

PART 70 OPERATING PERMIT OFFICE OF AIR QUALITY

**Central Soya Company, Inc.
1200 North 2nd Street
Decatur, Indiana 46733**

(herein known as the Permittee) is hereby authorized to operate subject to the conditions contained herein, the source described in Section A (Source Summary) of this permit.

This permit is issued in accordance with 326 IAC 2 and 40 CFR Part 70 Appendix A and contains the conditions and provisions specified in 326 IAC 2-7 as required by 42 U.S.C. 7401, et. seq. (Clean Air Act as amended by the 1990 Clean Air Act Amendments), 40 CFR Part 70.6, IC 13-15 and IC 13-17.

Operation Permit No.: T001-5610-00005	
Issued by: Original signed by Janet G. McCabe, Assistant Commissioner Office of Air Quality	Issuance Date: July 3, 2002 Expiration Date: July 3, 2007

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SECTION A SOURCE SUMMARY

This permit is based on information requested by the Indiana Department of Environmental Management (IDEM), Office of Air Quality (OAQ). The information describing the source contained in conditions A.1 through A.3 is descriptive information and does not constitute enforceable conditions. However, the Permittee should be aware that a physical change or a change in the method of operation that may render this descriptive information obsolete or inaccurate may trigger requirements for the Permittee to obtain additional permits or seek modification of this permit pursuant to 326 IAC 2, or change other applicable requirements presented in the permit application.

A.1 General Information [326 IAC 2-7-4(c)] [326 IAC 2-7-5(15)] [326 IAC 2-7-1(22)]

The Permittee owns and operates a stationary grain handling, animal feed production, soybean meal production, and soybean oil extraction plant.

Responsible Official:	Doyle R. Smith
Source Address:	1200 North 2 nd Street, Decatur, Indiana 46733
Mailing Address:	P.O. Box 1002, Decatur, Indiana 46733
General Source Phone Number:	(219)724-2101
SIC Code:	2075, 5153, 2048
County Location:	Adams
Source Location Status:	Attainment for all criteria pollutants
Source Status:	Part 70 Permit Program Major Source, under PSD Rules;

A.2 Emission Units and Pollution Control Equipment Summary [326 IAC 2-7-4(c)(3)] [326 IAC 2-7-5(15)]

This stationary source consists of the following emission units and pollution control devices:

NOTE: All throughputs and capacities are included in a IDEM, OAQ confidential file as the source considers them confidential.

- (a) Truck Dump #2, identified as 1EL1, constructed in 1980, using a baghouse for particulate matter (PM) control, and exhausting to stack 1EL;
- (b) The following grain elevator components, together identified as 2EL1, using a baghouse and oil suppressant for PM control, and exhausting to stack 2EL:
 - (1) One (1) dryer megatex enclosed conveyor, constructed in 1997;
 - (2) One (1) dryer rotex, constructed in 1978;
 - (3) One (1) screening bin hammermill, constructed in 1978;
 - (4) One (1) #1 scalperator, constructed prior to 1977;
 - (5) One (1) #2 scalperator, constructed prior to 1977;
 - (6) One (1) #3 scalperator, constructed prior to 1977;
 - (7) One (1) ext. screening bin, constructed prior to 1977;
 - (8) One (1) screening bin, constructed prior to 1977;
 - (9) One (1) solvent screening leg, constructed prior to 1977;

- (10) One (1) #1 leg, constructed prior to 1977;
 - (11) One (1) #2 leg, constructed prior to 1977;
 - (12) One (1) #3 leg, constructed prior to 1977;
 - (13) One (1) west to east Hi-Roller, constructed in 1992;
 - (14) One (1) west to east belt loader, constructed prior to 1977;
 - (15) One (1) dry bean leg, constructed prior to 1977;
 - (16) One (1) #1 dryer Hi-Roller, constructed in 1994;
 - (17) One (1) weaver's belt, constructed in 1994; and
 - (18) One (1) 102 belt, constructed in 1994;
- (c) The following grain elevator components, together identified as 5EL1, using a baghouse and oil suppressant for PM control, and exhausting to stack 5EL:
- (1) One (1) north tripper buggy, constructed in 1978;
 - (2) One (1) north galley belt loader, constructed in 1978;
 - (3) One (1) east west belt, constructed in 1995; and
 - (4) One (1) bin 102, constructed prior to 1977;
- (d) One (1) north west receiving house enclosed conveyor identified as 8EL1, constructed in 1995, using oil suppressant for PM control, with no aspiration;
- (e) The following grain elevator components, together identified as 10EL1, using a baghouse and oil suppressant for PM control, and exhausting to stack 10EL:
- (1) One (1) rail loadout, constructed in 1984;
 - (2) One (1) north leg, constructed prior to 1960; and
 - (3) One (1) south leg, constructed prior to 1960;
- (f) The following grain elevator components, together identified as 14EL1, using a baghouse and oil suppressant for PM control, and exhausting to stack 14EL:
- (1) One (1) jumbo silo east galley belt, constructed prior to 1977;
 - (2) One (1) jumbo silo west galley belt, constructed in 1993; and
 - (3) One (1) jumbo silo crossover galley belt, constructed prior to 1977;
- (g) One (1) grain dryer #2, identified as 19EL1, constructed in 1995, using self-cleaning screens for PM control, and exhausting to stack 19EL;

- (h) One (1) natural gas dryer #2 associated with grain dryer #2, identified as 19EL2, constructed in 1995, and exhausting to stack 19EL;
- (i) One (1) truck dump #7, identified as 20EL1, constructed in 1997, consisting of one (1) weight scale truck unloading pit, and two (2) enclosed bucket elevator legs, using two (2) baghouses in parallel for PM control, and exhausting to stack 20EL;
- (j) Silo bin vents, identified as 3EL1, constructed prior to 1977, using soybean oil as a dust suppressant, and exhausting to stack 3EL;
- (k) Silo direct loadout, identified as 4EL1, constructed prior to 1977, using soybean oil as a dust suppressant, and exhausting to stack 4EL;
- (l) One (1) south tripper buggy, one (1) south galley belt loader, and one (1) north south belt, identified as 6EL1, all constructed prior to 1977, using a baghouse and oil suppressant for PM control, and exhausting to stack 6EL;
- (m) One (1) south west receiving house enclosed conveyor, identified as 7EL1, constructed in 1995, using oil suppressant for PM control with no aspiration;
- (n) One (1) truck dump #3, identified as 9EL1, constructed in 1976, using a baghouse for PM control, and exhausting to stack 9EL;
- (o) One (1) truck dump #5, identified as 12EL1, constructed prior to 1977, using a baghouse for PM control, and exhausting to stack 12EL;
- (p) One (1) jumbo silo east tunnel belt, one (1) jumbo silo west tunnel belt, and one (1) jumbo silo crossover tunnel belt, identified as 13EL1, all constructed prior to 1977, using a baghouse and oil suppressant for PM control, and exhausting to stack 13EL;
- (q) One (1) truck dump #6, identified as 15EL1, constructed prior to 1977, using a baghouse for PM control, and exhausting to stack 15EL;
- (r) Two (2) grain dryers, # 4 and #5, identified as 17EL1, constructed in the 1960's, using self-cleaning screens for PM control, and exhausting to stack 17EL;
- (s) Two (2) natural gas fired dryers, #4 and #5, associated with grain dryers #4 and #5 respectively, identified as 17EL2, constructed in the 1960's, and exhausting to stack 17EL;
- (t) One (1) Lec. Dept. filter aid unit, identified as 204RO1, constructed in 1980, with a maximum capacity of 2.5 tons of diatomaceous earth per hour, using a baghouse for PM control, and exhausting to stack 204RO;
- (u) Daily use bins, identified as 102EO1, constructed in 1976, using a baghouse for PM control, and exhausting to stack 102EO;
- (v) Filter aid silos, identified as 103EO1, constructed in 1976, using a baghouse for PM control, and exhausting to stack 103EO;
- (w) One (1) natural gas fired hydrogen generator furnace, identified as 107EO1, constructed in 1992, and exhausting to stack 107EO;
- (x) Salt conveying, identified as 4SP1, constructed in 1981, using a baghouse for PM control, and exhausting to stack 4SP;

- (y) Lime conveying, identified as 5SP1, constructed in 1981, using a baghouse for PM control, and exhausting to stack 5SP;
- (z) One (1) vertical pellet cooler, constructed in 1967, and one (1) horizontal pellet cooler, constructed in the 1950's, identified as 1EF1, using a cyclone for PM control;
- (aa) One (1) corn grinding equipment, identified as 2EF1, constructed in 1992, using a cyclone for PM control.
- (bb) Ingredient grinding equipment, identified as 2EF2, constructed in the early 1970's;
- (cc) Feed Ingredient receiving, identified as 3EF1, constructed in the early 1970's;
- (dd) Bulk loadout, identified as 4EF1, constructed in the early 1970's;
- (ee) One (1) micro room, identified as 5EF1, constructed in the 1940's;
- (ff) Six (6) flaking rolls, #1, #2, #3, #4, #5, and #6, constructed in 1996, and B flake n/s drag, constructed in 1991, all identified together as 1EX1, sharing Vox filters with 1EX2 for PM control, and exhausting to stack 1EX;
- (gg) One (1) flaking roll #14 and flaking roll discharge #14, identified as 1EX2, constructed in 1991, sharing Vox filters with 1EX1 for PM control, and exhausting to stack 1EX;
- (hh) One (1) 'A' conditioner, identified as 2EX1, constructed in the 1930's, with no PM control, and exhausting to stack 2EX;
- (ii) The following soybean processing equipment, together identified as 3EX1, sharing a cyclone with 3EX2 for PM control, and exhausting to stack 3EX:
 - (1) Four (4) flaking rolls, #9, #10, #11, and #12, constructed in 1978;
 - (2) One (1) flaking roll #13, constructed in 1985;
 - (3) One (1) 'A' flake n/s drag, constructed in 1993; and
 - (4) One (1) 'A' flake e/w drag, constructed in 1993;
- (jj) One (1) north run around drag, identified as 3EX2, constructed in 1984, sharing a cyclone with 3EX1, and exhausting to stack 3EX;
- (kk) The following soybean processing equipment, together identified as 4EX1, sharing a baghouse with 4EX2 and 4EX3 for PM control, and exhausting to stack 4EX:
 - (1) One (1) whole bean scale, constructed in 1989;
 - (2) One (1) 'A' whole bean leg, constructed in 1997;
 - (3) One (1) 'A' surge bin, constructed prior to 1979;
 - (4) One (1) whole bean drag, constructed in 1981; and
 - (5) One (1) 'B' surge bin, constructed prior to 1979;

- (ll) A run around rework screw, identified as 4EX2, constructed in 1991, sharing a baghouse with 4EX1 and 4EX3 for PM control, and exhausting to stack 4EX;
- (mm) The following soybean processing equipment, together identified as 4EX3, sharing a baghouse with 4EX1 and 4EX2 for PM control, and exhausting to stack 4EX:
 - (1) One (1) hull refining screw conveyor, constructed in 1991;
 - (2) One (1) hull refining process, constructed in 1991; and
 - (3) One (1) hull grinding process, constructed in 1987;
- (nn) Dehulling equipment, identified as 5EX1, constructed in 1997, sharing a baghouse with 5EX2 and 5EX3 for PM control, and exhausting to stack 5EX;
- (oo) Hot dehulling equipment, identified as 5EX2, constructed in 1991, sharing a baghouse with 5EX1 and 5EX3 for PM control, and exhausting to stack 5EX;
- (pp) Screening aspiration, identified as 5EX3, constructed in 1988, sharing a baghouse with 5EX1 and 5EX2 for PM control, and exhausting to stack 5EX;
- (qq) Truck loadout, identified as 6EX1, constructed in 1982, replaced in 1999, using a baghouse for PM control, and exhausting to stack 6EX;
- (rr) The following soybean processing equipment, together identified as 7EX1, using a baghouse for PM control, and exhausting to stack 7EX:
 - (1) One (1) north megamill, constructed in 1993;
 - (2) One (1) south megamill, constructed in 1993; and
 - (3) One (1) stedman grinder, constructed in 1983;
- (ss) One (1) leg No. 2, one (1) mixing conveyor, and one (1) bin drag, together identified as 9EX1, all constructed in 1983, using a baghouse for PM control, and exhausting to stack 9EX;
- (tt) The following soybean processing equipment, together identified as 10EX1, using a baghouse for PM control, and exhausting to stack 10EX:
 - (1) One (1) leg No. 3, constructed in the 1950's;
 - (2) One (1) tunnel drag, constructed in 1983; and
 - (3) One (1) meal loadout drag, constructed in 1982;
- (uu) One (1) kaolin bin, identified as 11EX1, constructed in the 1950's, using a baghouse for PM control, and exhausting to stack 11EX;
- (ww) One (1) meal loadout bin, identified as 12EX1, constructed in 1982, using a baghouse for PM control, and exhausting to stack 12EX;
- (www) One (1) pre-DT section on top of 'A' top dryer section, constructed in 1996, and exhausting to 'A' top dryer section for PM control and one (1) 'A' top dryer section, identified as 13EX1,

- constructed in 1980, using a cyclone for PM control, exhausting to stack 13EX, with hexane emissions directed to stack 24EX;
- (xx) One (1) 'A' middle dryer section, identified as 13EX2, constructed in 1980, using a cyclone for PM control, exhausting to stack 13EX, with hexane emissions directed to stack 24EX;
 - (yy) One (1) 'A' bottom cooler section, identified as 13EX3, constructed in 1980, using a cyclone for PM control, exhausting to stack 13EX, with hexane emissions directed to stack 24EX;
 - (zz) One (1) pre-DT section on top of 'B' top dryer section, constructed in 1996, and exhausting to 'B' top dryer section for PM control, and one (1) 'B' top dryer section, identified as 14EX1, constructed in 1980, using a cyclone for PM control, exhausting to stack 14EX, with hexane emissions directed to stack 24EX;
 - (aaa) One (1) 'B' middle dryer section, identified as 14EX2, constructed in 1980, using a cyclone for PM control, exhausting to stack 14EX, with hexane emissions directed to stack 24EX;
 - (bbb) One (1) 'B' bottom cooler section, identified as 14EX3, constructed in 1980, using a cyclone for PM control, exhausting to stack 14EX, with hexane emissions directed to stack 24EX;
 - (ccc) One (1) meal cooler, identified as 21EX, constructed in 1996, using two (2) cyclones for PM control and exhausting to stacks 21EX-A and 21EX-B, with hexane emissions directed to stack 24EX;
 - (ddd) One (1) belt to storage bowls, one (1) large storage bowl, and one (1) small storage bowl, identified as 16EX1, 16EX2, and 16EX3, respectively, all constructed in 1982, with no PM control, and exhausting to stack 16EX;
 - (eee) Whole bean bins, identified as 18EX1, constructed in the 1940's, with no PM control, and exhausting to stack 18EX;
 - (fff) Meal storage silos with bin vents, identified as 23EX1, constructed in the 1950's, and one (1) bin vent filter, exhausting to stack 23EX;
 - (ggg) One (1) zinc receiving bin, identified as 25EX1, constructed in 1994, sharing a bin vent filter with 25EX2 for PM control, and exhausting to stack 25EX;
 - (hhh) One (1) zinc surge bin, identified as 25EX2, constructed in 1994, sharing a bin vent filter with 25EX1 for PM control, and exhausting to stack 25EX;
 - (iii) One (1) rumen conveyor, identified as 8EX1, constructed in 1994, using a cyclone for PM control, and exhausting to stack 8EX;
 - (jjj) One (1) rotary reactor, identified as 27EX1, constructed in the 1994, using a cyclone for PM control, and exhausting to stack 27EX;
 - (kkk) Rumen loadout bins, identified as 29EX1, constructed in 1994, using a bin vent filter for PM control, and exhausting to stack 29EX;
 - (lll) Rumen rework surge bin, identified as 30EX1, constructed in 1994, using a polyethylene fabric filter for PM control, and exhausting to stack 30EX;

- (mmm) One (1) natural gas fired Dowtherm heater #1, identified as 105EO1, constructed in 1969, and exhausting to stack 105EO;
- (nnn) One (1) natural gas fired Dowtherm heater #2, identified as 106EO1, constructed in 1976, and exhausting to stack 106EO;
- (ooo) One (1) natural gas fired steam generator #3, identified as 108EO1, constructed in 1994, and exhausting to stack 108EO;
- (ppp) One (1) B & W coal fired boiler, identified as 1SP1, constructed in 1950, using multiple cyclones for PM control, and exhausting to stack 1SP;
- (qqq) One (1) Keeler coal fired boiler, identified as 2SP1, constructed in 1963, using multiple cyclones for PM control, and exhausting to stack 1SP;
- (rrr) One (1) Murray natural gas fired, vegetable oil-fired, waste oil-fired, and hazardous chemical fired boiler, identified as 3SP1, constructed in 1968, and exhausting to stack 1SP;
- (sss) Hexane recovery, identified as 24EX1, constructed in 1980, with hexane emissions controlled by a mineral oil absorber, and exhausting to stack 24EX;
- (ttt) One (1) pre DT section on top of 'A' top dryer section, constructed in 1996, and one (1) 'A' DTDC top dryer section, constructed in 1980, both identified as 24EX2, with hexane emissions controlled by a mineral oil absorber and exhausting to stack 24EX;
- (uuu) One (1) 'A' DTDC middle dryer section, identified as 24EX3, constructed in 1980, with hexane emissions controlled by a mineral oil absorber, and exhausting to stack 24EX;
- (ww) One (1) 'A' DTDC bottom cooler section, identified as 24EX4, constructed in 1980, with hexane emissions controlled by a mineral oil absorber, and exhausting to stack 24EX;
- (www) One (1) pre-DT section on top of 'B' top dryer section, constructed in 1996, and one (1) 'B' DTDC top dryer section, constructed in 1980, both identified as 24EX5, with hexane emissions controlled by a mineral oil absorber, and exhausting to stack 24EX;
- (xxx) One (1) 'B' DTDC middle dryer section, identified as 24EX6, constructed in 1980, with hexane emissions controlled by a mineral oil absorber, and exhausting to stack 24EX;
- (yyy) One (1) 'B' DTDC bottom cooler section, identified as 24EX7, constructed in 1980, with hexane emissions controlled by a mineral oil absorber, and exhausting to stack 24EX;
- (zzz) One (1) meal cooler, identified as 21EX, constructed in 1996, with hexane emissions controlled by a mineral oil absorber, and exhausting to sack 24EX;
- (aaaa) Hexane storage tank, identified as 24EX8, constructed in 1995, and vented to the mineral oil absorber inlet;
- (bbbb) Wastewater system containing hexane, identified as 24EX9, constructed in 1980, and exhausting at the plant treatment facility;
- (cccc) One (1) refined oil hot well, identified as 24EX10, constructed in 1975, and exhausting to stack 24EX;

- (dddd) One (1) sampling/hexane unloading port, identified as 24EX11, and with no control;
- (eeee) One (1) grain dryer #1, identified as 16EL1, constructed in 1986, using self-cleaning screens for PM control, and exhausting to stack 16EL;
- (ffff) One (1) natural gas dryer #1 associated with grain dryer #1, identified as 16EL2, constructed in 1986, and exhausting to stack 16EL;
- (gggg) One (1) outside conditioner, identified as 17EX1, constructed in 1991, sharing a cyclone with 17EX2 for PM control, and exhausting to stack 17EX; and
- (hhhh) The following soybean processing equipment, together identified as 17EX2, modified in 1987, sharing a cyclone with 17EX1 for PM control, and exhausting to stack 17EX:
 - (1) One (1) flaking roll #8, constructed in 1981; and
 - (2) One (1) 'B' flke e/w drag, constructed in 1980.

A.3 Specifically Regulated Insignificant Activities [326 IAC 2-7-1(21)] [326 IAC 2-7-4(c)] [326 IAC 2-7-5(15)]

This stationary source also includes the following insignificant activities which are specifically regulated, as defined in 326 IAC 2-7-1(21):

- (a) Paved and unpaved roads and parking lots with public access [326 IAC 6-4].

A.4 Part 70 Permit Applicability [326 IAC 2-7-2]

This stationary source is required to have a Part 70 permit by 326 IAC 2-7-2 (Applicability) because:

- (a) It is a major source, as defined in 326 IAC 2-7-1(22);
- (b) It is a source in a source category designated by the United States Environmental Protection Agency (U.S. EPA) under 40 CFR 70.3 (Part 70 - Applicability).

SECTION B GENERAL CONDITIONS

B.1 Definitions [326 IAC 2-7-1]

Terms in this permit shall have the definition assigned to such terms in the referenced regulation. In the absence of definitions in the referenced regulation, the applicable definitions found in the statutes or regulations (IC 13-11, 326 IAC 1-2 and 326 IAC 2-7) shall prevail.

B.2 Permit Term [326 IAC 2-7-5(2)] [326 IAC 2-1.1-9.5]

This permit is issued for a fixed term of five (5) years from the original date, as determined in accordance with IC 4-21.5-3-5(f) and IC 13-15-5-3. Subsequent revisions, modifications, or amendments of this permit do not affect the expiration date.

B.3 Enforceability [326 IAC 2-7-7]

Unless otherwise stated, all terms and conditions in this permit, including any provisions designed to limit the source's potential to emit, are enforceable by IDEM, the United States Environmental Protection Agency (U.S. EPA) and by citizens in accordance with the Clean Air Act.

B.4 Termination of Right to Operate [326 IAC 2-7-10] [326 IAC 2-7-4(a)]

The Permittee's right to operate this source terminates with the expiration of this permit unless a timely and complete renewal application is submitted at least nine (9) months prior to the date of expiration of the source's existing permit, consistent with 326 IAC 2-7-3 and 326 IAC 2-7-4(a).

B.5 Severability [326 IAC 2-7-5(5)]

The provisions of this permit are severable; a determination that any portion of this permit is invalid shall not affect the validity of the remainder of the permit.

B.6 Property Rights or Exclusive Privilege [326 IAC 2-7-5(6)(D)]

This permit does not convey any property rights of any sort or any exclusive privilege.

B.7 Duty to Supplement and Provide Information [326 IAC 2-7-4(b)] [326 IAC 2-7-5(6)(E)] [326 IAC 2-7-6(6)]

(a) The Permittee, upon becoming aware that any relevant facts were omitted or incorrect information was submitted in the permit application, shall promptly submit such supplementary facts or corrected information to:

Indiana Department of Environmental Management
Permits Branch, Office of Air Quality
100 North Senate Avenue, P. O. Box 6015
Indianapolis, Indiana 46206-6015

The submittal by the Permittee does require the certification by the "responsible official" as defined by 326 IAC 2-7-1(34).

(b) The Permittee shall furnish to IDEM, OAQ, within a reasonable time, any information that IDEM, OAQ, may request in writing to determine whether cause exists for modifying, revoking and reissuing, or terminating this permit, or to determine compliance with this permit. The submittal by the Permittee does require the certification by the "responsible official" as defined by 326 IAC 2-7-1(34). Upon request, the Permittee shall also furnish to IDEM, OAQ, copies of records required to be kept by this permit or, for information claimed to be confidential, the Permittee may furnish such records directly to the U. S. EPA along with a claim of confidentiality. [326 IAC 2-7-5(6)(E)]

- (c) The Permittee may include a claim of confidentiality in accordance with 326 IAC 17.1. When furnishing copies of requested records directly to U. S. EPA, the Permittee may assert a claim of confidentiality in accordance with 40 CFR 2, Subpart B.

B.8 Compliance with Permit Conditions [326 IAC 2-7-5(6)(A)] [326 IAC 2-7-5(6)(B)]

- (a) The Permittee must comply with all conditions of this permit. Noncompliance with any provisions of this permit is grounds for:
 - (1) Enforcement action;
 - (2) Permit termination, revocation and reissuance, or modification; or
 - (3) Denial of a permit renewal application.
- (b) Noncompliance with any provision of this permit, except any provision specifically designated as not federally enforceable, constitutes a violation of the Clean Air Act.
- (c) It shall not be a defense for the Permittee in an enforcement action that it would have been necessary to halt or reduce the permitted activity in order to maintain compliance with the conditions of this permit.
- (d) An emergency does constitute an affirmative defense in an enforcement action provided the Permittee complies with the applicable requirements set forth in Section B, Emergency Provisions.

B.9 Certification [326 IAC 2-7-4(f)] [326 IAC 2-7-6(1)] [326 IAC 2-7-5(3)(C)]

- (a) Where specifically designated by this permit or required by an applicable requirement, any application form, report, or compliance certification submitted shall contain certification by a responsible official of truth, accuracy, and completeness. This certification shall state that, based on information and belief formed after reasonable inquiry, the statements and information in the document are true, accurate, and complete.
- (b) One (1) certification shall be included, using the attached Certification Form, with each submittal requiring certification.
- (c) A responsible official is defined at 326 IAC 2-7-1(34).

B.10 Annual Compliance Certification [326 IAC 2-7-6(5)]

- (a) The Permittee shall annually submit a compliance certification report which addresses the status of the source's compliance with the terms and conditions contained in this permit, including emission limitations, standards, or work practices. The initial certification shall cover the time period from the date of final permit issuance through December 31 of the same year. All subsequent certifications shall cover the time period from January 1 to December 31 of the previous year, and shall be submitted in letter form no later than July 1 of each year to:

Indiana Department of Environmental Management
Compliance Branch, Office of Air Quality
100 North Senate Avenue, P. O. Box 6015
Indianapolis, Indiana 46206-6015

and

United States Environmental Protection Agency, Region V

Air and Radiation Division, Air Enforcement Branch - Indiana (AE-17J)
77 West Jackson Boulevard
Chicago, Illinois 60604-3590

- (b) The annual compliance certification report required by this permit shall be considered timely if the date postmarked on the envelope or certified mail receipt, or affixed by the shipper on the private shipping receipt, is on or before the date it is due. If the document is submitted by any other means, it shall be considered timely if received by IDEM, OAQ, on or before the date it is due.
- (c) The annual compliance certification report shall include the following:
- (1) The appropriate identification of each term or condition of this permit that is the basis of the certification;
 - (2) The compliance status;
 - (3) Whether compliance was continuous or intermittent;
 - (4) The methods used for determining the compliance status of the source, currently and over the reporting period consistent with 326 IAC 2-7-5(3); and
 - (5) Such other facts, as specified in Sections D of this permit, as IDEM, OAQ, may require to determine the compliance status of the source.

The submittal by the Permittee does require the certification by the "responsible official" as defined by 326 IAC 2-7-1(34).

B.11 Preventive Maintenance Plan [326 IAC 2-7-5(1),(3) and (13)] [326 IAC 2-7-6(1) and (6)] [326 IAC 1-6-3]

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- (a) If required by specific condition(s) in Section D of this permit, the Permittee shall prepare and maintain Preventive Maintenance Plans (PMPs) within ninety (90) days after issuance of this permit, including the following information on each facility:
- (1) Identification of the individual(s) responsible for inspecting, maintaining, and repairing emission control devices;
 - (2) A description of the items or conditions that will be inspected and the inspection schedule for said items or conditions; and
 - (3) Identification and quantification of the replacement parts that will be maintained in inventory for quick replacement.

If, due to circumstances beyond the Permittee's control, the PMPs cannot be prepared and maintained within the above time frame, the Permittee may extend the date an additional ninety (90) days provided the Permittee notifies:

Indiana Department of Environmental Management
Compliance Branch, Office of Air Quality
100 North Senate Avenue, P. O. Box 6015
Indianapolis, Indiana 46206-6015

The PMP and the PMP extension notification do not require the certification by the "responsible official" as defined by 326 IAC 2-7-1(34).

- (b) The Permittee shall implement the PMPs as necessary to ensure that failure to implement a PMP does not cause or contribute to a violation of any limitation on emissions or potential to emit.
- (c) A copy of the PMPs shall be submitted to IDEM, OAQ, upon request and within a reasonable time, and shall be subject to review and approval by IDEM, OAQ. IDEM, OAQ, may require the Permittee to revise its PMPs whenever lack of proper maintenance causes or contributes to any violation. The PMP does not require the certification by the "responsible official" as defined by 326 IAC 2-7-1(34).
- (d) Records of preventive maintenance shall be retained for a period of at least five (5) years. These records shall be kept at the source location for a minimum of three (3) years. The records may be stored elsewhere for the remaining two (2) years as long as they are available upon request. If the Commissioner makes a request for records to the Permittee, the Permittee shall furnish the records to the Commissioner within a reasonable time.

B.12 Emergency Provisions [326 IAC 2-7-16]

- (a) An emergency, as defined in 326 IAC 2-7-1(12), is not an affirmative defense for an action brought for noncompliance with a federal or state health-based emission limitation.
- (b) An emergency, as defined in 326 IAC 2-7-1(12), constitutes an affirmative defense to an action brought for noncompliance with a technology-based emission limitation if the affirmative defense of an emergency is demonstrated through properly signed, contemporaneous operating logs or other relevant evidence that describe the following:
 - (1) An emergency occurred and the Permittee can, to the extent possible, identify the causes of the emergency;
 - (2) The permitted facility was at the time being properly operated;
 - (3) During the period of an emergency, the Permittee took all reasonable steps to minimize levels of emissions that exceeded the emission standards or other requirements in this permit;
 - (4) For each emergency lasting one (1) hour or more, the Permittee notified IDEM, OAQ, within four (4) daytime business hours after the beginning of the emergency, or after the emergency was discovered or reasonably should have been discovered;

Telephone Number: 1-800-451-6027 (ask for Office of Air Quality, Compliance Section), or

Telephone Number: 317-233-5674 (ask for Compliance Section)

Facsimile Number: 317-233-5967

- (5) For each emergency lasting one (1) hour or more, the Permittee submitted the attached Emergency Occurrence Report Form or its equivalent, either by mail or facsimile to:

Indiana Department of Environmental Management
Compliance Branch, Office of Air Quality
100 North Senate Avenue, P. O. Box 6015
Indianapolis, Indiana 46206-6015

within two (2) working days of the time when emission limitations were exceeded due to the emergency.

The notice fulfills the requirement of 326 IAC 2-7-5(3)(C)(ii) and must contain the following:

- (A) A description of the emergency;
- (B) Any steps taken to mitigate the emissions; and
- (C) Corrective actions taken.

The notification which shall be submitted by the Permittee does not require the certification by the "responsible official" as defined by 326 IAC 2-7-1(34).

- (6) The Permittee immediately took all reasonable steps to correct the emergency.
- (c) In any enforcement proceeding, the Permittee seeking to establish the occurrence of an emergency has the burden of proof.
- (d) This emergency provision supersedes 326 IAC 1-6 (Malfunctions). This permit condition is in addition to any emergency or upset provision contained in any applicable requirement.
- (e) IDEM, OAQ, may require that the Preventive Maintenance Plans required under 326 IAC 2-7-4-(c)(10) be revised in response to an emergency.
- (f) Failure to notify IDEM, OAQ, by telephone or facsimile of an emergency lasting more than one (1) hour in accordance with (b)(4) and (5) of this condition shall constitute a violation of 326 IAC 2-7 and any other applicable rules.
- (g) If the emergency situation causes a deviation from a technology-based limit, the Permittee may continue to operate the affected emitting facilities during the emergency provided the Permittee immediately takes all reasonable steps to correct the emergency and minimize emissions.

B.13 Permit Shield [326 IAC 2-7-15] [326 IAC 2-7-20] [326 IAC 2-7-12]

- (a) Pursuant to 326 IAC 2-7-15, the Permittee has been granted a permit shield. The permit shield provides that compliance with the conditions of this permit shall be deemed in compliance with any applicable requirements as of the date of permit issuance, provided that either the applicable requirements are included and specifically identified in this permit or the permit contains an explicit determination or concise summary of a determination that other specifically identified requirements are not applicable. The Indiana statutes from IC 13 and rules from 326 IAC, referenced in conditions in this permit, are those applicable at the time the permit was issued. The issuance or possession of this permit shall not alone constitute a defense against an alleged violation of any law, regulation or standard, except for the requirement to obtain a Part 70 permit under 326 IAC 2-7 or for applicable requirements for which a permit shield has been granted.

This permit shield does not extend to applicable requirements which are promulgated after the date of issuance of this permit unless this permit has been modified to reflect such new requirements.

- (b) If, after issuance of this permit, it is determined that the permit is in nonconformance with an applicable requirement that applied to the source on the date of permit issuance, IDEM, OAQ, shall immediately take steps to reopen and revise this permit and issue a compliance order to the Permittee to ensure expeditious compliance with the applicable

requirement until the permit is reissued. The permit shield shall continue in effect so long as the Permittee is in compliance with the compliance order.

- (c) No permit shield shall apply to any permit term or condition that is determined after issuance of this permit to have been based on erroneous information supplied in the permit application. Erroneous information means information that the Permittee knew to be false, or in the exercise of reasonable care should have been known to be false, at the time the information was submitted.
- (d) Nothing in 326 IAC 2-7-15 or in this permit shall alter or affect the following:
 - (1) The provisions of Section 303 of the Clean Air Act (emergency orders), including the authority of the U.S. EPA under Section 303 of the Clean Air Act;
 - (2) The liability of the Permittee for any violation of applicable requirements prior to or at the time of this permit's issuance;
 - (3) The applicable requirements of the acid rain program, consistent with Section 408(a) of the Clean Air Act; and
 - (4) The ability of U.S. EPA to obtain information from the Permittee under Section 114 of the Clean Air Act.
- (e) This permit shield is not applicable to any change made under 326 IAC 2-7-20(b)(2) (Sections 502(b)(10) of the Clean Air Act changes) and 326 IAC 2-7-20(c)(2) (trading based on State Implementation Plan (SIP) provisions).
- (f) This permit shield is not applicable to modifications eligible for group processing until after IDEM, OAQ, has issued the modifications. [326 IAC 2-7-12(c)(7)]
- (g) This permit shield is not applicable to minor Part 70 permit modifications until after IDEM, OAQ, has issued the modification. [326 IAC 2-7-12(b)(7)]

B.14 Prior Permits Superseded [326 IAC 2-1.1-9.5]

- (a) All terms and conditions of previous permits issued pursuant to permitting programs approved into the state implementation plan have been either
 - (1) incorporated as originally stated,
 - (2) revised, or
 - (3) deletedby this permit.
- (b) All previous registrations and permits are superseded by this permit.

B.15 Deviations from Permit Requirements and Conditions [326 IAC 2-7-5(3)(C)(ii)]

- (a) Deviations from any permit requirements (for emergencies see Section B - Emergency Provisions), the probable cause of such deviations, and any response steps or preventive measures taken shall be reported to:

Indiana Department of Environmental Management
Compliance Data Section, Office of Air Quality
100 North Senate Avenue, P.O. Box 6015
Indianapolis, Indiana 46206-6015

using the attached Quarterly Deviation and Compliance Monitoring Report, or its equivalent. A deviation required to be reported pursuant to an applicable requirement that exists independent of this permit shall be reported according to the schedule stated in the applicable requirement and do not need to be included in this report.

The Quarterly Deviation and Compliance Monitoring Report does require the certification by the "responsible official" as defined by 326 IAC 2-7-1(34).

- (b) A deviation is an exceedance of a permit limitation or a failure to comply with a requirement of the permit.
- (c) Emergencies shall be included in the Quarterly Deviation and Compliance Monitoring Report.

B.16 Permit Modification, Reopening, Revocation and Reissuance, or Termination [326 IAC 2-7-5(6)(C)]
[326 IAC 2-7-8(a)] [326 IAC 2-7-9]

- (a) This permit may be modified, reopened, revoked and reissued, or terminated for cause. The filing of a request by the Permittee for a Part 70 permit modification, revocation and reissuance, or termination, or of a notification of planned changes or anticipated noncompliance does not stay any condition of this permit. [326 IAC 2-7-5(6)(C)] The notification by the Permittee does require the certification by the "responsible official" as defined by 326 IAC 2-7-1(34).
- (b) This permit shall be reopened and revised under any of the circumstances listed in IC 13-15-7-2 or if IDEM, OAQ, determines any of the following:
 - (1) That this permit contains a material mistake.
 - (2) That inaccurate statements were made in establishing the emissions standards or other terms or conditions.
 - (3) That this permit must be revised or revoked to assure compliance with an applicable requirement. [326 IAC 2-7-9(a)(3)]
- (c) Proceedings by IDEM, OAQ, to reopen and revise this permit shall follow the same procedures as apply to initial permit issuance and shall affect only those parts of this permit for which cause to reopen exists. Such reopening and revision shall be made as expeditiously as practicable. [326 IAC 2-7-9(b)]
- (d) The reopening and revision of this permit, under 326 IAC 2-7-9(a), shall not be initiated before notice of such intent is provided to the Permittee by IDEM, OAQ, at least thirty (30) days in advance of the date this permit is to be reopened, except that IDEM, OAQ, may provide a shorter time period in the case of an emergency. [326 IAC 2-7-9(c)]

B.17 Permit Renewal [326 IAC 2-7-4]

- (a) The application for renewal shall be submitted using the application form or forms prescribed by IDEM, OAQ, and shall include the information specified in 326 IAC 2-7-4. Such information shall be included in the application for each emission unit at this source, except those emission units included on the trivial or insignificant activities list contained in

326 IAC 2-7-1(21) and 326 IAC 2-7-1(40). The renewal application does require the certification by the "responsible official" as defined by 326 IAC 2-7-1(34).

Request for renewal shall be submitted to:

Indiana Department of Environmental Management
Permits Branch, Office of Air Quality
100 North Senate Avenue, P.O. Box 6015
Indianapolis, Indiana 46206-6015

(b) Timely Submittal of Permit Renewal [326 IAC 2-7-4(a)(1)(D)]

(1) A timely renewal application is one that is:

(A) Submitted at least nine (9) months prior to the date of the expiration of this permit; and

(B) If the date postmarked on the envelope or certified mail receipt, or affixed by the shipper on the private shipping receipt, is on or before the date it is due. If the document is submitted by any other means, it shall be considered timely if received by IDEM, OAQ, on or before the date it is due.

(2) If IDEM, OAQ, upon receiving a timely and complete permit application, fails to issue or deny the permit renewal prior to the expiration date of this permit, this existing permit shall not expire and all terms and conditions shall continue in effect, including any permit shield provided in 326 IAC 2-7-15, until the renewal permit has been issued or denied.

(c) Right to Operate After Application for Renewal [326 IAC 2-7-3]

If the Permittee submits a timely and complete application for renewal of this permit, the source's failure to have a permit is not a violation of 326 IAC 2-7 until IDEM, OAQ, takes final action on the renewal application, except that this protection shall cease to apply if, subsequent to the completeness determination, the Permittee fails to submit by the deadline specified in writing by IDEM, OAQ, any additional information identified as being needed to process the application.

(d) United States Environmental Protection Agency Authority [326 IAC 2-7-8(e)]

If IDEM, OAQ, fails to act in a timely way on a Part 70 permit renewal, the U.S. EPA may invoke its authority under Section 505(e) of the Clean Air Act to terminate or revoke and reissue a Part 70 permit.

B.18 Permit Amendment or Modification [326 IAC 2-7-11] [326 IAC 2-7-12]

(a) Permit amendments and modifications are governed by the requirements of 326 IAC 2-7-11 or 326 IAC 2-7-12 whenever the Permittee seeks to amend or modify this permit.

(b) Any application requesting an amendment or modification of this permit shall be submitted to:

Indiana Department of Environmental Management
Permits Branch, Office of Air Quality
100 North Senate Avenue, P.O. Box 6015
Indianapolis, Indiana 46206-6015

Any such application shall be certified by the "responsible official" as defined by 326 IAC 2-7-1(34).

- (c) The Permittee may implement administrative amendment changes addressed in the request for an administrative amendment immediately upon submittal of the request. [326 IAC 2-7-11(c)(3)]

B.19 Permit Revision Under Economic Incentives and Other Programs [326 IAC 2-7-5(8)] [326 IAC 2-7-12 (b)(2)]

- (a) No Part 70 permit revision shall be required under any approved economic incentives, marketable Part 70 permits, emissions trading, and other similar programs or processes for changes that are provided for in a Part 70 permit.
- (b) Notwithstanding 326 IAC 2-7-12(b)(1)(D)(i) and 326 IAC 2-7-12(c)(1), minor Part 70 permit modification procedures may be used for Part 70 modifications involving the use of economic incentives, marketable Part 70 permits, emissions trading, and other similar approaches to the extent that such minor Part 70 permit modification procedures are explicitly provided for in the applicable State Implementation Plan (SIP) or in applicable requirements promulgated or approved by the U.S. EPA.

B.20 Operational Flexibility [326 IAC 2-7-20] [326 IAC 2-7-10.5]

- (a) The Permittee may make any change or changes at the source that are described in 326 IAC 2-7-20(b), (c), or (e), without a prior permit revision, if each of the following conditions is met:

- (1) The changes are not modifications under any provision of Title I of the Clean Air Act;
- (2) Any preconstruction approval required by 326 IAC 2-7-10.5 has been obtained;
- (3) The changes do not result in emissions which exceed the emissions allowable under this permit (whether expressed herein as a rate of emissions or in terms of total emissions);
- (4) The Permittee notifies the:

Indiana Department of Environmental Management
Permits Branch, Office of Air Quality
100 North Senate Avenue, P. O. Box 6015
Indianapolis, Indiana 46206-6015

and

United States Environmental Protection Agency, Region V
Air and Radiation Division, Regulation Development Branch - Indiana (AR-18J)
77 West Jackson Boulevard
Chicago, Illinois 60604-3590

in advance of the change by written notification at least ten (10) days in advance of the proposed change. The Permittee shall attach every such notice to the Permittee's copy of this permit; and

- (5) The Permittee maintains records on-site which document, on a rolling five (5) year basis, all such changes and emissions trading that are subject to 326 IAC 2-7-

20(b), (c), or (e) and makes such records available, upon reasonable request, for public review.

Such records shall consist of all information required to be submitted to IDEM, OAQ, in the notices specified in 326 IAC 2-7-20(b), (c)(1), and (e)(2).

- (b) The Permittee may make Section 502(b)(10) of the Clean Air Act changes (this term is defined at 326 IAC 2-7-1(36)) without a permit revision, subject to the constraint of 326 IAC 2-7-20(a). For each such Section 502(b)(10) of the Clean Air Act change, the required written notification shall include the following:
- (1) A brief description of the change within the source;
 - (2) The date on which the change will occur;
 - (3) Any change in emissions; and
 - (4) Any permit term or condition that is no longer applicable as a result of the change.

The notification which shall be submitted is not considered an application form, report or compliance certification. Therefore, the notification by the Permittee does not require the certification by the "responsible official" as defined by 326 IAC 2-7-1(34).

- (c) Emission Trades [326 IAC 2-7-20(c)]
The Permittee may trade increases and decreases in emissions in the source, where the applicable SIP provides for such emission trades without requiring a permit revision, subject to the constraints of Section (a) of this condition and those in 326 IAC 2-7-20(c).
- (d) Alternative Operating Scenarios [326 IAC 2-7-20(d)]
The Permittee may make changes at the source within the range of alternative operating scenarios that are described in the terms and conditions of this permit in accordance with 326 IAC 2-7-5(9). No prior notification of IDEM, OAQ, or U.S. EPA is required.

B.21 Source Modification Requirement [326 IAC 2-7-10.5]

A modification, construction, or reconstruction is governed by 326 IAC 2 and 326 IAC 2-7-10.5.

B.22 Inspection and Entry [326 IAC 2-7-6] [IC 13-14-2-2]

Upon presentation of proper identification cards, credentials, and other documents as may be required by law, and subject to the Permittee's right under all applicable laws and regulations to assert that the information collected by the agency is confidential and entitled to be treated as such, the Permittee shall allow IDEM, OAQ, U.S. EPA, or an authorized representative to perform the following:

- (a) Enter upon the Permittee's premises where a Part 70 source is located, or emissions related activity is conducted, or where records must be kept under the conditions of this permit;
- (b) Have access to and copy any records that must be kept under the conditions of this permit;
- (c) Inspect any facilities, equipment (including monitoring and air pollution control equipment), practices, or operations regulated or required under this permit;

- (d) Sample or monitor substances or parameters for the purpose of assuring compliance with this permit or applicable requirements; and
- (e) Utilize any photographic, recording, testing, monitoring, or other equipment for the purpose of assuring compliance with this permit or applicable requirements.

B.23 Transfer of Ownership or Operational Control [326 IAC 2-7-11]

- (a) The Permittee must comply with the requirements of 326 IAC 2-7-11 whenever the Permittee seeks to change the ownership or operational control of the source and no other change in the permit is necessary.
- (b) Any application requesting a change in the ownership or operational control of the source shall contain a written agreement containing a specific date for transfer of permit responsibility, coverage and liability between the current and new Permittee. The application shall be submitted to:

Indiana Department of Environmental Management
Permits Branch, Office of Air Quality
100 North Senate Avenue, P.O. Box 6015
Indianapolis, Indiana 46206-6015

The application which shall be submitted by the Permittee does require the certification by the "responsible official" as defined by 326 IAC 2-7-1(34).

- (c) The Permittee may implement administrative amendment changes addressed in the request for an administrative amendment immediately upon submittal of the request. [326 IAC 2-7-11(c)(3)]

B.24 Annual Fee Payment [326 IAC 2-7-19] [326 IAC 2-7-5(7)]

- (a) The Permittee shall pay annual fees to IDEM, OAQ, within thirty (30) calendar days of receipt of a billing. Pursuant to 326 IAC 2-7-19(b), if the Permittee does not receive a bill from IDEM, OAQ, the applicable fee is due April 1 of each year.
- (b) Except as provided in 326 IAC 2-7-19(e), failure to pay may result in administrative enforcement action or revocation of this permit.
- (c) The Permittee may call the following telephone numbers: 1-800-451-6027 or 317-233-0425 (ask for OAQ, Technical Support and Modeling Section), to determine the appropriate permit fee.

SECTION C SOURCE OPERATION CONDITIONS

Entire Source

Emission Limitations and Standards [326 IAC 2-7-5(1)]

C.1 Particulate Matter Emission Limitations For Processes with Process Weight Rates Less Than One Hundred (100) pounds per hour [326 IAC 6-3-2(c)]

Pursuant to 326 IAC 6-3-2(c), the allowable particulate matter emissions rate from any process not already regulated by 326 IAC 6-1 or any New Source Performance Standard, and which has a maximum process weight rate less than 100 pounds per hour shall not exceed 0.551 pounds per hour.

C.2 Opacity [326 IAC 5-1]

Pursuant to 326 IAC 5-1-2 (Opacity Limitations), except as provided in 326 IAC 5-1-3 (Temporary Alternative Opacity Limitations), opacity shall meet the following, unless otherwise stated in this permit:

- (a) Opacity shall not exceed an average of forty percent (40%) in any one (1) six (6) minute averaging period as determined in 326 IAC 5-1-4.
- (b) Opacity shall not exceed sixty percent (60%) for more than a cumulative total of fifteen (15) minutes (sixty (60) readings as measured according to 40 CFR 60, Appendix A, Method 9 or fifteen (15) one (1) minute nonoverlapping integrated averages for a continuous opacity monitor) in a six (6) hour period.

C.3 Open Burning [326 IAC 4-1] [IC 13-17-9]

The Permittee shall not open burn any material except as provided in 326 IAC 4-1-3, 326 IAC 4-1-4 or 326 IAC 4-1-6. The previous sentence notwithstanding, the Permittee may open burn in accordance with an open burning approval issued by the Commissioner under 326 IAC 4-1-4.1. 326 IAC 4-1-3 (a)(2)(A) and (B) are not federally enforceable.

C.4 Incineration [326 IAC 4-2] [326 IAC 9-1-2]

The Permittee shall not operate an incinerator or incinerate any waste or refuse except as provided in 326 IAC 4-2 and 326 IAC 9-1-2. 326 IAC 9-1-2 is not federally enforceable.

C.5 Fugitive Dust Emissions [326 IAC 6-4]

The Permittee shall not allow fugitive dust to escape beyond the property line or boundaries of the property, right-of-way, or easement on which the source is located, in a manner that would violate 326 IAC 6-4 (Fugitive Dust Emissions). 326 IAC 6-4-2(4) is not federally enforceable.

C.6 Operation of Equipment [326 IAC 2-7-6(6)]

Except as otherwise provided by statute or rule, or in this permit, all air pollution control equipment listed in this permit and used to comply with an applicable requirement shall be operated at all times that the emission units vented to the control equipment are in operation.

C.7 Stack Height [326 IAC 1-7]

The Permittee shall comply with the applicable provisions of 326 IAC 1-7 (Stack Height Provisions), for all exhaust stacks through which a potential (before controls) of twenty-five (25) tons per year or more of particulate matter or sulfur dioxide is emitted. The provisions of 326 IAC 1-7-2, 326 IAC 1-7-3(c) and (d), 326 IAC 1-7-4(d), (e), and (f), and 326 IAC 1-7-5(d) are not federally enforceable.

C.8 Asbestos Abatement Projects [326 IAC 14-10] [326 IAC 18] [40 CFR 61, Subpart M]

- (a) Notification requirements apply to each owner or operator. If the combined amount of regulated asbestos containing material (RACM) to be stripped, removed or disturbed is at least 260 linear feet on pipes or 160 square feet on other facility components, or at least thirty-five (35) cubic feet on all facility components, then the notification requirements of 326 IAC 14-10-3 are mandatory. All demolition projects require notification whether or not asbestos is present.

- (b) The Permittee shall ensure that a written notification is sent on a form provided by the Commissioner at least ten (10) working days before asbestos stripping or removal work or before demolition begins, per 326 IAC 14-10-3, and shall update such notice as necessary, including, but not limited to the following:
 - (1) When the amount of affected asbestos containing material increases or decreases by at least twenty percent (20%); or
 - (2) If there is a change in the following:
 - (A) Asbestos removal or demolition start date;
 - (B) Removal or demolition contractor; or
 - (C) Waste disposal site.

- (c) The Permittee shall ensure that the notice is postmarked or delivered according to the guidelines set forth in 326 IAC 14-10-3(2).

- (d) The notice shall include a signed certification from the owner or operator that the information provided in this notification is correct and that only Indiana licensed workers and project supervisors will be used to implement the asbestos removal project. The notifications do not require a certification by the "responsible official" as defined by 326 IAC 2-7-1(34).

All required notifications shall be submitted to:

Indiana Department of Environmental Management
Asbestos Section, Office of Air Quality
100 North Senate Avenue, P.O. Box 6015
Indianapolis, Indiana 46206-6015

The notice shall include a signed certification from the owner or operator that the information provided in this notification is correct and that only Indiana licensed workers and project supervisors will be used to implement the asbestos removal project. The notifications do not require a certification by the "responsible official" as defined by 326 IAC 2-7-1(34).

- (e) **Procedures for Asbestos Emission Control**
The Permittee shall comply with the applicable emission control procedures in 326 IAC 14-10-4 and 40 CFR 61.145(c). Per 326 IAC 14-10-4, emission control requirements are applicable for any removal or disturbance of RACM greater than three (3) linear feet on pipes or three (3) square feet on any other facility components or a total of at least 0.75 cubic feet on all facility components.

- (f) **Indiana Accredited Asbestos Inspector**

The Permittee shall comply with 326 IAC 14-10-1(a) that requires the owner or operator, prior to a renovation/demolition, to use an Indiana Accredited Asbestos Inspector to thoroughly inspect the affected portion of the facility for the presence of asbestos. The requirement that the inspector be accredited, pursuant to the provisions of 40 CFR 61, Subpart M, is federally enforceable.

Testing Requirements [326 IAC 2-7-6(1)]

C.9 Performance Testing [326 IAC 3-6]

- (a) All testing shall be performed according to the provisions of 326 IAC 3-6 (Source Sampling Procedures), except as provided elsewhere in this permit, utilizing any applicable procedures and analysis methods specified in 40 CFR 51, 40 CFR 60, 40 CFR 61, 40 CFR 63, 40 CFR 75, or other procedures approved by IDEM, OAQ.

A test protocol, except as provided elsewhere in this permit, shall be submitted to:

Indiana Department of Environmental Management
Compliance Data Section, Office of Air Quality
100 North Senate Avenue, P. O. Box 6015
Indianapolis, Indiana 46206-6015

no later than thirty-five (35) days prior to the intended test date. The protocol submitted by the Permittee does not require certification by the "responsible official" as defined by 326 IAC 2-7-1(34).

- (b) The Permittee shall notify IDEM, OAQ of the actual test date at least fourteen (14) days prior to the actual test date. The notification submitted by the Permittee does not require certification by the "responsible official" as defined by 326 IAC 2-7-1(34).
- (c) Pursuant to 326 IAC 3-6-4(b), all test reports must be received by IDEM, OAQ not later than forty-five (45) days after the completion of the testing. An extension may be granted by IDEM, OAQ, if the source submits to IDEM, OAQ, a reasonable written explanation not later than five (5) days prior to the end of the initial forty-five (45) day period.

Compliance Requirements [326 IAC 2-1.1-11]

C.10 Compliance Requirements [326 IAC 2-1.1-11]

The commissioner may require stack testing, monitoring, or reporting at any time to assure compliance with all applicable requirements. Any monitoring or testing shall be performed in accordance with 326 IAC 3 or other methods approved by the commissioner or the U. S. EPA.

Compliance Monitoring Requirements [326 IAC 2-7-5(1)] [326 IAC 2-7-6(1)]

C.11 Compliance Monitoring [326 IAC 2-7-5(3)] [326 IAC 2-7-6(1)]

Unless otherwise specified in this permit, all monitoring and record keeping requirements not already legally required shall be implemented within ninety (90) days of permit issuance. If required by Section D, the Permittee shall be responsible for installing any necessary equipment and initiating any required monitoring related to that equipment. If due to circumstances beyond its control, that equipment cannot be installed and operated within ninety (90) days, the Permittee may extend the compliance schedule related to the equipment for an additional ninety (90) days provided the Permittee notifies:

Indiana Department of Environmental Management
Compliance Branch, Office of Air Quality

100 North Senate Avenue, P. O. Box 6015
Indianapolis, Indiana 46206-6015

in writing, prior to the end of the initial ninety (90) day compliance schedule, with full justification of the reasons for the inability to meet this date.

The notification which shall be submitted by the Permittee does require the certification by the "responsible official" as defined by 326 IAC 2-7-1(34).

Unless otherwise specified in the approval for the new emission unit(s), compliance monitoring for new emission units or emission units added through a source modification shall be implemented when operation begins.

C.12 Monitoring Methods [326 IAC 3] [40 CFR 60] [40 CFR 63]

Any monitoring or testing required by Section D of this permit shall be performed according to the provisions of 326 IAC 3, 40 CFR 60, Appendix A, 40 CFR 60 Appendix B, 40 CFR 63, or other approved methods as specified in this permit.

C.13 Pressure Gauge and Other Instrument Specifications [326 IAC 2-1.1-11] [326 IAC 2-7-5(3)] [326 IAC 2-7-6(1)]

- (a) Whenever a condition in this permit requires the measurement of pressure drop across any part of the unit or its control device, the gauge employed shall have a scale such that the expected normal reading shall be no less than twenty percent (20%) of full scale and be accurate within plus or minus two percent ($\pm 2\%$) of full scale reading.
- (b) Whenever a condition in this permit requires the measurement of a flow rate, the instrument employed shall have a scale such that the expected normal reading shall be no less than twenty percent (20%) of full scale and be accurate within plus or minus two percent ($\pm 2\%$) of full scale reading.
- (c) The Permittee may request the IDEM, OAQ approve the use of a pressure gauge or other instrument that does not meet the above specifications provided the Permittee can demonstrate an alternative pressure gauge or other instrument specification will adequately ensure compliance with permit conditions requiring the measurement of pressure drop or other parameters.

Corrective Actions and Response Steps [326 IAC 2-7-5] [326 IAC 2-7-6]

C.14 Emergency Reduction Plans [326 IAC 1-5-2] [326 IAC 1-5-3]

Pursuant to 326 IAC 1-5-2 (Emergency Reduction Plans; Submission):

- (a) The Permittee shall prepare written emergency reduction plans (ERPs) consistent with safe operating procedures.
- (b) These ERPs shall be submitted for approval to:

Indiana Department of Environmental Management
Compliance Branch, Office of Air Quality
100 North Senate Avenue, P.O. Box 6015
Indianapolis, Indiana 46206-6015

within ninety (90) days after the date of issuance of this permit.

The ERP does require the certification by the “responsible official” as defined by 326 IAC 2-7-1(34).

- (c) If the ERP is disapproved by IDEM, OAQ, the Permittee shall have an additional thirty (30) days to resolve the differences and submit an approvable ERP.
- (d) These ERPs shall state those actions that will be taken, when each episode level is declared, to reduce or eliminate emissions of the appropriate air pollutants.
- (e) Said ERPs shall also identify the sources of air pollutants, the approximate amount of reduction of the pollutants, and a brief description of the manner in which the reduction will be achieved.
- (f) Upon direct notification by IDEM, OAQ, that a specific air pollution episode level is in effect, the Permittee shall immediately put into effect the actions stipulated in the approved ERP for the appropriate episode level. [326 IAC 1-5-3]

C.15 Risk Management Plan [326 IAC 2-7-5(12)] [40 CFR 68.215]

If a regulated substance, subject to 40 CFR 68, is present at a source in more than a threshold quantity, 40 CFR 68 is an applicable requirement and the Permittee shall submit:

- (a) A compliance schedule for meeting the requirements of 40 CFR 68; or
- (b) As a part of the annual compliance certification submitted under 326 IAC 2-7-6(5), a certification statement that the source is in compliance with all the requirements of 40 CFR 68, including the registration and submission of a Risk Management Plan (RMP).

All documents submitted pursuant to this condition shall include the certification by the “responsible official” as defined by 326 IAC 2-7-1(34).

C.16 Compliance Response Plan - Preparation, Implementation, Records, and Reports [326 IAC 2-7-5] [326 IAC 2-7-6]

- (a) The Permittee is required to prepare a Compliance Response Plan (CRP) for each compliance monitoring condition of this permit. A CRP shall be submitted to IDEM, OAQ upon request. The CRP shall be prepared within ninety (90) days after issuance of this permit by the Permittee, supplemented from time to time by the Permittee, maintained on site, and comprised of:
 - (1) Reasonable response steps that may be implemented in the event that a response step is needed pursuant to the requirements of Section D of this permit, and an expected timeframe for taking reasonable response steps.
 - (2) If, at any time, the Permittee takes reasonable response steps that are not set forth in the Permittee’s current Compliance Response Plan and the Permittee documents such response in accordance with subsection (e) below, the Permittee shall amend its Compliance Response Plan to include such response steps taken.
- (b) For each compliance monitoring condition of this permit, reasonable response steps shall be taken when indicated by the provisions of that compliance monitoring condition as follows:
 - (1) Reasonable response steps shall be taken as set forth in the Permittee’s current Compliance Response Plan; or

- (2) If none of the reasonable response steps listed in the Compliance Response Plan is applicable or responsive to the excursion, the Permittee shall devise and implement additional response steps as expeditiously as practical. Taking such additional response steps shall not be considered a deviation from this permit so long as the Permittee documents such response steps in accordance with this condition.
 - (3) If the Permittee determines that additional response steps would necessitate that the emissions unit or control device be shut down, the IDEM, OAQ shall be promptly notified of the expected date of the shut down, the status of the applicable compliance monitoring parameter with respect to normal, and the results of the actions taken up to the time of notification.
 - (4) Failure to take reasonable response steps shall constitute a violation of the permit.
- (c) The Permittee is not required to take any further response steps for any of the following reasons:
- (1) A false reading occurs due to the malfunction of the monitoring equipment and prompt action was taken to correct the monitoring equipment.
 - (2) The Permittee has determined that the compliance monitoring parameters established in the permit conditions are technically inappropriate, has previously submitted a request for a minor permit modification to the permit, and such request has not been denied.
 - (3) An automatic measurement was taken when the process was not operating.
 - (4) The process has already returned or is returning to operating within "normal" parameters and no response steps are required.
- (d) When implementing reasonable steps in response to a compliance monitoring condition, if the Permittee determines that an exceedance of an emission limitation has occurred, the Permittee shall report such deviations pursuant to Section B-Deviations from Permit Requirements and Conditions.
- (e) The Permittee shall record all instances when response steps are taken. In the event of an emergency, the provisions of 326 IAC 2-7-16 (Emergency Provisions) requiring prompt corrective action to mitigate emissions shall prevail.
- (f) Except as otherwise provided by a rule or provided specifically in Section D, all monitoring as required in Section D shall be performed when the emission unit is operating, except for time necessary to perform quality assurance and maintenance activities.

C.17 Actions Related to Noncompliance Demonstrated by a Stack Test [326 IAC 2-7-5] [326 IAC 2-7-6]

- (a) When the results of a stack test performed in conformance with Section C - Performance Testing, of this permit exceed the level specified in any condition of this permit, the Permittee shall take appropriate response actions. The Permittee shall submit a description of these response actions to IDEM, OAQ, within thirty (30) days of receipt of the test results. The Permittee shall take appropriate action to minimize excess emissions from the affected facility while the response actions are being implemented.
- (b) A retest to demonstrate compliance shall be performed within one hundred twenty (120) days of receipt of the original test results. Should the Permittee demonstrate to IDEM,

OAQ that retesting in one-hundred and twenty (120) days is not practicable, IDEM, OAQ may extend the retesting deadline.

- (c) IDEM, OAQ reserves the authority to take any actions allowed under law in response to noncompliant stack tests.

The documents submitted pursuant to this condition do require the certification by the “responsible official” as defined by 326 IAC 2-7-1(34).

Record Keeping and Reporting Requirements [326 IAC 2-7-5(3)] [326 IAC 2-7-19]

C.18 Emission Statement [326 IAC 2-7-5(3)(C)(iii)] [326 IAC 2-7-5(7)] [326 IAC 2-7-19(c)] [326 IAC 2-6]

- (a) The Permittee shall submit an annual emission statement certified pursuant to the requirements of 326 IAC 2-6, that must be received by July 1 of each year and must comply with the minimum requirements specified in 326 IAC 2-6-4. The annual emission statement shall meet the following requirements:

- (1) Indicate estimated actual emissions of criteria pollutants from the source, in compliance with 326 IAC 2-6 (Emission Reporting);
- (2) Indicate estimated actual emissions of other regulated pollutants (as defined by 326 IAC 2-7-1) from the source, for purposes of Part 70 fee assessment.

- (b) The annual emission statement covers the twelve (12) consecutive month time period starting January 1 and ending December 31. The annual emission statement must be submitted to:

Indiana Department of Environmental Management
Technical Support and Modeling Section, Office of Air Quality
100 North Senate Avenue, P. O. Box 6015
Indianapolis, Indiana 46206-6015

The emission statement does require the certification by the “responsible official” as defined by 326 IAC 2-7-1(34).

- (c) The annual emission statement required by this permit shall be considered timely if the date postmarked on the envelope or certified mail receipt, or affixed by the shipper on the private shipping receipt, is on or before the date it is due. If the document is submitted by any other means, it shall be considered timely if received by IDEM, OAQ, on or before the date it is due.

C.19 General Record Keeping Requirements [326 IAC 2-7-5(3)] [326 IAC 2-7-6]

- (a) Records of all required data, reports and support information shall be retained for a period of at least five (5) years from the date of monitoring sample, measurement, report, or application. These records shall be kept at the source location for a minimum of three (3) years. The records may be stored elsewhere for the remaining two (2) years as long as they are available upon request. If the Commissioner makes a request for records to the Permittee, the Permittee shall furnish the records to the Commissioner within a reasonable time.

- (b) Unless otherwise specified in this permit, all record keeping requirements not already legally required shall be implemented within ninety (90) days of permit issuance.

C.20 General Reporting Requirements [326 IAC 2-7-5(3)(C)] [326 IAC 2-1.1-11]

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- (a) The source shall submit the attached Quarterly Deviation and Compliance Monitoring Report or its equivalent. Any deviation from permit requirements, the date(s) of each deviation, the cause of the deviation, and the response steps taken must be reported. This report shall be submitted within thirty (30) days of the end of the reporting period. The Quarterly Deviation and Compliance Monitoring Report shall include the certification by the "responsible official" as defined by 326 IAC 2-7-1(34).
- (b) The report required in (a) of this condition and reports required by conditions in Section D of this permit shall be submitted to:
- Indiana Department of Environmental Management
Compliance Data Section, Office of Air Quality
100 North Senate Avenue, P. O. Box 6015
Indianapolis, Indiana 46206-6015
- (c) Unless otherwise specified in this permit, any notice, report, or other submission required by this permit shall be considered timely if the date postmarked on the envelope or certified mail receipt, or affixed by the shipper on the private shipping receipt, is on or before the date it is due. If the document is submitted by any other means, it shall be considered timely if received by IDEM, OAQ, on or before the date it is due.
- (d) Unless otherwise specified in this permit, all reports required in Section D of this permit shall be submitted within thirty (30) days of the end of the reporting period. All reports do require the certification by the "responsible official" as defined by 326 IAC 2-7-1(34).
- (e) The first report shall cover the period commencing on the date of issuance of this permit and ending on the last day of the reporting period. Reporting periods are based on calendar years.

Stratospheric Ozone Protection

C.21 Compliance with 40 CFR 82 and 326 IAC 22-1

Pursuant to 40 CFR 82 (Protection of Stratospheric Ozone), Subpart F, except as provided for motor vehicle air conditioners in Subpart B, the Permittee shall comply with the standards for recycling and emissions reduction:

- (a) Persons opening appliances for maintenance, service, repair, or disposal must comply with the required practices pursuant to 40 CFR 82.156.
- (b) Equipment used during the maintenance, service, repair, or disposal of appliances must comply with the standards for recycling and recovery equipment pursuant to 40 CFR 82.158.
- (c) Persons performing maintenance, service, repair, or disposal of appliances must be certified by an approved technician certification program pursuant to 40 CFR 82.161.

SECTION D.1 FACILITY OPERATION CONDITIONS

Facility Description [326 IAC 2-7-5(15)]:

- (a) Truck Dump #2, identified as 1EL1, constructed in 1980, using a baghouse for particulate matter (PM) control, and exhausting to stack 1EL;
- (b) The following grain elevator components, together identified as 2EL1, using a baghouse and oil suppressant for PM control, and exhausting to stack 2EL:
 - (1) One (1) dryer megatex enclosed conveyor, constructed in 1997;
 - (2) One (1) dryer rotex, constructed in 1978;
 - (3) One (1) screening bin hammermill, constructed in 1978;
 - (4) One (1) #1 scalperator, constructed prior to 1977;
 - (5) One (1) #2 scalperator, constructed prior to 1977;
 - (6) One (1) #3 scalperator, constructed prior to 1977;
 - (7) One (1) ext. screening bin, constructed prior to 1977;
 - (8) One (1) screening bin, constructed prior to 1977;
 - (9) One (1) solvent screening leg, constructed prior to 1977;
 - (10) One (1) #1 leg, constructed prior to 1977;
 - (11) One (1) #2 leg, constructed prior to 1977;
 - (12) One (1) #3 leg, constructed prior to 1977;
 - (13) One (1) west to east Hi-Roller, constructed in 1992;
 - (14) One (1) west to east belt loader, constructed prior to 1977;
 - (15) One (1) dry bean leg, constructed prior to 1977;
 - (16) One (1) #1 dryer Hi-Roller, constructed in 1994;
 - (17) One (1) weaver's belt, constructed in 1994; and
 - (18) One (1) 102 belt, constructed in 1994;
- (c) The following grain elevator components, together identified as 5EL1, using a baghouse and oil suppressant for PM control, and exhausting to stack 5EL:
 - (1) One (1) north tripper buggy, constructed in 1978;
 - (2) One (1) north galley belt loader, constructed in 1978;
 - (3) One (1) east west belt, constructed in 1995; and

SECTION D.1 FACILITY OPERATION CONDITIONS (Continued)

Facility Description [326 IAC 2-7-5(15)]:

- (4) One (1) bin 102, constructed prior to 1977;
- (d) One (1) north west receiving house enclosed conveyor identified as 8EL1, constructed in 1995, using oil suppressant for PM control, with no aspiration;
- (e) The following grain elevator components, together identified as 10EL1, using a baghouse and oil suppressant for PM control, and exhausting to stack 10EL:
 - (1) One (1) rail loadout, constructed in 1984;
 - (2) One (1) north leg, constructed prior to 1960; and
 - (3) One (1) south leg, constructed prior to 1960;
- (f) The following grain elevator components, together identified as 14EL1, using a baghouse and oil suppressant for PM control, and exhausting to stack 14EL:
 - (1) One (1) jumbo silo east galley belt, constructed prior to 1977;
 - (2) One (1) jumbo silo west galley belt, constructed in 1993; and
 - (3) One (1) jumbo silo crossover galley belt, constructed prior to 1977;
- (g) One (1) grain dryer #2, identified as 19EL1, constructed in 1995, using self-cleaning screens for PM control, and exhausting to stack 19EL;
- (h) One (1) natural gas dryer #2 associated with grain dryer #2, identified as 19EL2, constructed in 1995, and exhausting to stack 19EL;
- (i) One (1) truck dump #7, identified as 20EL1, constructed in 1997, consisting of one (1) weigh scale truck unloading pit, and two (2) enclosed bucket elevator legs, using two (2) baghouses in parallel for PM control, and exhausting to stack 20EL.

(The information describing the process contained in this facility description box is descriptive information and does not constitute enforceable conditions.)

Emission Limitations and Standards [326 IAC 2-7-5(1)]

D.1.1 General Provisions Relating to NSPS [326 IAC 12-1][40 CFR Part 60, Subpart A]

The provisions of 40 CFR Part 60, Subpart A - General Provisions, which are incorporated by reference in 326 IAC 12-1, apply to the affected facilities described in this section except when otherwise specified in 40 CFR Part 60, Subpart DD.

D.1.2 New Source Performance Standards (NSPS) Grain Elevators [326 IAC 12][40 CFR Subpart DD 60.302]

Pursuant to 40 CFR Part 60, Subpart DD 60.302(b), process emission gases discharged into the atmosphere from the following units:

- (a) Unit 1EL1: Truck Dump #2;

- (b) Unit 10EL1: Rail loadout; and
- (c) Unit 20EL1: Truck Dump #7.

shall not exceed particulate matter (PM) concentrations of 0.01 gr/dscf. Process emission gases from these facilities shall not exhibit greater than 0 percent opacity.

D.1.3 PSD Limit [326 IAC 2-2] [40 CFR 52.21]

Pursuant to CP001-4673-00005, issued May 10, 1996, the amount of soybean grains processed after the grain dryers shall be limited to less than 1,368,750 tons per twelve (12) consecutive month period. This limit, in combination with the limits in Conditions D.2.2 and D.5.3, restricts the net increases of PM and PM10 emissions for the modification in 1996 to below the PSD significant levels of twenty-five (25) and fifteen (15) tons per year, respectively, and also satisfies the requirements of 326 IAC 6-3-2 (Process Operations). This limit is equivalent to the following hourly limits for unit 19EL: less than 1.36 pounds per hour of PM; and less than 0.283 pounds per hour of PM10. This will render the requirements of 326 IAC 2-2 (Prevention of Significant Deterioration) and 40 CFR 52.21 not applicable.

D.1.4 Particulate Matter (PM) [326 IAC 6-3-2]

Pursuant to 326 IAC 6-3-2 (Process Operations), the particulate matter (PM) from the following units shall be limited by the equation following this table:

Unit	Description
2EL1	Dryer Rotex Feed Drag, Dryer Rotex, Screening Bin Hammermill, #1, #2, and #3 Scalperators, Solvent Screening Leg, #1, #2, and #2 Leg, West to East Belt Head Section, West to East Belt Loader, Dry Bean Leg, #1 Dryer Hi-Roller, Weaver's Belt, 102 Belt
5EL1	North Tripper Buggy, West Workhouse Turnhead, North Galley Belt Loader, East West Belt, West Workhouse to East Workhouse Belt Loader
8EL1	North West Receiving House Tunnel Belt
14EL1	Jumbo Silo East Galley Belt, Jumbo Silo West Galley Belt, Jumbo Silo Crossover Galley Belt
19EL1	Grain Dryer #2

Interpolation and extrapolation of the data for the process weight rate in excess of 60,000 pounds per hour shall be accomplished by use of the equation:

$$E = 55.0 P^{0.11} - 40 \quad \text{where } E = \text{rate of emission in pounds per hour; and}$$

$$P = \text{process weight rate in tons per hour}$$

The individual limitations are included in a IDEM, OAQ confidential file because the process weight rates are considered confidential by the source.

D.1.5 Preventive Maintenance Plan [326 IAC 2-7-5(13)]

A Preventive Maintenance Plan, in accordance with Section B - Preventive Maintenance Plan, of this permit, is required for this facility and its control device.

Compliance Determination Requirements

D.1.6 Particulate Matter (PM)

- (a) In order to comply with Conditions D.1.2, D.1.3, and D.1.4, the baghouses for PM control shall be in operation and control emissions from 1EL1, 2EL1, 5EL1, 10EL1, 14EL1, and 20EL1 at all times that the processes are in operation.

- (b) In order to comply with Conditions D.1.2, D.1.3, and D.1.4, the self-cleaning screens for PM control shall be in operation and control emissions from 19EL1 at all times that the process is in operation.
- (c) In order to comply with Conditions D.1.2, D.1.3, and D.1.4, dust control oil shall be applied at all times that 2EL1, 5EL1, 1EL1, 10EL1, and 14EL1 are in operation.

Compliance Monitoring Requirements [326 IAC 2-7-6(1)] [326 IAC 2-7-5(1)]

D.1.7 Visible Emissions Notations

- (a) Once per shift visible emission notations of Unit 1EL1, 2EL1, 5EL1, 10EL1, 14EL1, 19EL1, and 20EL1 stack exhaust shall be performed during normal daylight operations when exhausting to the atmosphere. A trained employee shall record whether emissions are normal or abnormal.
- (b) For processes operated continuously, "normal" means those conditions prevailing, or expected to prevail, eighty percent (80%) of the time the process is in operation, not counting startup or shut down time.
- (c) In the case of batch or discontinuous operations, readings shall be taken during that part of the operation that would normally be expected to cause the greatest emissions.
- (d) A trained employee is an employee who has worked at the plant at least one (1) month and has been trained in the appearance and characteristics of normal visible emissions for that specific process.
- (e) The Compliance Response Plan for these processes shall contain troubleshooting contingency and response steps for when an abnormal emission is observed. Failure to take response steps in accordance with Section C - Compliance Response Plan - Preparation, Implementation, Records, and Reports, shall be considered a violation of this permit.

D.1.8 Parametric Monitoring

The Permittee shall record the total static pressure drop across the baghouses used in conjunction with 1EL1, 2EL1, 5EL1, 10EL1, 14EL1, and 20EL1 at least once per shift when the processes are in operation when venting to the atmosphere. When for any one reading, the pressure drop across the baghouses is outside the normal range of 3.0 and 6.0 inches of water or a range established during the latest stack test, the Permittee shall take reasonable response steps in accordance with Section C - Compliance Response Plan - Preparation, Implementation, Records, and Reports. A pressure reading that is outside the above mentioned range is not a deviation from this permit. Failure to take response steps in accordance with Section C - Compliance Response Plan - Preparation, Implementation, Records, and Reports, shall be considered a violation of this permit.

The instrument used for determining the pressure shall comply with Section C - Pressure Gauge and Other Instrument Specifications, of this permit, shall be subject to approval by IDEM, OAQ, and shall be calibrated at least once every six (6) months.

D.1.9 Baghouse and Self-Cleaning Screen Inspections

An inspection shall be performed once per year of all bags and self-cleaning screens controlling the facilities when venting to the atmosphere. Inspections are optional when venting to the indoors. All defective bags and screens shall be replaced.

D.1.10 Broken or Failed Bag or Screen Detection

In the event that bag failure has been observed:

- (a) For multi-compartment units, the affected compartments will be shut down immediately until the failed units have been repaired or replaced. Operations may continue only if there are no visible emissions or if the event qualifies as an emergency and the Permittee satisfies the emergency provisions of this permit (Section B- Emergency Provisions). Within eight (8) business hours of the determination of failure, response steps according to the timetable described in the Compliance Response Plan shall be initiated. For any failure with corresponding response steps and timetable not described in the Compliance Response Plan, response steps shall be devised within eight (8) business hours of discovery of the failure and shall include a timetable for completion. Failure to take response steps in accordance with Section C - Compliance Response Plan - Preparation, Implementation, Records, and Reports, shall be considered a violation of this permit.
- (b) For single compartment baghouses, failed units and the associated process will be shut down immediately until the failed units have been repaired or replaced. Operations may continue only if the event qualifies as an emergency and the Permittee satisfies the requirements of the emergency provisions of this permit (Section B - Emergency Provisions).

Record Keeping and Reporting Requirement [326 IAC 2-7-5(3)] [326 IAC 2-7-19]

D.1.11 Record Keeping Requirements

- (a) To document compliance with Condition D.1.3, the Permittee shall maintain records of the amount of soybean grains processed after the grain dryers. This is the same record that is required in Conditions D.2.11(a) and D.5.12(a).
- (b) To document compliance with Condition D.1.7, the Permittee shall maintain records of once per shift visible emission notations of the stack exhaust.
- (c) To document compliance with Condition D.1.8, the Permittee shall maintain once per shift records of the total pressure drop across the baghouse during normal operation when venting to the atmosphere.
- (d) To document compliance with Condition D.1.9, the Permittee shall maintain records of the results of the inspections required under Condition D.1.9 and the dates the vents are redirected.
- (e) All records shall be maintained in accordance with Section C - General Record Keeping Requirements, of this permit.

D.1.12 Reporting Requirements

A quarterly summary of the information to document compliance with Condition D.1.3 shall be submitted to the address listed in Section C - General Reporting Requirements, of this permit, using the reporting forms located at the end of this permit, or their equivalent, within thirty (30) days after the end of the quarter being reported. The report submitted by the Permittee does require the certification by the "responsible official" as defined by 326 IAC 2-7-1(34). This is the same report as required in Condition D.2.11 and D.5.12.

SECTION D.2 FACILITY OPERATION CONDITIONS

Facility Description [326 IAC 2-7-5(15)]:

- (j) Silo bin vents, identified as 3EL1, constructed prior to 1977, using soybean oil as a dust suppressant, and exhausting to stack 3EL;
- (k) Silo direct loadout, identified as 4EL1, constructed prior to 1977, using soybean oil as a dust suppressant, and exhausting to stack 4EL;
- (l) One (1) south tripper buggy, one (1) south galley belt loader, and one (1) north south belt, identified as 6EL1, all constructed prior to 1977, using a baghouse and oil suppressant for PM control, and exhausting to stack 6EL;
- (m) One (1) south west receiving house enclosed conveyor, identified as 7EL1, constructed in 1995, using oil suppressant for PM control with no aspiration;
- (n) One (1) truck dump #3, identified as 9EL1, constructed in 1976, using a baghouse for PM control, and exhausting to stack 9EL;
- (o) One (1) truck dump #5, identified as 12EL1, constructed prior to 1977, using a baghouse for PM control, and exhausting to stack 12EL;
- (p) One (1) jumbo silo east tunnel belt, one (1) jumbo silo west tunnel belt, and one (1) jumbo silo crossover tunnel belt, identified as 13EL1, all constructed prior to 1977, using a baghouse and oil suppressant for PM control, and exhausting to stack 13EL;
- (q) One (1) truck dump #6, identified as 15EL1, constructed prior to 1977, using a baghouse for PM control, and exhausting to stack 15EL;
- (r) Two (2) grain dryers, # 4 and #5, identified as 17EL1, constructed in the 1960's, using self-cleaning screens for PM control, and exhausting to stack 17EL;
- (s) Two (2) natural gas fired dryers, #4 and #5, associated with grain dryers #4 and #5 respectively, identified as 17EL2, constructed in the 1960's, and exhausting to stack 17EL;
- (t) One (1) Lec. Dept. filter aid unit, identified as 204RO1, constructed in 1980, with a maximum capacity of 2.5 tons of diatomaceous earth per hour, using a baghouse for PM control, and exhausting to stack 204RO;
- (u) Daily use bins, identified as 102EO1, constructed in 1976, using a baghouse for PM control, and exhausting to stack 102EO;
- (v) Filter aid silos, identified as 103EO1, constructed in 1976, using a baghouse for PM control, and exhausting to stack 103EO;
- (w) One (1) natural gas fired hydrogen generator furnace, identified as 107EO1, constructed in 1992, and exhausting to stack 107EO;
- (x) Salt conveying, identified as 4SP1, constructed in 1981, using a baghouse for PM control, and exhausting to stack 4SP;
- (y) Lime conveying, identified as 5SP1, constructed in 1981, using a baghouse for PM control, and exhausting to stack 5SP;

SECTION D.2 FACILITY OPERATION CONDITIONS (Continued)

Facility Description [326 IAC 2-7-5(15)]:

- (z) One (1) vertical pellet cooler, constructed in 1967, and one (1) horizontal pellet cooler, constructed in the 1950's, identified as 1EF1, using a cyclone for PM control;
- (aa) One (1) corn grinding equipment, identified as 2EF1, constructed in 1992, using a cyclone for PM control.
- (bb) Ingredient grinding equipment, identified as 2EF2, constructed in the early 1970's;
- (cc) Feed Ingredient receiving, identified as 3EF1, constructed in the early 1970's;
- (dd) Bulk loadout, identified as 4EF1, constructed in the early 1970's;
- (ee) One (1) micro room, identified as 5EF1, constructed in the 1940's;
- (ff) Six (6) flaking rolls, #1, #2, #3, #4, #5, and #6, constructed in 1996, and B flake n/s drag, constructed in 1991, all identified together as 1EX1, sharing Vox filters with 1EX2 for PM control, and exhausting to stack 1EX;
- (gg) One (1) flaking roll #14 and flaking roll discharge #14, identified as 1EX2, constructed in 1991, sharing Vox filters with 1EX1 for PM control, and exhausting to stack 1EX;
- (hh) One (1) 'A' conditioner, identified as 2EX1, constructed in the 1930's, with no PM control, and exhausting to stack 2EX;
- (ii) The following soybean processing equipment, together identified as 3EX1, sharing a cyclone with 3EX2 for PM control, and exhausting to stack 3EX:
 - (1) Four (4) flaking rolls, #9, #10, #11, and #12, constructed in 1978;
 - (2) One (1) flaking roll #13, constructed in 1985;
 - (3) One (1) 'A' flake n/s drag, constructed in 1993; and
 - (4) One (1) 'A' flake e/w drag, constructed in 1993;
- (jj) One (1) north run around drag, identified as 3EX2, constructed in 1984, sharing a cyclone with 3EX1, and exhausting to stack 3EX;
- (kk) The following soybean processing equipment, together identified as 4EX1, sharing a baghouse with 4EX2 and 4EX3 for PM control, and exhausting to stack 4EX:
 - (1) One (1) whole bean scale, constructed in 1989;
 - (2) One (1) 'A' whole bean leg, constructed in 1997;
 - (3) One (1) 'A' surge bin, constructed prior to 1979;
 - (4) One (1) whole bean drag, constructed in 1981; and
 - (5) One (1) 'B' surge bin, constructed prior to 1979;

SECTION D.2 FACILITY OPERATION CONDITIONS (Continued)

Facility Description [326 IAC 2-7-5(15)]:

- (ll) A run around rework screw, identified as 4EX2, constructed in 1991, sharing a baghouse with 4EX1 and 4EX3 for PM control, and exhausting to stack 4EX;
- (mm) The following soybean processing equipment, together identified as 4EX3, sharing a baghouse with 4EX1 and 4EX2 for PM control, and exhausting to stack 4EX:
 - (1) One (1) hull refining screw conveyor, constructed in 1991;
 - (2) One (1) hull refining process, constructed in 1991; and
 - (3) One (1) hull grinding process, constructed in 1987;
- (nn) Dehulling equipment, identified as 5EX1, constructed in 1997, sharing a baghouse with 5EX2 and 5EX3 for PM control, and exhausting to stack 5EX;
- (oo) Hot dehulling equipment, identified as 5EX2, constructed in 1991, sharing a baghouse with 5EX1 and 5EX3 for PM control, and exhausting to stack 5EX;
- (pp) Screening aspiration, identified as 5EX3, constructed in 1988, sharing a baghouse with 5EX1 and 5EX2 for PM control, and exhausting to stack 5EX;
- (qq) Truck loadout, identified as 6EX1, constructed in 1982, replaced in 1999, using a baghouse for PM control, and exhausting to stack 6EX;
- (rr) The following soybean processing equipment, together identified as 7EX1, using a baghouse for PM control, and exhausting to stack 7EX:
 - (1) One (1) north megamill, constructed in 1993;
 - (2) One (1) south megamill, constructed in 1993; and
 - (3) One (1) stedman grinder, constructed in 1983;
- (ss) One (1) leg No. 2, one (1) mixing conveyor, and one (1) bin drag, together identified as 9EX1, all constructed in 1983, using a baghouse for PM control, and exhausting to stack 9EX;
- (tt) The following soybean processing equipment, together identified as 10EX1, using a baghouse for PM control, and exhausting to stack 10EX:
 - (1) One (1) leg No. 3, constructed in the 1950's;
 - (2) One (1) tunnel drag, constructed in 1983; and
 - (3) One (1) meal loadout drag, constructed in 1982;
- (uu) One (1) kaolin bin, identified as 11EX1, constructed in the 1950's, using a baghouse for PM control, and exhausting to stack 11EX;
- (wv) One (1) meal loadout bin, identified as 12EX1, constructed in 1982, using a baghouse for PM control, and exhausting to stack 12EX;

SECTION D.2 FACILITY OPERATION CONDITIONS (Continued)

Facility Description [326 IAC 2-7-5(15)]:

- (ww) One (1) pre-DT section on top of 'A' top dryer section, constructed in 1996, and exhausting to 'A' top dryer section for PM control and one (1) 'A' top dryer section, identified as 13EX1, constructed in 1980, using a cyclone for PM control, exhausting to stack 13EX, with hexane emissions directed to stack 24EX;
- (xx) One (1) 'A' middle dryer section, identified as 13EX2, constructed in 1980, using a cyclone for PM control, exhausting to stack 13EX, with hexane emissions directed to stack 24EX;
- (yy) One (1) 'A' bottom cooler section, identified as 13EX3, constructed in 1980, using a cyclone for PM control, exhausting to stack 13EX, with hexane emissions directed to stack 24EX;
- (zz) One (1) pre-DT section on top of 'B' top dryer section, constructed in 1996, and exhausting to 'B' top dryer section for PM control, and one (1) 'B' top dryer section, identified as 14EX1, constructed in 1980, using a cyclone for PM control, exhausting to stack 14EX, with hexane emissions directed to stack 24EX;
- (aaa) One (1) 'B' middle dryer section, identified as 14EX2, constructed in 1980, using a cyclone for PM control, exhausting to stack 14EX, with hexane emissions directed to stack 24EX;
- (bbb) One (1) 'B' bottom cooler section, identified as 14EX3, constructed in 1980, using a cyclone for PM control, exhausting to stack 14EX, with hexane emissions directed to stack 24EX;
- (ccc) One (1) meal cooler, identified as 21EX, constructed in 1996, using two (2) cyclones for PM control and exhausting to stacks 21EX-A and 21EX-B, with hexane emissions directed to stack 24EX;
- (ddd) One (1) belt to storage bowls, one (1) large storage bowl, and one (1) small storage bowl, identified as 16EX1, 16EX2, and 16EX3, respectively, all constructed in 1982, with no PM control, and exhausting to stack 16EX;
- (eee) Whole bean bins, identified as 18EX1, constructed in the 1940's, with no PM control, and exhausting to stack 18EX;
- (fff) Meal storage silos with bin vents, identified as 23EX1, constructed in the 1950's, and one (1) bin vent filter, exhausting to stack 23EX;
- (ggg) One (1) zinc receiving bin, identified as 25EX1, constructed in 1994, sharing a bin vent filter with 25EX2 for PM control, and exhausting to stack 25EX;
- (hhh) One (1) zinc surge bin, identified as 25EX2, constructed in 1994, sharing a bin vent filter with 25EX1 for PM control, and exhausting to stack 25EX;
- (iii) One (1) rumen conveyor, identified as 8EX1, constructed in 1994, using a cyclone for PM control, and exhausting to stack 8EX;
- (jjj) One (1) rotary reactor, identified as 27EX1, constructed in the 1994, using a cyclone for PM control, and exhausting to stack 27EX;
- (kkk) Rumen loadout bins, identified as 29EX1, constructed in 1994, using a bin vent filter for PM control, and exhausting to stack 29EX;

SECTION D.2 FACILITY OPERATION CONDITIONS (Continued)

Facility Description [326 IAC 2-7-5(15)]:

(III) Rumen rework surge bin, identified as 30EX1, constructed in 1994, using a polyethylene fabric filter for PM control, and exhausting to stack 30EX;

(The information describing the process contained in this facility description box is descriptive information and does not constitute enforceable conditions.)

Emission Limitations and Standards [326 IAC 2-7-5(1)]

D.2.1 Particulate Matter (PM) [326 IAC 6-3-2]

Pursuant to 326 IAC 6-3-2 (Process Operations), the particulate matter (PM) from the following units shall not exceed the pound per hour emission rate calculated using the equation following this table:

Unit	Description
3EL1	Silo Bin Vents
4EL1	Silo Direct Loadout
6EL1	South Tripper Buggy, South Galley Belt Loader, North South Belt
7EL1	South West Receiving House Tunnel Belt
9EL1	Truck Dump #3
12EL1	Truck Dump #5
13EL1	Jumbo Silo East Tunnel Belt, Jumbo Silo West Tunnel Belt, Jumbo Silo Crossover Tunnel Belt
15EL1	Truck Dump #6
16EL1	Grain Dryer #1
17EL1	Grain Dryer #4 and #5
204RO1	Lec. Dept. Filter Aid Unit
102EO1	Daily Use Bins
103EO1	Filter Aid Silos
4SP1	Salt Conveying
5SP1	Lime Conveying
1EF1	Vertical Pellet Cooler and Horizontal Pellet Cooler
2EF1	Corn Grinding Equipment
2EF2	Ingredient Grinding Equipment
5EF1	Micro Room
1EX1	Flaking Roll #1, #2, #3, #4, #5, #6, B Flake N/S Drag
1EX2	Flaking Roll #14, Flaking Roll Discharge #14
2EX1	'A' Conditioner
3EX1	Flaking Roll #9, #10, #11, #12, #13, 'A' Flake N/S Drag, 'A' Flake E/W Drag
3EX2	North Run Around Drag
4EX1	Whole Bean Scale, 'A' Whole Bean Leg, 'A' Surge Bin, Whole Bean Drag, 'B' Surge Bin
4EX2	Run Around Rework Screw
4EX3	Hull Refining Screw Conveyor, Hull Refining Process, Hull Grinding Process
5EX1	Dehulling Equipment

Unit	Description
5EX2	Hot Dehulling Equipment
5EX3	Screening
6EX1	Truck Loadout
7EX1	North Megamill, South Megamill, Stedman Grinder
9EX1	Leg No. 2, Mixing Conveyor, Bin Drag
10EX1	Leg No.3, tunnel drag, meal loadout drag
11EX1	Kaolin Bin
12EX1	Meal Loadout Bin
13EX1	Pre-DT and 'A' Top Dryer Section
13EX2	'A' Middle Dryer Section
13EX3	'A' Bottom Cooler Section
14EX1	Pre-DT and 'B' Top Dryer Section
14EX2	'B' Middle Dryer Section
14EX3	'B' Bottom Cooler Section
16EX1	Belt to Storage Bowls
16EX2	Large Storage Bowl
16EX3	Small Storage Bowl
18EX1	Whole Bean Bins
21EX1	A and B Cooler
23EX1	Meal Storage Silos
25EX1	Zinc Receiving Bin
25EX2	Zinc Surge Bin
27EX1	Rotary Reactor
8EX1	Rumen Conveyor
29EX1	Rumen Loadout Bins
30EX1	Rumen Surge Bin

Interpolation of the data for the process weight rate up to sixty thousand (60,000) pounds per hour shall be accomplished by use of the equation:

$$E = 4.10 P^{0.67} \quad \text{where } E = \text{rate of emission in pounds per hour and} \\ P = \text{process weight rate in tons per hour}$$

and

Interpolation and extrapolation of the data for the process weight rate in excess of sixty thousand (60,000) pounds per hour shall be accomplished by use of the equation:

$$E = 55.0 P^{0.11} - 40 \quad \text{where } E = \text{rate of emission in pounds per hour} \\ P = \text{process weight rate in tons per hour}$$

The individual limitations are included in a IDEM, OAQ confidential file because the process weight rates are considered confidential by the source.

Pursuant to CP001-4673-00005, issued May 10, 1996, the amount of soybean grains processed after the grain dryers shall be limited to less than 1,368,750 tons per twelve (12) consecutive month period. This limit, in combination with the limits in Conditions D.1.3 and D.5.3, restricts the net increases of PM and PM10 emissions from the modification in 1996 to below the PSD significant levels of twenty-five (25) and fifteen (15) tons per year, respectively, and also satisfies the requirements of 326 IAC 6-3-2 (Process Operations). This limit is equivalent to the following individual limits:

Unit	PM Limit (lb/hr)	PM10 Limit (lb/hr)
1EX	0.516	0.320
4EX	1.181	0.230
5EX	1.684	0.255
7EX	0.351	0.254
13EX	7.38	4.43
14EX	7.38	4.43
21EX	17.7	10.8
23EX	3.28	1.64
6EX	0.056	0.008

This will render the requirements of 326 IAC 2-2 (Prevention of Significant Deterioration) and 40 CFR 52.21 not applicable.

D.2.3 Preventive Maintenance Plan [326 IAC 2-7-5(13)]

A Preventive Maintenance Plan, in accordance with Section B - Preventive Maintenance Plan, of this permit, is required for this facility and its control device.

Compliance Determination Requirements

D.2.4 Particulate Matter (PM)

- (a) In order to comply with Conditions D.2.1 and D.2.2, the baghouses, filters, and cyclones for PM control shall be in operation and control emissions from the listed facilities at all times that the facilities are in operation.
- (b) In order to comply with Conditions D.2.1 and D.2.2, dust control oil shall be applied at all times that facilities whose descriptions above mention oil dust suppressant are in operation.
- (c) In order to comply with Conditions D.2.1 and D.2.2, the self-cleaning screens for PM control shall be in operation and control emissions from the facilities whose descriptions above mention the use of self-cleaning screens at all times that these facilities are in operation.

Compliance Monitoring Requirements [326 IAC 2-7-6(1)] [326 IAC 2-7-5(1)]

D.2.5 Visible Emissions Notations

- (a) Once per shift visible emission notations of 3EL, 4EL, 6EL, 9EL, 12EL, 13EL, 15EL, 17EL, 103EO, 4SP, 5SP, 1EX, 3EX, 4EX, 5EX, 6EX, 7EX, 9EX, 10EX, 11EX, 12EX, 13EX, 14EX, 21EX-A, 21EX-B, 23EX, 25EX, 8EX, 27EX, 29EX, and 30EX stack exhaust shall be performed during normal daylight operations when exhausting to the atmosphere. A trained employee shall record whether emissions are normal or abnormal.

- (b) For processes operated continuously, "normal" means those conditions prevailing, or expected to prevail, eighty percent (80%) of the time the process is in operation, not counting startup or shut down time.
- (c) In the case of batch or discontinuous operations, readings shall be taken during that part of the operation that would normally be expected to cause the greatest emissions.
- (d) A trained employee is an employee who has worked at the plant at least one (1) month and has been trained in the appearance and characteristics of normal visible emissions for that specific process.
- (e) The Compliance Response Plan for these processes shall contain troubleshooting contingency and response steps for when an abnormal emission is observed. Failure to take response steps in accordance with Section C - Compliance Response Plan - Preparation, Implementation, Records, and Reports, shall be considered a violation of this permit.

D.2.6 Parametric Monitoring

The Permittee shall record the total static pressure drop across the baghouses and filters controlling 6EL, 9EL, 12EL, 13EL, 15EL, 103EO, 4SP, 5SP, 1EX, 3EX, 4EX, 5EX, 6EX, 7EX, 9EX, 10EX, 11EX, 12EX, 25EX, 29EX, and 30EX at least once per shift when the processes are in operation when venting to the atmosphere. When for any one reading, the pressure drop across the baghouses is outside the normal range of 3.0 and 6.0 inches of water or a range established during the latest stack test, the Permittee shall take reasonable response steps in accordance with Section C - Compliance Response Plan - Preparation, Implementation, Records, and Reports. A pressure reading that is outside the above mentioned range is not a deviation from this permit. Failure to take response steps in accordance with Section C - Compliance Response Plan - Preparation, Implementation, Records, and Reports, shall be considered a violation of this permit.

The instrument used for determining the pressure shall comply with Section C - Pressure Gauge and Other Instrument Specifications, of this permit, shall be subject to approval by IDEM, OAQ, and shall be calibrated at least once every six (6) months.

D.2.7 Baghouse, Filters, and Self-Cleaning Screen Inspections

An inspection shall be performed once per year of all bags, filters, and self-cleaning screens controlling the facilities when venting to the atmosphere. Inspections are optional when venting to the indoors. All defective bags and screens shall be replaced.

D.2.8 Broken or Failed Bag, Filter, or Screen Detection

In the event that bag or screen failure has been observed:

- (a) For multi-compartment units, the affected compartments will be shut down immediately until the failed units have been repaired or replaced. Operations may continue only if there are no visible emissions or if the event qualifies as an emergency and the Permittee satisfies the emergency provisions of this permit (Section B- Emergency Provisions). Within eight (8) business hours of the determination of failure, response steps according to the timetable described in the Compliance Response Plan shall be initiated. For any failure with corresponding response steps and timetable not described in the Compliance Response Plan, response steps shall be devised within eight (8) business hours of discovery of the failure and shall include a timetable for completion. Failure to take response steps in accordance with Section C - Compliance Response Plan - Preparation, Implementation, Records, and Reports, shall be considered a violation of this permit.

- (b) For single compartment baghouses, filters, and screens, failed units and the associated process will be shut down immediately until the failed units have been repaired or replaced. Operations may continue only if the event qualifies as an emergency and the Permittee satisfies the requirements of the emergency provisions of this permit (Section B - Emergency Provisions).

D.2.9 Cyclone Inspections

An inspection shall be performed once per year of all cyclones controlling the processes when venting to the atmosphere. Inspections are optional when venting to the indoors.

D.2.10 Cyclone Failure Detection

In the event that cyclone failure has been observed:

Failed units and the associated process will be shut down immediately until the failed units have been repaired or replaced. Operations may continue only if the event qualifies as an emergency and the Permittee satisfies the requirements of the emergency provisions of this permit (Section B - Emergency Provisions). Failure to take response steps in accordance with Section C - Compliance Response Plan - Preparation, Implementation, Records, and Reports, shall be considered a violation of this permit.

Record Keeping and Reporting Requirement [326 IAC 2-7-5(3)] [326 IAC 2-7-19]

D.2.11 Record Keeping Requirements

- (a) To document compliance with Condition D.2.2, the Permittee shall maintain records of the amount of soybean grains processed after the grain dryers. This records is the same record that is required in Conditions D.1.11(a) and D.5.12(a).
- (b) To document compliance with Condition D.2.5, the Permittee shall maintain records of once per shift visible emission notations of the stack exhaust.
- (c) To document compliance with Condition D.2.6, the Permittee shall maintain once per shift records of the total pressure drop across the baghouse during normal operation when venting to the atmosphere.
- (d) To document compliance with Conditions D.2.7 and D.2.9, the Permittee shall maintain records of the results of the inspections required under Conditions D.2.7 and D.2.9 and the dates the vents are redirected.
- (e) All records shall be maintained in accordance with Section C - General Record Keeping Requirements, of this permit.

D.2.12 Reporting Requirements

A quarterly summary of the information to document compliance with Condition D.2.2 shall be submitted to the address listed in Section C - General Reporting Requirements, of this permit, using the reporting forms located at the end of this permit, or their equivalent, within thirty (30) days after the end of the quarter being reported. The report submitted by the Permittee does require the certification by the "responsible official" as defined by 326 IAC 2-7-1(34). This is the same report as required in Condition D.1.11 and D.5.12.

SECTION D.3 FACILITY OPERATION CONDITIONS

Facility Description [326 IAC 2-7-5(15)]:

- (mmm) One (1) natural gas fired Dowtherm heater #1, identified as 105EO1, constructed in 1969, and exhausting to stack 105EO;
- (nnn) One (1) natural gas fired Dowtherm heater #2, identified as 106EO1, constructed in 1976, and exhausting to stack 106EO;
- (ooo) One (1) natural gas fired steam generator #3, identified as 108EO1, constructed in 1994, and exhausting to stack 108EO;
- (ppp) One (1) B & W coal fired boiler, identified as 1SP1, constructed in 1950, using multiple cyclones for PM control, and exhausting to stack 1SP;
- (qqq) One (1) Keeler coal fired boiler, identified as 2SP1, constructed in 1963, using multiple cyclones for PM control, and exhausting to stack 1SP;
- (rrr) One (1) Murray natural gas fired, vegetable oil-fired, waste oil-fired, and hazardous chemical fired boiler, identified as 3SP1, constructed in 1968, and exhausting to stack 1SP;

(The information describing the process contained in this facility description box is descriptive information and does not constitute enforceable conditions.)

Emission Limitations and Standards [326 IAC 2-7-5(1)]

D.3.1 Particulate Matter Limitation (PM) [326 IAC 6-2-3] [326 IAC 6-2-4]

- (a) 326 IAC 6-2-3 (Particulate Emission Limitations for Sources of Indirect Heating) applies to the B&W boiler, Keeler boiler, and Murray boiler because they were constructed prior to September 21, 1983, the applicability date for this rule. Pursuant to this rule, the following particulate emission limitations exist:

Year	Unit	PM Limit (lb/MMBtu)
1950	1SP1 - B&W Boiler	0.8
1963	2SP1 - Keeler Boiler	0.8
1968	3SP1 - Murray Boiler	0.8

- (b) 326 IAC 6-2-4 (Particulate Emission Limitations for Source of Indirect Heating) applies to the natural gas fired steam generator #3 (108EO1) because it was constructed after September 21, 1983, the applicability date for this rule. Pursuant to this rule, the particulate emissions from this source shall be limited to less than 0.25 pound per million British thermal unit heat input.

D.3.2 Sulfur Dioxide (SO₂) [326 IAC 7-1.1-1]

Pursuant to 326 IAC 7-1.1-1, the sulfur dioxide emissions from the B&W boiler and Keeler boiler, when combusting coal, shall be less than 6.0 lb/MMBtu.

D.3.3 Particulate Matter (PM) [326 IAC 12-1] [40 CFR 60, Subpart Dc]

Although the natural gas fired steam generator #3 (108EO1) is subject to 40 CFR Part 60, Subpart Dc, there are no emission limitations applicable, only record keeping requirements described in D.3.7.

D.3.4 Preventive Maintenance Plan [326 IAC 2-7-5(13)]

A Preventive Maintenance Plan, in accordance with Section B - Preventive Maintenance Plan, of this permit, is required for this facility and its control device.

Compliance Determination Requirements

D.3.5 Sulfur Dioxide Emissions and Sulfur Content [326 IAC 7-2]

Pursuant to 326 IAC 7-2, the Permittee shall demonstrate that the sulfur dioxide emissions do not exceed six (6.0) pounds per MMBtu. Compliance shall be determined utilizing the following options:

- (a) Providing vendor analysis of coal delivered, if accompanied by a certification from the fuel supplier as described under 40 CFR 60.48c(f)(3). The certification shall include:
 - (1) The name of the coal supplier; and
 - (2) The location of the coal when the sample was collected for analysis to determine the properties of the coal, specifically including whether the coal was sampled as delivered to the affected facility or whether the coal was collected from coal in storage at the mine, at a coal preparation plant, at a coal supplier's facility, or at another location. The certification shall include the name of the coal mine (and coal seam), coal storage facility, or coal preparation plant (where the sample was collected); and
 - (3) The results of the analysis of the coal from which the shipment came (or of the shipment itself) including the sulfur content, moisture content, ash content, and heat content; and
 - (4) The methods used to determine the properties of the coal; or
- (b) Coal sampling and analyzing shall be performed using one of the following procedures:
 - (1) Minimum Coal Sampling Requirements and Analysis Methods:
 - (A) The coal sample acquisition point shall be at a location where representative samples of the total coal flow to be combusted by the facility or facilities may be obtained. A single as-bunkered or as-burned sampling station may be used to represent the coal to be combusted by multiple facilities using the same stockpile feed system;
 - (B) Coal shall be sampled at least three (3) times per day and at least one (1) time per eight (8) hour period unless no coal is bunkered during the proceeding eight (8) hours;
 - (C) Minimum sample size shall be five hundred (500) grams;
 - (D) Samples shall be composited and analyzed at the end of each calendar month;
 - (E) Preparation of the coal sample, heat content analysis, and sulfur content analysis shall be determined pursuant to 326 IAC 3-7-2(c), (d), (e); or
 - (2) Sample and analyze the coal pursuant to 326 IAC 3-7-3; or

- (c) Upon written notification to IDEM by a facility owner or operator, continuous emission monitoring data collected and reported pursuant to 326 IAC 3-5-1 may be used as the means for determining compliance with the emissions limitations in 326 IAC 7-2. Upon such notification, the other requirements of 326 IAC 7-2 shall not apply. [326 IAC 7-2-1(c)]
- (d) Compliance may also be determined by conducting a stack test for sulfur dioxide emissions from the boiler, using 40 CFR 60, Appendix A, Method 6 in accordance with the procedures in 326 IAC 3-6, which is conducted with such frequency as to generate the amount of information required by (a) or (b) above. [326 IAC 7-2-1(b)]

A determination of noncompliance pursuant to any of the methods specified in (a), (b), (c), or (d) above shall not be refuted by evidence of compliance pursuant to the other method. This rule is not federally enforceable.

D.3.6 Used Oil Requirements [329 IAC 13-8]

Pursuant to 329 IAC 13-3-2 (Used Oil Specifications), used oil burned for energy recovery that is classified as off-specification used oil fuel shall comply with the provisions of 329 IAC 13-8 (Used Oil Burners Who Burn Off-specification Used Oil For Energy Recovery), including:

- (1) Receipt of an EPA identification number as outlined in 329 IAC 13-8-3 (Notification),
- (2) Compliance with the used oil storage requirements specified in 329 IAC 13-8-5 (Used Oil Storage), and
- (3) Maintain records pursuant to 329 IAC 13-8-6 (Tracking).
- (4) The waste oil burned in the Murray boiler shall comply with the used oil requirements specified in 329 IAC 13 (Used Oil Management). The burning of mixtures of used oil and hazardous waste that is regulated by 329 IAC 3.1 is prohibited at this source.

Compliance Monitoring Requirements [326 IAC 2-7-6(1)] [326 IAC 2-7-5(1)]

D.3.7 Visible Emissions Notations

- (a) Once per shift visible emission notations of 1SP stack exhaust shall be performed during normal daylight operations when combusting coal and exhausting to the atmosphere. A trained employee shall record whether emissions are normal or abnormal.
- (b) For processes operated continuously, "normal" means those conditions prevailing, or expected to prevail, eighty percent (80%) of the time the process is in operation, not counting startup or shut down time.
- (c) In the case of batch or discontinuous operations, readings shall be taken during that part of the operation that would normally be expected to cause the greatest emissions.
- (d) A trained employee is an employee who has worked at the plant at least one (1) month and has been trained in the appearance and characteristics of normal visible emissions for that specific process.
- (e) The Compliance Response Plan for these processes shall contain troubleshooting contingency and response steps for when an abnormal emission is observed. Failure to take response steps in accordance with Section C - Compliance Response Plan - Preparation, Implementation, Records, and Reports, shall be considered a violation of this permit.

Record Keeping and Reporting Requirements [326 IAC 2-7-5(3)] [326 IAC 2-7-19]

D.3.8 Record Keeping Requirements

- (a) To document compliance with Condition D.3.2, the Permittee shall maintain records in accordance with (1) through (4) below. Records maintained for (1) through (4) shall be taken monthly and shall be complete and sufficient to establish compliance with the PM and SO₂ emission limits established in Condition D.3.2.
 - (1) Calendar dates covered in the compliance determination period;
 - (2) Actual coal usage since last compliance determination period;
 - (3) Sulfur content and heat content; and
 - (4) Sulfur dioxide emission rates.
- (b) Pursuant to 40 CFR Part 60, Subpart Dc, the owner or operator of 108EO1 shall record and maintain records of amounts of fuel combusted during each day.
- (c) To document compliance with Condition D.3.7, the Permittee shall maintain records of visible emission notations of the boiler stack exhaust while combusting coal.
- (d) All records shall be maintained in accordance with Section C - General Record Keeping Requirements, of this permit.

D.3.9 Reporting Requirements

- (a) A certification, signed by the responsible official, that certifies all of the fuels combusted during the period for units 105EO1, 106EO1, 108EO1, 1SP1, 2SP1, and 3SP1. The natural gas-fired boiler certification does require the certification by the "responsible official" as defined by 326 IAC 2-7-1(34);
- (b) The natural gas boiler certification shall be submitted to the address listed in Section C - General Reporting Requirements, of this permit, using the reporting forms located at the end of this permit, or their equivalent, within thirty (30) days after the end of the six (6) month period being reported.
- (c) Pursuant to 326 IAC 7-2, for the B&W boiler and Keeler boiler, a quarterly report of the calendar month average coal sulfur content, coal heat content, the sulfur dioxide emission rate in pounds per million Btu, and the total monthly coal consumption shall be submitted to the address listed in Section C - General Reporting Requirements, of this permit, using the reporting forms located at the end of this permit, or their equivalent, within thirty (30) days after the end of the quarter being reported. The report submitted by the Permittee does require the certification by the "responsible official" as defined by 326 IAC 2-7-1(34).

SECTION D.4 FACILITY OPERATION CONDITIONS

Facility Description [326 IAC 2-7-5(15)]:

- (sss) Hexane recovery, identified as 24EX1, constructed in 1980, with hexane emissions controlled by a mineral oil absorber, and exhausting to stack 24EX;
- (ttt) One (1) pre-DT section on top of 'A' top dryer section, constructed in 1996, and one (1) 'A' DTDC top dryer section, constructed in 1980, both identified as 24EX2, with hexane emissions controlled by a mineral oil absorber and exhausting to stack 24EX;
- (uuu) One (1) 'A' DTDC middle dryer section, identified as 24EX3, constructed in 1980, with hexane emissions controlled by a mineral oil absorber, and exhausting to stack 24EX;
- (ww) One (1) 'A' DTDC bottom cooler section, identified as 24EX4, constructed in 1980, with hexane emissions controlled by a mineral oil absorber, and exhausting to stack 24EX;
- (www) One (1) pre-DT section on top of 'B' top dryer section, constructed in 1996, and one (1) 'B' DTDC top dryer section, constructed in 1980, both identified as 24EX5, with hexane emissions controlled by a mineral oil absorber, and exhausting to stack 24EX;
- (xxx) One (1) 'B' DTDC middle dryer section, identified as 24EX6, constructed in 1980, with hexane emissions controlled by a mineral oil absorber, and exhausting to stack 24EX;
- (yyy) One (1) 'B' DTDC bottom cooler section, identified as 24EX7, constructed in 1980, with hexane emissions controlled by a mineral oil absorber, and exhausting to stack 24EX;
- (zzz) One (1) meal cooler, identified as 21EX, constructed in 1996, with hexane emissions controlled by a mineral oil absorber, and exhausting to sack 24EX;
- (aaaa) Hexane storage tank, identified as 24EX8, constructed in 1995, and vented to the mineral oil absorber inlet;
- (bbbb) Wastewater system containing hexane, identified as 24EX9, constructed in 1980, and exhausting at the plant treatment facility;
- (cccc) One (1) refined oil hot well, identified as 24EX10, constructed in 1975, and exhausting to stack 24EX;
- (dddd) One (1) sampling/hexane unloading port, identified as 24EX11, and with no control.

(The information describing the process contained in this facility description box is descriptive information and does not constitute enforceable conditions.)

Emission Limitations and Standards [326 IAC 2-7-5(1)]

D.4.1 Volatile Organic Compounds (VOC) [326 IAC 8-1-6]

Pursuant to CP(002)2005, issued August 23, 1991, and 326 IAC 8-1-6 (New Facilities; General Reduction Requirements), the VOC emissions from the hexane emitting units shall be controlled by a mineral oil absorption system with a control efficiency of 99.9%.

D.4.2 PSD Limit [326 IAC 2-2][40CFR 52.21]

Pursuant to CP(002)2005, issued August 23, 1991, the hexane usage for all of the oil extraction facilities (24EX1-24EX11) combined shall be limited to less than 330,000 gallons per twelve (12) consecutive month period to ensure that the increase in hexane emissions from these units remains below 39.2 tons per year. This will ensure that 326 IAC 2-2 (Prevention of Significant Deterioration) and 40 CFR 52.21 does not apply to this modification.

D.4.3 Storage Vessels [40 CFR 60, Subpart Kb][326 IAC 12]

Pursuant to 40 CFR Part 60, Subpart Kb, records must be kept for the hexane storage tank identified as 24EX8. The record keeping requirements are specified in the Record Keeping Requirements condition of this section. No other subpart Kb provisions apply.

D.4.4 General Provisions Relating to HAPs [326 IAC 20-1-1][40 CFR 63, Subpart A]

The provisions of 40 CFR 63, Subpart A - General Provisions, which are incorporated as 326 IAC 20-1-1, apply to the facility described in this section except when otherwise specified in 40 CFR 63, Subpart GGGG.

D.4.5 Solvent Extraction for Vegetable Oil Production NESHAP [40 CFR Part 63, Subpart GGGG][326 IAC 14]

Pursuant to 40 CFR Part 63, Subpart GGGG (National Emission Standards for Hazardous Air Pollutants: Solvent Extraction for Vegetable Oil Production), the hexane emissions for the soybean conventional oilseed process is limited to 0.2 gallons of hexane lost per ton of oilseed processed. This limitation is a solvent loss factor to be applied in comparison to a loss of solvent at a n-hexane content of 64%. The compliance date for this rule is April 12, 2004. Compliance with the hexane limit shall be demonstrated using the following equation found in 40 CFR 63.2840:

$$\text{Compliance Ratio} = \frac{\text{Actual HAP Loss}}{\text{Allowable HAP Loss}}$$

This equation can also be expressed as a function of total solvent loss as shown below and found in 40 CFR 63.2840:

$$\text{Compliance Ratio} = \frac{f * \text{Actual Solvent Loss}}{0.64 * \sum (\text{Oilseed}_i * (\text{SLF})_i)}$$

where f = The weighted average volume fraction of HAP in solvent received during the previous 12 operating months, as determined in 40 CFR 63.2854, dimensionless;

0.64 = The average volume fraction of HAP in solvent in the baseline performance data, dimensionless;

Actual Solvent Loss = Gallons of actual solvent loss during previous 12 operating months, as determined in 40 CFR 63.2853;

Oilseed = Tons of each oilseed type "i" processed during the previous 12 operating months, as shown in 40 CFR 63.2855; and

SLF = The corresponding solvent loss factor (gal/ton) for oilseed "i" as shown in Table 1 of 40 CFR 63.2840.

After 12 operating months, the source shall calculate the compliance ratio by the end of each calendar month following an operating month using the second equation. When calculating the compliance ratio, the following conditions shall be considered:

- (1) If the source processes any quantity of listed oilseeds in a calendar month and the source is not operating under an initial startup period or malfunction period subject to 40 CFR 63.2850, then the source shall categorize the month as an operating month, as defined in 40 CFR 63.2872.
- (2) The 12-month compliance ratio may include operating months occurring prior to a source shutdown and operating months that follow after the source resumes operation.
- (3) If the source shuts down and processes no listed oilseed for an entire calendar month, then the source shall categorize the month as a nonoperating month, as defined in 40 CFR 63.2872. Exclude any nonoperating months from the compliance ratio determination.
- (4) If the source is subject to an initial startup period as defined in 40 CFR 60.2872, the source shall exclude from the compliance ratio determination any solvent and oilseed information recorded for the initial startup period.
- (5) If the source is subject to a malfunction period as defined in 40 CFR 63.2872, the source shall exclude from the compliance ratio determination any solvent and oilseed information recorded for the malfunction period.

If the compliance ratio is less than or equal to 1.00, the source is in compliance with the HAP emission requirement for the previous operating month.

D.4.6 Preventive Maintenance Plan [326 IAC 2-7-5(13)]

A Preventive Maintenance Plan, in accordance with Section B - Preventive Maintenance Plan, of this permit, is required for this facility and any control devices.

Compliance Determination Requirements

D.4.7 Volatile Organic Compounds (VOC)

In order to comply with Conditions D.4.1 and D.4.2, the mineral oil absorber for VOC control shall be in operation and control emissions from the listed facilities at all times when the facilities are in operation.

D.4.8 Testing Requirements [326 IAC 2-7-6(1),(6)] [326 IAC 2-1.1-11]

During the period between 30 and 36 months after issuance of this permit, in order to demonstrate compliance with Conditions D.4.1, the Permittee shall perform VOC testing for the mineral absorption system to demonstrate compliance with the 99.9% control efficiency utilizing methods as approved by the Commissioner. This test shall be repeated at least once every five (5) years from the date of this valid compliance demonstration. Testing shall be conducted in accordance with Section C- Performance Testing.

D.4.9 Compliance Requirements [40 CFR Part 63, Subpart GGGG]

(a) Pursuant to 40 CFR 63.2850, the source shall:

- (1) Submit the following necessary notifications in accordance with 40 CFR 63.2860:
 - (A) Initial notifications for existing source by August 10, 2001. The source submitted the initial notification on August 6, 2001; and
 - (B) Notification of compliance status, no later than 60 days after determining your initial 12 operating months compliance ratio. For an existing source,

such as this source, the notification must be submitted no later than June 12, 2004 or the date as stated in 40 CFR 63.2860.

- (2) Develop and implement a plan for demonstrating compliance in accordance with 40 CFR 63.2851.
 - (3) Develop a written startup, shutdown, and malfunction (SSM) plan in accordance with the provisions in 40 CFR 63.2852.
 - (4) Maintain all the necessary records used to demonstrate compliance with this subpart in accordance with 40 CFR 63.2862.
 - (5) Submit the following reports:
 - (A) Annual compliance certifications in accordance with 40 CFR 63.2861(a);
 - (B) Periodic SSM reports in accordance with 40 CFR 63.261(c); and
 - (C) Immediate SSM reports in accordance with 40 CFR 63.261(d).
 - (6) Submit all notifications and reports and maintain all records required by the General Provisions for performance testing on the control device that destroys solvent.
- (b) A malfunction as defined in 40 CFR 63.2 is a sudden, infrequent, and not reasonably preventable failure of air pollution control equipment or process equipment to function in a usual manner. If the existing source experiences an unscheduled shutdown as a result of a malfunction, continues to operate during a malfunction (including the period reasonable necessary to correct the malfunction), or starts up after a shutdown resulting from a malfunction, then the source must meet the requirements associated with one of two compliance options. Routine or scheduled process startups and shutdowns resulting from, but not limited to, market demands, maintenance activities, and switching types of oilseed processed, are not startups or shutdowns resulting from a malfunction and, therefore do not qualify for this provision. Within 15 days of the beginning date of the malfunction, the source must choose to comply with one of the following options listed:
- (1) Normal operation. The source must meet all of the requirements listed in 40 CFR 63.2850(a) and (b).
 - (2) Malfunction period. Throughout the malfunction period, the source must meet all of the requirements listed in 40 CFR 63.2850(a) and Table 1 of 40 CFR 63.2850 for sources operating during a malfunction period. At the end of the malfunction period, the source must then meet all of the requirements of Table 1 of 40 CFR 63.2850 for sources under normal operation.

D.4.10 Compliance Plan [40 CFR Part 63, Subpart GGGG]

- (a) Pursuant to 40 CFR 63.2851, the source must develop and implement a written plan for demonstrating compliance that provides the detailed procedures the source will follow to monitor and record data necessary for demonstrating compliance with this subpart. Procedures followed for quantifying solvent loss from the source and amount of oilseed processed vary from source to source because of site-specific factors such as equipment design characteristics and operating conditions. Typical procedures include one or more accurate measurement methods such as weigh scales, volumetric displacement, and material mass balance. Because the industry does not have a uniform set of procedures,

the source must develop and implement a site-specific plan for demonstrating compliance before the compliance date for the source. The source shall keep the plan on-site and readily available as long as the source is operational. If the owner makes any changes to the plan for demonstrating compliance, the previous versions of the plan must be kept and made readily available for inspection for at least 5 years after each revision. The plan for demonstrating compliance must include the following:

- (1) The name and address of the owner or operator;
 - (2) The physical address of the vegetable oil production process;
 - (3) A detailed description of all methods of measurement the source will use to determine solvent losses, HAP content of solvent, and the tons of each type of oilseed processed;
 - (4) When each measurement will be made;
 - (5) Examples of each calculation the source will use to determine compliance status. Include examples how to convert data measured with one parameter to the terms for use in compliance determination;
 - (6) Example logs of how data will be recorded; and
 - (7) A plan to ensure that the data continue to meet compliance demonstration needs.
- (b) IDEM, OAQ may require the source to revise the plan for demonstrating compliance. IDEM, OAQ may require reasonable revisions if the procedures lack detail, are inconsistent or do not accurately determine solvent loss, HAP content of the solvent, or the tons of oilseed processed.

D.4.11 Startup, Shutdown, and Malfunction Plan [40 CFR Part 63, Subpart GGGG]

Pursuant to 40 CFR 63.2852, the source must develop a written SSM plan in accordance with 40 CFR 63.6(e)(3) and implement the plan, when applicable. The SSM plan must be completed before the compliance date for the source. The source must keep the SSM plan on-site and readily available as long as the source is operational. The SSM plan provides detailed procedures for operating and maintaining the source to minimize emissions during a qualifying SSM event for which the source chooses the 40 CFR 63.2580(e)(2) malfunction period, or the 40 CFR 63.2850(c)(2) or (d)(2) initial startup period. The SSM plan must specify a program of corrective action for malfunctioning process and air pollution control equipment and reflect the best practices now in use by the industry to minimize emissions. Some or all of the procedure may come from plans the source has developed for other purposes such as a Standard Operating Procedure manual or an Occupational Safety and Health Administration Process Safety Management plan. To qualify as a SSM plan, other such plans must meet all the applicable requirements of this NESHAP.

Compliance Monitoring Requirements [326 IAC 2-7-6(1)] [326 IAC 2-7-5(1)]

D.4.12 Monitoring

- (a) To document compliance with Conditions D.4.1 and D.4.2, the mineral oil absorption vent VOC (hexane) emission rate shall be determined daily by measuring the airflow rate and the concentration of hexane in the air stream. This concentration will be determined daily by measuring percent Lower Explosive Limit (LEL). If the air flow meter proves unreliable, airflow can be determined by calculations.

- (b) Additional inspections and preventive measures shall be performed as prescribed in the Preventive Maintenance Plan.

Record Keeping and Reporting Requirements [326 IAC 2-7-5(3)] [326 IAC 2-7-19]

D.4.13 Record Keeping Requirements

- (a) To document compliance with Condition D.4.1 and D.4.12, the Permittee shall maintain records of the mineral oil absorption vent VOC (hexane) emission rate as determined according to Condition D.4.12;
- (b) To document compliance with Condition D.4.2, the Permittee shall maintain records of the hexane usage for the oil extraction facilities.
- (c) To document compliance with Condition D.4.3, the Permittee shall maintain a record showing the dimension of the storage vessel and an analysis showing the capacity of the storage vessel.
- (d) To document compliance with Condition D.4.5 and 40 CFR Part 63, Subpart GGGG, the Permittee shall comply with the following:
 - (1) The following information must be kept on-site and readily available as long as the source is operational:
 - (A) Compliance Plan; and
 - (B) Startup, Shutdown, and Malfunction Plan.
 - (2) For the solvent inventory, the following information must be recorded in accordance with the source plan for demonstrating compliance:
 - (A) Dates that define each operating status period during a calendar month;
 - (B) The operating status of the source such as normal operation, nonoperating, initial startup period, malfunction period, or exempt operation for each recorded time interval;
 - (C) The gallons of extraction solvent in the inventory on the beginning and ending dates of each normal operating period;
 - (D) The gallons of all extraction solvent received, purchased, and recovered during each calendar month;
 - (E) All extraction solvent inventory adjustments, additions or subtractions. The owner must document the reason for the adjustment and justify the quantity of the adjustment;
 - (F) The total solvent loss for each calendar month, regardless of the source operating status; and
 - (G) The actual solvent loss in gallons for each operating month.
 - (3) For the weighted average volume fraction of HAP in the extraction solvent, the owner must record the following items:

- (A) The gallons of extraction solvent received in each delivery;
 - (B) The volume fraction of each HAP exceeding 1 percent by volume in each delivery of extraction solvent; and
 - (C) The weighted average volume fraction of HAP in extraction solvent received since the end of the last operating month as determined in accordance with 40 CFR 63.2854(b)(2).
- (4) For each type of listed oilseed processed, record the following items, in accordance with the source plan for demonstrating compliance:
- (A) The dates that define each operating period. The dates must be the same as the dates entered for the extraction solvent inventory.
 - (B) The operating status of the source such as normal operation, nonoperating, initial startup period, malfunction period, or exempt operation for each recorded time interval. On the log for each type of listed oilseed that is being processed during a normal operating period, the owner shall record which type of listed oilseed is being processed in addition to the source operating status.
 - (C) The oilseed inventory for the type of listed oilseed being processed on the beginning and ending dates of each normal operating period.
 - (D) The tons of each type of oilseed received at the affected source each normal operating period.
 - (E) All listed oilseed inventory adjustments, additions, or subtractions for normal operating periods. The owner must document the reason for adjustment and justify the quantity of the adjustment.
 - (F) The tons of each type of listed oilseed processed during each operating month.
- (5) After the source has processed listed oilseed for 12 operating months, and is not operating during an initial startup period as described in 40 CFR 63.2850(c)(2) or (d)(2), or a malfunction period as described in 40 CFR 63.2850(e)(2), the following items must be recorded by the end of the calendar month following each operating month:
- (A) The 12 operating months rolling sum of the actual solvent loss in gallons as described in 40 CFR 63.2853(c).
 - (B) The weighted average volume fraction of HAP in extraction solvent received for the previous 12 operating months as described in 40 CFR 63.2854(b)(3).
 - (C) The 12 operating months rolling sum of each type of listed oilseed processes at the affected source in tons as described in 40 CFR 63.2855(c).
 - (D) A determination of the compliance ratio. Using the values from 40 CFR 63.2853, 63.2854, 63.2855 and Table 1 of 40 CFR 63.2840, calculate the compliance ratio using equation 2 of 40 CFR 63.2840.

- (E) A statement of whether the source is in compliance with all of the requirements of the subpart. This includes a determination of whether the source has met all of the applicable requirements of 40 CFR 63.2850.
- (6) For each SSM event subject to an initial startup period as described in 40 CFR 63.2850(c)(2) or (d)(2), or a malfunction period as described in 40 CFR 63.2850(e)(2), the following items shall be recorded by the end of the calendar month following each month in which the initial startup period or malfunction period occurred:
 - (A) A description and date of the SSM event, its duration, and reason it qualifies as an initial startup or malfunction;
 - (B) An estimate of the solvent loss in gallons for the duration of the initial startup or malfunction period with supporting documentation; and
 - (C) A checklist or other mechanism to indicate whether the SSM plan was followed during the initial startup or malfunction period.
- (e) All records shall be maintained in accordance with Section C - General Record Keeping Requirements, of this permit.

D.4.14 Reporting Requirements

- (a) A quarterly summary of the information to document compliance with Condition D.4.2 shall be submitted to the address listed in Section C - General Reporting Requirements, of this permit, using the reporting forms located at the end of this permit, or their equivalent, within thirty (30) days after the end of the quarter being reported. The report submitted by the Permittee does require the certification by the "responsible official" as defined by 326 IAC 2-7-1(34).
- (b) To document compliance with 40 CFR Part 63, Subpart GGGG, the Permittee must submit annual compliance certifications. The first annual compliance certification is due no later than 60 days after determining the initial 12 operating months compliance ratio. For an existing source, such as this source, the notification must be submitted no later than 50 calendar months after the effective date of this subpart, April 12, 2001 or the date as stated in 40 CFR 63.2860. Each subsequent annual compliance certification is due 12 months after the previous annual compliance certification. The annual compliance certification provides the compliance status for each operating month during the 12 calendar months period ending 60 days or the time frame as stated in 40 CFR 63.2860 prior to the date on which the report is due. The annual certification shall include the following information:
 - (1) The name and address of the owner or operator.
 - (2) The physical address of the vegetable oil production process.
 - (3) Each listed oilseed type processed during the 12 calendar months period covered by the report.
 - (4) Each HAP identified under 40 CFR 63.2854(a) as being present in concentrations greater than 1 percent by volume in each delivery of solvent received during the 12 calendar months period covered by the report.
 - (5) A statement designating the source as major source of HAP.

- (6) A compliance certification to indicate whether the source was in compliance for each compliance determination made during the 12 calendar period covered by the report. For each such compliance determination, the source must include a certification of the following items:
 - (A) The source is following the procedures described in the plan for demonstrating compliance.
 - (B) The compliance ratio is less than or equal to 1.00.
- (c) To document compliance with 40 CFR Part 63, Subpart GGGG, the Permittee shall submit a deviation notification report for each compliance determination made in which the ratio exceeded 1.00 as determined under 40 CFR 63.2840(c). The report shall be submitted by the end of each month following the calendar month in which the deviation was determined. The deviation notification shall include the following:
 - (1) The name and address of the owner or operator.
 - (2) The physical address of the vegetable oil production process.
 - (3) Each listed oilseed type processed during the 12 calendar months period for which a deviation was determined.
 - (4) The compliance ratio comprising the deviation. The owner may reduce the frequency of submittal of the deviation notification report if the IDEM, OAQ does not object as provided in 40 CFR 63.10(e)(3)(iii).
- (d) To document compliance with 40 CFR Part 63, Subpart GGGG, if the Permittee chooses to operate the source under an initial startup period subject to 40 CFR 63.2850(c)(2) or (d)(2) or a malfunction period subject to 40 CFR 63.2850(e)(2), the Permittee shall submit a periodic SSM report by the end of the calendar month following each month in which the initial startup period or malfunction period occurred. The periodic SSM report shall include the following:
 - (1) The name, title, and signature of the source's responsible official who is certifying that the report accurately states all actions taken during the initial startup or malfunction period were consistent with the SSM plan.
 - (2) A description of the events occurring during the time period, the date and duration of the events, and the reason the time interval qualifies as an initial startup period or malfunction period.
 - (3) An estimate of the solvent loss during the initial startup or malfunction period with supporting documentation.
- (e) To document compliance with 40 CFR Part 63, Subpart GGGG, if the Permittee handles a SSM during an initial startup period subject to 40 CFR 63.2850(c)(2) or (d)(2) or a malfunction period subject to 40 CFR 63.2850(e)(2) differently from procedures in the SSM plan, then the Permittee shall submit an immediate SSM report. Immediate SSM reports consist of a telephone call or facsimile transmission to the responsible agency within 2 working days after starting actions inconsistent with the SSM plan, followed by a letter within 7 working days after the end of the event. The letter shall include the following:

- (1) The name, title, and signature of the source's responsible official who is certifying that the accuracy of the report, an explanation of the event, and the reasons for not following the SSM plan.
- (2) A description and date of the SSM event, its duration, and reason it qualifies as a SSM.
- (3) An estimate of the solvent loss for the duration of the SSM event with supporting documentation.

SECTION D.5 FACILITY OPERATION CONDITIONS

Facility Description [326 IAC 2-7-5(15)]:

- (eeee) One (1) grain dryer #1, identified as 16EL1, constructed in 1986, using self-cleaning screens for PM control, and exhausting to stack 16EL;
- (ffff) One (1) natural gas dryer #1 associated with grain dryer #1, identified as 16EL2, constructed in 1986, and exhausting to stack 16EL;
- (gggg) One (1) outside conditioner, identified as 17EX1, constructed in 1991, sharing a cyclone with 17EX2 for PM control, and exhausting to stack 17EX; and
- (hhhh) The following soybean processing equipment, together identified as 17EX2, modified in 1987, sharing a cyclone with 17EX1 for PM control, and exhausting to stack 17EX:
 - (1) One (1) flaking roll #8, constructed in 1981; and
 - (2) One (1) 'B' flke e/w drag, constructed in 1980.

(The information describing the process contained in this facility description box is descriptive information and does not constitute enforceable conditions.)

Emission Limitations and Standards [326 IAC 2-7-5(1)]

D.5.1 General Provisions Relating to NSPS [326 IAC 12-1][40 CFR Part 60, Subpart A]

The provisions of 40 CFR Part 60, Subpart A - General Provisions, which are incorporated by reference in 326 IAC 12-1, apply to the affected facilities described in this section except when otherwise specified in 40 CFR Part 60, Subpart DD.

D.5.2 New Source Performance Standards (NSPS) Grain Elevators [326 IAC 12][40 CFR Subpart DD 60.302]

Pursuant to 40 CFR Part 60, Subpart DD 60.302 is applicable to 16EL1 (#1 grain dryer) and 19EL1 (#2 grain dryer). However, pursuant to 40 CFR Part 60, Subpart DD 60.302(a) there are no applicable requirements for these column grain dryers because the column grain dryers have 0.083 inch diameter screen openings in the column plate, which is less than 0.094 inch diameter openings.

D.5.3 PSD Limit [326 IAC 2-2] [40 CFR 52.21]

Pursuant to CP001-4673-00005, issued May 10, 1996, the amount of soybean grains processed after the grain dryers shall be limited to less than 1,368,750 tons per twelve (12) consecutive month period. This limit, in combination with the limits in Conditions D.1.3 and D.2.2, restricts the net increases of PM and PM10 emissions to below the PSD thresholds and also satisfies the requirements of 326 IAC 6-3-2 (Process Operations). This limit is equivalent to limiting unit 17EX to less than 2.51 pounds per hour of PM and less than 1.52 pounds per hour of PM10. This will render the requirements of 326 IAC 2-2 (Prevention of Significant Deterioration) and 40 CFR 52.21 not applicable.

D.5.4 Particulate Matter (PM) [326 IAC 6-3-2]

Pursuant to 326 IAC 6-3-2 (Process Operations), the particulate matter (PM) from the following units shall be limited by the following equation:

Unit	Description
16EL1	Grain Dryer #1
17EX1	Outside Conditioner
17EX2	Flaking Roll #8, 'B' Flake E/W Drag

The pounds per hour limitation was calculated with the following equation:

Interpolation of the data for the process weight rate up to sixty thousand (60,000) pounds per hour shall be accomplished by use of the equation:

$$E = 4.10 P^{0.67} \quad \text{where } E = \text{rate of emission in pounds per hour and} \\ P = \text{process weight rate in tons per hour}$$

and

Interpolation and extrapolation of the data for the process weight rate in excess of 60,000 pounds per hour shall be accomplished by use of the equation:

$$E = 55.0 P^{0.11} - 40 \quad \text{where } E = \text{rate of emission in pounds per hour; and} \\ P = \text{process weight rate in tons per hour}$$

The individual limitations are included in a IDEM, OAQ confidential file because the source considers the process weight weights confidential.

D.5.5 Preventive Maintenance Plan [326 IAC 2-7-5(13)]

A Preventive Maintenance Plan, in accordance with Section B - Preventive Maintenance Plan, of this permit, is required for this facility and its control device.

Compliance Determination Requirements

D.5.6 Particulate Matter (PM)

- (a) In order to comply with Conditions D.5.3 and D.5.4, the self-cleaning screens for PM control shall be in operation and control emissions from 16EL1 at all times that the process is in operation.
- (b) In order to comply with Conditions D.5.3 and D.5.4, the cyclones for PM control shall be in operation and control emissions from the listed facilities at all times that the facilities are in operation.

Compliance Monitoring Requirements [326 IAC 2-7-6(1)] [326 IAC 2-7-5(1)]

D.5.7 Visible Emissions Notations

- (a) Once per shift visible emission notations of unit 16EL and 17EX stack exhaust shall be performed during normal daylight operations when exhausting to the atmosphere. A trained employee shall record whether emissions are normal or abnormal.
- (b) For processes operated continuously, "normal" means those conditions prevailing, or expected to prevail, eighty percent (80%) of the time the process is in operation, not counting startup or shut down time.
- (c) In the case of batch or discontinuous operations, readings shall be taken during that part of the operation that would normally be expected to cause the greatest emissions.

- (d) A trained employee is an employee who has worked at the plant at least one (1) month and has been trained in the appearance and characteristics of normal visible emissions for that specific process.
- (e) The Compliance Response Plan for these processes shall contain troubleshooting contingency and response steps for when an abnormal emission is observed. Failure to take response steps in accordance with Section C - Compliance Response Plan - Preparation, Implementation, Records, and Reports, shall be considered a violation of this permit.

D.5.8 Self-Cleaning Screen Inspections

An inspection shall be performed once per year of all self-cleaning screens controlling the facilities when venting to the atmosphere. All defective screens shall be replaced.

D.5.9 Broken or Failed Screen Detection

In the event that bag failure has been observed:

- (a) For multi-compartment units, the affected compartments will be shut down immediately until the failed units have been repaired or replaced. Operations may continue only if there are no visible emissions or if the event qualifies as an emergency and the Permittee satisfies the emergency provisions of this permit (Section B- Emergency Provisions). Within eight (8) business hours of the determination of failure, response steps according to the timetable described in the Compliance Response Plan shall be initiated. For any failure with corresponding response steps and timetable not described in the Compliance Response Plan, response steps shall be devised within eight (8) business hours of discovery of the failure and shall include a timetable for completion. Failure to take response steps in accordance with Section C - Compliance Response Plan - Preparation, Implementation, Records, and Reports, shall be considered a violation of this permit.
- (b) For single compartment baghouses, failed units and the associated process will be shut down immediately until the failed units have been repaired or replaced. Operations may continue only if the event qualifies as an emergency and the Permittee satisfies the requirements of the emergency provisions of this permit (Section B - Emergency Provisions).

D.5.10 Cyclone Inspections

An inspection shall be performed once per year of all cyclones controlling the processes when venting to the atmosphere. Inspections are optional when venting to the indoors.

D.5.11 Cyclone Failure Detection

In the event that cyclone failure has been observed:

Failed units and the associated process will be shut down immediately until the failed units have been repaired or replaced. Operations may continue only if the event qualifies as an emergency and the Permittee satisfies the requirements of the emergency provisions of this permit (Section B - Emergency Provisions). Failure to take response steps in accordance with Section C - Compliance Response Plan - Preparation, Implementation, Records, and Reports, shall be considered a violation of this permit.

Record Keeping and Reporting Requirement [326 IAC 2-7-5(3)] [326 IAC 2-7-19]

D.5.12 Record Keeping Requirements

- (a) To document compliance with Condition D.5.3, the Permittee shall maintain records of the amount of soybean grains processed after the grain dryers. This records is the same record that is required in Conditions D.1.11(a) and D.2.11(a).
- (b) To document compliance with Condition D.5.7, the Permittee shall maintain records of once per shift visible emission notations of the stack exhaust.
- (c) To document compliance with Conditions D.5.8 and D.5.10, the Permittee shall maintain records of the results of the inspections required under Conditions D.5.8 and D.5.10 and the dates the vents are redirected.
- (d) All records shall be maintained in accordance with Section C - General Record Keeping Requirements, of this permit.

D.5.13 Reporting Requirements

A quarterly summary of the information to document compliance with Condition D.5.3 shall be submitted to the address listed in Section C - General Reporting Requirements, of this permit, using the reporting forms located at the end of this permit, or their equivalent, within thirty (30) days after the end of the quarter being reported. The report submitted by the Permittee does require the certification by the "responsible official" as defined by 326 IAC 2-7-1(34). This is the same report as required by Conditions D.1.11 and D.2.12.

INDIANA DEPARTMENT OF ENVIRONMENTAL MANAGEMENT OFFICE OF AIR QUALITY

PART 70 OPERATING PERMIT CERTIFICATION

Source Name: Central Soya Company, Inc.
Source Address: 1200 North 2nd Street, Decatur, Indiana 46733
Mailing Address: P.O. Box 1002, Decatur, Indiana 46733
Part 70 Permit No.: T001-5610-00005

This certification shall be included when submitting monitoring, testing reports/results or other documents as required by this permit.

Please check what document is being certified:

- 9 Annual Compliance Certification Letter
- 9 Test Result (specify) _____
- 9 Report (specify) _____
- 9 Notification (specify) _____
- 9 Affidavit (specify) _____
- 9 Other (specify) _____

I certify that, based on information and belief formed after reasonable inquiry, the statements and information in the document are true, accurate, and complete.

Signature:

Printed Name:

Title/Position:

Phone:

Date:

**INDIANA DEPARTMENT OF ENVIRONMENTAL MANAGEMENT
OFFICE OF AIR QUALITY
COMPLIANCE BRANCH
100 North Senate Avenue
P.O. Box 6015
Indianapolis, Indiana 46206-6015
Phone: 317-233-5674
Fax: 317-233-5967**

**PART 70 OPERATING PERMIT
EMERGENCY OCCURRENCE REPORT**

Source Name: Central Soya Company, Inc.
Source Address: 1200 North 2nd Street, Decatur, Indiana 46733
Mailing Address: P.O. Box 1002, Decatur, Indiana 46733
Part 70 Permit No.: T001-5610-00005

This form consists of 2 pages

Page 1 of 2

- 9** This is an emergency as defined in 326 IAC 2-7-1(12)
- C** The Permittee must notify the Office of Air Quality (OAQ), within four (4) business hours (1-800-451-6027 or 317-233-5674, ask for Compliance Section); and
 - C** The Permittee must submit notice in writing or by facsimile within two (2) days (Facsimile Number: 317-233-5967), and follow the other requirements of 326 IAC 2-7-16.

If any of the following are not applicable, mark N/A

Facility/Equipment/Operation:

Control Equipment:

Permit Condition or Operation Limitation in Permit:

Description of the Emergency:

Describe the cause of the Emergency:

If any of the following are not applicable, mark N/A

Page 2 of 2

Date/Time Emergency started:
Date/Time Emergency was corrected:
Was the facility being properly operated at the time of the emergency? Y N Describe:
Type of Pollutants Emitted: TSP, PM-10, SO ₂ , VOC, NO _x , CO, Pb, other:
Estimated amount of pollutant(s) emitted during emergency:
Describe the steps taken to mitigate the problem:
Describe the corrective actions/response steps taken:
Describe the measures taken to minimize emissions:
If applicable, describe the reasons why continued operation of the facilities are necessary to prevent imminent injury to persons, severe damage to equipment, substantial loss of capital investment, or loss of product or raw materials of substantial economic value:

Form Completed by: _____

Title / Position: _____

Date: _____

Phone: _____

A certification is not required for this report.

**INDIANA DEPARTMENT OF ENVIRONMENTAL MANAGEMENT
OFFICE OF AIR QUALITY
COMPLIANCE DATA SECTION**

**PART 70 OPERATING PERMIT
SEMI-ANNUAL NATURAL GAS FIRED BOILER CERTIFICATION**

Source Name: Central Soya Company, Inc.
Source Address: 1200 North 2nd Street, Decatur, Indiana 46733
Mailing Address: P.O. Box 1002, Decatur, Indiana 46733
Part 70 Permit No.: T001-5610-00005

9	Natural Gas Only
9	Alternate Fuel burned
	From: _____ To: _____

I certify that, based on information and belief formed after reasonable inquiry, the statements and information in the document are true, accurate, and complete.
Signature:
Printed Name:
Title/Position:
Phone:
Date:

A certification by the responsible official as defined by 326 IAC 2-7-1(34) is required for this report.

**INDIANA DEPARTMENT OF ENVIRONMENTAL MANAGEMENT
 OFFICE OF AIR QUALITY
 COMPLIANCE DATA SECTION**

Part 70 Quarterly Report

Source Name: Central Soya Company, Inc.
 Source Address: 1200 North 2nd Street, Decatur, Indiana 46733
 Mailing Address: P.O. Box 1002, Decatur, Indiana 46733
 Part 70 Permit No.: T001-5610-00005
 Facility: Oil Extraction Facilities
 Parameter: Hexane Usage
 Limit: Less than 330,000 gallons per year

YEAR: _____

Month	Column 1	Column 2	Column 1 + Column
	This Month	Previous 11 Months	12 Month Total
Month 1			
Month 2			
Month 3			

- 9 No deviation occurred in this quarter.
- 9 Deviation/s occurred in this quarter.
 Deviation has been reported on: _____

Submitted by: _____
 Title / Position: _____
 Signature: _____
 Date: _____
 Phone: _____

Attach a signed certification to complete this report.

**INDIANA DEPARTMENT OF ENVIRONMENTAL MANAGEMENT
 OFFICE OF AIR QUALITY
 COMPLIANCE DATA SECTION**

Part 70 Quarterly Report

Source Name: Central Soya Company, Inc.
 Source Address: 1200 North 2nd Street, Decatur, Indiana 46733
 Mailing Address: P.O. Box 1002, Decatur, Indiana 46733
 Part 70 Permit No.: T001-5610-00005
 Facility: Grain Processing Facilities
 Parameter: Soybean grain processed after the grain dryers
 Limit: Less than 1,368,750 tons per year

YEAR: _____

Month	Column 1	Column 2	Column 1 + Column
	This Month	Previous 11 Months	12 Month Total
Month 1			
Month 2			
Month 3			

- 9 No deviation occurred in this quarter.
- 9 Deviation/s occurred in this quarter.
 Deviation has been reported on: _____

Submitted by: _____
 Title / Position: _____
 Signature: _____
 Date: _____
 Phone: _____

Attach a signed certification to complete this report.

**INDIANA DEPARTMENT OF ENVIRONMENTAL MANAGEMENT
OFFICE OF AIR QUALITY
COMPLIANCE DATA SECTION**

**PART 70 OPERATING PERMIT
QUARTERLY DEVIATION AND COMPLIANCE MONITORING REPORT**

Source Name: Central Soya Company, Inc.
Source Address: 1200 North 2nd Street, Decatur, Indiana 46733
Mailing Address: P.O. Box 1002, Decatur, Indiana 46733
Part 70 Permit No.: T001-5610-00005

Months: _____ to _____ Year: _____

Page 1 of 2

This report is an affirmation that the source has met all the requirements stated in this permit. This report shall be submitted quarterly based on a calendar year. Any deviation from the requirements, the date(s) of each deviation, the probable cause of the deviation, and the response steps taken must be reported. Deviations that are required to be reported by an applicable requirement shall be reported according to the schedule stated in the applicable requirement and do not need to be included in this report. Additional pages may be attached if necessary. If no deviations occurred, please specify in the box marked "No deviations occurred this reporting period".

9 NO DEVIATIONS OCCURRED THIS REPORTING PERIOD.

9 THE FOLLOWING DEVIATIONS OCCURRED THIS REPORTING PERIOD

Permit Requirement (specify permit condition #)

Date of Deviation:

Duration of Deviation:

Number of Deviations:

Probable Cause of Deviation:

Response Steps Taken:

Permit Requirement (specify permit condition #)

Date of Deviation:

Duration of Deviation:

Number of Deviations:

Probable Cause of Deviation:

Response Steps Taken:

Permit Requirement (specify permit condition #)	
Date of Deviation:	Duration of Deviation:
Number of Deviations:	
Probable Cause of Deviation:	
Response Steps Taken:	
Permit Requirement (specify permit condition #)	
Date of Deviation:	Duration of Deviation:
Number of Deviations:	
Probable Cause of Deviation:	
Response Steps Taken:	
Permit Requirement (specify permit condition #)	
Date of Deviation:	Duration of Deviation:
Number of Deviations:	
Probable Cause of Deviation:	
Response Steps Taken:	

Form Completed By: _____

Title/Position: _____

Date: _____

Phone: _____

Attach a signed certification to complete this report.

July 3, 2002

**Indiana Department of Environmental Management
Office of Air Quality**

Addendum to the
Technical Support Document for Part 70 Permit

Source Background and Description

Source Name:	Central Soya Company, Inc.
Source Location:	1200 North 2 nd Street, Decatur, IN 46733
County:	Adams
SIC Code:	2075, 5153, 2048
Operation Permit No.:	T001-5610-00005
Permit Reviewer:	ERG/KC

On January 4, 2002, the Office of Air Quality (OAQ) had a notice published in the Decatur Daily Democrat in Decatur, Indiana, stating that Central Soya Company, Inc. had applied for a Part 70 Permit to operate a grain handling, animal feed production, soybean meal production, and soybean oil extraction plant with control. The notice also stated that OAQ proposed to issue a permit for this operation and provided information on how the public could review the proposed permit and other documentation. Finally, the notice informed interested parties that there was a period of thirty (30) days to provide comments on whether or not this permit should be issued as proposed.

On January 30, 2002, Central Soya Company, Inc. submitted comments on the proposed Part 70 Permit. The summary of the comments is as follows:

Comment 1:

Central Soya requests that the unit description in A.2(b)(1) be changed from "rotex feed drag" to "megatex enclosed conveyor" and that the unit description in A.(b)(13) be changed from "belt head section" to "Hi-Roller." They also requested that it be noted that the drag was replaced with the conveyor in 1997 and the belt head section was replaced with the Hi-Roller in 1992.

Response to Comment 1:

IDEM made the following changes as a result of this comment:

A.2 Emission Units and Pollution Control Equipment Summary [326 IAC 2-7-4(c)(3)] [326 IAC 2-7-5(15)]

This stationary source consists of the following emission units and pollution control devices:

NOTE: All throughputs and capacities are included in a IDEM, OAQ confidential file as the source considers them confidential.

(b) The following grain elevator components, together identified as 2EL1, using a baghouse and oil pressant for PM control, and exhausting to stack 2EL:

- (1) One (1) dryer ~~rotex feed drag~~ **megatex enclosed conveyor**, constructed in ~~1979~~ **1997**;
- (13) One (1) west to east ~~belt head section~~ **Hi-Roller**, constructed ~~prior to 1977 in~~ **1992**;

SECTION D.1 FACILITY OPERATION CONDITIONS

Facility Description [326 IAC 2-7-5(15)]:

- (b) The following grain elevator components, together identified as 2EL1, using a baghouse and oil suppressant for PM control, and exhausting to stack 2EL:
 - (1) One (1) dryer ~~rotex feed drag~~ **megatex enclosed conveyor**, constructed in ~~1979~~ **1997**;
 - (13) One (1) west to east ~~belt head section~~ **Hi-Roller**, constructed ~~prior to 1977 in~~ **1992**;

Comment 2:

Central Soya requests that the items listed as A.2(c)(2), A.2(c)(6), and A.2(c)(7) be deleted as they were replaced by the Hi-Roller mentioned in Comment 1.

Response to Comment 2:

The following changes were made to the permit as a result of this comment:

A.2 Emission Units and Pollution Control Equipment Summary [326 IAC 2-7-4(c)(3)] [326 IAC 2-7-5(15)]

This stationary source consists of the following emission units and pollution control devices:

NOTE: All throughputs and capacities are included in a IDEM, OAQ confidential file as the source considers them confidential.

- (c) The following grain elevator components, together identified as 5EL1, using a baghouse and oil suppressant for PM control, and exhausting to stack 5EL:
 - (1) One (1) north tripper buggy, constructed in 1978;
 - ~~(2) One (1) west workhouse turnhead, constructed in 1978;~~
 - ~~(3)~~ **(2)** One (1) north galley belt loader, constructed in 1978;
 - ~~(4)~~ **(3)** One (1) east west belt, constructed in 1995; **and**
 - ~~(5)~~ **(4)** One (1) bin 102, constructed prior to 1977;
 - ~~(6) One (1) north south belt, constructed prior to 1977; and~~
 - ~~(7) One (1) west workhouse to east workhouse belt loader, constructed prior to 1977;~~

SECTION D.1 FACILITY OPERATION CONDITIONS

Facility Description [326 IAC 2-7-5(15)]:

- (c) The following grain elevator components, together identified as 5EL1, using a baghouse and oil suppressant for PM control, and exhausting to stack 5EL:
- (1) One (1) north tripper buggy, constructed in 1978;
 - ~~(2) One (1) west workhouse turnhead, constructed in 1978;~~
 - (3 2) One (1) north galley belt loader, constructed in 1978;
 - ~~(4 3) One (1) east west belt, constructed in 1995; and~~
 - (5 4) One (1) bin 102, constructed prior to 1977;
 - ~~(6) One (1) north south belt, constructed prior to 1977; and~~
 - ~~(7) One (1) west workhouse to east workhouse belt loader, constructed prior to 1977;~~

Comment 3:

Central Soya noted that the incorrect stack and unit identifier are referenced in A.2(i). They would like 15EX and 15EX1 to be changed to 20EL and 20 EL1, respectively.

Response to Comment 3:

The following changes were made as a result of this comment:

A.2 Emission Units and Pollution Control Equipment Summary [326 IAC 2-7-4(c)(3)] [326 IAC 2-7-5(15)]

This stationary source consists of the following emission units and pollution control devices:

NOTE: All throughputs and capacities are included in a IDEM, OAQ confidential file as the source considers them confidential.

- (i) One (1) truck dump #7, identified as ~~15EX1~~ 20EL1, constructed in 1997, consisting of one (1) weight scale truck unloading pit, and two (2) enclosed bucket elevator legs, using a baghouse for PM control, and exhausting to stack ~~15EX 20EL~~;

SECTION D.1 FACILITY OPERATION CONDITIONS

Facility Description [326 IAC 2-7-5(15)]:

- (i) One (1) truck dump #7, identified as ~~15EX1~~ 20EL1, constructed in 1997, consisting of one (1) weight scale truck unloading pit, and two (2) enclosed bucket elevator legs, using a baghouse for PM control, and exhausting to stack ~~15EX 20EL~~;

D.1.2 New Source Performance Standards (NSPS) Grain Elevators [326 IAC 12] [40 CFR Subpart DD 60.302]

- (a) Pursuant to 40 CFR Part 60, Subpart DD 60.302(b), process emission gases discharged into the atmosphere from the following units:

(7) Unit ~~45EX4~~ **20EL1**; Truck Dump #7.

D.1.4 Particulate Matter (PM) [326 IAC 6-3-2]

Pursuant to 326 IAC 6-3-2 (Process Operations), the particulate matter (PM) from the following units shall be limited by the equation following this table:

Unit	Description
45EX4 20EL1	Truck Dump #7

D.1.6 Particulate Matter (PM)

(a) In order to comply with Conditions D.1.2, D.1.3, and D.1.4, the baghouses for PM control shall be in operation and control emissions from 1EL1, 2EL1, 5EL1, 10EL1, 14EL1, and ~~45EX4~~ **20EL1** at all times that the processes are in operation.

D.1.8 Parametric Monitoring

The Permittee shall record the total static pressure drop across the baghouses used in conjunction with 1EL1, 2EL1, 5EL1, 10EL1, 14EL1, ~~45EX4~~ and **20EL1** at least once per shift when the processes are in operation when venting to the atmosphere. When for any one reading, the pressure drop across the baghouses is outside the normal range of 0.25 and 12.0 inches of water or a range established during the latest stack test, the Permittee shall take reasonable response steps in accordance with Section C - Compliance Response Plan - Failure to Take Response Steps. A pressure reading that is outside the above mentioned range is not a deviation from this permit. Failure to take response steps in accordance with Section C - Compliance Response Plan - Failure to Take Response Steps, shall be considered a violation of this permit.

Comment 4:

Central Soya requests that the unit described in A.2(k) (4EL1) be deleted from the significant activity list and placed in the insignificant activity list because the source is a fugitive source of particulate emissions and qualifies as an insignificant activity.

Response to Comment 4:

No change was made as a result of this comment. Even though unit 4EL1 is a fugitive source, it has the potential to emit greater than five (5) tons per year of PM10. Therefore this source cannot be considered an insignificant activity.

Comment 5:

Central Soya requests that the description "vegetable oil" in A.2(rrr) be changed to "vegetable oil, waste oils, and hazardous chemicals." These changes are consistent with IDEM authorizations dating back to 1981 and are consistent with USEPA ID No. 005 129 499.

Response to Comment 5:

The following changes were made as a result of this comment:

A.2 Emission Units and Pollution Control Equipment Summary [326 IAC 2-7-4(c)(3)] [326 IAC 2-7-5(15)]

This stationary source consists of the following emission units and pollution control devices:

NOTE: All throughputs and capacities are included in a IDEM, OAQ confidential file as the source considers them confidential.

- (rrr) One (1) Murray natural gas fired, and vegetable oil fired, **waste-oil fired, and hazardous chemical fired** boiler, identified as 3SP1, constructed in 1968, and exhausting to stack 1SP;

SECTION D.3 FACILITY OPERATION CONDITIONS

Facility Description [326 IAC 2-7-5(15)]:

- (rrr) One (1) Murray natural gas fired, and vegetable oil fired, **waste-oil fired, and hazardous chemical fired** boiler, identified as 3SP1, constructed in 1968, and exhausting to stack 1SP;

D.3.6 Used Oil Requirements [329 IAC 13-8]

Pursuant to 329 IAC 13-3-2 (Used Oil Specifications), used oil burned for energy recovery that is classified as off-specification used oil fuel shall comply with the provisions of 329 IAC 13-8 (Used Oil Burners Who Burn Off-specification Used Oil For Energy Recovery), including:

- (1) Receipt of an EPA identification number as outlined in 329 IAC 13-8-3 (Notification),
- (2) Compliance with the used oil storage requirements specified in 329 IAC 13-8-5 (Used Oil Storage), and
- (3) Maintain records pursuant to 329 IAC 13-8-6 (Tracking).
- (4) The waste oil burned in the Murray boiler shall comply with the used oil requirements specified in 329 IAC 13 (Used Oil Management). The burning of mixtures of used oil and hazardous waste that is regulated by 329 IAC 3.1 is prohibited at this source.

Comment 6:

Central Soya requests a modification to Condition B.22(a) (Inspection and Entry). They would like the condition to read as follows: During any reasonable business hour and following the facility safety rules, enter upon the Permittee's premises where a Part 70 source is located, or emissions related activity is conducted, or where records must be kept under the conditions of this permit. The source requests this change to ensure the safety of outside persons entering the facility. Since the facility is regulated under OSHA's PSM rules for hazardous chemicals, the facility is required to ensure that all persons entering the PSM areas are trained, aware of the hazards, and follow all safety rules provided for their protection as well as the protection of the facility.

Response to Comment 6:

No change was made as a result of this comment as inspections can occur at any time. IDEM, OAQ agrees that inspectors need to follow facility safety rules. The Permittee can discuss facility safety rules with the inspector. Based on these discussions with the Permittee, the inspector will then determine what is necessary to perform his job.

Comment 7:

Central Soya requests that Condition B.22(e) (Inspection and Entry) be modified to read as follows: Utilize photographic, recording, testing, monitoring, or other equipment, that meets the facility safety requirements for the purpose of assuring compliance with this permit or applicable requirements. This change is requested in order to ensure the safety of outside persons entering the facility as well as to ensure the protection of the facility.

Response to Comment 7:

No change was made as a result of this comment. IDEM, OAQ agrees that inspectors need to use safe equipment. The Permittee can work with the inspector at the time of inspection to determine what equipment to use. Based on discussions with the Permittee, the inspector will then determine what equipment is appropriate to accomplish his job.

Comment 8:

Central Soya requests that unit 8EL1 be deleted from Condition D.1.2 (New Source Performance Standards (NSPS) Grain Elevators) and from Condition D.1.4 (Particulate Matter) because the unit is a closed conveyor with no aspiration or discharge to the atmosphere. The source also requests that unit 7EL1 be deleted from Condition D.2.1 (Particulate Matter) because this unit is a closed conveyor with no aspiration or discharge to the atmosphere.

Response to Comment 8:

No change was made as a result of this comment. Unit 8EL1 is no longer subject to 40 CFR 60, Subpart DD pursuant to comment 25. Even though unit 8EL1 and 7EL1 are totally enclosed, there is still the potential for the units to emit particulate matter. Therefore the units are still subject to 326 IAC 6-3-2.

Comment 9:

Central Soya requests that Conditions D.1.7, D.2.5, D.3.6, and D.5.7 (Visible Emissions Notations) be changed to require the notations once per day rather than once per shift. They also request that the corresponding record keeping requirements in Conditions D.1.11, D.2.11, D.3.7 and D.5.12 be changed to reflect this change. Central Soya notes that some departments only operate one shift per day and others operate on 12 hour shifts. They feel that this change to the condition will reduce confusion and is consistent with other Title V permits issued by IDEM.

Response to Comment 9:

The visible emissions notations are used to indicate compliance with 326 IAC 5-1 and 326 IAC 6. This requirement is designed as a trigger that the source perform some corrective action on the facility if visible emissions are abnormal, to ensure continuous compliance with emission limitation. IDEM believes that once per shift notations are reasonable and adequate in order to ensure compliance with permit requirements. Therefore, when more than one shift occurs during daylight hours, visible emissions notations shall be made during each shift during normal daylight hours. Even though some departments only operate one shift a day, the condition must still require visible emission notations once per shift during daylight hours in order to demonstrate compliance in case the department chooses to operate more than one shift per day in the future.

Comment 10:

Central Soya requests that visible emissions notations be required for only units 1EL1, 2EL1, 5EL1, 10EL1, 14EL1, and 20EL1 to be consistent with Condition D.1.6(a).

Response to Comment 10:

The OAQ believes that it is reasonable to require compliance monitoring for the following units that rely on control devices to comply with allowable emissions at the level of: 1EL1, 2EL1, 5EL1, 10EL1, 14EL1, 19EL1, and 20EL1, not just the units listed in Condition D.1.6(a) which each are controlled by a baghouse. This is consistent with IDEM guidance. In order to clarify which units need visible emissions notations, the following change was made to the permit:

D.1.7 Visible Emissions Notations

- (a) Once per shift visible emission notations of ~~the facility stack~~ **Unit 1EL1, 2EL1, 5EL1, 10EL1, 14EL1, 19EL1, and 20EL1 stack** exhaust shall be performed during normal daylight operations when exhausting to the atmosphere. A trained employee shall record whether emissions are normal or abnormal.

Comment 11:

Central Soya requests that the once per shift pressure drop reading required in Conditions D.1.8 and D.2.6 (Parametric Monitoring) be changed to once per week. The source also requests that the corresponding record keeping requirements in Conditions D.1.11 and D.2.11 be changed to reflect this change in monitoring frequency. They feel that visible emissions notations will provide adequate monitoring and will likely reveal potential problems faster than pressure drop deviations. Pressure drop deviations are normally better predictors of long-term baghouse performance. Additionally, the source feels that changing this requirement is consistent with other Title V permits issued for similar sources in Indiana.

Response to Comment 11:

Monitoring of the static pressure drop can alert the operator to relative changes (such as dust cake resistance) over a period of time. The operator can use this information to chart trends and determine if the unit is operating within the optimal range as determined by baseline testing of the unit and manufacturer's specifications. Pressure drop is an indicator of a variety of conditions within the baghouse. Any deviations from the normal operational range of the unit, whether gradual or sudden, should alert the operator that the unit needs maintenance. The Compliance Response Plan should include response steps to anticipate corrective actions when abnormal conditions arise. Both gradual and sudden changes in the pressure drop could result in damage to the bags or baghouse if not properly addressed. The OAQ does not believe that a weekly monitoring frequency is adequate to indicate compliance with 326 IAC 6. Therefore, the OAQ believes that pressure drop readings should be taken at least once per shift. The requirements to measure the pressure drops across the baghouses will remain unchanged in the permit.

Comment 12:

Central Soya requests that the instrument calibration frequency in Conditions D.1.8 and D.2.6 (Parametric Monitoring) be changed from once every six months to annually. The source feels that visual emissions monitoring should be sufficient to detect any problems that might exist and the types of monitoring equipment employed are unlikely to drift from calibration in the time period indicated.

Response to Comment 12:

No change was made as a result of this comment. The once per shift pressure drop monitoring is necessary to ensure compliance with 326 IAC 6 and to alert the operator of potential baghouse problems. In order to accurately assess compliance, the instrument used for determining compliance must be properly calibrated. IDEM, OAQ feels that calibrations once every six months is necessary for proper calibration.

Comment 13:

Central Soya requests that the baghouse and self-cleaning screen inspections required in Conditions D.1.9 and D.2.7 (Baghouse and Self-Cleaning Screen Inspections), the self-cleaning screen inspections in

Condition D.5.8 (Self-Cleaning Screen Inspections) and the cyclone inspections required in Conditions D.2.9 and D.5.10 (Cyclone Inspections) be changed from quarterly to annually. They feel this change is necessary because some inspections require shutdown of continuous operating equipment, most under vacuum to prevent leaks, that will cause greater increases in emissions of other pollutants. The source also feels that the visual emissions notations and pressure drop readings should be sufficient to detect any problem that may exist.

Response to Comment 13:

The following changes were made as a result of this comment.

D.1.9 Baghouse and Self-Cleaning Screen Inspections

An inspection shall be performed ~~each calendar quarter~~ **once per year** of all bags and self-cleaning screens controlling the facilities when venting to the atmosphere. ~~A baghouse and self-cleaning screen inspections shall be performed within three months of redirecting vents to the atmosphere and every three months thereafter.~~ Inspections are optional when venting to the indoors. All defective bags and screens shall be replaced.

D.2.7 Baghouse and Self-Cleaning Screen Inspections

An inspection shall be performed ~~each calendar quarter~~ **once per year** of all bags and self-cleaning screens controlling the facilities when venting to the atmosphere. ~~A baghouse or self-cleaning screen inspection shall be performed within three months of redirecting vents to the atmosphere and every three months thereafter.~~ Inspections are optional when venting to the indoors. All defective bags and screens shall be replaced.

D.2.9 Cyclone Inspections

An inspection shall be performed ~~each calendar quarter~~ **once per year** of all cyclones controlling the processes when venting to the atmosphere. ~~A cyclone inspection shall be performed within three months of redirecting vents to the atmosphere and every three months thereafter.~~ Inspections are optional when venting to the indoors.

D.5.8 Self-Cleaning Screen Inspections

An inspection shall be performed ~~each calendar quarter~~ **once per year** of all self-cleaning screens controlling the facilities when venting to the atmosphere. ~~A self-cleaning screen inspection shall be performed within three months of redirecting vents to the atmosphere and every three months thereafter.~~ Inspections are optional when venting to the indoors. All defective screens shall be replaced.

D.5.10 Cyclone Inspections

An inspection shall be performed ~~each calendar quarter~~ **once per year** of all cyclones controlling the processes when venting to the atmosphere. ~~A cyclone inspection shall be performed within three months of redirecting vents to the atmosphere and every three months thereafter.~~ Inspections are optional when venting to the indoors.

Comment 14:

Central Soya requests that the description of Unit 21EX1 in Condition D.2.1 (Particulate Matter) be changed from "aspirators" to "A and B cooler" in order to more accurately describe the unit. The source also noted that the descriptions for Units 27EX1 and 8EX1 were switched. They would like this error corrected.

Response to Comment 14:

IDEM agrees with the comment and the following changes were made:

D.2.1 Particulate Matter (PM) [326 IAC 6-3-2]

Pursuant to 326 IAC 6-3-2 (Process Operations), the particulate matter (PM) from the following units shall not exceed the pound per hour emission rate calculated using the equation following this table:

Unit	Description
21EX1	Aspirators A and B Cooler
23EX1	Meal Storage Silos
25EX1	Zinc Receiving Bin
25EX2	Zinc Surge Bin
27EX1	Rumen Conveyor Rotary Reactor
8EX1	Rotary Reactor Rumen Conveyor
29EX1	Rumen Loadout Bins
30EX1	Rumen Surge Bin

Comment 15:

Central Soya requests that the visible emissions monitoring contained in Condition D.2.5 (Visible Emissions Notations) only be required for the following units: 9EL, 12EL, 15EL, 1EX, 3EX, 4EX, 5EX, 6EX, 7EX, 13EX, 14EX, 21EXA, and 21EXB. The source requests monitoring for only these units because they believe these are the only units in this section that are above the thresholds for monitoring established by IDEM guidance.

Response to Comment 15:

The OAQ believes that it is reasonable to require compliance monitoring for the following units that rely on control devices to comply with allowable emissions at the level of: 3EL, 4EL, 6EL, 9EL, 12EL, 13EL, 15EL, 17EL, 103EO, 4SP, 5SP, 1EX, 3EX, 4EX, 5EX, 6EX, 7EX, 9EX, 10EX, 11EX, 12EX, 13EX, 14EX, 21EX-A, 21EX-B, 23EX, 25EX, 8EX, 27EX, 29EX, and 30EX. Visible emissions notations are not required for the following controlled units because they have allowable emissions pursuant to 326 IAC 6-3-2 that are low: 204RO, 102EO, 1EF, and 2EF. Visible emissions notations are not required for the following units because they have no control device and have low actual emissions: 7EL, 2EX, 3EF, 4EF, 5EF, 16EX, and 18EX. Therefore the following changes were made to this permit:

D.2.5 Visible Emissions Notations

- (a) Once per shift visible emission notations of ~~the 3EL, 4EL, 6EL, 9EL, 12EL, 13EL, 15EL, 17EL, 103EO, 4SP, 5SP, 1EX, 3EX, 4EX, 5EX, 6EX, 7EX, 9EX, 10EX, 11EX, 12EX, 13EX, 14EX, 21EX-A, 21EX-B, 23EX, 25EX, 8EX, 27EX, 29EX, and 30EX~~ stack exhaust shall be performed during normal daylight operations when exhausting to the atmosphere. A trained employee shall record whether emissions are normal or abnormal.

Comment 16:

Central Soya requests that parametric monitoring only be required for the following stacks: 9EL, 12EL, 15EL, 1EX, 3EX, 4EX, 5EX, 6EX, 7EX, 13EX, 14EX, 21EXA, and 21EXB. The source requests monitoring for only these units because they believe that these are the only units in this section that are above the thresholds for monitoring established by IDEM guidance.

Response to Comment 16:

The OAQ believes that it is reasonable to require compliance monitoring for the following units that rely on a baghouse to comply with allowable emissions at the level of: 6EL, 9EL, 12EL, 13EL, 15EL, 103EO, 4SP, 5SP, 1EX, 3EX, 4EX, 5EX, 6EX, 7EX, 9EX, 10EX, 11EX, 12EX, 25EX, 29EX, and 30EX. This is consistent with IDEM guidance. To clarify this, the following change was made to the permit:

D.2.6 Parametric Monitoring

The Permittee shall record the total static pressure drop across the baghouses ~~used in conjunction with the processes~~ **controlling 6EL, 9EL, 12EL, 13EL, 15EL, 103EO, 4SP, 5SP, 1EX, 3EX, 4EX, 5EX, 6EX, 7EX, 9EX, 10EX, 11EX, 12EX, 25EX, 29EX, and 30EX** at least once per shift when the processes are in operation when venting to the atmosphere. When for any one reading, the pressure drop across the baghouses is outside the normal range of 0.25 and 12.0 inches of water or a range established during the latest stack test, the Permittee shall take reasonable response steps in accordance with Section C - Compliance Response Plan - Failure to Take Response Steps. A pressure reading that is outside the above mentioned range is not a deviation from this permit. Failure to take response steps in accordance with Section C - Compliance Response Plan - Failure to Take Response Steps, shall be considered a violation of this permit.

Comment 17:

Central Soya requests that visible emissions notations in Condition D.3.6 only be required for unit 1SP. The source requests monitoring for only this unit because they believe that this unit is the only unit in this section that is above the thresholds for monitoring established by IDEM guidance.

Response to Comment 17:

Visible emissions notations are required whenever a unit combusts coal. Therefore, the following changes were made to Condition D.3.6 (Visible Emissions Notations) to clarify this:

D.3.6 Visible Emissions Notations

- (a) Once per shift visible emission notations of ~~the 1SP~~ stack exhaust shall be performed during normal daylight operations when combusting coal and exhausting to the atmosphere. A trained employee shall record whether emissions are normal or abnormal.

Comment 18:

Central Soya requests that the requirement for the semi-annual natural gas certification in Condition D.3.8(a) be removed or the boiler that needs this certification be clarified. The source noted that units 105EO1, 106EO1, and 108EO1 are only capable of firing natural gas so they feel that a certification will serve little purpose. They also noted that units 1SP and 2SP have the capability to burn natural gas and coal, but they have additional record keeping and reporting requirements.

Response to Comment 18

The natural gas certification is used in lieu of requiring visible emissions notations when a unit is combusting natural gas. Therefore this certification is required for all boilers listed in this section. In order to clarify this, the following change was made to the permit:

D.3.8 Reporting Requirements

- (a) A certification, signed by the responsible official, that certifies all of the fuels combusted during the period **for units 105EO1, 106EO1, 108EO1, 1SP1, 2SP1, and 3SP1**. The

natural gas-fired boiler certification does require the certification by the “responsible official” as defined by 326 IAC 2-7-1(34);

Comment 19

Central Soya requests that the reference to PM in Condition D.4.7 (Volatile Organic Compounds) be removed as the mineral oil absorber controls VOC not PM.

Response to Comment 19

The reference to PM was inadvertently placed in Condition D.4.7 (Volatile Organic Compounds). This error was corrected as follows:

D.4.7 Volatile Organic Compounds (VOC)

In order to comply with Conditions D.4.1 and D.4.2, the mineral oil absorber for ~~PM~~ **VOC** control shall be in operation and control emissions from the listed facilities at all times when the facilities are in operation.

Comment 20

Central Soya noted that it is unclear for which facility the testing requirement in Condition D.4.8 (Testing Requirements) is intended to apply. Central Soya believes that the combination of parametric monitoring and the overall VOC loss limit calculated by material balance (and limited to 330,000 gallons per year) provides sufficient information to determine compliance. Therefore, they request that the testing requirement be deleted.

Response to Comment 20

The testing requirement is to determine compliance with the mineral oil absorption system control efficiency of 99.9%. The mass balance calculations are acceptable for estimation purposes but they do not guarantee actual efficient performance of the control devices. Therefore, the testing is required to demonstrate that the mineral oil absorption system can achieve a control efficiency of 99.9% even at worst case conditions. Therefore, the testing requirement will remain in the permit, but the following change was made to clarify what unit the testing is for.

D.4.8 Testing Requirements [326 IAC 2-7-6(1),(6)] [326 IAC 2-1.1-11]

During the period between 30 and 36 months after issuance of this permit, in order to demonstrate compliance with Conditions D.4.1, the Permittee shall perform VOC testing **for the mineral absorption system to demonstrate compliance with the 99.9% control efficiency** utilizing methods as approved by the Commissioner. This test shall be repeated at least once every five (5) years from the date of this valid compliance demonstration. Testing shall be conducted in accordance with Section C- Performance Testing.

Comment 21

Central Soya requests that the submittal date for the notification of compliance status in Condition D.4.9 (Compliance Requirements) be changed from June 12, 2004 to June 30, 2004. The source stated that notification of compliance for an existing source is generally no later than 51 calendar months after the effective date of the NESHAP; 36 months for compliance, 12 operating months to record data, 1 month to calculate compliance ratio, and 2 months to complete the report. The source stated that EPA is in the process of administratively amending the rule to clarify the incorrect statement in the final rule. The source would also like this change to be reflected in Condition D.4.14(b) (Reporting Requirements).

Response to Comment 21

40 CFR 63.2860 currently states that the Permittee must submit the notification no later than 50 calendar months after the effective date of this NESHAP (June 12, 2001). However, since the EPA is in the process of changing this, the following change was made to the permit:

D.4.9 Compliance Requirements [40 CFR Part 63, Subpart GGGG]

- (a) Pursuant to 40 CFR 63.2850, the source shall:
- (1) Submit the following necessary notifications in accordance with 40 CFR 63.2860:
 - (B) Notification of compliance status, no later than 60 days after determining your initial 12 operating months compliance ratio. For an existing source, such as this source, the notification must be submitted no later than June 12, 2004 **or the date as stated in 40 CFR 63.2860.**

D.4.14 Reporting Requirements

- (b) To document compliance with 40 CFR Part 63, Subpart GGGG, the Permittee must submit annual compliance certifications. The first annual compliance certification is due no later than 60 days after determining the initial 12 operating months compliance ratio. For an existing source, such as this source, the notification must be submitted no later than 50 calendar months after the effective date of this subpart, April 12, 2001 **or the date as stated in 40 CFR 63.2860.** Each subsequent annual compliance certification is due 12 months after the previous annual compliance certification. The annual compliance certification provides the compliance status for each operating month during the 12 calendar months period ending 60 days **or the time frame as stated in 40 CFR 63.2860** prior to the date on which the report is due. The annual certification shall include the following information:

Comment 22

Central Soya requests that the requirement in Condition D.4.12(a) (Monitoring) to measure the LEL once per shift be changed to once per day. Since the emission rate is required to be determined daily by measuring the air flow rate and the concentration of hexane in the air stream and this concentration is determined by measuring the LEL, there is no reason why the LEL should be measured more frequently than the emission rate is to be determined.

Response to Comment 22

Since the emission rate is to be determined daily and LEL concentration is needed for this determination, the LEL only needs to be measured once per day. The following change was made as a result of this comment:

D.4.12 Monitoring

- (a) To document compliance with Conditions D.4.1 and D.4.2, the mineral oil absorption vent VOC (hexane) emission rate shall be determined daily by measuring the airflow rate and the concentration of hexane in the air stream. This concentration will be determined ~~once per shift~~ **daily** by measuring percent Lower Explosive Limit (LEL). If the air flow meter proves unreliable, airflow can be determined by calculations.

Comment 23

Central Soya requests that the requirement for visible emission notations in Condition D.5.7 be limited just to unit 17EX. The source requests monitoring for only this unit because they believe that this is the only unit in this section that is above the thresholds for monitoring established by IDEM guidance.

Response to Comment 23

The OAQ believes that it is reasonable to require compliance monitoring for the following units that rely on control devices to comply with allowable emissions at the level of: 16EL and 17EX. This is consistent with IDEM guidance. To clarify this, the following change was made to the permit:

D.5.7 Visible Emissions Notations

- (a) Once per shift visible emission notations of ~~the facility~~ **unit 16EL and 17EX** stack exhaust shall be performed during normal daylight operations when exhausting to the atmosphere. A trained employee shall record whether emissions are normal or abnormal.

Comment 24

Central Soya noted that the Quarterly Report form for the grain processing facilities states that the soybean grain processed after the grain dryers should be limited to less than 1,368,750 gallons per year when the limit should be 1368,750 tons per year. They would like this error to be corrected.

Response to Comment 24

The error was corrected as follows:

INDIANA DEPARTMENT OF ENVIRONMENTAL MANAGEMENT OFFICE OF AIR QUALITY COMPLIANCE DATA SECTION

Part 70 Quarterly Report

Source Name:	Central Soya Company, Inc.
Source Address:	1200 North 2 nd Street, Decatur, Indiana 46733
Mailing Address:	P.O. Box 1002, Decatur, Indiana 46733
Part 70 Permit No.:	T001-5610-00005
Facility:	Grain Processing Facilities
Parameter:	Soybean grain processed after the grain dryers
Limit:	Less than 1,368,750 gallons tons per year

Comment 25

The source claimed that Unit 1EL1 (Truck Dump #2), Unit 2EL1 (Dryer megatex enclosed conveyor, #1 Dryer HI-Roller, Weaver's belt, and 102 Belt), Unit 5EL1 (North tripper buggy, North galley belt loader, and East west belt), Unit 8EL1 (North west receiving house tunnel belt), Unit 10EL1 (Rail Loadout), and Unit 14EL1 (Jumbo silo west galley belt) are not subject to 40 CFR 60, Subpart DD as indicated in Condition D.1.2 (New Source Performance Standards (NSPS) Grain Elevators). The source stated that the construction on Unit 2EL1, 5EL1, 8EL1 and 14EL1 replaced units with closed conveyors and thus, the potential emissions were reduced. For this reason, the source claimed that the construction did not meet the definition of modification and therefore the units are not subject to the NSPS. The source also claimed that the construction on Unit 1EL1 and Unit 10EL1 did not meet the definition of replacement because the cost of the repairs on these units did not exceed 6.5% of the cost of the entire grain elevator. For the reasons described above, the source would like Unit 1EL1, Unit 2EL1, Unit 5EL1, Unit 8EL1, Unit 10EL1 and Unit 14EL1 to be removed from Condition D.1.2.

Response to Comment 25

The applicability section of 40 CFR 60, Subpart DD defines the affected facility as "all grain handling operations." Thus, replacing individual units in and of itself would not trigger NSPS, unless the replacement qualified as a modification or reconstruction. IDEM agrees that since the construction on Unit 2EL1, 5EL1, 8EL1 and 14EL1 reduced the potential to emit from these units and did not increase the capacity of the grain elevator, the construction did not meet the definition of modification. Therefore, these units are not subject to 40 CFR 60, Subpart DD and have been removed from Condition D.1.2.

IDEM disagrees with the source's claim that the construction on Unit 10EL1 did not meet the definition of modification. 40 CFR 60.14(e)(2) states that the following shall not by itself be considered a modification: "An increase in production rate of an existing facility, if that increase can be accomplished without a capital expenditure on that facility." The source is claiming that the changes to Unit 10EL1 increased the production rate of an existing facility without a capital expenditure. However, to determine if a capital expenditure was made, the source is comparing the cost of the repairs to the cost of the entire grain elevator. This analysis is incorrect. According to the applicability section of 40 CFR 60, Subpart DD, the affected facilities are "each truck unloading station, truck loading station, barge and ship unloading station, barge and ship loading station, railcar loading station, railcar unloading station, grain dryer, and all grain handling operations." Since the NSPS defines the affected facility narrowly, to determine if a capital expenditure was made, the cost of the repairs to Unit 10EL1 need to be compared to the railcar loading station to determine if the costs exceeded 6.5%. The source has not provided sufficient evidence that the costs of repairs to Unit 10EL1 do not constitute a replacement. For this reason, Unit 10EL1 was not deleted from Condition D.1.2 as requested by the source.

IDEM also disagrees that Unit 1EL1 should be deleted from Condition D.1.2. As previously mentioned, according to the applicability section of 40 CFR 60, Subpart DD, the affected facilities are "each truck unloading station, truck loading station, barge and ship unloading station, barge and ship loading station, railcar loading station, railcar unloading station, grain dryer, and all grain handling operations." Unit 1EL1 meets the definition of a truck unloading station as defined in Subpart DD and, based on the information provided by Central Soya, was constructed in 1980 to replace another truck unloading station. Because of the truck unloading station is the affected facility, the replacement of the truck unloading station constitutes construction of a new unit. For this reason, Unit 1EL1 is subject to the NSPS as was therefore not deleted from Condition D.1.2 as requested by the source.

Additionally, since truck dump #2, rail loadout, and truck dump #7 are all controlled units with emissions venting through a stack, emissions from these units are not considered fugitive. For this reason, the following change was made to the permit.

D.1.2 New Source Performance Standards (NSPS) Grain Elevators [326 IAC 12] [40 CFR Subpart DD 60.302]

~~(a)~~ Pursuant to 40 CFR Part 60, Subpart DD 60.302(b), process emission gases discharged into the atmosphere from the following units:

~~(1 a)~~ Unit 1EL1: Truck Dump #2;

~~(2)~~ Unit 2EL1: Dryer rotex feed drag, #1 dryer HI-Roller, Weaver's belt, 102 Belt;

~~(3)~~ Unit 5EL1: North tripper buggy, West workhouse turnhead, North galley belt loader, East-west belt;

~~(4)~~ Unit 8EL1: North west receiving house tunnel belt;

~~(5 b)~~ Unit 10EL1: Rail loadout; **and**

~~(6)~~ Unit 14EL1: Jumbo silo west galley belt; and

(7 c) Unit 20EL1; Truck Dump #7.

shall not exceed particulate matter (PM) concentrations of 0.01 gr/dscf. Process emission gases from these facilities shall not exhibit greater than 0 percent opacity.

~~(b) Pursuant to 40 CFR Part 60, Subpart DD 60.302(e)(1), fugitive emissions from Truck Dump #2, Rail loadout and Truck Dump #7 shall not exhibit greater than 5% opacity.~~

Upon further review, IDEM, OAQ made the following changes to the permit. The Table of Contents was updated as needed to reflect these changes.

Updates 1 through 5 have been made to incorporate the Article 2 rule revisions that were adopted on October 3, 2001, and became effective on January 19th, 2002. For more information about this rulemaking, refer to the October 2001 Air Pollution Control Board Packet which can be found on the internet at <http://www.state.in.us/idem/air/rules/apcb/packets/index.html>. The rule revisions were published in the February 1, 2002 Indiana Register which can be found on the internet at <http://www.IN.gov/legislative/register/index-25.html>.

1. Add the new rule cite to B.2 Permit Term.

B.2 Permit Term [326 IAC 2-7-5(2)] [326 IAC 2-1.1-9.5]

This permit is issued for a fixed term of five (5) years from the original date, as determined in accordance with IC 4-21.5-3-5(f) and IC 13-15-5-3. Subsequent revisions, modifications, or amendments of this permit do not affect the expiration date.

2. B.12 Emergency Provisions (a)(b) and (g) have been revised to reflect rule changes to 326 IAC 2-7-16. This section of the rule is now consistent with 40 CFR 70.6(g) and provides an affirmative defense to an action brought for non-compliance with technology based emission limitations only.

B.12 Emergency Provisions [326 IAC 2-7-16]

(a) An emergency, as defined in 326 IAC 2-7-1(12), is not an affirmative defense for an action brought for noncompliance with a federal or state health-based emission limitation, ~~except as provided in 326 IAC 2-7-16.~~

(b) An emergency, as defined in 326 IAC 2-7-1(12), constitutes an affirmative defense to an action brought for noncompliance with a ~~health-based or~~ technology-based emission limitation if the affirmative defense of an emergency is demonstrated through properly signed, contemporaneous operating logs or other relevant evidence that describe the following:

(g) ~~Operations may continue during an emergency only if the following conditions are met:~~

~~(1) If the emergency situation causes a deviation from a technology-based limit, the Permittee may continue to operate the affected emitting facilities during the emergency provided the Permittee immediately takes all reasonable steps to correct the emergency and minimize emissions.~~

~~(2) If an emergency situation causes a deviation from a health-based limit, the Permittee may not continue to operate the affected emissions facilities unless:~~

~~(A) The Permittee immediately takes all reasonable steps to correct the emergency situation and to minimize emissions; and~~

~~(B) Continued operation of the facilities is necessary to prevent imminent injury to persons, severe damage to equipment, substantial loss of capital investment, or loss of product or raw materials of substantial economic value.~~

~~Any operation shall continue no longer than the minimum time required to prevent the situations identified in (g)(2)(B) of this condition.~~

3. B.14 Multiple Exceedances has been deleted, because 326 IAC 2-7-5(1)(E) has been repealed, because it conflicted with 40 CFR 70.6(a)(6).

~~B.14 Multiple Exceedances [326 IAC 2-7-5(1)(E)]~~

~~Any exceedance of a permit limitation or condition contained in this permit, which occurs contemporaneously with an exceedance of an associated surrogate or operating parameter established to detect or assure compliance with that limit or condition, both arising out of the same act or occurrence, shall constitute a single potential violation of this permit.~~

4. B.14 Prior Permits Superseded was added to the permit to help clarify the intent of the new rule 326 IAC 2-1.1-9.5.

B.14 Prior Permits Superseded [326 IAC 2-1.1-9.5]

(a) All terms and conditions of previous permits issued pursuant to permitting programs approved into the state implementation plan have been either

(1) incorporated as originally stated,

(2) revised, or

(3) deleted

by this permit.

(b) All previous registrations and permits are superseded by this permit.

5. Remove (b) from B.13 Permit Shield. Since B.14 Prior Permits Superseded has been added to the permit, it is not necessary for this statement to be in this condition.

~~B.13 Permit Shield [326 IAC 2-7-15] [326 IAC 2-7-20] [326 IAC 2-7-12]~~

~~(b) This permit shall be used as the primary document for determining compliance with applicable requirements established by previously issued permits. All previously issued operating permits are superseded by this permit.~~

2. In C.17 (c)(2) "administrative amendment" has been revised to "minor permit modification", because 326 IAC 2-7-11(a)(7) has been repealed. The title Compliance Monitoring Plan - Failure to Take Response Steps has been changed to Compliance Response Plan - Preparation, Implementation, Records, and Reports throughout the permit. This change in the title was made throughout the permit when ever the condition was mentioned.

C.17 Compliance Response Plan - Failure to Take Response Steps Preparation, Implementation, Records, and Reports [326 IAC 2-7-5] [326 IAC 2-7-6]

(c) The Permittee is not required to take any further response steps for any of the following reasons:

- (2) The Permittee has determined that the compliance monitoring parameters established in the permit conditions are technically inappropriate, has previously submitted a request for ~~an administrative amendment~~ **a minor permit modification** to the permit, and such request has not been denied.

3. For clarification purposes, the following changes were made to Conditions D.1.11(c) and D.2.11(c) (Record Keeping Requirements):

D.1.11 Record Keeping Requirements

- (c) To document compliance with Condition D.1.8, the Permittee shall maintain once per shift records of the total ~~inlet and outlet~~ pressure drop **across the baghouse** during normal operation when venting to the atmosphere.

D.2.11 Record Keeping Requirements

- (c) To document compliance with Condition D.1.8, the Permittee shall maintain once per shift records of the total ~~inlet and outlet~~ pressure drop **across the baghouse** during normal operation when venting to the atmosphere.

4. The following change was made to Condition D.2.1 (Particulate Matter) in order to better describe the equipment:

D.2.1 Particulate Matter (PM) [326 IAC 6-3-2]

Pursuant to 326 IAC 6-3-2 (Process Operations), the particulate matter (PM) from the following units shall not exceed the pound per hour emission rate calculated using the equation following this table:

Unit	Description
1EF1	Vertical Pellet Cooler and Horizontal Pellet Cooler
4EX3	Hull Refining Screw Conveyor, Hull Refining Process, Hull Refining Grinding Process

5. The following errors were corrected:

D.1.7 Visible Emissions Notations

- (e) The Compliance Response Plan for ~~this unit~~ **these processes** shall contain troubleshooting contingency and response steps for when an abnormal emission is observed. Failure to take response steps in accordance with Section C - Compliance ~~Monitoring Response~~ **Plan - Failure to Take Response Steps Preparation, Implementation, Records, and Reports**, shall be considered a violation of this permit.

D.2.5 Visible Emissions Notations

- (e) The Compliance Response Plan for ~~this unit~~ **these processes** shall contain troubleshooting contingency and response steps for when an abnormal emission is observed. Failure to take response steps in accordance with Section C - Compliance ~~Monitoring Response~~ **Plan - Failure to Take Response Steps Preparation, Implementation, Records, and Reports**, shall be considered a violation of this permit.

D.3.6 Visible Emissions Notations

- (e) The Compliance Response Plan for ~~this unit~~ **these processes** shall contain troubleshooting contingency and response steps for when an abnormal emission is observed. Failure to take response steps in accordance with Section C - Compliance ~~Monitoring Response~~ **Plan - Failure to Take Response Steps Preparation, Implementation, Records, and Reports**, shall be considered a violation of this permit.

D.5.7 Visible Emissions Notations

-
- (e) The Compliance Response Plan for ~~this unit~~ **these processes** shall contain troubleshooting contingency and response steps for when an abnormal emission is observed. Failure to take response steps in accordance with Section C - Compliance **Monitoring Response Plan - Failure to Take Response Steps Preparation, Implementation, Records, and Reports**, shall be considered a violation of this permit.

6. The following errors in facility description were corrected:

A.2 Emission Units and Pollution Control Equipment Summary [326 IAC 2-7-4(c)(3)] [326 IAC 2-7-5(15)]

This stationary source consists of the following emission units and pollution control devices:

NOTE: All throughputs and capacities are included in a IDEM, OAQ confidential file as the source considers them confidential.

- (i) One (1) truck dump #7, identified as 15EX1, constructed in 1997, consisting of one (1) weight scale truck unloading pit, and two (2) enclosed bucket elevator legs, using ~~a baghouse~~ **two (2) baghouses in parallel** for PM control, and exhausting to stack 15EX;
- (ff) Six (6) flaking rolls, #1, #2, #3, #4, #5, and #6, constructed in 1996, and B flake n/s drag, constructed in 1991, all identified together as 1EX1, sharing ~~a baghouse~~ **Vox filters** with 1EX2 for PM control, and exhausting to stack 1EX;
- (gg) One (1) flaking roll #14 and flaking roll discharge #14, identified as 1EX2, constructed in 1991, sharing ~~a baghouse~~ **Vox filters** with 1EX1 for PM control, and exhausting to stack 1EX;
- (ggg) One (1) zinc receiving bin, identified as 25EX1, constructed in 1994, sharing a ~~baghouse~~ **bin vent filter** with 25EX2 for PM control, and exhausting to stack 25EX;
- (hhh) One (1) zinc surge bin, identified as 25EX2, constructed in 1994, sharing a ~~baghouse~~ **bin vent filter** with 25EX1 for PM control, and exhausting to stack 25EX;
- (kkk) Rumen loadout bins, identified as 29EX1, constructed in 1994, using a ~~baghouse~~ **bin vent filter** for PM control, and exhausting to stack 29EX; ~~and~~
- (lll) Rumen rework surge bin, identified as 30EX1, constructed in 1994, using a ~~baghouse~~ **polyethylene fabric filter** for PM control, and exhausting to stack 30EX;

SECTION D.1 FACILITY OPERATION CONDITIONS

Facility Description [326 IAC 2-7-5(15)]:

- (i) One (1) truck dump #7, identified as 15EX1, constructed in 1997, consisting of one (1) weight scale truck unloading pit, and two (2) enclosed bucket elevator legs, using ~~a baghouse~~ **two (2) baghouses in parallel** for PM control, and exhausting to stack 15EX;

SECTION D.2 FACILITY OPERATION CONDITIONS

Facility Description [326 IAC 2-7-5(15)]:

- (ff) Six (6) flaking rolls, #1, #2, #3, #4, #5, and #6, constructed in 1996, and B flake n/s drag, constructed in 1991, all identified together as 1EX1, sharing a ~~baghouse~~ **Vox filters** with 1EX2 for PM control, and exhausting to stack 1EX;
- (gg) One (1) flaking roll #14 and flaking roll discharge #14, identified as 1EX2, constructed in 1991, sharing a ~~baghouse~~ **Vox filters** with 1EX1 for PM control, and exhausting to stack 1EX;
- (ggg) One (1) zinc receiving bin, identified as 25EX1, constructed in 1994, sharing a ~~baghouse bin vent filter~~ with 25EX2 for PM control, and exhausting to stack 25EX;
- (hhh) One (1) zinc surge bin, identified as 25EX2, constructed in 1994, sharing a ~~baghouse bin vent filter~~ with 25EX1 for PM control, and exhausting to stack 25EX;
- (kkk) Rumen loadout bins, identified as 29EX1, constructed in 1994, using a ~~baghouse bin vent filter~~ for PM control, and exhausting to stack 29EX; ~~and~~
- (lll) Rumen rework surge bin, identified as 30EX1, constructed in 1994, using a ~~baghouse~~ **polyethylene fabric filter** for PM control, and exhausting to stack 30EX;

D.2.4 Particulate Matter (PM)

- (a) In order to comply with Conditions D.2.1 and D.2.2, the baghouses, **filters**, and cyclones for PM control shall be in operation and control emissions from the listed facilities at all times that the facilities are in operation.

D.2.6 Parametric Monitoring

The Permittee shall record the total static pressure drop across the baghouses **and filters** used in conjunction with the processes at least once per shift when the processes are in operation when venting to the atmosphere. When for any one reading, the pressure drop across the baghouses is outside the normal range of 0.25 and 12.0 inches of water or a range established during the latest stack test, the Permittee shall take reasonable response steps in accordance with Section C - Compliance Response Plan - ~~Failure to Take Response Steps~~ **Preparation, Implementation, Records, and Reports**. A pressure reading that is outside the above mentioned range is not a deviation from this permit. Failure to take response steps in accordance with Section C - Compliance Response Plan - ~~Failure to Take Response Steps~~ **Preparation, Implementation, Records, and Reports**, shall be considered a violation of this permit.

D.2.7 Baghouse, Filter, and Self-Cleaning Screen Inspections

An inspection shall be performed once per year of all bags, **filters**, and self-cleaning screens controlling the facilities when venting to the atmosphere. Inspections are optional when venting to the indoors. All defective bags and screens shall be replaced.

D.2.8 Broken or Failed Bag, Filter, or Screen Detection

In the event that bag or screen failure has been observed:

- (a) For multi-compartment units, the affected compartments will be shut down immediately until the failed units have been repaired or replaced. Operations may continue only if there are no visible emissions or if the event qualifies as an emergency and the Permittee satisfies the emergency provisions of this permit (Section B- Emergency Provisions). Within eight (8) business hours of the determination of failure, response steps according to the timetable described in the Compliance Response Plan shall be initiated. For any

failure with corresponding response steps and timetable not described in the Compliance Response Plan, response steps shall be devised within eight (8) business hours of discovery of the failure and shall include a timetable for completion. Failure to take response steps in accordance with Section C - Compliance ~~Monitoring~~ **Response Plan - Failure to Take Response Steps Preparation, Implementation, Records, and Reports**, shall be considered a violation of this permit.

- (b) For single compartment baghouses, **filters, and screens**, failed units and the associated process will be shut down immediately until the failed units have been repaired or replaced. Operations may continue only if the event qualifies as an emergency and the Permittee satisfies the requirements of the emergency provisions of this permit (Section B - Emergency Provisions).

- 7. The pressure drop range contained in the Parametric Monitoring conditions was changed from 0.25 and 12 inches of water to 3 and 6 inches of water. This change was made because Central Soya could not provide adequate documentation that the baghouses would still be operating properly within the range of 0.25 and 12 inches of water.

D.1.8 Parametric Monitoring

The Permittee shall record the total static pressure drop across the baghouses used in conjunction with 1EL1, 2EL1, 5EL1, 10EL1, 14EL1, 20EL1 at least once per shift when the processes are in operation when venting to the atmosphere. When for any one reading, the pressure drop across the baghouses is outside the normal range of ~~0.25~~ **3.0** and ~~12.0~~ **6.0** inches of water or a range established during the latest stack test, the Permittee shall take reasonable response steps in accordance with Section C - Compliance Response Plan - Preparation, Implementation, Records, and Reports. A pressure reading that is outside the above mentioned range is not a deviation from this permit. Failure to take response steps in accordance with Section C - Compliance Response Plan - Preparation, Implementation, Records, and Reports, shall be considered a violation of this permit.

D.2.6 Parametric Monitoring

The Permittee shall record the total static pressure drop across the baghouses controlling 6EL, 9EL, 12EL, 13EL, 15EL, 103EO, 4SP, 5SP, 1EX, 3EX, 4EX, 5EX, 6EX, 7EX, 9EX, 10EX, 11EX, 12EX, 25EX, 29EX, and 30EX at least once per shift when the processes are in operation when venting to the atmosphere. When for any one reading, the pressure drop across the baghouses is outside the normal range of ~~0.25~~ **3.0** and ~~12.0~~ **6.0** inches of water or a range established during the latest stack test, the Permittee shall take reasonable response steps in accordance with Section C - Compliance Response Plan - Preparation, Implementation, Records, and Reports. A pressure reading that is outside the above mentioned range is not a deviation from this permit. Failure to take response steps in accordance with Section C - Compliance Response Plan - Preparation, Implementation, Records, and Reports, shall be considered a violation of this permit.

- 12. Since Unit 1EL1, Unit 10EL1, and 20EL1 are subject to the requirements of 40 CFR 60, Subpart DD, these units are not subject to 326 IAC 6-3-2. Therefore the following changes were made to the permit:

D.1.4 Particulate Matter (PM) [326 IAC 6-3-2]

Pursuant to 326 IAC 6-3-2 (Process Operations), the particulate matter (PM) from the following units shall be limited by the equation following this table:

Unit	Description
4EL1	Truck Dump #2

Unit	Description
2EL1	Dryer Rotex Feed Drag, Dryer Rotex, Screening Bin Hammermill, #1, #2, and #3 Scalperators, Solvent Screening Leg, #1, #2, and #2 Leg, West to East Belt Head Section, West to East Belt Loader, Dry Bean Leg, #1 Dryer Hi-Roller, Weaver's Belt, 102 Belt
5EL1	North Tripper Buggy, West Workhouse Turnhead, North Galley Belt Loader, East West Belt, West Workhouse to East Workhouse Belt Loader
8EL1	North West Receiving House Tunnel Belt
10EL1	Rail Loadout, North 12,000 bu leg, South 12,000 bu leg
14EL1	Jumbo Silo East Galley Belt, Jumbo Silo West Galley Belt, Jumbo Silo Crossover Galley Belt
19EL1	Grain Dryer #2
20EL1	Truck Dump #7

Interpolation and extrapolation of the data for the process weight rate in excess of 60,000 pounds per hour shall be accomplished by use of the equation:

$$E = 55.0 P^{0.11} - 40 \quad \text{where} \quad E = \text{rate of emission in pounds per hour; and} \\ P = \text{process weight rate in tons per hour}$$

The individual limitations are included in a IDEM, OAQ confidential file because the process weight rates are considered confidential by the source.

Indiana Department of Environmental Management Office of Air Quality

Technical Support Document (TSD) for a Part 70 Operating Permit

Source Background and Description

Source Name: Central Soya Company, Inc.
Source Location: 1200 North 2nd Street, Decatur, Indiana 46733
County: Adams
SIC Code: 2075, 5153, 2048
Operation Permit No.: T001-5610-00005
Permit Reviewer: ERG/KC

The Office of Air Quality (OAQ) has reviewed a Part 70 permit application from Central Soya Company, Inc. relating to the operation of a grain handling, animal feed production, soybean meal production, and soybean oil extraction plant.

Permitted Emission Units and Pollution Control Equipment

The source consists of the following permitted emission units and pollution control devices:

NOTE: All throughputs and capacities are included in a IDEM, OAQ confidential file as the source considers them confidential.

- (a) Truck Dump #2, identified as 1EL1, constructed in 1980, using a baghouse for particulate matter (PM) control, and exhausting to stack 1EL;
- (b) The following grain elevator components, together identified as 2EL1, using a baghouse and oil suppressant for PM control, and exhausting to stack 2EL:
 - (1) One (1) dryer rotex feed drag, constructed in 1979;
 - (2) One (1) dryer rotex, constructed in 1978;
 - (3) One (1) screening bin hammermill, constructed in 1978;
 - (4) One (1) #1 scalperator, constructed prior to 1977;
 - (5) One (1) #2 scalperator, constructed prior to 1977;
 - (6) One (1) #3 scalperator, constructed prior to 1977;
 - (7) One (1) ext. screening bin, constructed prior to 1977;

- (8) One (1) screening bin, constructed prior to 1977;
 - (9) One (1) solvent screening leg, constructed prior to 1977;
 - (10) One (1) #1 leg, constructed prior to 1977;
 - (11) One (1) #2 leg, constructed prior to 1977;
 - (12) One (1) #3 leg, constructed prior to 1977;
 - (13) One (1) west to east belt head section, constructed prior to 1977;
 - (14) One (1) west to east belt loader, constructed prior to 1977;
 - (15) One (1) dry bean leg, constructed prior to 1977;
 - (16) One (1) #1 dryer Hi-Roller, constructed in 1994;
 - (17) One (1) weaver's belt, constructed in 1994; and
 - (18) One (1) 102 belt, constructed in 1994;
- (c) The following grain elevator components, together identified as 5EL1, using a baghouse and oil suppressant for PM control, and exhausting to stack 5EL:
- (1) One (1) north tripper buggy, constructed in 1978;
 - (2) One (1) west workhouse turnhead, constructed in 1978;
 - (3) One (1) north galley belt loader, constructed in 1978;
 - (4) One (1) east west belt, constructed in 1995;
 - (5) One (1) bin 102, constructed prior to 1977;
 - (6) One (1) north south belt, constructed prior to 1977; and
 - (7) One (1) west workhouse to east workhouse belt loader, constructed prior to 1977;
- (d) One (1) north west receiving house enclosed conveyor identified as 8EL1, constructed in 1995, using oil suppressant for PM control, with no aspiration;
- (e) The following grain elevator components, together identified as 10EL1, using a baghouse and oil suppressant for PM control, and exhausting to stack 10EL:
- (1) One (1) rail loadout, constructed in 1984;
 - (2) One (1) north leg, constructed prior to 1960; and
 - (3) One (1) south leg, constructed prior to 1960;
- (f) The following grain elevator components, together identified as 14EL1, using a baghouse and oil suppressant for PM control, and exhausting to stack 14EL:

- (1) One (1) jumbo silo east galley belt, constructed prior to 1977;
- (2) One (1) jumbo silo west galley belt, constructed in 1993; and
- (3) One (1) jumbo silo crossover galley belt, constructed prior to 1977;
- (g) One (1) grain dryer #2, identified as 19EL1, constructed in 1995, using self-cleaning screens for PM control, and exhausting to stack 19EL;
- (h) One (1) natural gas dryer #2 associated with grain dryer #2, identified as 19EL2, constructed in 1995, and exhausting to stack 19EL;
- (i) One (1) truck dump #7, identified as 15EX1, constructed in 1997, consisting of one (1) weight scale truck unloading pit, and two (2) enclosed bucket elevator legs, using a baghouse for PM control, and exhausting to stack 15EX;
- (j) Silo bin vents, identified as 3EL1, constructed prior to 1977, using soybean oil as a dust suppressant, and exhausting to stack 3EL;
- (k) Silo direct loadout, identified as 4EL1, constructed prior to 1977, using soybean oil as a dust suppressant, and exhausting to stack 4EL;
- (l) One (1) south tripper buggy, one (1) south galley belt loader, and one (1) north south belt, identified as 6EL1, all constructed prior to 1977, using a baghouse and oil suppressant for PM control, and exhausting to stack 6EL;
- (m) One (1) south west receiving house enclosed conveyor, identified as 7EL1, constructed in 1995, using oil suppressant for PM control with no aspiration;
- (n) One (1) truck dump #3, identified as 9EL1, constructed in 1976, using a baghouse for PM control, and exhausting to stack 9EL;
- (o) One (1) truck dump #5, identified as 12EL1, constructed prior to 1977, using a baghouse for PM control, and exhausting to stack 12EL;
- (p) One (1) jumbo silo east tunnel belt, one (1) jumbo silo west tunnel belt, and one (1) jumbo silo crossover tunnel belt, identified as 13EL1, all constructed prior to 1977, using a baghouse and oil suppressant for PM control, and exhausting to stack 13EL;
- (q) One (1) truck dump #6, identified as 15EL1, constructed prior to 1977, using a baghouse for PM control, and exhausting to stack 15EL;
- (r) Two (2) grain dryers, # 4 and #5, identified as 17EL1, constructed in the 1960's, using self-cleaning screens for PM control, and exhausting to stack 17EL;
- (s) Two (2) natural gas fired dryers, #4 and #5, associated with grain dryers #4 and #5 respectively, identified as 17EL2, constructed in the 1960's, and exhausting to stack 17EL;
- (t) One (1) Lec. Dept. filter aid unit, identified as 204RO1, constructed in 1980, with a maximum capacity of 2.5 tons of diatomaceous earth per hour, using a baghouse for PM control, and exhausting to stack 204RO;
- (u) Daily use bins, identified as 102EO1, constructed in 1976, using a baghouse for PM control, and exhausting to stack 102EO;

- (v) Filter aid silos, identified as 103EO1, constructed in 1976, using a baghouse for PM control, and exhausting to stack 103EO;
- (w) One (1) natural gas fired hydrogen generator furnace, identified as 107EO1, constructed in 1992, and exhausting to stack 107EO;
- (x) Salt conveying, identified as 4SP1, constructed in 1981, using a baghouse for PM control, and exhausting to stack 4SP;
- (y) Lime conveying, identified as 5SP1, constructed in 1981, using a baghouse for PM control, and exhausting to stack 5SP;
- (z) One (1) vertical pellet cooler, constructed in 1967, and one (1) horizontal pellet cooler, constructed in the 1950's, identified as 1EF1, using a cyclone for PM control;
- (aa) One (1) corn grinding equipment, identified as 2EF1, constructed in 1992, using a cyclone for PM control.
- (bb) Ingredient grinding equipment, identified as 2EF2, constructed in the early 1970's;
- (cc) Feed Ingredient receiving, identified as 3EF1, constructed in the early 1970's;
- (dd) Bulk loadout, identified as 4EF1, constructed in the early 1970's;
- (ee) One (1) micro room, identified as 5EF1, constructed in the 1940's;
- (ff) Six (6) flaking rolls, #1, #2, #3, #4, #5, and #6, constructed in 1996, and B flake n/s drag, constructed in 1991, all identified together as 1EX1, sharing a baghouse with 1EX2 for PM control, and exhausting to stack 1EX;
- (gg) One (1) flaking roll #14 and flaking roll discharge #14, identified as 1EX2, constructed in 1991, sharing a baghouse with 1EX1 for PM control, and exhausting to stack 1EX;
- (hh) One (1) 'A' conditioner, identified as 2EX1, constructed in the 1930's, with no PM control, and exhausting to stack 2EX;
- (ii) The following soybean processing equipment, together identified as 3EX1, sharing a cyclone with 3EX2 for PM control, and exhausting to stack 3EX:
 - (1) Four (4) flaking rolls, #9, #10, #11, and #12, constructed in 1978;
 - (2) One (1) flaking roll #13, constructed in 1985;
 - (3) One (1) 'A' flake n/s drag, constructed in 1993; and
 - (4) One (1) 'A' flake e/w drag, constructed in 1993;
- (jj) One (1) north run around drag, identified as 3EX2, constructed in 1984, sharing a cyclone with 3EX1, and exhausting to stack 3EX;
- (kk) The following soybean processing equipment, together identified as 4EX1, sharing a baghouse with 4EX2 and 4EX3 for PM control, and exhausting to stack 4EX:
 - (1) One (1) whole bean scale, constructed in 1989;

- (2) One (1) 'A' whole bean leg, constructed in 1997;
 - (3) One (1) 'A' surge bin, constructed prior to 1979;
 - (4) One (1) whole bean drag, constructed in 1981; and
 - (5) One (1) 'B' surge bin, constructed prior to 1979;
- (ll) A run around rework screw, identified as 4EX2, constructed in 1991, sharing a baghouse with 4EX1 and 4EX3 for PM control, and exhausting to stack 4EX;
- (mm) The following soybean processing equipment, together identified as 4EX3, sharing a baghouse with 4EX1 and 4EX2 for PM control, and exhausting to stack 4EX:
- (1) One (1) hull refining screw conveyor, constructed in 1991;
 - (2) One (1) hull refining process, constructed in 1991; and
 - (3) One (1) hull grinding process, constructed in 1987;
- (nn) Dehulling equipment, identified as 5EX1, constructed in 1997, sharing a baghouse with 5EX2 and 5EX3 for PM control, and exhausting to stack 5EX;
- (oo) Hot dehulling equipment, identified as 5EX2, constructed in 1991, sharing a baghouse with 5EX1 and 5EX3 for PM control, and exhausting to stack 5EX;
- (pp) Screening aspiration, identified as 5EX3, constructed in 1988, sharing a baghouse with 5EX1 and 5EX2 for PM control, and exhausting to stack 5EX;
- (qq) Truck loadout, identified as 6EX1, constructed in 1982, replaced in 1999, using a baghouse for PM control, and exhausting to stack 6EX;
- (rr) The following soybean processing equipment, together identified as 7EX1, using a baghouse for PM control, and exhausting to stack 7EX:
- (1) One (1) north megamill, constructed in 1993;
 - (2) One (1) south megamill, constructed in 1993; and
 - (3) One (1) stedman grinder, constructed in 1983;
- (ss) One (1) leg No. 2, one (1) mixing conveyor, and one (1) bin drag, together identified as 9EX1, all constructed in 1983, using a baghouse for PM control, and exhausting to stack 9EX;
- (tt) The following soybean processing equipment, together identified as 10EX1, using a baghouse for PM control, and exhausting to stack 10EX:
- (1) One (1) leg No. 3, constructed in the 1950's;
 - (2) One (1) tunnel drag, constructed in 1983; and
 - (3) One (1) meal loadout drag, constructed in 1982;

- (uu) One (1) kaolin bin, identified as 11EX1, constructed in the 1950's, using a baghouse for PM control, and exhausting to stack 11EX;
- (w) One (1) meal loadout bin, identified as 12EX1, constructed in 1982, using a baghouse for PM control, and exhausting to stack 12EX;
- (ww) One (1) pre-DT section on top of 'A' top dryer section, constructed in 1996, and exhausting to 'A' top dryer section for PM control and one (1) 'A' top dryer section, identified as 13EX1, constructed in 1980, using a cyclone for PM control, exhausting to stack 13EX, with hexane emissions directed to stack 24EX;
- (xx) One (1) 'A' middle dryer section, identified as 13EX2, constructed in 1980, using a cyclone for PM control, exhausting to stack 13EX, with hexane emissions directed to stack 24EX;
- (yy) One (1) 'A' bottom cooler section, identified as 13EX3, constructed in 1980, using a cyclone for PM control, exhausting to stack 13EX, with hexane emissions directed to stack 24EX;
- (zz) One (1) pre-DT section on top of 'B' top dryer section, constructed in 1996, and exhausting to 'B' top dryer section for PM control, and one (1) 'B' top dryer section, identified as 14EX1, constructed in 1980, using a cyclone for PM control, exhausting to stack 14EX, with hexane emissions directed to stack 24EX;
- (aaa) One (1) 'B' middle dryer section, identified as 14EX2, constructed in 1980, using a cyclone for PM control, exhausting to stack 14EX, with hexane emissions directed to stack 24EX;
- (bbb) One (1) 'B' bottom cooler section, identified as 14EX3, constructed in 1980, using a cyclone for PM control, exhausting to stack 14EX, with hexane emissions directed to stack 24EX;
- (ccc) One (1) meal cooler, identified as 21EX, constructed in 1996, using two (2) cyclones for PM control and exhausting to stacks 21EX-A and 21EX-B, with hexane emissions directed to stack 24EX;
- (ddd) One (1) belt to storage bowls, one (1) large storage bowl, and one (1) small storage bowl, identified as 16EX1, 16EX2, and 16EX3, respectively, all constructed in 1982, with no PM control, and exhausting to stack 16EX;
- (eee) Whole bean bins, identified as 18EX1, constructed in the 1940's, with no PM control, and exhausting to stack 18EX;
- (fff) Meal storage silos with bin vents, identified as 23EX1, constructed in the 1950's, and one (1) bin vent filter exhausting to stack 23EX;
- (ggg) One (1) zinc receiving bin, identified as 25EX1, constructed in 1994, sharing a baghouse with 25EX2 for PM control, and exhausting to stack 25EX;
- (hhh) One (1) zinc surge bin, identified as 25EX2, constructed in 1994, sharing a baghouse with 25EX1 for PM control, and exhausting to stack 25EX;
- (iii) One (1) rumen conveyor, identified as 8EX1, constructed in 1994, using a cyclone for PM control, and exhausting to stack 8EX;

- (jjj) One (1) rotary reactor, identified as 27EX1, constructed in the 1994, using a cyclone for PM control, and exhausting to stack 27EX;
- (kkk) Rumen loadout bins, identified as 29EX1, constructed in 1994, using a baghouse for PM control, and exhausting to stack 29EX; and
- (lll) Rumen rework surge bin, identified as 30EX1, constructed in 1994, using a baghouse for PM control, and exhausting to stack 30EX;
- (mmm) One (1) natural gas fired Dowtherm heater #1, identified as 105EO1, constructed in 1969, and exhausting to stack 105EO;
- (nnn) One (1) natural gas fired Dowtherm heater #2, identified as 106EO1, constructed in 1976, and exhausting to stack 106EO;
- (ooo) One (1) natural gas fired steam generator #3, identified as 108EO1, constructed in 1994, and exhausting to stack 108EO;
- (ppp) One (1) B & W coal fired boiler, identified as 1SP1, constructed in 1950, using multiple cyclones for PM control, and exhausting to stack 1SP;
- (qqq) One (1) Keeler coal fired boiler, identified as 2SP1, constructed in 1963, using multiple cyclones for PM control, and exhausting to stack 1SP;
- (rrr) One (1) Murray natural gas fired and vegetable oil fired boiler, identified as 3SP1, constructed in 1968, and exhausting to stack 1SP;
- (sss) Hexane recovery, identified as 24EX1, constructed in 1980, with hexane emissions controlled by a mineral oil absorber, and exhausting to stack 24EX;
- (ttt) One (1) pre DT section on top of 'A' top dryer section, constructed in 1996, and one (1) 'A' DTDC top dryer section, constructed in 1980, both identified as 24EX2, with hexane emissions controlled by a mineral oil absorber and exhausting to stack 24EX;
- (uuu) One (1) 'A' DTDC middle dryer section, identified as 24EX3, constructed in 1980, with hexane emissions controlled by a mineral oil absorber, and exhausting to stack 24EX;
- (vvv) One (1) 'A' DTDC bottom cooler section, identified as 24EX4, constructed in 1980, with hexane emissions controlled by a mineral oil absorber, and exhausting to stack 24EX;
- (www) One (1) pre-DT section on top of 'B' top dryer section, constructed in 1996, and one (1) 'B' DTDC top dryer section, constructed in 1980, both identified as 24EX5, with hexane emissions controlled by a mineral oil absorber, and exhausting to stack 24EX;
- (xxx) One (1) 'B' DTDC middle dryer section, identified as 24EX6, constructed in 1980, with hexane emissions controlled by a mineral oil absorber, and exhausting to stack 24EX;
- (yyy) One (1) 'B' DTDC bottom cooler section, identified as 24EX7, constructed in 1980, with hexane emissions controlled by a mineral oil absorber, and exhausting to stack 24EX;
- (zzz) One (1) meal cooler, identified as 21EX, constructed in 1996, with hexane emissions controlled by a mineral oil absorber, and exhausting to sack 24EX;

- (aaaa) Hexane storage tank, identified as 24EX8, constructed in 1995, and vented to the mineral oil absorber inlet;
- (bbbb) Wastewater system containing hexane, identified as 24EX9, constructed in 1980, and exhausting at the plant treatment facility;
- (cccc) One (1) refined oil hot well, identified as 24EX10, constructed in 1975, and exhausting to stack 24EX;
- (dddd) One (1) sampling/hexane unloading port, identified as 24EX11, and with no control.

Unpermitted Emission Units and Pollution Control Equipment

The source also consists of the following unpermitted facilities/units:

NOTE: All throughputs and capacities are included in a IDEM, OAQ confidential file as the source considers them confidential.

- (eeee) One (1) grain dryer #1, identified as 16EL1, constructed in 1986, using self-cleaning screens for PM control, and exhausting to stack 16EL;
- (ffff) One (1) natural gas dryer #1 associated with grain dryer #1, identified as 16EL2, constructed in 1986, and exhausting to stack 16EL;
- (gggg) One (1) outside conditioner, identified as 17EX1, constructed in 1991, sharing a cyclone with 17EX2 for PM control, and exhausting to stack 17EX; and
- (hhhh) The following soybean processing equipment, together identified as 17EX2, modified in 1987, sharing a cyclone with 17EX1 for PM control, and exhausting to stack 17EX:
 - (1) One (1) flaking roll #8, constructed in 1981; and
 - (2) One (1) 'B' flke e/w drag, constructed in 1980.

New Emission Units and Pollution Control Equipment Receiving Advanced Source Modification Approval

There are no new emission units and pollution control equipment receiving advanced source modification approval at this source during this review process.

Insignificant Activities

The source also consists of the following insignificant activities, as defined in 326 IAC 2-7-1(21):

- (a) Paved and unpaved roads and parking lots with public access [326 IAC 6-4];
- (b) Degreasing operations that do not exceed 145 gallons per 12 months, except if subject to 326 IAC 20-6 [326 IAC 8-3-2; 326 IAC 8-3-5];
- (c) Natural gas-fired combustion sources with heat input equal to or less than ten million (10,000,000) British thermal units per hour;

- (d) Propane or liquified petroleum gas, or butane-fired combustion sources with heat input equal to or less than six million (6,000,000) British thermal units per hour;
- (e) Combustion source flame safety purging on start-up;
- (f) A gasoline fuel transfer and dispensing operation handling less than or equal to 1,300 gallons per day, such as filling of tanks, locomotives, automobiles, having a storage capacity less than or equal to 10,500 gallons;
- (g) A petroleum fuel, other than gasoline, dispensing facility having a storage capacity less than or equal to 10,500 gallons, and dispensing less than or equal to 23,000 gallons per month;
- (h) Vessels storing lubricating oils, hydraulic oils, machining oils, and machining fluids;
- (i) Machining where an aqueous cutting coolant continuously floods the machining interface;
- (j) Cleaners and solvents characterized as follows:
 - (1) having a vapor pressure equal to or less than 2 kPa; 15 mmHg; or 0.3 psi measured at 38 degrees C (100EF); or
 - (2) having a vapor pressure equal to or less than 0.7 kPa; 5 mmHg; or 0.1 psi measured at 20 degrees C (68EF);the use of which for all cleaners and solvents combined does not exceed 145 gallons per 12 months;
- (k) Closed loop heating and cooling systems;
- (l) Activities associated with the treatment of wastewater streams with an oil and grease content less than or equal to 1% by volume;
- (m) Water based adhesives that are less than or equal to 5% by volume of VOCs, excluding HAPs;
- (n) Noncontact cooling tower systems with natural draft cooling towers not regulated under a NESHAP;
- (o) Replacement or repair of electrostatic precipitators, bags in baghouses, and filters in other filtrations equipment;
- (p) Heat exchanger cleaning and repair;
- (q) Process vessel degreasing and cleaning to prepare for internal repairs;
- (r) Underground conveyors;
- (s) Coal bunker and coal scale exhausts and associated dust collector vents;
- (t) Asbestos abatement projects regulated by 326 IAC 14-10;

- (u) Purging of gas lines and vessels that is related to routine maintenance and repair of buildings, structures, or vehicles at the source where air emissions from those activities would not be associated with any production process;
- (v) Equipment used to collect any material that might be released during a malfunction, process upset, or spill cleanup, including catch tanks, temporary liquid separators, tanks, and fluid handling equipment;
- (w) Blowdown for any of the following: sight glass; boiler; compressors; pumps; and cooling tower;
- (x) Stationary fire pumps;
- (y) Purge double block and bleed valves;
- (z) Filter or coalescer media changeout;
- (aa) Vents from ash transport systems not operated at positive pressure;
- (bb) A laboratory as defined in 326 IAC 2-7-1(20)(c); and
- (cc) Emission units with PM and PM10 emissions less than five (5) tons per year, SO₂, NO_x, and VOC emissions less than ten (10) tons per year, CO emissions less than twenty-five (25) tons per year, lead emissions less than two-tenths (0.2) tons per year, single HAP emissions less than one (1) ton per year, and combination of HAPs emissions less than two and a half (2.5) tons per year:
 - (1) One (1) acetic anhydride storage tank.

Existing Approvals

The source has been operating under previous approvals including, but not limited to, the following:

- (a) AA001-9930-00005, issued September 17, 1998;
- (b) 001-8851-00005, issued October 17, 1997;
- (c) CP001-8851I-00005, issued September 4, 1997;
- (d) CP001-4673-00005, issued May 10, 1996;
- (e) AA001-4894-00005, issued October 20, 1995;
- (f) CP001-4673I-00005, issued August 1, 1995;
- (g) AA001-4696-00005, issued July 13, 1995;
- (h) E001-4205-00005, issued December 8, 1994;
- (i) AA001-4065-0005, issued September 19, 1994;
- (j) CP001-3582-00005, issued September 13, 1994;
- (k) CP001-3431-00005, issued October 6, 1994;

- (l) 001-3197-00005, issued September 30, 1993;
- (m) CP001-3151-00005, issued September 3, 1993;
- (n) CP001-2426-00005, issued March 20, 1992;
- (o) CP001-2441-00005, issued March 13, 1992;
- (p) CP002-2005-00005, issued August 23, 1991;
- (q) PC(01)1597, issued December 16, 1985;
- (r) PC(01)1595, issued November 6, 1985;
- (s) OP01-07-88-0121, issued January 8, 1985;
- (t) CP001-1546-00005, issued April 10, 1984;
- (u) 01-07-85-0109;
- (v) Exempt construction, issued October 21, 1987;
- (w) Amendment to OP01-07-85-0108, issued July 19, 1983;
- (x) Amendment to OP01-07-85-0108, issued March 8, 1982;
- (y) Amendment to OP01-07-85-0108, issued March 3, 1982;
- (z) Amendment to OP01-07-85-0108, issued October 5, 1981;
- (aa) OP01-07-85-0108, issued August 25, 1981;
- (bb) OP01-07-85-0107, issued August 25, 1981; and
- (cc) Registered construction, issued June 4, 1980.

All conditions from previous approvals were incorporated into this Part 70 permit except all limits were converted from tons per year to tons per twelve (12) consecutive month period to match IDEM's current policy.

Enforcement Issue

- (a) IDEM is aware that equipment has been constructed and operated prior to receipt of the proper permit. If these units had been constructed under current regulations, they would have been considered significant source modifications under 326 IAC 2-7-10.5 because their uncontrolled potential to emit PM is greater than twenty-five (25) tons per year. The subject equipment is listed in this Technical Support Document under the condition entitled Unpermitted Emission Units and Pollution Control Equipment.
- (b) IDEM is reviewing this matter and will take appropriate action. This proposed permit is intended to satisfy the requirements of the construction permit rules.

Recommendation

The staff recommends to the Commissioner that the Part 70 permit be approved. This recommendation is based on the following facts and conditions:

Unless otherwise stated, information used in this review was derived from the application and additional information submitted by the applicant.

An administratively complete Part 70 permit application for the purposes of this review was received on March 28, 1996.

A notice of completeness letter was mailed to the source on July 25, 1996.

Emission Calculations

All calculations are included in a IDEM, OAQ confidential file because the capacities and throughputs are considered confidential by the source.

Potential To Emit

Pursuant to 326 IAC 2-1.1-1(16), Potential to Emit is defined as “the maximum capacity of a stationary source to emit any air pollutant under its physical and operational design. Any physical or operational limitation on the capacity of a source to emit an air pollutant, including air pollution control equipment and restrictions on hours of operation or type or amount of material combusted, stored, or processed shall be treated as part of its design if the limitation is enforceable by the U. S. EPA.”

This table reflects the PTE before controls. Control equipment is not considered federally enforceable until it has been required in a federally enforceable permit.

Pollutant	Potential To Emit (tons/year)
PM	40,840
PM-10	11,000
SO ₂	998
VOC	764
CO	204
NO _x	463

Note: For the purpose of determining Title V applicability for particulates, PM-10, not PM, is the regulated pollutant in consideration.

HAPs	Potential To Emit (tons/year)
Hexane	758
Lead	1.5x10 ⁻²
Cadmium	2.16x10 ⁻³
Formaldehyde	7.2x10 ⁻²
Chromium	4.5x10 ⁻²
Benzene	1.83x10 ⁻³
Dichlorobenzene	1.05x10 ⁻³
Toluene	2.96x10 ⁻³
Manganese	3.31x10 ⁻⁴
Nickel	1.83x10 ⁻³

HAPs	Potential To Emit (tons/year)
TOTAL	758

- (a) The potential to emit (as defined in 326 IAC 2-1.1-1(16)) of PM10, SO₂, VOC, CO and NO_x are equal to or greater than 100 tons per year. Therefore, the source is subject to the provisions of 326 IAC 2-7.
- (b) The potential to emit (as defined in 326 IAC 2-1.1-1(16)) of any single HAP is equal to or greater than ten (10) tons per year and the potential to emit (as defined in 326 IAC 2-7-1(29)) of a combination HAPs is greater than or equal to twenty-five (25) tons per year. Therefore, the source is subject to the provisions of 326 IAC 2-7.
- (c) Fugitive Emissions
 Since this type of operation is not one of the twenty-eight (28) listed source categories under 326 IAC 2-2 and since there are no applicable New Source Performance Standards that were in effect on August 7, 1980, the fugitive emissions are not counted toward determination of PSD and Emission Offset applicability.

Actual Emissions

The following table shows the actual emissions from the source. This information reflects the 1999 OAQ emission data.

Pollutant	Actual Emissions (tons/year)
PM-10	153
SO ₂	585
VOC	451
CO	103
NO _x	409
Lead	0.07

Potential to Emit After Issuance

The table below summarizes the potential to emit, reflecting all limits, of the significant emission units after controls. The control equipment is considered federally enforceable only after issuance of this Part 70 operating permit.

Process/Facility	Potential to Emit After Issuance (tons/year)						
	PM	PM-10	SO ₂	VOC	CO	NO _x	Total HAPs
1EL1	Less than 0.01 gr/dscf (NSPS)	Less than 0.01 gr/dscf (NSPS)					
2EL1	Less than 0.01 gr/dscf (NSPS)	Less than 0.01 gr/dscf (NSPS)					

Process/Facility	Potential to Emit After Issuance (tons/year)						
	PM	PM-10	SO ₂	VOC	CO	NO _x	Total HAPs
5EL1	Less than 0.01 gr/dscf (NSPS)	Less than 0.01 gr/dscf (NSPS)					
8EL1	Less than 0.01 gr/dscf (NSPS)	Less than 0.01 gr/dscf (NSPS)					
10EL1	Less than 0.01 gr/dscf (NSPS)	Less than 0.01 gr/dscf (NSPS)					
14EL1	Less than 0.01 gr/dscf (NSPS)	Less than 0.01 gr/dscf (NSPS)					
19EL1	Not greater than 5.96 (PSD limit)	Not greater than 1.24 (PSD limit)					
19EL2							
15EX1	326 IAC 6-3-2	326 IAC 6-3-2					
3EL1	326 IAC 6-3-2	326 IAC 6-3-2					
4EL1	326 IAC 6-3-2	326 IAC 6-3-2					
6EL1	326 IAC 6-3-2	326 IAC 6-3-2					
7EL1	326 IAC 6-3-2	326 IAC 6-3-2					
9EL1	326 IAC 6-3-2	326 IAC 6-3-2					
12EL1	326 IAC 6-3-2	326 IAC 6-3-2					
13EL1	326 IAC 6-3-2	326 IAC 6-3-2					
15EL1	326 IAC 6-3-2	326 IAC 6-3-2					
17EL1	326 IAC 6-3-2	326 IAC 6-3-2					
17EL2							
204RO1	326 IAC 6-3-2	326 IAC 6-3-2					
102EO1	326 IAC 6-3-2	326 IAC 6-3-2					

Process/Facility	Potential to Emit After Issuance (tons/year)						
	PM	PM-10	SO ₂	VOC	CO	NO _x	Total HAPs
103EO1	326 IAC 6-3-2	326 IAC 6-3-2					
107EO1							
108EO1							
4SP1	326 IAC 6-3-2	326 IAC 6-3-2					
5SP1	326 IAC 6-3-2	326 IAC 6-3-2					
1EX1 and 1EX2	Less than 2.26 (PSD limit)	Less than 1.40 (PSD limit)					
2EX1	326 IAC 6-3-2	326 IAC 6-3-2					
3EX1	326 IAC 6-3-2	326 IAC 6-3-2					
3EX2	326 IAC 6-3-2	326 IAC 6-3-2					
4EX1, 4EX2, 4EX3	Less than 5.17 (PSD limit)	Less than 1.01 (PSD limit)					
5EX1, 5EX2, 5EX3	Less than 7.38 (PSD limit)	Less than 1.12 (PSD limit)					
6EX1	Less than 0.25 (PSD limit)	Less than 0.04 (PSD limit)					
7EX1	Less than 1.54 (PSD limit)	Less than 1.11 (PSD limit)					
9EX1	326 IAC 6-3-2	326 IAC 6-3-2					
10EX1	326 IAC 6-3-2	326 IAC 6-3-2					
11EX1	326 IAC 6-3-2	326 IAC 6-3-2					
12EX1	326 IAC 6-3-2	326 IAC 6-3-2					
13EX1, 13EX2, 13EX3	Less than 31.89 (PSD limit)	Less than 19.40 (PSD limit)					

Process/Facility	Potential to Emit After Issuance (tons/year)						
	PM	PM-10	SO ₂	VOC	CO	NO _x	Total HAPs
14EX1, 14EX2, 14EX3	Less than 31.89 (PSD limit)	Less than 31.89 (PSD limit)					
16EX1	326 IAC 6-3- 2	326 IAC 6-3-2					
16EX2	326 IAC 6-3- 2	326 IAC 6-3-2					
16EX3	326 IAC 6-3- 2	326 IAC 6-3-2					
18EX1	326 IAC 6-3- 2	326 IAC 6-3-2					
21EX1	326 IAC 6-3- 2	326 IAC 6-3-2					
23EX1	Less than 14.67 (PSD limit)	Less than 7.18 (PSD limit)					
25EX1	326 IAC 6-3- 2	326 IAC 6-3-2					
25EX2	326 IAC 6-3- 2	326 IAC 6-3-2					
27EX1	326 IAC 6-3- 2	326 IAC 6-3-2					
8EX1	326 IAC 6-3- 2	326 IAC 6-3-2					
29EX1	326 IAC 6-3- 2	326 IAC 6-3-2					
30EX1	326 IAC 6-3- 2	326 IAC 6-3-2					
105EO1	Less than 0.8 lb/MMBtu	Less than 0.8 lb/MMBtu					
1SP1	Less than 0.8 lb/MMBtu	Less than 0.8 lb/MMBtu	Less than 6.0 lb/MMBtu				
2SP1	Less than 0.8 lb/MMBtu	Less than 0.8 lb/MMBtu	Less than 6.0 lb/MMBtu				
3SP1	Less than 0.8 lb/MMBtu	Less than 0.8 lb/MMBtu					

Process/Facility	Potential to Emit After Issuance (tons/year)						
	PM	PM-10	SO ₂	VOC	CO	NO _x	Total HAPs
24EX1, 24EX2, 24EX3, 24EX5, 24EX6, 24EX7, 24EX9, 24EX10, 24EX11				(1) Less than 330,000 gal of hexane per year (2) Less than 0.2 gallons of hexane lost per ton of oilseed processed			(1) Less than 330,000 gal of hexane per year (2) Less than 0.2 gallons of hexane lost per ton of oilseed processed
24EX8				Less than 25 (registration)			
16EL1	326 IAC 6-3-2	326 IAC 6-3-2					
16EL2							
17EX1, 17EX2	Less than 11.00 (PSD limit)	Less than 6.66 (PSD limit)					
1EF1	326 IAC 6-3-2	326 IAC 6-3-2					
2EF1	326 IAC 6-3-2	326 IAC 6-3-2					
2EF2	326 IAC 6-3-2	326 IAC 6-3-2					
3EF1	326 IAC 6-3-2	326 IAC 6-3-2					
4EF1	326 IAC 6-3-2	326 IAC 6-3-2					
5EF1	326 IAC 6-3-2	326 IAC 6-3-2					
106EO1	Less than 0.6 lb/MMBtu	Less than 0.6 lb/MMBtu					
Total Emissions	Greater than 250	Greater than 250	Greater than 250	Greater than 250	Greater than 100, Less than 250	Greater than 250	Greater than 10 for a single HAP, Greater than 25 for a combination of HAPs

Note: The PM and PM10 limit is simply listed as 326 IAC 6-3-2 because the process weight rates are considered confidential by the source. Therefore the limits are not specified.

County Attainment Status

The source is located in Adams County.

Pollutant	Status
PM-10	Attainment
SO ₂	Attainment
NO ₂	Attainment
Ozone	Attainment
CO	Attainment
Lead	Attainment

- (a) Volatile organic compounds (VOC) and oxides of nitrogen (NO_x) are precursors for the formation of ozone. Therefore, VOC and NO_x emissions are considered when evaluating the rule applicability relating to the ozone standards. Adams County has been designated as attainment or unclassifiable for ozone. Therefore, VOC and NO_x emissions were reviewed pursuant to the requirements for Prevention of Significant Deterioration (PSD), 326 IAC 2-2 and 40 CFR 52.21.
- (b) Adams County has been classified as attainment or unclassifiable for PM₁₀, SO₂, NO₂, CO, and lead. Therefore, these emissions were reviewed pursuant to the requirements for Prevention of Significant Deterioration (PSD), 326 IAC 2-2 and 40 CFR 52.21.
- (c) Fugitive Emissions
 Since this type of operation is not one of the 28 listed source categories under 326 IAC 2-2 and since there are no applicable New Source Performance Standards that were in effect on August 7, 1980, the fugitive emissions are not counted toward determination of PSD and Emission Offset applicability.

Part 70 Permit Conditions

This source is subject to the requirements of 326 IAC 2-7, pursuant to which the source has to meet the following:

- (a) Emission limitations and standards, including those operational requirements and limitations that assure compliance with all applicable requirements at the time of issuance of Part 70 permits.
- (b) Monitoring and related record keeping requirements which assume that all reasonable information is provided to evaluate continuous compliance with the applicable requirements.

Federal Rule Applicability

- (a) Unit 1EL1, 2EL1, 5EL1, 8EL1, 10EL1, and 14EL1 are subject to 40 CFR Part 60, Subpart DD (Standards of Performance for Grain Elevators) because they are located at a grain elevator and were constructed after August 3, 1978. Pursuant to this rule, the following limitations apply:

Unit	Description	PM Limit (gr/dscf)	Opacity Limit (%)
1EL1	Truck Dump #2	0.01	0 (stack) 5 (fugitive)
2EL1	Dryer rotex feed drag, #1 dryer HI-Roller, Weaver's belt, 102 Belt	0.01	0 (stack)
5EL1	North Tripper Buggy, West Workhouse Turnhead, North Galley Belt Loader, East West Belt	0.01	0 (stack)

Unit	Description	PM Limit (gr/dscf)	Opacity Limit (%)
8EL1	North West Receiving House Tunnel Belt	0.01	0 (stack)
10EL1	Rail Loadout	0.01	0 (stack) 5 (fugitive)
14EL1	Jumbo Silo West Galley Belt	0.01	0 (stack)
15EX1	Truck Dump #7	0.01	0 (stack) 5 (fugitive)

The provisions of 40 CFR, Subpart A - General Provisions, which are incorporated by reference in 326 IAC 12-1, apply to the affected facilities described here except when otherwise specified in 40 CFR Part 60, Subpart DD.

The following grain handling facilities are not subject to 40 CFR Part 60, Subpart DD because they were constructed prior to August 3, 1978: 3EL1, 4EL1, 6EL1, 7EL1, 9EL1, 12EL1, 13EL1, 15EL1, and 17EL1.

- (b) 40 CFR Part 60, Subpart DD (Standards of Performance for Grain Elevators) is applicable to 16EL1 (#1 grain dryer) and 19EL1 (#2 grain dryer). However, there are no applicable requirements for these column grain dryers due to 60.302(a)(1). The column grain dryers have 0.083 inch diameter screen openings in the column plate, which is less than 0.094 inch diameter openings.

The provisions of 40 CFR Part 60, Subpart A - General Provisions, which are incorporated by reference in 326 IAC 12-1, apply to the affected facilities described here except when otherwise specified in 40 CFR Part 60, Subpart DD.

- (c) The hexane storage tank, identified as 24EX8, is subject to 40 CFR 60, Subpart Kb (Volatile Organic Liquid (VOL) Storage Vessels (including petroleum liquid storage vessels for Which Construction Commenced after July 23, 1984]) because it was constructed in 1995, which is after the applicability date of the rule, and has a capacity greater than 40 cubic meters. However because the capacity is less than 75 cubic meters, no specific emission limitations or standards apply. Only record keeping requirements apply. The Permittee shall maintain a record showing the dimension of the storage vessel and an analysis showing the capacity of the storage vessel.
- (d) 40 CFR Part 60, Subpart Dc (Standards of Performance for Small Industrial-Commercial-Institutional Steam Generating Units) is applicable to this source. The natural gas fired steam generator #3 (108EO1) is subject to the rule because it was constructed after June 9, 1989 and has a capacity greater than 10 million British thermal units. Pursuant to this rule, the owner or operator shall maintain records of the amounts of fuel combusted each day. The #1 Dowtherm heater (105EO1) and the #2 Dowtherm heater (106EO1) are not subject to this rule because they are not steam generating units and were constructed prior to June 9, 1989. The Keeler Boiler (2SP1) is not subject to this rule because it was constructed prior to June 9, 1989.
- (e) 40 CFR Part 60, Subpart Db (Standards of Performance for Industrial-Commercial-Institutional Steam Generating Units) is not applicable to this source. The B&W Boiler (1SP1) and the Murray Boiler (3SP1) are not subject to this rule even though the both have maximum capacities greater than 100 million British thermal units per hour because they were constructed before the applicability date of this rule, June 19, 1984.

- (f) 40 CFR Part 63, Subpart GGGG (National Emission Standards for Hazardous Air Pollutants: Solvent Extraction for Vegetable Oil Production) is applicable to this source because the source operates a vegetable oil production process that is a major source of HAPs. Pursuant to this rule, hexane emissions for the soybean conventional oilseed process (24EX1 - 24EX11) are limited to 0.2 gallons of hexane lost per ton of oilseed processed. The limitation is a solvent loss factor to be applied in comparison to a loss solvent at a n-hexane content of 64%. The compliance date for this rule is April 12, 2004. Compliance with the hexane limit shall be demonstrated using the following equation found in 40 CFR 63.2840:

$$\text{Compliance Ratio} = \frac{\text{Actual HAP Loss}}{\text{Allowable HAP Loss}}$$

This equation can also be expressed as a function of total solvent loss as shown below and found in 40 CFR 63.2840:

$$\text{Compliance Ratio} = \frac{f * \text{Actual Solvent Loss}}{0.64 * \sum (\text{Oilseed}_i * (\text{SLF})_i)}$$

where f = The weighted average volume fraction of HAP in solvent received during the previous 12 operating months, as determined in 40 CFR 63.2854, dimensionless;

0.64 = The average volume fraction of HAP in solvent in the baseline performance data, dimensionless;

Actual Solvent Loss = Gallons of actual solvent loss during previous 12 operating months, as determined in 40 CFR 63.2853;

Oilseed = Tons of each oilseed type "i" processed during the previous 12 operating months, as shown in 40 CFR 63.2855; and

SLF = The corresponding solvent loss factor (gal/ton) for oilseed "i" as shown in Table 1 of 40 CFR 63.2840.

After 12 operating months, the source shall calculate the compliance ratio by the end of each calendar month following an operating month using the second equation. When calculating the compliance ratio, the following conditions shall be considered:

- (1) If the source processes any quantity of listed oilseeds in a calendar month and the source is not operating under an initial startup period or malfunction period subject to 40 CFR 63.2850, then the source shall categorize the month as an operating month, as defined in 40 CFR 63.2872.
- (2) The 12-month compliance ratio may include operating months occurring prior to a source shutdown and operating months that follow after the source resumes operation.
- (3) If the source shuts down and processes no listed oilseed for an entire calendar month, then the source shall categorize the month as a nonoperating month, as defined in 40 CFR 63.2872. Exclude any nonoperating months from the compliance ratio determination.

- (4) If the source is subject to an initial startup period as defined in 40 CFR 60.2872, the source shall exclude from the compliance ratio determination any solvent and oilseed information recorded for the initial startup period.
- (5) If the source is subject to a malfunction period as defined in 40 CFR 63.2872, the source shall exclude from the compliance ratio determination any solvent and oilseed information recorded for the malfunction period.

If the compliance ratio is less than or equal to 1.00, the source is in compliance with the HAP emission requirement for the previous operating month.

- (g) The insignificant degreasing operations are not subject to the requirements of 40 CFR Part 63, Subpart T (National Emission Standards for Halogenated Solvent Cleaning) because they use solvents that do not contain specified halogenated HAPs greater than 5% by weight.
- (h) This source is not subject to the provisions of 40 CFR 64, Compliance Assurance Monitoring. In order for this rule to apply, a specific emissions unit must meet three criteria for a given pollutant: 1) the unit is subject to an emission limitation or standard for the applicable regulated air pollutant, 2) the unit uses a control device to achieve compliance with any such emission limitation or standard, and, 3) the unit has potential pre-control device emissions of the applicable regulated air pollutant that are equal to or greater than 100 percent of the amount required for a source to be classified as a major source. The B&W Boiler, Keeler Boiler, and Murray Boiler all have emissions of greater than one hundred (100) tons per year. The Murray boiler is subject to an emission limit under 326 IAC 6-2, however, it does not use a control device to comply with the limit. The B&W boiler and Keeler Boiler are also subject to an emission limit under 326 IAC 6-2 and do use a control device to achieve compliance with this limit. However, the Part 70 application was submitted prior to April 20, 1998 and therefore the source is not subject to the provisions of 40 CFR 64, Compliance Assurance Monitoring.

State Rule Applicability - Entire Source

326 IAC 2-2 (Prevention of Significant Deterioration (PSD))

- (a) PM10, SO2, VOC, CO, and NOx potential emissions are all greater than two hundred and fifty (250) tons per year. Therefore, the source is a major source under Prevention of Significant Deterioration (PSD) rules.
- (b) Pursuant to CP001-4673-00005, issued May 10, 1996, and the administrative amendment to this permit, AA001-9930-00005, issued September 17, 1998, the amount of soybean grains processed after the grain dryers shall be limited to less than 1,368,750 tons per twelve (12) consecutive month period and the hourly limits are as follows:

Unit	PM Limit (lb/hr)	PM10 Limit (lb/hr)
19EL	1.36	0.283
1EX	0.516	0.320
17EX	2.51	1.52
4EX	1.181	0.230
5EX	1.684	0.255
7EX	0.351	0.254

13EX	7.38	4.43
14EX	7.38	4.43
21EX	17.7	10.8
22EX	0.468	0.234
23EX	3.28	1.64
6EX	0.056	0.008

These limits restrict the net increases of PM and PM10 emissions from the modification in 1996 to below the PSD significant levels of twenty-five (25) and fifteen (15) tons per year, respectively, and also satisfy the requirements of 326 IAC 6-3-2 (Process Operations). This will render the requirements of 326 IAC 2-2 (Prevention of Significant Deterioration) and 40 CFR 52.21 not applicable.

- (c) Pursuant to CP(002)2005, issued August 23, 1991, the hexane losses from all of the oil extraction facilities (24EX1-24EX11) combined shall be limited to less than 330,000 gallons per twelve (12) consecutive month period to ensure that the increase in hexane emissions from these units remain below 39.2 tons per year. This will ensure that 326 IAC 2-2 (Prevention of Significant Deterioration) and 40 CFR 52.21 does not apply to this modification.

326 IAC 2-4.1-1 (Major Sources of HAP, New Source Toxic Control)

This source is not subject to 326 IAC 2-4.1-1 (Major Sources of HAP, New Source Toxic Control) because the source was constructed prior to the applicable date of July 27, 1997. Also, there have been no reconstruction of existing process lines or no new process lines added that have increased single HAP emissions to greater than ten (10) tons per year or combination HAP emissions to greater than twenty-five (25) tons per year.

326 IAC 2-6 (Emission Reporting)

This source is subject to 326 IAC 2-6 (Emission Reporting), because it has the potential to emit more than one hundred (100) tons per year of PM10, SO₂, VOC, CO, and NO_x. Pursuant to this rule, the owner/operator of the source must annually submit an emission statement for the source. The annual statement must be received by July 1 of each year and contain the minimum requirement as specified in 326 IAC 2-6-4. The submittal should cover the period defined in 326 IAC 2-6-2(8)(Emission Statement Operating Year).

326 IAC 5-1 (Opacity Limitations)

Pursuant to 326 IAC 5-1-2 (Opacity Limitations), except as provided in 326 IAC 5-1-3 (Temporary Alternative Opacity Limitations), opacity shall meet the following, unless otherwise stated in this permit:

- (a) Opacity shall not exceed an average of forty percent (40%) any one (1) six (6) minute averaging period as determined in 326 IAC 5-1-4.
- (b) Opacity shall not exceed sixty percent (60%) for more than a cumulative total of fifteen (15) minutes (sixty (60) readings as measured according to 40 CFR 60, Appendix A, Method 9 or fifteen (15) one (1) minute nonoverlapping integrated averages for a continuous opacity monitor) in a six (6) hour period.

326 IAC 6-3-2 (Process Operations)

Pursuant to 326 IAC 6-3-2 (Process Operations), the particulate matter (PM) from the following units shall be limited by the equation that follows the table:

Unit	Description
1EL1	Truck Dump #2
2EL1	Dryer Rotex Feed Drag, Dryer Rotex, Screening Bin Hammermill, #1, #2, and #3 Scalperators, Solvent Screening Leg, #1, #2, and #2 Leg, West to East Belt Head Section, West to East Belt Loader, Dry Bean Leg, #1 Dryer Hi-Roller, Weaver's Belt, 102 Belt
3EL1	Silo Bin Vents
4EL1	Silo Direct Loadout
5EL1	North Tripper Buggy, West Workhouse Turnhead, North Galley Belt Loader, East West Belt, West Workhouse to East Workhouse Belt Loader
6EL1	South Tripper Buggy, South Galley Belt Loader, North South Belt
7EL1	South West Receiving House Tunnel Belt
8EL1	North West Receiving House Tunnel Belt
9EL1	Truck Dump #3
10EL1	Rail Loadout, North 12,000 bu leg, South 12,000 bu leg
12EL1	Truck Dump #5
13EL1	Jumbo Silo East Tunnel Belt, Jumbo Silo West Tunnel Belt, Jumbo Silo Crossover Tunnel Belt
14EL1	Jumbo Silo East Galley Belt, Jumbo Silo West Galley Belt, Jumbo Silo Crossover Galley Belt
15EL1	Truck Dump #6
16EL1	Grain Dryer #1
17EL1	Grain Dryer #4 and #5
19EL1	Grain Dryer #2
204RO1	Lec. Dept. Filter Aid Unit
102EO1	Daily Use Bins
103EO1	Filter Aid Silos
4SP1	Salt Conveying
5SP1	Lime Conveying
1EX1	Flaking Roll #1, #2, #3, #4, #5, #6, B Flake N/S Drag
1EX2	Flaking Roll #14, Flaking Roll Discharge #14
2EX1	'A' Conditioner
3EX1	Flaking Roll #9, #10, #11, #12, #13, 'A' Flake N/S Drag, 'A' Flake E/W Drag
3EX2	North Run Around Drag
4EX1	Whole Bean Scale, 'A' Whole Bean Leg, 'A' Surge Bin, Whole Bean Drag, 'B' Surge Bin
4EX2	Run Around Rework Screw

Unit	Description
4EX3	Hull Refining Screw Conveyor, Hull Refining Process, Hull Refining Process
5EX1	Dehulling Equipment
5EX2	Hot Dehulling Equipment
5EX3	Screening
6EX1	Truck Loadout
7EX1	North Megamill, South Megamill, Stedman Grinder
9EX1	Leg No. 2, Mixing Conveyor, Bin Drag
10EX1	Leg No.3, tunnel drag, meal loadout drag
11EX1	Kaolin Bin
12EX1	Meal Loadout Bin
13EX1	Pre-DT and 'A' Top Dryer Section
13EX2	'A' Middle Dryer Section
13EX3	'A' Bottom Cooler Section
14EX1	Pre-DT and 'B' Top Dryer Section
14EX2	'B' Middle Dryer Section
14EX3	'B' Bottom Cooler Section
16EX1	Belt to Storage Bowls
16EX2	Large Storage Bowl
16EX3	Small Storage Bowl
17EX1	Outside Conditioner
17EX2	Flaking Roll #8, 'B' Flake E/W Drag
18EX1	Whole Bean Bins
21EX1	Aspirators
23EX1	Meal Storage Silos
24EX2	'A' DTDC Top Dryer Section
24EX3	'A' DTDC Bottom Dryer Section
24EX4	'A' DTDC Cooler Section
24EX5	'B' DTDC Top Dryer Section
24EX6	'B' DTDC Bottom Dryer Section
24EX7	'B' DTDC Cooler Section
25EX1	Zinc Receiving Bin
25EX2	Zinc Surge Bin
27EX1	Rumen Conveyor

Unit	Description
8EX1	Rotary Reactor
29EX1	Rumen Loadout Bins
30EX1	Rumen Surge Bin
1EF1	Vertical Pellet Cooler
2EF1	Corn Grinding Equipment
2EF2	Ingredient Grinding Equipment
5EF1	Micro Room

Interpolation of the data for the process weight rate up to sixty thousand (60,000) pounds per hour shall be accomplished by use of the equation:

$$E = 4.10 P^{0.67} \quad \text{where } E = \text{rate of emission in pounds per hour and} \\ P = \text{process weight rate in tons per hour}$$

and

Interpolation and extrapolation of the data for the process weight rate in excess of sixty thousand (60,000) pounds per hour shall be accomplished by use of the equation:

$$E = 55.0 P^{0.11} - 40 \quad \text{where } E = \text{rate of emission in pounds per hour and} \\ P = \text{process weight rate in tons per hour}$$

The individual limits are included in a IDEM, OAQ confidential file because the and process weight rates are considered confidential by the source.

The baghouses, cyclones, and oil suppressants shall be in operation at all times that the units are in operation, in order to comply with this limit.

State Rule Applicability - Boilers

326 IAC 6-2-3 (Particulate Emission Limitations for Sources of Indirect Heating)

326 IAC 6-2-3 (Particulate Emission Limitations for Sources of Indirect Heating) applies to the B&W boiler, Keeler boiler, and Murray boiler because they were constructed prior to September 21, 1983, the applicability date for this rule. Pursuant to this rule, the following particulate emission limitations exist:

Year	Unit	PM Limit (lb/MMBTU)
1950	1SP1 - B&W Boiler	0.8 ¹
1963	2SP1 - Keeler Boiler	0.8 ¹
1968	3SP1 - Murray Boiler	0.8 ¹

¹ 0.8 lb/MMBTU is the lesser of the calculated limit using the equation and 0.8.

The following equation was used to calculate the listed limits:

$$Pt = \underline{\hspace{1cm}} C X a X h \underline{\hspace{1cm}}$$

$$76.5 \times Q^{0.75} \times N^{0.25}$$

where Pt = Pounds of particulate matter emitted per million Btu heat input (lb/MMBtu);
C = Maximum ground level concentration (50);
a = Plume rise factor (0.67);
h = Stack height (ft);
Q = Total source maximum operating capacity (MMBtu/hr); and
N = Number of stacks.

Q and h for each boiler are included in a IDEM, OAQ confidential file.

326 IAC 6-2-4 (Particulate Emission Limitations for Source of Indirect Heating)

326 IAC 6-2-4 (Particulate Emission Limitations for Source of Indirect Heating) applies to the natural gas fired steam generator #3 (108EO1) because it was constructed after September 21, 1983, the applicability date for this rule. Pursuant to this rule, the particulate emissions from this source shall be limited to less than 0.25 pound per million British thermal unit heat input. This limitation was calculated using the following equation:

$$Pt = \frac{1.09}{Q^{0.26}}$$

where Pt = Pounds of particulate matter emitted per million Btu heat input (lb/MMBtu); and
Q = Total source maximum operating capacity (MMBtu/hr).

326 IAC 7-1 (Sulfur Dioxide Emission Limitations)

- (a) The B&W boiler (1SP1) and Keeler boiler (2SP1) are both subject to 326 IAC 7 (Sulfur Dioxide Emission Limitations) because they have the potential to emit greater than twenty-five (25) tons per year of sulfur dioxide. Pursuant to this rule, the sulfur dioxide emissions from the boilers, when combusting coal, shall be less than 6.0 lb/MMBtu.
- (b) The Murray boiler (3SP1), the #1 Dowtherm heater (105EO1), and the #2 Dowtherm heater (106EO1) are not subject to 326 IAC 7-1 (Sulfur Dioxide Emission Limitations) because they do not have the potential to emit greater than twenty-five (25) tons per year of sulfur dioxide.

State Rule Applicability - Oil Extraction Facilities

326 IAC 8-1-6 (New Facilities; General Reduction Requirements)

- (a) Pursuant to CP(002)2005, the hexane emitting units (24EX1-24EX11) are subject to 326 IAC 8-1-6 (New Facilities; General Reduction Requirements). Therefore the source must comply with BACT for these equipment, which has been determined to be 99.9% VOC control through the use of a mineral oil absorption system.
- (b) The volatile organic compound (VOC) emissions from 24EX8 are less than twenty-five (25) tons per year. This renders the requirements of 326 IAC 8-1-6 not applicable.

326 IAC 8-6 (Organic Solvent Emission Limitations)

This source is not subject to 326 IAC 8-6 (Organic Solvent Emission Limitations) because it is located in Adams County and was constructed after January 1, 1980.

Testing Requirements

- (a) Testing is required for the oil extraction system because it has the potential to emit greater than forty percent (40%) of the source's total potential to emit, before controls, of VOC, the

major pollutant. Testing is required to ensure that the oil absorption unit is controlling emissions at an efficiency of 99.9% as required under 326 IAC 8-1-6 (New Facilities; General Reduction Requirements).

- (b) SO₂ compliance testing is required for the B&W boiler and Keeler boiler because 326 IAC 7-2 requires it.
- (c) Testing is not required for the remaining units at the source because no other unit individually has the potential to emit greater than forty percent (40%) of the source's total potential to emit, before controls, of a major pollutant. The B&W and Keeler boilers do have the potential to emit greater than 100 tons per year of PM, PM₁₀, SO₂, and NO_x, however AP-42 emission factors indicate that these equipment are in compliance with 326 IAC 7-1 and 326 IAC 6-2-3 and there is no other evidence that the source is not in compliance with these rules.

Compliance Requirements

Permits issued under 326 IAC 2-7 are required to ensure that sources can demonstrate compliance with applicable state and federal rules on a more or less continuous basis. All state and federal rules contain compliance provisions, however, these provisions do not always fulfill the requirement for a more or less continuous demonstration. When this occurs IDEM, OAQ, in conjunction with the source, must develop specific conditions to satisfy 326 IAC 2-7-5. As a result, compliance requirements are divided into two sections: Compliance Determination Requirements and Compliance Monitoring Requirements.

Compliance Determination Requirements in Section D of the permit are those conditions that are found more or less directly within state and federal rules and the violation of which serves as grounds for enforcement action. If these conditions are not sufficient to demonstrate continuous compliance, they will be supplemented with Compliance Monitoring Requirements, also Section D of the permit. Unlike Compliance Determination Requirements, failure to meet Compliance Monitoring conditions would serve as a trigger for corrective actions and not grounds for enforcement action. However, a violation in relation to a compliance monitoring condition will arise through a source's failure to take the appropriate corrective actions within a specific time period.

The compliance monitoring requirements applicable to this source are as follows:

1. 1EL-10EL, 12EL-15EL, 17EL, 19EL, 204RO1, 102EO1, 103EO1, 107EO1, 108EO1, 4SP1, 5SP1, 1EX-14EX, 16EX, 18EX, 21EX, 23EX, 25EX, 27EX, 29EX, and 30EX have applicable compliance monitoring conditions as specified below:
 - (a) Once per shift visible emissions notations of the unit stack exhaust shall be performed during normal daylight operations. A trained employee will record whether emissions are normal or abnormal. For processes operated continuously "normal" means those conditions prevailing, or expected to prevail, eighty percent (80%) of the time the process is in operation, not counting startup or shut down time. In the case of batch or discontinuous operations, readings shall be taken during that part of the operation that would normally be expected to cause the greatest emissions. A trained employee is an employee who has worked at the plant at least one (1) month and has been trained in the appearance and characteristics of normal visible emissions for that specific process. The Compliance Response Plan for this unit shall contain troubleshooting contingency and response steps for when an abnormal emission is observed.

- (b) The Permittee shall record the total static pressure drop across the baghouses controlling the listed units, at least once per shift when the units are in operation. When for any one reading, the pressure drop across the baghouses is outside the normal range of 0.25 to 12.0 inches of water or a range established during the latest stack test, the Permittee shall take reasonable response steps in accordance with Section C - Compliance Response Plan - Failure to Take Response Steps. A pressure reading that is outside the above mentioned range is not a deviation from this permit. Failure to take response steps in accordance with Section C - Compliance Response Plan - Failure to Take Response Steps, shall be considered a violation of this permit.
 - (c) An inspection shall be performed each calendar quarter of all bags, cyclones, and self-cleaning screens controlling the facilities when venting to the atmosphere. A baghouse, cyclone, and self-cleaning screen inspection shall be performed within three months of redirecting vents to the atmosphere and every three months thereafter. Inspections are optional when venting to the indoors. All defective bags, cyclones, and screens shall be replaced.
 - (d) In the event that bag or screen failure has been observed:
 - (1) For multi-compartment units, the affected compartments will be shut down immediately until the failed units have been repaired or replaced. Operations may continue only if there are no visible emissions or if the event qualifies as an emergency and the Permittee satisfies the emergency provisions of this permit (Section B- Emergency Provisions). Within eight (8) business hours of the determination of failure, response steps according to the timetable described in the Compliance Response Plan shall be initiated. For any failure with corresponding response steps and timetable not described in the Compliance Response Plan, response steps shall be devised within eight (8) business hours of discovery of the failure and shall include a timetable for completion. Failure to take response steps in accordance with Section C - Compliance Monitoring Plan - Failure to Take Response Steps, shall be considered a violation of this permit.
 - (2) For single compartment baghouses, failed units and the associated process will be shut down immediately until the failed units have been repaired or replaced. Operations may continue only if the event qualifies as an emergency and the Permittee satisfies the requirements of the emergency provisions of this permit (Section B - Emergency Provisions).
 - (e) In the event that cyclone failure has been observed:

Failed units and the associated process will be shut down immediately until the failed units have been repaired or replaced. Operations may continue only if the event qualifies as an emergency and the Permittee satisfies the requirements of the emergency provisions of this permit (Section B - Emergency Provisions). Failure to take response steps in accordance with Section C - Compliance Monitoring Plan - Failure to Take Response Steps, shall be considered a violation of this permit.
2. 1EL-10EL, 12EL-15EL, 17EL, 19EL, 204RO1, 102EO1, 103EO1, 107EO1, 108EO1, 4SP1, 5SP1, 1EX-14EX, 16EX, 18EX, 21EX, 23EX, 25EX, 27EX, 29EX, and 30EX have applicable compliance monitoring conditions as specified below:

- (a) Once per shift visible emissions notations of the unit stack exhaust shall be performed during normal daylight operations when combusting coal. A trained employee will record whether emissions are normal or abnormal. For processes operated continuously "normal" means those conditions prevailing, or expected to prevail, eighty percent (80%) of the time the process is in operation, not counting startup or shut down time. In the case of batch or discontinuous operations, readings shall be taken during that part of the operation that would normally be expected to cause the greatest emissions. A trained employee is an employee who has worked at the plant at least one (1) month and has been trained in the appearance and characteristics of normal visible emissions for that specific process. The Compliance Response Plan for this unit shall contain troubleshooting contingency and response steps for when an abnormal emission is observed.
3. 24EX1-24EX11 have applicable compliance monitoring conditions as specified below:
 - (a) The mineral oil absorption vent VOC (hexane) emission rate shall be determined daily by measuring the airflow rate and the concentration of hexane in the air stream. This concentration will be determined once per shift by measuring percent Lower Explosive Limit (LEL). If the air flow meter proves unreliable, airflow can be determined by calculations.
4. 16EL, 17EX, and 1EF-5EF have applicable compliance monitoring conditions as specified below:
 - (a) Once per shift visible emissions notations of the unit stack exhaust shall be performed during normal daylight operations. A trained employee will record whether emissions are normal or abnormal. For processes operated continuously "normal" means those conditions prevailing, or expected to prevail, eighty percent (80%) of the time the process is in operation, not counting startup or shut down time. In the case of batch or discontinuous operations, readings shall be taken during that part of the operation that would normally be expected to cause the greatest emissions. A trained employee is an employee who has worked at the plant at least one (1) month and has been trained in the appearance and characteristics of normal visible emissions for that specific process. The Compliance Response Plan for this unit shall contain troubleshooting contingency and response steps for when an abnormal emission is observed.
 - (b) An inspection shall be performed each calendar quarter of all cyclones and self-cleaning screens controlling the facilities when venting to the atmosphere. A cyclone and self-cleaning screen inspection shall be performed within three months of redirecting vents to the atmosphere and every three months thereafter. Inspections are optional when venting to the indoors. All defective cyclones and screens shall be replaced.
 - (c) In the event that screen failure has been observed:
 - (1) For multi-compartment units, the affected compartments will be shut down immediately until the failed units have been repaired or replaced. Operations may continue only if there are no visible emissions or if the event qualifies as an emergency and the Permittee satisfies the emergency provisions of this permit (Section B- Emergency Provisions). Within eight (8) business hours of the determination of failure, response steps according to the timetable described in the Compliance Response

Plan shall be initiated. For any failure with corresponding response steps and timetable not described in the Compliance Response Plan, response steps shall be devised within eight (8) business hours of discovery of the failure and shall include a timetable for completion. Failure to take response steps in accordance with Section C - Compliance Monitoring Plan - Failure to Take Response Steps, shall be considered a violation of this permit.

- (2) For single compartment units, failed units and the associated process will be shut down immediately until the failed units have been repaired or replaced. Operations may continue only if the event qualifies as an emergency and the Permittee satisfies the requirements of the emergency provisions of this permit (Section B - Emergency Provisions).

- (d) In the event that cyclone failure has been observed:

Failed units and the associated process will be shut down immediately until the failed units have been repaired or replaced. Operations may continue only if the event qualifies as an emergency and the Permittee satisfies the requirements of the emergency provisions of this permit (Section B - Emergency Provisions). Failure to take response steps in accordance with Section C - Compliance Monitoring Plan - Failure to Take Response Steps, shall be considered a violation of this permit.

These monitoring conditions are necessary because the baghouses, cyclones, self-cleaning screens, and the mineral oil absorption unit for the source must operate properly to ensure compliance with 326 IAC 6-3 (Process Operations), 326 IAC 2-2 (Prevention of Significant Deterioration), 40 CFR 52.21, 326 IAC 8-1-6 (New Facilities; General Reduction Requirements) and 326 IAC 2-7 (Part 70).

Conclusion

The operation of this grain handling, animal feed production, soybean meal production, and soybean oil extraction plant shall be subject to the conditions of the attached proposed Part 70 Permit No. T001-5610-00005.

TABLE 6 TO SUBPART CCCC.—APPLICABILITY OF GENERAL PROVISIONS TO SUBPART CCCC—
Continued

Citation	Subject	Applicable to subpart CCCC?
§ 63.2	Definitions	Yes.
§ 63.3	Units and Abbreviations	Yes.
§ 63.4	Prohibited Activities and Circumvention	Yes.
§ 63.5	Construction and Reconstruction	Yes.
§ 63.6	Compliance With Standards and Maintenance Requirements.	1. For § 63.6(e) and (f), requirements for startup, shutdown, and malfunctions apply only to malfunctions. 2. § 63.6(h) does not apply. 3. Otherwise, all apply.
§ 63.7	Performance Testing Requirements	1. § 63.7(a)(1)–(2) and (e)(3) do not apply, instead specified in this subpart. 2. Otherwise, all apply.
§ 63.8	Monitoring Requirements	1. § 63.8(a)(2) is modified by § 63.2163. 2. § 63.8(a)(4) does not apply. 3. For § 63.8(c)(1), requirements for startup, shutdown, and malfunctions apply only to malfunctions, and no report pursuant to § 63.10(d)(5)(i) is required. 4. For § 63.8(d), requirements for startup, shutdown, and malfunctions apply only to malfunctions. 5. § 63.8(c)(4)(i), (c)(5), (e)(5)(ii), and (g)(5), do not apply. 6. § 63.8(c)(4)(ii), (c)(6)–(8), (e)(4), and (g)(1)–(4) do not apply, instead specified in this subpart. 7. Otherwise, all apply.
§ 63.9	Notification Requirements	1. § 63.9(b)(2) does not apply because rule omits requirements for initial notification for sources that start up prior to May 21, 2001 2. § 63.9(f) does not apply. 3. Otherwise, all apply.
§ 63.10	Recordkeeping and Reporting Requirements	1. For § 63.10(b)(2)(i)–(v), (c)(9)–(15), and (d)(5), requirements for startup, shutdown, and malfunctions apply only to malfunctions. 2. § 63.10(b)(2)(vii) and (c)(1)–(6) do not apply, instead specified in this subpart. 3. § 63.10(c)(7)–(8), (d)(3), (e)(2)(ii)–(4), (e)(3)–(4) do not apply. 4. Otherwise, all apply.
§ 63.11	Flares	No.
§ 63.12	Delegation	Yes.
§ 63.13	Addresses	Yes.
§ 63.14	Incorporation by Reference	Yes.
§ 63.15	Availability of Information	Yes.

Subpart GGGG—National Emission Standards for Hazardous Air Pollutants: Solvent Extraction for Vegetable Oil Production

SOURCE: 66 FR 19011, Apr. 12, 2001, unless otherwise noted.

WHAT THIS SUBPART COVERS

§ 63.2830 What is the purpose of this subpart?

This subpart establishes national emission standards for hazardous air pollutants (NESHAP) for emissions during vegetable oil production. This

subpart limits hazardous air pollutant (HAP) emissions from specified vegetable oil production processes. This subpart also establishes requirements to demonstrate initial and continuous compliance with the emission standards.

§ 63.2831 Where can I find definitions of key words used in this subpart?

You can find definitions of key words used in this subpart in § 63.2872.

§ 63.2832 Am I subject to this subpart?

(a) You are an affected source subject to this subpart if you meet all of the criteria listed in paragraphs (a)(1) and (2) of this section:

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(1) You own or operate a vegetable oil production process that is a major source of HAP emissions or is collocated within a plant site with other sources that are individually or collectively a major source of HAP emissions.

(i) A *vegetable oil production process* is defined in §63.2872. In general, it is the collection of continuous process equipment and activities that produce crude vegetable oil and meal products by removing oil from oilseeds listed in Table 1 to §63.2840 through direct contact with an organic solvent, such as a hexane isomer blend.

(ii) A major source of HAP emissions is a plant site that emits or has the potential to emit any single HAP at a rate of 10 tons (9.07 megagrams) or more per year or any combination of HAP at a rate of 25 tons (22.68 megagrams) or more per year.

(2) Your vegetable oil production process processes any combination of eight types of oilseeds listed in paragraphs (a)(2)(i) through (viii) of this section:

- (i) Corn germ;
- (ii) Cottonseed;
- (iii) Flax;
- (iv) Peanut;
- (v) Rapeseed (for example, canola);
- (vi) Safflower;
- (vii) Soybean; and

(viii) Sunflower.

(b) You are not subject to this subpart if your vegetable oil production process meets any of the criteria listed in paragraphs (b)(1) through (4) of this section:

(1) It uses only mechanical extraction techniques that use no organic solvent to remove oil from a listed oilseed.

(2) It uses only batch solvent extraction and batch desolventizing equipment.

(3) It processes only agricultural products that are not listed oilseeds as defined in §63.2872.

(4) It functions only as a research and development facility and is not a major source.

(c) As listed in §63.1(c)(5) of the General Provisions, if your HAP emissions increase such that you become a major source, then you are subject to all of the requirements of this subpart.

§ 63.2833. Is my source categorized as existing or new?

(a) This subpart applies to each existing and new affected source. You must categorize your vegetable oil production process as either an existing or a new source in accordance with the criteria in Table 1 of this section, as follows:

TABLE 1 TO § 63.2833.—CATEGORIZING YOUR SOURCE AS EXISTING OR NEW

If your affected source...	And if...	Then your affected source...
(1) was constructed or began construction before May 26, 2000.	reconstruction has not occurred	is an existing source.
(2) began reconstruction, as defined in §63.2, on or after May 26, 2000.	(i) reconstruction was part of a scheduled plan to comply with the existing source requirements of this subpart; and (ii) reconstruction was completed no later than 3 years after the effective date of this subpart.	remains an existing source.
(3) began a significant modification, as defined in §63.2872, at any time on an existing source.	the modification does not constitute reconstruction.	remains an existing source.
(4) began a significant modification, as defined in §63.2872, at any time on a new source.	the modification does not constitute reconstruction.	remains a new source.
(5) began reconstruction on or after May 26, 2000.	reconstruction was completed later than 3 years after the effective date of this subpart.	is a new source
(6) began construction on or after May 26, 2000.	is a new source.

(b) *Reconstruction of a source.* Any affected source is reconstructed if com-

ponents are replaced so that the criteria in the definition of *reconstruction*

in § 63.2 are satisfied. In general, a vegetable oil production process is reconstructed if the fixed capital cost of the new components exceeds 50 percent of the fixed capital cost for constructing a new vegetable oil production process, and it is technically and economically feasible for the reconstructed source to meet the relevant new source requirements of this subpart. The effect of reconstruction on the categorization of your existing and new affected source is described in paragraphs (b)(1) and (2) of this section:

(1) After reconstruction of an existing source, the affected source is recategorized as a new source and becomes subject to the new source requirements of this subpart.

(2) After reconstruction of a new source, the affected source remains categorized as a new source and remains subject to the new source requirements of this subpart.

(c) *Significant modification of a source.* A significant modification to an affected source is a term specific to this subpart and is defined in § 63.2872.

(1) In general, a significant modification to your source consists of adding new equipment or the modification of existing equipment within the affected source that significantly affects solvent losses from the affected source. Examples include adding or replacing extractors, desolventizer-toasters (con-

ventional and specialty), and meal dryer-coolers. All other significant modifications must meet the criteria listed in paragraphs (c)(1)(i) and (ii) of this section:

(i) The fixed capital cost of the modification represents a significant percentage of the fixed capital cost of building a comparable new vegetable oil production process.

(ii) It does not constitute reconstruction as defined in § 63.2.

(2) A significant modification has no effect on the categorization of your source as existing and new. An existing source remains categorized as an existing source and subject to the existing source requirements of this subpart. A new source remains categorized as a new source and subject to the new source requirements of this subpart.

(d) Changes in the type of oilseed processed by your affected source does not affect the categorization of your source as new or existing. Recategorizing an affected source from existing to new occurs only when you add or modify process equipment within the source which meets the definition of *reconstruction*.

§ 63.2834 When do I have to comply with the standards in this subpart?

You must comply with this subpart in accordance with one of the schedules in Table 1 of this section, as follows:

TABLE 1 OF § 63.2834.—COMPLIANCE DATES FOR EXISTING AND NEW SOURCES

If your affected source is categorized as...	And if...	Then your compliance date is...
(a) an existing source	3 years after the effective date of this subpart.
(b) a new source	you startup your affected source before the effective date of this subpart.	the effective date of this subpart.
(c) a new source	you startup your affected source on or after the effective date of this subpart.	your startup date.

STANDARDS

§ 63.2840 What emission requirements must I meet?

(a)(1) The emission requirements limit the number of gallons of HAP lost per ton of listed oilseeds processed. For each operating month, you must calculate a compliance ratio which compares your actual HAP loss to your allowable HAP loss for the previous 12

operating months as shown in Equation 1 of this section. An operating month, as defined in § 63.2872, is any calendar month in which a source processes a listed oilseed, excluding any entire calendar month in which the source operated under an initial startup period subject to § 63.2850(c)(2) or (d)(2) or a malfunction period subject to § 63.2850(e)(2). Equation 1 of this section follows:

$$\text{Compliance Ratio} = \frac{\text{Actual Hap Loss}}{\text{Allowable Hap Loss}} \quad (\text{Eq. 1})$$

(2) Equation 1 of this section can also be expressed as a function of total solvent loss as shown in Equation 2 of this section. Equation 2 of this section follows:

$$\text{Compliance Ratio} = \frac{f * \text{Actual Solvent Loss}}{0.64 * \sum_{i=1}^n ((\text{Oilseed})_i * (\text{SLF})_i)} \quad (\text{Eq. 2})$$

Where:

f = The weighted average volume fraction of HAP in solvent received during the previous 12 operating months, as determined in §63.2854, dimensionless.

0.64 = The average volume fraction of HAP in solvent in the baseline performance data, dimensionless.

Actual Solvent Loss = Gallons of actual solvent loss during previous 12

operating months, as determined in §63.2853.

Oilseed = Tons of each oilseed type ‘i’ processed during the previous 12 operating months, as shown in §63.2855.

SLF = The corresponding solvent loss factor (gal/ton) for oilseed ‘i’ listed in Table 1 of this section, as follows:

TABLE 1 OF § 63.2840.—OILSEED SOLVENT LOSS FACTORS FOR DETERMINING ALLOWABLE HAP LOSS

Type of oilseed process	A source that..	Oilseed solvent loss factor (gal/ton)	
		Existing sources	New sources
(i) Corn Germ, Wet Milling	processes corn germ that has been separated from other corn components using a “wet” process of centrifuging a slurry steeped in a dilute sulfuric acid solution.	0.4	0.3
(ii) Corn Germ, Dry Milling	processes corn germ that has been separated from the other corn components using a “dry” process of mechanical chafing and air sifting.	0.7	0.7
(iii) Cottonseed, Large	processes 120,000 tons or more of a combination of cottonseed and other listed oilseeds during all normal operating periods in a 12 operating month period.	0.5	0.4
(iv) Cottonseed, Small	processes less than 120,000 tons of a combination of cottonseed and other listed oilseeds during all normal operating periods in a 12 operating month period.	0.7	0.4
(v) Flax	processes flax	0.6	0.6
(vi) Peanuts	processes peanuts	1.2	0.7
(vii) Rapeseed	processes rapeseed	0.7	0.3
(viii) Safflower	processes safflower	0.7	0.7
(ix) Soybean, Conventional	uses a conventional style desolventizer to produce crude soybean oil products and soybean animal feed products.	0.2	0.2
(x) Soybean, Specialty	uses a special style desolventizer to produce soybean meal products for human and animal consumption.	1.7	1.5

TABLE 1 OF § 63.2840.—OILSEED SOLVENT LOSS FACTORS FOR DETERMINING ALLOWABLE HAP LOSS—Continued

Type of oilseed process	A source that...	Oilseed solvent loss factor (gal/ton)	
		Existing sources	New sources
(xi) Soybean, Combination Plant with Low Specialty Production.	processes soybeans in both specialty and conventional desolventizers and the quantity of soybeans processed in specialty desolventizers during normal operating periods is less than 3.3 percent of total soybeans processed during all normal operating periods in a 12 operating month period. The corresponding solvent loss factor is an overall value and applies to the total quantity of soybeans processed..	0.25	0.25
(xii) Sunflower	processes sunflower	0.4	0.3

(b) When your source has processed listed oilseed for 12 operating months, calculate the compliance ratio by the end of each calendar month following an operating month using Equation 2 of this section. When calculating your compliance ratio, consider the conditions and exclusions in paragraphs (b)(1) through (6) of this section:

(1) If your source processes any quantity of listed oilseeds in a calendar month and the source is not operating under an initial startup period or malfunction period subject to § 63.2850, then you must categorize the month as an operating month, as defined in § 63.2872.

(2) The 12-month compliance ratio may include operating months occurring prior to a source shutdown and operating months that follow after the source resumes operation.

(3) If your source shuts down and processes no listed oilseed for an entire calendar month, then you must categorize the month as a nonoperating month, as defined in § 63.2872. Exclude any nonoperating months from the compliance ratio determination.

(4) If your source is subject to an initial startup period as defined in § 63.2872, exclude from the compliance ratio determination any solvent and oilseed information recorded for the initial startup period.

(5) If your source is subject to a malfunction period as defined in § 63.2872, exclude from the compliance ratio determination any solvent and oilseed information recorded for the malfunction period.

(6) For sources processing cottonseed or specialty soybean, the solvent loss factor you use to determine the compliance ratio may change each operating month depending on the tons of oilseed processed during all normal operating periods in a 12 operating month period.

(c) If the compliance ratio is less than or equal to 1.00, your source was in compliance with the HAP emission requirements for the previous operating month.

(d) To determine the compliance ratio in Equation 2 of this section, you must select the appropriate oilseed solvent loss factor from Table 1 of this section. First, determine whether your source is new or existing using Table 1 of § 63.2833. Then, under the appropriate existing or new source column, select the oilseed solvent loss factor that corresponds to each type oilseed or process operation for each operating month.

COMPLIANCE REQUIREMENTS

§ 63.2850 How do I comply with the hazardous air pollutant emission standards?

(a) *General requirements.* The requirements in paragraphs (a)(1)(i) through (iv) of this section apply to all affected sources:

(1) Submit the necessary notifications in accordance with § 63.2860, which include:

- (i) Initial notifications for existing sources.
- (ii) Initial notifications for new and reconstructed sources.

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(iii) Initial notifications for significant modifications to existing or new sources.

(iv) Notification of compliance status.

(2) Develop and implement a plan for demonstrating compliance in accordance with § 63.2851.

(3) Develop a written startup, shutdown and malfunction (SSM) plan in accordance with the provisions in § 63.2852.

(4) Maintain all the necessary records you have used to demonstrate compliance with this subpart in accordance with § 63.2862.

(5) Submit the reports in paragraphs (a)(5)(i) through (iii) of this section:

(i) Annual compliance certifications in accordance with § 63.2861(a).

(ii) Periodic SSM reports in accordance with § 63.2861(c).

(iii) Immediate SSM reports in accordance with § 63.2861(d).

(6) Submit all notifications and reports and maintain all records required by the General Provisions for performance testing if you add a control device that destroys solvent.

(b) *Existing sources under normal operation.* You must meet all of the requirements listed in paragraph (a) of this section and Table 1 of this section for sources under normal operation, and the schedules for demonstrating compliance for existing sources under normal operation in Table 2 of this section.

(c) *New sources.* Your new source, including a source that is categorized as new due to reconstruction, must meet the requirements associated with one of two compliance options. Within 15 days of the startup date, you must choose to comply with one of the options listed in paragraph (c)(1) or (2) of this section:

(1) *Normal operation.* Upon startup of your new source, you must meet all of the requirements listed in § 63.2850(a) and Table 1 of this section for sources under normal operation, and the schedules for demonstrating compliance for new sources under normal operation in Table 2 of this section.

(2) *Initial startup period.* For up to 6 calendar months after the startup date of your new source, you must meet all of the requirements listed in paragraph

(a) of this section and Table 1 of this section for sources operating under an initial startup period, and the schedules for demonstrating compliance for new sources operating under an initial startup period in Table 2 of this section. After a maximum of 6 calendar months, your new source must then meet all of the requirements listed in Table 1 of this section for sources under normal operation.

(d) *Existing or new sources that have been significantly modified.* Your existing or new source that has been significantly modified must meet the requirements associated with one of two compliance options. Within 15 days of the modified source startup date, you must choose to comply with one of the options listed in paragraph (d)(1) or (2) of this section:

(1) *Normal operation.* Upon startup of your significantly modified existing or new source, you must meet all of the requirements listed in paragraph (a) of this section and Table 1 of this section for sources under normal operation, and the schedules for demonstrating compliance for an existing or new source that has been significantly modified in Table 2 of this section.

(2) *Initial startup period.* For up to 3 calendar months after the startup date of your significantly modified existing or new source, you must meet all of the requirements listed in paragraph (a) of this section and Table 1 of this section for sources operating under an initial startup period, and the schedules for demonstrating compliance for a significantly modified existing or new source operating under an initial startup period in Table 2 of this section. After a maximum of 3 calendar months, your new or existing source must meet all of the requirements listed in Table 1 of this section for sources under normal operation.

(e) *Existing or new sources experiencing a malfunction.* A malfunction is defined in § 63.2. In general, it means any sudden, infrequent, and not reasonably preventable failure of air pollution control equipment or process equipment to function in a usual manner. If your existing or new source experiences an unscheduled shutdown as a result of a malfunction, continues to operate during a malfunction (including

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the period reasonably necessary to correct the malfunction), or starts up after a shutdown resulting from a malfunction, then you must meet the requirements associated with one of two compliance options. Routine or scheduled process startups and shutdowns resulting from, but not limited to, market demands, maintenance activities, and switching types of oilseed processed, are not startups or shutdowns resulting from a malfunction and, therefore, do not qualify for this provision. Within 15 days of the beginning date of the malfunction, you must choose to comply with one of the options listed in paragraphs (e)(1) through (2) of this section:

(1) *Normal operation.* Your source must meet all of the requirements listed in paragraph (a) of this section and one of the options listed in paragraphs (e)(1)(i) through (iii) of this section:

(i) Existing source normal operation requirements in paragraph (b) of this section.

(ii) New source normal operation requirements in paragraph (c)(1) of this section.

(iii) Normal operation requirements for sources that have been significantly modified in paragraph (d)(1) of this section.

(2) *Malfunction period.* Throughout the malfunction period, you must meet all of the requirements listed in paragraph (a) of this section and Table 1 of this section for sources operating during a malfunction period. At the end of the malfunction period, your source must then meet all of the requirements listed in Table 1 of this section for sources under normal operation. Table 1 of this section follows:

TABLE 1 OF § 63.2850.—REQUIREMENTS FOR COMPLIANCE WITH HAP EMISSION STANDARDS

Are you required to . . .	For periods of normal operation?	For initial startup periods subject to § 63.2850(c)(2) or (d)(2)?	For malfunction periods subject to § 63.2850(e)(2)?
(a) Operate and maintain your source in accordance with your SSM plan as described in § 63.2852?	No, your source is not subject to the SSM plan, but rather the HAP emission limits of this standard.	Yes, throughout the entire initial startup period.	Yes, throughout the entire malfunction period.
(b) Determine and record the extraction solvent loss in gallons from your source?	Yes, as described in § 63.2853.	Yes, as described in § 63.2862(e).	Yes, as described in § 63.2862(e).
(c) Record the volume fraction of HAP present at greater than 1 percent by volume and gallons of extraction solvent in shipment received?	Yes	Yes	Yes.
(d) Determine and record the tons of each oilseed type processed by your source?	Yes, as described in § 63.2855.	No	No.
(e) Determine the weighted average volume fraction of HAP in extraction solvent received as described in § 63.2854 by the end of the following calendar month?	Yes	No. Except for solvent received by a new or reconstructed source commencing operation under an initial startup period, the HAP volume fraction in any solvent received during an initial startup period is included in the weighted average HAP determination for the next operating month.	No, the HAP volume fraction in any solvent received during a malfunction period is included in the weighted average HAP determination for the next operating month.
(f) Determine and record the actual solvent loss, weighted average volume fraction HAP, oilseed processed and compliance ratio for each 12 operating month period as described in § 63.2840 by the end of the following calendar month?	Yes,	No, these requirements are not applicable because your source is not required to determine the compliance ratio with data recorded for an initial startup period.	No, these requirements are not applicable because your source is not required to determine the compliance ratio with data recorded for a malfunction period.

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**TABLE 1 OF § 63.2850.—REQUIREMENTS FOR COMPLIANCE WITH HAP EMISSION STANDARDS—
Continued**

Are you required to . . .	For periods of normal operation?	For initial startup periods subject to § 63.2850(c)(2) or (d)(2)?	For malfunction periods subject to § 63.2850(e)(2)?
(g) Submit a Notification of Compliance Status or Annual Compliance Certification as appropriate?.	Yes, as described in §§ 63.2860(d) and 63.2861(a).	No. However, you may be required to submit an annual compliance certification for previous operating months, if the deadline for the annual compliance certification happens to occur during the initial startup period.	No. However, you may be required to submit an annual compliance certification for previous operating months, if the deadline for the annual compliance certification happens to occur during the malfunction period.
(h) Submit a Deviation Notification Report by the end of the calendar month following the month in which you determined that the compliance ratio exceeds 1.00 as described in § 63.2861(b)?.	Yes	No, these requirements are not applicable because your source is not required to determine the compliance ratio with data recorded for an initial startup period.	No, these requirements are not applicable because your source is not required to determine the compliance ratio with data recorded for a malfunction period.
(i) Submit a Periodic SSM Report as described in § 63.2861(c)?.	No, a SSM activity is not categorized as normal operation.	Yes	Yes.
(j) Submit an Immediate SSM Report as described in § 63.2861(d)?.	No, a SSM activity is not categorized as normal operation.	Yes, only if your source does not follow the SSM plan.	Yes, only if your source does not follow the SSM plan.

TABLE 2 OF § 63.2850.—SCHEDULES FOR DEMONSTRATING COMPLIANCE UNDER VARIOUS SOURCE OPERATING MODES

If your source is . . .	and is operating under. . .	then your record-keeping schedule. . .	You must determine your first compliance ratio by the end of the calendar month following. . .	Base your first compliance ratio on information recorded. . .
(a) Existing	Normal operation	Begins on the compliance date.	The first 12 operating months after the compliance date.	During the first 12 operating months after the compliance date.
(b) New	(1) Normal operation	Begins on the startup date of your new source.	The first 12 operating months after the startup date of the new source.	During the first 12 operating months after the startup date of the new source.
	(2) An initial startup period.	Begins on the startup date of your new source.	The first 12 operating months after termination of the initial startup period, which can last for up to 6 months.	During the first 12 operating months after the initial startup period, which can last for up to 6 months.
(c) Existing or new that has been significantly modified.	(1) Normal operation	Resumes on the startup date of the modified source.	The first operating month after the startup date of the modified source.	During the previous 11 operating months prior to the significant modification and the first operating month following the initial startup date of the source.
	(2) An initial startup period.	Resumes on the startup date of the modified source.	The first operating month after termination of the initial startup period, which can last up to 3 months.	During the 11 operating months before the significant modification and the first operating month after the initial startup period.

§ 63.2851 What is a plan for demonstrating compliance?

(a) You must develop and implement a written plan for demonstrating compliance that provides the detailed procedures you will follow to monitor and record data necessary for demonstrating compliance with this subpart. Procedures followed for quantifying solvent loss from the source and amount of oilseed processed vary from source to source because of site-specific factors such as equipment design characteristics and operating conditions. Typical procedures include one or more accurate measurement methods such as weigh scales, volumetric displacement, and material mass balances. Because the industry does not have a uniform set of procedures, you must develop and implement your own site-specific plan for demonstrating compliance before the compliance date for your source. You must also incorporate the plan for demonstrating compliance by reference in the source's title V permit and keep the plan on-site and readily available as long as the source is operational. If you make any changes to the plan for demonstrating compliance, then you must keep all previous versions of the plan and make them readily available for inspection for at least 5 years after each revision. The plan for demonstrating compliance must include the items in paragraphs (a)(1) through (7) of this section:

- (1) The name and address of the owner or operator.
- (2) The physical address of the vegetable oil production process.
- (3) A detailed description of all methods of measurement your source will use to determine your solvent losses, HAP content of solvent, and the tons of each type of oilseed processed.
- (4) When each measurement will be made.
- (5) Examples of each calculation you will use to determine your compliance status. Include examples of how you will convert data measured with one parameter to other terms for use in compliance determination.
- (6) Example logs of how data will be recorded.
- (7) A plan to ensure that the data continue to meet compliance demonstration needs.

(b) The responsible agency of these NESHAP may require you to revise your plan for demonstrating compliance. The responsible agency may require reasonable revisions if the procedures lack detail, are inconsistent or do not accurately determine solvent loss, HAP content of the solvent, or the tons of oilseed processed.

§ 63.2852 What is a startup, shutdown, and malfunction plan?

You must develop a written SSM plan in accordance with § 63.6(e)(3) and implement the plan, when applicable. You must complete the SSM plan before the compliance date for your source. You must also incorporate the SSM plan by reference in your source's title V permit and keep the SSM plan on-site and readily available as long as the source is operational. The SSM plan provides detailed procedures for operating and maintaining your source to minimize emissions during a qualifying SSM event for which the source chooses the § 63.2850(e)(2) malfunction period, or the § 63.2850(c)(2) or (d)(2) initial startup period. The SSM plan must specify a program of corrective action for malfunctioning process and air pollution control equipment and reflect the best practices now in use by the industry to minimize emissions. Some or all of the procedures may come from plans you developed for other purposes such as a Standard Operating Procedure manual or an Occupational Safety and Health Administration Process Safety Management plan. To qualify as a SSM plan, other such plans must meet all the applicable requirements of these NESHAP.

§ 63.2853 How do I determine the actual solvent loss?

By the end of each calendar month following an operating month, you must determine the total solvent loss in gallons for the previous operating month. The total solvent loss for an operating month includes all solvent losses that occur during normal operating periods within the operating month. If you have determined solvent losses for 12 or more operating months, then you must also determine the 12 operating months rolling sum of actual solvent loss in gallons by summing the

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monthly actual solvent loss for the previous 12 operating months. The 12 operating months rolling sum of solvent loss is the “actual solvent loss,” which is used to calculate your compliance ratio as described in §63.2840.

(a) To determine the actual solvent loss from your source, follow the procedures in your plan for demonstrating compliance to determine the items in paragraphs (a)(1) through (7) of this section:

(1) *The dates that define each operating status period during a calendar month.* The dates that define each operating status period include the beginning date of each calendar month and the date of any change in the source operating status. If the source maintains the same operating status during an entire calendar month, these dates are the beginning and ending dates of the calendar month. If, prior to the effective

date of this rule, your source determines the solvent loss on an *accounting month*, as defined in §63.2872, rather than a calendar month basis, and you have 12 complete accounting months of approximately equal duration in a calendar year, you may substitute the accounting month time interval for the calendar month time interval. If you choose to use an accounting month rather than a calendar month, you must document this measurement frequency selection in your plan for demonstrating compliance, and you must remain on this schedule unless you request and receive written approval from the agency responsible for these NESHAP.

(2) *Source operating status.* You must categorize the operating status of your source for each recorded time interval in accordance with criteria in Table 1 of this section, as follows:

TABLE 1 OF § 63.2853.—CATEGORIZING YOUR SOURCE OPERATING STATUS

If during a recorded time interval . . .	then your source operating status is . . .
(i) Your source processes any amount of listed oilseed and source is not operating under an initial startup operating period or a malfunction period subject to §63.2850(c)(2), (d)(2), or (e)(2).	A normal operating period.
(ii) Your source processes no agricultural product and your source is not operating under an initial startup period or malfunction period subject to §63.2850(c)(2), (d)(2), or (e)(2).	A nonoperating period.
(iii) You choose to operate your source under an initial startup period subject to §63.2850(c)(2) or (d)(2).	An initial startup period.
(iv) You choose to operate your source under a malfunction period subject to §63.2850(e)(2).	A malfunction period.
(v) Your source processes agricultural products not defined as listed oilseed.	An exempt period.

(3) *Measuring the beginning and ending solvent inventory.* You are required to measure and record the solvent inventory on the beginning and ending dates of each normal operating period that occurs during an operating month. An operating month is any calendar month with at least one normal operating period. You must consistently follow the procedures described in your plan for demonstrating compliance, as specified in §63.2851, to determine the extraction solvent inventory, and maintain readily available records of the actual solvent loss inventory, as described in §63.2862(c)(1). In general, you must measure and record the solvent inventory only when the source is actively processing any type of agricul-

tural product. When the source is not active, some or all of the solvent working capacity is transferred to solvent storage tanks which can artificially inflate the solvent inventory.

(4) *Gallons of extraction solvent received.* Record the total gallons of extraction solvent received in each shipment. For most processes, the gallons of solvent received represents purchases of delivered solvent added to the solvent storage inventory. However, if your process refines additional vegetable oil from off-site sources, recovers solvent from the off-site oil, and adds it to the on-site solvent inventory, then you must determine the quantity of recovered solvent and include it in

the gallons of extraction solvent received.

(5) *Solvent inventory adjustments.* In some situations, solvent losses determined directly from the measured solvent inventory and quantity of solvent received is not an accurate estimate of the “actual solvent loss” for use in determining compliance ratios. In such cases, you may adjust the total solvent loss for each normal operating period as long as you provide a reasonable justification for the adjustment. Situations that may require adjustments of the total solvent loss include, but are not limited to, situations in paragraphs (a)(5)(i) and (ii) of this section:

(i) *Solvent destroyed in a control device.* You may use a control device to reduce solvent emissions to meet the emission standard. The use of a control device does not alter the emission limit for the source. If you use a control device that reduces solvent emissions through destruction of the solvent instead of recovery, then determine the gallons of solvent that enter the control device and are destroyed there during each normal operating period. All solvent destroyed in a control device during a normal operating period can be subtracted from the total solvent loss. Examples of destructive emission control devices include catalytic incinerators, boilers, or flares. Identify and describe, in your plan for demonstrating compliance, each type of reasonable and sound measurement method that you use to quantify the gallons of solvent entering and exiting the control device and to determine the destruction efficiency of the control device. You may use design evaluations to document the gallons of solvent destroyed or removed by the control device instead of performance testing under § 63.7. The

design evaluations must be based on the procedures and options described in § 63.985(b)(1)(i)(A) through (C) or § 63.11, as appropriate. All data, assumptions, and procedures used in such evaluations must be documented and available for inspection. If you use performance testing to determine solvent flow rate to the control device or destruction efficiency of the device, follow the procedures as outlined in § 63.997(e)(1) and (2). Instead of periodic performance testing to demonstrate continued good operation of the control device, you may develop a monitoring plan, following the procedures outlined in § 63.988(c) and using operational parametric measurement devices such as fan parameters, percent measurements of lower explosive limits, and combustion temperature.

(ii) Changes in solvent working capacity. In records you keep on-site, document any process modifications resulting in changes to the solvent working capacity in your vegetable oil production process. *Solvent working capacity* is defined in § 63.2872. In general, solvent working capacity is the volume of solvent normally retained in solvent recovery equipment such as the extractor, desolventizer-toaster, solvent storage, working tanks, mineral oil absorber, condensers, and oil/solvent distillation system. If the change occurs during a normal operating period, you must determine the difference in working solvent volume and make a one-time documented adjustment to the solvent inventory.

(b) Use Equation 1 of this section to determine the actual solvent loss occurring from your affected source for all normal operating periods recorded within a calendar month. Equation 1 of this section follows:

$$\text{Monthly Actual Solvent (gal)} = \sum_{i=1}^n (\text{SOLV}_B - \text{SOLV}_E + \text{SOLV}_R \pm \text{SOLV}_A)_i \quad (\text{Eq. 1})$$

Where:
 SOLV_B = Gallons of solvent in the inventory at the beginning of normal

operating period “i” as determined in paragraph (a)(3) of this section.

$SOLV_E$ = Gallons of solvent in the inventory at the end of normal operating period "i" as determined in paragraph (a)(3) of this section.

$SOLV_R$ = Gallons of solvent received between the beginning and ending inventory dates of normal operating period "i" as determined in paragraph (a)(4) of this section.

$SOLV_A$ = Gallons of solvent added or removed from the extraction solvent inventory during normal operating period "i" as determined in paragraph (a)(5) of this section.

n = Number of normal operating periods in a calendar month.

(c) The actual solvent loss is the total solvent losses during normal operating periods for the previous 12 operating months. You determine your actual solvent loss by summing the monthly actual solvent losses for the previous 12 operating months. You must record the actual solvent loss by the end of each calendar month following an operating month. Use the actual solvent loss in Equation 2 of § 63.2840 to determine the compliance ratio. Actual solvent loss does not include losses that occur during operating status periods listed in paragraphs (c)(1) through (4) of this section. If any one of these four operating status periods span an entire month, then the month is treated as nonoperating and there is no compliance ratio determination.

(1) Nonoperating periods as described in paragraph (a)(2)(ii) of this section.

(2) Initial startup periods as described in § 63.2850(c)(2) or (d)(2).

(3) Malfunction periods as described in § 63.2850(e)(2).

(4) Exempt operation periods as described in paragraph (a)(2)(v) of this section.

§ 63.2854 How do I determine the weighted average volume fraction of HAP in the actual solvent loss?

(a) This section describes the information and procedures you must use to determine the weighted average volume fraction of HAP in extraction solvent received for use in your vegetable oil production process. By the end of each calendar month following an operating month, determine the weighted average volume fraction of HAP in ex-

traction solvent received since the end of the previous operating month. If you have determined the monthly weighted average volume fraction of HAP in solvent received for 12 or more operating months, then also determine an overall weighted average volume fraction of HAP in solvent received for the previous 12 operating months. Use the volume fraction of HAP determined as a 12 operating months weighted average in Equation 2 of § 63.2840 to determine the compliance ratio.

(b) To determine the volume fraction of HAP in the extraction solvent determined as a 12 operating months weighted average, you must comply with paragraphs (b)(1) through (3) of this section:

(1) Record the volume fraction of each HAP comprising more than 1 percent by volume of the solvent in each delivery of solvent, including solvent recovered from off-site oil. To determine the HAP content of the material in each delivery of solvent, the reference method is EPA Method 311 of appendix A of this part. You may use EPA Method 311, an approved alternative method, or any other reasonable means for determining the HAP content. Other reasonable means of determining HAP content include, but are not limited to, a material safety data sheet or a manufacturer's certificate of analysis. A certificate of analysis is a legal and binding document provided by a solvent manufacturer. The purpose of a certificate of analysis is to list the test methods and analytical results that determine chemical properties of the solvent and the volume percentage of all HAP components present in the solvent at quantities greater than 1 percent by volume. You are not required to test the materials that you use, but the Administrator may require a test using EPA Method 311 (or an approved alternative method) to confirm the reported HAP content. However, if the results of an analysis by EPA Method 311 are different from the HAP content determined by another means, the EPA Method 311 results will govern compliance determinations.

(2) Determine the weighted average volume fraction of HAP in the extraction solvent each operating month. The

weighted average volume fraction of HAP for an operating month includes all solvent received since the end of the last operating month, regardless of the operating status at the time of the delivery. Determine the monthly weighted average volume fraction of HAP by summing the products of the HAP vol-

ume fraction of each delivery and the volume of each delivery and dividing the sum by the total volume of all deliveries as expressed in Equation 1 of this section. Record the result by the end of each calendar month following an operating month. Equation 1 of this section follows:

$$\text{Monthly Weighted Average HAP Content of Extraction Solvent (volume fraction)} = \frac{\sum_{i=1}^n (\text{Received}_i * \text{Content}_i)}{\text{Total Received}} \quad (\text{Eq. 1})$$

Where:

Received_i = Gallons of extraction solvent received in delivery "i."

Content_i = The volume fraction of HAP in extraction solvent delivery "i."

Total Received = Total gallons of extraction solvent received since the end of the previous operating month.

n = Number of extraction solvent deliveries since the end of the previous operating month.

(3) Determine the volume fraction of HAP in your extraction solvent as a 12

operating months weighted average. When your source has processed oilseed for 12 operating months, sum the products of the monthly weighted average HAP volume fraction and corresponding volume of solvent received, and divide the sum by the total volume of solvent received for the 12 operating months, as expressed by Equation 2 of this section. Record the result by the end of each calendar month following an operating month and use it in Equation 2 of §63.2840 to determine the compliance ratio. Equation 2 of this section follows:

$$\text{12-Month Weighted Average of HAP Content in Solvent Received (volume fraction)} = \frac{\sum_{i=1}^{12} (\text{Received}_i * \text{Content}_i)}{\text{Total Received}} \quad (\text{Eq. 2})$$

Where:

Received_i = Gallons of extraction solvent received in operating month "i" as determined in accordance with §63.2853(a)(4).

Content_i = Average volume fraction of HAP in extraction solvent received in operating month "i" as determined in accordance with paragraph (b)(1) of this section.

Total Received = Total gallons of extraction solvent received during the previous 12 operating months.

§63.2855 How do I determine the quantity of oilseed processed?

All oilseed measurements must be determined on an *as received* basis, as defined in §63.2872. The *as received* basis refers to the oilseed chemical and physical characteristics as initially received by the source and prior to any oilseed handling and processing. By the end of each calendar month following an operating month, you must determine the tons as received of each listed oilseed processed for the operating month. The total oilseed processed for an operating month includes the total

of each oilseed processed during all normal operating periods that occur within the operating month. If you have determined the tons of oilseed processed for 12 or more operating months, then you must also determine the 12 operating months rolling sum of each type oilseed processed by summing the tons of each type of oilseed processed for the previous 12 operating months. The 12 operating months rolling sum of each type of oilseed processed is used to calculate the compliance ratio as described in § 63.2840.

(a) To determine the tons as received of each type of oilseed processed at your source, follow the procedures in your plan for demonstrating compliance to determine the items in paragraphs (a)(1) through (5) of this section:

(1) *The dates that define each operating status period.* The dates that define each operating status period include the beginning date of each calendar month and the date of any change in the source operating status. If, prior to the effective date of this rule, your source determines the oilseed inventory on an accounting month rather than a calendar month basis, and you have 12 complete accounting months of approximately equal duration in a calendar year, you may substitute the accounting month time interval for the calendar month time interval. If you choose to use an accounting month rather than a calendar month, you must document this measurement frequency selection in your plan for demonstrating compliance, and you must remain on this schedule unless you request and receive written approval from the agency responsible for these NESHAP. The dates on each oilseed inventory log must be consistent with the dates recorded for the solvent inventory.

(2) *Source operating status.* You must categorize the source operation for each recorded time interval. The source operating status for each time interval recorded on the oilseed inventory for each type of oilseed must be consistent with the operating status recorded on the solvent inventory logs as described in § 63.2853(a)(2).

(3) *Measuring the beginning and ending inventory for each oilseed.* You are required to measure and record the oil-

seed inventory on the beginning and ending dates of each normal operating period that occurs during an operating month. An operating month is any calendar month with at least one normal operating period. You must consistently follow the procedures described in your plan for demonstrating compliance, as specified in § 63.2851, to determine the oilseed inventory on an as received basis and maintain readily available records of the oilseed inventory as described by § 63.2862(c)(3).

(4) *Tons of each oilseed received.* Record the type of oilseed and tons of each shipment of oilseed received and added to your on-site storage.

(5) *Oilseed inventory adjustments.* In some situations, determining the quantity of oilseed processed directly from the measured oilseed inventory and quantity of oilseed received is not an accurate estimate of the tons of oilseed processed for use in determining compliance ratios. For example, spoiled and molded oilseed removed from storage but not processed by your source will result in an overestimate of the quantity of oilseed processed. In such cases, you must adjust the oilseed inventory and provide a justification for the adjustment. Situations that may require oilseed inventory adjustments include, but are not limited to, the situations listed in paragraphs (a)(5)(i) through (v) of this section:

(i) Oilseed that mold or otherwise become unsuitable for processing.

(ii) Oilseed you sell before it enters the processing operation.

(iii) Oilseed destroyed by an event such as a process malfunction, fire, or natural disaster.

(iv) Oilseed processed through operations prior to solvent extraction such as screening, dehulling, cracking, drying, and conditioning; but that are not routed to the solvent extractor for further processing.

(v) Periodic physical measurements of inventory. For example, some sources periodically empty oilseed storage silos to physically measure the current oilseed inventory. This periodic measurement procedure typically results in a small inventory correction. The correction factor, usually less than

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1 percent, may be used to make an adjustment to the source's oilseed inventory that was estimated previously with indirect measurement techniques. To make this adjustment, your plan for demonstrating compliance must provide for such an adjustment.

(b) Use Equation 1 of this section to determine the quantity of each oilseed type processed at your affected source during normal operating periods recorded within a calendar month. Equation 1 of this section follows:

$$\text{Monthly Quantity of Each Oilseed Processed (tons)} = \sum_{n=1}^n (\text{SEED}_B - \text{SEED}_E + \text{SEED}_R \pm \text{SEED}_A) \quad (\text{Eq. 1})$$

Where:

SEED_B = Tons of oilseed in the inventory at the beginning of normal operating period "i" as determined in accordance with paragraph (a)(3) of this section.

SEED_E = Tons of oilseed in the inventory at the end of normal operating period "i" as determined in accordance with paragraph (a)(3) of this section.

SEED_R = Tons of oilseed received during normal operating period "i" as determined in accordance with paragraph (a)(4) of this section.

SEED_A = Tons of oilseed added or removed from the oilseed inventory during normal operating period "i" as determined in accordance with paragraph (a)(5) of this section.

n = Number of normal operating periods in the calendar month during which this type oilseed was processed.

(c) The quantity of each oilseed processed is the total tons of each type of listed oilseed processed during normal operating periods in the previous 12 operating months. You determine the tons of each oilseed processed by summing the monthly quantity of each oilseed processed for the previous 12 operating months. You must record the 12 operating months quantity of each type of oilseed processed by the end of each calendar month following an operating month. Use the 12 operating months quantity of each type of oilseed processed to determine the compliance ratio as described in § 63.2840. The quantity of oilseed processed does not include oilseed processed during the operating status periods in paragraphs (c)(1) through (4) of this section:

(1) Nonoperating periods as described in § 63.2853 (a)(2)(ii).

(2) Initial startup periods as described in § 63.2850(c)(2) or (d)(2).

(3) Malfunction periods as described in § 63.2850(e)(2).

(4) Exempt operation periods as described in § 63.2853 (a)(2)(v).

(5) If any one of these four operating status periods span an entire calendar month, then the calendar month is treated as a nonoperating month and there is no compliance ratio determination.

NOTIFICATIONS, REPORTS, AND RECORDS

§ 63.2860 What notifications must I submit and when?

You must submit the one-time notifications listed in paragraphs (a) through (d) of this section to the responsible agency:

(a) *Initial notification for existing sources.* For an existing source, submit an initial notification to the agency responsible for these NESHAP no later than 120 days after the effective date of this subpart. In the notification, include the items in paragraphs (a)(1) through (5) of this section:

(1) The name and address of the owner or operator.

(2) The physical address of the vegetable oil production process.

(3) Identification of the relevant standard, such as the vegetable oil production NESHAP, and compliance date.

(4) A brief description of the source including the types of listed oilseeds processed, nominal operating capacity, and type of desolventizer(s) used.

(5) A statement designating the source as a major source of HAP or a

demonstration that the source meets the definition of an area source. An area source is a source that is not a major source and is not collocated within a plant site with other sources that are individually or collectively a major source.

(b) *Initial notifications for new and reconstructed sources.* New or reconstructed sources must submit a series of notifications before, during, and after source construction per the schedule listed in § 63.9. The information requirements for the notifications are the same as those listed in the General Provisions with the exceptions listed in paragraphs (b)(1) and (2) of this section:

(1) The application for approval of construction does not require the specific HAP emission data required in § 63.5(d)(1)(ii)(H) and (iii), (d)(2) and (d)(3)(ii). The application for approval of construction would include, instead, a brief description of the source including the types of listed oilseeds processed, nominal operating capacity, and type of desolventizer(s) used.

(2) The notification of actual startup date must also include whether you have elected to operate under an initial startup period subject to § 63.2850(c)(2) and provide an estimate and justification for the anticipated duration of the initial startup period.

(c) *Significant modification notifications.* Any existing or new source that plans to undergo a significant modification as defined in § 63.2872 must submit two reports as described in paragraphs (c)(1) and (2) of this section:

(1) Initial notification. You must submit an initial notification to the agency responsible for these NESHAP 30 days prior to initial startup of the significantly modified source. The initial notification must demonstrate that the proposed changes qualify as a significant modification. The initial notification must include the items in paragraphs (c)(1)(i) and (ii) of this section:

(i) The expected startup date of the modified source.

(ii) A description of the significant modification including a list of the equipment that will be replaced or modified. If the significant modification involves changes other than adding or replacing extractors,

desolventizer-toasters (conventional and specialty), and meal dryer-coolers, then you must also include the fixed capital cost of the new components, expressed as a percentage of the fixed capital cost to build a comparable new vegetable oil production process; supporting documentation for the cost estimate; and documentation that the proposed changes will significantly affect solvent losses.

(2) Notification of actual startup. You must submit a notification of actual startup date within 15 days after initial startup of the modified source. The notification must include the items in paragraphs (c)(2)(i) through (iv) of this section:

(i) The initial startup date of the modified source.

(ii) An indication whether you have elected to operate under an initial startup period subject to § 63.2850(d)(2).

(iii) The anticipated duration of any initial startup period.

(iv) A justification for the anticipated duration of any initial startup period.

(d) *Notification of compliance status.* As an existing, new, or reconstructed source, you must submit a notification of compliance status report to the responsible agency no later than 60 days after determining your initial 12 operating months compliance ratio. If you are an existing source, you generally must submit this notification no later than 50 calendar months after the effective date of these NESHAP (36 calendar months for compliance, 12 operating months to record data, and 2 calendar months to complete the report). If you are a new or reconstructed source, the notification of compliance status is generally due no later than 20 calendar months after initial startup (6 calendar months for the initial startup period, 12 operating months to record data, and 2 calendar months to complete the report). The notification of compliance status must contain the items in paragraphs (d)(1) through (6) of this section:

(1) The name and address of the owner or operator.

(2) The physical address of the vegetable oil production process.

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(3) Each listed oilseed type processed during the previous 12 operating months.

(4) Each HAP identified under § 63.2854(a) as being present in concentrations greater than 1 percent by volume in each delivery of solvent received during the 12 operating months period used for the initial compliance determination.

(5) A statement designating the source as a major source of HAP or a demonstration that the source qualifies as an area source. An area source is a source that is not a major source and is not collocated within a plant site with other sources that are individually or collectively a major source.

(6) A compliance certification indicating whether the source complied with all of the requirements of this subpart throughout the 12 operating months used for the initial source compliance determination. This certification must include a certification of the items in paragraphs (d)(6)(i) through (iii) of this section:

(i) The plan for demonstrating compliance (as described in § 63.2851) and SSM plan (as described in § 63.2852) are complete and available on-site for inspection.

(ii) You are following the procedures described in the plan for demonstrating compliance.

(iii) The compliance ratio is less than or equal to 1.00.

§ 63.2861 What reports must I submit and when?

After the initial notifications, you must submit the reports in paragraphs (a) through (d) of this section to the agency responsible for these NESHAP at the appropriate time intervals:

(a) *Annual compliance certifications.* The first annual compliance certification is due 12 calendar months after you submit the notification of compliance status. Each subsequent annual compliance certification is due 12 calendar months after the previous annual compliance certification. The annual compliance certification provides the compliance status for each operating month during the 12 calendar months period ending 60 days prior to the date on which the report is due. Include the information in paragraphs (a)(1)

through (6) of this section in the annual certification:

(1) The name and address of the owner or operator.

(2) The physical address of the vegetable oil production process.

(3) Each listed oilseed type processed during the 12 calendar months period covered by the report.

(4) Each HAP identified under § 63.2854(a) as being present in concentrations greater than 1 percent by volume in each delivery of solvent received during the 12 calendar months period covered by the report.

(5) A statement designating the source as a major source of HAP or a demonstration that the source qualifies as an area source. An area source is a source that is not a major source and is not collocated within a plant site with other sources that are individually or collectively a major source.

(6) A compliance certification to indicate whether the source was in compliance for each compliance determination made during the 12 calendar months period covered by the report. For each such compliance determination, you must include a certification of the items in paragraphs (a)(6)(i) through (ii) of this section:

(i) You are following the procedures described in the plan for demonstrating compliance.

(ii) The compliance ratio is less than or equal to 1.00.

(b) *Deviation notification report.* Submit a deviation report for each compliance determination you make in which the compliance ratio exceeds 1.00 as determined under § 63.2840(c). Submit the deviation report by the end of the month following the calendar month in which you determined the deviation. The deviation notification report must include the items in paragraphs (b)(1) through (4) of this section:

(1) The name and address of the owner or operator.

(2) The physical address of the vegetable oil production process.

(3) Each listed oilseed type processed during the 12 operating months period for which you determined the deviation.

(4) The compliance ratio comprising the deviation. You may reduce the frequency of submittal of the deviation

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notification report if the agency responsible for these NESHAP does not object as provided in § 63.10(e)(3)(iii).

(c) *Periodic startup, shutdown, and malfunction report.* If you choose to operate your source under an initial startup period subject to § 63.2850(c)(2) or (d)(2) or a malfunction period subject to § 63.2850(e)(2), you must submit a periodic SSM report by the end of the calendar month following each month in which the initial startup period or malfunction period occurred. The periodic SSM report must include the items in paragraphs (c)(1) through (3) of this section:

(1) The name, title, and signature of a source's responsible official who is certifying that the report accurately states that all actions taken during the initial startup or malfunction period were consistent with the SSM plan.

(2) A description of events occurring during the time period, the date and duration of the events, and reason the time interval qualifies as an initial startup period or malfunction period.

(3) An estimate of the solvent loss during the initial startup or malfunction period with supporting documentation.

(d) *Immediate SSM reports.* If you handle a SSM during an initial startup period subject to § 63.2850(c)(2) or (d)(2) or a malfunction period subject to § 63.2850(e)(2) differently from procedures in the SSM plan, then you must submit an immediate SSM report. Immediate SSM reports consist of a telephone call or facsimile transmission to the responsible agency within 2 working days after starting actions inconsistent with the SSM plan, followed by a letter within 7 working days after the end of the event. The letter must include the items in paragraphs (d)(1) through (3) of this section:

(1) The name, title, and signature of a source's responsible official who is certifying the accuracy of the report, an explanation of the event, and the reasons for not following the SSM plan.

(2) A description and date of the SSM event, its duration, and reason it qualifies as a SSM.

(3) An estimate of the solvent loss for the duration of the SSM event with supporting documentation.

§ 63.2862 What records must I keep?

(a) You must satisfy the record-keeping requirements of this section by the compliance date for your source specified in Table 1 of § 63.2834.

(b) Prepare a plan for demonstrating compliance (as described in § 63.2851) and a SSM plan (as described in § 63.2852). In these two plans, describe the procedures you will follow in obtaining and recording data, and determining compliance under normal operations or a SSM subject to the § 63.2850(c)(2) or (d)(2) initial startup period or the § 63.2850(e)(2) malfunction period. Complete both plans before the compliance date for your source and keep them on-site and readily available as long as the source is operational.

(c) If your source processes any listed oilseed, record the items in paragraphs (c)(1) through (5) of this section:

(1) For the solvent inventory, record the information in paragraphs (c)(1)(i) through (vii) of this section in accordance with your plan for demonstrating compliance:

(i) Dates that define each operating status period during a calendar month.

(ii) The operating status of your source such as normal operation, non-operating, initial startup period, malfunction period, or exempt operation for each recorded time interval.

(iii) Record the gallons of extraction solvent in the inventory on the beginning and ending dates of each normal operating period.

(iv) The gallons of all extraction solvent received, purchased, and recovered during each calendar month.

(v) All extraction solvent inventory adjustments, additions or subtractions. You must document the reason for the adjustment and justify the quantity of the adjustment.

(vi) The total solvent loss for each calendar month, regardless of the source operating status.

(vii) The actual solvent loss in gallons for each operating month.

(2) For the weighted average volume fraction of HAP in the extraction solvent, you must record the items in paragraphs (c)(2)(i) through (iii) of this section:

(i) The gallons of extraction solvent received in each delivery.

(ii) The volume fraction of each HAP exceeding 1 percent by volume in each delivery of extraction solvent.

(iii) The weighted average volume fraction of HAP in extraction solvent received since the end of the last operating month as determined in accordance with § 63.2854(b)(2).

(3) For each type of listed oilseed processed, record the items in paragraphs (c)(3)(i) through (vi) of this section, in accordance with your plan for demonstrating compliance:

(i) The dates that define each operating status period. These dates must be the same as the dates entered for the extraction solvent inventory.

(ii) The operating status of your source such as normal operation, non-operating, initial startup period, malfunction period, or exempt operation for each recorded time interval. On the log for each type of listed oilseed that is not being processed during a normal operating period, you must record which type of listed oilseed is being processed in addition to the source operating status.

(iii) The oilseed inventory for the type of listed oilseed being processed on the beginning and ending dates of each normal operating period.

(iv) The tons of each type of listed oilseed received at the affected source each normal operating period.

(v) All listed oilseed inventory adjustments, additions or subtractions for normal operating periods. You must document the reason for the adjustment and justify the quantity of the adjustment.

(vi) The tons of each type of listed oilseed processed during each operating month.

(d) After your source has processed listed oilseed for 12 operating months, and you are not operating during an initial startup period as described in § 63.2850(c)(2) or (d)(2), or a malfunction period as described in § 63.2850(e)(2), record the items in paragraphs (d)(1) through (5) of this section by the end of the calendar month following each operating month:

(1) The 12 operating months rolling sum of the actual solvent loss in gallons as described in § 63.2853(c).

(2) The weighted average volume fraction of HAP in extraction solvent

received for the previous 12 operating months as described in § 63.2854(b)(3).

(3) The 12 operating months rolling sum of each type of listed oilseed processed at the affected source in tons as described in § 63.2855(c).

(4) A determination of the compliance ratio. Using the values from §§ 63.2853, 63.2854, 63.2855, and Table 1 of § 63.2840, calculate the compliance ratio using Equation 2 of § 63.2840.

(5) A statement of whether the source is in compliance with all of the requirements of this subpart. This includes a determination of whether you have met all of the applicable requirements in § 63.2850.

(e) For each SSM event subject to an initial startup period as described in § 63.2850(c)(2) or (d)(2), or a malfunction period as described in § 63.2850(e)(2), record the items in paragraphs (e)(1) through (3) of this section by the end of the calendar month following each month in which the initial startup period or malfunction period occurred:

(1) A description and date of the SSM event, its duration, and reason it qualifies as an initial startup or malfunction.

(2) An estimate of the solvent loss in gallons for the duration of the initial startup or malfunction period with supporting documentation.

(3) A checklist or other mechanism to indicate whether the SSM plan was followed during the initial startup or malfunction period.

§ 63.2863 In what form and how long must I keep my records?

(a) Your records must be in a form suitable and readily available for review in accordance with § 63.10(b)(1).

(b) As specified in § 63.10(b)(1), you must keep each record for 5 years following the date of each occurrence, measurement, maintenance, corrective action, report, or record.

(c) You must keep each record on-site for at least 2 years after the date of each occurrence, measurement, maintenance, corrective action, report, or record, in accordance with § 63.10(b)(1). You can keep the records off-site for the remaining 3 years.

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OTHER REQUIREMENTS AND INFORMATION

§§ 63.1 through 63.15 apply to you. Table 1 of § 63.2870 follows:

§ 63.2870 What parts of the General Provisions apply to me?

Table 1 of this section shows which parts of the General Provisions in

TABLE 1 OF § 63.2870.—APPLICABILITY OF 40 CFR PART 63, SUBPART A, TO 40 CFR, PART 63, SUBPART GGGG

General provisions citation	Subject of citation	Brief description of requirement	Applies to subpart	Explanation
§ 63.1	Applicability	Initial applicability determination; applicability after standard established; permit requirements; extensions; notifications.	Yes	
§ 63.2	Definitions	Definitions for part 63 standards	Yes	Except as specifically provided in this subpart.
§ 63.3	Units and abbreviations	Units and abbreviations for part 63 standards.	Yes.	
§ 63.4	Prohibited activities and circumvention.	Prohibited activities; compliance date; circumvention; severability.	Yes	
§ 63.5	Construction/reconstruction	Applicability; applications; approvals	Yes	Except for subsections of § 63.5 as listed below.
§ 63.5(c)	[Reserved]			
§ 63.5(d)(1)(ii)(H)	Application for approval	Type and quantity of HAP, operating parameters.	No	All sources emit HAP. Subpart GGGG does not require control from specific emission points.
§ 63.5(d)(1)(ii)(I)	[Reserved]			
§ 63.5(d)(1)(iii), (d)(2), (d)(3)(ii).		Application for approval	No	The requirements of the application for approval for new, reconstructed and significantly modified sources are described in § 63.2860(b) and (c) of subpart GGGG. General provision requirements for identification of HAP emission points or estimates of actual emissions are not required. Descriptions of control and methods, and the estimated and actual control efficiency of such do not apply. Requirements for describing control equipment and the estimated and actual control efficiency of such equipment apply only to control equipment to which the subpart GGGG requirements for quantifying.
§ 63.6	Applicability of General Provisions	Applicability	Yes	Except for subsections of § 63.6 as listed below.
§ 63.6(b)(1)–(3)	Compliance dates, new and reconstructed sources.		No	Section 63.2834 of subpart GGGG specifies the compliance dates for new and reconstructed sources.
§ 63.6(b)(6)	[Reserved]			
§ 63.6(c)(3)–(4)	[Reserved]			
§ 63.6(d)	[Reserved]			
§ 63.6(e)	Operation and maintenance requirements.		Yes	Implement your SSM plan, as specified in § 63.2851.
§ 63.6(f)–(g)	Compliance with nonopacity emission standards except during SSM.	Comply with emission standards at all times except during SSM.	No	Subpart GGGG does not have nonopacity requirements.
§ 63.6(h)	Opacity/Visible emission (VE) standards.		No	Subpart GGGG has no opacity or VE standards.
§ 63.6(i)	Compliance extension	Procedures and criteria for responsible agency to grant compliance extension.	Yes	
§ 63.6(j)	Presidential compliance exemption	President may exempt source category from requirement to comply with subpart.	Yes	

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§ 63.7	Performance testing requirements	Schedule, conditions, notifications and procedures.	Yes	Subpart GGGG requires performance testing only if the source applies additional control that destroys solvent. Section 63.2850(a)(6) requires sources to follow the performance testing guidelines of the General Provisions if a control is added.
§ 63.8	Monitoring requirements		No	Subpart GGGG does not require monitoring other than as specified therein.
§ 63.9	Notification requirements	Applicability and state delegation	Yes	Except for subsections of § 63.9 as listed below.
§ 63.9(b)(2)	Notification requirements	Initial notification requirements for existing sources.	No	Section 63.2860(a) of subpart GGGG specifies the requirements of the initial notification for existing sources.
§ 63.9(b)(3)–(5)	Notification requirements	Notification requirement for certain new/reconstructed sources.	Yes	Except the information requirements differ as described in § 63.2860(b) of subpart GGGG.
§ 63.9(e)	Notification of performance test	Notify responsible agency 60 days ahead.	Yes	Applies only if performance testing is performed.
§ 63.9(f)	Notification of VE/opacity observations.	Notify responsible agency 30 days ahead.	No	Subpart GGGG has no opacity or VE standards.
§ 63.9(g)	Additional notifications when using a continuous monitoring system (CMS).	Notification of performance evaluation; Notification using COMS data; notification that exceeded criterion for relative accuracy.	No	Subpart GGGG has no CMS requirements.
§ 63.9(h)	Notification of compliance status	Contents	No	Section 63.2860(d) of subpart GGGG specifies requirements for the notification of compliance status.
§ 63.10	Recordkeeping/reporting	Schedule for reporting, record storage	Yes	Except for subsections of § 63.10 as listed below.
§ 63.10(b)(2)(i)	Recordkeeping	Record SSM event	Yes	Applicable to periods when sources must implement their SSM plan as specified in subpart GGGG.
§ 63.10(b)(2)(ii)–(iii)	Recordkeeping	Malfunction of air pollution equipment	No	Applies only if air pollution control equipment has been added to the process and is necessary for the source to meet the emission limit.
§ 63.10(b)(2)(vi)	Recordkeeping	CMS recordkeeping	No	Subpart GGGG has no CMS requirements.
§ 63.10(b)(2)(viii)–(ix)	Recordkeeping	Conditions of performance test	Yes	Applies only if performance tests are performed. Subpart GGGG does not have any CMS opacity or VE observation requirements.
§ 63.10(b)(2)(x)–(xii)	Recordkeeping	CMS, performance testing, and opacity and VE observations recordkeeping.	No	Subpart GGGG does not require CMS.
§ 63.10(c)	Recordkeeping	Additional CMS recordkeeping	No	Subpart GGGG does not require CMS.
§ 63.10(d)(2)	Reporting	Reporting performance test results	Yes	Applies only if performance testing is performed.
§ 63.10(d)(3)	Reporting	Reporting opacity or VE observations	No	Subpart GGGG has no opacity or VE standards.
§ 63.10(d)(4)	Reporting	Progress reports	Yes	Applies only if a condition of compliance extension exists.
§ 63.10(d)(5)	Reporting	SSM reporting	No	Section 63.2861(c) and (d) specify SSM reporting requirements.
§ 63.10(e)	Reporting	Additional CMS reports	No	Subpart GGGG does not require CMS.
§ 63.11	Control device requirements	Requirements for flares	Yes	Applies only if your source uses a flare to control solvent emissions. Subpart GGGG does not require flares.

TABLE 1 OF § 63.2870.—APPLICABILITY OF 40 CFR PART 63, SUBPART A, TO 40 CFR, PART 63, SUBPART GGGG—Continued

General provisions citation	Subject of citation	Brief description of requirement	Applies to subpart	Explanation
§ 63.12	State authority and delegations	State authority to enforce standards ..	Yes	
§ 63.13	State/regional addresses	Addresses where reports, notifica- tions, and requests are sent.	Yes	
§ 63.14	Incorporation by reference	Test methods incorporated by ref- erence.	Yes	
§ 63.15	Availability of information and con- fidentiality.	Public and confidential information	Yes	

§ 63.2870

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§ 63.2871 Who implements and enforces this subpart?

(a) This subpart can be implemented by us, the U.S. EPA, or a delegated authority such as your State, local, or tribal agency. If the U.S. EPA Administrator has delegated authority to your State, local, or tribal agency, then that agency, as well as the U.S. EPA, has the authority to implement and enforce this subpart. You should contact your U.S. EPA Regional Office to find out if this subpart is delegated to your State, local, or tribal agency.

(b) In delegating implementation and enforcement authority of this subpart to a State, local, or tribal agency under section 40 CFR part 63, subpart E, the authorities contained in paragraph (c) of this section are retained by the Administrator of the U.S. EPA and are not transferred to the State, local, or tribal agency.

(c) The authorities that will not be delegated to State, local, or tribal agencies are as follows:

- (1) Approval of alternative non-opacity emissions standards under § 63.6(g).
- (2) Approval of alternative opacity standards under § 63.6(h)(9).
- (3) Approval of major alternatives to test methods under § 63.7(e)(2)(ii) and (f) and as defined in § 63.90.
- (4) Approval of major alternatives to monitoring under § 63.8(f) and as defined in § 63.90.
- (5) Approval of major alternatives to recordkeeping and reporting under § 63.10(f) and as defined in § 63.90.

§ 63.2872 What definitions apply to this subpart?

Terms used in this subpart are defined in the sources listed:

- (a) The Clean Air Act, section 112(a).
- (b) In 40 CFR 63.2, the NESHAP General Provisions.
- (c) In this section as follows:

Accounting month means a time interval defined by a business firm during which corporate economic and financial factors are determined on a consistent and regular basis. An accounting month will consist of approximately 4 to 5 calendar weeks and each accounting month will be of approximate equal duration. An accounting month may not correspond exactly to a

calendar month, but 12 accounting months will correspond exactly to a calendar year.

Actual solvent loss means the gallons of solvent lost from a source during 12 operating months as determined in accordance with § 63.2853.

Agricultural product means any commercially grown plant or plant product.

Allowable HAP loss means the gallons of HAP that would have been lost from a source if the source was operating at the solvent loss factor for each listed oilseed type. The allowable HAP loss in gallons is determined by multiplying the tons of each oilseed type processed during the previous 12 operating months, as determined in accordance with § 63.2855, by the corresponding oilseed solvent loss factor (gal/ton) listed in Table 1 of § 63.2840, and by the dimensionless constant 0.64, and summing the result for all oilseed types processed.

Area source means any source that does not meet the major source definition.

As received is the basis upon which all oilseed measurements must be determined and refers to the oilseed chemical and physical characteristics as initially received by the source and prior to any oilseed handling and processing.

Batch operation means any process that operates in a manner where the addition of raw material and withdrawal of product do not occur simultaneously. Typically, raw material is added to a process, operational steps occur, and a product is removed from the process. More raw material is then added to the process and the cycle repeats.

Calendar month means 1 month as specified in a calendar.

Compliance date means the date on which monthly compliance recordkeeping begins. For existing sources, recordkeeping typically begins 3 years after the effective date of the subpart. For new and reconstructed sources, recordkeeping typically begins upon initial startup, except as noted in § 63.2834.

Compliance ratio means a ratio of the actual HAP loss in gallons from the previous 12 operating months to an allowable HAP loss in gallons, which is

determined by using oilseed solvent loss factors in Table 1 of § 63.2840, the weighted average volume fraction of HAP in solvent received for the previous 12 operating months, and the tons of each type of listed oilseed processed in the previous 12 operating months. Months during which no listed oilseed is processed, or months during which the § 63.2850(c)(2) or (d)(2) initial startup period or the § 63.2850(e)(2) malfunction period applies, are excluded from this calculation. Equation 2 of § 63.2840 is used to calculate this value. If the value is less than or equal to 1.00, the source is in compliance. If the value is greater than 1.00, the source is deviating from compliance.

Continuous operation means any process that adds raw material and withdraws product simultaneously. Mass, temperature, concentration and other properties typically approach steady-state conditions.

Conventional desolventizer means a desolventizer toaster that operates with indirect and direct-contact steam to remove solvent from the extracted meal. Oilseeds processed in a conventional desolventizer produce crude vegetable oil and crude meal products, such as animal feed.

Corn germ dry milling means a source that processes corn germ that has been separated from the other corn components using a “dry” process of mechanical chafing and air sifting.

Corn germ wet milling means a source that processes corn germ that has been separated from other corn components using a “wet” process of centrifuging a slurry steeped in a dilute sulfurous acid solution.

Exempt period means a period of time during which a source processes agricultural products not defined as listed oilseed.

Extraction solvent means an organic chemical medium used to remove oil from an oilseed. Typically, the extraction solvent is a commercial grade of hexane isomers which have an approximate HAP content of 64 percent by volume.

Hazardous air pollutant (HAP) means any substance or mixture of substances listed as a hazardous air pollutant under section 112(b) of the Clean Air Act, as of April 12, 2001.

Initial startup date means the first calendar day that a new, reconstructed or significantly modified source processes any listed oilseed.

Initial startup period means a period of time from the initial startup date of a new, reconstructed or significantly modified source, for which you choose to operate the source under an initial startup period subject to § 63.2850(c)(2) or (d)(2). During an initial startup period, a source is in compliance with the standards by following the operating and maintenance procedures listed for minimizing HAP emissions in the source’s SSM plan rather than being subject to a HAP emission limit. The initial startup period following initial startup of a new or reconstructed source may not exceed 6 calendar months. The initial startup period following a significant modification may not exceed 3 calendar months. Solvent and oilseed inventory information recorded during the initial startup period is excluded from use in any compliance ratio determinations.

Large cottonseed plant means a vegetable oil production process that processes 120,000 tons or more of cottonseed and other listed oilseed during all normal operating periods in a 12 operating months period used to determine compliance.

Malfunction period means a period of time between the beginning and end of a process malfunction and the time reasonably necessary for a source to correct the malfunction for which you choose to operate the source under a malfunction period subject to § 63.2850(e)(2). This period may include the duration of an unscheduled process shutdown, continued operation during a malfunction, or the subsequent process startup after a shutdown resulting from a malfunction. During a malfunction period, a source complies with the standards by following the operating and maintenance procedures described for minimizing HAP emissions in the source’s SSM plan rather than being subject to a HAP emission limit. Therefore, solvent and oilseed inventory information recorded during a malfunction period is excluded from use in any compliance ratio determinations.

Mechanical extraction means removing vegetable oil from oilseeds using only mechanical devices such as presses or screws that physically force the oil from the oilseed. Mechanical extraction techniques use no organic solvents to remove oil from an oilseed.

Nonoperating period means any period of time in which a source processes no agricultural product. This operating status does not apply during any period in which the source operates under an initial startup period as described in § 63.2850(c)(2) or (d)(2), or a malfunction period, as described in § 63.2850(e)(2).

Normal operating period means any period of time in which a source processes a listed oilseed that is not categorized as an initial startup period as described in § 63.2850(c)(2) or (d)(2), or a malfunction period, as described in § 63.2850(e)(2). At the beginning and ending dates of a normal operating period, solvent and oilseed inventory information is recorded and included in the compliance ratio determination.

Oilseed or listed oilseed means the following agricultural products: corn germ, cottonseed, flax, peanut, rapeseed (for example, canola), safflower, soybean, and sunflower.

Oilseed solvent loss factor means a ratio expressed as gallons of solvent loss per ton of oilseed processed. The solvent loss factors are presented in Table 1 of § 63.2840 and are used to determine the allowable HAP loss.

Operating month means any calendar or accounting month in which a source processes any quantity of listed oilseed, excluding any entire calendar or accounting month in which the source operated under an initial startup period as described in § 63.2850(c)(2) or (d)(2), or a malfunction period as described in § 63.2850(e)(2). An operating month may include time intervals characterized by several types of operating status. However, an operating month must have at least one normal operating period.

Significant modification means the addition of new equipment or the modification of existing equipment that:

- (1) Significantly affects solvent losses from your vegetable oil production process;
- (2) The fixed capital cost of the new components represents a significant

percentage of the fixed capital cost of building a comparable new vegetable oil production process;

(3) The fixed capital cost of the new equipment does not constitute reconstruction as defined in § 63.2; and

(4) Examples of significant modifications include replacement of or major changes to solvent recovery equipment such as extractors, desolventizer-toasters/dryer-coolers, flash desolventizers, and distillation equipment associated with the mineral oil system, and equipment affecting desolventizing efficiency and steady-state operation of your vegetable oil production process such as flaking mills, oilseed heating and conditioning equipment, and cracking mills.

Small cottonseed plant means a vegetable oil production process that processes less than 120,000 tons of cottonseed and other listed oilseed during all normal operating periods in a 12 operating months period used to determine compliance.

Solvent extraction means removing vegetable oil from listed oilseed using an organic solvent in a direct-contact system.

Solvent working capacity means the volume of extraction solvent normally retained in solvent recovery equipment. Examples include components such as the solvent extractor, desolventizer-toaster, solvent storage and working tanks, mineral oil absorption system, condensers, and oil/solvent distillation system.

Specialty desolventizer means a desolventizer that removes excess solvent from soybean meal using vacuum conditions, energy from superheated solvent vapors, or reduced operating conditions (e.g., temperature) as compared to the typical operation of a conventional desolventizer. Soybeans processed in a specialty desolventizer result in high-protein vegetable meal products for human and animal consumption, such as calf milk replacement products and meat extender products.

Vegetable oil production process means the equipment comprising a continuous process for producing crude vegetable oil and meal products, including specialty soybean products, in which oil is removed from listed oilseeds through

direct contact with an organic solvent. Process equipment typically includes the following components: oilseed preparation operations (including conditioning, drying, dehulling, and cracking), solvent extractors, desolventizer-toasters, meal dryers, meal coolers, meal conveyor systems, oil distillation units, solvent evaporators and condensers, solvent recovery system (also referred to as a mineral oil absorption system), vessels storing solvent-laden materials, and crude meal packaging and storage vessels. A vegetable oil production process does not include vegetable oil refining operations (including operations such as bleaching, hydrogenation, and deodorizing) and operations that engage in additional chemical treatment of crude soybean meals produced in specialty desolventizer units (including operations such as soybean isolate production).

APPENDIX A TO PART 63—TEST METHODS

METHOD 301—FIELD VALIDATION OF POLLUTANT MEASUREMENT METHODS FROM VARIOUS WASTE MEDIA

1. Applicability and principle

1.1 *Applicability.* This method, as specified in the applicable subpart, is to be used whenever a source owner or operator (hereafter referred to as an “analyst”) proposes a test method to meet a U.S. Environmental Protection Agency (EPA) requirement in the absence of a validated method. This Method includes procedures for determining and documenting the quality, i.e., systematic error (bias) and random error (precision), of the measured concentrations from an effected source. This method is applicable to various waste media (i.e., exhaust gas, wastewater, sludge, etc.).

1.1.1 If EPA currently recognizes an appropriate test method or considers the analyst’s test method to be satisfactory for a particular source, the Administrator may waive the use of this protocol or may specify a less rigorous validation procedure. A list of validated methods may be obtained by contacting the Emission Measurement Technical Information Center (EMTIC), Mail Drop 19, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711, (919) 541-0200. Procedures for obtaining a waiver are in Section 12.0.

1.1.2 This method includes optional procedures that may be used to expand the applicability of the proposed method. Section 7.0 involves ruggedness testing (Laboratory Evaluation), which demonstrates the sensi-

tivity of the method to various parameters. Section 8.0 involves a procedure for including sample stability in bias and precision for assessing sample recovery and analysis times; Section 9.0 involves a procedure for the determination of the practical limit of quantitation for determining the lower limit of the method. These optional procedures are required for the waiver consideration outlined in Section 12.0.

1.2 *Principle.* The purpose of these procedures is to determine bias and precision of a test method at the level of the applicable standard. The procedures involve (a) introducing known concentrations of an analyte or comparing the test method against a validated test method to determine the method’s bias and (b) collecting multiple or collocated simultaneous samples to determine the method’s precision.

1.2.1 *Bias.* Bias is established by comparing the method’s results against a reference value and may be eliminated by employing a correction factor established from the data obtained during the validation test. An offset bias may be handled accordingly. Methods that have bias correction factors outside 0.7 to 1.3 are unacceptable. Validated method to proposed method comparisons, section 6.2, requires a more restrictive test of central tendency and a lower correction factor allowance of 0.90 to 1.10.

1.2.2 *Precision.* At the minimum, paired sampling systems shall be used to establish precision. The precision of the method at the level of the standard shall not be greater than 50 percent relative standard deviation. For a validated method to proposed method equivalency comparisons, section 6.2, the analyst must demonstrate that the precision of the proposed test method is as precise as the validated method for acceptance.

2. Definitions

2.1 *Negative bias.* Bias resulting when the measured result is less than the “true” value.

2.2 *Paired sampling system.* A sampling system capable of obtaining two replicate samples that were collected as closely as possible in sampling time and sampling location.

2.3 *Positive bias.* Bias resulting when the measured result is greater than the “true” value.

2.4 *Proposed method.* The sampling and analytical methodology selected for field validation using the method described herein.

2.5 *Quadruplet sampling system.* A sampling system capable of obtaining four replicate samples that were collected as closely as possible in sampling time and sampling location.

2.6 *Surrogate compound.* A compound that serves as a model for the types of compounds being analyzed (i.e., similar chemical structure, properties, behavior). The model can be

distinguished by the method from the compounds being analyzed.

3. Reference Material

The reference materials shall be obtained or prepared at the level of the standard. Additional runs with higher and lower reference material concentrations may be made to expand the applicable range of the method, in accordance with the ruggedness test procedures.

3.1 *Exhaust Gas Tests.* The analyst shall obtain a known concentration of the reference material (i.e., analyte of concern) from an independent source such as a specialty gas manufacturer, specialty chemical company, or commercial laboratory. A list of vendors may be obtained from EMTIC (see Section 1.1.1). The analyst should obtain the manufacturer's stability data of the analyte concentration and recommendations for recertification.

3.2 *Other Waste Media Tests.* The analyst shall obtain pure liquid components of the reference materials (i.e., analytes of concern) from an independent manufacturer and dilute them in the same type matrix as the source waste. The pure reference materials shall be certified by the manufacturer as to purity and shelf life. The accuracy of all diluted reference material concentrations shall be verified by comparing their response to independently-prepared materials (independently prepared in this case means prepared from pure components by a different analyst).

3.3 *Surrogate Reference Materials.* The analyst may use surrogate compounds, e.g., for highly toxic or reactive organic compounds, provided the analyst can demonstrate to the Administrator's satisfaction that the surrogate compound behaves as the analyte. A surrogate may be an isotope or one that contains a unique element (e.g., chlorine) that is not present in the source or a derivation of the toxic or reactive compound, if the derivative formation is part of the method's procedure. Laboratory experiments or literature data may be used to show behavioral acceptability.

3.4 *Isotopically Labeled Materials.* Isotope mixtures may contain the isotope and the natural analyte. For best results, the isotope labeled analyte concentration should be more than five times the natural concentration of the analyte.

4. EPA Performance Audit Material

4.1 To assess the method bias independently, the analyst shall use (in addition to the reference material) an EPA performance audit material, if it is available. The analyst may contact EMTIC (see section 1.1.1) to receive a list of currently available EPA audit materials. If the analyte is listed, the analyst should request the audit material at

least 30 days before the validation test. If an EPA audit material is not available, request documentation from the validation report reviewing authority that the audit material is currently not available from EPA. Include this documentation with the field validation report.

4.2 The analyst shall sample and analyze the performance audit sample three times according to the instructions provided with the audit sample. The analyst shall submit the three results with the field validation report. Although no acceptance criteria are set for these performance audit results, the analyst and reviewing authority may use them to assess the relative error of sample recovery, sample preparation, and analytical procedures and then consider the relative error in evaluating the measured emissions.

5. Procedure for Determination of Bias and Precision in the Field

The analyst shall select one of the sampling approaches below to determine the bias and precision of the data. After analyzing the samples, the analyst shall calculate the bias and precision according to the procedure described in section 6.0. When sampling a stationary source, follow the probe placement procedures in section 5.4.

5.1 *Isotopic Spiking.* This approach shall be used only for methods that require mass spectrometry (MS) analysis. Bias and precision are calculated by procedures described in section 6.1.

5.1.1 *Number of Samples and Sampling Runs.* Collect a total of 12 replicate samples by either obtaining six sets of paired samples or three sets of quadruplet samples.

5.1.2 *Spiking Procedure.* Spike all 12 samples with the reference material at the level of the standard. Follow the appropriate spiking procedures listed below for the applicable waste medium.

5.1.2.1 *Exhaust Gas Testing.* The spike shall be introduced as close to the tip of the sampling probe as possible.

5.1.2.1.1 *Gaseous Reference Material with Sorbent or Impinger Sampling Trains.* Sample the reference material (in the laboratory or in the field) at a concentration which is close to the allowable concentration standard for the time required by the method, and then sample the gas stream for an equal amount of time. The time for sampling both the reference material and gas stream should be equal; however, the time should be adjusted to avoid sorbent breakthrough.

5.1.2.1.2 *Gaseous Reference Material with Sample Container (Bag or Canister).* Spike the sample containers after completion of each test run with an amount equal to the allowable concentration standard of the emission point. The final concentration of the reference material shall approximate the level of the emission concentration in the stack. The volume amount of reference material

shall be less than 10 percent of the sample volume.

5.1.2.1.3 *Liquid and Solid Reference Material with Sorbent or Impinger Trains.* Spike the trains with an amount equal to the allowable concentration standard before sampling the stack gas. The spiking should be done in the field; however, it may be done in the laboratory.

5.1.2.1.4 *Liquid and Solid Reference Material with Sample Container (Bag or Canister).* Spike the containers at the completion of each test run with an amount equal to the level of the emission standard.

5.1.2.2 *Other Waste Media.* Spike the 12 replicate samples with the reference material either before or directly after sampling in the field.

5.2 *Comparison Against a Validated Test Method.* Bias and precision are calculated using the procedures described in section 6.2. This approach shall be used when a validated method is available and an alternative method is being proposed.

5.2.1 *Number of Samples and Sampling Runs.* Collect nine sets of replicate samples using a paired sampling system (a total of 18 samples) or four sets of replicate samples using a quadruplet sampling system (a total of 16 samples). In each sample set, the validated test method shall be used to collect and analyze half of the samples.

5.2.2 *Performance Audit Exception.* Conduct the performance audit as required in section 4.0 for the validated test method. Conducting a performance audit on the test method being evaluated is recommended.

5.3 *Analyte Spiking.* This approach shall be used when sections 5.1 and 5.2 are not applicable. Bias and precision are calculated using the procedures described in Section 6.3.

5.3.1 *Number of Samples and Sampling Runs.* Collect a total of 24 samples using the quadruplet sampling system (a total of 6 sets of replicate samples).

5.3.2 In each quadruplet set, spike half of the samples (two out of the four) with the reference material according to the applicable procedure in section 5.1.2.1 or 5.1.2.2.

5.4 *Probe Placement and Arrangement for Stationary Source Stack or Duct Sampling.* The probes shall be placed in the same horizontal plane. For paired sample probes the arrangement should be that the probe tip is 2.5 cm from the outside edge of the other with a pitot tube on the outside of each probe. Other paired arrangements for the pitot tube may be acceptable. For quadruplet sampling probes, the tips should be in a 6.0 cm × 6.0 cm square area measured from the center line of the opening of the probe tip with a single pitot tube in the center or two pitot tubes with their location on either side of the probe tip configuration. An alternative arrangement should be proposed whenever the cross-sectional area of the probe tip configura-

tion is approximately 5 percent of the stack or duct cross-sectional area.

6. Calculations

Data resulting from the procedures specified in section 5.0 shall be treated as follows to determine bias, correction factors, relative standard deviations, precision, and data acceptance.

6.1 *Isotopic Spiking.* Analyze the data for isotopic spiking tests as outlined in sections 6.1.1 through 6.1.6.

6.1.1 Calculate the numerical value of the bias using the results from the analysis of the isotopically spiked field samples and the calculated value of the isotopically labeled spike:

$$B = CS - S_m \quad \text{Eq. 301-1}$$

where:

B=Bias at the spike level.

S_m =Mean of the measured values of the isotopically spiked samples.

CS=Calculated value of the isotopically labeled spike.

6.1.2 Calculate the standard deviation of the S_i values as follows:

$$SD = \sqrt{\frac{\sum (S_i - S_m)^2}{(n-1)}}$$

Eq. 301-2

where:

S_i =Measured value of the isotopically labeled analyte in the i th field sample,

n =Number of isotopically spiked samples, 12.

6.1.3. Calculate the standard deviation of the mean (SDM) as follows:

$$SDM = \frac{SD}{\sqrt{n}}$$

Eq. 301-3

6.1.4 Test the bias for statistical significance by calculating the t-statistic,

$$t = \frac{|B|}{SDM}$$

Eq. 301-4

and compare it with the critical value of the two-sided t-distribution at the 95-percent confidence level and $n-1$ degrees of freedom. This critical value is 2.201 for the eleven degrees of freedom when the procedure specified in section 5.1.2 is followed. If the calculated t-value is greater than the critical value the bias is statistically significant and the analyst should proceed to evaluate the correction factor.

6.1.5 *Calculation of a Correction Factor.* If the t-test does not show that the bias is statistically significant, use all analytical results without correction and proceed to the precision evaluation. If the method's bias is statistically significant, calculate the correction factor, CF, using the following equation:

$$CF = \frac{1}{1 + \frac{B}{CS}}$$

Eq. 301-5

If the CF is outside the range of 0.70 to 1.30, the data and method are considered unacceptable. For correction factors within the range, multiply all analytical results by the CF to obtain the final values.

6.1.6 *Calculation of the Relative Standard Deviation (Precision).* Calculate the relative standard deviation as follows:

$$RSD = \left(\frac{SD}{S_m} \right) \times 100$$

Eq. 301-6

where S_m is the measured mean of the isotopically labeled spiked samples.

6.2 *Comparison with Validated Method.* Analyze the data for comparison with a validated method as outlined in sections 6.2.1 or 6.2.2, as appropriate. Conduct these procedures in order to determine if a proposed method produces results equivalent to a validated method. Make all necessary bias corrections for the validated method, as appropriate. If the proposed method fails either test, the method results are unacceptable, and conclude that the proposed method is not as precise or accurate as the validated method. For highly variable sources, additional precision checks may be necessary. The analyst should consult with the Administrator if a highly variable source is suspected.

6.2.1 *Paired Sampling Systems.*

6.2.1.1. *Precision.* Determine the acceptance of the proposed method's variance with respect to the variability of the validated method results. If a significant difference is determined, the proposed method and the results are rejected. Proposed methods demonstrating F-values equal to or less than the critical value have acceptable precision.

6.2.1.2 Calculate the variance of the proposed method, S_p^2 , and the variance of the validated method, S_v^2 , using the following equation:

$$S_{(pov)}^2 = SD^2 \quad \text{Eq. 301-7}$$

where:

SD_v = Standard deviation provided with the validated method,

SD_p = Standard deviation of the proposed method calculated using Equation 301-9a.

6.2.1.3 *The F-test.* Determine if the variance of the proposed method is significantly different from that of the validated method by calculating the F-value using the following equation:

$$F = \frac{S_p^2}{S_v^2}$$

Eq. 301-8

Compare the experimental F value with the critical value of F. The critical value is 1.0 when the procedure specified in section 5.2.1 for paired trains is followed. If the calculated F is greater than the critical value, the difference in precision is significant and the data and proposed method are unacceptable.

6.2.1.4 *Bias Analysis.* Test the bias for statistical significance by calculating the t-statistic and determine if the mean of the differences between the proposed method and the validated method is significant at the 80-percent confidence level. This procedure requires the standard deviation of the validated method, SD_v , to be known. Employ the value furnished with the method. If the standard deviation of the validated method is not available, the paired replicate sampling procedure may not be used. Determine the mean of the paired sample differences, d_m , and the standard deviation, SD_d , of the differences, d_i 's, using Equation 301-2 where: d_i replaces S_i , d_m replaces S_m . Calculate the standard deviation of the proposed method, SD_p , as follows:

$$SD_p = SD_d - SD_v \quad \text{Eq. 301-9a}$$

(If $SD_v > SD_d$, let $SD = SD_d/1.414$).

Calculate the value of the t-statistic using the following equation:

$$t = \frac{d_m}{\left(\frac{SD_p}{\sqrt{n}} \right)}$$

Eq. 301-9

where n is the total number of paired samples. For the procedure in section 5.2.1, n equals nine. Compare the calculated t-statistic with the corresponding value from the table of the t-statistic. When nine runs are conducted, as specified in section 5.2.1, the critical value of the t-statistic is 1.397 for eight degrees of freedom. If the calculated t-value is greater than the critical value the bias is statistically significant and the analyst should proceed to evaluate the correction factor.

6.2.1.5 *Calculation of a Correction Factor.* If the statistical test cited above does not show a significant bias with respect to the reference method, assume that the proposed

method is unbiased and use all analytical results without correction. If the method's bias is statistically significant, calculate the correction factor, CF, as follows:

$$CF = \frac{1}{1 + \frac{d_m}{V_m}}$$

Eq. 301-10

where V_m is the mean of the validated method's values.

Multiply all analytical results by CF to obtain the final values. The method results, and the method, are unacceptable if the correction factor is outside the range of 0.9 to 1.10.

6.2.2 *Quadruplet Replicate Sampling Systems.*

6.2.2.1 *Precision.* Determine the acceptance of the proposed method's variance with respect to the variability of the validated method results. If a significant difference is determined the proposed method and the results are rejected.

6.2.2.2 Calculate the variance of the proposed method, S_p^2 , using the following equation:

$$S^2 = \frac{\sum d_i^2}{2n}$$

Eq. 301-11

where the d_i 's are the differences between the validated method values and the proposed method values.

6.2.2.3 *The F-test.* Determine if the variance of the proposed method is more variable than that of the validated method by calculating the F-value using Equation 301-8. Compare the experimental F value with the critical value of F. The critical value is 1.0 when the procedure specified in section 5.2.2 for quadruplet trains is followed. The calculated F should be less than or equal to the critical value. If the difference in precision is significant the results and the proposed method are unacceptable.

6.2.2.4 *Bias Analysis.* Test the bias for statistical significance at the 80 percent confidence level by calculating the t-statistic. Determine the bias (mean of the differences between the proposed method and the validated method, d_m) and the standard deviation, SD_d , of the differences. Calculate the standard deviation of the differences, SD_d , using Equation 301-2 and substituting d_i for S_i . The following equation is used to calculate d_i :

$$d_i = \frac{(V_{1i} + V_{2i})}{2} - \frac{(P_{1i} + P_{2i})}{2}$$

Eq. 301-12

and: V_{1i} =First measured value of the validated method in the i th test sample.

P_{1i} =First measured value of the proposed method in the i th test sample.

Calculate the t-statistic using Equation 301-9 where n is the total number of test sample differences (d_i). For the procedure in section 5.2.2, n equals four. Compare the calculated t-statistic with the corresponding value from the table of the t-statistic and determine if the mean is significant at the 80-percent confidence level. When four runs are conducted, as specified in section 5.2.2, the critical value of the t-statistic is 1.638 for three degrees of freedom. If the calculated t-value is greater than the critical value the bias is statistically significant and the analyst should proceed to evaluate the correction factor.

6.2.2.5 *Correction Factor Calculation.* If the method's bias is statistically significant, calculate the correction factor, CF, using Equation 301-10. Multiply all analytical results by CF to obtain the final values. The method results, and the method, are unacceptable if the correction factor is outside the range of 0.9 to 1.10.

6.3 *Analyte Spiking.* Analyze the data for analyte spike testing as outlined in Sections 6.3.1 through 6.3.3.

6.3.1 *Precision.*

6.3.1.1 *Spiked Samples.* Calculate the difference, d_i , between the pairs of the spiked proposed method measurements for each replicate sample set. Determine the standard deviation (SD_s) of the spiked values using the following equation:

$$SD_s = \sqrt{\frac{\sum d_i^2}{2n}}$$

Eq. 301-13

where: n = Number of runs.

Calculate the relative standard deviation of the proposed spiked method using Equation 301-6 where S_m is the measured mean of the analyte spiked samples. The proposed method is unacceptable if the RSD is greater than 50 percent.

6.3.1.2 *Unspiked Samples.* Calculate the standard deviation of the unspiked values using Equation 301-13 and the relative standard deviation of the proposed unspiked method using Equation 301-6 where S_m is the measured mean of the analyte spiked samples. The RSD must be less than 50 percent.

6.3.2 *Bias*. Calculate the numerical value of the bias using the results from the analysis of the spiked field samples, the unspiked field samples, and the calculated value of the spike:

$$B = S_m - M_m - CS$$

Eq. 301-14

where: B = Bias at the spike level.

S_m = Mean of the spiked samples.

M_m = Mean of the unspiked samples.

CS = Calculated value of the spiked level.

6.3.2.1 Calculate the standard deviation of the mean using the following equation where SD_s and SD_u are the standard deviations of the spiked and unspiked sample values respectively as calculated using Equation 301-13.

$$SD = \sqrt{SD_s^2 + SD_u^2}$$

Eq. 301-15

6.3.2.2 Test the bias for statistical significance by calculating the t-statistic using Equation 301-4 and comparing it with the critical value of the two-sided t-distribution at the 95-percent confidence level and n-1 degrees of freedom. This critical value is 2.201 for the eleven degrees of freedom.

6.3.3 *Calculation of a Correction Factor*. If the t-test shows that the bias is not statistically significant, use all analytical results without correction. If the method's bias is statistically significant, calculate the correction factor using Equation 301-5. Multiply all analytical results by CF to obtain the final values.

7. Ruggedness Testing (Optional)

7.1 *Laboratory Evaluation*.

7.1.1 Ruggedness testing is a useful and cost-effective laboratory study to determine the sensitivity of a method to certain parameters such as sample collection rate, interferant concentration, collecting medium temperature, or sample recovery temperature. This Section generally discusses the principle of the ruggedness test. A more detailed description is presented in citation 10 of Section 13.0.

7.1.2 In a ruggedness test, several variables are changed simultaneously rather than one variable at a time. This reduces the number of experiments required to evaluate the effect of a variable. For example, the effect of seven variables can be determined in eight experiments rather than 128 (W.J. Youden, *Statistical Manual of the Association of Official Analytical Chemists*, Association of Official Analytical Chemists, Washington, DC, 1975, pp. 33-36).

7.1.3 Data from ruggedness tests are helpful in extending the applicability of a test method to different source concentrations or source categories.

8. Procedure for Including Sample Stability in Bias and Precision Evaluations

8.1 *Sample Stability*.

8.1.1 The test method being evaluated must include procedures for sample storage and the time within which the collected samples shall be analyzed.

8.1.2 This section identifies the procedures for including the effect of storage time in bias and precision evaluations. The evaluation may be deleted if the test method specifies a time for sample storage.

8.2 *Stability Test Design*. The following procedures shall be conducted to identify the effect of storage times on analyte samples. Store the samples according to the procedure specified in the test method. When using the analyte spiking procedures (section 5.3), the study should include equal numbers of spiked and unspiked samples.

8.2.1 *Stack Emission Testing*.

8.2.1.1 For sample container (bag or canister) and impinger sampling systems, sections 5.1 and 5.3, analyze six of the samples at the minimum storage time. Then analyze the same six samples at the maximum storage time.

8.2.1.2 For sorbent and impinger sampling systems, sections 5.1 and 5.3, that require extraction or digestion, extract or digest six of the samples at the minimum storage time and extract or digest six other samples at the maximum storage time. Analyze an aliquot of the first six extracts (digestates) at both the minimum and maximum storage times. This will provide some freedom to analyze extract storage impacts.

8.2.1.3 For sorbent sampling systems, sections 5.1 and 5.3, that require thermal desorption, analyze six samples at the minimum storage time. Analyze another set of six samples at the maximum storage time.

8.2.1.4 For systems set up in accordance with section 5.2, the number of samples analyzed at the minimum and maximum storage times shall be half those collected (8 or 9). The procedures for samples requiring extraction or digestion should parallel those in section 8.2.1.

8.2.2 *Other Waste Media Testing*. Analyze half of the replicate samples at the minimum storage time and the other half at the maximum storage time in order to identify the effect of storage times on analyte samples.

9. Procedure for Determination of Practical Limit of Quantitation (Optional)

9.1 *Practical Limit of Quantitation*.

9.1.1 The practical limit of quantitation (PLQ) is the lowest level above which quantitative results may be obtained with an acceptable degree of confidence. For this protocol, the PLQ is defined as 10 times the standard deviation, s_o , at the blank level. This PLQ corresponds to an uncertainty of

±30 percent at the 99-percent confidence level.

9.1.2 The PLQ will be used to establish the lower limit of the test method.

9.2 *Procedure I for Estimating s_o* . This procedure is acceptable if the estimated PLQ is no more than twice the calculated PLQ. If the PLQ is greater than twice the calculated PLQ use Procedure II.

9.2.1 Estimate the PLQ and prepare a test standard at this level. The test standard could consist of a dilution of the reference material described in section 3.0.

9.2.2 Using the normal sampling and analytical procedures for the method, sample and analyze this standard at least seven times in the laboratory.

9.2.3 Calculate the standard deviation, s_o , of the measured values.

9.2.4 Calculate the PLQ as 10 times s_o .

9.3 *Procedure II for Estimating s_o* . This procedure is to be used if the estimated PLQ is more than twice the calculated PLQ.

9.3.1 Prepare two additional standards at concentration levels lower than the standard used in Procedure I.

9.3.2 Sample and analyze each of these standards at least seven times.

9.3.3 Calculate the standard deviation for each concentration level.

9.3.4 Plot the standard deviations of the three test standards as a function of the standard concentrations.

9.3.5 Draw a best-fit straight line through the data points and extrapolate to zero concentration. The standard deviation at zero concentration is S_o .

9.3.6 Calculate the PLQ as 10 times S_o .

10.0 Field Validation Report Requirements

The field validation report shall include a discussion of the regulatory objectives for the testing which describe the reasons for the test, applicable emission limits, and a description of the source. In addition, validation results shall include:

10.1 Summary of the results and calculations shown in section 6.0.

10.2 Reference material certification and value(s).

10.3 Performance audit results or letter from the reviewing authority stating the audit material is currently not available.

10.4 Laboratory demonstration of the quality of the spiking system.

10.5 Discussion of laboratory evaluations.

10.6 Discussion of field sampling.

10.7 Discussion of sample preparations and analysis.

10.8 Storage times of samples (and extracts, if applicable).

10.9 Reasons for eliminating any results.

11. Followup Testing

The correction factor calculated in section 6.0 shall be used to adjust the sample con-

centrations in all followup tests conducted at the same source. These tests shall consist of at least three replicate samples, and the average shall be used to determine the pollutant concentration. The number of samples to be collected and analyzed shall be as follows, depending on the validated method precision level:

11.1 Validated relative standard deviation (RSD) $\leq \pm 15$ Percent. Three replicate samples.

11.2 Validated RSD $\leq \pm 30$ Percent. Six replicate samples.

11.3 Validated RSD $\leq \pm 50$ Percent. Nine replicate samples.

11.4 Equivalent method. Three replicate samples.

12. Procedure for Obtaining a Waiver

12.1 *Waivers*. These procedures may be waived or a less rigorous protocol may be granted for site-specific applications. The following are three example situations for which a waiver may be considered.

12.1.1 *"Similar" Sources*. If the test method has been validated previously at a "similar" source, the procedures may be waived provided the requester can demonstrate to the satisfaction of the Administrator that the sources are "similar." The methods's applicability to the "similar" source may be demonstrated by conducting a ruggedness test as described in section 6.0.

12.1.2 *"Documented" Methods*. In some cases, bias and precision may have been documented through laboratory tests or protocols different from this method. If the analyst can demonstrate to the satisfaction of the Administrator that the bias and precision apply to a particular application, the Administrator may waive these procedures or parts of the procedures.

12.1.3 *"Conditional" Test Methods*. When the method has been demonstrated to be valid at several sources, the analyst may seek a "conditional" method designation from the Administrator. "Conditional" method status provides an automatic waiver from the procedures provided the test method is used within the stated applicability.

12.2 *Application for Waiver*. In general, the requester shall provide a thorough description of the test method, the intended application, and results of any validation or other supporting documents. Because of the many potential situations in which the Administrator may grant a waiver, it is neither possible nor desirable to prescribe the exact criteria for a waiver. At a minimum, the requester is responsible for providing the following.

12.2.1 A clearly written test method, preferably in the format of 40 CFR part 60, appendix A Test Methods. The method must include an applicability statement, concentration range, precision, bias (accuracy), and time in which samples must be analyzed.

12.2.2.2 Summaries (see section 10.0) of previous validation tests or other supporting documents. If a different procedure from that described in this method was used, the requester shall provide appropriate documents substantiating (to the satisfaction of the Administrator) the bias and precision values.

12.2.2.3 Results of testing conducted with respect to sections 7.0, 8.0, and 9.0.

12.2.3 Discussion of the applicability statement and arguments for approval of the waiver. This discussion should address as applicable the following: Applicable regulation, emission standards, effluent characteristics, and process operations.

12.3 *Requests for Waiver.* Each request shall be in writing and signed by the analyst. Submit requests to the Director, OAQPS, Technical Support Division, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

13. Bibliography

1. Albritton, J.R., G.B. Howe, S.B. Tompkins, R.K.M. Jayanty, and C.E. Decker, 1989. Stability of Parts-Per-Million Organic Cylinder Gases and Results of Source Test Analysis Audits, Status Report No. 11. Environmental Protection Agency Contract 68-02-4125. Research Triangle Institute, Research Triangle Park, NC. September.
2. DeWees, W.G., P.M. Grohse, K.K. Luk, and F.E. Butler. 1989. Laboratory and Field Evaluation of a Methodology for Speciating Nickel Emissions from Stationary Sources. EPA Contract 68-02-4442. Prepared for Atmospheric Research and Environmental Assessment Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711. January.
3. Keith, L.H., W. Crummer, J. Deegan Jr., R.A. Libby, J.K. Taylor, and G. Wentler. 1983. Principles of Environmental Analysis. American Chemical Society, Washington, DC.
4. Maxwell, E.A. 1974. Estimating variances from one or two measurements on each sample. *Amer. Statistician* 28:96-97.
5. Midgett, M.R. 1977. How EPA Validates NSPS Methodology. *Environ. Sci. & Technol.* 11(7):655-659.
6. Mitchell, W.J., and M.R. Midgett. 1976. Means to evaluate performance of stationary source test methods. *Environ. Sci. & Technol.* 10:85-88.
7. Plackett, R.L., and J.P. Burman. 1946. The design of optimum multifactorial experiments. *Biometrika*, 33:305.
8. Taylor, J.K. 1987. Quality Assurance of Chemical Measurements. Lewis Publishers, Inc., pp. 79-81.
9. U.S. Environmental Protection Agency. 1978. Quality Assurance Handbook for Air Pollution Measurement Systems: Volume III. Stationary Source Specific Methods. Publication No. EPA-600/4-77-027b. Office of Research and Development Publications, 26 West St. Clair St., Cincinnati, OH 45268.
10. U.S. Environmental Protection Agency. 1981. A Procedure for Establishing Traceability of Gas Mixtures to Certain National Bureau of Standards Standard Reference Materials. Publication No. EPA-600/7-81-010. Available from the U.S. EPA, Quality Assurance Division (MD-77), Research Triangle Park, NC 27711.
11. U.S. Environmental Protection Agency. 1991. Protocol for The Field Validation of Emission Concentrations From Stationary Sources. Publication No. 450/4-90-015. Available from the U.S. EPA, Emission Measurement Technical Information Center, Technical Support Division (MD-14), Research Triangle Park, NC 27711.
12. Youdon, W.J. Statistical techniques for collaborative tests. In: Statistical Manual of the Association of Official Analytical Chemists, Association of Official Analytical Chemists, Washington, DC, 1975, pp. 33-36.

METHOD 303—DETERMINATION OF VISIBLE EMISSIONS FROM BY-PRODUCT COKE OVEN BATTERIES

NOTE: This method is not inclusive with respect to observer certification. Some material is incorporated by reference from other methods in appendix A to 40 CFR part 60. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of Method 9.

1.0 Scope and Application

1.1 Applicability. This method is applicable for the determination of visible emissions (VE) from the following by-product coke oven battery sources: charging systems during charging; doors, topside port lids, and offtake systems on operating coke ovens; and collecting mains. This method is also applicable for qualifying observers for visually determining the presence of VE.

2.0 Summary of Method

2.1 A certified observer visually determines the VE from coke oven battery sources. Certification procedures are presented. This method does not require that opacity of emissions be determined or that magnitude be differentiated.

3.0 Definitions

3.1 *Bench* means the platform structure in front of the oven doors.

3.2 *By-product Coke Oven Battery* means a source consisting of a group of ovens connected by common walls, where coal undergoes destructive distillation under positive pressure to produce coke and coke oven gas, from which by-products are recovered.

3.3 *Charge or charging period* means the period of time that commences when coal begins to flow into an oven through a topside port and ends when the last charging port is recapped.

3.4 *Charging system* means an apparatus used to charge coal to a coke oven (e.g., a larry car for wet coal charging systems).

3.5 *Coke oven door* means each end enclosure on the push side and the coking side of an oven. The chuck, or leveler-bar, door is considered part of the push side door. The coke oven door area includes the entire area on the vertical face of a coke oven between the bench and the top of the battery between two adjacent buck stays.

3.6 *Coke side* means the side of a battery from which the coke is discharged from ovens at the end of the coking cycle.

3.7 *Collecting main* means any apparatus that is connected to one or more offtake systems and that provides a passage for conveying gases under positive pressure from the by-product coke oven battery to the by-product recovery system.

3.8 *Consecutive charges* means charges observed successively, excluding any charge during which the observer's view of the charging system or topside ports is obscured.

3.9 *Damper-off* means to close off the gas passage between the coke oven and the collecting main, with no flow of raw coke oven gas from the collecting main into the oven or into the oven's offtake system(s).

3.10 *Decarbonization period* means the period of time for combusting oven carbon that commences when the oven lids are removed from an empty oven or when standpipe caps of an oven are opened. The period ends with the initiation of the next charging period for that oven.

3.11 *Larry car* means an apparatus used to charge coal to a coke oven with a wet coal charging system.

3.12 *Log average* means logarithmic average as calculated in Section 12.4.

3.13 *Offtake system* means any individual oven apparatus that is stationary and provides a passage for gases from an oven to a coke oven battery collecting main or to another oven. Offtake system components include the standpipe and standpipe caps, goosenecks, stationary jumper pipes, mini-standpipes, and standpipe and gooseneck connections.

3.14 *Operating oven* means any oven not out of operation for rebuild or maintenance work extensive enough to require the oven to be skipped in the charging sequence.

3.15 *Oven* means a chamber in the coke oven battery in which coal undergoes destructive distillation to produce coke.

3.16 *Push side* means the side of the battery from which the coke is pushed from ovens at the end of the coking cycle.

3.17 *Run* means the observation of visible emissions from topside port lids, offtake systems, coke oven doors, or the charging of a single oven in accordance with this method.

3.18 *Shed* means an enclosure that covers the side of the coke oven battery, captures emissions from pushing operations and from leaking coke oven doors on the coke side or push side of the coke oven battery, and routes the emissions to a control device or system.

3.19 *Standpipe cap* means An apparatus used to cover the opening in the gooseneck of an offtake system.

3.20 *Topside port lid* means a cover, removed during charging or decarbonizing, that is placed over the opening through which coal can be charged into the oven of a by-product coke oven battery.

3.21 *Traverse time* means accumulated time for a traverse as measured by a stopwatch. Traverse time includes time to stop and write down oven numbers but excludes time waiting for obstructions of view to clear or for time to walk around obstacles.

3.22 *Visible Emissions or VE* means any emission seen by the unaided (except for corrective lenses) eye, excluding steam or condensing water.

4.0 Interferences [Reserved]

5.0 Safety

5.1 *Disclaimer.* This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 *Safety Training.* Because coke oven batteries have hazardous environments, the training materials and the field training (Section 10.0) shall cover the precautions required by the company to address health and safety hazards. Special emphasis shall be given to the Occupational Safety and Health Administration (OSHA) regulations pertaining to exposure of coke oven workers (see Reference 3 in Section 16.0). In general, the regulation requires that special fire-retardant clothing and respirators be worn in certain restricted areas of the coke oven battery. The OSHA regulation also prohibits certain activities, such as chewing gum, smoking, and eating in these areas.

6.0 *Equipment and Supplies [Reserved]*7.0 *Reagents and Standards [Reserved]*8.0 *Sample Collection, Preservation, Transport, and Storage [Reserved]*9.0 *Quality Control [Reserved]*10.0 *Calibration and Standardization*

Observer certification and training requirements are as follows:

10.1 Certification Procedures. This method requires only the determination of whether VE occur and does not require the determination of opacity levels; therefore, observer certification according to Method 9 in appendix A to part 60 of this chapter is not required to obtain certification under this method. However, in order to receive Method 303 observer certification, the first-time observer (trainee) shall have attended the lecture portion of the Method 9 certification course. In addition, the trainee shall successfully complete the Method 303 training course, satisfy the field observation requirement, and demonstrate adequate performance and sufficient knowledge of Method 303. The Method 303 training course shall be conducted by or under the sanction of the EPA and shall consist of classroom instruction and field observations, and a proficiency test.

10.1.1 The classroom instruction shall familiarize the trainees with Method 303 through lecture, written training materials, and a Method 303 demonstration video. A successful completion of the classroom portion of the Method 303 training course shall be demonstrated by a perfect score on a written test. If the trainee fails to answer all of the questions correctly, the trainee may review the appropriate portion of the training materials and retake the test.

10.1.2 The field observations shall be a minimum of 12 hours and shall be completed before attending the Method 303 certification course. Trainees shall observe the operation of a coke oven battery as it pertains to Method 303, including topside operations, and shall also practice conducting Method 303 or similar methods. During the field observations, trainees unfamiliar with coke battery operations shall receive instruction from an experienced coke oven observer familiar with Method 303 or similar methods and with the operation of coke batteries. The trainee must verify completion of at least 12 hours of field observation prior to attending the Method 303 certification course.

10.1.3 All trainees must demonstrate proficiency in the application of Method 303 to a panel of three certified Method 303 observers, including an ability to differentiate coke oven emissions from condensing water vapor and smoldering coal. Each panel member shall have at least 120 days experience in

reading visible emissions from coke ovens. The visible emissions inspections that will satisfy the experience requirement must be inspections of coke oven battery fugitive emissions from the emission points subject to emission standards under subpart L of this part (*i.e.*, coke oven doors, topside port lids, offtake system(s), and charging operations), using either Method 303 or predecessor State or local test methods. A "day's experience" for a particular inspection is a day on which one complete inspection was performed for that emission point under Method 303 or a predecessor State or local method. A "day's experience" does not mean 8 or 10 hours performing inspections, or any particular time expressed in minutes or hours that may have been spent performing them. Thus, it would be possible for an individual to qualify as a Method 303 panel member for some emission points, but not others (*e.g.*, an individual might satisfy the experience requirement for coke oven doors, but not topside port lids). Until November 15, 1994, the EPA may waive the certification requirement (but not the experience requirement) for panel members. The composition of the panel shall be approved by the EPA. The panel shall observe the trainee in a series of training runs and a series of certification runs. There shall be a minimum of 1 training run for doors, topside port lids, and offtake systems, and a minimum of 5 training runs (*i.e.*, 5 charges) for charging. During training runs, the panel can advise the trainee on proper procedures. There shall be a minimum of 3 certification runs for doors, topside port lids, and offtake systems, and a minimum of 15 certification runs for charging (*i.e.*, 15 charges). The certification runs shall be unassisted. Following the certification test runs, the panel shall approve or disapprove certification based on the trainee's performance during the certification runs. To obtain certification, the trainee shall demonstrate to the satisfaction of the panel a high degree of proficiency in performing Method 303. To aid in evaluating the trainee's performance, a checklist, provided by the EPA, will be used by the panel members.

10.2 Observer Certification/Recertification. The coke oven observer certification is valid for 1 year from date of issue. The observer shall recertify annually by viewing the training video and answering all of the questions on the certification test correctly. Every 3 years, an observer shall be required to pass the proficiency test in Section 10.1.3 in order to be certified.

10.3 The EPA (or applicable enforcement agency) shall maintain records reflecting a certified observer's successful completion of the proficiency test, which shall include the completed proficiency test checklists for the certification runs.

10.4 An owner or operator of a coke oven battery subject to subpart L of this part may observe a training and certification program under this section.

11.0 Procedure

11.1 Procedure for Determining VE from Charging Systems During Charging.

11.1.1 Number of Oven Charges. Refer to §63.309(c)(1) of this part for the number of oven charges to observe. The observer shall observe consecutive charges. Charges that are nonconsecutive can only be observed when necessary to replace observations terminated prior to the completion of a charge because of visual interferences. (See Section 11.1.5).

11.1.2 Data Records. Record all the information requested at the top of the charging system inspection sheet (Figure 303-1). For each charge, record the identification number of the oven being charged, the approximate beginning time of the charge, and the identification of the larry car used for the charge.

11.1.3 Observer Position. Stand in an area or move to positions on the topside of the coke oven battery with an unobstructed view of the entire charging system. For wet coal charging systems or non-pipeline coal charging systems, the observer should have an unobstructed view of the emission points of the charging system, including larry car hoppers, drop sleeves, and the topside ports of the oven being charged. Some charging systems are configured so that all emission points can only be seen from a distance of five ovens. For other batteries, distances of 8 to 12 ovens are adequate.

11.1.4 Observation. The charging period begins when coal begins to flow into the oven and ends when the last charging port is recapped. During the charging period, observe all of the potential sources of VE from the entire charging system. For wet coal charging systems or non-pipeline coal charging systems, sources of VE typically include the larry car hoppers, drop sleeves, slide gates, and topside ports on the oven being charged. Any VE from an open standpipe cap on the oven being charged is included as charging VE.

11.1.4.1 Using an accumulative-type stopwatch with unit divisions of at least 0.5 seconds, determine the total time VE are observed as follows. Upon observing any VE emerging from any part of the charging system, start the stopwatch. Stop the watch when VE are no longer observed emerging, and restart the watch when VE reemerges.

11.1.4.2 When VE occur simultaneously from several points during a charge, consider the sources as one. Time overlapping VE as continuous VE. Time single puffs of VE only for the time it takes for the puff to emerge from the charging system. Continue to time VE in this manner for the entire charging

period. Record the accumulated time to the nearest 0.5 second under "Visible emissions, seconds" on Figure 303-1.

11.1.5 Visual Interference. If fugitive VE from other sources at the coke oven battery site (*e.g.*, door leaks or condensing water vapor from the coke oven wharf) prevent a clear view of the charging system during a charge, stop the stopwatch and make an appropriate notation under "Comments" on Figure 303-1. Label the observation an observation of an incomplete charge, and observe another charge to fulfill the requirements of Section 11.1.1.

11.1.6 VE Exemptions. Do not time the following VE:

11.1.6.1 The VE from burning or smoldering coal spilled on top of the oven, topside port lid, or larry car surfaces;

NOTE: The VE from smoldering coal are generally white or gray. These VE generally have a plume of less than 1 meter long. If the observer cannot safely and with reasonable confidence determine that VE are from charging, do not count them as charging emissions.

11.1.6.2 The VE from the coke oven doors or from the leveler bar; or

11.1.6.3 The VE that drift from the top of a larry car hopper if the emissions had already been timed as VE from the drop sleeve.

NOTE: When the slide gate on a larry car hopper closes after the coal has been added to the oven, the seal may not be airtight. On occasions, a puff of smoke observed at the drop sleeves is forced past the slide gate up into the larry car hopper and may drift from the top; time these VE either at the drop sleeves or the hopper. If the larry car hopper does not have a slide gate or the slide gate is left open or partially closed, VE may quickly pass through the larry car hopper without being observed at the drop sleeves and will appear as a strong surge of smoke; time these as charging VE.

11.1.7 Total Time Record. Record the total time that VE were observed for each charging operation in the appropriate column on the charging system inspection sheet.

11.1.8 Determination of Validity of a Set of Observations. Five charging observations (runs) obtained in accordance with this method shall be considered a valid set of observations for that day. No observation of an incomplete charge shall be included in a daily set of observations that is lower than the lowest reading for a complete charge. If both complete and incomplete charges have been observed, the daily set of observations shall include the five highest values observed. Four or three charging observations (runs) obtained in accordance with this method shall be considered a valid set of charging observations only where it is not possible to obtain five charging observations, because visual interferences (see Section

11.1.5) or inclement weather prevent a clear view of the charging system during charging. However, observations from three or four charges that satisfy these requirements shall not be considered a valid set of charging observations if use of such set of observations in a calculation under Section 12.4 would cause the value of A to be less than 145.

11.1.9 Log Average. For each day on which a valid daily set of observations is obtained, calculate the daily 30-day rolling log average of seconds of visible emissions from the charging operation for each battery using these data and the 29 previous valid daily sets of observations, in accordance with Section 12.4.

11.2. Procedure for Determining VE from Coke Oven Door Areas. The intent of this procedure is to determine VE from coke oven door areas by carefully observing the door area from a standard distance while walking at a normal pace.

11.2.1 Number of Runs. Refer to §63.309(c)(1) of this part for the appropriate number of runs.

11.2.2 Battery Traverse. To conduct a battery traverse, walk the length of the battery on the outside of the pusher machine and quench car tracks at a steady, normal walking pace, pausing to make appropriate entries on the door area inspection sheet (Figure 303-2). A single test run consists of two timed traverses, one for the coke side and one for the push side. The walking pace shall be such that the duration of the traverse does not exceed an average of 4 seconds per oven door, excluding time spent moving around stationary obstructions or waiting for other obstructions to move from positions blocking the view of a series of doors. Extra time is allowed for each leak (a maximum of 10 additional seconds for each leaking door) for the observer to make the proper notation. A walking pace of 3 seconds per oven door has been found to be typical. Record the actual traverse time with a stopwatch.

11.2.2.1 Include in the traverse time only the time spent observing the doors and recording door leaks. To measure actual traverse time, use an accumulative-type stopwatch with unit divisions of 0.5 seconds or less. Exclude interruptions to the traverse and time required for the observer to move to positions where the view of the battery is unobstructed, or for obstructions, such as the door machine, to move from positions blocking the view of a series of doors.

11.2.2.2 Various situations may arise that will prevent the observer from viewing a door or a series of doors. Prior to the door inspection, the owner or operator may elect to temporarily suspend charging operations for the duration of the inspection, so that all of the doors can be viewed by the observer. The observer has two options for dealing with obstructions to view: (a) Stop the stopwatch

and wait for the equipment to move or the fugitive emissions to dissipate before completing the traverse; or (b) stop the stopwatch, skip the affected ovens, and move to an unobstructed position to continue the traverse. Restart the stopwatch and continue the traverse. After the completion of the traverse, if the equipment has moved or the fugitive emissions have dissipated, inspect the affected doors. If the equipment is still preventing the observer from viewing the doors, then the affected doors may be counted as not observed. If option (b) is used because of doors blocked by machines during charging operations, then, of the affected doors, exclude the door from the most recently charged oven from the inspection. Record the oven numbers and make an appropriate notation under "Comments" on the door area inspection sheet (Figure 303-2).

11.2.2.3 When batteries have sheds to control emissions, conduct the inspection from outside the shed unless the doors cannot be adequately viewed. In this case, conduct the inspection from the bench. Be aware of special safety considerations pertinent to walking on the bench and follow the instructions of company personnel on the required equipment and procedures. If possible, conduct the bench traverse whenever the bench is clear of the door machine and hot coke guide.

11.2.3 Observations. Record all the information requested at the top of the door area inspection sheet (Figure 303-2), including the number of non-operating ovens. Record the clock time at the start of the traverse on each side of the battery. Record which side is being inspected (*i.e.*, coke side or push side). Other information may be recorded at the discretion of the observer, such as the location of the leak (*e.g.*, top of the door, chuck door, etc.), the reason for any interruption of the traverse, or the position of the sun relative to the battery and sky conditions (*e.g.*, overcast, partly sunny, etc.).

11.2.3.1 Begin the test run by starting the stopwatch and traversing either the coke side or the push side of the battery. After completing one side, stop the watch. Complete this procedure on the other side. If inspecting more than one battery, the observer may view the push sides and the coke sides sequentially.

11.2.3.2 During the traverse, look around the entire perimeter of each oven door. The door is considered leaking if VE are detected in the coke oven door area. The coke oven door area includes the entire area on the vertical face of a coke oven between the bench and the top of the battery between two adjacent buck stays (*e.g.*, the oven door, chuck door, between the masonry brick, buck stay or jamb, or other sources). Record the oven number and make the appropriate notation on the door area inspection sheet (Figure 303-2).

NOTE: Multiple VE from the same door area (*e.g.*, VE from both the chuck door and the push side door) are counted as only one emitting door, not as multiple emitting doors.

11.2.3.3 Do not record the following sources as door area VE:

11.2.3.3.1 VE from ovens with doors removed. Record the oven number and make an appropriate notation under "Comments;"

11.2.3.3.2 VE from ovens taken out of service. The owner or operator shall notify the observer as to which ovens are out of service. Record the oven number and make an appropriate notation under "Comments;" or

11.2.3.3.3 VE from hot coke that has been spilled on the bench as a result of pushing.

11.2.4 Criteria for Acceptance. After completing the run, calculate the maximum time allowed to observe the ovens using the equation in Section 12.2. If the total traverse time exceeds T, void the run, and conduct another run to satisfy the requirements of §63.309(c)(1) of this part.

11.2.5 Percent Leaking Doors. For each day on which a valid observation is obtained, calculate the daily 30-day rolling average for each battery using these data and the 29 previous valid daily observations, in accordance with Section 12.5.

11.3 Procedure for Determining VE from Topside Port Lids and Offtake Systems.

11.3.1 Number of Runs. Refer to §63.309(c)(1) of this part for the number of runs to be conducted. Simultaneous runs or separate runs for the topside port lids and offtake systems may be conducted.

11.3.2 Battery Traverse. To conduct a topside traverse of the battery, walk the length of the battery at a steady, normal walking pace, pausing only to make appropriate entries on the topside inspection sheet (Figure 303-3). The walking pace shall not exceed an average rate of 4 seconds per oven, excluding time spent moving around stationary obstructions or waiting for other obstructions to move from positions blocking the view. Extra time is allowed for each leak for the observer to make the proper notation. A walking pace of 3 seconds per oven is typical. Record the actual traverse time with a stopwatch.

11.3.3 Topside Port Lid Observations. To observe lids of the ovens involved in the charging operation, the observer shall wait to view the lids until approximately 5 minutes after the completion of the charge. Record all the information requested on the topside inspection sheet (Figure 303-3). Record the clock time when traverses begin and end. If the observer's view is obstructed during the traverse (*e.g.*, steam from the coke wharf, larry car, etc.), follow the guidelines given in Section 11.2.2.2.

11.3.3.1 To perform a test run, conduct a single traverse on the topside of the battery. The observer shall walk near the center of

the battery but may deviate from this path to avoid safety hazards (such as open or closed charging ports, luting buckets, lid removal bars, and topside port lids that have been removed) and any other obstacles. Upon noting VE from the topside port lid(s) of an oven, record the oven number and port number, then resume the traverse. If any oven is dampered-off from the collecting main for decarbonization, note this under "Comments;" for that particular oven.

NOTE: Count the number of topside ports, not the number of points, exhibiting VE, *i.e.*, if a topside port has several points of VE, count this as one port exhibiting VE.

11.3.3.2 Do not count the following as topside port lid VE:

11.3.3.2.1 VE from between the brickwork and oven lid casing or VE from cracks in the oven brickwork. Note these VE under "Comments;"

11.3.3.2.2 VE from topside ports involved in a charging operation. Record the oven number, and make an appropriate notation (*e.g.*, not observed because ports open for charging) under "Comments;"

11.3.3.2.3 Topside ports having maintenance work done. Record the oven number and make an appropriate notation under "Comments;" or

11.3.3.2.4 Condensing water from wet-sealing material. Ports with only visible condensing water from wet-sealing material are counted as observed but not as having VE.

11.3.3.2.5 Visible emissions from the flue inspection ports and caps.

11.3.4 Offtake Systems Observations. To perform a test run, traverse the battery as in Section 11.3.3.1. Look ahead and back two to four ovens to get a clear view of the entire offtake system for each oven. Consider visible emissions from the following points as offtake system VE: (a) the flange between the gooseneck and collecting main ("saddle"), (b) the junction point of the standpipe and oven ("standpipe base"), (c) the other parts of the offtake system (*e.g.*, the standpipe cap), and (d) the junction points with ovens and flanges of jumper pipes.

11.3.4.1 Do not stray from the traverse line in order to get a "closer look" at any part of the offtake system unless it is to distinguish leaks from interferences from other sources or to avoid obstacles.

11.3.4.2 If the centerline does not provide a clear view of the entire offtake system for each oven (*e.g.*, when standpipes are longer than 15 feet), the observer may conduct the traverse farther from (rather than closer to) the offtake systems.

11.3.4.3 Upon noting a leak from an offtake system during a traverse, record the oven number. Resume the traverse. If the oven is dampered-off from the collecting

main for decarbonization and VE are observed, note this under "Comments" for that particular oven.

11.3.4.4 If any part or parts of an offtake system have VE, count it as one emitting offtake system. Each stationary jumper pipe is considered a single offtake system.

11.3.4.5 Do not count standpipe caps open for a decarbonization period or standpipes of an oven being charged as source of offtake system VE. Record the oven number and write "Not observed" and the reason (*i.e.*, decarb or charging) under "Comments."

NOTE: VE from open standpipes of an oven being charged count as charging emissions. All VE from closed standpipe caps count as offtake leaks.

11.3.5 Criteria for Acceptance. After completing the run (allow 2 traverses for batteries with double mains), calculate the maximum time allowed to observe the topside port lids and/or offtake systems using the equation in Section 12.3. If the total traverse time exceeds T, void the run and conduct another run to satisfy the requirements of §63.309(c)(1) of this part.

11.3.6 In determining the percent leaking topside port lids and percent leaking offtake systems, do not include topside port lids or offtake systems with VE from the following ovens:

11.3.6.1 Empty ovens, including ovens undergoing maintenance, which are properly dampered off from the main.

11.3.6.2 Ovens being charged or being pushed.

11.3.6.3 Up to 3 full ovens that have been dampered off from the main prior to pushing.

11.3.6.4 Up to 3 additional full ovens in the pushing sequence that have been dampered off from the main for offtake system cleaning, for decarbonization, for safety reasons, or when a charging/pushing schedule involves widely separated ovens (*e.g.*, a Marquard system); or that have been dampered off from the main for maintenance near the end of the coking cycle. Examples of reasons that ovens are dampered off for safety reasons are to avoid exposing workers in areas with insufficient clearance between standpipes and the larry car, or in areas where workers could be exposed to flames or hot gases from open standpipes, and to avoid the potential for removing a door on an oven that is not dampered off from the main.

11.3.7 Percent Leaking Topside Port Lids and Offtake Systems. For each day on which a valid observation is obtained, calculate the daily 30-day rolling average for each battery using these data and the 29 previous valid daily observations, in accordance with Sections 12.6 and 12.7.

11.4 Procedure for Determining VE from Collecting Mains.

11.4.1 Traverse. To perform a test run, traverse both the collecting main catwalk

and the battery topside along the side closest to the collecting main. If the battery has a double main, conduct two sets of traverses for each run, *i.e.*, one set for each main.

11.4.2 Data Recording. Upon noting VE from any portion of a collection main, identify the source and approximate location of the source of VE and record the time under "Collecting main" on Figure 303-3; then resume the traverse.

11.4.3 Collecting Main Pressure Check. After the completion of the door traverse, the topside port lids, and offtake systems, compare the collecting main pressure during the inspection to the collecting main pressure during the previous 8 to 24 hours. Record the following: (a) the pressure during inspection, (b) presence of pressure deviation from normal operations, and (c) the explanation for any pressure deviation from normal operations, if any, offered by the operators. The owner or operator of the coke battery shall maintain the pressure recording equipment and conduct the quality assurance/quality control (QA/QC) necessary to ensure reliable pressure readings and shall keep the QA/QC records for at least 6 months. The observer may periodically check the QA/QC records to determine their completeness. The owner or operator shall provide access to the records within 1 hour of an observer's request.

12.0 Data Analysis and Calculations

12.1 Nomenclature.

A = 150 or the number of valid observations (runs). The value of A shall not be less than 145, except for purposes of determinations under §63.306(c) (work practice plan implementation) or §63.306(d) (work practice plan revisions) of this part. No set of observations shall be considered valid for such a recalculation that otherwise would not be considered a valid set of observations for a calculation under this paragraph.

D_i = Number of doors on non-operating ovens.

D_{no} = Number of doors not observed.

D_{ob} = Total number of doors observed on operating ovens.

D_t = Total number of oven doors on the battery.

$e = 2.72$

J = Number of stationary jumper pipes.

L = Number of doors with VE.

L_b = Yard-equivalent reading.

L_s = Number of doors with VE observed from the bench under sheds.

L_y = Number of doors with VE observed from the yard.

$L_{y'}$ = Number of doors with VE observed from the yard on the push side.

ln = Natural logarithm.

N = Total number of ovens in the battery.

N_i = Total number of inoperable ovens.

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P_{NO} = Number of ports not observed.
 P_{Ovn} = Number of ports per oven.
 P_{VE} = Number of topside port lids with VE.
 PLD = Percent leaking coke oven doors for the test run.
 PLL = Percent leaking topside port lids for the run.
 PLO = Percent leaking offtake systems.
 T = Total time allowed for traverse, seconds.
 T_{Ovn} = Number of offtake systems (excluding jumper pipes) per oven.

T_{NO} = Number of offtake systems not observed.
 T_{VE} = Number of offtake systems with VE.
 X_i = Seconds of VE during the i th charge.
 Z = Number of topside port lids or offtake systems with VE.

12.2 Criteria for Acceptance for VE Determinations from Coke Oven Door Areas. After completing the run, calculate the maximum time allowed to observe the ovens using the following equation:

$$T = (4 \times D_t) + (10 \times L) \quad \text{Eq. 303-1}$$

12.3 Criteria for Acceptance for VE Determinations from Topside Port Lids and Offtake Systems. After completing the run (allow 2 traverses for batteries with double

mains), calculate the maximum time allowed to observe the topside port lids and/or offtake systems by the following equation:

$$T = (4 \times N) + (10 \times Z) \quad \text{Eq. 303-2}$$

12.4 Average Duration of VE from Charging Operations. Use Equation 303-3 to calculate the daily 30-day rolling log average of seconds of visible emissions from the charg-

ing operation for each battery using these current day's observations and the 29 previous valid daily sets of observations.

$$\text{logarithmic average} = e^y - 1 = \frac{\ln(X_1 + 1) + \ln(X_2 + 1) + \dots + \ln(X_A + 1)}{A} \quad \text{Eq. 303-3}$$

12.5 Percent Leaking Doors (PLD). Determine the total number of doors for which ob-

servations were made on the coke oven battery as follows:

$$D_{ob} = (2 \times N) - (D_i + D_{no}) \quad \text{Eq. 303-4}$$

12.5.1 For each test run (one run includes both the coke side and the push side traverses), sum the number of doors with door area VE. For batteries subject to an approved alternative standard under §63.305 of

this part, calculate the push side and the coke side PLD separately.

12.5.2 Calculate percent leaking doors by using Equation 303-5:

$$PLD = \frac{L_y}{D_{ob}} \times 100 \quad \text{Eq. 303-5}$$

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12.5.3 When traverses are conducted from the bench under sheds, calculate the coke side and the push side separately. Use Equation 303-6 to calculate a yard-equivalent reading:

$$L_b = L_s - (N \times 0.06) \quad \text{Eq. 303-6}$$

If L_b is less than zero, use zero for L_b in Equation 303-7 in the calculation of PLD. 12.5.3.1 Use Equation 303-7 to calculate PLD:

$$PLD = \frac{L_b + L_y}{D_{ob}} \times 100 \quad \text{Eq. 303-7}$$

Round off PLD to the nearest hundredth of 1 percent and record as the percent leaking coke oven doors for the run. day rolling average percent leaking doors for each battery using these current day's observations and the 29 previous valid daily sets of observations.

12.5.3.2 Average Percent Leaking Doors. Use Equation 303-8 to calculate the daily 30-

$$PLD_{(30\text{-day})} = \frac{(PLD_1 + PLD_2 + \dots + PLD_{30})}{30} \quad \text{Eq. 303-8}$$

12.6 Topside Port Lids. Determine the percent leaking topside port lids for each run as follows:

$$PLL = \frac{P_{VE}}{P_{ovn}(N - N_i) - P_{NO}} \times 100 \quad \text{Eq. 303-9}$$

12.6.1 Round off this percentage to the nearest hundredth of 1 percent and record this percentage as the percent leaking topside port lids for the run. the daily 30-day rolling average percent leaking topside port lids for each battery using these current day's observations and the 29 previous valid daily sets of observations.

12.6.2 Average Percent Leaking Topside Port Lids. Use Equation 303-10 to calculate

$$PLL_{(30\text{-day})} = \frac{(PLL_1 + PLL_2 + \dots + PLL_{30})}{30} \quad \text{Eq. 303-10}$$

12.7 Offtake Systems. Determine the percent leaking offtake systems for the run as follows:

$$PLO = \frac{T_{VE}}{T_{ovn}(N - N_i) + J - T_{NO}} \times 100 \quad \text{Eq. 303-11}$$

12.7.1 Round off this percentage to the nearest hundredth of 1 percent and record this percentage as the percent leaking offtake systems for the run.

12.7.2 Average Percent Leaking Offtake Systems. Use Equation 303-12 to calculate

the daily 30-day rolling average percent leaking offtake systems for each battery using these current day's observations and the 29 previous valid daily sets of observations.

$$PLO (30\text{-day}) = \frac{(PLO_1 + PLO_2 \dots + PLO_{30})}{30} \quad \text{Eq. 303-12}$$

13.0 *Method Performance.* [Reserved]

14.0 *Pollution Prevention.* [Reserved]

15.0 *Waste Management.* [Reserved]

16.0 *References.*

1. Missan, R., and A. Stein. Guidelines for Evaluation of Visible Emissions Certification, Field Procedures, Legal Aspects, and Background Material. U.S. Environmental Protection Agency. EPA Publication No. EPA-340/1-75-007. April 1975.

2. Wohlschlegel, P., and D. E. Wagoner. Guideline for Development of a Quality Assurance Program: Volume IX—Visual Determination of Opacity Emission from Stationary Sources. U.S. Environmental Protection Agency. EPA Publication No. EPA-650/4-74-005i. November 1975.

3. U.S. Occupational Safety and Health Administration. Code of Federal Regulations. Title 29, Chapter XVII, Section 1910.1029(g). Washington, D.C. Government Printing Office. July 1, 1990.

4. U.S. Environmental Protection Agency. National Emission Standards for Hazardous Air Pollutants; Coke Oven Emissions from Wet-Coal Charged By-Product Coke Oven Batteries; Proposed Rule and Notice of Public Hearing. Washington, D.C. FEDERAL REGISTER. Vol. 52, No. 78 (13586). April 23, 1987.

17.0 *Tables, Diagrams, Flowcharts, and Validation Data*

Company name: _____
 Battery no.: _____ Date: _____ Run no.: _____
 City, State: _____
 Observer name: _____
 Company representative(s): _____

Charge No.	Oven No.	Clock time	Visible emissions, seconds	Comments

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Charge No.	Oven No.	Clock time	Visible emissions, seconds	Comments

Figure 303-1. Charging System Inspection

Company name: _____
 Battery no.: _____
 Date: _____
 City, State: _____
 Total no. of ovens in battery: _____
 Observer name: _____
 Certification expiration date: _____
 Inoperable ovens: _____
 Company representative(s): _____
 Traverse time CS: _____
 Traverse time PS: _____
 Valid run (Y or N): _____

Time traverse started/ completed	PS/CS	Door No.	Comments (No. of blocked doors, interruptions to traverse, etc.)

Figure 303-2. Door Area Inspection.

Company name: _____
 Battery no.: _____
 Date: _____
 City, State: _____
 Total no. of ovens in battery: _____
 Observer name: _____

Certification expiration date: _____
 Inoperable ovens: _____
 Company representative(s): _____
 Total no. of lids: _____
 Total no. of oftakes: _____
 Total no. of jumper pipes: _____
 Ovens not observed: _____
 Total traverse time: _____
 Valid run (Y or N): _____

Time traverse started/ completed	Type of Inspection (lids, oftakes, collecting main)	Location of VE (Oven #/Port #)	Comments

Figure 303-3. Topside Inspection

METHOD 303A—DETERMINATION OF VISIBLE EMISSIONS FROM NONRECOVERY COKE OVEN BATTERIES

NOTE: This method does not include all of the specifications pertaining to observer certification. Some material is incorporated by reference from other methods in this part and in appendix A to 40 CFR Part 60. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of Method 9 and Method 303.

1.0 Scope and Application

1.1 Applicability. This method is applicable for the determination of visible emis-

sions (VE) from leaking doors at non-recovery coke oven batteries.

2.0 Summary of Method

2.1 A certified observer visually determines the VE from coke oven battery sources while walking at a normal pace. This method does not require that opacity of emissions be determined or that magnitude be differentiated.

3.0 Definitions

3.1 Bench means the platform structure in front of the oven doors.

3.2 Coke oven door means each end enclosure on the push side and the coking side of an oven.

3.3 *Coke side* means the side of a battery from which the coke is discharged from ovens at the end of the coking cycle.

3.4 *Nonrecovery coke oven battery* means a source consisting of a group of ovens connected by common walls and operated as a unit, where coal undergoes destructive distillation under negative pressure to produce coke, and which is designed for the combustion of coke oven gas from which by-products are not recovered.

3.5 *Operating oven* means any oven not out of operation for rebuild or maintenance work extensive enough to require the oven to be skipped in the charging sequence.

3.6 *Oven* means a chamber in the coke oven battery in which coal undergoes destructive distillation to produce coke.

3.7 *Push side* means the side of the battery from which the coke is pushed from ovens at the end of the coking cycle.

3.8 *Run* means the observation of visible emissions from coke oven doors in accordance with this method.

3.9 *Shed* means an enclosure that covers the side of the coke oven battery, captures emissions from pushing operations and from leaking coke oven doors on the coke side or push side of the coke oven battery, and routes the emissions to a control device or system.

3.10 *Traverse time* means accumulated time for a traverse as measured by a stopwatch. Traverse time includes time to stop and write down oven numbers but excludes time waiting for obstructions of view to clear or for time to walk around obstacles.

3.11 *Visible Emissions or VE* means any emission seen by the unaided (except for corrective lenses) eye, excluding steam or condensing water.

4.0 *Interferences. [Reserved]*

5.0 *Safety*

5.1 *Disclaimer.* This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 *Safety Training.* Because coke oven batteries have hazardous environments, the training materials and the field training (Section 10.0) shall cover the precautions required by the company to address health and safety hazards. Special emphasis shall be given to the Occupational Safety and Health Administration (OSHA) regulations pertaining to exposure of coke oven workers (see Reference 3 in Section 16.0). In general, the regulation requires that special fire-retardant clothing and respirators be worn in certain restricted areas of the coke oven bat-

tery. The OSHA regulation also prohibits certain activities, such as chewing gum, smoking, and eating in these areas.

6.0 *Equipment and Supplies. [Reserved]*

7.0 *Reagents and Standards [Reserved]*

8.0 *Sample Collection, Preservation, Transport, and Storage. [Reserved]*

9.0 *Quality Control. [Reserved]*

10.0 *Calibration and Standardization.*

10.1 *Training.* This method requires only the determination of whether VE occur and does not require the determination of opacity levels; therefore, observer certification according to Method 9 in Appendix A to Part 60 is not required. However, the first-time observer (trainee) shall have attended the lecture portion of the Method 9 certification course. Furthermore, before conducting any VE observations, an observer shall become familiar with nonrecovery coke oven battery operations and with this test method by observing for a minimum of 4 hours the operation of a nonrecovery coke oven battery in the presence of personnel experienced in performing Method 303 assessments.

11.0 *Procedure*

The intent of this procedure is to determine VE from coke oven door areas by carefully observing the door area while walking at a normal pace.

11.1 *Number of Runs.* Refer to §63.309(c)(1) of this part for the appropriate number of runs.

11.2 *Battery Traverse.* To conduct a battery traverse, walk the length of the battery on the outside of the pusher machine and quench car tracks at a steady, normal walking pace, pausing to make appropriate entries on the door area inspection sheet (Figure 303A-1). The walking pace shall be such that the duration of the traverse does not exceed an average of 4 seconds per oven door, excluding time spent moving around stationary obstructions or waiting for other obstructions to move from positions blocking the view of a series of doors. Extra time is allowed for each leak (a maximum of 10 additional seconds for each leaking door) for the observer to make the proper notation. A walking pace of 3 seconds per oven door has been found to be typical. Record the actual traverse time with a stopwatch. A single test run consists of two timed traverses, one for the coke side and one for the push side.

11.2.1 Various situations may arise that will prevent the observer from viewing a door or a series of doors. The observer has two options for dealing with obstructions to view: (a) Wait for the equipment to move or the fugitive emissions to dissipate before

completing the traverse; or (b) skip the affected ovens and move to an unobstructed position to continue the traverse. Continue the traverse. After the completion of the traverse, if the equipment has moved or the fugitive emissions have dissipated, complete the traverse by inspecting the affected doors. Record the oven numbers and make an appropriate notation under "Comments" on the door area inspection sheet (Figure 303A-1).

NOTE: Extra time incurred for handling obstructions is not counted in the traverse time.

11.2.2 When batteries have sheds to control pushing emissions, conduct the inspection from outside the shed, if the shed allows such observations, or from the bench. Be aware of special safety considerations pertinent to walking on the bench and follow the instructions of company personnel on the required equipment and operations procedures. If possible, conduct the bench traverse whenever the bench is clear of the door machine and hot coke guide.

11.3 Observations. Record all the information requested at the top of the door area inspection sheet (Figure 303A-1), including the number of non-operating ovens. Record which side is being inspected, *i.e.*, coke side or push side. Other information may be recorded at the discretion of the observer, such as the location of the leak (*e.g.*, top of the door), the reason for any interruption of the traverse, or the position of the sun relative to the battery and sky conditions (*e.g.*, overcast, partly sunny, etc.).

11.3.1 Begin the test run by traversing either the coke side or the push side of the

battery. After completing one side, traverse the other side.

11.3.2 During the traverse, look around the entire perimeter of each oven door. The door is considered leaking if VE are detected in the coke oven door area. The coke oven door area includes the entire area on the vertical face of a coke oven between the bench and the top of the battery and the adjacent doors on both sides. Record the oven number and make the appropriate notation on the door area inspection sheet (Figure 303A-1).

11.3.3 Do not record the following sources as door area VE:

11.3.3.1 VE from ovens with doors removed. Record the oven number and make an appropriate notation under "Comments";

11.3.3.2 VE from ovens where maintenance work is being conducted. Record the oven number and make an appropriate notation under "Comments"; or

11.3.3.3 VE from hot coke that has been spilled on the bench as a result of pushing.

12.0 Data Analysis and Calculations

Same as Method 303, Section 12.1, 12.2, 12.3, 12.4, and 12.5.

13.0 Method Performance. [Reserved]

14.0 Pollution Prevention. [Reserved]

15.0 Waste Management. [Reserved]

16.0 References

Same as Method 303, Section 16.0.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

Company name: _____
 Battery no.: _____
 Date: _____
 City, State: _____
 Total no. of ovens in battery: _____
 Observer name: _____
 Certification expiration date: _____
 Inoperable ovens: _____
 Company representative(s): _____
 Traverse time CS: _____
 Traverse time PS: _____
 Valid run (Y or N): _____

Time traverse started/ completed	PS/CS	Door No.	Comments (No. of blocked doors, interruptions to traverse, etc.)

Time traverse started/ completed	PS/CS	Door No.	Comments (No. of blocked doors, interruptions to traverse, etc.)

Figure 303A-1. Door Area Inspection

METHOD 304A: DETERMINATION OF BIODEGRADATION RATES OF ORGANIC COMPOUNDS (VENT OPTION)

1.0 Scope and Application

1.1 Applicability. This method is applicable for the determination of biodegradation rates of organic compounds in an activated sludge process. The test method is designed to evaluate the ability of an aerobic biological reaction system to degrade or destroy specific components in waste streams. The method may also be used to determine the effects of changes in wastewater composition on operation. The biodegradation rates determined by utilizing this method are not representative of a full-scale system. The rates measured by this method shall be used in conjunction with the procedures listed in appendix C of this part to calculate the fraction emitted to the air versus the fraction biodegraded.

2.0 Summary of Method

2.1 A self-contained benchtop bioreactor system is assembled in the laboratory. A sample of mixed liquor is added and the waste stream is then fed continuously. The benchtop bioreactor is operated under conditions nearly identical to the target full-scale activated sludge process. Bioreactor temperature, dissolved oxygen concentration, average residence time in the reactor, waste composition, biomass concentration, and biomass composition of the full-scale process

are the parameters which are duplicated in the benchtop bioreactor. Biomass shall be removed from the target full-scale activated sludge unit and held for no more than 4 hours prior to use in the benchtop bioreactor. If antifoaming agents are used in the full-scale system, they shall also be used in the benchtop bioreactor. The feed flowing into and the effluent exiting the benchtop bioreactor are analyzed to determine the biodegradation rates of the target compounds. The flow rate of the exit vent is used to calculate the concentration of target compounds (utilizing Henry's law) in the exit gas stream. If Henry's law constants for the compounds of interest are not known, this method cannot be used in the determination of the biodegradation rate and Method 304B is the suggested method. The choice of analytical methodology for measuring the compounds of interest at the inlet and outlet to the benchtop bioreactor are left to the discretion of the source, except where validated methods are available.

3.0 Definitions. [Reserved]

4.0 Interferences. [Reserved]

5.0 Safety

5.1 If explosive gases are produced as a by-product of biodegradation and could realistically pose a hazard, closely monitor headspace concentration of these gases to ensure laboratory safety. Placement of the

benchtop bioreactor system inside a laboratory hood is recommended regardless of by-products produced.

6.0. Equipment and Supplies

NOTE: Figure 304A-1 illustrates a typical laboratory apparatus used to measure biodegradation rates. While the following description refers to Figure 304A-1, the EPA recognizes that alternative reactor configurations, such as alternative reactor shapes and locations of probes and the feed inlet, will also meet the intent of this method. Ensure that the benchtop bioreactor system is self-contained and isolated from the atmosphere (except for the exit vent stream) by leak-checking fittings, tubing, etc.

6.1 Benchtop Bioreactor. The biological reaction is conducted in a biological oxidation reactor of at least 6 liters capacity. The benchtop bioreactor is sealed and equipped with internal probes for controlling and monitoring dissolved oxygen and internal temperature. The top of the reactor is equipped for aerators, gas flow ports, and instrumentation (while ensuring that no leaks to the atmosphere exist around the fittings).

6.2 Aeration gas. Aeration gas is added to the benchtop bioreactor through three diffusers, which are glass tubes that extend to the bottom fifth of the reactor depth. A pure oxygen pressurized cylinder is recommended in order to maintain the specified oxygen concentration. Install a blower (*e.g.*, Diaphragm Type, 15 SCFH capacity) to blow the aeration gas into the reactor diffusers. Measure the aeration gas flow rate with a rotameter (*e.g.*, 0-15 SCFH recommended). The aeration gas will rise through the benchtop bioreactor, dissolving oxygen into the mixture in the process. The aeration gas must provide sufficient agitation to keep the solids in suspension. Provide an exit for the aeration gas from the top flange of the benchtop bioreactor through a water-cooled (*e.g.*, Allihn-type) vertical condenser. Install the condenser through a gas-tight fitting in the benchtop bioreactor closure. Install a splitter which directs a portion of the gas to an exit vent and the rest of the gas through an air recycle pump back to the benchtop bioreactor. Monitor and record the flow rate through the exit vent at least 3 times per day throughout the day.

6.3 Wastewater Feed. Supply the wastewater feed to the benchtop bioreactor in a collapsible low-density polyethylene container or collapsible liner in a container (*e.g.*, 20 L) equipped with a spigot cap (collapsible containers or liners of other material may be required due to the permeability of some volatile compounds through polyethylene). Obtain the wastewater feed by sampling the wastewater feed in the target process. A representative sample of wastewater shall be obtained from the piping lead-

ing to the aeration tank. This sample may be obtained from existing sampling valves at the discharge of the wastewater feed pump, or collected from a pipe discharging to the aeration tank, or by pumping from a well-mixed equalization tank upstream from the aeration tank. Alternatively, wastewater can be pumped continuously to the laboratory apparatus from a bleed stream taken from the equalization tank of the full-scale treatment system.

6.3.1 Refrigeration System. Keep the wastewater feed cool by ice or by refrigeration to 4 °C. If using a bleed stream from the equalization tank, refrigeration is not required if the residence time in the bleed stream is less than five minutes.

6.3.2 Wastewater Feed Pump. The wastewater is pumped from the refrigerated container using a variable-speed peristaltic pump drive equipped with a peristaltic pump head. Add the feed solution to the benchtop bioreactor through a fitting on the top flange. Determine the rate of feed addition to provide a retention time in the benchtop bioreactor that is numerically equivalent to the retention time in the full-scale system. The wastewater shall be fed at a rate sufficient to achieve 90 to 100 percent of the full-scale system residence time.

6.3.3 Treated wastewater feed. The benchtop bioreactor effluent exits at the bottom of the reactor through a tube and proceeds to the clarifier.

6.4 Clarifier. The effluent flows to a separate closed clarifier that allows separation of biomass and effluent (*e.g.*, 2-liter pear-shaped glass separatory funnel, modified by removing the stopcock and adding a 25-mm OD glass tube at the bottom). Benchtop bioreactor effluent enters the clarifier through a tube inserted to a depth of 0.08 m (3 in.) through a stopper at the top of the clarifier. System effluent flows from a tube inserted through the stopper at the top of the clarifier to a drain (or sample bottle when sampling). The underflow from the clarifier leaves from the glass tube at the bottom of the clarifier. Flexible tubing connects this fitting to the sludge recycle pump. This pump is coupled to a variable speed pump drive. The discharge from this pump is returned through a tube inserted in a port on the side of the benchtop bioreactor. An additional port is provided near the bottom of the benchtop bioreactor for sampling the reactor contents. The mixed liquor from the benchtop bioreactor flows into the center of the clarifier. The clarified system effluent separates from the biomass and flows through an exit near the top of the clarifier. There shall be no headspace in the clarifier.

6.5 Temperature Control Apparatus. Capable of maintaining the system at a temperature equal to the temperature of the full-scale system. The average temperature

should be maintained within ± 2 °C of the set point.

6.5.1 Temperature Monitoring Device. A resistance type temperature probe or a thermocouple connected to a temperature read-out with a resolution of 0.1 °C or better.

6.5.2 Benchtop Bioreactor Heater. The heater is connected to the temperature control device.

6.6 Oxygen Control System. Maintain the dissolved oxygen concentration at the levels present in the full-scale system. Target full-scale activated sludge systems with dissolved oxygen concentration below 2 mg/L are required to maintain the dissolved oxygen concentration in the benchtop bioreactor within 0.5 mg/L of the target dissolved oxygen level. Target full-scale activated sludge systems with dissolved oxygen concentration above 2 mg/L are required to maintain the dissolved oxygen concentration in the benchtop bioreactor within 1.5 mg/L of the target dissolved oxygen concentration; however, for target full-scale activated sludge systems with dissolved oxygen concentrations above 2 mg/L, the dissolved oxygen concentration in the benchtop bioreactor may not drop below 1.5 mg/L. If the benchtop bioreactor is outside the control range, the dissolved oxygen is noted and the reactor operation is adjusted.

6.6.1 Dissolved Oxygen Monitor. Dissolved oxygen is monitored with a polarographic probe (gas permeable membrane) connected to a dissolved oxygen meter (*e.g.*, 0 to 15 mg/L, 0 to 50 °C).

6.6.2 Benchtop Bioreactor Pressure Monitor. The benchtop bioreactor pressure is monitored through a port in the top flange of the reactor. This is connected to a gauge control with a span of 13-cm water vacuum to 13-cm water pressure or better. A relay is activated when the vacuum exceeds an adjustable setpoint which opens a solenoid valve (normally closed), admitting oxygen to the system. The vacuum setpoint controlling oxygen addition to the system shall be set at approximately 2.5 ± 0.5 cm water and maintained at this setting except during brief periods when the dissolved oxygen concentration is adjusted.

6.7 Connecting Tubing. All connecting tubing shall be Teflon or equivalent in impermeability. The only exception to this specification is the tubing directly inside the pump head of the wastewater feed pump, which may be Viton, Silicone or another type of flexible tubing.

NOTE: Mention of trade names or products does not constitute endorsement by the U.S. Environmental Protection Agency.

7.0 Reagents and Standards

7.1 Wastewater. Obtain a representative sample of wastewater at the inlet to the full-scale treatment plant if there is an existing full-scale treatment plant (see section 6.3). If

there is no existing full-scale treatment plant, obtain the wastewater sample as close to the point of determination as possible. Collect the sample by pumping the wastewater into the 20-L collapsible container. The loss of volatiles shall be minimized from the wastewater by collapsing the container before filling, by minimizing the time of filling, and by avoiding a headspace in the container after filling. If the wastewater requires the addition of nutrients to support the biomass growth and maintain biomass characteristics, those nutrients are added and mixed with the container contents after the container is filled.

7.2 Biomass. Obtain the biomass or activated sludge used for rate constant determination in the bench-scale process from the existing full-scale process or from a representative biomass culture (*e.g.*, biomass that has been developed for a future full-scale process). This biomass is preferentially obtained from a thickened acclimated mixed liquor sample. Collect the sample either by bailing from the mixed liquor in the aeration tank with a weighted container, or by collecting aeration tank effluent at the effluent overflow weir. Transport the sample to the laboratory within no more than 4 hours of collection. Maintain the biomass concentration in the benchtop bioreactor at the level of the full-scale system ± 10 percent throughout the sampling period of the test method.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Benchtop Bioreactor Operation. Charge the mixed liquor to the benchtop bioreactor, minimizing headspace over the liquid surface to minimize entrainment of mixed liquor in the circulating gas. Fasten the benchtop bioreactor headplate to the reactor over the liquid surface. Maintain the temperature of the contents of the benchtop bioreactor system at the temperature of the target full-scale system, ± 2 °C, throughout the testing period. Monitor and record the temperature of the benchtop bioreactor contents at least to the nearest 0.1 °C.

8.1.1 Wastewater Storage. Collect the wastewater sample in the 20-L collapsible container. Store the container at 4 °C throughout the testing period. Connect the container to the benchtop bioreactor feed pump.

8.1.2 Wastewater Flow Rate.

8.1.2.1 The hydraulic residence time of the aeration tank is calculated as the ratio of the volume of the tank (L) to the flow rate (L/min). At the beginning of a test, the container shall be connected to the feed pump and solution shall be pumped to the benchtop bioreactor at the required flow rate to achieve the calculated hydraulic residence time of wastewater in the aeration tank.

$$Q_{\text{test}} = Q_{\text{fs}} \frac{L}{V_{\text{fs}}} \quad \text{Eq. 304A-1}$$

Where:

Q_{test} = wastewater flow rate (L/min)

Q_{fs} = average flow rate of full-scale process (L/min)

V_{fs} = volume of full-scale aeration tank (L)

8.1.2.2 The target flow rate in the test apparatus is the same as the flow rate in the target full-scale process multiplied by the ratio of benchtop bioreactor volume (e.g., 6 L) to the volume of the full-scale aeration tank. The hydraulic residence time shall be maintained at 90 to 100 percent of the residence time maintained in the full-scale unit. A nominal flow rate is set on the pump based on a pump calibration. Changes in the elasticity of the tubing in the pump head and the accumulation of material in the tubing affect this calibration. The nominal pumping rate shall be changed as necessary based on volumetric flow measurements. Discharge the benchtop bioreactor effluent to a wastewater storage, treatment, or disposal facility, except during sampling or flow measurement periods.

8.1.3 Sludge Recycle Rate. Set the sludge recycle rate at a rate sufficient to prevent accumulation in the bottom of the clarifier. Set the air circulation rate sufficient to maintain the biomass in suspension.

8.1.4 Benchtop Bioreactor Operation and Maintenance. Temperature, dissolved oxygen concentration, exit vent flow rate, benchtop bioreactor effluent flow rate, and air circulation rate shall be measured and recorded three times throughout each day of benchtop bioreactor operation. If other parameters (such as pH) are measured and maintained in the target full-scale unit, these parameters, where appropriate, shall be monitored and maintained to target full-scale specifications in the benchtop bioreactor. At the beginning of each sampling period (Section 8.2), sample the benchtop bioreactor contents for suspended solids analysis. Take this sample by loosening a clamp on a length of tubing attached to the lower side port. Determine the suspended solids gravimetrically by the Gooch crucible/glass fiber filter method for total suspended solids, in accordance with Standard Methods³ or equivalent. When necessary, sludge shall be wasted from the lower side port of the benchtop bioreactor, and the volume that is wasted shall be replaced with an equal volume of the reactor effluent. Add thickened activated sludge mixed liquor as necessary to the benchtop bioreactor to increase the suspended solids concentration to the desired level. Pump this mixed liquor to the benchtop bioreactor through the upper side port (Item 24 in Figure 304A-1). Change

the membrane on the dissolved oxygen probe before starting the test. Calibrate the oxygen probe immediately before the start of the test and each time the membrane is changed.

8.1.5 Inspection and Correction Procedures. If the feed line tubing becomes clogged, replace with new tubing. If the feed flow rate is not within 5 percent of target flow any time the flow rate is measured, reset pump or check the flow measuring device and measure flow rate again until target flow rate is achieved.

8.2 Test Sampling. At least two and one half hydraulic residence times after the system has reached the targeted specifications shall be permitted to elapse before the first sample is taken. Effluent samples of the clarifier discharge (Item 20 in Figure 304A-1) and the influent wastewater feed are collected in 40-mL septum vials to which two drops of 1:10 hydrochloric acid (HCl) in water have been added. Sample the clarifier discharge directly from the drain line. These samples will be composed of the entire flow from the system for a period of several minutes. Feed samples shall be taken from the feed pump suction line after temporarily stopping the benchtop bioreactor feed, removing a connector, and squeezing the collapsible feed container. Store both influent and effluent samples at 4 °C immediately after collection and analyze within 8 hours of collection.

8.2.1 Frequency of Sampling. During the test, sample and analyze the wastewater feed and the clarifier effluent at least six times. The sampling intervals shall be separated by at least 8 hours. During any individual sampling interval, sample the wastewater feed simultaneously with or immediately after the effluent sample. Calculate the relative standard deviation (RSD) of the amount removed (*i.e.*, effluent concentration—wastewater feed concentration). The RSD values shall be < 15 percent. If an RSD value is > 15 percent, continue sampling and analyzing influent and effluent sets of samples until the RSD values are within specifications.

8.2.2 Sampling After Exposure of System to Atmosphere. If, after starting sampling procedures, the benchtop bioreactor system is exposed to the atmosphere (due to leaks, maintenance, etc.), allow at least one hydraulic residence time to elapse before resuming sampling.

9.0 Quality Control

9.1 Dissolved Oxygen. Fluctuation in dissolved oxygen concentration may occur for

numerous reasons, including undetected gas leaks, increases and decreases in mixed liquor suspended solids resulting from cell growth and solids loss in the effluent stream, changes in diffuser performance, cycling of effluent flow rate, and overcorrection due to faulty or sluggish dissolved oxygen probe response. Control the dissolved oxygen concentration in the benchtop bioreactor by changing the proportion of oxygen in the circulating aeration gas. Should the dissolved oxygen concentration drift below the designated experimental condition, bleed a small amount of aeration gas from the system on the pressure side (i.e., immediately upstream of one of the diffusers). This will create a vacuum in the system, triggering the pressure sensitive relay to open the solenoid valve and admit oxygen to the system.

Should the dissolved oxygen concentration drift above the designated experimental condition, slow or stop the oxygen input to the system until the dissolved oxygen concentration approaches the correct level.

9.2 Sludge Wasting.

9.2.1 Determine the suspended solids concentration (section 8.1.4) at the beginning of a test, and once per day thereafter during the test. If the test is completed within a two day period, determine the suspended solids concentration after the final sample set is taken. If the suspended solids concentration exceeds the specified concentration, remove a fraction of the sludge from the benchtop bioreactor. The required volume of mixed liquor to remove is determined as follows:

$$V_w = V_r \left(\frac{S_m - S_s}{S_m} \right) \quad \text{Eq. 304A-2}$$

Where:

V_w is the wasted volume (Liters),
 V_r is the volume of the benchtop bioreactor (Liters),
 S_m is the measured solids (g/L), and
 S_s is the specified solids (g/L).

9.2.2 Remove the mixed liquor from the benchtop bioreactor by loosening a clamp on the mixed liquor sampling tube and allowing the required volume to drain to a graduated flask. Clamp the tube when the correct vol-

ume has been wasted. Replace the volume of the liquid wasted by pouring the same volume of effluent back into the benchtop bioreactor. Dispose of the waste sludge properly.

9.3 Sludge Makeup. In the event that the suspended solids concentration is lower than the specifications, add makeup sludge back into the benchtop bioreactor. Determine the amount of sludge added by the following equation:

$$V_w = V_r \left(\frac{S_s - S_m}{S_w} \right) \quad \text{Eq. 304A-3}$$

Where:

V_w is the volume of sludge to add (Liters),
 V_r is the volume of the benchtop bioreactor (Liters),
 S_w is the solids in the makeup sludge (g/L),
 S_m is the measured solids (g/L), and S_s is the specified solids (g/L).

10.0 Calibration and Standardization

10.1 Wastewater Pump Calibration. Determine the wastewater flow rate by collecting the system effluent for a time period of at least one hour, and measuring the volume with a graduated cylinder. Record the collection time period and volume collected. Determine flow rate. Adjust the pump speed to deliver the specified flow rate.

10.2 Calibration Standards. Prepare calibration standards from pure certified standards in an aqueous medium. Prepare and analyze three concentrations of calibration standards for each target component (or for a mixture of components) in triplicate daily throughout the analyses of the test samples. At each concentration level, a single calibration shall be within 5 percent of the average of the three calibration results. The low and medium calibration standards shall bracket the expected concentration of the effluent (treated) wastewater. The medium and high standards shall bracket the expected influent concentration.

11.0 Analytical Procedures

11.1 Analysis. If the identity of the compounds of interest in the wastewater is not known, a representative sample of the wastewater shall be analyzed in order to identify all of the compounds of interest present. A gas chromatography/mass spectrometry screening method is recommended.

11.1.1 After identifying the compounds of interest in the wastewater, develop and/or use one or more analytical techniques capable of measuring each of those compounds (more than one analytical technique may be required, depending on the characteristics of the wastewater). Test Method 18, found in appendix A of 40 CFR 60, may be used as a guideline in developing the analytical technique. Purge and trap techniques may be used for analysis providing the target components are sufficiently volatile to make this technique appropriate. The limit of quantitation for each compound shall be determined (see reference 1). If the effluent concentration of any target compound is below the limit of quantitation determined for that compound, the operation of the Method 304 unit may be altered to attempt to increase the effluent concentration above the limit of quantitation. Modifications to the method shall be approved prior to the test. The request should be addressed to Method 304 contact, Emissions Measurement Center, Mail Drop 19, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

12.0 Data Analysis and Calculations

12.1 Nomenclature. The following symbols are used in the calculations.

C_i = Average inlet feed concentration for a compound of interest, as analyzed (mg/L)

C_o = Average outlet (effluent) concentration for a compound of interest, as analyzed (mg/L)

X = Biomass concentration, mixed liquor suspended solids (g/L)

t = Hydraulic residence time in the benchtop bioreactor (hours)

V = Volume of the benchtop bioreactor (L)

Q = Flow rate of wastewater into the benchtop bioreactor, average (L/hour)

12.2 Residence Time. The hydraulic residence time of the benchtop bioreactor is equal to the ratio of the volume of the benchtop bioreactor (L) to the flow rate (L/h):

$$t = \frac{V}{Q} \quad \text{Eq. 304A-4}$$

12.3 Rate of Biodegradation. Calculate the rate of biodegradation for each component with the following equation:

$$\text{Rate} \left(\frac{\text{mg}}{\text{L-h}} \right) = \frac{C_i - C_o}{t} \quad \text{Eq. 304A-5}$$

12.4 First-Order Biorate Constant. Calculate the first-order biorate constant (K1) for each component with the following equation:

$$K1 \left(\frac{\text{L}}{\text{g-h}} \right) = \frac{C_i - C_o}{t C_o X} \quad \text{Eq. 304A-6}$$

12.5 Relative Standard Deviation (RSD). Determine the standard deviation of both

the influent and effluent sample concentrations (S) using the following equation:

$$\text{RSD} = \frac{100}{\bar{S}} \left(\sum_{i=1}^n \frac{(S_i - \bar{S})^2}{(n-1)} \right)^{1/2} \quad \text{Eq. 304A-7}$$

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12.6 Determination of Percent Air Emissions and Percent Biodegraded. Use the results from this test method and follow the applicable procedures in appendix C of 40 CFR part 63, entitled, "Determination of the Fraction Biodegraded (F_{bio}) in a Biological Treatment Unit" to determine F_{bio} .

13.0 *Method Performance, [Reserved]*

14.0 *Pollution Prevention, [Reserved]*

15.0 *Waste Management, [Reserved]*

16.0 References

1. "Guidelines for data acquisition and data quality evaluation in Environmental Chemistry," Daniel MacDoughal, Analytical Chemistry, Volume 52, p. 2242, 1980.

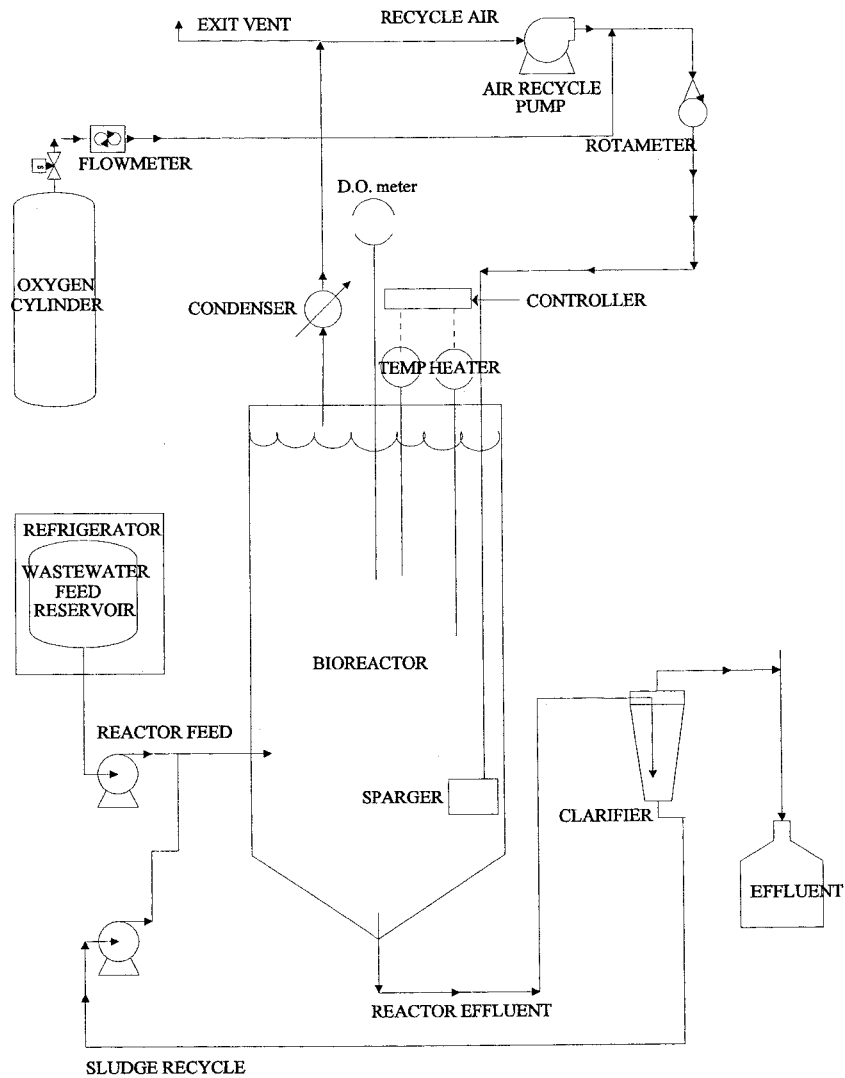
2. Test Method 18, 40 CFR 60, appendix A.

3. Standard Methods for the Examination of Water and Wastewater, 16th Edition, Method 209C, Total Suspended Solids Dried at 103–105 °C, APHA, 1985.

4. Water7, Hazardous Waste Treatment, Storage, and Disposal Facilities (TSDF)—Air Emission Models, U.S. Environmental Protection Agency, EPA-450/3-87-026, Review Draft, November 1989.

5. Chemdat7, Hazardous Waste Treatment, Storage, and Disposal Facilities (TSDF)—Air Emission Models, U.S. Environmental Protection Agency, EPA-450/3-87-026, Review Draft, November 1989.

17.0 *Tables, Diagrams, Flowcharts, and Validation Data*



EPA METHOD 304A VENT BIOREACTOR SYSTEM

METHOD 304B: DETERMINATION OF BIODEGRADATION RATES OF ORGANIC COMPOUNDS (SCRUBBER OPTION)

1.0 Scope and Application

1.1 Applicability. This method is applicable for the determination of biodegradation rates of organic compounds in an activated sludge process. The test method is designed to evaluate the ability of an aerobic biological

reaction system to degrade or destroy specific components in waste streams. The method may also be used to determine the effects of changes in wastewater composition on operation. The biodegradation rates determined by utilizing this method are not representative of a full-scale system. Full-scale systems embody biodegradation and air emissions in competing reactions. This method measures biodegradation in absence

of air emissions. The rates measured by this method shall be used in conjunction with the procedures listed in appendix C of this part to calculate the fraction emitted to the air versus the fraction biodegraded.

2.0 Summary of Method

2.1 A self-contained benchtop bioreactor system is assembled in the laboratory. A sample of mixed liquor is added and the waste stream is then fed continuously. The benchtop bioreactor is operated under conditions nearly identical to the target full-scale activated sludge process, except that air emissions are not a factor. The benchtop bioreactor temperature, dissolved oxygen concentration, average residence time in the reactor, waste composition, biomass concentration, and biomass composition of the target full-scale process are the parameters which are duplicated in the laboratory system. Biomass shall be removed from the target full-scale activated sludge unit and held for no more than 4 hours prior to use in the benchtop bioreactor. If antifoaming agents are used in the full-scale system, they shall also be used in the benchtop bioreactor. The feed flowing into and the effluent exiting the benchtop bioreactor are analyzed to determine the biodegradation rates of the target compounds. The choice of analytical methodology for measuring the compounds of interest at the inlet and outlet to the benchtop bioreactor are left to the discretion of the source, except where validated methods are available.

3.0 Definitions. [Reserved]

4.0 Interferences. [Reserved]

5.0 Safety

5.1 If explosive gases are produced as a by-product of biodegradation and could realistically pose a hazard, closely monitor headspace concentration of these gases to ensure laboratory safety. Placement of the benchtop bioreactor system inside a laboratory hood is recommended regardless of by-products produced.

6.0 Equipment and Supplies

NOTE: Figure 304B-1 illustrates a typical laboratory apparatus used to measure biodegradation rates. While the following description refers to Figure 304B-1, the EPA recognizes that alternative reactor configurations, such as alternative reactor shapes and locations of probes and the feed inlet, will also meet the intent of this method. Ensure that the benchtop bioreactor system is self-contained and isolated from the atmosphere by leak-checking fittings, tubing, etc.

6.1 Benchtop Bioreactor. The biological reaction is conducted in a biological oxidation reactor of at least 6-liters capacity. The benchtop bioreactor is sealed and equipped

with internal probes for controlling and monitoring dissolved oxygen and internal temperature. The top of the benchtop bioreactor is equipped for aerators, gas flow ports, and instrumentation (while ensuring that no leaks to the atmosphere exist around the fittings).

6.2 Aeration gas. Aeration gas is added to the benchtop bioreactor through three diffusers, which are glass tubes that extend to the bottom fifth of the reactor depth. A pure oxygen pressurized cylinder is recommended in order to maintain the specified oxygen concentration. Install a blower (*e.g.*, Diaphragm Type, 15 SCFH capacity) to blow the aeration gas into the benchtop bioreactor diffusers. Measure the aeration gas flow rate with a rotameter (*e.g.*, 0-15 SCFH recommended). The aeration gas will rise through the benchtop bioreactor, dissolving oxygen into the mixture in the process. The aeration gas must provide sufficient agitation to keep the solids in suspension. Provide an exit for the aeration gas from the top flange of the benchtop bioreactor through a water-cooled (*e.g.*, Allihn-type) vertical condenser. Install the condenser through a gas-tight fitting in the benchtop bioreactor closure. Design the system so that at least 10 percent of the gas flows through an alkaline scrubber containing 175 mL of 45 percent by weight solution of potassium hydroxide (KOH) and 5 drops of 0.2 percent alizarin yellow dye. Route the balance of the gas through an adjustable scrubber bypass. Route all of the gas through a 1-L knock-out flask to remove entrained moisture and then to the intake of the blower. The blower recirculates the gas to the benchtop bioreactor.

6.3 Wastewater Feed. Supply the wastewater feed to the benchtop bioreactor in a collapsible low-density polyethylene container or collapsible liner in a container (*e.g.*, 20 L) equipped with a spigot cap (collapsible containers or liners of other material may be required due to the permeability of some volatile compounds through polyethylene). Obtain the wastewater feed by sampling the wastewater feed in the target process. A representative sample of wastewater shall be obtained from the piping leading to the aeration tank. This sample may be obtained from existing sampling valves at the discharge of the wastewater feed pump, or collected from a pipe discharging to the aeration tank, or by pumping from a well-mixed equalization tank upstream from the aeration tank. Alternatively, wastewater can be pumped continuously to the laboratory apparatus from a bleed stream taken from the equalization tank of the full-scale treatment system.

6.3.1 Refrigeration System. Keep the wastewater feed cool by ice or by refrigeration to 4 °C. If using a bleed stream from the

equalization tank, refrigeration is not required if the residence time in the bleed stream is less than five minutes.

6.3.2 Wastewater Feed Pump. The wastewater is pumped from the refrigerated container using a variable-speed peristaltic pump drive equipped with a peristaltic pump head. Add the feed solution to the benchtop bioreactor through a fitting on the top flange. Determine the rate of feed addition to provide a retention time in the benchtop bioreactor that is numerically equivalent to the retention time in the target full-scale system. The wastewater shall be fed at a rate sufficient to achieve 90 to 100 percent of the target full-scale system residence time.

6.3.3 Treated wastewater feed. The benchtop bioreactor effluent exits at the bottom of the reactor through a tube and proceeds to the clarifier.

6.4 Clarifier. The effluent flows to a separate closed clarifier that allows separation of biomass and effluent (*e.g.*, 2-liter pear-shaped glass separatory funnel, modified by removing the stopcock and adding a 25-mm OD glass tube at the bottom). Benchtop bioreactor effluent enters the clarifier through a tube inserted to a depth of 0.08 m (3 in.) through a stopper at the top of the clarifier. System effluent flows from a tube inserted through the stopper at the top of the clarifier to a drain (or sample bottle when sampling). The underflow from the clarifier leaves from the glass tube at the bottom of the clarifier. Flexible tubing connects this fitting to the sludge recycle pump. This pump is coupled to a variable speed pump drive. The discharge from this pump is returned through a tube inserted in a port on the side of the benchtop bioreactor. An additional port is provided near the bottom of the benchtop bioreactor for sampling the reactor contents. The mixed liquor from the benchtop bioreactor flows into the center of the clarifier. The clarified system effluent separates from the biomass and flows through an exit near the top of the clarifier. There shall be no headspace in the clarifier.

6.5 Temperature Control Apparatus. Capable of maintaining the system at a temperature equal to the temperature of the full-scale system. The average temperature should be maintained within ± 2 °C of the set point.

6.5.1 Temperature Monitoring Device. A resistance type temperature probe or a thermocouple connected to a temperature read-out with a resolution of 0.1 °C or better.

6.5.2 Benchtop Bioreactor Heater. The heater is connected to the temperature control device.

6.6 Oxygen Control System. Maintain the dissolved oxygen concentration at the levels present in the full-scale system. Target full-scale activated sludge systems with dissolved oxygen concentration below 2 mg/L are required to maintain the dissolved oxy-

gen concentration in the benchtop bioreactor within 0.5 mg/L of the target dissolved oxygen level. Target full-scale activated sludge systems with dissolved oxygen concentration above 2 mg/L are required to maintain the dissolved oxygen concentration in the benchtop bioreactor within 1.5 mg/L of the target dissolved oxygen concentration; however, for target full-scale activated sludge systems with dissolved oxygen concentrations above 2 mg/L, the dissolved oxygen concentration in the benchtop bioreactor may not drop below 1.5 mg/L. If the benchtop bioreactor is outside the control range, the dissolved oxygen is noted and the reactor operation is adjusted.

6.6.1 Dissolved Oxygen Monitor. Dissolved oxygen is monitored with a polarographic probe (gas permeable membrane) connected to a dissolved oxygen meter (*e.g.*, 0 to 15 mg/L, 0 to 50 °C).

6.6.2 Benchtop Bioreactor Pressure Monitor. The benchtop bioreactor pressure is monitored through a port in the top flange of the reactor. This is connected to a gauge control with a span of 13-cm water vacuum to 13-cm water pressure or better. A relay is activated when the vacuum exceeds an adjustable setpoint which opens a solenoid valve (normally closed), admitting oxygen to the system. The vacuum setpoint controlling oxygen addition to the system shall be set at approximately 2.5 ± 0.5 cm water and maintained at this setting except during brief periods when the dissolved oxygen concentration is adjusted.

6.7 Connecting Tubing. All connecting tubing shall be Teflon or equivalent in impermeability. The only exception to this specification is the tubing directly inside the pump head of the wastewater feed pump, which may be Viton, Silicone or another type of flexible tubing.

NOTE: Mention of trade names or products does not constitute endorsement by the U.S. Environmental Protection Agency.

7.0. Reagents and Standards

7.1 Wastewater. Obtain a representative sample of wastewater at the inlet to the full-scale treatment plant if there is an existing full-scale treatment plant (See Section 6.3). If there is no existing full-scale treatment plant, obtain the wastewater sample as close to the point of determination as possible. Collect the sample by pumping the wastewater into the 20-L collapsible container. The loss of volatiles shall be minimized from the wastewater by collapsing the container before filling, by minimizing the time of filling, and by avoiding a headspace in the container after filling. If the wastewater requires the addition of nutrients to support the biomass growth and maintain biomass characteristics, those nutrients are added and mixed with the container contents after the container is filled.

7.2 Biomass. Obtain the biomass or activated sludge used for rate constant determination in the bench-scale process from the existing full-scale process or from a representative biomass culture (*e.g.*, biomass that has been developed for a future full-scale process). This biomass is preferentially obtained from a thickened acclimated mixed liquor sample. Collect the sample either by bailing from the mixed liquor in the aeration tank with a weighted container, or by collecting aeration tank effluent at the effluent overflow weir. Transport the sample to the laboratory within no more than 4 hours of collection. Maintain the biomass concentration in the benchtop bioreactor at the level of the target full-scale system +10 percent throughout the sampling period of the test method.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Benchtop Bioreactor Operation. Charge the mixed liquor to the benchtop bioreactor, minimizing headspace over the liquid surface to minimize entrainment of

mixed liquor in the circulating gas. Fasten the benchtop bioreactor headplate to the reactor over the liquid surface. Maintain the temperature of the contents of the benchtop bioreactor system at the temperature of the target full-scale system, ± 2 °C, throughout the testing period. Monitor and record the temperature of the reactor contents at least to the nearest 0.1 °C.

8.1.1 Wastewater Storage. Collect the wastewater sample in the 20-L collapsible container. Store the container at 4 °C throughout the testing period. Connect the container to the benchtop bioreactor feed pump.

8.1.2 Wastewater Flow Rate.

8.1.2.1 The hydraulic residence time of the aeration tank is calculated as the ratio of the volume of the tank (L) to the flow rate (L/min). At the beginning of a test, the container shall be connected to the feed pump and solution shall be pumped to the benchtop bioreactor at the required flow rate to achieve the calculated hydraulic residence time of wastewater in the aeration tank.

$$Q_{\text{test}} = Q_{\text{fs}} \frac{L}{V_{\text{fs}}} \quad \text{Eq. 304B-1}$$

Where:

Q_{test} = wastewater flow rate (L/min)

Q_{fs} = average flow rate of full-scale process (L/min)

V_{fs} = volume of full-scale aeration tank (L)

8.1.2.2 The target flow rate in the test apparatus is the same as the flow rate in the target full-scale process multiplied by the ratio of benchtop bioreactor volume (*e.g.*, 6 L) to the volume of the full-scale aeration tank. The hydraulic residence time shall be maintained at 90 to 100 percent of the residence time maintained in the target full-scale unit. A nominal flow rate is set on the pump based on a pump calibration. Changes in the elasticity of the tubing in the pump head and the accumulation of material in the tubing affect this calibration. The nominal pumping rate shall be changed as necessary based on volumetric flow measurements. Discharge the benchtop bioreactor effluent to a wastewater storage, treatment, or disposal facility, except during sampling or flow measurement periods.

8.1.3 Sludge Recycle Rate. Set the sludge recycle rate at a rate sufficient to prevent accumulation in the bottom of the clarifier. Set the air circulation rate sufficient to maintain the biomass in suspension.

8.1.4 Benchtop Bioreactor Operation and Maintenance. Temperature, dissolved oxygen

concentration, flow rate, and air circulation rate shall be measured and recorded three times throughout each day of testing. If other parameters (such as pH) are measured and maintained in the target full-scale unit, these parameters shall, where appropriate, be monitored and maintained to full-scale specifications in the benchtop bioreactor. At the beginning of each sampling period (section 8.2), sample the benchtop bioreactor contents for suspended solids analysis. Take this sample by loosening a clamp on a length of tubing attached to the lower side port. Determine the suspended solids gravimetrically by the Gooch crucible/glass fiber filter method for total suspended solids, in accordance with Standard Methods³ or equivalent. When necessary, sludge shall be wasted from the lower side port of the benchtop bioreactor, and the volume that is wasted shall be replaced with an equal volume of the benchtop bioreactor effluent. Add thickened activated sludge mixed liquor as necessary to the benchtop bioreactor to increase the suspended solids concentration to the desired level. Pump this mixed liquor to the benchtop bioreactor through the upper side port (Item 24 in Figure 304B-1). Change the membrane on the dissolved oxygen probe before starting the test. Calibrate the oxygen probe immediately before the start of the test and each time the membrane is changed.

The scrubber solution shall be replaced each weekday with 175 mL 45 percent W/W KOH solution to which five drops of 0.2 percent alizarin yellow indicator in water have been added. The potassium hydroxide solution in the alkaline scrubber shall be changed if the alizarin yellow dye color changes.

8.1.5 Inspection and Correction Procedures. If the feed line tubing becomes clogged, replace with new tubing. If the feed flow rate is not within 5 percent of target flow any time the flow rate is measured, reset pump or check the flow measuring device and measure flow rate again until target flow rate is achieved.

8.2 Test Sampling. At least two and one half hydraulic residence times after the system has reached the targeted specifications shall be permitted to elapse before the first sample is taken. Effluent samples of the clarifier discharge (Item 20 in Figure 304B-1) and the influent wastewater feed are collected in 40-mL septum vials to which two drops of 1:10 hydrochloric acid (HCl) in water have been added. Sample the clarifier discharge directly from the drain line. These samples will be composed of the entire flow from the system for a period of several minutes. Feed samples shall be taken from the feed pump suction line after temporarily stopping the benchtop bioreactor feed, removing a connector, and squeezing the collapsible feed container. Store both influent and effluent samples at 4 °C immediately after collection and analyze within 8 hours of collection.

8.2.1 Frequency of Sampling. During the test, sample and analyze the wastewater feed and the clarifier effluent at least six times. The sampling intervals shall be separated by at least 8 hours. During any individual sampling interval, sample the wastewater feed simultaneously with or immediately after the effluent sample. Calculate the RSD of the amount removed (*i.e.*, effluent concentration—wastewater feed concentration). The RSD values shall be <15 percent. If an RSD value is >15 percent, continue sampling and analyzing influent and effluent sets of samples until the RSD values are within specifications.

8.2.2 Sampling After Exposure of System to Atmosphere. If, after starting sampling procedures, the benchtop bioreactor system is exposed to the atmosphere (due to leaks, maintenance, etc.), allow at least one hydraulic residence time to elapse before resuming sampling.

9.0 Quality Control

9.1 Dissolved Oxygen. Fluctuation in dissolved oxygen concentration may occur for numerous reasons, including undetected gas leaks, increases and decreases in mixed liquor suspended solids resulting from cell growth and solids loss in the effluent stream, changes in diffuser performance, cycling of effluent flow rate, and overcorrection due to faulty or sluggish dissolved oxygen probe response. Control the dissolved oxygen concentration in the benchtop bioreactor by changing the proportion of oxygen in the circulating aeration gas. Should the dissolved oxygen concentration drift below the designated experimental condition, bleed a small amount of aeration gas from the system on the pressure side (*i.e.*, immediately upstream of one of the diffusers). This will create a vacuum in the system, triggering the pressure sensitive relay to open the solenoid valve and admit oxygen to the system. Should the dissolved oxygen concentration drift above the designated experimental condition, slow or stop the oxygen input to the system until the dissolved oxygen concentration approaches the correct level.

9.2 Sludge Wasting.

9.2.1 Determine the suspended solids concentration (section 8.1.4) at the beginning of a test, and once per day thereafter during the test. If the test is completed within a two day period, determine the suspended solids concentration after the final sample set is taken. If the suspended solids concentration exceeds the specified concentration, remove a fraction of the sludge from the benchtop bioreactor. The required volume of mixed liquor to remove is determined as follows:

$$V_w = V_r \left(\frac{S_m - S_s}{S_m} \right) \quad \text{Eq. 304B-2}$$

Where:

V_w is the wasted volume (Liters),
 V_r is the volume of the benchtop bioreactor (Liters),
 S_m is the measured solids (g/L), and
 S_s is the specified solids (g/L).

9.2.2 Remove the mixed liquor from the benchtop bioreactor by loosening a clamp on the mixed liquor sampling tube and allowing the required volume to drain to a graduated flask. Clamp the tube when the correct volume has been wasted. Replace the volume of

the liquid wasted by pouring the same volume of effluent back into the benchtop bioreactor. Dispose of the waste sludge properly.

9.3 Sludge Makeup. In the event that the suspended solids concentration is lower than

the specifications, add makeup sludge back into the benchtop bioreactor. Determine the amount of sludge added by the following equation:

$$V_w = V_r \left(\frac{S_s - S_m}{S_w} \right) \quad \text{Eq. 304B-3}$$

Where:

V_w is the volume of sludge to add (Liters),
 V_r is the volume of the benchtop bioreactor (Liters),
 S_w is the solids in the makeup sludge (g/L),
 S_m is the measured solids (g/L), and
 S_s is the specified solids (g/L).

10.0 Calibration and Standardizations

10.1 Wastewater Pump Calibration. Determine the wastewater flow rate by collecting the system effluent for a time period of at least one hour, and measuring the volume with a graduated cylinder. Record the collection time period and volume collected. Determine flow rate. Adjust the pump speed to deliver the specified flow rate.

10.2 Calibration Standards. Prepare calibration standards from pure certified standards in an aqueous medium. Prepare and analyze three concentrations of calibration standards for each target component (or for a mixture of components) in triplicate daily throughout the analyses of the test samples. At each concentration level, a single calibration shall be within 5 percent of the average of the three calibration results. The low and medium calibration standards shall bracket the expected concentration of the effluent (treated) wastewater. The medium and high standards shall bracket the expected influent concentration.

11.0 Analytical Test Procedures

11.1 Analysis. If the identity of the compounds of interest in the wastewater is not known, a representative sample of the wastewater shall be analyzed in order to identify all of the compounds of interest present. A gas chromatography/mass spectrometry screening method is recommended.

11.1.1 After identifying the compounds of interest in the wastewater, develop and/or use one or more analytical technique capable of measuring each of those compounds (more

than one analytical technique may be required, depending on the characteristics of the wastewater). Method 18, found in appendix A of 40 CFR 60, may be used as a guideline in developing the analytical technique. Purge and trap techniques may be used for analysis providing the target components are sufficiently volatile to make this technique appropriate. The limit of quantitation for each compound shall be determined.¹ If the effluent concentration of any target compound is below the limit of quantitation determined for that compound, the operation of the Method 304 unit may be altered to attempt to increase the effluent concentration above the limit of quantitation. Modifications to the method shall be approved prior to the test. The request should be addressed to Method 304 contact, Emissions Measurement Center, Mail Drop 19, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

12.0 Data Analysis and Calculations

12.1 Nomenclature. The following symbols are used in the calculations.

C_i = Average inlet feed concentration for a compound of interest, as analyzed (mg/L)
 C_o = Average outlet (effluent) concentration for a compound of interest, as analyzed (mg/L)
 X = Biomass concentration, mixed liquor suspended solids (g/L)
 t = Hydraulic residence time in the benchtop bioreactor (hours)
 V = Volume of the benchtop bioreactor (L)
 Q = Flow rate of wastewater into the benchtop bioreactor, average (L/hour)

12.2 Residence Time. The hydraulic residence time of the benchtop bioreactor is equal to the ratio of the volume of the benchtop bioreactor (L) to the flow rate (L/h)

$$t = \frac{V}{Q} \quad \text{Eq. 304B-4}$$

12.3 Rate of Biodegradation. Calculate the rate of biodegradation for each component with the following equation:

$$\text{Rate} \left(\frac{\text{mg}}{\text{L-h}} \right) = \frac{C_i - C_o}{t} \quad \text{Eq. 304B-5}$$

12.4 First-Order Biorate Constant. Calculate the first-order biorate constant (K1) for each component with the following equation:

$$K1 \left(\frac{\text{L}}{\text{g-h}} \right) = \frac{C_i - C_o}{t C_o X} \quad \text{Eq. 304B-6}$$

12.5 Relative Standard Deviation (RSD). Determine the standard deviation of both the influent and effluent sample concentrations (S) using the following equation:

$$\text{RSD} = \frac{100}{\bar{S}} \left(\frac{\sum_{i=1}^n (S_i - \bar{S})^2}{(n-1)} \right)^{1/2} \quad \text{Eq. 304B-7}$$

12.6 Determination of Percent Air Emissions and Percent Biodegraded. Use the results from this test method and follow the applicable procedures in appendix C of 40 CFR Part 63, entitled, "Determination of the Fraction Biodegraded (F_{bio}) in a Biological Treatment Unit" to determine F_{bio} .

13.0 Method Performance. [Reserved]

14.0 Pollution Prevention. [Reserved]

15.0 Waste Management. [Reserved]

16.0 References

1. "Guidelines for data acquisition and data quality evaluation in Environmental Chemistry", Daniel MacDoughal, Analytical Chemistry, Volume 52, p. 2242, 1980.

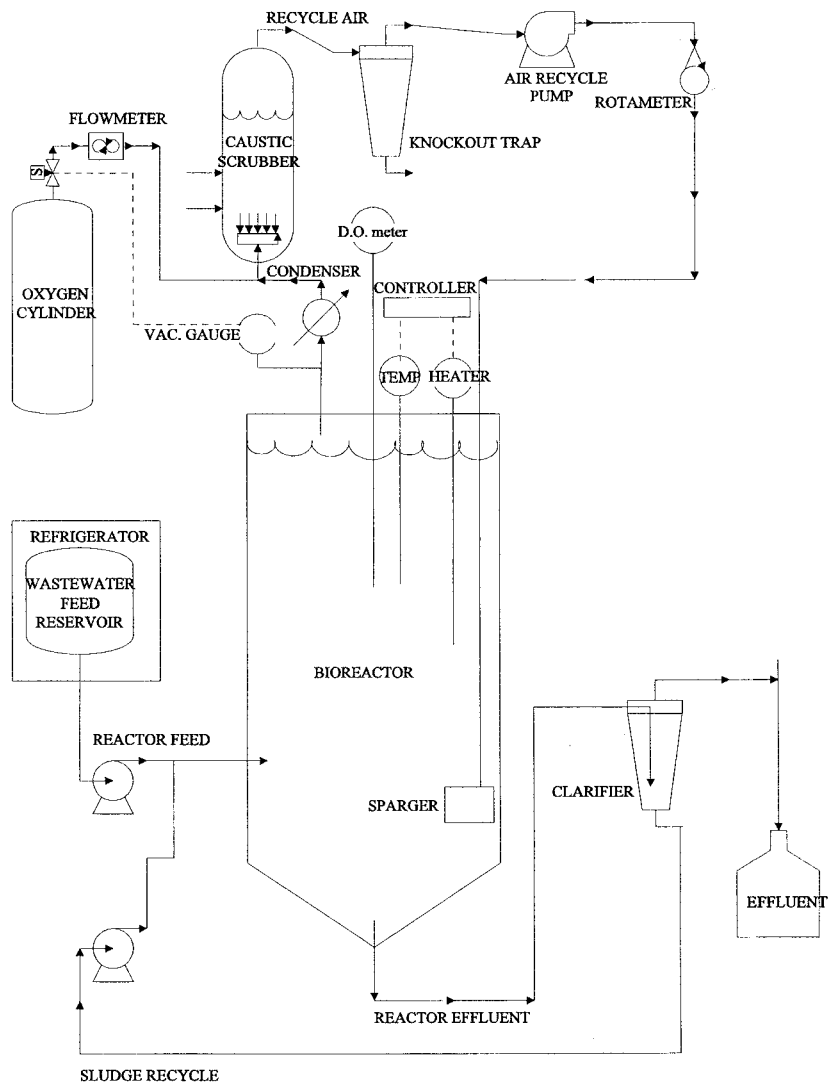
2. Test Method 18, 40 CFR 60, Appendix A.

3. Standard Methods for the Examination of Water and Wastewater, 16th Edition, Method 209C, Total Suspended Solids Dried at 103-105 °C, APHA, 1985.

4. Water-7, Hazardous Waste Treatment, Storage, and Disposal Facilities (TSDF)—Air Emission Models, U.S. Environmental Protection Agency, EPA-450/3-87-026, Review Draft, November 1989.

5. Chemdat7, Hazardous Waste Treatment, Storage, and Disposal Facilities (TSDF)—Air Emission Models, U.S. Environmental Protection Agency, EPA-450/3-87-026, Review Draft, November 1989.

17.0 Tables, Diagrams, Flowcharts, and Validation Data



EPA METHOD 304B BIOREACTOR SYSTEM

METHOD 305: MEASUREMENT OF EMISSION POTENTIAL OF INDIVIDUAL VOLATILE ORGANIC COMPOUNDS IN WASTE

NOTE: This method does not include all of the specifications (e.g., equipment and supplies) and procedures (e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in 40 CFR Part 60, Appendix

A. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least Method 25D.

1.0 Scope and Application

1.1 Analyte. Volatile Organics. No CAS No. assigned.

1.2 Applicability. This procedure is used to determine the emission potential of individual volatile organics (VOs) in waste.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 The heated purge conditions established by Method 25D (40 CFR Part 60, Appendix A) are used to remove VOs from a 10 gram sample of waste suspended in a 50/50 solution of polyethylene glycol (PEG) and water. The purged VOs are quantified by using the sample collection and analytical techniques (*e.g.* gas chromatography) appropriate for the VOs present in the waste. The recovery efficiency of the sample collection and analytical technique is determined for each waste matrix. A correction factor is determined for each compound (if acceptable recovery criteria requirements are met of 70 to 130 percent recovery for every target compound), and the measured waste concentration is corrected with the correction factor for each compound. A minimum of three replicate waste samples shall be analyzed.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

6.1 Method 25D Purge Apparatus.

6.1.1 Purge Chamber. The purge chamber shall accommodate the 10 gram sample of waste suspended in a matrix of 50 mL of PEG and 50 mL of deionized, hydrocarbon-free water. Three fittings are used on the glass chamber top. Two #7 Ace-threads are used for the purge gas inlet and outlet connections. A #50 Ace-thread is used to connect the top of the chamber to the base (see Figure 305-1). The base of the chamber has a side-arm equipped with a #22 Sovirel fitting to allow for easy sample introductions into the chamber. The dimensions of the chamber are shown in Figure 305-1.

6.1.2 Flow Distribution Device (FDD). The FDD enhances the gas-to-liquid contact for improved purging efficiency. The FDD is a 6 mm OD (0.2 in) by 30 cm (12 in) long glass tube equipped with four arm bubblers as shown in Figure 305-1. Each arm shall have an opening of 1 mm (0.04 in) in diameter.

6.1.3 Coalescing Filter. The coalescing filter serves to discourage aerosol formation of sample gas once it leaves the purge chamber.

The glass filter has a fritted disc mounted 10 cm (3.9 in) from the bottom. Two #7 Ace-threads are used for the inlet and outlet connections. The dimensions of the chamber are shown in Figure 305-2.

6.1.4 Oven. A forced convection airflow oven capable of maintaining the purge chamber and coalescing filter at 75 ± 2 °C (167 ± 3.6 °F).

6.1.5 Toggle Valve. An on/off valve constructed from brass or stainless steel rated to 100 psig. This valve is placed in line between the purge nitrogen source and the flow controller.

6.1.6 Flow Controller. High-quality stainless steel flow controller capable of restricting a flow of nitrogen to 6 ± 0.06 L/min (0.2 ± 0.002 ft³/min) at 40 psig.

6.1.7 Polyethylene Glycol Cleaning System.

6.1.7.1 Round-Bottom Flask. One liter, three-neck glass round-bottom flask for cleaning PEG. Standard taper 24/40 joints are mounted on each neck.

6.1.7.2 Heating Mantle. Capable of heating contents of the 1-L flask to 120 °C (248 °F).

6.1.7.3 Nitrogen Bubbler. Teflon® or glass tube, 0.25 in OD (6.35 mm).

6.1.7.4 Temperature Sensor. Partial immersion glass thermometer.

6.1.7.5 Hose Adapter. Glass with 24/40 standard tapered joint.

6.2 Volatile Organic Recovery System.

6.2.1 Splitter Valve (Optional). Stainless steel cross-pattern valve capable of splitting nominal flow rates from the purge flow of 6 L/min (0.2 ft³/min). The valve shall be maintained at 75 ± 2 °C (167 ± 3.6 °F) in the heated zone and shall be placed downstream of the coalescing filter. It is recommended that 0.125 in OD (3.175 mm) tubing be used to direct the split vent flow from the heated zone. The back pressure caused by the 0.125 in OD (3.175 mm) tubing is critical for maintaining proper split valve operation.

NOTE: The splitter valve design is optional; it may be used in cases where the concentration of a pollutant would saturate the adsorbents.

6.2.2 Injection Port. Stainless steel 1/4 in OD (6.35 mm) compression fitting tee with a 6 mm (0.2 in) septum fixed on the top port. The injection port is the point of entry for the recovery study solution. If using a gaseous standard to determine recovery efficiency, connect the gaseous standard to the injection port of the tee.

6.2.3 Knockout Trap (Optional but Recommended). A 25 mL capacity glass reservoir body with a full-stem impinger (to avoid leaks, a modified midget glass impinger with a screw cap and ball/socket clamps on the inlet and outlet is recommended). The empty impinger is placed in an ice water bath between the injection port and the sorbent cartridge. Its purpose is to reduce the water

content of the purge gas (saturated at 75 °C (167 °F)) before the sorbent cartridge.

6.2.4 Insulated Ice Bath. A 350 mL dewar or other type of insulated bath is used to maintain ice water around the knockout trap.

6.2.5 Sorbent Cartridges. Commercially available glass or stainless steel cartridge packed with one or more appropriate sorbents. The amount of adsorbent packed in the cartridge depends on the breakthrough volume of the test compounds but is limited by back pressure caused by the packing (not to exceed 7 psig). More than one sorbent cartridge placed in series may be necessary depending upon the mixture of the measured components.

6.2.6 Volumetric Glassware. Type A glass 10 mL volumetric flasks for measuring a final volume from the water catch in the knockout trap.

6.2.7 Thermal Desorption Unit. A clam-shell type oven, used for the desorption of direct thermal desorption sorbent tubes. The oven shall be capable of increasing the temperature of the desorption tubes rapidly to recommended desorption temperature.

6.2.8 Ultrasonic Bath. Small bath used to agitate sorbent material and desorption solvent. Ice water shall be used in the bath because of heat transfer caused by operation of the bath.

6.2.9 Desorption Vials. Four-dram (15 mL) capacity borosilicate glass vials with Teflon-lined caps.

6.3 Analytical System. A gas chromatograph (GC) is commonly used to separate and quantify compounds from the sample collection and recovery procedure. Method 18 (40 CFR Part 60, Appendix A) may be used as a guideline for determining the appropriate GC column and GC detector based on the test compounds to be determined. Other types of analytical instrumentation may be used (HPLC) in lieu of GC systems as long as the recovery efficiency criteria of this method are met.

6.3.1 Gas Chromatograph (GC). The GC shall be equipped with a constant-temperature liquid injection port or a heated sampling loop/valve system, as appropriate. The GC oven shall be temperature-programmable over the useful range of the GC column. The choice of detectors is based on the test compounds to be determined.

6.3.2 GC Column. Select the appropriate GC column based on (1) literature review or previous experience, (2) polarity of the analytes, (3) capacity of the column, or (4) resolving power (*e.g.*, length, diameter, film thickness) required.

6.3.3 Data System. A programmable electronic integrator for recording, analyzing, and storing the signal generated by the detector.

7.0 Reagents and Standards

7.1 Method 25D Purge Apparatus.

7.1.1 Polyethylene Glycol (PEG). Ninety-eight percent pure organic polymer with an average molecular weight of 400 g/mol. Volatile organics are removed from the PEG prior to use by heating to 120 ± 5 °C (248 ± 9 °F) and purging with pure nitrogen at 1 L/min (0.04 ft³/min) for 2 hours. After purging and heating, the PEG is maintained at room temperature under a nitrogen purge maintained at 1 L/min (0.04 ft³/min) until used. A typical apparatus used to clean the PEG is shown in Figure 305-3.

7.1.2 Water. Organic-free deionized water is required.

7.1.3 Nitrogen. High-purity nitrogen (less than 0.5 ppm total hydrocarbons) is used to remove test compounds from the purge matrix. The source of nitrogen shall be regulated continuously to 40 psig before the on/off toggle valve.

7.2 Volatile Organic Recovery System.

7.2.1 Water. Organic-free deionized water is required.

7.2.2 Desorption Solvent (when used). Appropriate high-purity (99.99 percent) solvent for desorption shall be used. Analysis shall be performed (utilizing the same analytical technique as that used in the analysis of the waste samples) on each lot to determine purity.

7.3 Analytical System. The gases required for GC operation shall be of the highest obtainable purity (hydrocarbon free). Consult the operating manual for recommended settings.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Assemble the glassware and associated fittings (see Figures 305-3 and 305-4, as appropriate) and leak-check the system (approximately 7 psig is the target pressure). After an initial leak check, mark the pressure gauge and use the initial checkpoint to monitor for leaks throughout subsequent analyses. If the pressure in the system drops below the target pressure at any time during analysis, that analysis shall be considered invalid.

8.2 Recovery Efficiency Determination. Determine the individual recovery efficiency (RE) for each of the target compounds in duplicate before the waste samples are analyzed. To determine the RE, generate a water blank (Section 11.1) and use the injection port to introduce a known volume of spike solution (or certified gaseous standard) containing all of the target compounds at the levels expected in the waste sample. Introduce the spike solution immediately after the nitrogen purge has been started (Section 8.3.2). Follow the procedures outlined in Section 8.3.3. Analyze the recovery efficiency samples using the techniques described in

Section 11.2. Determine the recovery efficiency (Equation 305–1, Section 12.2) by comparing the amount of compound recovered to the theoretical amount spiked. Determine the RE twice for each compound; the relative standard deviation, (RSD) shall be ≤ 10 percent for each compound. If the RSD for any compound is not ≤ 10 percent, modify the sampling/analytical procedure and complete an RE study in duplicate, or continue determining RE until the RSD meets the acceptable criteria. The average RE shall be $0.70 \leq RE \leq 1.30$ for each compound. If the average RE does not meet these criteria, an alternative sample collection and/or analysis technique shall be developed and the recovery efficiency determination shall be repeated for that compound until the criteria are met for every target compound. Example modifications of the sampling/analytical system include changing the adsorbent material, changing the desorption solvent, utilizing direct thermal desorption of test compounds from the sorbent tubes, utilizing another analytical technique.

8.3 Sample Collection and Recovery.

8.3.1 The sample collection procedure in Method 25D shall be used to collect (into a preweighed vial) 10 g of waste into PEG, cool, and ship to the laboratory. Remove the sample container from the cooler and wipe the exterior to remove any ice or water. Weigh the container and sample to the nearest 0.01 g and record the weight. Pour the sample from the container into the purge

flask. Rinse the sample container three times with approximately 6 mL of PEG (or the volume needed to total 50 mL of PEG in the purge flask), transferring the rinses to the purge flask. Add 50 mL of organic-free deionized water to the purge flask. Cap the purge flask tightly in between each rinse and after adding all the components into the flask.

8.3.2 Allow the oven to equilibrate to 75 ± 2 °C (167 ± 3.6 °F). Begin the sample recovery process by turning the toggle valve on, thus allowing a 6 L/min flow of pure nitrogen through the purge chamber.

8.3.3 Stop the purge after 30 min. Immediately remove the sorbent tube(s) from the apparatus and cap both ends. Remove the knockout trap and transfer the water catch to a 10 mL volumetric flask. Rinse the trap with organic-free deionized water and transfer the rinse to the volumetric flask. Dilute to the 10 mL mark with water. Transfer the water sample to a sample vial and store at 4 °C (39.2 °F) with zero headspace. The analysis of the contents of the water knockout trap is optional for this method. If the target compounds are water soluble, analysis of the water is recommended; meeting the recovery efficiency criteria in these cases would be difficult without adding the amount captured in the knockout trap.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
8.1	Sampling equipment leak-check	Ensures accurate measurement of sample volume.
8.2	Recovery efficiency (RE) determination for each measured compound..	Ensures accurate sample collection and analysis.
8.3	Calibration of analytical instrument with at least 3 calibration standards..	Ensures linear measurement of compounds over the instrument span.

10.0 Calibration and Standardization

10.1 The analytical instrument shall be calibrated with a minimum of three levels of standards for each compound whose concentrations bracket the concentration of test compounds from the sorbent tubes. Liquid calibration standards shall be used for calibration in the analysis of the solvent extracts. The liquid calibration standards shall be prepared in the desorption solvent matrix. The calibration standards may be prepared and injected individually or as a mixture. If thermal desorption and focusing (onto another sorbent or cryogen focusing) are used, a certified gaseous mixture or a series of gaseous standards shall be used for calibration of the instrument. The gaseous standards shall be focused and analyzed in the same manner as the samples.

10.2 The analytical system shall be certified free from contaminants before a cali-

bration is performed (see Section 11.1). The calibration standards are used to determine the linearity of the analytical system. Perform an initial calibration and linearity check by analyzing the three calibration standards for each target compound in triplicate starting with the lowest level and continuing to the highest level. If the triplicate analyses do not agree within 5 percent of their average, additional analyses will be needed until the 5 percent criteria is met. Calculate the response factor (Equation 305–3, Section 12.4) from the average area counts of the injections for each concentration level. Average the response factors of the standards for each compound. The linearity of the detector is acceptable if the response factor of each compound at a particular concentration is within 10 percent of the overall mean response factor for that compound.

Analyze daily a mid-level calibration standard in duplicate and calculate a new response factor. Compare the daily response factor average to the average response factor calculated for the mid-level calibration during the initial linearity check; repeat the three-level calibration procedure if the daily average response factor differs from the initial linearity check mid-level response factor by more than 10 percent. Otherwise, proceed with the sample analysis.

11.0 Analytical Procedure

11.1 Water Blank Analysis. A water blank shall be analyzed daily to determine the cleanliness of the purge and recovery system. A water blank is generated by adding 60 mL of organic-free deionized water to 50 mL of PEG in the purge chamber. Treat the blank as described in Sections 8.3.2 and 8.3.3. The purpose of the water blank is to insure that no contaminants exist in the sampling and analytical apparatus which would interfere with the quantitation of the target compounds. If contaminants are present, locate the source of contamination, remove it, and repeat the water blank analysis.

11.2 Sample Analysis. Sample analysis in the context of this method refers to techniques to remove the target compounds from the sorbent tubes, separate them using a chromatography technique, and quantify them with an appropriate detector. Two types of sample extraction techniques typically used for sorbents include solvent desorption or direct thermal desorption of test compounds to a secondary focusing unit (either sorbent or cryogen based). The test compounds are then typically transferred to a GC system for analysis. Other analytical systems may be used (e.g., HPLC) in lieu of GC systems as long as the recovery efficiency criteria of this method are met.

11.2.1 Recover the test compounds from the sorbent tubes that require solvent desorption by transferring the adsorbent material to a sample vial containing the desorption solvent. The desorption solvent shall be the same as the solvent used to prepare calibration standards. The volume of solvent depends on the amount of adsorbed material to be desorbed (1.0 mL per 100 mg of adsorbent material) and also on the amount of test compounds present. Final volume adjustment and or dilution can be made so that the concentration of test compounds in the desorption solvent is bracketed by the concentration of the calibration solutions. Ultrasonicate the desorption solvent for 15 min in an ice bath. Allow the sample to sit for a period of time so that the adsorbent material can settle to the bottom of the vial. Transfer the solvent with a pasteur pipet (minimizing the amount of adsorbent material taken) to another vial and store at 4 °C (39.2 °F).

11.2.2 Analyze the desorption solvent or direct thermal desorption tubes from each sample using the same analytical parameters used for the calibration standard. Calculate the total weight detected for each compound (Equation 305-4, Section 12.5). The slope (area/amount) and y-intercept are calculated from the line bracketed between the two closest calibration points. Correct the concentration of each waste sample with the appropriate recovery efficiency factor and the split flow ratio (if used). The final concentration of each individual test compound is calculated by dividing the corrected measured weight for that compound by the weight of the original sample determined in Section 8.3.1 (Equation 305-5, Section 12.6).

11.2.3 Repeat the analysis for the three samples collected in Section 8.3. Report the corrected concentration of each of the waste samples, average waste concentration, and relative standard deviation (Equation 305-6, Section 12.7).

12.0 Data Analysis and Calculations.

12.1 Nomenclature.

- A_s = Mean area counts of test compound in standard.
- A_U = Mean area counts of test compound in sample desorption solvent.
- b = Y-intercept of the line formed between the two closest calibration standards that bracket the concentration of the sample.
- C_T = Amount of test compound (μg) in calibration standard.
- C_F = Correction for adjusting final amount of sample detected for losses during individual sample runs.
- F_P = Nitrogen flow through the purge chamber (6 L/min).
- F_S = Nitrogen split flow directed to the sample recovery system (use 6 L/min if split flow design was not used).
- PPM = Final concentration of test compound in waste sample [$\mu\text{g/g}$ (which is equivalent to parts per million by weight (ppmw))].
- RE = Recovery efficiency for adjusting final amount of sample detected for losses due to inefficient trapping and desorption techniques.
- R.F. = Response factor for test compound, calculated from a calibration standard.
- S = Slope of the line (area counts/ C_T) formed between two closest calibration points that bracket the concentration of the sample.
- W_C = Weight of test compound expected to be recovered in spike solution based on theoretical amount (μg).
- W_E = Weight of vial and PEG (g).
- W_F = Weight of vial, PEG and waste sample (g).
- W_S = Weight of original waste sample (g).

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W_T = Corrected weight of test compound measured (μg) in sample.
 W_X = Weight of test compound measured during analysis of recovery efficiency spike samples (μg).

12.2 Recovery efficiency for determining trapping/desorption efficiency of individual test compounds in the spike solution, decimal value.

$$\text{RE} = \frac{W_X}{W_C} \quad \text{Eq. 305-1}$$

12.3 Weight of waste sample (g).

$$W_S = W_F - W_E \quad \text{Eq. 305-2}$$

12.4 Response factor for individual test compounds.

$$\text{RF} = \frac{C_T}{A_S} \quad \text{Eq. 305-3}$$

12.5 Corrected weight of a test compound in the sample, in μg .

$$W_T = \frac{A_u - b}{S} \times \frac{1}{\text{RE}} \times \frac{F_p}{F_s} \quad \text{Eq. 305-4}$$

12.6 Final concentration of a test compound in the sample in ppmw.

$$\text{PPM} = \frac{W_T}{W_S} \quad \text{Eq. 305-5}$$

12.7 Relative standard deviation (RSD) calculation.

$$\text{RSD} = \frac{100}{\text{PPM}} \sqrt{\frac{\sum_{i=1}^n (\text{PPM}_i - \overline{\text{PPM}})^2}{n-1}} \quad \text{Eq. 305-6}$$

13.0 Method Performance. [Reserved]

14.0 Pollution Prevention. [Reserved]

15.0 Waste Management. [Reserved]

16.0 References. [Reserved]

17.0 Tables, Diagrams, Flowcharts, and Validation Data

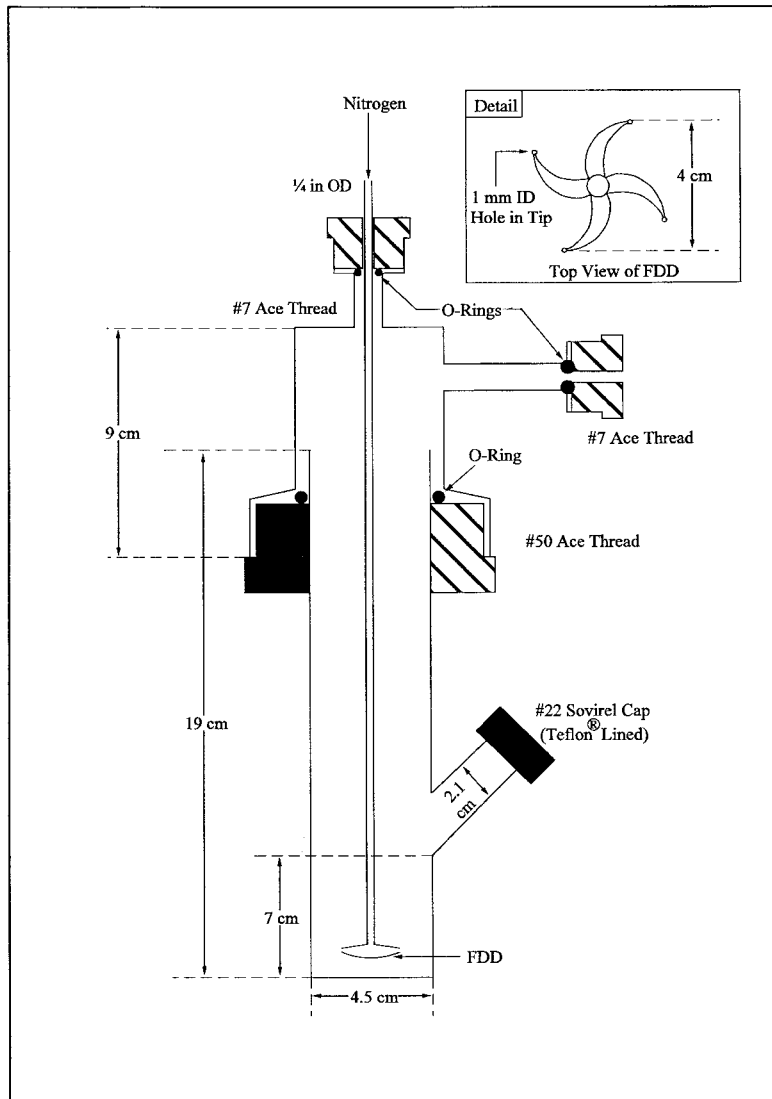


Figure 305-1. Schematic of Purge Chamber.

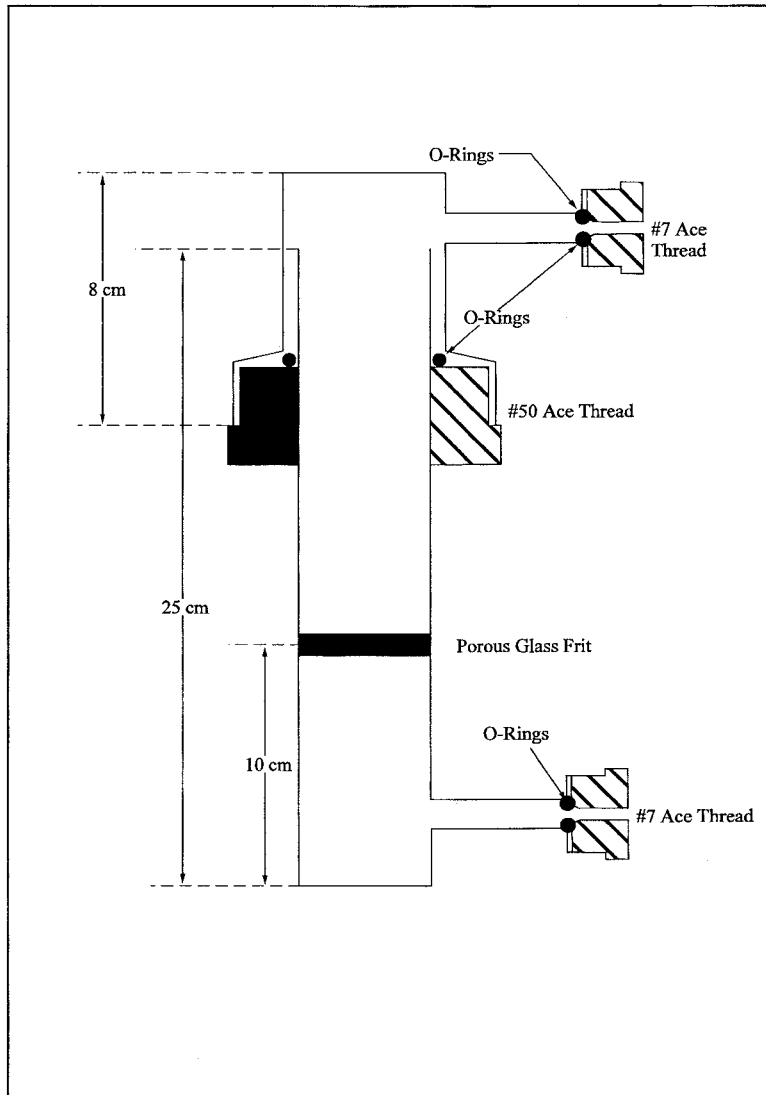


Figure 305-2. Schematic of Coalescing Filter.

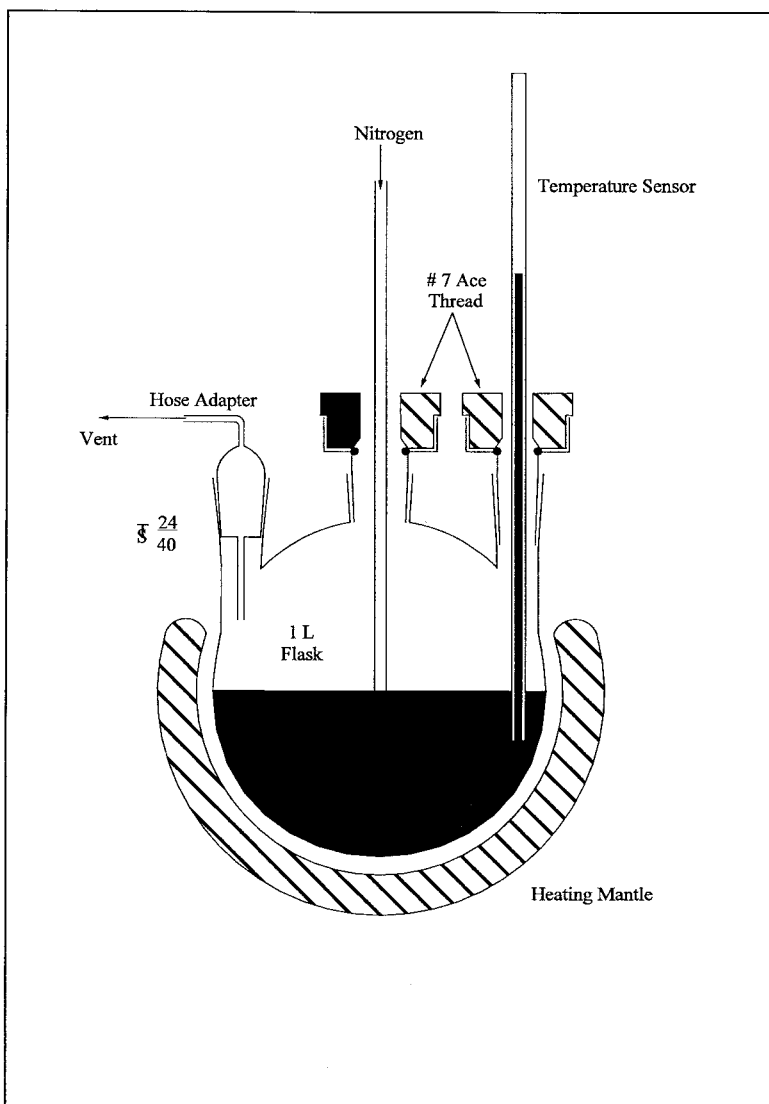


Figure 305-3. Schematic of PEG Cleaning System.

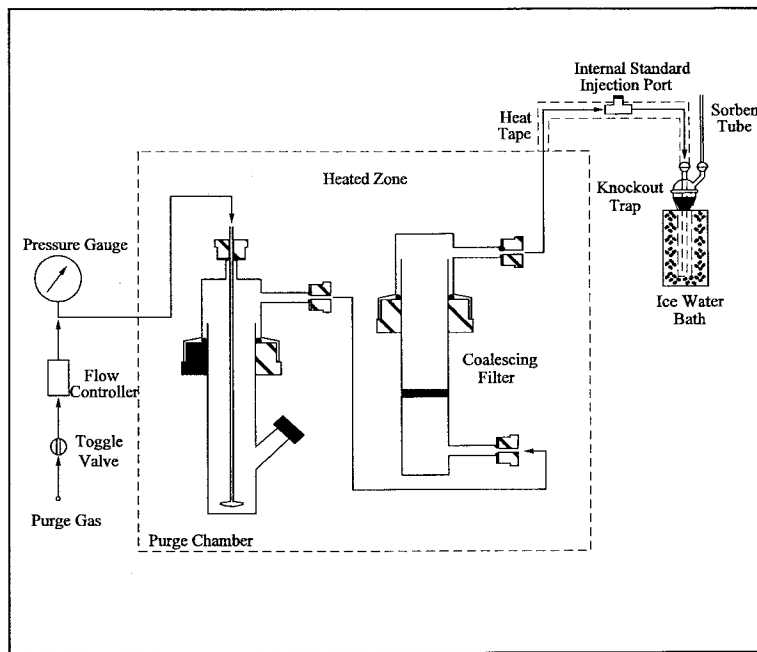


Figure 305-4. Schematic of Purge and Recovery Apparatus.

METHOD 306—DETERMINATION OF CHROMIUM EMISSIONS FROM DECORATIVE AND HARD CHROMIUM ELECTROPLATING AND CHROMIUM ANODIZING OPERATIONS—ISOKINETIC METHOD

Note: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in 40 CFR Part 60, Appendix A. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least Method 5.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Chromium	7440-47-3	See Sec. 13.2.

1.2 Applicability. This method applies to the determination of chromium (Cr) in emissions from decorative and hard chrome electroplating facilities, chromium anodizing operations, and continuous chromium plating operations at iron and steel facilities.

1.3 Data Quality Objectives. [Reserved]

2.0 Summary of Method

2.1 Sampling. An emission sample is extracted isokinetically from the source using an unheated Method 5 sampling train (40 CFR Part 60, Appendix A), with a glass nozzle and probe liner, but with the filter omit-

ted. The sample time shall be at least two hours. The Cr emissions are collected in an alkaline solution containing 0.1 N sodium hydroxide (NaOH) or 0.1 N sodium bicarbonate (NaHCO₃). The collected samples are recovered using an alkaline solution and are then transported to the laboratory for analysis.

2.2 Analysis.

2.2.1 Total chromium samples with high chromium concentrations ($\geq 35 \mu\text{g/L}$) may be analyzed using inductively coupled plasma emission spectrometry (ICP) at 267.72 nm.

NOTE: The ICP analysis is applicable for this method only when the solution analyzed

has a Cr concentration greater than or equal to 35 µg/L or five times the method detection limit as determined according to Appendix B in 40 CFR Part 136.

2.2.2 Alternatively, when lower total chromium concentrations (<35 µg/L) are encountered, a portion of the alkaline sample solution may be digested with nitric acid and analyzed by graphite furnace atomic absorption spectroscopy (GFAAS) at 357.9 nm.

2.2.3 If it is desirable to determine hexavalent chromium (Cr⁺⁶) emissions, the samples may be analyzed using an ion chromatograph equipped with a post-column reactor (IC/PCR) and a visible wavelength detector. To increase sensitivity for trace levels of Cr⁺⁶, a preconcentration system may be used in conjunction with the IC/PCR.

3.0 Definitions

3.1 *Total Chromium*—measured chromium content that includes both major chromium oxidation states (Cr⁺³, Cr⁺³).

3.2 *May*—Implies an optional operation.

3.3 *Digestion*—The analytical operation involving the complete (or nearly complete) dissolution of the sample in order to ensure the complete solubilization of the element (analyte) to be measured.

3.4 *Interferences*—Physical, chemical, or spectral phenomena that may produce a high or low bias in the analytical result.

3.5 *Analytical System*—All components of the analytical process including the sample digestion and measurement apparatus.

3.6 *Sample Recovery*—The quantitative transfer of sample from the collection apparatus to the sample preparation (digestion, etc.) apparatus. This term should not be confused with analytical recovery.

3.7 *Matrix Modifier*—A chemical modification to the sample during GFAAS determinations to ensure that the analyte is not lost during the measurement process (prior to the atomization stage)

3.8 *Calibration Reference Standards*—Quality control standards used to check the accuracy of the instrument calibration curve prior to sample analysis.

3.9 *Continuing Check Standard*—Quality control standards used to verify that unacceptable drift in the measurement system has not occurred.

3.10 *Calibration Blank*—A blank used to verify that there has been no unacceptable shift in the baseline either immediately following calibration or during the course of the analytical measurement.

3.11 *Interference Check*—An analytical/measurement operation that ascertains whether a measurable interference in the sample exists.

3.12 *Interelement Correction Factors*—Factors used to correct for interfering elements that produce a false signal (high bias).

3.13 *Duplicate Sample Analysis*—Either the repeat measurement of a single solution or

the measurement of duplicate preparations of the same sample. It is important to be aware of which approach is required for a particular type of measurement. For example, no digestion is required for the ICP determination and the duplicate instrument measurement is therefore adequate whereas duplicate digestion/instrument measurements are required for GFAAS.

3.14 *Matrix Spiking*—Analytical spikes that have been added to the actual sample matrix either before (Section 9.2.5.2) or after (Section 9.1.6). Spikes added to the sample *prior* to a preparation technique (*e.g.*, digestion) allow for the assessment of an overall method accuracy while those added *after* only provide for the *measurement* accuracy determination.

4.0 Interferences

4.1 ICP Interferences.

4.1.1 *ICP Spectral Interferences*. Spectral interferences are caused by: overlap of a spectral line from another element; unresolved overlap of molecular band spectra; background contribution from continuous or recombination phenomena; and, stray light from the line emission of high-concentrated elements. Spectral overlap may be compensated for by correcting the raw data with a computer and measuring the interfering element. At the 267.72 nm Cr analytical wavelength, iron, manganese, and uranium are potential interfering elements. Background and stray light interferences can usually be compensated for by a background correction adjacent to the analytical line. Unresolved overlap requires the selection of an alternative chromium wavelength. Consult the instrument manufacturer's operation manual for interference correction procedures.

4.1.2 *ICP Physical Interferences*. High levels of dissolved solids in the samples may cause significant inaccuracies due to salt buildup at the nebulizer and torch tips. This problem can be controlled by diluting the sample or by extending the rinse times between sample analyses. Standards shall be prepared in the same solution matrix as the samples (*i.e.*, 0.1 N NaOH or 0.1 N NaHCO₃).

4.1.3 *ICP Chemical Interferences*. These include molecular compound formation, ionization effects and solute vaporization effects, and are usually not significant in the ICP procedure, especially if the standards and samples are matrix matched.

4.2 GFAAS Interferences.

4.2.1 *GFAAS Chemical Interferences*. Low concentrations of calcium and/or phosphate may cause interferences; at concentrations above 200 µg/L, calcium's effect is constant

and eliminates the effect of phosphate. Calcium nitrate is therefore added to the concentrated analyte to ensure a known constant effect. Other matrix modifiers recommended by the instrument manufacturer may also be considered.

4.2.2 GFAAS Cyanide Band Interferences. Nitrogen should not be used as the purge gas due to cyanide band interference.

4.2.3 GFAAS Spectral Interferences. Background correction may be required because of possible significant levels of nonspecific absorption and scattering at the 357.9 nm analytical wavelength.

4.2.4 GFAAS Background Interferences. Zeeman or Smith-Hieftje background correction is recommended for interferences resulting from high levels of dissolved solids in the alkaline impinger solutions.

4.3 IC/PCR Interferences.

4.3.1 IC/PCR Chemical Interferences. Components in the sample matrix may cause Cr^{+6} to convert to trivalent chromium (Cr^{+3}) or cause Cr^{+3} to convert to Cr^{+6} . The chromatographic separation of Cr^{+6} using ion chromatography reduces the potential for other metals to interfere with the post column reaction. For the IC/PCR analysis, only compounds that coelute with Cr^{+6} and affect the diphenylcarbazide reaction will cause interference.

4.3.2 IC/PCR Background Interferences. Periodic analyses of reagent water blanks are used to demonstrate that the analytical system is essentially free of contamination. Sample cross-contamination can occur when high-level and low-level samples or standards are analyzed alternately and can be eliminated by thorough purging of the sample loop. Purging of the sample can easily be achieved by increasing the injection volume to ten times the size of the sample loop.

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Hexavalent chromium compounds have been listed as carcinogens although chromium (III) compounds show little or no toxicity. Chromium can be a skin and respiratory irritant.

6.0 Equipment and Supplies

6.1 Sampling Train.

6.1.1 A schematic of the sampling train used in this method is shown in Figure 306-1. The train is the same as shown in Method 5, Section 6.0 (40 CFR Part 60, Appendix A) except that the probe liner is unheated, the

particulate filter is omitted, and quartz or borosilicate glass must be used for the probe nozzle and liner in place of stainless steel.

6.1.2 Probe fittings of plastic such as Teflon, polypropylene, etc. are recommended over metal fittings to prevent contamination. If desired, a single combined probe nozzle and liner may be used, but such a single glass assembly is not a requirement of this methodology.

6.1.3 Use 0.1 N NaOH or 0.1 N NaHCO_3 in the impingers in place of water.

6.1.4 Operating and maintenance procedures for the sampling train are described in APTD-0576 of Method 5. Users should read the APTD-0576 document and adopt the outlined procedures.

6.1.5 Similar collection systems which have been approved by the Administrator may be used.

6.2 Sample Recovery. Same as Method 5, [40 CFR Part 60, Appendix A], with the following exceptions:

6.2.1 Probe-Liner and Probe-Nozzle Brushes. Brushes are not necessary for sample recovery. If a probe brush is used, it must be non-metallic.

6.2.2 Sample Recovery Solution. Use 0.1 N NaOH or 0.1 N NaHCO_3 , whichever is used as the impinger absorbing solution, in place of acetone to recover the sample.

6.2.3 Sample Storage Containers. Polyethylene, with leak-free screw cap, 250 mL, 500 mL or 1,000 mL.

6.3 Analysis.

6.3.1 General. For analysis, the following equipment is needed.

6.3.1.1 Phillips Beakers. (Phillips beakers are preferred, but regular beakers may also be used.)

6.3.1.2 Hot Plate.

6.3.1.3 Volumetric Flasks. Class A, various sizes as appropriate.

6.3.1.4 Assorted Pipettes.

6.3.2 Analysis by ICP.

6.3.2.1 ICP Spectrometer. Computer-controlled emission spectrometer with background correction and radio frequency generator.

6.3.2.2 Argon Gas Supply. Welding grade or better.

6.3.3 Analysis by GFAAS.

6.3.3.1 Chromium Hollow Cathode Lamp or Electrodeless Discharge Lamp.

6.3.3.2 Graphite Furnace Atomic Absorption Spectrophotometer.

6.3.3.3 Furnace Autosampler.

6.3.4 Analysis by IC/PCR.

6.3.4.1 IC/PCR System. High performance liquid chromatograph pump, sample injection valve, post-column reagent delivery and mixing system, and a visible detector, capable of operating at 520 nm-540 nm, all with a non-metallic (or inert) flow path. An electronic peak area mode is recommended, but

other recording devices and integration techniques are acceptable provided the repeatability criteria and the linearity criteria for the calibration curve described in Section 10.4 can be satisfied. A sample loading system is required if preconcentration is employed.

6.3.4.2 Analytical Column. A high performance ion chromatograph (HPIC) non-metallic column with anion separation characteristics and a high loading capacity designed for separation of metal chelating compounds to prevent metal interference. Resolution described in Section 11.6 must be obtained. A non-metallic guard column with the same ion-exchange material is recommended.

6.3.4.3 Preconcentration Column (for older instruments). An HPIC non-metallic column with acceptable anion retention characteristics and sample loading rates must be used as described in Section 11.6.

6.3.4.4 Filtration Apparatus for IC/PCR.

6.3.4.4.1 Teflon, or equivalent, filter holder to accommodate 0.45- μ m acetate, or equivalent, filter, if needed to remove insoluble particulate matter.

6.3.4.4.2 0.45- μ m Filter Cartridge. For the removal of insoluble material. To be used just prior to sample injection/analysis.

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, all reagents should conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society (ACS reagent grade). Where such specifications are not available, use the best available grade. Reagents should be checked by the appropriate analysis prior to field use to assure that contamination is below the analytical detection limit for the ICP or GFAAS total chromium analysis; and that contamination is below the analytical detection limit for Cr⁺⁶ using IC/PCR for direct injection or, if selected, preconcentration.

7.1 Sampling.

7.1.1 Water. Reagent water that conforms to ASTM Specification D1193-77 or 91 Type II (incorporated by reference see §63.14). All references to water in the method refer to reagent water unless otherwise specified. It is recommended that water blanks be checked prior to preparing the sampling reagents to ensure that the Cr content is less than three (3) times the anticipated detection limit of the analytical method.

7.1.2 Sodium Hydroxide (NaOH) Absorbing Solution, 0.1 N. Dissolve 4.0 g of sodium hydroxide in 1 liter of water to obtain a pH of approximately 8.5.

7.1.3 Sodium Bicarbonate (NaHCO₃) Absorbing Solution, 0.1 N. Dissolve approximately 8.5 g of sodium bicarbonate in 1 liter of water to obtain a pH of approximately 8.3.

7.1.4 Chromium Contamination.

7.1.4.1 The absorbing solution shall not exceed the QC criteria noted in Section 7.1.1 (≤ 3 times the instrument detection limit).

7.1.4.2 When the Cr⁺⁶ content in the field samples exceeds the blank concentration by at least a factor of ten (10), Cr⁺⁶ blank concentrations ≥ 10 times the detection limit will be allowed.

NOTE: At sources with high concentrations of acids and/or SO₂, the concentration of NaOH or NaHCO₃ should be ≥ 0.5 N to insure that the pH of the solution remains at or above 8.5 for NaOH and 8.0 for NaHCO₃ during and after sampling.

7.1.5 Silica Gel. Same as in Method 5.

7.2 Sample Recovery.

7.2.1 0.1 N NaOH or 0.1 N NaHCO₃. Use the same solution for the sample recovery that is used for the impinger absorbing solution.

7.2.2 pH Indicator Strip, for IC/PCR. pH indicator capable of determining the pH of solutions between the pH range of 7 and 12, at 0.5 pH increments.

7.3 Sample Preparation and Analysis.

7.3.1 Nitric Acid (HNO₃), Concentrated, for GFAAS. Trace metals grade or better HNO₃ must be used for reagent preparation. The ACS reagent grade HNO₃ is acceptable for cleaning glassware.

7.3.2 HNO₃, 1.0% (v/v), for GFAAS. Prepare, by slowly stirring, 10 mL of concentrated HNO₃ into 800 mL of reagent water. Dilute to 1,000 mL with reagent water. The solution shall contain less than 0.001 mg Cr/L.

7.3.3 Calcium Nitrate Ca(NO₃)₂ Solution (10 μ g Ca/mL) for GFAAS analysis. Prepare the solution by weighing 40.9 mg of Ca(NO₃)₂ into a 1 liter volumetric flask. Dilute with reagent water to 1 liter.

7.3.4 Matrix Modifier, for GFAAS. See instrument manufacturer's manual for suggested matrix modifier.

7.3.5 Chromatographic Eluent, for IC/PCR. The eluent used in the analytical system is ammonium sulfate based.

7.3.5.1 Prepare by adding 6.5 mL of 29 percent ammonium hydroxide (NH₄OH) and 33 g of ammonium sulfate ((NH₄)₂SO₄) to 500 mL of reagent water. Dilute to 1 liter with reagent water and mix well.

7.3.5.2 Other combinations of eluents and/or columns may be employed provided peak resolution, repeatability, linearity, and analytical sensitivity as described in Sections 9.3 and 11.6 are acceptable.

7.3.6 Post-Column Reagent, for IC/PCR. An effective post-column reagent for use with the chromatographic eluent described in Section 7.3.5 is a diphenylcarbazide (DPC)-based system. Dissolve 0.5 g of 1,5-diphenylcarbazide in 100 mL of ACS grade methanol. Add 500 mL of reagent water containing 50 mL of 96 percent spectrophotometric grade sulfuric acid. Dilute to 1 liter with reagent water.

7.3.7 Chromium Standard Stock Solution (1000 mg/L). Procure a certified aqueous standard or dissolve 2.829 g of potassium dichromate ($K_2Cr_2O_7$), in reagent water and dilute to 1 liter.

7.3.8 Calibration Standards for ICP or IC/PCR. Prepare calibration standards for ICP or IC/PCR by diluting the Cr standard stock solution (Section 7.3.7) with 0.1 N NaOH or 0.1 N $NaHCO_3$, whichever is used as the impinging absorbing solution, to achieve a matrix similar to the actual field samples. Suggested levels are 0, 50, 100, and 200 μg Cr/L for ICP, and 0, 1, 5, and 10 μg Cr^{+6} /L for IC/PCR.

7.3.9 Calibration Standards for GFAAS. Chromium solutions for GFAAS calibration shall contain 1.0 percent (v/v) HNO_3 . The zero standard shall be 1.0 percent (v/v) HNO_3 . Calibration standards should be prepared daily by diluting the Cr standard stock solution (Section 7.3.7) with 1.0 percent HNO_3 . Use at least four standards to make the calibration curve. Suggested levels are 0, 10, 50, and 100 μg Cr/L.

7.4 Glassware Cleaning Reagents.

7.4.1 HNO_3 , Concentrated. ACS reagent grade or equivalent.

7.4.2 Water. Reagent water that conforms to ASTM Specification D1193-77 or 91 Type II.

7.4.3 HNO_3 , 10 percent (v/v). Add by stirring 500 mL of concentrated HNO_3 into a flask containing approximately 4,000 mL of reagent water. Dilute to 5,000 mL with reagent water. Mix well. The reagent shall contain less than 2 μg Cr/L.

7.5 Quality Assurance Audit Samples.

7.5.1 When making compliance determinations, and upon availability, audit samples shall be obtained from the appropriate EPA regional Office or from the responsible enforcement authority and analyzed in conjunction with the field samples.

7.5.2 If EPA or National Institute of Standards and Technology (NIST) reference audit sample are not available, a mid-range standard, prepared from an independent commercial source, may be used.

NOTE: To order audit samples, contact the responsible enforcement authority at least 30 days prior to the test date to allow sufficient time for the audit sample to be delivered.

8.0 Sample Collection, Preservation, Holding Times, Storage, and Transport

NOTE: Prior to sample collection, consideration should be given to the type of analysis (Cr^{+6} or total Cr) that will be performed. Which analysis option(s) will be performed will determine which sample recovery and storage procedures will be required to process the sample (See Figures 306-3 and 306-4).

8.1 Sample Collection. Same as Method 5 (40 CFR part 60, Appendix A), with the following exceptions.

8.1.1 Omit the particulate filter and filter holder from the sampling train. Use a glass

nozzle and probe liner instead of stainless steel. Do not heat the probe. Place 100 mL of 0.1 N NaOH or 0.1 N $NaHCO_3$ in each of the first two impingers, and record the data for each run on a data sheet such as shown in Figure 306-2.

8.1.2 Clean all glassware prior to sampling in hot soapy water designed for laboratory cleaning of glassware. Next, rinse the glassware three times with tap water, followed by three additional rinses with reagent water. Then soak the glassware in 10% (v/v) HNO_3 solution for a minimum of 4 hours, rinse three times with reagent water, and allow to air dry. Cover all glassware openings where contamination can occur with Parafilm, or equivalent, until the sampling train is assembled for sampling.

8.1.3 Train Operation. Follow the basic procedures outlined in Method 5 in conjunction with the following instructions. Train sampling rate shall not exceed 0.030 m^3/min (1.0 cfm) during a run.

8.2 Sample Recovery. Follow the basic procedures of Method 5, with the exceptions noted.

8.2.1 A particulate filter is not recovered from this train.

8.2.2 Tester shall select either the total Cr or Cr^{+6} sample recovery option.

8.2.3 Samples to be analyzed for both total Cr and Cr^{+6} , shall be recovered using the Cr^{+6} sample option (Section 8.2.6).

8.2.4 A field reagent blank shall be collected for either of the Cr or the Cr^{+6} analysis. If both analyses (Cr and Cr^{+6}) are to be conducted on the samples, collect separate reagent blanks for each analysis.

NOTE: Since particulate matter is not usually present at chromium electroplating and/or chromium anodizing operations, it is not necessary to filter the Cr^{+6} samples unless there is observed sediment in the collected solutions. If it is necessary to filter the Cr^{+6} solutions, please refer to Method 0061, Determination of Hexavalent Chromium Emissions From Stationary Sources, Section 7.4, Sample Preparation in SW-846 (see Reference 1).

8.2.5 Total Cr Sample Option.

8.2.5.1 Container No. 1. Measure the volume of the liquid in the first, second, and third impingers and quantitatively transfer into a labeled sample container.

8.2.5.2 Use approximately 200 to 300 mL of the 0.1 N NaOH or 0.1 N $NaHCO_3$ absorbing solution to rinse the probe nozzle, probe liner, three impingers, and connecting glassware; add this rinse to Container No. 1.

8.2.6 Cr^{+6} Sample Option.

8.2.6.1 Container No. 1. Measure and record the pH of the absorbing solution contained in the first impinger at the end of the sampling run using a pH indicator strip. The pH of the solution must be ≥ 8.5 for NaOH and ≥ 8.0 for $NaHCO_3$. If it is not, discard the collected sample, increase the normality of the

NaOH or NaHCO₃ impinger absorbing solution to 0.5 N or to a solution normality approved by the Administrator and collect another air emission sample.

8.2.6.2 After determining the pH of the first impinger solution, combine and measure the volume of the liquid in the first, second, and third impingers and quantitatively transfer into the labeled sample container. Use approximately 200 to 300 mL of the 0.1 N NaOH or 0.1 N NaHCO₃ absorbing solution to rinse the probe nozzle, probe liner, three impingers, and connecting glassware; add this rinse to Container No. 1.

8.2.7 Field Reagent Blank.

8.2.7.1 Container No. 2.

8.2.7.2 Place approximately 500 mL of the 0.1 N NaOH or 0.1 N NaHCO₃ absorbing solution into a labeled sample container.

8.3 Sample Preservation, Storage, and Transport.

8.3.1 Total Cr Sample Option. Samples to be analyzed for total Cr need not be refrigerated.

8.3.2 Cr⁺⁶ Sample Option. Samples to be analyzed for Cr⁺⁶ must be shipped and stored at 4 °C. Allow Cr⁺⁶ samples to return to ambient temperature prior to analysis.

8.4 Sample Holding Times.

8.4.1 Total Cr Sample Option. Samples to be analyzed for total Cr shall be analyzed within 60 days of collection.

8.4.2 Cr⁺⁶ Sample Option. Samples to be analyzed for Cr⁺⁶ shall be analyzed within 14 days of collection.

9.0 Quality Control

9.1 ICP Quality Control.

9.1.1 ICP Calibration Reference Standards. Prepare a calibration reference standard using the same alkaline matrix as the calibration standards; it should be at least 10 times the instrumental detection limit.

9.1.1.1 This reference standard must be prepared from a different Cr stock solution source than that used for preparation of the calibration curve standards.

9.1.1.2 Prior to sample analysis, analyze at least one reference standard.

9.1.1.3 The calibration reference standard must be measured within 10 percent of its true value for the curve to be considered valid.

9.1.1.4 The curve must be validated before sample analyses are performed.

9.1.2 ICP Continuing Check Standard.

9.1.2.1 Perform analysis of the check standard with the field samples as described in Section 11.2 (at least after every 10 samples, and at the end of the analytical run).

9.1.2.2 The check standard can either be the mid-range calibration standard or the reference standard. The results of the check standard shall agree within 10 percent of the expected value; if not, terminate the analyses, correct the problem, recalibrate the instrument, and rerun all samples analyzed

subsequent to the last acceptable check standard analysis.

9.1.3 ICP Calibration Blank.

9.1.3.1 Perform analysis of the calibration blank with the field samples as described in Section 11.2 (at least after every 10 samples, and at the end of the analytical run).

9.1.3.2 The results of the calibration blank shall agree within three standard deviations of the mean blank value. If not, analyze the calibration blank two more times and average the results. If the average is not within three standard deviations of the background mean, terminate the analyses, correct the problem, recalibrate, and reanalyze all samples analyzed subsequent to the last acceptable calibration blank analysis.

9.1.4 ICP Interference Check. Prepare an interference check solution that contains known concentrations of interfering elements that will provide an adequate test of the correction factors in the event of potential spectral interferences.

9.1.4.1 Two potential interferences, iron and manganese, may be prepared as 1000 µg/mL and 200 µg/mL solutions, respectively. The solutions should be prepared in dilute HNO₃ (1-5 percent). Particular care must be used to ensure that the solutions and/or salts used to prepare the solutions are of ICP grade purity (*i.e.*, that no measurable Cr contamination exists in the salts/solutions). Commercially prepared interfering element check standards are available.

9.1.4.2 Verify the interelement correction factors every three months by analyzing the interference check solution. The correction factors are calculated according to the instrument manufacturer's directions. If the interelement correction factors are used properly, no false Cr should be detected.

9.1.4.3 Negative results with an absolute value greater than three (3) times the detection limit are usually the results of the background correction position being set incorrectly. Scan the spectral region to ensure that the correction position has not been placed on an interfering peak.

9.1.5 ICP Duplicate Sample Analysis. Perform one duplicate sample analysis for each compliance sample batch (3 runs).

9.1.5.1 As there is no sample preparation required for the ICP analysis, a duplicate analysis is defined as a repeat analysis of one of the field samples. The selected sample shall be analyzed using the same procedures that were used to analyze the original sample.

9.1.5.2 Duplicate sample analyses shall agree within 10 percent of the original measurement value.

9.1.5.3 Report the original analysis value for the sample and report the duplicate analysis value as the QC check value. If agreement is not achieved, perform the duplicate analysis again. If agreement is not achieved the second time, perform corrective action

to identify and correct the problem before analyzing the sample for a third time.

9.1.6 ICP Matrix Spiking. Spiked samples shall be prepared and analyzed daily to ensure that there are no matrix effects, that samples and standards have been matrix-matched, and that the laboratory equipment is operating properly.

9.1.6.1 Spiked sample recovery analyses should indicate a recovery for the Cr spike of between 75 and 125 percent.

9.1.6.2 Cr levels in the spiked sample should provide final solution concentrations that are within the linear portion of the calibration curve, as well as, at a concentration level at least: equal to that of the original sample; and, ten (10) times the detection limit.

9.1.6.3 If the spiked sample concentration meets the stated criteria but exceeds the linear calibration range, the spiked sample must be diluted with the field absorbing solution.

9.1.6.4 If the recoveries for the Cr spiked samples do not meet the specified criteria, perform corrective action to identify and correct the problem prior to reanalyzing the samples.

9.1.7 ICP Field Reagent Blank.

9.1.7.1 Analyze a minimum of one matrix-matched field reagent blank (Section 8.2.4) per sample batch to determine if contamination or memory effects are occurring.

9.1.7.2 If contamination or memory effects are observed, perform corrective action to identify and correct the problem before re-analyzing the samples.

9.1.8 Audit Sample Analysis.

9.1.8.1 When the method is used to analyze samples to demonstrate compliance with a source emission regulation, an audit sample must be analyzed, subject to availability.

9.1.8.2 Concurrently analyze the audit sample and the compliance samples in the same manner to evaluate the technique of the analyst and the standards preparation.

9.1.8.3 The same analyst, analytical reagents, and analytical system shall be used for the compliance samples and the audit sample. If this condition is met, duplicate auditing of subsequent compliance analyses for the same enforcement agency within a 30-day period is waived. An audit sample set may not be used to validate different sets of compliance samples under the jurisdiction of separate enforcement agencies, unless prior arrangements have been made with both enforcement agencies.

9.1.9 Audit Sample Results.

9.1.9.1 Calculate the audit sample concentrations and submit results using the instructions provided with the audit samples.

9.1.9.2 Report the results of the audit samples and the compliance determination samples along with their identification numbers, and the analyst's name to the responsible enforcement authority. Include this informa-

tion with reports of any subsequent compliance analyses for the same enforcement authority during the 30-day period.

9.1.9.3 The concentrations of the audit samples obtained by the analyst shall agree within the values specified by the compliance auditor. If the specified range is not met, reanalyze the compliance and audit samples, and include initial and reanalysis values in the test report.

9.1.9.4 Failure to meet the specified range may require retests unless the audit problems are resolved. However, if the audit results do not affect the compliance or non-compliance status of the affected facility, the Administrator may waive the reanalysis requirement, further audits, or retests and accept the results of the compliance test. While steps are being taken to resolve audit analysis problems, the Administrator may also choose to use the data to determine the compliance or noncompliance status of the affected facility.

9.2 GFAAS Quality Control.

9.2.1 GFAAS Calibration Reference Standards. The calibration curve must be verified by using at least one calibration reference standard (made from a reference material or other independent standard material) at or near the mid-range of the calibration curve.

9.2.1.1 The calibration curve must be validated before sample analyses are performed.

9.2.1.2 The calibration reference standard must be measured within 10 percent of its true value for the curve to be considered valid.

9.2.2 GFAAS Continuing Check Standard.

9.2.2.1 Perform analysis of the check standard with the field samples as described in Section 11.4 (at least after every 10 samples, and at the end of the analytical run).

9.2.2.2 These standards are analyzed, in part, to monitor the life and performance of the graphite tube. Lack of reproducibility or a significant change in the signal for the check standard may indicate that the graphite tube should be replaced.

9.2.2.3 The check standard may be either the mid-range calibration standard or the reference standard.

9.2.2.4 The results of the check standard shall agree within 10 percent of the expected value.

9.2.2.5 If not, terminate the analyses, correct the problem, recalibrate the instrument, and reanalyze all samples analyzed subsequent to the last acceptable check standard analysis.

9.2.3 GFAAS Calibration Blank.

9.2.3.1 Perform analysis of the calibration blank with the field samples as described in Section 11.4 (at least after every 10 samples, and at the end of the analytical run).

9.2.3.2 The calibration blank is analyzed to monitor the life and performance of the graphite tube as well as the existence of any memory effects. Lack of reproducibility or a

significant change in the signal, may indicate that the graphite tube should be replaced.

9.2.3.3 The results of the calibration blank shall agree within three standard deviations of the mean blank value.

9.2.3.4 If not, analyze the calibration blank two more times and average the results. If the average is not within three standard deviations of the background mean, terminate the analyses, correct the problem, recalibrate, and reanalyze all samples analyzed subsequent to the last acceptable calibration blank analysis.

9.2.4 GFAAS Duplicate Sample Analysis. Perform one duplicate sample analysis for each compliance sample batch (3 runs).

9.2.4.1 A digested aliquot of the selected sample is processed and analyzed using the identical procedures that were used for the whole sample preparation and analytical efforts.

9.2.4.2 Duplicate sample analyses results incorporating duplicate digestions shall agree within 20 percent for sample results exceeding ten (10) times the detection limit.

9.2.4.3 Report the original analysis value for the sample and report the duplicate analysis value as the QC check value.

9.2.4.4 If agreement is not achieved, perform the duplicate analysis again. If agreement is not achieved the second time, perform corrective action to identify and correct the problem before analyzing the sample for a third time.

9.2.5 GFAAS Matrix Spiking.

9.2.5.1 Spiked samples shall be prepared and analyzed daily to ensure that (1) correct procedures are being followed, (2) there are no matrix effects and (3) all equipment is operating properly.

9.2.5.2 Cr spikes are added prior to any sample preparation.

9.2.5.3 Cr levels in the spiked sample should provide final solution concentrations that are within the linear portion of the calibration curve, as well as, at a concentration level at least: equal to that of the original sample; and, ten (10) times the detection limit.

9.2.5.4 Spiked sample recovery analyses should indicate a recovery for the Cr spike of between 75 and 125 percent.

9.2.5.5 If the recoveries for the Cr spiked samples do not meet the specified criteria, perform corrective action to identify and correct the problem prior to reanalyzing the samples.

9.2.6 GFAAS Method of Standard Additions.

9.2.6.1 Method of Standard Additions. Perform procedures in Section 5.4 of Method 12 (40 CFR Part 60, Appendix A)

9.2.6.2 Whenever sample matrix problems are suspected and standard/sample matrix matching is not possible or whenever a new sample matrix is being analyzed, perform

referenced procedures to determine if the method of standard additions is necessary.

9.2.7 GFAAS Field Reagent Blank.

9.2.7.1 Analyze a minimum of one matrix-matched field reagent blank (Section 8.2.4) per sample batch to determine if contamination or memory effects are occurring.

9.2.7.2 If contamination or memory effects are observed, perform corrective action to identify and correct the problem before re-analyzing the samples.

9.2.8 Audit Sample Analysis.

9.2.8.1 When the method is used to analyze samples to demonstrate compliance with a source emission regulation, an audit sample must be analyzed, subject to availability.

9.2.8.2 Concurrently analyze the audit sample and the compliance samples in the same manner to evaluate the technique of the analyst and the standards preparation.

9.2.8.3 The same analyst, analytical reagents, and analytical system shall be used for the compliance samples and the audit sample. If this condition is met, duplicate auditing of subsequent compliance analyses for the same enforcement agency within a 30-day period is waived. An audit sample set may not be used to validate different sets of compliance samples under the jurisdiction of separate enforcement agencies, unless prior arrangements have been made with both enforcement agencies.

9.2.9 Audit Sample Results.

9.2.9.1 Calculate the audit sample concentrations and submit results using the instructions provided with the audit samples.

9.2.9.2 Report the results of the audit samples and the compliance determination samples along with their identification numbers, and the analyst's name to the responsible enforcement authority. Include this information with reports of any subsequent compliance analyses for the same enforcement authority during the 30-day period.

9.2.9.3 The concentrations of the audit samples obtained by the analyst shall agree within the values specified by the compliance auditor. If the specified range is not met, reanalyze the compliance and audit samples, and include initial and reanalysis values in the test report.

9.2.9.4 Failure to meet the specified range may require retests unless the audit problems are resolved. However, if the audit results do not affect the compliance or non-compliance status of the affected facility, the Administrator may waive the reanalysis requirement, further audits, or retests and accept the results of the compliance test. While steps are being taken to resolve audit analysis problems, the Administrator may also choose to use the data to determine the compliance or noncompliance status of the affected facility.

9.3 IC/PCR Quality Control.

9.3.1 IC/PCR Calibration Reference Standards.

9.3.1.1 Prepare a calibration reference standard at a concentration that is at or near the mid-point of the calibration curve using the same alkaline matrix as the calibration standards. This reference standard should be prepared from a different Cr stock solution than that used to prepare the calibration curve standards. The reference standard is used to verify the accuracy of the calibration curve.

9.3.1.2 The curve must be validated before sample analyses are performed. Prior to sample analysis, analyze at least one reference standard with an expected value within the calibration range.

9.3.1.3 The results of this reference standard analysis must be within 10 percent of the true value of the reference standard for the calibration curve to be considered valid.

9.3.2 IC/PCR Continuing Check Standard and Calibration Blank.

9.3.2.1 Perform analysis of the check standard and the calibration blank with the field samples as described in Section 11.6 (at least after every 10 samples, and at the end of the analytical run).

9.3.2.2 The result from the check standard must be within 10 percent of the expected value.

9.3.2.3 If the 10 percent criteria is exceeded, excessive drift and/or instrument degradation may have occurred, and must be corrected before further analyses can be performed.

9.3.2.4 The results of the calibration blank analyses must agree within three standard deviations of the mean blank value.

9.3.2.5 If not, analyze the calibration blank two more times and average the results.

9.3.2.6 If the average is not within three standard deviations of the background mean, terminate the analyses, correct the problem, recalibrate, and reanalyze all samples analyzed subsequent to the last acceptable calibration blank analysis.

9.3.3 IC/PCR Duplicate Sample Analysis.

9.3.3.1 Perform one duplicate sample analysis for each compliance sample batch (3 runs).

9.3.3.2 An aliquot of the selected sample is prepared and analyzed using procedures identical to those used for the emission samples (for example, filtration and/or, if necessary, preconcentration).

9.3.3.3 Duplicate sample injection results shall agree within 10 percent for sample results exceeding ten (10) times the detection limit.

9.3.3.4 Report the original analysis value for the sample and report the duplicate analysis value as the QC check value.

9.3.3.5 If agreement is not achieved, perform the duplicate analysis again.

9.3.3.6 If agreement is not achieved the second time, perform corrective action to

identify and correct the problem prior to analyzing the sample for a third time.

9.3.4 ICP/PCR Matrix Spiking. Spiked samples shall be prepared and analyzed with each sample set to ensure that there are no matrix effects, that samples and standards have been matrix-matched, and that the equipment is operating properly.

9.3.4.1 Spiked sample recovery analysis should indicate a recovery of the Cr⁺⁶ spike between 75 and 125 percent.

9.3.4.2 The spiked sample concentration should be within the linear portion of the calibration curve and should be equal to or greater than the concentration of the original sample. In addition, the spiked sample concentration should be at least ten (10) times the detection limit.

9.3.4.3 If the recoveries for the Cr⁺⁶ spiked samples do not meet the specified criteria, perform corrective action to identify and correct the problem prior to reanalyzing the samples.

9.3.5 IC/PCR Field Reagent Blank.

9.3.5.1 Analyze a minimum of one matrix-matched field reagent blank (Section 8.2.4) per sample batch to determine if contamination or memory effects are occurring.

9.3.5.2 If contamination or memory effects are observed, perform corrective action to identify and correct the problem before reanalyzing the samples.

9.3.6 Audit Sample Analysis.

9.3.6.1 When the method is used to analyze samples to demonstrate compliance with source emission regulation, an audit sample must be analyzed, subject to availability.

9.3.6.2 Concurrently analyze the audit sample and the compliance samples in the same manner to evaluate the technique of the analyst and the standards preparation.

9.3.6.3 The same analyst, analytical reagents, and analytical system shall be used for the compliance samples and the audit sample. If this condition is met, duplicate auditing of subsequent compliance analyses for the same enforcement agency within a 30-day period is waived. An audit sample set may not be used to validate different sets of compliance samples under the jurisdiction of separate enforcement agencies, unless prior arrangements have been made with both enforcement agencies.

9.3.7 Audit Sample Results.

9.3.7.1 Calculate the audit sample concentrations and submit results using the instructions provided with the audit samples.

9.3.7.2 Report the results of the audit samples and the compliance determination samples along with their identification numbers, and the analyst's name to the responsible enforcement authority. Include this information with reports of any subsequent compliance analyses for the same enforcement authority during the 30-day period.

9.3.7.3 The concentrations of the audit samples obtained by the analyst shall agree

within the values specified by the compliance auditor. If the specified range is not met, reanalyze the compliance and audit samples, and include initial and reanalysis values in the test report.

9.3.7.4 Failure to meet the specified range may require retests unless the audit problems are resolved. However, if the audit results do not affect the compliance or non-compliance status of the affected facility, the Administrator may waive the reanalysis requirement, further audits, or retests and accept the results of the compliance test. While steps are being taken to resolve audit analysis problems, the Administrator may also choose to use the data to determine the compliance or noncompliance status of the affected facility.

10.0 Calibration and Standardization

10.1 Sampling Train Calibration. Perform calibrations described in Method 5, (40 CFR Part 60, Appendix A). The alternate calibration procedures described in Method 5, may also be used.

10.2 ICP Calibration.

10.2.1 Calibrate the instrument according to the instrument manufacturer's recommended procedures, using a calibration blank and three standards for the initial calibration.

10.2.2 Calibration standards should be prepared fresh daily, as described in Section 7.3.8. Be sure that samples and calibration standards are matrix matched. Flush the system with the calibration blank between each standard.

10.2.3 Use the average intensity of multiple exposures (3 or more) for both standardization and sample analysis to reduce random error.

10.2.4 Employing linear regression, calculate the correlation coefficient.

10.2.5 The correlation coefficient must equal or exceed 0.995.

10.2.6 If linearity is not acceptable, prepare and rerun another set of calibration standards or reduce the range of the calibration standards, as necessary.

10.3 GFAAS Calibration.

10.3.1 For instruments that measure directly in concentration, set the instrument software to display the correct concentration, if applicable.

10.3.2 Curve must be linear in order to correctly perform the method of standard additions which is customarily performed automatically with most instrument computer-based data systems.

10.3.3 The calibration curve (direct calibration or standard additions) must be prepared daily with a minimum of a calibration blank and three standards that are prepared fresh daily.

10.3.4 The calibration curve acceptance criteria must equal or exceed 0.995.

10.3.5 If linearity is not acceptable, prepare and rerun another set of calibration standards or reduce the range of calibration standards, as necessary.

10.4 IC/PCR Calibration.

10.4.1 Prepare a calibration curve using the calibration blank and three calibration standards prepared fresh daily as described in Section 7.3.8.

10.4.2 The calibration curve acceptance criteria must equal or exceed 0.995.

10.4.3 If linearity is not acceptable, remake and/or rerun the calibration standards. If the calibration curve is still unacceptable, reduce the range of the curve.

10.4.4 Analyze the standards with the field samples as described in Section 11.6.

11.0 Analytical Procedures

NOTE: The method determines the chromium concentration in $\mu\text{g Cr/mL}$. It is important that the analyst measure the field sample volume prior to analyzing the sample. This will allow for conversion of $\mu\text{g Cr/mL}$ to $\mu\text{g Cr/sample}$.

11.1 ICP Sample Preparation.

11.1.1 The ICP analysis is performed directly on the alkaline impinger solution; acid digestion is not necessary, provided the samples and standards are matrix matched.

11.1.2 The ICP analysis should only be employed when the solution analyzed has a Cr concentration greater than 35 $\mu\text{g/L}$ or five times the method detection limit as determined according to Appendix B in 40 CFR Part 136 or by other commonly accepted analytical procedures.

11.2 ICP Sample Analysis.

11.2.1 The ICP analysis is applicable for the determination of total chromium only.

11.2.2 ICP Blanks. Two types of blanks are required for the ICP analysis.

11.2.2.1 Calibration Blank. The calibration blank is used in establishing the calibration curve. For the calibration blank, use either 0.1 N NaOH or 0.1 N NaHCO_3 , whichever is used for the impinger absorbing solution. The calibration blank can be prepared fresh in the laboratory; it does not have to be prepared from the same batch of solution that was used in the field. A sufficient quantity should be prepared to flush the system between standards and samples.

11.2.2.2 Field Reagent Blank. The field reagent blank is collected in the field during the testing program. The field reagent blank (Section 8.2.4) is an aliquot of the absorbing solution prepared in Section 7.1.2. The reagent blank is used to assess possible contamination resulting from sample processing.

11.2.3 ICP Instrument Adjustment.

11.2.3.1 Adjust the ICP instrument for proper operating parameters including wavelength, background correction settings (if

necessary), and interfering element correction settings (if necessary).

11.2.3.2 The instrument must be allowed to become thermally stable before beginning measurements (usually requiring at least 30 min of operation prior to calibration). During this warmup period, the optical calibration and torch position optimization may be performed (consult the operator's manual).

11.2.4 ICP Instrument Calibration.

11.2.4.1 Calibrate the instrument according to the instrument manufacturer's recommended procedures, and the procedures specified in Section 10.2.

11.2.4.2 Prior to analyzing the field samples, reanalyze the highest calibration standard as if it were a sample.

11.2.4.3 Concentration values obtained should not deviate from the actual values or from the established control limits by more than 5 percent, whichever is lower (see Sections 9.1 and 10.2).

11.2.4.4 If they do, follow the recommendations of the instrument manufacturer to correct the problem.

11.2.5 ICP Operational Quality Control Procedures.

11.2.5.1 Flush the system with the calibration blank solution for at least 1 min before the analysis of each sample or standard.

11.2.5.2 Analyze the continuing check standard and the calibration blank after each batch of 10 samples.

11.2.5.3 Use the average intensity of multiple exposures for both standardization and sample analysis to reduce random error.

11.2.6 ICP Sample Dilution.

11.2.6.1 Dilute and reanalyze samples that are more concentrated than the linear calibration limit or use an alternate, less sensitive Cr wavelength for which quality control data have already been established.

11.2.6.2 When dilutions are performed, the appropriate factors must be applied to sample measurement results.

11.2.7 Reporting Analytical Results. All analytical results should be reported in $\mu\text{g Cr/mL}$ using three significant figures. Field sample volumes (mL) must be reported also.

11.3 GFAAS Sample Preparation.

11.3.1 GFAAS Acid Digestion. An acid digestion of the alkaline impinger solution is required for the GFAAS analysis.

11.3.1.1 In a beaker, add 10 mL of concentrated HNO_3 to a 100 mL sample aliquot that has been well mixed. Cover the beaker with a watch glass. Place the beaker on a hot plate and reflux the sample to near dryness. Add another 5 mL of concentrated HNO_3 to complete the digestion. Again, carefully reflux the sample volume to near dryness. Rinse the beaker walls and watch glass with reagent water.

11.3.1.2 The final concentration of HNO_3 in the solution should be 1 percent (v/v).

11.3.1.3 Transfer the digested sample to a 50-mL volumetric flask. Add 0.5 mL of con-

centrated HNO_3 and 1 mL of the 10 $\mu\text{g/mL}$ of $\text{Ca}(\text{NO}_3)_2$. Dilute to 50 mL with reagent water.

11.3.2 HNO_3 Concentration. A different final volume may be used based on the expected Cr concentration, but the HNO_3 concentration must be maintained at 1 percent (v/v).

11.4 GFAAS Sample Analysis.

11.4.1 The GFAAS analysis is applicable for the determination of total chromium only.

11.4.2 GFAAS Blanks. Two types of blanks are required for the GFAAS analysis.

11.4.2.1 Calibration Blank. The 1.0 percent HNO_3 is the calibration blank which is used in establishing the calibration curve.

11.4.2.2 Field Reagent Blank. An aliquot of the 0.1 N NaOH solution or the 0.1 N NaHCO_3 prepared in Section 7.1.2 is collected for the field reagent blank. The field reagent blank is used to assess possible contamination resulting from processing the sample.

11.4.2.2.1 The reagent blank must be subjected to the entire series of sample preparation and analytical procedures, including the acid digestion.

11.4.2.2.2 The reagent blank's final solution must contain the same acid concentration as the sample solutions.

11.4.3 GFAAS Instrument Adjustment.

11.4.3.1 The 357.9 nm wavelength line shall be used.

11.4.3.2 Follow the manufacturer's instructions for all other spectrophotometer operating parameters.

11.4.4 Furnace Operational Parameters. Parameters suggested by the manufacturer should be employed as guidelines.

11.4.4.1 Temperature-sensing mechanisms and temperature controllers can vary between instruments and/or with time; the validity of the furnace operating parameters must be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to higher-than-necessary temperature settings or losses in sensitivity due to less than optimum settings can be minimized.

11.4.4.2 Similar verification of furnace operating parameters may be required for complex sample matrices (consult instrument manual for additional information). Calibrate the GFAAS system following the procedures specified in Section 10.3.

11.4.5 GFAAS Operational Quality Control Procedures.

11.4.5.1 Introduce a measured aliquot of digested sample into the furnace and atomize.

11.4.5.2 If the measured concentration exceeds the calibration range, the sample should be diluted with the calibration blank solution (1.0 percent HNO_3) and reanalyzed.

11.4.5.3 Consult the operator's manual for suggested injection volumes. The use of multiple injections can improve accuracy and assist in detecting furnace pipetting errors.

11.4.5.4 Analyze a minimum of one matrix-matched reagent blank per sample batch to determine if contamination or any memory effects are occurring.

11.4.5.5 Analyze a calibration blank and a continuing check standard after approximately every batch of 10 sample injections.

11.4.6 GFAAS Sample Dilution.

11.4.6.1 Dilute and reanalyze samples that are more concentrated than the instrument calibration range.

11.4.6.2 If dilutions are performed, the appropriate factors must be applied to sample measurement results.

11.4.7 Reporting Analytical Results.

11.4.7.1 Calculate the Cr concentrations by the method of standard additions (see operator's manual) or, from direct calibration. All dilution and/or concentration factors must be used when calculating the results.

11.4.7.2 Analytical results should be reported in $\mu\text{g Cr/mL}$ using three significant figures. Field sample volumes (mL) must be reported also.

11.5 IC/PCR Sample Preparation.

11.5.1 Sample pH. Measure and record the sample pH prior to analysis.

11.5.2 Sample Filtration. Prior to preconcentration and/or analysis, filter all field samples through a 0.45- μm filter. The filtration step should be conducted just prior to sample injection/analysis.

11.5.2.1 Use a portion of the sample to rinse the syringe filtration unit and acetate filter and then collect the required volume of filtrate.

11.5.2.2 Retain the filter if total Cr is to be determined also.

11.5.3 Sample Preconcentration (older instruments).

11.5.3.1 For older instruments, a preconcentration system may be used in conjunction with the IC/PCR to increase sensitivity for trace levels of Cr^{+6} .

11.5.3.2 The preconcentration is accomplished by selectively retaining the analyte on a solid absorbent, followed by removal of the analyte from the absorbent (consult instrument manual).

11.5.3.3 For a manual system, position the injection valve so that the eluent displaces the concentrated Cr^{+6} sample, transferring it from the preconcentration column and onto the IC anion separation column.

11.6 IC/PCR Sample Analyses.

11.6.1 The IC/PCR analysis is applicable for hexavalent chromium measurements only.

11.6.2 IC/PCR Blanks. Two types of blanks are required for the IC/PCR analysis.

11.6.2.1 Calibration Blank. The calibration blank is used in establishing the analytical curve. For the calibration blank, use either

0.1 N NaOH or 0.1 N NaHCO_3 , whichever is used for the impinger solution. The calibration blank can be prepared fresh in the laboratory; it does not have to be prepared from the same batch of absorbing solution that is used in the field.

11.6.2.2 Field Reagent Blank. An aliquot of the 0.1 N NaOH solution or the 0.1 N NaHCO_3 solution prepared in Section 7.1.2 is collected for the field reagent blank. The field reagent blank is used to assess possible contamination resulting from processing the sample.

11.6.3 Stabilized Baseline. Prior to sample analysis, establish a stable baseline with the detector set at the required attenuation by setting the eluent and post-column reagent flow rates according to the manufacturers recommendations.

NOTE: As long as the ratio of eluent flow rate to PCR flow rate remains constant, the standard curve should remain linear. Inject a sample of reagent water to ensure that no Cr^{+6} appears in the water blank.

11.6.4 Sample Injection Loop. Size of injection loop is based on standard/sample concentrations and the selected attenuator setting.

11.6.4.1 A 50- μL loop is normally sufficient for most higher concentrations.

11.6.4.2 The sample volume used to load the injection loop should be at least 10 times the loop size so that all tubing in contact with the sample is thoroughly flushed with the new sample to prevent cross contamination.

11.6.5 IC/PCR Instrument Calibration.

11.6.5.1 First, inject the calibration standards prepared, as described in Section 7.3.8 to correspond to the appropriate concentration range, starting with the lowest standard first.

11.6.5.2 Check the performance of the instrument and verify the calibration using data gathered from analyses of laboratory blanks, calibration standards, and a quality control sample.

11.6.5.3 Verify the calibration by analyzing a calibration reference standard. If the measured concentration exceeds the established value by more than 10 percent, perform a second analysis. If the measured concentration still exceeds the established value by more than 10 percent, terminate the analysis until the problem can be identified and corrected.

11.6.6 IC/PCR Instrument Operation.

11.6.6.1 Inject the calibration reference standard (as described in Section 9.3.1), followed by the field reagent blank (Section 8.2.4), and the field samples.

11.6.6.1.1 Standards (and QC standards) and samples are injected into the sample loop of the desired size (use a larger size loop for greater sensitivity). The Cr^{+6} is collected on the resin bed of the column.

11.6.6.1.2 After separation from other sample components, the Cr⁺⁶ forms a specific complex in the post-column reactor with the DPC reaction solution, and the complex is detected by visible absorbance at a maximum wavelength of 540 nm.

11.6.6.1.3 The amount of absorbance measured is proportional to the concentration of the Cr⁺⁶ complex formed.

11.6.6.1.4 The IC retention time and the absorbance of the Cr⁺⁶ complex with known Cr⁺⁶ standards analyzed under identical conditions must be compared to provide both qualitative and quantitative analyses.

11.6.6.1.5 If a sample peak appears near the expected retention time of the Cr⁺⁶ ion, spike the sample according to Section 9.3.4 to verify peak identity.

11.6.7 IC/PCR Operational Quality Control Procedures.

11.6.7.1 Samples should be at a pH ≥ 8.5 for NaOH and ≥ 8.0 if using NaHCO₃; document any discrepancies.

11.6.7.2 Refrigerated samples should be allowed to equilibrate to ambient temperature prior to preparation and analysis.

11.6.7.3 Repeat the injection of the calibration standards at the end of the analytical run to assess instrument drift. Measure areas or heights of the Cr⁺⁶/DPC complex chromatogram peaks.

11.6.7.4 To ensure the precision of the sample injection (manual or autosampler), the response for the second set of injected standards must be within 10 percent of the average response.

11.6.7.5 If the 10 percent criteria duplicate injection cannot be achieved, identify the source of the problem and rerun the calibration standards.

11.6.7.6 Use peak areas or peak heights from the injections of calibration standards to generate a linear calibration curve. From the calibration curve, determine the concentrations of the field samples.

11.6.8 IC/PCR Sample Dilution.

11.6.8.1 Samples having concentrations higher than the established calibration range must be diluted into the calibration range and re-analyzed.

11.6.8.2 If dilutions are performed, the appropriate factors must be applied to sample measurement results.

11.6.9 Reporting Analytical Results. Results should be reported in $\mu\text{g Cr}^{+6}/\text{mL}$ using three significant figures. Field sample volumes (mL) must be reported also.

12.0 Data Analysis and Calculations

12.1 Pretest Calculations.

12.1.1 Pretest Protocol (Site Test Plan).

12.1.1.1 The pretest protocol should define and address the test data quality objectives (DQOs), with all assumptions, that will be re-

quired by the end user (enforcement authority); what data are needed? why are the data needed? how will the data be used? what are method detection limits? and what are estimated target analyte levels for the following test parameters.

12.1.1.1.1 Estimated source concentration for total chromium and/or Cr⁺⁶.

12.1.1.1.2 Estimated minimum sampling time and/or volume required to meet method detection limit requirements (Appendix B 40 CFR Part 136) for measurement of total chromium and/or Cr⁺⁶.

12.1.1.1.3 Demonstrate that planned sampling parameters will meet DQOs. The protocol must demonstrate that the planned sampling parameters calculated by the tester will meet the needs of the source and the enforcement authority.

12.1.1.2 The pre-test protocol should include information on equipment, logistics, personnel, process operation, and other resources necessary for an efficient and coordinated test.

12.1.1.3 At a minimum, the pre-test protocol should identify and be approved by the source, the tester, the analytical laboratory, and the regulatory enforcement authority. The tester should not proceed with the compliance testing before obtaining approval from the enforcement authority.

12.1.2 Post Test Calculations.

12.1.2.1 Perform the calculations, retaining one extra decimal figure beyond that of the acquired data. Round off figures after final calculations.

12.1.2.2 Nomenclature.

C_s = Concentration of Cr in sample solution, $\mu\text{g Cr}/\text{mL}$.

C_{cr} = Concentration of Cr in stack gas, dry basis, corrected to standard conditions, mg/dscm .

D = Digestion factor, dimension less.

F = Dilution factor, dimension less.

M_{Cr} = Total Cr in each sample, μg .

V_{ad} = Volume of sample aliquot after digestion, mL.

V_{af} = Volume of sample aliquot after dilution, mL.

V_{bd} = Volume of sample aliquot submitted to digestion, mL.

V_{br} = Volume of sample aliquot before dilution, mL.

V_{mL} = Volume of impinger contents plus rinses, mL.

V_{m(std)} = Volume of gas sample measured by the dry gas meter, corrected to standard conditions, dscm .

12.1.2.3 Dilution Factor. The dilution factor is the ratio of the volume of sample aliquot after dilution to the volume before dilution. This ratio is given by the following equation:

$$F = \frac{V_{af}}{V_{bf}} \quad \text{Eq. 306-1}$$

12.1.2.4 Digestion Factor. The digestion factor is the ratio of the volume of sample aliquot after digestion to the volume before

digestion. This ratio is given by Equation 306-2.

$$D = \frac{V_{ad}}{V_{bd}} \quad \text{Eq. 306-2}$$

12.1.2.5 Total Cr in Sample. Calculate M_{Cr}, the total µg Cr in each sample, using the following equation:

$$M_{Cr} = V_{mL} \times C_S \times F \times D \quad \text{Eq. 306-3}$$

12.1.2.6 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop. Same as Method 5.

12.1.2.7 Dry Gas Volume, Volume of Water Vapor, Moisture Content. Same as Method 5.

12.1.2.8 Cr Emission Concentration (C_{Cr}). Calculate C_{Cr}, the Cr concentration in the stack gas, in mg/dscm on a dry basis, corrected to standard conditions using the following equation:

$$C_{Cr} = \frac{M_{Cr}}{V_{m(std)}} \times 10^{-3} \frac{\text{mg}}{\mu\text{g}} \quad \text{Eq. 306-4}$$

12.1.2.9 Isokinetic Variation, Acceptable Results. Same as Method 5.

13.0 Method Performance

13.1 Range. The recommended working range for all of the three analytical techniques starts at five times the analytical detection limit (see also Section 13.2.2). The upper limit of all three techniques can be extended indefinitely by appropriate dilution.

13.2 Sensitivity.

13.2.1 Analytical Sensitivity. The estimated instrumental detection limits listed are provided as a guide for an instrumental limit. The actual method detection limits are sample and instrument dependent and may vary as the sample matrix varies.

13.2.1.2 ICP Analytical Sensitivity. The minimum estimated detection limits for ICP, as reported in Method 6010A and the recently revised Method 6010B of SW-846 (Reference 1), are 7.0 µg Cr/L and 4.7 µg Cr/L, respectively.

13.2.1.3 GFAAS Analytical Sensitivity. The minimum estimated detection limit for

GFAAS, as reported in Methods 7000A and 7191 of SW-846 (Reference 1), is 1 µg Cr/L.

13.2.1.4 IC/PCR Analytical Sensitivity. The minimum detection limit for IC/PCR with a preconcentrator, as reported in Methods 0061 and 7199 of SW-846 (Reference 1), is 0.05 µg Cr⁺⁶/L.

1.3.2.1.5 Determination of Detection Limits. The laboratory performing the Cr⁺⁶ measurements must determine the method detection limit on a quarterly basis using a suitable procedure such as that found in 40 CFR, Part 136, Appendix B. The determination should be made on samples in the appropriate alkaline matrix. Normally this involves the preparation (if applicable) and consecutive measurement of seven (7) separate aliquots of a sample with a concentration <5 times the expected detection limit. The detection limit is 3.14 times the standard deviation of these results.

13.2.2 In-stack Sensitivity. The in-stack sensitivity depends upon the analytical detection limit, the volume of stack gas sampled, the total volume of the impinger absorbing solution plus the rinses, and, in some cases, dilution or concentration factors from sample preparation. Using the analytical detection limits given in Sections 13.2.1.1, 13.2.1.2, and 13.2.1.3; a stack gas sample volume of 1.7 dscm; a total liquid sample volume of 500 mL; and the digestion concentration factor of 1/2 for the GFAAS analysis; the corresponding in-stack detection limits are 0.0014 mg Cr/dscm to 0.0021 mg Cr/dscm for ICP, 0.00015 mg Cr/dscm for GFAAS, and 0.000015 mg Cr⁺⁶/dscm for IC/PCR with preconcentration.

NOTE: It is recommended that the concentration of Cr in the analytical solutions be at least five times the analytical detection limit to optimize sensitivity in the analyses. Using this guideline and the same assumptions for impinger sample volume, stack gas sample volume, and the digestion concentration factor for the GFAAS analysis (500 mL, 1.7 dscm, and 1/2, respectively), the recommended minimum stack concentrations for optimum sensitivity are 0.0068 mg Cr/dscm to 0.0103 mg Cr/dscm for ICP, 0.00074 mg Cr/dscm for GFAAS, and 0.000074 mg Cr⁺⁶/dscm for IC/PCR with preconcentration. If required, the in-stack detection limits can be improved by either increasing the stack gas sample volume, further reducing the volume of the digested sample for GFAAS, improving the analytical detection limits, or any combination of the three.

13.3 Precision.

13.3.1 The following precision data have been reported for the three analytical methods. In each case, when the sampling precision is combined with the reported analytical precision, the resulting overall precision may decrease.

13.3.2 Bias data is also reported for GFAAS.

13.4 ICP Precision.

13.4.1 As reported in Method 6010B of SW-846 (Reference 1), in an EPA round-robin Phase 1 study, seven laboratories applied the ICP technique to acid/distilled water matrices that had been spiked with various metal concentrates. For true values of 10, 50, and 150 µg Cr/L; the mean reported values were 10, 50, and 149 µg Cr/L; and the mean percent relative standard deviations were 18, 3.3, and 3.8 percent, respectively.

13.4.2 In another multi laboratory study cited in Method 6010B, a mean relative standard of 8.2 percent was reported for an aqueous sample concentration of approximately 3750 µg Cr/L.

13.5 GFAAS Precision. As reported in Method 7191 of SW-846 (Reference 1), in a single laboratory (EMSL), using Cincinnati, Ohio tap water spiked at concentrations of

19, 48, and 77 µg Cr/L, the standard deviations were ±0.1, ±0.2, and ±0.8, respectively. Recoveries at these levels were 97 percent, 101 percent, and 102 percent, respectively.

13.6 IC/PCR Precision. As reported in Methods 0061 and 7199 of SW-846 (Reference 1), the precision of IC/PCR with sample preconcentration is 5 to 10 percent. The overall precision for sewage sludge incinerators emitting 120 ng/dscm of Cr⁺⁶ and 3.5 µg/dscm of total Cr was 25 percent and 9 percent, respectively; and for hazardous waste incinerators emitting 300 ng/dscm of Cr⁺⁶ the precision was 20 percent.

14.0 Pollution Prevention

14.1 The only materials used in this method that could be considered pollutants are the chromium standards used for instrument calibration and acids used in the cleaning of the collection and measurement containers/labware, in the preparation of standards, and in the acid digestion of samples. Both reagents can be stored in the same waste container.

14.2 Cleaning solutions containing acids should be prepared in volumes consistent with use to minimize the disposal of excessive volumes of acid.

14.3 To the extent possible, the containers/vessels used to collect and prepare samples should be cleaned and reused to minimize the generation of solid waste.

15.0 Waste Management

15.1 It is the responsibility of the laboratory and the sampling team to comply with all federal, state, and local regulations governing waste management, particularly the discharge regulations, hazardous waste identification rules, and land disposal restrictions; and to protect the air, water, and land by minimizing and controlling all releases from field operations.

15.2 For further information on waste management, consult The Waste Management Manual for Laboratory Personnel and Less is Better—Laboratory Chemical Management for Waste Reduction, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street NW, Washington, DC 20036.

16.0 References

1. "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Third Edition," as amended by Updates I, II, IIA, IIB, and III. Document No. 955-001-000001. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, DC, November 1986.

2. Cox, X.B., R.W. Linton, and F.E. Butler. Determination of Chromium Speciation in Environmental Particles—A Multi-technique

Study of Ferrochrome Smelter Dust. Accepted for publication in Environmental Science and Technology.

3. Same as Section 17.0 of Method 5, References 2, 3, 4, 5, and 7.

4. California Air Resources Board, "Determination of Total Chromium and Hexavalent Chromium Emissions from Stationary Sources." Method 425, September 12, 1990.

5. *The Merck Index*. Eleventh Edition. Merck & Co., Inc., 1989.

6. Walpole, R.E., and R.H. Myers. "Probability and Statistics for Scientists and Engineers." 3rd Edition. MacMillan Publishing Co., New York, N.Y., 1985.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

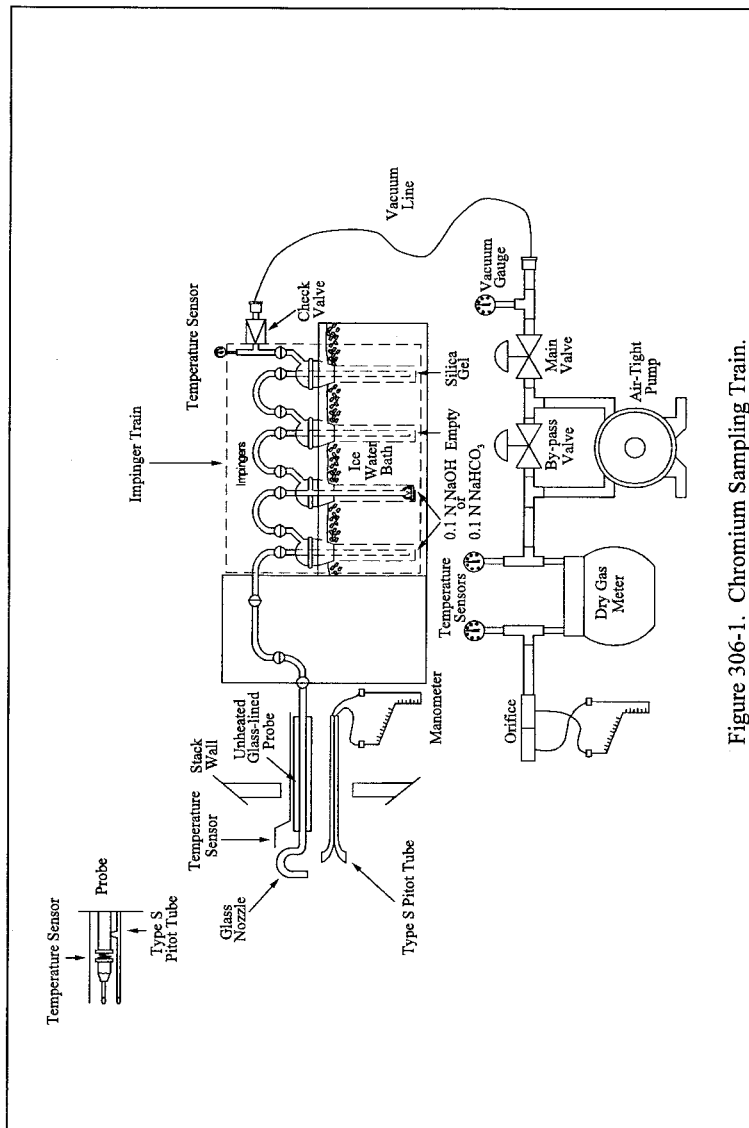


Figure 306-1. Chromium Sampling Train.

Plant _____

Location _____

Operator _____

Date _____

Run No. _____

Sample box No. _____

Meter box No. _____

Meter, d_i _____

C factor _____

Pitot tube coefficient, C_p _____

Ambient temperature _____

Barometric pressure _____

Assumed moisture, % _____

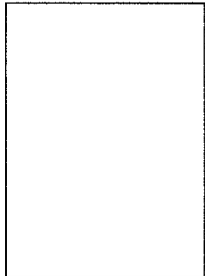
Probe length, (ft.) _____

Nozzle identification No. _____

Average calibrated nozzle diameter, (in.) _____

Leak rate, (cfm) _____

Static pressure, (in. Hg) _____



SCHEMATIC OF STACK CROSS SECTION

Transverse point number	Sampling time min.	Vacuum (in. Hg)	Stack temperature (T_s) (°F)	Velocity head (ΔP_v) (in. H ₂ O)	Pressure differential across orifice meter (in. H ₂ O)	Gas meter reading (ft ³)	Gas sample temperature at dry gas meter		Temperature of gas leaving condenser or last impinger (°F)
							Inlet (°F)	Outlet (°F)	
Total								Avg.	Avg.
Average								Avg.	Avg.

Figure 306-2. Chromium Field Data Sheet.

METHOD 306A—DETERMINATION OF CHROMIUM EMISSIONS FROM DECORATIVE AND HARD CHROMIUM ELECTROPLATING AND CHROMIUM ANODIZING OPERATIONS

NOTE: This method does not include all of the specifications (e.g., equipment and supplies) and procedures (e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from

other methods in 40 CFR Part 60, Appendix A and in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least Methods 5 and 306.

1.0 Scope and Application

- 1.1 Analyte. Chromium. CAS Number (7440-47-3).
- 1.2 Applicability.

1.2.1 This method applies to the determination of chromium (Cr) in emissions from decorative and hard chromium electroplating facilities, chromium anodizing operations, and continuous chromium plating at iron and steel facilities. The method is less expensive and less complex to conduct than Method 306. Correctly applied, the precision and bias of the sample results should be comparable to those obtained with the isokinetic Method 306. This method is applicable for the determination of air emissions under nominal ambient moisture, temperature, and pressure conditions.

1.2.2 The method is also applicable to electroplating and anodizing sources controlled by wet scrubbers.

1.3 Data Quality Objectives.

1.3.1 Pretest Protocol.

1.3.1.1 The pretest protocol should define and address the test data quality objectives (DQOs), with all assumptions, that will be required by the end user (enforcement authority); what data are needed? why are the data needed? how will data be used? what are method detection limits? and what are estimated target analyte levels for the following test parameters.

1.3.1.1.1 Estimated source concentration for total chromium and/or Cr⁺⁶.

1.3.1.1.2 Estimated minimum sampling time and/or volume required to meet method detection limit requirements (Appendix B 40 CFR Part 136) for measurement of total chromium and/or Cr⁺⁶.

1.3.1.1.3 Demonstrate that planned sampling parameters will meet DQOs. The protocol must demonstrate that the planned sampling parameters calculated by the tester will meet the needs of the source and the enforcement authority.

1.3.1.2 The pre-test protocol should include information on equipment, logistics, personnel, process operation, and other resources necessary for an efficient and coordinated performance test.

1.3.1.3 At a minimum, the pre-test protocol should identify and be approved by the source, the tester, the analytical laboratory, and the regulatory enforcement authority. The tester should not proceed with the compliance testing before obtaining approval from the enforcement authority.

2.0 Summary of Method

2.1 Sampling.

2.1.1 An emission sample is extracted from the source at a constant sampling rate determined by a critical orifice and collected in a sampling train composed of a probe and impingers. The proportional sampling time at the cross sectional traverse points is varied according to the stack gas velocity at each point. The total sample time must be at least two hours.

2.1.2 The chromium emission concentration is determined by the same analytical

procedures described in Method 306: inductively-coupled plasma emission spectrometry (ICP), graphite furnace atomic absorption spectrometry (GFAAS), or ion chromatography with a post-column reactor (IC/PCR).

2.1.2.1 Total chromium samples with high chromium concentrations (≥ 35 $\mu\text{g/L}$) may be analyzed using inductively coupled plasma emission spectrometry (ICP) at 267.72 nm.

NOTE: The ICP analysis is applicable for this method only when the solution analyzed has a Cr concentration greater than or equal to 35 $\mu\text{g/L}$ or five times the method detection limit as determined according to Appendix B in 40 CFR Part 136.

2.1.2.2 Alternatively, when lower total chromium concentrations (< 35 $\mu\text{g/L}$) are encountered, a portion of the alkaline sample solution may be digested with nitric acid and analyzed by graphite furnace atomic absorption spectroscopy (GFAAS) at 357.9 nm.

2.1.2.3 If it is desirable to determine hexavalent chromium (Cr⁺⁶) emissions, the samples may be analyzed using an ion chromatograph equipped with a post-column reactor (IC/PCR) and a visible wavelength detector. To increase sensitivity for trace levels of Cr⁺⁶, a preconcentration system may be used in conjunction with the IC/PCR.

3.0 Definitions

3.1 *Total Chromium*—measured chromium content that includes both major chromium oxidation states (Cr+3, Cr+6).

3.2 *May*—Implies an optional operation.

3.3 *Digestion*—The analytical operation involving the complete (or nearly complete) dissolution of the sample in order to ensure the complete solubilization of the element (analyte) to be measured.

3.4 *Interferences*—Physical, chemical, or spectral phenomena that may produce a high or low bias in the analytical result.

3.5 *Analytical System*—All components of the analytical process including the sample digestion and measurement apparatus.

3.6 *Sample Recovery*—The quantitative transfer of sample from the collection apparatus to the sample preparation (digestion, etc.) apparatus. This term should not be confused with analytical recovery.

4.0 Interferences

4.1 Same as in Method 306, Section 4.0.

5.0 Safety

5.1 *Disclaimer*. This method may involve hazardous materials, operations, and equipment. This test method does not purport to address all of the safety issues associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Chromium and some chromium compounds have been listed as carcinogens although Chromium (III) compounds show little or no toxicity. Chromium is a skin and respiratory irritant.

6.0 Equipment and Supplies

NOTE: Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

6.1 Sampling Train. A schematic of the sampling train is shown in Figure 306A-1. The individual components of the train are available commercially, however, some fabrication and assembly are required.

6.1.1 Probe Nozzle/Tubing and Sheath.

6.1.1.1 Use approximately 6.4-mm ($\frac{1}{4}$ -in.) inside diameter (ID) glass or rigid plastic tubing approximately 20 cm (8 in.) in length with a short 90 degree bend at one end to form the sampling nozzle. Grind a slight taper on the nozzle end before making the bend. Attach the nozzle to flexible tubing of sufficient length to enable collection of a sample from the stack.

6.1.1.2 Use a straight piece of larger diameter rigid tubing (such as metal conduit or plastic water pipe) to form a sheath that begins about 2.5 cm (1 in.) from the 90 ° bend on the nozzle and encases and supports the flexible tubing.

6.1.2 Type S Pitot Tube. Same as Method 2, Section 6.1 (40 CFR Part 60, Appendix A).

6.1.3 Temperature Sensor.

6.1.3.1 A thermocouple, liquid-filled bulb thermometer, bimetallic thermometer, mercury-in-glass thermometer, or other sensor capable of measuring temperature to within 1.5 percent of the minimum absolute stack temperature.

6.1.3.2 The temperature sensor shall either be positioned near the center of the stack, or be attached to the pitot tube as directed in Section 6.3 of Method 2.

6.1.4 Sample Train Connectors.

6.1.4.1 Use thick wall flexible plastic tubing (polyethylene, polypropylene, or polyvinyl chloride) ~ 6.4-mm ($\frac{1}{4}$ -in.) to 9.5-mm ($\frac{3}{8}$ -in.) ID to connect the train components.

6.1.4.2 A combination of rigid plastic tubing and thin wall flexible tubing may be used as long as tubing walls do not collapse when leak-checking the train. Metal tubing cannot be used.

6.1.5 Impingers. Three, one-quart capacity, glass canning jars with vacuum seal lids, or three Greenburg-Smith (GS) design impingers connected in series, or equivalent, may be used.

6.1.5.1 One-quart glass canning jar. Three separate jar containers are required: (1) the first jar contains the absorbing solution; (2) the second is empty and is used to collect any reagent carried over from the first container; and (3) the third contains the desiccant drying agent.

6.1.5.2 Canning Jar Connectors. The jar containers are connected by leak-tight inlet and outlet tubes installed in the lids of each container for assembly with the train. The tubes may be made of ~ 6.4 mm ($\frac{1}{4}$ -in.) ID glass or rigid plastic tubing. For the inlet tube of the first impinger, heat the glass or plastic tubing and draw until the tubing separates. Fabricate the necked tip to form an orifice tip that is approximately 2.4 mm ($\frac{3}{32}$ -in.) ID.

6.1.5.2.1 When assembling the first container, place the orifice tip end of the tube approximately 4.8 mm ($\frac{1}{16}$ -in.) above the inside bottom of the jar.

6.1.5.2.2 For the second container, the inlet tube need not be drawn and sized, but the tip should be approximately 25 mm (1 in.) above the bottom of the jar.

6.1.5.2.3 The inlet tube of the third container should extend to approximately 12.7 mm ($\frac{1}{2}$ -in.) above the bottom of the jar.

6.1.5.2.4 Extend the outlet tube for each container approximately 50 mm (2 in.) above the jar lid and downward through the lid, approximately 12.7 mm ($\frac{1}{2}$ -in.) beneath the bottom of the lid.

6.1.5.3 Greenburg-Smith Impingers. Three separate impingers of the Greenburg-Smith (GS) design as described in Section 6.0 of Method 5 are required. The first GS impinger shall have a standard tip (orifice/plate), and the second and third GS impingers shall be modified by replacing the orifice/plate tube with a 13 mm ($\frac{1}{2}$ -in.) ID glass tube, having an unrestricted opening located 13 mm ($\frac{1}{2}$ -in.) from the bottom of the outer flask.

6.1.5.4 Greenburg-Smith Connectors. The GS impingers shall be connected by leak-free ground glass "U" tube connectors or by leak-free non-contaminating flexible tubing. The first impinger shall contain the absorbing solution, the second is empty and the third contains the desiccant drying agent.

6.1.6 Manometer. Inclined/vertical type, or equivalent device, as described in Section 6.2 of Method 2 (40 CFR Part 60, Appendix A).

6.1.7 Critical Orifice. The critical orifice is a small restriction in the sample line that is located upstream of the vacuum pump. The orifice produces a constant sampling flow rate that is approximately 0.021 cubic meters per minute (m^3/min) or 0.75 cubic feet per minute (cfm).

6.1.7.1 The critical orifice can be constructed by sealing a 2.4-mm ($\frac{3}{32}$ -in.) ID brass tube approximately 14.3 mm ($\frac{1}{16}$ -in.) in length inside a second brass tube that is approximately 8 mm ($\frac{5}{16}$ -in.) ID and 14.3-mm ($\frac{1}{16}$ -in.) in length.

6.1.7.2 Materials other than brass can be used to construct the critical orifice as long as the flow through the sampling train can be maintained at approximately 0.021 cubic meter per minute (0.75) cfm.

6.1.8 Connecting Hardware. Standard pipe and fittings, 9.5-mm ($\frac{3}{8}$ -in.), 6.4-mm ($\frac{1}{4}$ -in.)

or 3.2-mm (1/8-in.) ID, may be used to assemble the vacuum pump, dry gas meter and other sampling train components.

6.1.9 Vacuum Gauge. Capable of measuring approximately 760 mm H_g (30 in. H_g) vacuum in 25.4 mm H_g (1 in. H_g) increments. Locate vacuum gauge between the critical orifice and the vacuum pump.

6.1.10 Pump Oiler. A glass oil reservoir with a wick mounted at the vacuum pump inlet that lubricates the pump vanes. The oiler should be an in-line type and not vented to the atmosphere. See EMTIC Guideline Document No. GD-041.WPD for additional information.

6.1.11 Vacuum Pump. Gast Model 0522-VI03-G18DX, or equivalent, capable of delivering at least 1.5 cfm at 15 in. H_g vacuum.

6.1.12 Oil Trap/Muffler. An empty glass oil reservoir without wick mounted at the pump outlet to control the pump noise and prevent oil from reaching the dry gas meter.

6.1.13 By-pass Fine Adjust Valve (Optional). Needle valve assembly 6.4-mm (1/4-in.), Whitey 1 RF 4-A, or equivalent, that allows for adjustment of the train vacuum.

6.1.13.1 A fine-adjustment valve is positioned in the optional pump by-pass system that allows the gas flow to recirculate through the pump. This by-pass system allows the tester to control/reduce the maximum leak-check vacuum pressure produced by the pump.

6.1.13.1.1 The tester must conduct the post test leak check at a vacuum equal to or greater than the maximum vacuum encountered during the sampling run.

6.1.13.1.2 The pump by-pass assembly is not required, but is recommended if the tester intends to leak-check the 306A train at the vacuum experienced during a run.

6.1.14 Dry Gas Meter. An Equimeter Model 110 test meter or, equivalent with temperature sensor(s) installed (inlet/outlet) to monitor the meter temperature. If only one temperature sensor is installed, locate the sensor at the outlet side of the meter. The dry gas meter must be capable of measuring the gaseous volume to within ±2% of the true volume.

NOTE: The Method 306 sampling train is also commercially available and may be used to perform the Method 306A tests. The sampling train may be assembled as specified in Method 306A with the sampling rate being operated at the delta H₀ specified for the calibrated orifice located in the meter box. The Method 306 train is then operated as described in Method 306A.

6.2 Barometer. Mercury aneroid barometer, or other barometer equivalent, capable of measuring atmospheric pressure to within ±2.5 mm H_g (0.1 in. H_g).

6.2.1 A preliminary check of the barometer shall be made against a mercury-in-glass reference barometer or its equivalent.

6.2.2 Tester may elect to obtain the absolute barometric pressure from a nearby National Weather Service station.

6.2.2.1 The station value (which is the absolute barometric pressure) must be adjusted for elevation differences between the weather station and the sampling location. Either subtract 2.5 mm H_g (0.1 in. H_g) from the station value per 30 m (100 ft) of elevation increase or add the same for an elevation decrease.

6.2.2.2 If the field barometer cannot be adjusted to agree within 0.1 in. H_g of the reference barometric, repair or discard the unit. The barometer pressure measurement shall be recorded on the sampling data sheet.

6.3 Sample Recovery. Same as Method 5, Section 6.2 (40 CFR Part 60, Appendix A), with the following exceptions:

6.3.1 Probe-Liner and Probe-Nozzle Brushes. Brushes are not necessary for sample recovery. If a probe brush is used, it must be non-metallic.

6.3.2 Wash Bottles. Polyethylene wash bottle, for sample recovery absorbing solution.

6.3.3 Sample Recovery Solution. Use 0.1 N NaOH or 0.1 N NaHCO₃, whichever is used as the impinger absorbing solution, to replace the acetone.

6.3.4 Sample Storage Containers.

6.3.4.1 Glass Canning Jar. The first canning jar container of the sampling train may serve as the sample shipping container. A new lid and sealing plastic wrap shall be substituted for the container lid assembly.

6.3.4.2 Polyethylene or Glass Containers. Transfer the Greenburg-Smith impinger contents to precleaned polyethylene or glass containers. The samples shall be stored and shipped in 250-mL, 500-mL or 1000-mL polyethylene or glass containers with leak-free, non metal screw caps.

6.3.5 pH Indicator Strip, for Cr⁺⁶ Samples. pH indicator strips, or equivalent, capable of determining the pH of solutions between the range of 7 and 12, at 0.5 pH increments.

6.3.6 Plastic Storage Containers. Air tight containers to store silica gel.

6.4 Analysis. Same as Method 306, Section 6.3.

7.0 Reagents and Standards.

NOTE: Unless otherwise indicated, all reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society (ACS reagent grade). Where such specifications are not available, use the best available grade. It is recommended, but not required, that reagents be checked by the appropriate analysis prior to field use to assure that contamination is below the analytical detection limit for the ICP or GFAAS total chromium analysis; and that contamination is below the analytical detection limit for

Cr⁺⁶ using IC/PCR for direct injection or, if selected, preconcentration.

7.1 Sampling.

7.1.1 Water. Reagent water that conforms to ASTM Specification D1193 Type II (incorporated by reference see §63.14). All references to water in the method refer to reagent water unless otherwise specified. It is recommended that water blanks be checked prior to preparing the sampling reagents to ensure that the Cr content is less than three (3) times the anticipated detection limit of the analytical method.

7.1.2 Sodium Hydroxide (NaOH) Absorbing Solution, 0.1 N. Dissolve 4.0 g of sodium hydroxide in 1 liter of water to obtain a pH of approximately 8.5.

7.1.3 Sodium Bicarbonate (NaHCO₃) Absorbing Solution, 0.1 N. Dissolve approximately 8.5 g of sodium bicarbonate in 1 liter of water to obtain a pH of approximately 8.3.

7.1.4 Chromium Contamination.

7.1.4.1 The absorbing solution shall not exceed the QC criteria noted in Method 306, Section 7.1.1 (≤3 times the instrument detection limit).

7.1.4.2 When the Cr⁺⁶ content in the field samples exceeds the blank concentration by at least a factor of ten (10), Cr⁺⁶ blank levels ≤10 times the detection limit will be allowed.

NOTE: At sources with high concentrations of acids and/or SO₂, the concentration of NaOH or NaHCO₃ should be ≥0.5 N to insure that the pH of the solution remains at or above 8.5 for NaOH and 8.0 for NaHCO₃ during and after sampling.

7.1.3 Desiccant. Silica Gel, 6-16 mesh, indicating type. Alternatively, other types of desiccants may be used, subject to the approval of the Administrator.

7.2 Sample Recovery. Same as Method 306, Section 7.2.

7.3 Sample Preparation and Analysis. Same as Method 306, Section 7.3.

7.4 Glassware Cleaning Reagents. Same as Method 306, Section 7.4.

7.5 Quality Assurance Audit Samples.

7.5.1 It is recommended, but not required, that a performance audit sample be analyzed in conjunction with the field samples. The audit sample should be in a suitable sample matrix at a concentration similar to the actual field samples.

7.5.2 When making compliance determinations, and upon availability, audit samples may be obtained from the appropriate EPA regional Office or from the responsible enforcement authority and analyzed in conjunction with the field samples.

NOTE: The responsible enforcement authority should be notified at least 30 days prior to the test date to allow sufficient time for the audit sample to be delivered.

8.0 Sample Collection, Recovery, Preservation, Holding Times, Storage, and Transport

NOTE: Prior to sample collection, consideration should be given as to the type of analysis (Cr⁺⁶ or total Cr) that will be performed. Deciding which analysis will be performed will enable the tester to determine which appropriate sample recovery and storage procedures will be required to process the sample.

8.1 Sample Collection.

8.1.1 Pretest Preparation.

8.1.1.1 Selection of Measurement Site. Locate the sampling ports as specified in Section 11.0 of Method 1 (40 CFR Part 60, Appendix A).

8.1.1.2 Location of Traverse Points.

8.1.1.2.1 Locate the traverse points as specified in Section 11.0 of Method 1 (40 CFR Part 60, Appendix A). Use a total of 24 sampling points for round ducts and 24 or 25 points for rectangular ducts. Mark the pitot and sampling probe to identify the sample traversing points.

8.1.1.2.2 For round ducts less than 12 inches in diameter, use a total of 16 points.

8.1.1.3 Velocity Pressure Traverse. Perform an initial velocity traverse before obtaining samples. The Figure 306A-2 data sheet may be used to record velocity traverse data.

8.1.1.3.1 To demonstrate that the flow rate is constant over several days of testing, perform complete traverses at the beginning and end of each day's test effort, and calculate the deviation of the flow rate for each daily period. The beginning and end flow rates are considered constant if the deviation does not exceed 10 percent. If the flow rate exceeds the 10 percent criteria, either correct the inconsistent flow rate problem, or obtain the Administrator's approval for the test results.

8.1.1.3.2 Perform traverses as specified in Section 8.0 of Method 2, but record only the Δp (velocity pressure) values for each sampling point. If a mass emission rate is desired, stack velocity pressures shall be recorded before and after each test, and an average stack velocity pressure determined for the testing period.

8.1.1.4 Verification of Absence of Cyclonic Flow. Check for cyclonic flow during the initial traverse to verify that it does not exist. Perform the cyclonic flow check as specified in Section 11.4 of Method 1 (40 CFR Part 60, Appendix A).

8.1.1.4.1 If cyclonic flow is present, verify that the absolute average angle of the tangential flow does not exceed 20 degrees. If the average value exceeds 20 degrees at the sampling location, the flow condition in the stack is unacceptable for testing.

8.1.1.4.2 Alternative procedures, subject to approval of the Administrator, *e.g.*, installing straightening vanes to eliminate the cyclonic flow, must be implemented prior to conducting the testing.

8.1.1.5 Stack Gas Moisture Measurements. *Not required.* Measuring the moisture content is optional when a mass emission rate is to be calculated.

8.1.1.5.1 The tester may elect to either measure the actual stack gas moisture during the sampling run or utilize a nominal moisture value of 2 percent.

8.1.1.5.2 For additional information on determining sampling train moisture, please refer to Method 4 (40 CFR Part 60, Appendix A).

8.1.1.6 Stack Temperature Measurements. If a mass emission rate is to be calculated, a temperature sensor must be placed either near the center of the stack, or attached to the pitot tube as described in Section 8.3 of Method 2. Stack temperature measurements, shall be recorded before and after each test,

and an average stack temperature determined for the testing period.

8.1.1.7 Point Sampling Times. Since the sampling rate of the train (0.75 cfm) is maintained constant by the critical orifice, it is necessary to calculate specific sampling times for each traverse point in order to obtain a proportional sample.

8.1.1.7.1 If the sampling period (3 runs) is to be completed in a single day, the point sampling times shall be calculated only once.

8.1.1.7.2 If the sampling period is to occur over several days, the sampling times must be calculated daily using the initial velocity pressure data recorded for that day. Determine the average of the Δp values obtained during the velocity traverse (Figure 306A-2).

8.1.1.7.3 If the stack diameter is less than 12 inches, use 7.5 minutes in place of 5 minutes in the equation and 16 sampling points instead of 24 or 25 points. Calculate the sampling times for each traverse point using the following equation:

$$\text{Minutes at point } n = \frac{\sqrt{\Delta p \text{ at Point } n}}{(\sqrt{\Delta p})_{\text{avg}}} \times 5 \text{ min.} \quad \text{Eq. 306A - 1}$$

Where:

n = Sampling point number.

Δp = Average pressure differential across pitot tube, mm H₂O (in. H₂O).

ΔP_{avg} = Average of Δp values, mm H₂O (in. H₂O).

NOTE: Convert the decimal fractions for minutes to seconds.

8.1.1.8 Pretest Preparation. It is recommended, but not required, that all items which will be in contact with the sample be cleaned prior to performing the testing to avoid possible sample contamination (positive chromium bias). These items include, but are not limited to: Sampling probe, connecting tubing, impingers, and jar containers.

8.1.1.8.1 Sample train components should be: (1) Rinsed with hot tap water; (2) washed with hot soapy water; (3) rinsed with tap water; (4) rinsed with reagent water; (5) soaked in a 10 percent (v/v) nitric acid solution for at least four hours; and (6) rinsed thoroughly with reagent water before use.

8.1.1.8.2 At a minimum, the tester should, rinse the probe, connecting tubing, and first and second impingers twice with either 0.1 N sodium hydroxide (NaOH) or 0.1 N sodium bicarbonate (NaHCO₃) and discard the rinse solution.

8.1.1.8.3 If separate sample shipping containers are to be used, these also should be

precleaned using the specified cleaning procedures.

8.1.1.9 Preparation of Sampling Train. Assemble the sampling train as shown in Figure 306A-1. Secure the nozzle-liner assembly to the outer sheath to prevent movement when sampling.

8.1.1.9.1 Place 250 mL of 0.1 N NaOH or 0.1 N NaHCO₃ absorbing solution into the first jar container or impinger. The second jar/impinger is to remain empty. Place 6 to 16 mesh indicating silica gel, or equivalent desiccant into the third jar/impinger until the container is half full (~ 300 to 400 g).

8.1.1.9.2 Place a small cotton ball in the outlet exit tube of the third jar to collect small silica gel particles that may dislodge and impair the pump and/or gas meter.

8.1.1.10 Pretest Leak-Check. A pretest leak-check is recommended, but not required. If the tester opts to conduct the pretest leak-check, the following procedures shall be performed: (1) Place the jar/impinger containers into an ice bath and wait 10 minutes for the ice to cool the containers before performing the leak check and/or start sampling; (2) to perform the leak check, seal the nozzle using a piece of clear plastic wrap placed over the end of a finger and switch on the pump; and (3) the train system leak rate should not exceed 0.02 cfm at a vacuum of 380 mm Hg (15 in. Hg) or greater. If the leak rate

does exceed the 0.02 cfm requirement, identify and repair the leak area and perform the leak check again.

NOTE: Use caution when releasing the vacuum following the leak check. Always allow air to slowly flow through the nozzle end of the train system while the pump is still operating. Switching off the pump with vacuum on the system may result in the silica gel being pulled into the second jar container.

8.1.1.11 Leak-Checks During Sample Run. If, during the sampling run, a component (e.g., jar container) exchange becomes necessary, a leak-check shall be conducted *immediately before* the component exchange is made. The leak-check shall be performed according to the procedure outlined in Section 8.1.1.10 of this method. If the leakage rate is found to be ≤ 0.02 cfm at the maximum operating vacuum, the results are acceptable. If, however, a higher leak rate is obtained, either record the leakage rate and correct the sample volume as shown in Section 12.3 of Method 5 or void the sample and initiate a replacement run. Following the component change, leak-checks are optional, but are recommended as are the pretest leak-checks.

8.1.1.12 Post Test Leak Check. Remove the probe assembly and flexible tubing from the first jar/impinger container. Seal the inlet tube of the first container using clear plastic wrap and switch on the pump. The vacuum in the line between the pump and the critical orifice must be ≥ 15 in. Hg. Record the vacuum gauge measurement along with the leak rate observed on the train system.

8.1.1.12.1 If the leak rate does not exceed 0.02 cfm, the results are acceptable and no sample volume correction is necessary.

8.1.1.12.2 If, however, a higher leak rate is obtained (>0.02 cfm), the tester shall either record the leakage rate and correct the sample volume as shown in Section 12.3 of Method 5, or void the sampling run and initiate a replacement run. After completing the leak-check, slowly release the vacuum at the first container while the pump is still operating. Afterwards, switch-off the pump.

8.1.2 Sample Train Operation.

8.1.2.1 Data Recording. Record all pertinent process and sampling data on the data sheet (see Figure 306A-3). Ensure that the process operation is suitable for sample collection.

8.1.2.2 Starting the Test. Place the probe/nozzle into the duct at the first sampling point and switch on the pump. Start the sampling using the time interval calculated for the first point. When the first point sampling time has been completed, move to the second point and continue to sample for the time interval calculated for that point; sample each point on the traverse in this manner. Maintain ice around the sample containers during the run.

8.1.2.3 Critical Flow. The sample line between the critical orifice and the pump must operate at a vacuum of ≥ 380 mm Hg (≥ 15 in. Hg) in order for critical flow to be maintained. This vacuum must be monitored and documented using the vacuum gauge located between the critical orifice and the pump.

NOTE: Theoretically, critical flow for air occurs when the ratio of the orifice outlet absolute pressure to the orifice inlet absolute pressure is less than a factor of 0.53. This means that the system vacuum should be at least ≥ 356 mm Hg (≥ 14 in. Hg) at sea level and ~ 305 mm Hg (~ 12 in. Hg) at higher elevations.

8.1.2.4 Completion of Test.

8.1.2.4.1 Circular Stacks. Complete the first port traverse and switch off the pump. Testers may opt to perform a leak-check between the port changes to verify the leak rate however, this is not mandatory. Move the sampling train to the next sampling port and repeat the sequence. Be sure to record the final dry gas meter reading after completing the test run. After performing the post test leak check, disconnect the jar/impinger containers from the pump and meter assembly and transport the probe, connecting tubing, and containers to the sample recovery area.

8.1.2.4.2 Rectangle Stacks. Complete each port traverse as per the instructions provided in 8.1.2.4.1.

NOTE: If an approximate mass emission rate is to be calculated, measure and record the stack velocity pressure and temperature before and after the test run.

8.2 Sample Recovery. After the train has been transferred to the sample recovery area, disconnect the tubing that connects the jar/impingers. The tester shall select either the total Cr or Cr⁺⁶ sample recovery option. Samples to be analyzed for both total Cr and Cr⁺⁶ shall be recovered using the Cr⁺⁶ sample option (Section 8.2.2).

NOTE: Collect a reagent blank sample for each of the total Cr or the Cr⁺⁶ analytical options. If both analyses (Cr and Cr⁺⁶) are to be conducted on the samples, collect separate reagent blanks for each analysis.

8.2.1 Total Cr Sample Option.

8.2.1.1 Shipping Container No. 1. The first jar container may either be used to store and transport the sample, or if GS impingers are used, samples may be stored and shipped in pre-cleaned 250-mL, 500-mL or 1000-mL polyethylene or glass bottles with leak-free, non-metal screw caps.

8.2.1.1.1 Unscrew the lid from the first jar/impinger container.

8.2.1.1.2 Lift the inner tube assembly almost out of the container, and using the wash bottle containing fresh absorbing solution, rinse the outside of the tube that was immersed in the container solution; rinse

the inside of the tube as well, by rinsing twice from the top of the tube down through the inner tube into the container.

8.2.1.2 Recover the contents of the second jar/impinger container by removing the lid and pouring any contents into the first shipping container.

8.2.1.2.1 Rinse twice, using fresh absorbing solution, the inner walls of the second container including the inside and outside of the inner tube.

8.2.1.2.2 Rinse the connecting tubing between the first and second sample containers with absorbing solution and place the rinses into the first container.

8.2.1.3 Position the nozzle, probe and connecting plastic tubing in a vertical position so that the tubing forms a "U".

8.2.1.3.1 Using the wash bottle, partially fill the tubing with fresh absorbing solution. Raise and lower the end of the plastic tubing several times to allow the solution to contact the internal surfaces. Do not allow the solution to overflow or part of the sample will be lost. Place the nozzle end of the probe over the mouth of the first container and elevate the plastic tubing so that the solution flows into the sample container.

8.2.1.3.2 Repeat the probe/tubing sample recovery procedure but allow the solution to flow out the opposite end of the plastic tubing into the sample container. Repeat the entire sample recovery procedure once again.

8.2.1.4 Use approximately 200 to 300 mL of the 0.1 N NaOH or 0.1 N NaHCO₃ absorbing solution during the rinsing of the probe nozzle, probe liner, sample containers, and connecting tubing.

8.2.1.5 Place a piece of clear plastic wrap over the mouth of the sample jar to seal the shipping container. Use a standard lid and band assembly to seal and secure the sample in the jar.

8.2.1.5.1 Label the jar clearly to identify its contents, sample number and date.

8.2.1.5.2 Mark the height of the liquid level on the container to identify any losses during shipping and handling.

8.2.1.5.3 Prepare a chain-of-custody sheet to accompany the sample to the laboratory.

8.2.2 Cr⁺⁶ Sample Option.

8.2.2.1 Shipping Container No. 1. The first jar container may either be used to store and transport the sample, or if GS impingers are used, samples may be stored and shipped in precleaned 250-mL, 500-mL or 1000-mL polyethylene or glass bottles with leak-free non-metal screw caps.

8.2.2.1.1 Unscrew and remove the lid from the first jar container.

8.2.2.1.2 Measure and record the pH of the solution in the first container by using a pH indicator strip. The pH of the solution must be ≥ 8.5 for NaOH and ≥ 8.0 for NaHCO₃. If not, discard the collected sample, increase the concentration of the NaOH or NaHCO₃ ab-

sorbing solution to 0.5 M and collect another air emission sample.

8.2.2.2 After measuring the pH of the first container, follow sample recovery procedures described in Sections 8.2.1.1 through 8.2.1.5.

NOTE: Since particulate matter is not usually present at chromium electroplating and/or chromium anodizing facilities, it is not necessary to filter the Cr⁺⁶ samples unless there is observed sediment in the collected solutions. If it is necessary to filter the Cr⁺⁶ solutions, please refer to the EPA Method 0061, Determination of Hexavalent Chromium Emissions from Stationary Sources, Section 7.4, Sample Preparation in SW-846 (see Reference 5) for procedure.

8.2.3 Silica Gel Container. Observe the color of the indicating silica gel to determine if it has been completely spent and make a notation of its condition/color on the field data sheet. Do not use water or other liquids to remove and transfer the silica gel.

8.2.4 Total Cr and/or Cr⁺⁶ Reagent Blank.

8.2.4.1 Shipping Container No. 2. Place approximately 500 mL of the 0.1 N NaOH or 0.1 N NaHCO₃ absorbing solution in a precleaned, labeled sample container and include with the field samples for analysis.

8.3 Sample Preservation, Storage, and Transport.

8.3.1 Total Cr Option. Samples that are to be analyzed for total Cr need not be refrigerated.

8.3.2 Cr⁺⁶ Option. Samples that are to be analyzed for Cr⁺⁶ must be shipped and stored at 4 °C (-40 °F).

NOTE: Allow Cr⁺⁶ samples to return to ambient temperature prior to analysis.

8.4 Sample Holding Times.

8.4.1 Total Cr Option. Samples that are to be analyzed for total chromium must be analyzed within 60 days of collection.

8.4.2 Cr⁺⁶ Option. Samples that are to be analyzed for Cr⁺⁶ must be analyzed within 14 days of collection.

9.0 Quality Control

9.1 Same as Method 306, Section 9.0.

10.0 Calibration and Standardization

NOTE: Tester shall maintain a performance log of all calibration results.

10.1 Pitot Tube. The Type S pitot tube assembly shall be calibrated according to the procedures outlined in Section 10.1 of Method 2.

10.2 Temperature Sensor. Use the procedure in Section 10.3 of Method 2 to calibrate the in-stack temperature sensor.

10.3 Metering System.

10.3.1 Sample Train Dry Gas Meter Calibration. Calibrations may be performed as described in Section 16.2 of Method 5 by either the manufacturer, a firm who provides calibration services, or the tester.

10.3.2 Dry Gas Meter Calibration Coefficient (Y_m). The meter calibration coefficient (Y_m) must be determined prior to the initial use of the meter, and following each field test program. If the dry gas meter is new, the manufacturer will have specified the Y_m value for the meter. This Y_m value can be used as the pretest value for the first test. For subsequent tests, the tester must use the Y_m value established during the pretest calibration.

10.3.3 Calibration Orifice. The manufacturer may have included a calibration orifice and a summary spreadsheet with the meter that may be used for calibration purposes. The spreadsheet will provide data necessary to determine the calibration for the orifice and meter (standard cubic feet volume, sample time, *etc.*). These data were produced when the initial Y_m value was determined for the meter.

10.3.4 Y_m Meter Value Verification or Meter Calibration.

10.3.4.1 The Y_m meter value may be determined by replacing the sampling train critical

orifice with the calibration orifice. Replace the critical orifice assembly by installing the calibration orifice in the same location. The inlet side of the calibration orifice is to be left open to the atmosphere and is *not* to be reconnected to the sample train during the calibration procedure.

10.3.4.2 If the vacuum pump is cold, switch on the pump and allow it to operate (become warm) for several minutes prior to starting the calibration. After stopping the pump, record the initial dry gas meter volume and meter temperature.

10.3.4.3 Perform the calibration for the number of minutes specified by the manufacturer's data sheet (usually 5 minutes). Stop the pump and record the final dry gas meter volume and temperature. Subtract the start volume from the stop volume to obtain the V_m and average the meter temperatures (t_m).

10.3.5 Y_m Value Calculation. Y_m is the calculated value for the dry gas meter. Calculate Y_m using the following equation:

$$Y_m = \frac{V_{m(\text{std}),\text{mfg}}}{V_m \left(\frac{T_{\text{std}}}{P_{\text{std}}} \right) \left(\frac{P_{\text{bar}}}{T_m} \right)}$$

$$Y_m = \frac{V_{m(\text{std}),\text{mfg}} T_m}{17.64 V_m P_{\text{bar}}} \quad \text{Eq. 306A-2}$$

Where:

P_{bar} = Barometric pressure at meter, mm Hg, (in. Hg).

P_{std} = Standard absolute pressure,

Metric = 760 mm Hg.

English = 29.92 in. Hg.

t_m = Average dry gas meter temperature, °C, (°F).

T_m = Absolute average dry gas meter temperature,

Metric °K = 273 + t_m (°C).

English °R = 460 + t_m (°F).

T_{std} = Standard absolute temperature,

Metric = 293 °K.

English = 528 °R.

V_m = Volume of gas sample as measured (actual) by dry gas meter, dcm, (dcf).

$V_{m(\text{std}),\text{mfg}}$ = Volume of gas sample measured by manufacturer's calibrated orifice and dry gas meter, corrected to standard conditions (pressure/temperature) dscm (dscf).

Y_m = Dry gas meter calibration factor, (dimensionless).

10.3.6 Y_m Comparison. Compare the Y_m value provided by the manufacturer (Section 10.3.3) or the pretest Y_m value to the post test Y_m value using the following equation:

$$\frac{Y_m(\text{manufacturer's or pretest value})}{Y_m(\text{post - test value})} \quad \text{Eq. 306A-3}$$

10.3.6.1 If this ratio is between 0.95 and 1.05, the designated Y_m value for the meter is acceptable for use in later calculations.

10.3.6.1.1 If the value is outside the specified range, the test series shall either be: 1) voided and the samples discarded; or 2) calculations for the test series shall be conducted using whichever meter coefficient value (i.e., manufacturers's/pretest Y_m value or post test Y_m value) produces the lowest sample volume.

10.3.6.1.2 If the post test dry gas meter Y_m value differs by more than 5% as compared to the pretest value, either perform the calibration again to determine acceptability or return the meter to the manufacturer for re-calibration.

10.3.6.1.3 The calibration may also be conducted as specified in Section 10.3 or Section 16.0 of Method 5 (40 CFR Part 60, Appendix A), except that it is only necessary to check the calibration at one flow rate of ~ 0.75 cfm.

10.3.6.1.4 The calibration of the dry gas meter must be verified after each field test program using the same procedures.

NOTE: The tester may elect to use the Y_m post test value for the next pretest Y_m value; e.g., Test 1 post test Y_m value and Test 2 pretest Y_m value would be the same.

10.4 Barometer. Calibrate against a mercury barometer that has been corrected for temperature and elevation.

10.5 ICP Spectrometer Calibration. Same as Method 306, Section 10.2.

10.6 GFAA Spectrometer Calibration. Same as Method 306, Section 10.3.

10.7 IC/PCR Calibration. Same as Method 306, Section 10.4.

11.0 Analytical Procedures

NOTE: The method determines the chromium concentration in $\mu\text{g Cr/mL}$. It is important that the analyst measure the volume of the field sample prior to analyzing the sample. This will allow for conversion of $\mu\text{g Cr/mL}$ to $\mu\text{g Cr/sample}$.

11.1 Analysis. Refer to Method 306 for sample preparation and analysis procedures.

12.0 Data Analysis and Calculations

12.1 Calculations. Perform the calculations, retaining one extra decimal point beyond that of the acquired data. When reporting final results, round number of figures consistent with the original data.

12.2 Nomenclature.

A = Cross-sectional area of stack, m^2 (ft^2).
 B_{ws} = Water vapor in gas stream, proportion by volume, dimensionless (assume 2 percent moisture = 0.02).
 C_p = Pitot tube coefficient; "S" type pitot coefficient usually 0.840, dimensionless.
 C_s = Concentration of Cr in sample solution, $\mu\text{g Cr/mL}$.

C_{Cr} = Concentration of Cr in stack gas, dry basis, corrected to standard conditions $\mu\text{g/dscm}$ (gr/dscf).

d = Diameter of stack, m (ft).

D = Digestion factor, dimensionless.

ER = Approximate mass emission rate, mg/hr (lb/hr).

F = Dilution factor, dimensionless.

L = Length of a square or rectangular duct, m (ft).

M_{Cr} = Total Cr in each sample, μg (gr).

M_s = Molecular weight of wet stack gas, wet basis, g/g-mole , (lb/lb-mole); in a nominal gas stream at 2% moisture the value is 28.62.

P_{bar} = Barometric pressure at sampling site, mm Hg (in. Hg).

P_s = Absolute stack gas pressure; in this case, usually the same value as the barometric pressure, mm Hg (in. Hg).

P_{std} = Standard absolute pressure:

Metric = 760 mm Hg.

English = 29.92 in. Hg.

Q_{std} = Average stack gas volumetric flow, dry, corrected to standard conditions, dscm/hr (dscf/hr).

t_m = Average dry gas meter temperature, $^{\circ}\text{C}$ ($^{\circ}\text{F}$).

T_m = Absolute average dry gas meter temperature:

Metric $^{\circ}\text{K} = 273 + t_m$ ($^{\circ}\text{C}$).

English $^{\circ}\text{R} = 460 + t_m$ ($^{\circ}\text{F}$).

t_s = Average stack temperature, $^{\circ}\text{C}$ ($^{\circ}\text{F}$).

T_s = Absolute average stack gas temperature: Metric $^{\circ}\text{K} = 273 + t_s$ ($^{\circ}\text{C}$). English $^{\circ}\text{R} = 460 + t_s$ ($^{\circ}\text{F}$).

T_{std} = Standard absolute temperature: Metric = 293 $^{\circ}\text{K}$. English = 528 $^{\circ}\text{R}$.

V_{ad} = Volume of sample aliquot after digestion (mL).

V_{af} = Volume of sample aliquot after dilution (mL).

V_{bd} = Volume of sample aliquot submitted to digestion (mL).

V_{br} = Volume of sample aliquot before dilution (mL).

V_m = Volume of gas sample as measured (actual, dry) by dry gas meter, dcm (dcf).

V_{mL} = Volume of impinger contents plus rinses (mL).

$V_{m(std)}$ = Volume of gas sample measured by the dry gas meter, corrected to standard conditions (temperature/pressure), dscm (dscf).

v_s = Stack gas average velocity, calculated by Method 2, Equation 2-9, m/sec (ft/sec).

W = Width of a square or rectangular duct, m (ft).

Y_m = Dry gas meter calibration factor, (dimensionless).

Δp = Velocity head measured by the Type S pitot tube, $\text{cm H}_2\text{O}$ (in. H_2O).

Δp_{avg} = Average of Δp values, $\text{mm H}_2\text{O}$ (in. H_2O).

12.3 Dilution Factor. The dilution factor is the ratio of the volume of sample aliquot after dilution to the volume before dilution.

The dilution factor is usually calculated by the laboratory. This ratio is derived by the following equation:

$$F = \frac{V_{af}}{V_{bf}} \quad \text{Eq. 306A-4}$$

12.4 Digestion Factor. The digestion factor is the ratio of the volume of sample aliquot after digestion to the volume before di-

gestion. The digestion factor is usually calculated by the laboratory. This ratio is derived by the following equation.

$$D = \frac{V_{ad}}{V_{bd}} \quad \text{Eq. 306A-5}$$

12.5 Total Cr in Sample. Calculate M_{Cr} , the total μg Cr in each sample, using the following equation:

$$M_{Cr} = V_{mL} \times C_S \times F \times D \quad \text{Eq. 306A-6}$$

12.6 Dry Gas Volume. Correct the sample volume measured by the dry gas meter to standard conditions (20 °C, 760 mm Hg or

68°F, 29.92 in. Hg) using the following equation:

$$V_{m(\text{std})} = V_m Y_m \left(\frac{T_{\text{std}}}{T_m} \right) \left(\frac{P_{\text{bar}}}{P_{\text{std}}} \right) = K_1 V_m Y_m \left(\frac{P_{\text{bar}}}{T_m} \right) \quad \text{Eq. 306A-7}$$

Where:

K_1 = Metric units—0.3855 °K/mm Hg.
English units—17.64 °R/in. Hg.

12.7 Cr Emission Concentration (C_{Cr}). Calculate C_{Cr} , the Cr concentration in the stack gas, in $\mu\text{g}/\text{dscm}$ ($\mu\text{g}/\text{dscf}$) on a dry basis, corrected to standard conditions, using the following equation:

$$C_{Cr} = \frac{M_{Cr}}{V_{m(\text{std})}} \quad \text{Eq. 306A-8}$$

Note: To convert $\mu\text{g}/\text{dscm}$ ($\mu\text{g}/\text{dscf}$) to mg/dscm (mg/dscf), divide by 1000.

12.8 Stack Gas Velocity.

12.8.1 K_p = Velocity equation constant:

$$\text{Metric } K_p = 34.97 \frac{\text{m}}{\text{sec}} \left[\frac{(\text{g/g-mole})(\text{mm Hg})}{(\text{° K})(\text{mm H}_2\text{O})} \right]^{1/2}$$

$$\text{English } K_p = 85.49 \frac{\text{ft}}{\text{sec}} \left[\frac{(\text{lb/lb-mole})(\text{in. Hg})}{(\text{° R})(\text{in. H}_2\text{O})} \right]^{1/2}$$

12.8.2 Average Stack Gas Velocity.

$$\begin{aligned} v_s &= K_p C_p (\sqrt{\Delta p})_{\text{avg}} \sqrt{\frac{T_{s(\text{avg})}}{P_s M_s}} \\ &= 34.97 C_p (\sqrt{\Delta p})_{\text{avg}} \sqrt{\frac{T_{s(\text{avg})}}{P_s M_s}} \quad \text{Eq. 306A-9} \end{aligned}$$

12.9 Cross sectional area of stack.

$$A = \frac{\Pi d^2}{4} \quad \text{or} \quad A = LW \quad \text{Eq. 306A-10}$$

12.10 Average Stack Gas Dry Volumetric Flow Rate.

NOTE: The emission rate may be based on a nominal stack moisture content of 2 percent (0.02). To calculate an emission rate, the

tester may elect to use either the nominal stack gas moisture value or the actual stack gas moisture collected during the sampling run.

Volumetric Flow Rate Equation:

$$Q_{\text{std}} = 3600 (1 - B_{\text{ws}}) v_s A \left(\frac{T_{\text{std}}}{T_{s(\text{avg})}} \right) \left(\frac{P_s}{P_{\text{std}}} \right) \quad \text{Eq. 306A-11}$$

Where:

3600 = Conversion factor, sec/hr.

$$Q_{\text{std}} = 62,234 v_s A \left(\frac{P_s}{T_{s(\text{avg})}} \right) \quad \text{Eq. 306A-12}$$

NOTE: To convert Q_{std} from dscm/hr (dscf/hr) to dscm/min (dscf/min), divide Q_{std} by 60.

12.11 Mass emission rate, mg/hr (lb/hr):

$$ER = C_{cr} \times Q_{std} \times 10^{-3} \text{ (mg / hr)} \quad \text{Eq. 306A-13}$$

$$ER = C_{cr} \times Q_{std} \times 1.43 \times 10^{-4} \text{ (lb / hr)} \quad \text{Eq. 306A-14}$$

13.0 Method Performance

13.1 Range. The recommended working range for all of the three analytical techniques starts at five times the analytical detection limit (see also Method 306, Section 13.2.2). The upper limit of all three techniques can be extended indefinitely by appropriate dilution.

13.2 Sensitivity.

13.2.1 Analytical Sensitivity. The estimated instrumental detection limits listed are provided as a guide for an instrumental limit. The actual method detection limits are sample and instrument dependent and may vary as the sample matrix varies.

13.2.1.1 ICP Analytical Sensitivity. The minimum estimated detection limits for ICP, as reported in Method 6010A and the recently revised Method 6010B of SW-846 (Reference 1), are 7.0 µg Cr/L and 4.7 µg Cr/L, respectively.

13.2.1.2 GFAAS Analytical Sensitivity. The minimum estimated detection limit for GFAAS, as reported in Methods 7000A and 7191 of SW-846 (Reference 1), is 1.0 µg Cr/L.

13.2.1.3 IC/PCR Analytical Sensitivity. The minimum detection limit for IC/PCR with a preconcentrator, as reported in Methods 0061 and 7199 of SW-846 (Reference 1), is 0.05 µg Cr⁺⁶/L.

13.2.2 In-stack Sensitivity. The in-stack sensitivity depends upon the analytical detection limit, the volume of stack gas sampled, and the total volume of the impinger absorbing solution plus the rinses. Using the analytical detection limits given in Sections 13.2.1.1, 13.2.1.2, and 13.2.1.3; a stack gas sample volume of 1.7 dscm; and a total liquid sample volume of 500 mL; the corresponding in-stack detection limits are 0.0014 mg Cr/dscm to 0.0021 mg Cr/dscm for ICP, 0.00029 mg Cr/dscm for GFAAS, and 0.000015 mg Cr^{+3e}/dscm for IC/PCR with preconcentration.

NOTE: It is recommended that the concentration of Cr in the analytical solutions be at least five times the analytical detection limit to optimize sensitivity in the analyses. Using this guideline and the same assumptions for impinger sample volume and stack gas sample volume (500 mL and 1.7 dscm, respectively), the recommended minimum stack concentrations for optimum sensitivity are 0.0068 mg Cr/dscm to 0.0103 mg Cr/dscm for ICP, 0.0015 mg Cr/dscm for GFAAS, and 0.000074 mg Cr⁺⁶ dscm for IC/PCR with preconcentration. If required, the in-stack detection limits can be improved by either increasing the sampling time, the stack gas sample volume, reducing the vol-

ume of the digested sample for GFAAS, improving the analytical detection limits, or any combination of the three.

13.3 Precision.

13.3.1 The following precision data have been reported for the three analytical methods. In each case, when the sampling precision is combined with the reported analytical precision, the resulting overall precision may decrease.

13.3.2 Bias data is also reported for GFAAS.

13.4 ICP Precision.

13.4.1 As reported in Method 6010B of SW-846 (Reference 1), in an EPA round-robin Phase 1 study, seven laboratories applied the ICP technique to acid/distilled water matrices that had been spiked with various metal concentrates. For true values of 10, 50, and 150 µg Cr/L; the mean reported values were 10, 50, and 149 µg Cr/L; and the mean percent relative standard deviations were 18, 3.3, and 3.8 percent, respectively.

13.4.2 In another multilaboratory study cited in Method 6010B, a mean relative standard of 8.2 percent was reported for an aqueous sample concentration of approximately 3750 µg Cr/L.

13.5 GFAAS Precision. As reported in Method 7191 of SW-846 (Reference 1), in a single laboratory (EMSL), using Cincinnati, Ohio tap water spiked at concentrations of 19, 48, and 77 µg Cr/L, the standard deviations were ±0.1, ±0.2, and ±0.8, respectively. Recoveries at these levels were 97 percent, 101 percent, and 102 percent, respectively.

13.6 IC/PCR Precision. As reported in Methods 0061 and 7199 of SW-846 (Reference 1), the precision of IC/PCR with sample preconcentration is 5 to 10 percent; the overall precision for sewage sludge incinerators emitting 120 ng/dscm of Cr⁺⁶ and 3.5 µg/dscm of total Cr is 25 percent and 9 percent, respectively; and for hazardous waste incinerators emitting 300 ng/dscm of Cr⁺⁶ the precision is 20 percent.

14.0 Pollution Prevention

14.1 The only materials used in this method that could be considered pollutants are the chromium standards used for instrument calibration and acids used in the cleaning of the collection and measurement containers/labware, in the preparation of standards, and in the acid digestion of samples. Both reagents can be stored in the same waste container.

14.2 Cleaning solutions containing acids should be prepared in volumes consistent

with use to minimize the disposal of excessive volumes of acid.

14.3 To the extent possible, the containers/vessels used to collect and prepare samples should be cleaned and reused to minimize the generation of solid waste.

15.0 Waste Management

15.1 It is the responsibility of the laboratory and the sampling team to comply with all federal, state, and local regulations governing waste management, particularly the discharge regulations, hazardous waste identification rules, and land disposal restrictions; and to protect the air, water, and land by minimizing and controlling all releases from field operations.

15.2 For further information on waste management, consult The Waste Management Manual for Laboratory Personnel and Less is Better-Laboratory Chemical Management for Waste Reduction, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street NW, Washington, DC 20036.

16.0 References

1. F.R. Clay, Memo, Impinger Collection Efficiency—Mason Jars vs. Greenburg-Smith Impingers, Dec. 1989.

2. Segall, R.R., W.G. DeWees, F.R. Clay, and J.W. Brown. Development of Screening Methods for Use in Chromium Emissions Measurement and Regulations Enforcement. In: Proceedings of the 1989 EPA/A&WMA International Symposium—Measurement of Toxic and Related Air Pollutants, A&WMA Publication VIP-13, EPA Report No. 600/9-89-060, p. 785.

3. Clay, F.R., Chromium Sampling Method. In: Proceedings of the 1990 EPA/A&WMA International Symposium—Measurement of Toxic and Related Air Pollutants, A&WMA Publication VIP-17, EPA Report No. 600/9-90-026, p. 576.

4. Clay, F.R., Proposed Sampling Method 306A for the Determination of Hexavalent Chromium Emissions from Electroplating and Anodizing Facilities. In: Proceedings of the 1992 EPA/A&WMA International Symposium—Measurement of Toxic and Related Air Pollutants, A&WMA Publication VIP-25, EPA Report No. 600/R-92/131, p. 209.

5. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Third Edition as amended by Updates I, II, IIA, IIB, and III. Document No. 955-001-000001. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, DC, November 1986.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

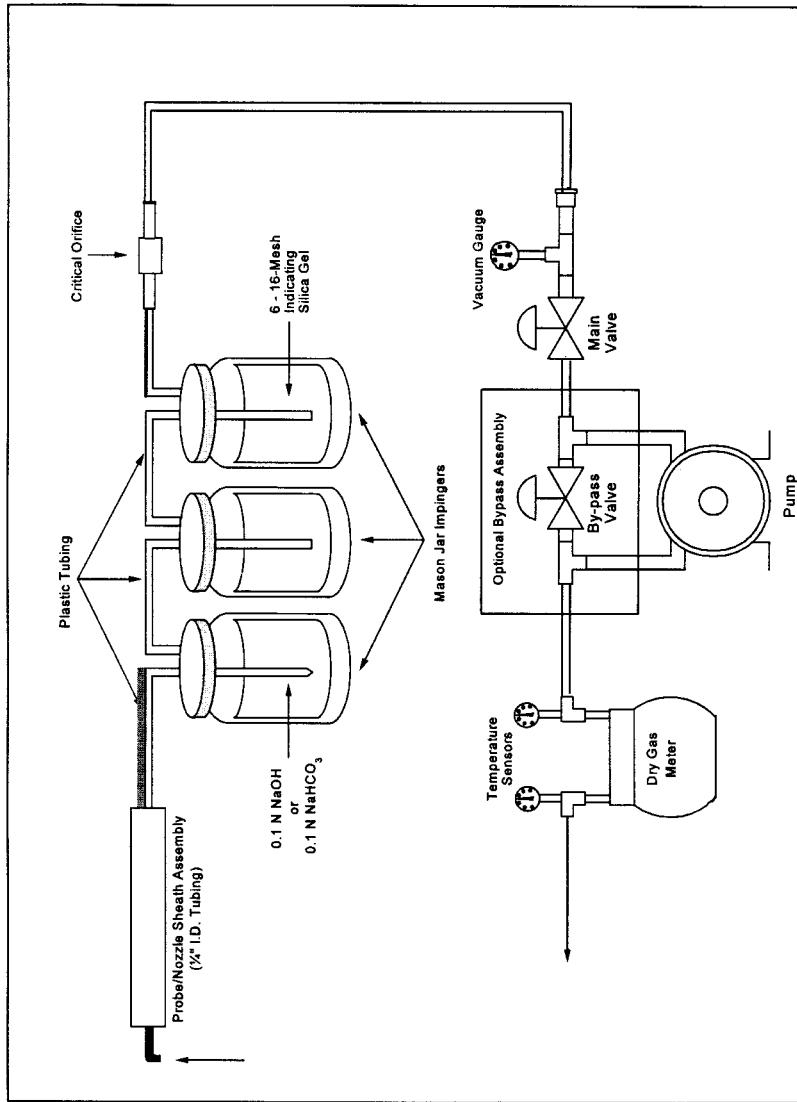


Figure 306A-1. Method 306A Sampling Train.

Plant _____

Date _____ Time _____

Location _____

Operator(s) _____

Beginning stack temperature, °F _____

Ending stack temperature, °F _____

Average stack temperature, °F _____

Schematic of Points _____

Circle one:

Before Run 1 Before Run 2 Before Run 3 After Run No. _____

Traverse Point Number	Cyclonic Flow Angle (Degrees)	Δ P	√Δ P	$\frac{\sqrt{\Delta P}}{\sqrt{\Delta P_{Avg}}} \times 5 \text{ min} = \text{Numerical Minutes}$	Decimal Part of Minute x 60 = Seconds	Whole Minutes + Seconds = Sample Time
Total			Total			
Avg			Avg			

Figure 306A-2. Velocity Traverse and Point Sample Time Calculation Sheet.

Plant _____
 Sampling Site _____
 Total Cr catch, M, μg _____
 Avg dry gas meter temp, T_m , $^{\circ}\text{F}$ _____
 Meter correction factor, Y_m _____
 Meter volume, V_m , ft^3 _____
 Barometric press, P_{bar} , in. Hg _____
 Start clock time _____
 Stop clock time _____

Date _____ Run Number _____
 Operator _____
 Stack radius, r , in. _____
 Avg delta p , Δp in., H_2O _____
 Stack temp, T_s , $^{\circ}\text{F}$ _____
 Leak rate before run, cfm _____
 Leak rate after run, cfm _____
 Stop meter volume, ft^3 _____
 Start meter volume, ft^3 _____

POINT NO	SAMPLE (MIN/SEC)	GAS METER TEMP (F)		CRITICAL ORIFICE VACUUM IN. HG	POINT NO	SAMPLE (MIN/SEC)	GAS METER TEMP (F)		CRITICAL ORIFICE VACUUM IN. HG
TOTAL					TOTAL				
AVG					AVG				

REMARKS _____

Figure 306A-3. Chromium Constant Sampling Rate Field Data Sheet.

METHOD 306B—SURFACE TENSION MEASUREMENT FOR TANKS USED AT DECORATIVE CHROMIUM ELECTROPLATING AND CHROMIUM ANODIZING FACILITIES

NOTE: This method does not include all of the specifications (e.g., equipment and supplies) and procedures (e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from

other methods in 40 CFR Part 60, Appendix A and in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least Methods 5 and 306.

1.0 Scope and Application

- 1.1 Analyte. Not applicable.
- 1.2 Applicability. This method is applicable to all decorative chromium plating and

chromium anodizing operations, and continuous chromium plating at iron and steel facilities where a wetting agent is used in the tank as the primary mechanism for reducing emissions from the surface of the plating solution.

2.0 Summary of Method

2.1 During an electroplating or anodizing operation, gas bubbles generated during the process rise to the surface of the liquid and burst. Upon bursting, tiny droplets of chromic acid become entrained in ambient air. The addition of a wetting agent to the tank bath reduces the surface tension of the liquid and diminishes the formation of these droplets.

2.2 This method determines the surface tension of the bath using a stalagmometer or a tensiometer to confirm that there is sufficient wetting agent present.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies

6.1 Stalagmometer. Any commercially available stalagmometer or equivalent surface tension measuring device may be used to measure the surface tension of the plating or anodizing tank liquid.

6.2 Tensiometer. A tensiometer may be used to measure the surface tension of the tank liquid provided the procedures specified in ASTM Method D 1331-89, Standard Test Methods for Surface and Interfacial Tension of Solutions of Surface Active Agents (incorporated by reference—see §63.14) are followed.

7.0 Reagents and Standards [Reserved]

8.0 Sample Collection, Sample Recovery, Sample Preservation, Sample Holding Times, Storage, and Transport [Reserved]

9.0 Quality Control [Reserved]

10.0 Calibration and Standardization [Reserved]

11.0 Analytical Procedure

11.1 Procedure. The surface tension of the tank bath may be measured by using a tensiometer, a stalagmometer or any other equiv-

alent surface tension measuring device approved by the Administrator for measuring surface tension in dynes per centimeter. If the tensiometer is used, the procedures specified in ASTM Method D 1331-89 must be followed. If a stalagmometer or other device is used to measure surface tension, the instructions provided with the measuring device must be followed.

11.2 Frequency of Measurements.

11.2.1 Measurements of the bath surface tension are performed using a progressive system which decreases the frequency of surface tension measurements required when the proper surface tension is maintained.

11.2.1.1 Initially, following the compliance date, surface tension measurements must be conducted once every 4 hours of tank operation for the first 40 hours of tank operation.

11.2.1.2 Once there are no exceedances during a period of 40 hours of tank operation, measurements may be conducted once every 8 hours of tank operation.

11.2.1.3 Once there are no exceedances during a second period of 40 consecutive hours of tank operation, measurements may be conducted once every 40 hours of tank operation on an on-going basis, until an exceedance occurs. The maximum time interval for measurements is once every 40 hours of tank operation.

11.2.2 If a measurement of the surface tension of the solution is above the 45 dynes per centimeter limit, or above an alternate surface tension limit established during the performance test, the time interval shall revert back to the original monitoring schedule of once every 4 hours. A subsequent decrease in frequency would then be allowed according to Section 11.2.1.

12.0 Data Analysis and Calculations

12.1 Log Book of Surface Tension Measurements and Fume Suppressant Additions.

12.1.1 The surface tension of the plating or anodizing tank bath must be measured as specified in Section 11.2.

12.1.2 The measurements must be recorded in the log book. In addition to the record of surface tension measurements, the frequency of fume suppressant maintenance additions and the amount of fume suppressant added during each maintenance addition must be recorded in the log book.

12.1.3 The log book will be readily available for inspection by regulatory personnel.

12.2 Instructions for Apparatus Used in Measuring Surface Tension.

12.2.1 Included with the log book must be a copy of the instructions for the apparatus used for measuring the surface tension of the plating or anodizing bath.

12.2.2 If a tensiometer is used, a copy of ASTM Method D 1331-89 must be included with the log book.

13.0 *Method Performance [Reserved]*

14.0 *Pollution Prevention [Reserved]*

15.0 *Waste Management [Reserved]*

16.0 *References [Reserved]*

17.0 *Tables, Diagrams, Flowcharts, and Validation Data [Reserved]*

METHOD 307—DETERMINATION OF EMISSIONS FROM HALOGENATED SOLVENT VAPOR CLEANING MACHINES USING A LIQUID LEVEL PROCEDURE

1. Applicability and Principle

1.1 *Applicability.* This method is applicable to the determination of the halogenated solvent emissions from solvent vapor cleaners in the idling mode.

1.2 *Principle.* The solvent level in the solvent cleaning machine is measured using inclined liquid level indicators. The change in liquid level corresponds directly to the

amount of solvent lost from the solvent cleaning machine.

2. Apparatus

NOTE: Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

2.1 *Inclined Liquid Level Indicator.* A schematic of the inclined liquid level indicators used in this method is shown in figure 307-1; two inclined liquid level indicators having 0.05 centimeters divisions or smaller shall be used. The liquid level indicators shall be made of glass, Teflon, or any similar material that will not react with the solvent being used. A 6-inch by 1-inch slope is recommended; however the slope may vary depending on the size and design of the solvent cleaning machine.

NOTE: It is important that the inclined liquid level indicators be constructed with ease of reading in mind. The inclined liquid level indicators should also be mounted so that they can be raised or lowered if necessary to suit the solvent cleaning machine size.

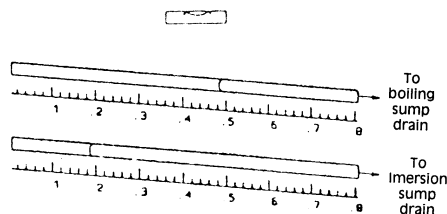


Figure 307-1. Inclined Liquid Level Indicator Apparatus.

2.2 *Horizontal Indicator.* Device to check the inclined liquid level indicators orientation relative to horizontal.

2.3 *Velocity Meter.* Hotwire and vane anemometers, or other devices capable of measuring the flow rates ranging from 0 to 15.2 meters per minute across the solvent cleaning machine.

3. Procedure

3.1 *Connection of the Inclined Liquid Level Indicator.* Connect one of the inclined liquid level indicators to the boiling sump drain and the other inclined liquid level indicator to the immersion sump drain using Teflon tubing and the appropriate fittings. A schematic diagram is shown in figure 307-2.

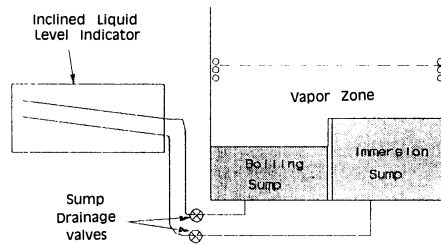


Figure 307-2. Solvent Cleaner Test Setup.

3.2 Positioning of Velocity Meter. Position the velocity meter so that it measures the flow rate of the air passing directly across the solvent cleaning machine.

3.3 Level the Inclined Liquid Level Indicators.

3.4 Initial Inclined Liquid Level Indicator Readings. Open the sump drainage valves. Allow the solvent cleaning machine to operate long enough for the vapor zone to form and the system to stabilize (check with manufacturer). Record the inclined liquid level indicators readings and the starting time on the data sheet. A sample data sheet is provided in figure 307-3.

Width of solvent vapor/air interface (W_v), m (ft) _____

Clock time	Boiling sump reading	Immersion sump reading	Flow rate reading

Figure 307-3. Data sheet.

- Date _____
- Run _____
- Solvent type _____
- Solvent density, g/m^3 (lb/ft^3) _____
- Length of boiling sump (S_B), m (ft) _____
- Width of boiling sump (W_B), m (ft) _____
- Length of immersion sump (S_I), m (ft) _____
- Width of immersion sump (W_I), m (ft) _____
- Length of solvent vapor/air interface (S_v), m (ft) _____

3.5 Final Inclined Liquid Level Indicator Readings. At the end of the 16-hour test run, check to make sure the inclined liquid level indicators are level; if not, make the necessary adjustments. Record the final inclined liquid level indicators readings and time.

3.6 Determination of Solvent Vapor/Air Interface Area for Each Sump. Determine the area of the solvent/air interface of the individual sumps. Whenever possible, physically measure these dimensions, rather than using factory specifications. A schematic of the dimensions of a solvent cleaning machine is provided in figure 307-4.

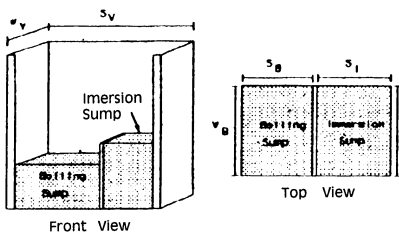


Figure 307-4. Solvent Cleaner Dimensions.

4. Calculations

4.1 Nomenclature.

- A_B = area of boiling sump interface, m^2 (ft^2).
- A_I = area of immersion sump interface, m^2 (ft^2).

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A_v = area of solvent/air interface, m^2 (ft^2).
 E = emission rate, kg/m^2-hr (lb/ft^2-hr).
 K = 100,000 $cm \cdot g/m \cdot kg$ for metric units.
 = 12 $in./ft$ for English units.
 L_{BF} = final boiling sump inclined liquid level indicators reading, cm ($in.$).
 L_{Bi} = initial boiling sump inclined liquid level indicators reading, cm ($in.$).
 L_{If} = final immersion sump inclined liquid level indicators reading, cm ($in.$).
 L_{Ii} = initial immersion sump inclined liquid level indicators reading, cm ($in.$).
 S_B = length of the boiling sump, m (ft).
 S_I = length of the immersion sump, m (ft).
 S_v = length of the solvent vapor/air interface, m (ft).
 W_B = width of the boiling sump, m (ft).
 W_I = width of the immersion sump, m (ft).
 W_v = width of the solvent vapor/air interface, m (ft).

ρ = density of solvent, g/m^3 (lb/ft^3).
 θ = test time, hr .
 4.2 Area of Sump Interfaces. Calculate the areas of the boiling and immersion sump interfaces as follows:

$$A_B = S_B W_B \quad \text{Eq. 307-1}$$

$$A_I = S_I W_I \quad \text{Eq. 307-2}$$

4.3 Area of Solvent/Air Interface. Calculate the area of the solvent vapor/air interface as follows:

$$A_v = S_v W_v \quad \text{Eq. 307-3}$$

4.4 Emission Rate. Calculate the emission rate as follows:

$$E = \frac{(L_{BF} - L_{Bi})\rho A_B + (L_{If} - L_{Ii})\rho A_I}{KA_v\theta}$$

Eq. 307-4

METHOD 308—PROCEDURE FOR DETERMINATION OF METHANOL EMISSION FROM STATIONARY SOURCES

1.0 Scope and Application

1.1 Analyte. Methanol. Chemical Abstract Service (CAS) No. 67-56-1.

1.2 Applicability. This method applies to the measurement of methanol emissions from specified stationary sources.

2.0 Summary of Method

A gas sample is extracted from the sampling point in the stack. The methanol is collected in deionized distilled water and adsorbed on silica gel. The sample is returned to the laboratory where the methanol in the water fraction is separated from other organic compounds with a gas chromatograph (GC) and is then measured by a flame ionization detector (FID). The fraction adsorbed on silica gel is extracted with an aqueous solution of n-propanol and is then separated and measured by GC/FID.

3.0 Definitions [Reserved]

4.0 Interferences [Reserved]

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations before performing this test method.

5.2 Methanol Characteristics. Methanol is flammable and a dangerous fire and explosion risk. It is moderately toxic by ingestion and inhalation.

6.0 Equipment and Supplies

6.1 Sample Collection. The following items are required for sample collection:

6.1.1 Sampling Train. The sampling train is shown in Figure 308-1 and component parts are discussed below.

6.1.1.1 Probe. Teflon®, approximately 6-millimeter (mm) (0.24 inch) outside diameter.

6.1.1.2 Impinger. A 30-milliliter (ml) mid-gel impinger. The impinger must be connected with leak-free glass connectors. Silicone grease may not be used to lubricate the connectors.

6.1.1.3 Adsorbent Tube. Glass tubes packed with the required amount of the specified adsorbent.

6.1.1.4 Valve. Needle valve, to regulate sample gas flow rate.

6.1.1.5 Pump. Leak-free diaphragm pump, or equivalent, to pull gas through the sampling train. Install a small surge tank between the pump and rate meter to eliminate the pulsation effect of the diaphragm pump on the rotameter.

6.1.1.6 Rate Meter. Rotameter, or equivalent, capable of measuring flow rate to within 2 percent of the selected flow rate of up to 1000 milliliter per minute (ml/min). Alternatively, the tester may use a critical orifice to set the flow rate.

6.1.1.7 Volume Meter. Dry gas meter (DGM), sufficiently accurate to measure the sample volume to within 2 percent, calibrated at the selected flow rate and conditions actually encountered during sampling, and equipped with a temperature sensor (dial thermometer, or equivalent) capable of measuring temperature accurately to within 3 °C (5.4 °F).

6.1.1.8 Barometer. Mercury (Hg), aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm (0.1 inch) Hg. See the NOTE in Method 5 (40 CFR part 60, appendix A), section 6.1.2.

6.1.1.9 Vacuum Gauge and Rotameter. At least 760-mm (30-inch) Hg gauge and 0- to 40-

ml/min rotameter, to be used for leak-check of the sampling train.

6.2 Sample Recovery. The following items are required for sample recovery:

6.2.1 Wash Bottles. Polyethylene or glass, 500-ml, two.

6.2.2 Sample Vials. Glass, 40-ml, with Teflon®-lined septa, to store impinger samples (one per sample).

6.2.3 Graduated Cylinder. 100-ml size.

6.3 Analysis. The following are required for analysis:

6.3.1 Gas Chromatograph. GC with an FID, programmable temperature control, and heated liquid injection port.

6.3.2 Pump. Capable of pumping 100 ml/min. For flushing sample loop.

6.3.3 Flow Meter. To monitor accurately sample loop flow rate of 100 ml/min.

6.3.4 Regulators. Two-stage regulators used on gas cylinders for GC and for cylinder standards.

6.3.5 Recorder. To record, integrate, and store chromatograms.

6.3.6 Syringes. 1.0- and 10-microliter (1) size, calibrated, for injecting samples.

6.3.7 Tubing Fittings. Stainless steel, to plumb GC and gas cylinders.

6.3.8 Vials. Two 5.0-ml glass vials with screw caps fitted with Teflon®-lined septa for each sample.

6.3.9 Pipettes. Volumetric type, assorted sizes for preparing calibration standards.

6.3.10 Volumetric Flasks. Assorted sizes for preparing calibration standards.

6.3.11 Vials. Glass 40-ml with Teflon®-lined septa, to store calibration standards (one per standard).

7.0 Reagents and Standards

NOTE: Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society. Where such specifications are not available, use the best available grade.

7.1 Sampling. The following are required for sampling:

7.1.1 Water. Deionized distilled to conform to the American Society for Testing and Materials (ASTM) Specification D 1193-77, Type 3. At the option of the analyst, the potassium permanganate (KMnO₄) test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

7.1.2 Silica Gel. Deactivated chromatographic grade 20/40 mesh silica gel packed in glass adsorbent tubes. The silica gel is packed in two sections. The front section contains 520 milligrams (mg) of silica gel, and the back section contains 260 mg.

7.2 Analysis. The following are required for analysis:

7.2.1 Water. Same as specified in section 7.1.1.

7.2.2 n-Propanol, 3 Percent. Mix 3 ml of n-propanol with 97 ml of water.

7.2.3 Methanol Stock Standard. Prepare a methanol stock standard by weighing 1 gram of methanol into a 100-ml volumetric flask. Dilute to 100 ml with water.

7.2.3.1 Methanol Working Standard. Prepare a methanol working standard by pipetting 1 ml of the methanol stock standard into a 100-ml volumetric flask. Dilute the solution to 100 ml with water.

7.2.3.2 Methanol Standards For Impinger Samples. Prepare a series of methanol standards by pipetting 1, 2, 5, 10, and 25 ml of methanol working standard solution respectively into five 50-ml volumetric flasks. Dilute the solutions to 50 ml with water. These standards will have 2, 4, 10, 20, and 50 µg/ml of methanol, respectively. After preparation, transfer the solutions to 40-ml glass vials capped with Teflon® septa and store the vials under refrigeration. Discard any excess solution.

7.2.3.3 Methanol Standards for Adsorbent Tube Samples. Prepare a series of methanol standards by first pipetting 10 ml of the methanol working standard into a 100-ml volumetric flask and diluting the contents to exactly 100 ml with 3 percent n-propanol solution. This standard will contain 10 µg/ml of methanol. Pipette 5, 15, and 25 ml of this standard, respectively, into four 50-ml volumetric flasks. Dilute each solution to 50 ml with 3 percent n-propanol solution. These standards will have 1, 3, and 5 µg/ml of methanol, respectively. Transfer all four standards into 40-ml glass vials capped with Teflon®-lined septa and store under refrigeration. Discard any excess solution.

7.2.4 GC Column. Capillary column, 30 meters (100 feet) long with an inside diameter (ID) of 0.53 mm (0.02 inch), coated with DB 624 to a film thickness of 3.0 micrometers, (µm) or an equivalent column. Alternatively, a 30-meter capillary column coated with polyethylene glycol to a film thickness of 1 µm such as AT-WAX or its equivalent.

7.2.5 Helium. Ultra high purity.

7.2.6 Hydrogen. Zero grade.

7.2.7 Oxygen. Zero grade.

8.0 Procedure

8.1 Sampling. The following items are required for sampling:

8.1.1 Preparation of Collection Train. Measure 20 ml of water into the midget impinger. The adsorbent tube must contain 520 mg of silica gel in the front section and 260 mg of silica gel in the backup section. Assemble the train as shown in Figure 308-1. An optional, second impinger that is left empty may be placed in front of the water-containing impinger to act as a condensate trap. Place crushed ice and water around the impinger.

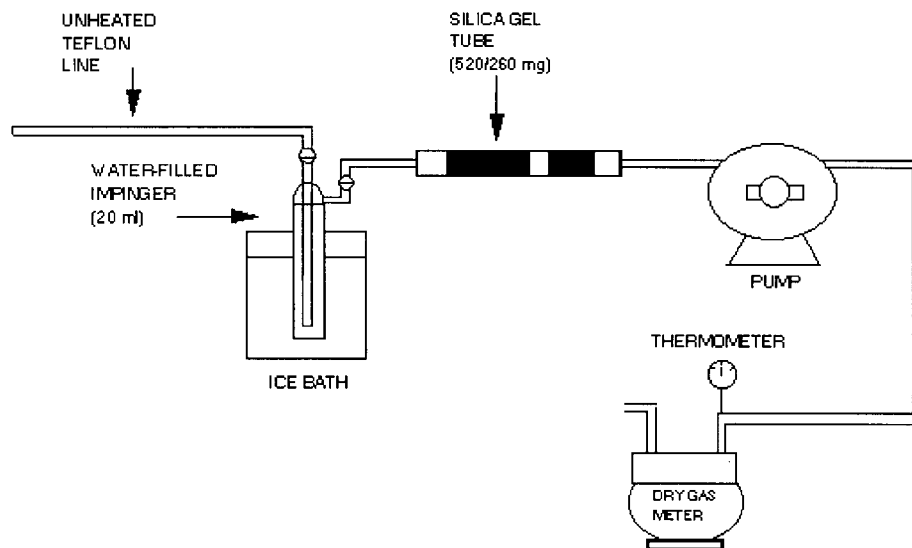


Figure 308.1. Sampling train schematic

8.1.2 Leak Check. A leak check prior to the sampling run is optional; however, a leak check after the sampling run is mandatory. The leak-check procedure is as follows:

Temporarily attach a suitable (e.g., 0-to 40-ml/min) rotameter to the outlet of the DGM, and place a vacuum gauge at or near the probe inlet. Plug the probe inlet, pull a vacuum of at least 250 mm (10 inch) Hg, and note the flow rate as indicated by the rotameter. A leakage rate not in excess of 2 percent of the average sampling rate is acceptable.

NOTE: Carefully release the probe inlet plug before turning off the pump.

8.1.3 Sample Collection. Record the initial DGM reading and barometric pressure. To begin sampling, position the tip of the Teflon® tubing at the sampling point, connect the tubing to the impinger, and start the pump. Adjust the sample flow to a constant rate between 200 and 1000 ml/min as indicated by the rotameter. Maintain this constant rate (± 10 percent) during the entire sampling run. Take readings (DGM, temperatures at DGM and at impinger outlet, and rate meter) at least every 5 minutes. Add more ice during the run to keep the temperature of the gases leaving the last impinger at 20 °C (68 °F) or less. At the conclusion of each run,

turn off the pump, remove the Teflon® tubing from the stack, and record the final readings. Conduct a leak check as in section 8.1.2. (This leak check is mandatory.) If a leak is found, void the test run or use procedures acceptable to the Administrator to adjust the sample volume for the leakage.

8.2 Sample Recovery. The following items are required for sample recovery:

8.2.1 Impinger. Disconnect the impinger. Pour the contents of the midget impinger into a graduated cylinder. Rinse the midget impinger and the connecting tubes with water, and add the rinses to the graduated cylinder. Record the sample volume. Transfer the sample to a glass vial and cap with a Teflon® septum. Discard any excess sample. Place the samples in an ice chest for shipment to the laboratory.

8.2.2 Adsorbent Tubes. Seal the silica gel adsorbent tubes and place them in an ice chest for shipment to the laboratory.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures. The following quality control measures are required:

Section	Quality control measure	Effect
8.1.2, 8.1.3, 10.1.	Sampling equipment leak check and calibration.	Ensures accurate measurement of sample volume.
10.2	GC calibration	Ensures precision of GC analysis.

9.2 Applicability. When the method is used to analyze samples to demonstrate compliance with a source emission regulation, an audit sample must be analyzed, subject to availability.

9.3 Audit Procedure. Analyze an audit sample with each set of compliance samples. Concurrently analyze the audit sample and a set of compliance samples in the same manner to evaluate the technique of the analyst and the standards preparation. The same analyst, analytical reagents, and analytical system shall be used both for the compliance samples and the EPA audit sample.

9.4 Audit Sample Availability. Audit samples will be supplied only to enforcement agencies for compliance tests. Audit samples may be obtained by writing: Source Test Audit Coordinator (MD-77B), Air Measurement Research Division, National Exposure Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711; or by calling the Source Test Audit Coordinator (STAC) at (919) 541-7834. The audit sample request must be made at least 30 days prior to the scheduled compliance sample analysis.

9.5 Audit Results. Calculate the audit sample concentration according to the calculation procedure provided in the audit instructions included with the audit sample.

Fill in the audit sample concentration and the analyst's name on the audit response form included with the audit instructions. Send one copy to the EPA Regional Office or the appropriate enforcement agency and a second copy to the STAC. The EPA Regional office or the appropriate enforcement agency will report the results of the audit to the laboratory being audited. Include this response with the results of the compliance samples in relevant reports to the EPA Regional Office or the appropriate enforcement agency.

10.0 Calibration and Standardization

10.1 Metering System. The following items are required for the metering system:

10.1.1 Initial Calibration.

10.1.1.1 Before its initial use in the field, first leak-check the metering system (drying tube, needle valve, pump, rotameter, and DGM) as follows: Place a vacuum gauge at the inlet to the drying tube, and pull a vacuum of 250 mm (10 inch) Hg; plug or pinch off the outlet of the flow meter, and then turn off the pump. The vacuum shall remain stable for at least 30 seconds. Carefully release the vacuum gauge before releasing the flow meter end.

10.1.1.2 Next, remove the drying tube, and calibrate the metering system (at the sampling flow rate specified by the method) as follows: Connect an appropriately sized wet test meter (e.g., 1 liter per revolution (0.035 cubic feet per revolution)) to the inlet of the drying tube. Make three independent calibrations runs, using at least five revolutions of the DGM per run. Calculate the calibration factor, Y (wet test meter calibration volume divided by the DGM volume, both volumes adjusted to the same reference temperature and pressure), for each run, and average the results. If any Y-value deviates by more than 2 percent from the average, the metering system is unacceptable for use. Otherwise, use the average as the calibration factor for subsequent test runs.

10.1.2 Posttest Calibration Check. After each field test series, conduct a calibration check as in section 10.1.1 above, except for the following variations: (a) The leak check is not to be conducted, (b) three, or more revolutions of the DGM may be used, and (c) only two independent runs need be made. If the calibration factor does not deviate by more than 5 percent from the initial calibration factor (determined in section 10.1.1), then the DGM volumes obtained during the test series are acceptable. If the calibration factor deviates by more than 5 percent, recalibrate the metering system as in section 10.1.1, and for the calculations, use the calibration factor (initial or recalibration) that yields the lower gas volume for each test run.

10.1.3 Temperature Sensors. Calibrate against mercury-in-glass thermometers.

10.1.4 Rotameter. The rotameter need not be calibrated, but should be cleaned and maintained according to the manufacturer's instruction.

10.1.5 Barometer. Calibrate against a mercury barometer.

10.2 Gas Chromatograph. The following procedures are required for the gas chromatograph:

10.2.1 Initial Calibration. Inject 1 μ l of each of the standards prepared in sections 7.2.3.3 and 7.2.3.4 into the GC and record the response. Repeat the injections for each standard until two successive injections agree within 5 percent. Using the mean response for each calibration standard, prepare a linear least squares equation relating the response to the mass of methanol in the sample. Perform the calibration before analyzing each set of samples.

10.2.2 Continuing Calibration. At the beginning of each day, analyze the mid level calibration standard as described in section 10.5.1. The response from the daily analysis must agree with the response from the initial calibration within 10 percent. If it does not, the initial calibration must be repeated.

11.0 Analytical Procedure

11.1 Gas Chromatograph Operating Conditions. The following operating conditions are required for the GC:

11.1.1 Injector. Configured for capillary column, splitless, 200 °C (392 °F).

11.1.2 Carrier. Helium at 10 ml/min.

11.1.3 Oven. Initially at 45 °C for 3 minutes; then raise by 10 °C to 70 °C; then raise by 70 °C/min to 200 °C.

11.2 Impinger Sample. Inject 1 μ l of the stored sample into the GC. Repeat the injection and average the results. If the sample response is above that of the highest calibration standard, either dilute the sample until it is in the measurement range of the calibration line or prepare additional calibration standards. If the sample response is below that of the lowest calibration standard, prepare additional calibration standards. If additional calibration standards are prepared, there shall be at least two that bracket the response of the sample. These standards should produce approximately 50 percent and 150 percent of the response of the sample.

11.3 Silica Gel Adsorbent Sample. The following items are required for the silica gel adsorbent samples:

11.3.1 Preparation of Samples. Extract the front and backup sections of the adsorbent tube separately. With a file, score the glass adsorbent tube in front of the first section of silica gel. Break the tube open. Remove and discard the glass wool. Transfer the first section of the silica gel to a 5-ml glass vial and stopper the vial. Remove the spacer between

the first and second section of the adsorbent tube and discard it. Transfer the second section of silica gel to a separate 5-ml glass vial and stopper the vial.

11.3.2 Desorption of Samples. Add 3 ml of the 10 percent n-propanol solution to each of the stoppered vials and shake or vibrate the vials for 30 minutes.

11.3.3 Inject a 1- μ l aliquot of the diluted sample from each vial into the GC. Repeat the injection and average the results. If the sample response is above that of the highest calibration standard, either dilute the sample until it is in the measurement range of the calibration line or prepare additional calibration standards. If the sample response is below that of the lowest calibration standard, prepare additional calibration standards. If additional calibration standards are prepared, there shall be at least two that bracket the response of the sample. These standards should produce approximately 50 percent and 150 percent of the response of the sample.

12.0 Data Analysis and Calculations

12.1 Nomenclature.

C_{af} =Concentration of methanol in the front of the adsorbent tube, μ g/ml.

C_{ab} =Concentration of methanol in the back of the adsorbent tube, μ g/ml.

C_i =Concentration of methanol in the impinger portion of the sample train, μ g/ml.

E =Mass emission rate of methanol, μ g/hr (lb/hr).

M_{tot} =Total mass of methanol collected in the sample train, μ g.

P_{bar} =Barometric pressure at the exit orifice of the DGM, mm Hg (in. Hg).

P_{std} =Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

Q_{std} =Dry volumetric stack gas flow rate corrected to standard conditions, dscm/hr (dscf/hr).

T_m =Average DGM absolute temperature, degrees K (°R).

T_{std} =Standard absolute temperature, 293 degrees K (528 °R).

V_{af} =Volume of front half adsorbent sample, ml.

V_{ab} =Volume of back half adsorbent sample, ml.

V_i =Volume of impinger sample, ml.

V_m =Dry gas volume as measured by the DGM, dry cubic meters (dcm), dry cubic feet (dcf).

$V_{m(std)}$ =Dry gas volume measured by the DGM, corrected to standard conditions, dry standard cubic meters (dscm), dry standard cubic feet (dscf).

12.2 Mass of Methanol. Calculate the total mass of methanol collected in the sampling train using Equation 308-1.

$$M_{\text{tot}} = V_i C_i + V_{\text{af}} C_{\text{af}} + V_{\text{ab}} C_{\text{ab}} \quad \text{Equation 308-1}$$

12.3 Dry Sample Gas Volume, Corrected to Standard Conditions. Calculate the volume of gas sampled at standard conditions using Equation 308-2.

$$V_m(\text{std}) = \frac{V_m Y T_{\text{std}} P_{\text{bar}}}{T_m P_{\text{std}}} \quad \text{Equation 308-2}$$

12.4 Mass Emission Rate of Methanol. Calculate the mass emission rate of methanol using Equation 308-3.

$$E = \frac{M_{\text{tot}} Q_{\text{sd}}}{V_m(\text{std})} \quad \text{Equation 308-3}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Bibliography

1. Rom, J.J. "Maintenance, Calibration, and Operation of Isokinetic Source Sampling Equipment." Office of Air Programs, Environmental Protection Agency. Research Triangle Park, NC. APTD-0576 March 1972.
2. Annual Book of ASTM Standards. Part 31; Water, Atmospheric Analysis. American Society for Testing and Materials. Philadelphia, PA. 1974. pp. 40-42.
3. Westlin, P.R. and R.T. Shigehara. "Procedure for Calibrating and Using Dry Gas Volume Meters as Calibration Standards." Source Evaluation Society Newsletter. 3(1):17-30. February 1978.
4. Yu, K.K. "Evaluation of Moisture Effect on Dry Gas Meter Calibration." Source Evaluation Society Newsletter. 5(1):24-28. February 1980.
5. NIOSH Manual of Analytical Methods, Volume 2. U.S. Department of Health and Human Services National Institute for Occupational Safety and Health. Center for Disease Control. 4676 Columbia Parkway, Cincinnati, OH 45226. (available from the Superintendent of Documents, Government Printing Office, Washington, DC 20402.)
6. Pinkerton, J.E. "Method for Measuring Methanol in Pulp Mill Vent Gases." National Council of the Pulp and Paper Industry for Air and Stream Improvement, Inc., New York, NY.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

[Reserved]

METHOD 310A—DETERMINATION OF RESIDUAL HEXANE THROUGH GAS CHROMATOGRAPHY

1.0 Scope and Application

- 1.1 This method is used to analyze any crumb rubber or water samples for residual hexane content.
- 1.2 The sample is heated in a sealed bottle with an internal standard and the vapor is analyzed by gas chromatography.

2.0 Summary of Method

2.1 This method, utilizing a capillary column gas chromatograph with a flame ionization detector, determines the concentration of residual hexane in rubber crumb samples.

3.0 Definitions

3.1 The definitions are included in the text as needed.

4.0 Interferences

4.1 There are no known interferences.

5.0 Safety

5.1 It is the responsibility of the user of this procedure to establish safety and health practices applicable to their specific operation.

6.0 Equipment and Supplies

6.1 Gas Chromatograph with a flame ionization detector and data handling station

equipped with a capillary column 30 meters long.

6.2 Chromatograph conditions for Sigma 1:

- 6.2.1 Helium pressure: 50# inlet A, 14# aux
- 6.2.2 Carrier flow: 25 cc/min
- 6.2.3 Range switch: 100x
- 6.2.4 DB: 1 capillary column

6.3 Chromatograph conditions for Hewlett-Packard GC:

- 6.3.1 Initial temperature: 40 °C
- 6.3.2 Initial time: 8 min
- 6.3.3 Rate: 0
- 6.3.4 Range: 2
- 6.3.5 DB: 1705 capillary column
- 6.4 Septum bottles and stoppers
- 6.5 Gas Syringe—0.5 cc

7.0 Reagents and Standards

7.1 Chloroform, 99.9+%, A.S.C. HPLC grade

8.0 Sample Collection, Preservation, and Storage

8.1 A representative sample should be caught in a clean 8 oz. container with a secure lid.

8.2 The container should be labeled with sample identification, date and time.

9.0 Quality Control

9.1 The instrument is calibrated by injecting calibration solution (Section 10.2 of this method) five times.

9.2 The retention time for components of interest and relative response of monomer to the internal standard is determined.

9.3 Recovery efficiency must be determined once for each sample type and whenever modifications are made to the method.

9.3.1 Determine the percent hexane in three separate dried rubber crumb samples.

9.3.2 Weigh a portion of each crumb sample into separate sample bottles and add a known amount of hexane (10 microliters) by microliter syringe and 20 microliters of internal standard. Analyze each by the described procedure and calculate the percent recovery of the known added hexane.

9.3.3 Repeat the previous step using twice the hexane level (20 microliters), analyze and calculate the percent recovery of the known added hexane.

9.3.4 Set up two additional sets of samples using 10 microliters and 20 microliters of hexane as before, but add an amount of water equal to the dry crumb used. Analyze and calculate percent recovery to show the effect of free water on the results obtained.

9.3.5 A value of R between 0.70 and 1.30 is acceptable.

9.3.6 R shall be used to correct all reported results for each compound by dividing the measured results of each compound by the R for that compound for the same sample type.

10.0 Calibration and Instrument Settings

10.1 Calibrate the chromatograph using a standard made by injecting 10 µl of fresh hexane and 20 µl of chloroform into a sealed septum bottle. This standard will be 0.6 wt.% total hexane based on 1 gram of dry rubber.

10.2 Analyze the hexane used and calculate the percentage of each hexane isomer (2-methylpentane, 3-methylpentane, n-hexane, and methylcyclopentane). Enter these percentages into the method calibration table.

10.3 Heat the standard bottle for 30 minutes in a 105 °C oven.

10.4 Inject about 0.25 cc of vapor into the gas chromatograph and after the analysis is finished, calibrate according to the procedures described by the instrument manufacturer.

11.0 Procedure

11.1 Using a cold mill set at a wide roller gap (125–150 mm), mill about 250 grams of crumb two times to homogenize the sample.

11.2 Weigh about 2 grams of wet crumb into a septum bottle and cap with a septum ring. Add 20 µl of chloroform with a syringe and place in a 105 °C oven for 45 minutes.

11.3 Run the moisture content on a separate portion of the sample and calculate the grams of dry rubber put into the septum bottle.

11.4 Set up the data station on the required method and enter the dry rubber weight in the sample weight field.

11.5 Inject a 0.25 cc vapor sample into the chromatograph and push the start button.

11.6 At the end of the analysis, the data station will print a report listing the concentration of each identified component.

11.7 To analyze water samples, pipet 5 ml of sample into the septum bottle, cap and add 20 µl of chloroform. Place in a 105 °C oven for 30 minutes.

11.8 Enter 5 grams into the sample weight field.

11.9 Inject a 0.25 cc vapor sample into the chromatograph and push the start button.

11.10 At the end of the analysis, the data station will print a report listing the concentration of each identified component.

12.0 Data Analysis and Calculation

12.1 For samples that are prepared as in section 11 of this method, ppm n-hexane is read directly from the computer.

12.2 The formulas for calculation of the results are as follows:

$$\text{ppm}_{\text{hexane}} = (A_{\text{hexane}} \times R_{\text{hexane}}) / (A_{\text{is}} \times R_{\text{is}})$$

Where:

A_{hexane} = area of hexane

R_{hexane} = response of hexane

A_{is} = area of the internal standard

R_{is} = response of the internal standard

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% hexane in crumb=(ppm_{hexane}/sample amount)100

12.3 Correct the results by the value of R (as determined in sections 9.3.4, 9.3.5, and 9.3.6 of this method).

13.0 Method Performance

13.1 The test has a standard deviation of 0.14 wt% at 0.66 wt% hexane. Spike recovery of 12 samples at two levels of hexane averaged 102.3%. Note: Recovery must be determined for each type of sample. The values given here are meant to be examples of method performance.

14.0 Pollution Prevention

14.1 Waste generation should be minimized where possible. Sample size should be

an amount necessary to adequately run the analysis.

15.0 Waste Management

15.1 All waste shall be handled in accordance with federal and state environmental regulations.

16.0 References and Publications

16.1 DSM Copolymer Test Method T-3380.

METHOD 310B—DETERMINATION OF RESIDUAL HEXANE THROUGH GAS CHROMATOGRAPHY

1.0 Scope and Application

Analyte	CAS No.	Matrix	Method sensitivity (5.5g sample size)
Hexane	110-54-3	Rubber crumb01 wt%.
Applicable Termonomer	Rubber crumb001 wt%.

1.1 Data Quality Objectives:

In the production of ethylene-propylene terpolymer crumb rubber, the polymer is recovered from solution by flashing off the solvent with steam and hot water. The resulting water-crumb slurry is then pumped to the finishing units. Certain amounts of solvent (hexane being the most commonly used solvent) and diene monomer remain in the crumb. The analyst uses the following procedure to determine those amounts.

2.0 Summary of Method

2.1 The crumb rubber sample is dissolved in toluene to which heptane has been added as an internal standard. Acetone is then added to this solution to precipitate the crumb, and the supernatant is analyzed for hexane and diene by a gas chromatograph equipped with a flame ionization detector (FID).

3.0 Definitions

3.1 Included in text as needed.

4.0 Interferences

4.1 None known.

4.2 Benzene, introduced as a contaminant in the toluene solvent, elutes between methyl cyclopentane and cyclohexane. However, the benzene peak is completely resolved.

4.3 2,2-dimethyl pentane, a minor component of the hexane used in our process, elutes just prior to methyl cyclopentane. It is included as "hexane" in the analysis whether it is integrated separately or included in the methyl cyclopentane peak.

5.0 Safety

5.1 This procedure does not purport to address all of the safety concerns associated with its use. It is the responsibility of the user of this procedure to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

5.2 Chemicals used in this analysis are flammable and hazardous (see specific toxicity information below). Avoid contact with sources of ignition during sample prep. All handling should be done beneath a hood. Playtex or nitrile gloves recommended.

5.3 Hexane is toxic by ingestion and inhalation. Vapor inhalation causes irritation of nasal and respiratory passages, headache, dizziness, nausea, central nervous system depression. Chronic overexposure can cause severe nerve damage. May cause irritation on contact with skin or eyes. May cause damage to kidneys.

5.4 Termonomer may be harmful by inhalation, ingestion, or skin absorption. Vapor or mist is irritating to the eyes, mucous membranes, and upper respiratory tract. Causes skin irritation.

5.5 Toluene is harmful or fatal if swallowed. Vapor harmful if inhaled. Symptoms: headache, dizziness, hallucinations, distorted perceptions, changes in motor activity, nausea, diarrhea, respiratory irritation, central nervous system depression, unconsciousness, liver, kidney and lung damage. Contact can cause severe eye irritation. May cause skin irritation. Causes irritation of eyes, nose, and throat.

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5.6 Acetone, at high concentrations or prolonged overexposure, may cause headache, dizziness, irritation of eyes and respiratory tract, loss of strength, and narcosis. Eye contact causes severe irritation; skin contact may cause mild irritation. Concentrations of 20,000 ppm are immediately dangerous to life and health.

5.7 Heptane is harmful if inhaled or swallowed. May be harmful if absorbed through the skin. Vapor or mist is irritating to the eyes, mucous membranes, and upper respiratory tract. Prolonged or repeated exposure to skin causes defatting and dermatitis.

5.8 The steam oven used to dry the polymer in this procedure is set at 110 °C. Wear leather gloves when removing bottles from the oven.

6.0 Equipment and Supplies

- 6.1 4000-ml volumetric flask
- 6.2 100-ml volumetric pipette
- 6.3 1000-ml volumetric flask
- 6.4 8-oz. French Square sample bottles with plastic-lined caps
- 6.5 Top-loading balance
- 6.6 Laboratory shaker
- 6.7 Laboratory oven set at 110 °C (steam oven)
- 6.8 Gas chromatograph, Hewlett-Packard 5890A, or equivalent, interfaced with HP 7673A (or equivalent) autosampler (equipped with nanoliter adapter and robotic arm), and HP 3396 series II or 3392A (or equivalent) integrator/controller.
- 6.9 GC column, capillary type, 50m × 0.53mm, methyl silicone, 5 micron film thickness, Quadrex, or equivalent.
- 6.10 Computerized data acquisition system, such as CIS/CALS

6.11 Crimp-top sample vials and HP p/n 5181-1211 crimp caps, or screw-top autosampler vials and screw tops.

6.12 Glass syringes, 5-ml, with “Luer-lock” fitting

6.13 Filters, PTFE, .45µm pore size, Gelman Acrodisc or equivalent, to fit on Luer-lock syringes (in 6.12, above).

7.0 Reagents and Standards

7.1 Reagent toluene, EM Science Omnisolv (or equivalent)

Purity Check: Prior to using any bottle of reagent toluene, analyze it according to section 11.2 of this method. Use the bottle only if hexane, heptane, and termonomer peak areas are less than 15 each (note that an area of 15 is equivalent to less than 0.01 wt% in a 10g sample).

7.2 Reagent acetone, EM Science Omnisolv HR-GC (or equivalent)

Purity Check: Prior to using any bottle of reagent acetone, analyze it according to section 11.2 of this method. Use the bottle only if hexane, heptane, and termonomer peak areas are less than 15 each.

7.3 Reagent heptane, Aldrich Chemical Gold Label, Cat #15,487-3 (or equivalent)

Purity Check: Prior to using any bottle of reagent heptane, analyze it according to section 11.2 of this method. Use the bottle only if hexane and termonomer peak areas are less than 5 each.

7.4 Internal standard solution—used as a concentrate for preparation of the more dilute Polymer Dissolving Solution. It contains 12.00g heptane/100ml of solution which is 120.0g per liter.

Preparation of internal standard solution (polymer dissolving stock solution):

Action	Notes
7.4.1 Tare a clean, dry 1-liter volumetric flask on the balance. Record the weight to three places.	If the 1-liter volumetric flask is too tall to fit in the balance case, you can shield the flask from drafts by inverting a paint bucket with a hole cut in the bottom over the balance cover. Allow the neck of the flask to project through the hole in the bucket.
7.4.2 Weigh 120.00 g of n-heptane into the flask. Record the total weight of the flask and heptane as well as the weight of heptane added.	Use 99+% n-heptane from Aldrich or Janssen Chimica.
7.4.3 Fill the flask close to the mark with toluene, about 1 to 2" below the mark.	Use EM Science Omnisolve toluene, Grade TX0737-1, or equivalent.
7.4.4 Shake the flask vigorously to mix the contents	Allow any bubbles to clear before proceeding to the next step.
7.4.5 Top off the flask to the mark with toluene. Shake vigorously, as in section 7.4.4 of this method, to mix well.	
7.4.6 Weigh the flask containing the solution on the three place balance record the weight	
7.4.7 Transfer the contents of the flask to a 1 qt Boston round bottle.	Discard any excess solution
7.4.8 Label the bottle with the identity of the contents, the weights of heptane and toluene used, the date of preparation and the preparer's name.	Be sure to include the words "Hexane in Crumb Polymer Dissolving Stock Solution" on the label.
7.4.9 Refrigerate the completed blend for the use of the routine Technicians.	

7.5 Polymer Dissolving Solution ("PDS")—Heptane (as internal standard) in toluene. This solution contains 0.3g of heptane internal standard per 100 ml of solution.

7.5.1 Preparation of Polymer Dissolving Solution. Fill a 4,000-ml volumetric flask about $\frac{3}{4}$ full with toluene.

7.5.2 Add 100 ml of the internal standard solution (section 7.4 of this method) to the flask using the 100ml pipette.

7.5.3 Fill the flask to the mark with toluene. Discard any excess.

7.5.4 Add a large magnetic stirring bar to the flask and mix by stirring.

7.5.5 Transfer the polymer solvent solution to the one-gallon labeled container with 50ml volumetric dispenser attached.

7.5.6 Purity Check: Analyze according to section 11.2. *NOTE:* You must "precipitate" the sample with an equal part of acetone (thus duplicating actual test conditions— see section 11.1 of this method, sample prep) before analyzing. Analyze the reagent 3 times to quantify the C_6 and termonomer interferences. Inspect the results to ensure good agreement among the three runs (within 10%).

7.5.7 Tag the bottle with the following information:

POLYMER DISSOLVING SOLUTION
FOR C_6 IN CRUMB ANALYSIS
PREPARER'S NAME
DATE
CALS FILE ID'S OF THE THREE
ANALYSES FOR PURITY (from section
7.5.6 of this method)

7.6 Quality Control Solution: the quality control solution is prepared by adding specific amounts of mixed hexanes (barge hexane), n-nonane and termonomer to some polymer dissolving solution. Nonane elutes in the same approximate time region as termonomer and is used to quantify in that region because it has a longer shelf life. Termonomer, having a high tendency to polymerize, is used in the QC solution only to ensure that both termonomer isomers elute at the proper time.

First, a concentrated stock solution is prepared; the final QC solution can then be prepared by diluting the stock solution.

7.6.1 In preparation of stock solution, fill a 1-liter volumetric flask partially with polymer dissolving solution (PDS)—see section 7.5 of this method. Add 20.0 ml barge hexane, 5.0 ml n-nonane, and 3 ml termonomer. Finish filling the volumetric to the mark with PDS.

7.6.2 In preparation of quality control solution, dilute the quality control stock solution (above) precisely 1:10 with PDS, i.e. 10 ml of stock solution made up to 100 ml (volumetric flask) with PDS. Pour the solution into a 4 oz. Boston round bottle and store in the refrigerator.

8.0 Sample Collection, Preservation and Storage

8.1 Line up facility to catch crumb samples. The facility is a special facility where the sample is drawn.

8.1.1 Ensure that the cock valve beneath facility is closed.

8.1.2 Line up the system from the slurry line cock valve to the cock valve at the nozzle on the stripper.

8.1.3 Allow the system to flush through facility for a period of 30 seconds.

8.2 Catch a slurry crumb sample.

8.2.1 Simultaneously close the cock valves upstream and downstream of facility.

8.2.2 Close the cock valve beneath the slurry line in service.

8.2.3 Line up the cooling tower water through the sample bomb water jacket to the sewer for a minimum of 30 minutes.

8.2.4 Place the sample catching basket beneath facility and open the cock valve underneath the bomb to retrieve the rubber crumb.

8.2.5 If no rubber falls by gravity into the basket, line up nitrogen to the bleeder upstream of the sample bomb and force the rubber into the basket.

8.2.6 Close the cock valve underneath the sample bomb.

8.3 Fill a plastic "Whirl-pak" sample bag with slurry crumb and send it to the lab immediately.

8.4 Once the sample reaches the lab, it should be prepped as soon as possible to avoid hexane loss through evaporation. Samples which have lain untouched for more than 30 minutes should be discarded.

9.0 Quality Control

Quality control is monitored via a computer program that tracks analyses of a prepared QC sample (from section 7.6.2 of this method). The QC sample result is entered daily into the program, which plots the result as a data point on a statistical chart. If the data point does not satisfy the "in-control" criteria (as defined by the lab quality facilitator), an "out-of-control" flag appears, mandating corrective action.

In addition, the area of the n-heptane peak is monitored so that any errors in making up the polymer dissolving solution will be caught and corrected. Refer to section 12.4 of this method.

9.1 Fill an autosampler vial with the quality control solution (from section 7.6.2 of this method) and analyze on the GC as normal (per section 11 of this method).

9.2 Add the concentrations of the 5 hexane isomers as they appear on the CALS print-out. Also include the 2,2-dimethyl-pentane peak just ahead of the methyl cyclopentane (the fourth major isomer) peak in the event that the peak integration split this peak out. Do not include the benzene peak in the sum.

Note the nonane concentration. Record both results (total hexane and nonane) in the QC computer program. If out of control, and GC appears to be functioning within normal parameters, reanalyze a fresh control sample. If the fresh QC is not in control, check stock solution for contaminants or make up a new QC sample with the toluene currently in use. If instrument remains out-of-control, more thorough GC troubleshooting may be needed.

Also, verify that the instrument has detected both isomers of termonomer (quantification not necessary—see section 7.0 of this method).

9.3 Recovery efficiency must be determined for high ethylene concentration, low ethylene concentration, E-P terpolymer, or oil extended samples and whenever modifications are made to the method. Recovery shall be between 70 and 130 percent. All test results must be corrected by the recovery efficiency value (R).

9.3.1 Approximately 10 grams of wet EPDM crumb (equivalent to about 5 grams of dry rubber) shall be added to six sample bottles containing 100 ml of hexane in crumb polymer dissolving solution (toluene containing 0.3 gram n-heptane/100 ml solution). The polymer shall be dissolved by agitating the bottles on a shaker for 4 hours. The polymer shall be precipitated using 100 ml acetone.

9.3.2 The supernatant liquid shall be decanted from the polymer. Care shall be taken to remove as much of the liquid phase from the sample as possible to minimize the effect of retained liquid phase upon the next cycle of the analysis. The supernatant liquid shall be analyzed by gas chromatography using an internal standard quantitation method with heptane as the internal standard.

9.3.3 The precipitated polymer from the steps described above shall be redissolved using toluene as the solvent. No heptane shall be added to the sample in the second dissolving step. The toluene solvent and acetone precipitant shall be determined to be free of interfering compounds.

9.3.4 The rubber which was dissolved in the toluene shall be precipitated with acetone as before, and the supernatant liquid decanted from the precipitated polymer. The liquid shall be analyzed by gas chromatography and the rubber phase dried in a steam-oven to determine the final polymer weight.

9.3.5 The ratios of the areas of the hexane peaks and of the heptane internal standard peak shall be calculated for each of the six samples in the two analysis cycles outlined above. The area ratios of the total hexane to heptane (R1) shall be determined for the two analysis cycles of the sample set. The ratio of the values of R1 from the second analysis cycle to the first cycle shall be determined to give a second ratio (R2).

10.0 Calibration and Standardization

The procedure for preparing a Quality Control sample with the internal standard in it is outlined in section 7.6 of this method.

10.1 The relative FID response factors for n-heptane, the internal standard, versus the various hexane isomers and termonomer are relatively constant and should seldom need to be altered. However Baseline construction is a most critical factor in the production of good data. For this reason, close attention should be paid to peak integration. Procedures for handling peak integration will depend upon the data system used.

10.2 If recalibration of the analysis is needed, make up a calibration blend of the internal standard and the analytes as detailed below and analyze it using the analytical method used for the samples.

10.2.1 Weigh 5 g heptane into a tared scintillation vial to five places.

10.2.2 Add 0.2 ml termonomer to the vial and reweigh.

10.2.3 Add 0.5 ml hexane to the vial and reweigh.

10.2.4 Cap, and shake vigorously to mix.

10.2.5 Calculate the weights of termonomer and of hexane added and divide their weights by the weight of the n-heptane added. The result is the known of given value for the calibration.

10.2.6 Add 0.4 ml of this mixture to a mixture of 100 ml toluene and 100 ml of acetone. Cap and shake vigorously to mix.

10.2.7 Analyze the sample.

10.2.8 Divide the termonomer area and the total areas of the hexane peaks by the n-heptane area. This result is the "found" value for the calibration.

10.2.9 Divide the appropriate "known" value from 10.2.5 by the found value from 10.2.8. The result is the response factor for the analyte in question. Previous work has shown that the standard deviation of the calibration method is about 1% relative.

11.0 Procedure

11.1 SAMPLE PREPARATION

11.1.1 Tare an 8oz sample bottle—Tag attached, cap off; record weight and sample ID on tag in pencil.

11.1.2 Place crumb sample in bottle: RLA-3; 10 g (gives a dry wt. of ~5.5 g).

11.1.3 Dispense 100ml of PDS into each bottle. **SAMPLE SHOULD BE PLACED INTO SOLUTION ASAP TO AVOID HEXANE LOSS**—Using "Dispensette" pipettor. *Before dispensing, "purge" the dispensette (25% of its volume) into a waste bottle to eliminate any voids.*

11.1.4 Tightly cap bottles and load samples into shaker.

11.1.5 Insure that "ON-OFF" switch on the shaker itself is "ON."

11.1.6 Locate shaker timer. Insure that toggle switch atop timer control box is in

the middle ("off") position. If display reads "04:00" (4 hours), move toggle switch to the left position. Shaker should begin operating.

11.1.7 After shaker stops, add 100 ml acetone to each sample to precipitate polymer. Shake minimum of 5 minutes on shaker—Vistalon sample may not have fully dissolved; nevertheless, for purposes of consistency, 4 hours is the agreed-upon dissolving time.

11.1.8 Using a 5-ml glass Luer-lock syringe and Acrodisc filter, filter some of the supernatant liquid into an autosampler vial; crimp the vial and load it into the GC autosampler for analysis (section 11.2 of this method)—The samples are filtered to prevent polymer buildup in the GC. Clean the syringes in toluene.

11.1.9 Decant remaining supernatant into a hydrocarbon waste sink, being careful not to discard any of the polymer. Place bottle of precipitate into the steam oven and dry for six hours—Some grades of Vistalon produce very small particles in the precipitate, thus making complete decanting impossible without discarding some polymer. In this case, decant as much as possible and put into the oven as is, allowing the oven to drive off remaining supernatant (this practice is avoided for environmental reasons). WARNING: OVEN IS HOT—110 °C (230 °F).

11.1.10 Cool, weigh and record final weight of bottle.

11.2 GC ANALYSIS

11.2.1 Initiate the CALS computer channel.

11.2.2 Enter the correct instrument method into the GC's integrator.

11.2.3 Load sample vial(s) into autosampler.

11.2.4 Start the integrator.

11.2.5 When analysis is complete, plot CALS run to check baseline skim.

12.0 Data Analysis and Calculations

12.1 Add the concentrations of the hexane peaks as they appear on the CALS printout. Do not include the benzene peak in the sum.

12.2 Subtract any hexane interferences found in the PDS (see section 7.5.6 of this method); record the result.

12.3 Note the termonomer concentration on the CALS printout. Subtract any termonomer interference found in the PDS and record this result in a "% termonomer by GC" column in a logbook.

12.4 Record the area (from CALS printout) of the heptane internal standard peak in a "C7 area" column in the logbook. This helps track instrument performance over the long term.

12.5 After obtaining the final dry weight of polymer used (Section 11.1.10 of this method), record that result in a "dry wt." column of the logbook (for oil extended polymer, the amount of oil extracted is added to the dry rubber weight).

12.6 Divide the %C6 by the dry weight to obtain the total PHR hexane in crumb. Similarly, divide the % termonomer by the dry weight to obtain the total PHR termonomer in crumb. Note that PHR is an abbreviation for "parts per hundred". Record both the hexane and termonomer results in the logbook.

12.7 Correct all results by the recovery efficiency value (R).

13.0 Method Performance

13.1 The method has been shown to provide 100% recovery of the hexane analyte. The method was found to give a 6% relative standard deviation when the same six portions of the same sample were carried through the procedure. Note: These values are examples; each sample type, as specified in Section 9.3, must be tested for sample recovery.

14.0 Pollution Prevention

14.1 Dispose of all hydrocarbon liquids in the appropriate disposal sink system; never pour hydrocarbons down a water sink.

14.2 As discussed in section 11.1.9 of this method, the analyst can minimize venting hydrocarbon vapor to the atmosphere by decanting as much hydrocarbon liquid as possible before oven drying.

15.0 Waste Management

15.1 The Technician conducting the analysis should follow the proper waste management practices for their laboratory location.

16.0 References

16.1 Baton Rouge Chemical Plant Analytical Procedure no. BRCP 1302

16.2 Material Safety Data Sheets (from chemical vendors) for hexane, ENB, toluene, acetone, and heptane

METHOD 310C—DETERMINATION OF RESIDUAL N-HEXANE IN EPDM RUBBER THROUGH GAS CHROMATOGRAPHY

1.0 Scope and Application

1.1 This method describes a procedure for the determination of residual hexane in EPDM wet crumb rubber in the 0.01–2% range by solvent extraction of the hexane followed by gas chromatographic analysis where the hexane is detected by flame ionization and quantified via an internal standard.

1.2 This method may involve hazardous materials operations and equipment. This method does not purport to address all the safety problems associated with it use, if any. It is the responsibility of the user to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2.0 Summary

2.1 Residual hexane contained in wet pieces of EPDM polymer is extracted with MIBK. A known amount of an internal standard (IS) is added to the extract which is subsequently analyzed via gas chromatography where the hexane and IS are separated and detected utilizing a megabore column and flame ionization detection (FID). From the response to the hexane and the IS, the amount of hexane in the EPDM polymer is calculated.

3.0 Definitions

- 3.1 Hexane—refers to n-hexane
- 3.2 Heptane—refers to n-heptane
- 3.3 MIBK—methyl isobutyl ketone (4 methyl 2—Pentanone)

4.0 Interferences

4.1 Material eluting at or near the hexane and/or the IS will cause erroneous results. Prior to extraction, solvent blanks must be analyzed to confirm the absence of interfering peaks.

5.0 Safety

5.1 Review Material Safety Data Sheets of the chemicals used in this method.

6.0 Equipment and Supplies

- 6.1 4 oz round glass jar with a wide mouth screw cap lid.
- 6.2 Vacuum oven.
- 6.3 50 ml pipettes.
- 6.4 A gas chromatograph with an auto sampler and a 50 meter, 0.53 ID, methyl silicone column with 5 micron phase thickness.
- 6.5 Shaker, large enough to hold 10, 4 oz. jars.
- 6.6 1000 and 4000 ml volumetric flasks.
- 6.7 Electronic integrator or equivalent data system.
- 6.8 GC autosampler vials.
- 6.9 50 uL syringe.

7.0 Reagents and Standards

- 7.1 Reagent grade Methyl-Iso-Butyl-Ketone (MIBK)
- 7.2 n-heptane, 99% + purity
- 7.3 n-hexane, 99% + purity

8.0 Sample Collection

8.1 Trap a sample of the EPDM crumb slurry in the sampling apparatus. Allow the crumb slurry to circulate through the sampling apparatus for 5 minutes; then close off the valves at the bottom and top of the sampling apparatus, trapping the crumb slurry. Run cooling water through the water jacket for a minimum of 30 minutes. Expel the cooled crumb slurry into a sample catching basket. If the crumb does not fall by gravity, force it out with demineralized water or ni-

trogen. Send the crumb slurry to the lab for analysis.

9.0 Quality Control

9.1 The Royalene crumb sample is extracted three times with MIBK containing an internal standard. The hexane from each extraction is added together to obtain a total hexane content. The percent hexane in the first extraction is then calculated and used as the recovery factor for the analysis.

9.2 Follow this test method through section 11.4 of the method. After removing the sample of the first extraction to be run on the gas chromatograph, drain off the remainder of the extraction solvent, retaining the crumb sample in the sample jar. Rinse the crumb with demineralized water to remove any MIBK left on the surface of the crumb. Repeat the extraction procedure with fresh MIBK with internal standard two more times.

9.3 After the third extraction, proceed to section 11.5 of this method and obtain the percent hexane in each extraction. Use the sample weight obtained in section 12.1 of this method to calculate the percent hexane in each of the extracts.

9.4 Add the percent hexane obtained from the three extractions for a total percent hexane in the sample.

9.5 Use the following equations to determine the recovery factor (R):

% Recovery of the first extraction=(% hexane in the first extract/total % hexane) \times 100

Recovery Factor (R)=(% Hexane Recovered in the first extract)/100

10.0 Calibration

10.1 Preparation of Internal Standard (IS) solution:

Accuracy weigh 30 grams of n-heptane into a 1000 ml volumetric flask. Dilute to the mark with reagent grade MIBK. Label this Solution "A". Pipette 100 mls. of Solution A into a 4 liter volumetric flask. Fill the flask to the mark with reagent MIBK. Label this Solution "B". Solution "B" will have a concentration of 0.75 mg/ml of heptane.

10.2 Preparation of Hexane Standard Solution (HS):

Using a 50 uL syringe, weigh by difference, 20 mg of n-hexane into a 50 ml volumetric flask containing approximately 40 ml of Solution B. Fill the flask to the mark with Solution B and mix well.

10.3 Conditions for GC analysis of standards and samples:

Temperature:
Initial=40 °C
Final=150 °C
Injector=160 °C
Detector=280 °C
Program Rate=5.0 °C/min

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Initial Time=5 minutes Final Time=6 minutes

Flow Rate=5.0 ml/min

Sensitivity=detecter response must be adjusted to keep the hexane and IS on scale.

10.4 Fill an autosampler vial with the HS, analyze it three times and calculate a Hexane Relative Response Factor (RF) as follows:

$$RF=(A_{IS} \times C_{HS} \times P_{HS})/(A_{HS} \times C_{IS} \times P_{IS}) \quad (1)$$

Where:

A_{IS} =Area of IS peak (Heptane)

A_{HS} =Area of peak (Hexane Standard)

C_{HS} =Mg of Hexane/50 ml HS

C_{IS} =Mg of Heptane/50 ml IS Solution B

P_{IS} =Purity of the IS n-heptane

P_{HS} =Purity of the HS n-hexane

11.0 Procedure

11.1 Weight 10 grams of wet crumb into a tared (W1), wide mouth 4 oz. jar.

11.2 Pipette 50 ml of Solution B into the jar with the wet crumb rubber.

11.3 Screw the cap on tightly and place it on a shaker for 4 hours.

11.4 Remove the sample from the shaker and fill an autosampler vial with the MIBK extract.

11.5 Analyze the sample two times.

11.6 Analyze the HS twice, followed by the samples. Inject the HS twice at the end of each 10 samples or at the end of the run.

12.0 Calculations

12.1 Drain off the remainder of the MIBK extract from the polymer in the 4 oz. jar. Retain all the polymer in the jar. Place the uncovered jar and polymer in a heated vacuum oven until the polymer is dry. Reweigh the jar and polymer (W2) and calculate the dried sample weight of the polymer as follows:

$$\text{Dried SW}=W2-W1 \quad (2)$$

12.2 Should the polymer be oil extended, pipette 10 ml of the MIBK extract into a tared evaporating dish (W1) and evaporate to dryness on a steam plate.

Reweigh the evaporating dish containing the extracted oil (W2). Calculate the oil content of the polymer as follows:

$$\text{Gram of oil extracted}=5(W2-W1) \quad (3)$$

$$\% \text{ Hexane in polymer}=(A_s \times RF \times C_{IS} \times P_{IS}) / (A_{IS} \times SW) \quad (4)$$

Where:

A_s =Area of sample hexane sample peak.

A_{IS} =Area of IS peak in sample.

C_{IS} =Concentration of IS in 50 ml.

P_{IS} =Purity of IS.

SW=Weight of dried rubber after extraction. (For oil extended polymer, the amount of oil extracted is added to the dry rubber weight).

$$\% \text{ Corrected Hexane}=(\% \text{ Hexane in Polymer})/R \quad (5)$$

R=Recovery factor determined in section 9 of this method.

13.0 Method Performance

13.1 Performance must be determined for each sample type by following the procedures in section 9 of this method.

14.0 Waste Generation

14.1 Waste generation should be minimized where possible.

15.0 Waste Management

15.1 All waste shall be handled in accordance with Federal and State environmental regulations.

16.0 References

[Reserved]

METHOD 311—ANALYSIS OF HAZARDOUS AIR POLLUTANT COMPOUNDS IN PAINTS AND COATINGS BY DIRECT INJECTION INTO A GAS CHROMATOGRAPH

1. Scope and Application

1.1 Applicability. This method is applicable for determination of most compounds designated by the U.S. Environmental Protection Agency as volatile hazardous air pollutants (HAP's) (See Reference 1) that are contained in paints and coatings. Styrene, ethyl acrylate, and methyl methacrylate can be measured by ASTM D 4827-93 or ASTM D 4747-87. Formaldehyde can be measured by ASTM PS 9-94 or ASTM D 1979-91. Toluene diisocyanate can be measured in urethane prepolymers by ASTM D 3432-89. Method 311 applies only to those volatile HAP's which are added to the coating when it is manufactured, not to those which may form as the coating cures (reaction products or cure volatiles). A separate or modified test procedure must be used to measure these reaction products or cure volatiles in order to determine the total volatile HAP emissions from a coating. Cure volatiles are a significant component of the total HAP content of some coatings. The term "coating" used in this method shall be understood to mean paints and coatings.

1.2 Principle. The method uses the principle of gas chromatographic separation and quantification using a detector that responds to concentration differences. Because there are many potential analytical systems or sets of operating conditions that may represent useable methods for determining the concentrations of the compounds cited in Section 1.1 in the applicable matrices, all systems that employ this principle, but differ only in details of equipment and operation, may be used as alternative methods, provided that the prescribed quality control, calibration, and method performance requirements are met. Certified product data sheets (CPDS) may also include information relevant to the analysis of the coating sample including, but not limited to, separation

column, oven temperature, carrier gas, injection port temperature, extraction solvent, and internal standard.

2. Summary of Method

Whole coating is added to dimethylformamide and a suitable internal standard compound is added. An aliquot of the sample mixture is injected onto a chromatographic column containing a stationary phase that separates the analytes from each other and from other volatile compounds contained in the sample. The concentrations of the analytes are determined by comparing the detector responses for the sample to the responses obtained using known concentrations of the analytes.

3. Definitions [Reserved]

4. Interferences

4.1 Coating samples of unknown composition may contain the compound used as the internal standard. Whether or not this is the case may be determined by following the procedures of Section 11 and deleting the addition of the internal standard specified in Section 11.5.3. If necessary, a different internal standard may be used.

4.2 The GC column and operating conditions developed for one coating formulation may not ensure adequate resolution of target analytes for other coating formulations. Some formulations may contain nontarget analytes that coelute with target analytes. If there is any doubt about the identification or resolution of any gas chromatograph (GC) peak, it may be necessary to analyze the sample using a different GC column or different GC operating conditions.

4.3 Cross-contamination may occur whenever high-level and low-level samples are analyzed sequentially. The order of sample analyses specified in Section 11.7 is designed to minimize this problem.

4.4 Cross-contamination may also occur if the devices used to transfer coating during the sample preparation process or for injecting the sample into the GC are not adequately cleaned between uses. All such devices should be cleaned with acetone or other suitable solvent and checked for plugs or cracks before and after each use.

5. Safety

5.1 Many solvents used in coatings are hazardous. Precautions should be taken to avoid unnecessary inhalation and skin or eye contact. This method may involve hazardous materials, operations, and equipment. This test method does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations in re-

gards to the performance of this test method.

5.2 Dimethylformamide is harmful if inhaled or absorbed through the skin. The user should obtain relevant health and safety information from the manufacturer. Dimethylformamide should be used only with adequate ventilation. Avoid contact with skin, eyes, and clothing. In case of contact, immediately flush skin or eyes with plenty of water for at least 15 minutes. If eyes are affected, consult a physician. Remove and wash contaminated clothing before reuse.

5.3 User's manuals for the gas chromatograph and other related equipment should be consulted for specific precautions to be taken related to their use.

6. Equipment and Supplies

NOTE: Certified product data sheets (CPDS) may also include information relevant to the analysis of the coating sample including, but not limited to, separation column, oven temperature, carrier gas, injection port temperature, extraction solvent, and internal standard.

6.1 Sample Collection.

6.1.1 Sampling Containers. Dual-seal sampling containers, four to eight fluid ounce capacity, should be used to collect the samples. Glass sample bottles or plastic containers with volatile organic compound (VOC) impermeable walls must be used for corrosive substances (e.g., etch primers and certain coating catalysts such as methyl ethyl ketone (MEK) peroxide). Sample containers, caps, and inner seal liners must be inert to the compounds in the sample and must be selected on a case-by-case basis.

6.1.1.1 Other routine sampling supplies needed include waterproof marking pens, tubing, scrapers/spatulas, clean rags, paper towels, cooler/ice, long handle tongs, and mixing/stirring paddles.

6.1.2 Personal safety equipment needed includes eye protection, respiratory protection, a hard hat, gloves, steel toe shoes, etc.

6.1.3 Shipping supplies needed include shipping boxes, packing material, shipping labels, strapping tape, etc.

6.1.4 Data recording forms and labels needed include coating data sheets and sample can labels.

NOTE: The actual requirements will depend upon the conditions existing at the source sampled.

6.2 Laboratory Equipment and Supplies.

6.2.1 Gas Chromatograph (GC). Any instrument equipped with a flame ionization detector and capable of being temperature programmed may be used. Optionally, other types of detectors (e.g., a mass spectrometer), and any necessary interfaces, may be used provided that the detector system

yields an appropriate and reproducible response to the analytes in the injected sample. Autosampler injection may be used, if available.

6.2.2 Recorder. If available, an electronic data station or integrator may be used to record the gas chromatogram and associated data. If a strip chart recorder is used, it must meet the following criteria: A 1 to 10 millivolt (mV) linear response with a full scale response time of 2 seconds or less and a maximum noise level of ± 0.03 percent of full scale. Other types of recorders may be used as appropriate to the specific detector installed provided that the recorder has a full scale response time of 2 seconds or less and a maximum noise level of ± 0.03 percent of full scale.

6.2.3 Column. The column must be constructed of materials that do not react with components of the sample (*e.g.*, fused silica, stainless steel, glass). The column should be of appropriate physical dimensions (*e.g.*, length, internal diameter) and contain sufficient suitable stationary phase to allow separation of the analytes. DB-5, DB-Wax, and FFAP columns are commonly used for paint analysis; however, it is the responsibility of each analyst to select appropriate columns and stationary phases.

6.2.4 Tube and Tube Fittings. Supplies to connect the GC and gas cylinders.

6.2.5 Pressure Regulators. Devices used to regulate the pressure between gas cylinders and the GC.

6.2.6 Flow Meter. A device used to determine the carrier gas flow rate through the GC. Either a digital flow meter or a soap film bubble meter may be used to measure gas flow rates.

6.2.7 Septa. Seals on the GC injection port through which liquid or gas samples can be injected using a syringe.

6.2.8 Liquid Charging Devices. Devices used to inject samples into the GC such as clean and graduated 1, 5, and 10 microliter (μ l) capacity syringes.

6.2.9 Vials. Containers that can be sealed with a septum in which samples may be prepared or stored. The recommended size is 25 ml capacity. Mininert® valves have been found satisfactory and are available from Pierce Chemical Company, Rockford, Illinois.

6.2.10 Balance. Device used to determine the weights of standards and samples. An analytical balance capable of accurately weighing to 0.0001 g is required.

7. Reagents and Standards

7.1 Purity of Reagents. Reagent grade chemicals shall be used in all tests. Unless otherwise specified, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used pro-

vided it is first ascertained that the reagent is of sufficient purity to permit its use without lessening the accuracy of determination.

7.2 Carrier Gas. Helium carrier gas shall have a purity of 99.995 percent or higher. High purity nitrogen may also be used. Other carrier gases that are appropriate for the column system and analyte may also be used. Ultra-high purity grade hydrogen gas and zero-grade air shall be used for the flame ionization detector.

7.3 Dimethylformamide (DMF). Solvent for all standards and samples. Some other suitable solvent may be used if DMF is not compatible with the sample or coelutes with a target analyte.

NOTE: DMF may coelute with ethylbenzene or p-xylene under the conditions described in the note under Section 6.2.3.

7.4 Internal Standard Materials. The internal standard material is used in the quantitation of the analytes for this method. It shall be gas chromatography spectrophotometric quality or, if this grade is not available, the highest quality available. Obtain the assay for the internal standard material and maintain at that purity during use. The recommended internal standard material is 1-propanol; however, selection of an appropriate internal standard material for the particular coating and GC conditions used is the responsibility of each analyst.

7.5 Reference Standard Materials. The reference standard materials are the chemicals cited in Section 1.1 which are of known identity and purity and which are used to assist in the identification and quantification of the analytes of this method. They shall be the highest quality available. Obtain the assays for the reference standard materials and maintain at those purities during use.

7.6 Stock Reference Standards. Stock reference standards are dilutions of the reference standard materials that may be used on a daily basis to prepare calibration standards, calibration check standards, and quality control check standards. Stock reference standards may be prepared from the reference standard materials or purchased as certified solutions.

7.6.1 Stock reference standards should be prepared in dimethylformamide for each analyte expected in the coating samples to be analyzed. The concentrations of analytes in the stock reference standards are not specified but must be adequate to prepare the calibration standards required in the method. A stock reference standard may contain more than one analyte provided all analytes are chemically compatible and no analytes coelute. The actual concentrations prepared must be known to within 0.1 percent (*e.g.*, 0.1000 ± 0.0001 g/g solution). The following procedure is suggested. Place about 35 ml of dimethylformamide into a

tared ground-glass stoppered 50 ml volumetric flask. Weigh the flask to the nearest 0.1 mg. Add 12.5 g of the reference standard material and reweigh the flask. Dilute to volume with dimethylformamide and reweigh. Stopper the flask and mix the contents by inverting the flask several times. Calculate the concentration in grams per gram of solution from the net gain in weights, correcting for the assayed purity of the reference standard material.

NOTE: Although a glass-stoppered volumetric flask is convenient, any suitable glass container may be used because stock reference standards are prepared by weight.

7.6.2 Transfer the stock reference standard solution into one or more Teflon-sealed screw-cap bottles. Store, with minimal headspace, at -10°C to 0°C and protect from light.

7.6.3 Prepare fresh stock reference standards every six months, or sooner if analysis results from daily calibration check standards indicate a problem. Fresh stock reference standards for very volatile HAP's may have to be prepared more frequently.

7.7 Calibration Standards. Calibration standards are used to determine the response of the detector to known amounts of reference material. Calibration standards must be prepared at a minimum of three concentration levels from the stock reference standards (see Section 7.6). Prepare the calibration standards in dimethylformamide (see Section 7.3). The lowest concentration standard should contain a concentration of analyte equivalent either to a concentration of no more than 0.01% of the analyte in a coating or to a concentration that is lower than the actual concentration of the analyte in the coating, whichever concentration is higher. The highest concentration standard should contain a concentration of analyte equivalent to slightly more than the highest concentration expected for the analyte in a coating. The remaining calibration standard should contain a concentration of analyte roughly at the midpoint of the range defined by the lowest and highest concentration calibration standards. The concentration range of the standards should thus correspond to the expected range of analyte concentrations in the prepared coating samples (see Section 11.5). Each calibration standard should contain each analyte for detection by this method expected in the actual coating samples (e.g., some or all of the compounds listed in Section 1.1 may be included). Each calibration standard should also contain an appropriate amount of internal standard material (response for the internal standard material is within 25 to 75 percent of full scale on the attenuation setting for the particular reference standard concentration level). Calibration Standards should be stored for 1 week only in sealed vials with minimal

headspace. If the stock reference standards were prepared as specified in Section 7.6, the calibration standards may be prepared by either weighing each addition of the stock reference standard or by adding known volumes of the stock reference standard and calculating the mass of the standard reference material added. Alternative 1 (Section 7.7.1) specifies the procedure to be followed when the stock reference standard is added by volume. Alternative 2 (Section 7.7.2) specifies the procedure to be followed when the stock reference standard is added by weight.

NOTE: To assist with determining the appropriate amount of internal standard to add, as required here and in other sections of this method, the analyst may find it advantageous to prepare a curve showing the area response versus the amount of internal standard injected into the GC.

7.7.1 Preparation Alternative 1. Determine the amount of each stock reference standard and dimethylformamide solvent needed to prepare approximately 25 ml of the specific calibration concentration level desired. To a tared 25 ml vial that can be sealed with a crimp-on or Mininert[®] valve, add the total amount of dimethylformamide calculated to be needed. As quickly as practical, add the calculated amount of each stock reference standard using new pipets (or pipet tips) for each stock reference standard. Reweigh the vial and seal it. Using the known weights of the standard reference materials per ml in the stock reference standards, the volumes added, and the total weight of all reagents added to the vial, calculate the weight percent of each standard reference material in the calibration standard prepared. Repeat this process for each calibration standard to be prepared.

7.7.2 Preparation Alternative 2. Determine the amount of each stock reference standard and dimethylformamide solvent needed to prepare approximately 25 ml of the specific calibration concentration level desired. To a tared 25 ml vial that can be sealed with a crimp-on or Mininert[®] valve, add the total amount of dimethylformamide calculated to be needed. As quickly as practical, add the calculated amount of a stock reference standard using a new pipet (or pipet tip) and reweigh the vial. Repeat this process for each stock reference standard to be added. Seal the vial after obtaining the final weight. Using the known weight percents of the standard reference materials in the stock reference standards, the weights of the stock reference standards added, and the total weight of all reagents added to the vial, calculate the weight percent of each standard reference material in the calibration standard prepared. Repeat this process for each calibration standard to be prepared.

8. Sample Collection, Preservation, Transport, and Storage

8.1 Copies of material safety data sheets (MSDS's) for each sample should be obtained prior to sampling. The MSDS's contain information on the ingredients, and physical and chemical properties data. The MSDS's also contain recommendations for proper handling or required safety precautions. Certified product data sheets (CPDS) may also include information relevant to the analysis of the coating sample including, but not limited to, separation column, oven temperature, carrier gas, injection port temperature, extraction solvent, and internal standard.

8.2 A copy of the blender's worksheet can be requested to obtain data on the exact coating being sampled. A blank coating data sheet form (see Section 18) may also be used. The manufacturer's formulation information from the product data sheet should also be obtained.

8.3 Prior to sample collection, thoroughly mix the coating to ensure that a representative, homogeneous sample is obtained. It is preferred that this be accomplished using a coating can shaker or similar device; however, when necessary, this may be accomplished using mechanical agitation or circulation systems.

8.3.1 Water-thinned coatings tend to incorporate or entrain air bubbles if stirred too vigorously; mix these types of coatings slowly and only as long as necessary to homogenize.

8.3.2 Each component of multicomponent coatings that harden when mixed must be sampled separately. The component mix ratios must be obtained at the facility at the time of sampling and submitted to the analytical laboratory.

8.4 Sample Collection. Samples must be collected in a manner that prevents or minimizes loss of volatile components and that does not contaminate the coating reservoir. A suggested procedure is as follows. Select a sample collection container which has a capacity at least 25 percent greater than the container in which the sample is to be transported. Make sure both sample containers are clean and dry. Using clean, long-handled tongs, turn the sample collection container upside down and lower it into the coating reservoir. The mouth of the sample collection container should be at approximately the midpoint of the reservoir (do not take the sample from the top surface). Turn the sample collection container over and slowly bring it to the top of the coating reservoir. Rapidly pour the collected coating into the sample container, filling it completely. It is important to fill the sample container completely to avoid any loss of volatiles due to volatilization into the headspace. Return any unused coating to the reservoir or dispose as appropriate.

NOTE: If a company requests a set of samples for its own analysis, a separate set of samples, using new sample containers, should be taken at the same time.

8.5 Once the sample is collected, place the sample container on a firm surface and insert the inner seal in the container by placing the seal inside the rim of the container, inverting a screw cap, and pressing down on the screw cap which will evenly force the inner seal into the container for a tight fit. Using clean towels or rags, remove all residual coating material from the outside of the sample container after inserting the inner seal. Screw the cap onto the container.

8.5.1 Affix a sample label (see Section 18) clearly identifying the sample, date collected, and person collecting the sample.

8.5.2 Prepare the sample for transportation to the laboratory. The sample should be maintained at the coating's recommended storage temperature specified on the Material Safety Data Sheet, or, if no temperature is specified, the sample should be maintained within the range of 5 °C to 38 °C.

8.9 The shipping container should adhere to U.S. Department of Transportation specification DOT 12-B. Coating samples are considered hazardous materials; appropriate shipping procedures should be followed.

9. Quality Control

9.1 Laboratories using this method should operate a formal quality control program. The minimum requirements of the program should consist of an initial demonstration of laboratory capability and an ongoing analysis of blanks and quality control samples to evaluate and document quality data. The laboratory must maintain records to document the quality of the data generated. When results indicate atypical method performance, a quality control check standard (see Section 9.4) must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

9.2 Before processing any samples, the analyst must demonstrate, through analysis of a reagent blank, that there are no interferences from the analytical system, glassware, and reagents that would bias the sample analysis results. Each time a set of analytical samples is processed or there is a change in reagents, a reagent blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement steps.

9.3 Required instrument quality control parameters are found in the following sections:

9.3.1 Baseline stability must be demonstrated to be ≤5 percent of full scale using the procedures given in Section 10.1.

9.3.2 The GC calibration is not valid unless the retention time (RT) for each analyte at each concentration is within ± 0.05 min of the retention time measured for that analyte in the stock standard.

9.3.3 The retention time (RT) of any sample analyte must be within ± 0.05 min of the average RT of the analyte in the calibration standards for the analyte to be considered tentatively identified.

9.3.4 The GC system must be calibrated as specified in Section 10.2.

9.3.5 A one-point daily calibration check must be performed as specified in Section 10.3.

9.4 To establish the ability to generate results having acceptable accuracy and precision, the analyst must perform the following operations.

9.4.1 Prepare a quality control check standard (QCCS) containing each analyte expected in the coating samples at a concentration expected to result in a response between 25 percent and 75 percent of the limits of the calibration curve when the sample is prepared as described in Section 11.5. The QCCS may be prepared from reference standard materials or purchased as certified solutions. If prepared in the laboratory, the QCCS must be prepared independently from the calibration standards.

9.4.2 Analyze three aliquots of the QCCS according to the method beginning in Section 11.5.3 and calculate the weight percent of each analyte using Equation 1, Section 12.

9.4.3 Calculate the mean weight percent (\bar{X}) for each analyte from the three results obtained in Section 9.4.2.

9.4.4 Calculate the percent accuracy for each analyte using the known concentrations (T_i) in the QCCS using Equation 3, Section 12.

9.4.5 Calculate the percent relative standard deviation (percent RSD) for each analyte using Equation 7, Section 12, substituting the appropriate values for the relative response factors (RRF's) in said equation.

9.4.6 If the percent accuracy (Section 9.4.4) for all analytes is within the range 90 percent to 110 percent and the percent RSD (Section 9.4.5) for all analytes is ≤ 20 percent, system performance is acceptable and sample analysis may begin. If these criteria are not met for any analyte, then system performance is not acceptable for that analyte and the test must be repeated for those analytes only. Repeated failures indicate a general problem with the measurement system that must be located and corrected. In this case, the entire test, beginning at Section 9.4.1, must be repeated after the problem is corrected.

9.5 Great care must be exercised to maintain the integrity of all standards. It is recommended that all standards be stored at -10 °C to 0 °C in screw-cap amber glass bottles with Teflon liners.

9.6 Unless otherwise specified, all weights are to be recorded within 0.1 mg.

10. Calibration and Standardization.

10.1 Column Baseline Drift. Before each calibration and series of determinations and before the daily calibration check, condition the column using procedures developed by the laboratory or as specified by the column supplier. Operate the GC at initial (i.e., before sample injection) conditions on the lowest attenuation to be used during sample analysis. Adjust the recorder pen to zero on the chart and obtain a baseline for at least one minute. Initiate the GC operating cycle that would be used for sample analysis. On the recorder chart, mark the pen position at the end of the simulated sample analysis cycle. Baseline drift is defined as the absolute difference in the pen positions at the beginning and end of the cycle in the direction perpendicular to the chart movement. Calculate the percent baseline drift by dividing the baseline drift by the chart width representing full-scale deflection and multiply the result by 100.

10.2 Calibration of GC. Bring all stock standards and calibration standards to room temperature while establishing the GC at the determined operating conditions.

10.2.1 Retention Times (RT's) for Individual Compounds.

NOTE: The procedures of this subsection are required only for the initial calibration. However, it is good laboratory practice to follow these procedures for some or all analytes before each calibration. The procedures were written for chromatograms output to a strip chart recorder. More modern instruments (e.g., integrators and electronic data stations) determine and print out or display retention times automatically.

The RT for each analyte should be determined before calibration. This provides a positive identification for each peak observed from the calibration standards. Inject an appropriate volume (see NOTE in Section 11.5.2) of one of the stock reference standards into the gas chromatograph and record on the chart the pen position at the time of the injection (see Section 7.6.1). Dilute an aliquot of the stock reference standard as required in dimethylformamide to achieve a concentration that will result in an on-scale response. Operate the gas chromatograph according to the determined procedures. Select the peak(s) that correspond to the analyte(s) [and internal standard, if used] and measure the retention time(s). If a chart recorder is used, measure the distance(s) on the chart from the injection point to the peak maxima. These distances, divided by the chart speed, are defined as the RT's of the analytes in question. Repeat this process for each of the stock reference standard solutions.

NOTE: If gas chromatography with mass spectrometer detection (GC-MS) is used, a stock reference standard may contain a group of analytes, provided all analytes are adequately separated during the analysis. Mass spectral library matching can be used to identify the analyte associated with each peak in the gas chromatogram. The retention time for the analyte then becomes the retention time of its peak in the chromatogram.

10.2.2 Calibration. The GC must be calibrated using a minimum of three concentration levels of each potential analyte. (See Section 7.7 for instructions on preparation of the calibration standards.) Beginning with the lowest concentration level calibration standard, carry out the analysis procedure as described beginning in Section 11.7. Repeat the procedure for each progressively higher concentration level until all calibration standards have been analyzed.

10.2.2.1 Calculate the RT's for the internal standard and for each analyte in the calibration standards at each concentration level as described in Section 10.2.1. The RT's for the internal standard must not vary by more than 0.10 minutes. Identify each analyte by comparison of the RT's for peak maxima to the RT's determined in Section 10.2.1.

10.2.2.2 Compare the retention times (RT's) for each potential analyte in the calibration standards for each concentration level to the retention times determined in Section 10.2.1. The calibration is not valid unless all RT's for all analytes meet the criteria given in Section 9.3.2.

10.2.2.3 Tabulate the area responses and the concentrations for the internal standard and each analyte in the calibration standards. Calculate the response factor for the internal standard (RF_{is}) and the response factor for each compound relative to the internal standard (RRF) for each concentration level using Equations 5 and 6, Section 12.

10.2.2.4 Using the RRF's from the calibration, calculate the percent relative standard deviation (percent RSD) for each analyte in the calibration standard using Equation 7, Section 12. The percent RSD for each individual calibration analyte must be less than 15 percent. This criterion must be met in order for the calibration to be valid. If the criterion is met, the mean RRF's determined above are to be used until the next calibration.

10.3 Daily Calibration Checks. The calibration curve (Section 10.2.2) must be checked and verified at least once each day that samples are analyzed. This is accomplished by analyzing a calibration standard that is at a concentration near the midpoint of the working range and performing the checks in Sections 10.3.1, 10.3.2, and 10.3.3.

10.3.1 For each analyte in the calibration standard, calculate the percent difference in the RRF from the last calibration using

Equation 8, Section 12. If the percent difference for each calibration analyte is less than 10 percent, the last calibration curve is assumed to be valid. If the percent difference for any analyte is greater than 5 percent, the analyst should consider this a warning limit. If the percent difference for any one calibration analyte exceeds 10 percent, corrective action must be taken. If no source of the problem can be determined after corrective action has been taken, a new three-point (minimum) calibration must be generated. This criterion must be met before quantitative analysis begins.

10.3.2 If the RF_{is} for the internal standard changes by more than ± 20 percent from the last daily calibration check, the system must be inspected for malfunctions and corrections made as appropriate.

10.3.3 The retention times for the internal standard and all calibration check analytes must be evaluated. If the retention time for the internal standard or for any calibration check analyte changes by more than 0.10 min from the last calibration, the system must be inspected for malfunctions and corrections made as required.

11. Procedure

11.1 All samples and standards must be allowed to warm to room temperature before analysis. Observe the given order of ingredient addition to minimize loss of volatiles.

11.2 Bring the GC system to the determined operating conditions and condition the column as described in Section 10.1.

NOTE: The temperature of the injection port may be an especially critical parameter. Information about the proper temperature may be found on the CPDS.

11.3 Perform the daily calibration checks as described in Section 10.3. Samples are not to be analyzed until the criteria in Section 10.3 are met.

11.4 Place the as-received coating sample on a paint shaker, or similar device, and shake the sample for a minimum of 5 minutes to achieve homogenization.

11.5 NOTE: The steps in this section must be performed rapidly and without interruption to avoid loss of volatile organics. These steps must be performed in a laboratory hood free from solvent vapors. All weights must be recorded to the nearest 0.1 mg.

11.5.1 Add 16 g of dimethylformamide to each of two tared vials (A and B) capable of being septum sealed.

11.5.2 To each vial add a weight of coating that will result in the response for the major constituent being in the upper half of the linear range of the calibration curve.

NOTE: The magnitude of the response obviously depends on the amount of sample injected into the GC as specified in Section 11.8. This volume must be the same as used

for preparation of the calibration curve, otherwise shifts in compound retention times may occur. If a sample is prepared that results in a response outside the limits of the calibration curve, new samples must be prepared; changing the volume injected to bring the response within the calibration curve limits is not permitted.

11.5.3 Add a weight of internal standard to each vial (A and B) that will result in the response for the internal standard being between 25 percent and 75 percent of the linear range of the calibration curve.

11.5.4 Seal the vials with crimp-on or Mininert® septum seals.

11.6 Shake the vials containing the prepared coating samples for 60 seconds. Allow the vials to stand undisturbed for ten minutes. If solids have not settled out on the bottom after 10 minutes, then centrifuge at 1,000 rpm for 5 minutes. The analyst also has the option of injecting the sample without allowing the solids to settle.

11.7 Analyses should be conducted in the following order: daily calibration check sample, method blank, up to 10 injections from sample vials (*i.e.*, one injection each from up to five pairs of vials, which corresponds to analysis of 5 coating samples).

11.8 Inject the prescribed volume of supernatant from the calibration check sample, the method blank, and the sample vials onto the chromatographic column and record the chromatograms while operating the system under the specified operating conditions.

NOTE: The analyst has the option of injecting the unseparated sample.

12. Data Analysis and Calculations

12.1 Qualitative Analysis. An analyte (*e.g.*, those cited in Section 1.1) is considered tentatively identified if two criteria are satisfied: (1) elution of the sample analyte within ± 0.05 min of the average GC retention time of the same analyte in the calibration standard; and (2) either (a) confirmation of the identity of the compound by spectral matching on a gas chromatograph equipped with a mass selective detector or (b) elution of the sample analyte within ± 0.05 min of the average GC retention time of the same analyte in the calibration standard analyzed on a dissimilar GC column.

12.1.1 The RT of the sample analyte must meet the criteria specified in Section 9.3.3.

12.1.2 When doubt exists as to the identification of a peak or the resolution of two or more components possibly comprising one peak, additional confirmatory techniques (listed in Section 12.1) must be used.

12.2 Quantitative Analysis. When an analyte has been identified, the quantification of that compound will be based on the internal standard technique.

12.2.1 A single analysis consists of one injection from each of two sample vials (A and B) prepared using the same coating. Calculate the concentration of each identified analyte in the sample as follows:

$$\text{HAP}_{\text{wt}\%} = 100 \times \frac{(A_x)(W_{\text{is}})}{(A_{\text{is}})(\overline{\text{RRF}}_x)(W_x)} \quad \text{Eq. (1)}$$

where:

HAP_{wt%} = weight percent of the analyte in coating.

A_x = Area response of the analyte in the sample.

W_{is} = Weight of internal standard added to sample, g.

A_{is} = Area response of the internal standard in the sample.

$\overline{\text{RRF}}_x$ = Mean relative response factor for the analyte in the calibration standards.

W_x = Weight of coating added to the sample solution, g.

12.2.2 Report results for duplicate analysis (sample vials A and B) without correction.

12.3 Precision Data. Calculate the percent difference between the measured concentrations of each analyte in vials A and B as follows.

12.3.1 Calculate the weight percent of the analyte in each of the two sample vials as described in Section 12.2.1.

12.3.2 Calculate the percent difference for each analyte as:

$$\% \text{Dif}_i = 100 \times \frac{|A_i - B_i|}{\frac{(A_i + B_i)}{2}} \quad \text{Eq. (2)}$$

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where A_i and B_i are the measured concentrations of the analyte in vials A and B.

12.4 Calculate the percent accuracy for analytes in the QCCS (See Section 9.4) as follows:

$$\% \text{ Accuracy}_x = 100 \times \frac{\bar{X}_x}{T_x} \quad \text{Eq. (3)}$$

where X_x is the mean measured value and T_x is the known true value of the analyte in the QCCS.

12.5 Obtain retention times (RT's) from data station or integrator or, for chromatograms from a chart recorder, calculate the RT's for analytes in the calibration standards (See Section 10.2.2.2) as follows:

$$\text{RT} = \frac{\text{Distance from injection to peak maximum}}{\text{Recorder chart speed}} \quad \text{Eq. (4)}$$

12.6 Calculate the response factor for the internal standard (See Section 10.2.2.3) as follows:

$$\text{RF}_{is} = \frac{A_{is}}{C_{is}} \quad \text{Eq. (5)}$$

where:

A_{is} = Area response of the internal standard.

C_{is} = Weight percent of the internal standard.

12.7 Calculate the relative response factors for analytes in the calibration standards (See Section 10.2.2.3) as follows:

where:

$$\text{RRF}_x = \frac{A_x}{\text{RF}_{is} C_x} \quad \text{Eq. (6)}$$

RRF_x = Relative response factor for an individual analyte.

A_x = Area response of the analyte being measured.

C_x = Weight percent of the analyte being measured.

12.8 Calculate the percent relative standard deviation of the relative response factors for analytes in the calibration standards (See Section 10.2.2.4) as follows:

$$\% \text{RSD} = 100 \times \frac{\sqrt{\frac{\sum_{i=1}^n (\text{RRF}_x - \overline{\text{RRF}_x})^2}{n-1}}}{\overline{\text{RRF}_x}} \quad \text{Eq. (7)}$$

where:

n = Number of calibration concentration levels used for an analyte.

RRF_x = Individual RRF for an analyte.

$\overline{\text{RRF}_x}$ = Mean of all RRF'_x s for an analyte.

12.9 Calculate the percent difference in the relative response factors between the cali-

bration curve and the daily calibration checks (See Section 10.3) as follows:

$$\% \text{ Difference} = \frac{|\overline{\text{RRF}}_x - \text{RRF}_c|}{\overline{\text{RRF}}_x} \times 100 \quad \text{Eq. (8)}$$

where:

$\overline{\text{RRF}}$ = mean relative response factor from last calibration.

RRF = relative response factor from calibration check standard.

13. *Measurement of Reaction Byproducts That are HAP.* [Reserved]

14. *Method Performance.* [Reserved]

15. *Pollution Prevention.* [Reserved]

16. *Waste Management*

16.1 The coating samples and laboratory standards and reagents may contain compounds which require management as hazardous waste. It is the laboratory's responsibility to ensure all wastes are managed in accordance with all applicable laws and regulations.

16.2 To avoid excessive laboratory waste, obtain only enough sample for laboratory analysis.

16.3 It is recommended that discarded waste coating solids, used rags, used paper towels, and other nonglass or nonsharp waste materials be placed in a plastic bag before disposal. A separate container, designated "For Sharp Objects Only," is recommended for collection of discarded glassware and other sharp-edge items used in the laboratory. It is recommended that unused or excess samples and reagents be placed in a solvent-resistant plastic or metal container with a lid or cover designed for flammable liquids. This container should not be stored in the area where analytical work is performed. It is recommended that a record be kept of all compounds placed in the container for identification of the contents upon disposal.

17. *References*

1. Clean Air Act Amendments, Public Law 101-549, Titles I-XI, November, 1990.

2. Standard Test Method for Water Content of Water-Reducible Paints by Direct Injection into a Gas Chromatograph. ASTM Designation D3792-79.

3. Standard Practice for Sampling Liquid Paints and Related Pigment Coatings. ASTM Designation D3925-81.

4. Standard Test Method for Determination of Dichloromethane and 1,1,1-Trichloroethane in Paints and Coatings by Direct Injection into a Gas Chromatograph. ASTM Designation D4457-85.

5. Standard Test Method for Determining the Unreacted Monomer Content of Latexes Using Capillary Column Gas Chromatography. ASTM Designation D4827-93.

6. Standard Test Method for Determining Unreacted Monomer Content of Latexes Using Gas-Liquid Chromatography. ASTM Designation D 4747-87.

7. Method 301—"Field Validation of Pollutant Measurement Methods from Various Waste Media," 40 CFR 63, Appendix A.

8. "Reagent Chemicals, American Chemical Society Specifications," American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards" by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY and the "United States Pharmacopeia."

18. *Tables, Diagrams, Flowcharts, and Validation Data*

Agency: _____
 Inspector: _____
 Date/Time: _____
 Sample ID#: _____
 Source ID: _____
 Coating Name/Type: _____
 Plant Witness: _____
 Type Analysis Required: _____
 Special Handling: _____

Sample Container Label

Coating Data

Date: _____
 Source: _____

Data	Sample ID No.	Sample ID No.
Coating:		
Supplier Name
Name and Color of Coating
Type of Coating (primer, clearcoat, etc.)
Identification Number for Coating
Coating Density (lbs/gal)

Data	Sample ID No.	Sample ID No.
Total Volatiles Content (wt percent)
Water Content (wt percent)
Exempt Solvents Content (wt percent)
VOC Content (wt percent)
Solids Content (vol percent)
Diluent Properties:		
Name:		
Identification Number
Diluent Solvent Density (lbs/gal)
VOC Content (wt percent)
Water Content (wt percent)
Exempt Solvent Content (wt percent)
Diluent/Solvent Ratio (gal diluent solvent/gal coating)

Stock Reference Standard
 Name of Reference Material: _____
 Supplier Name: _____
 Lot Number: _____
 Purity: _____
 Name of Solvent Material: _____
Dimethylformamide
 Supplier Name: _____
 Lot Number: _____
 Purity: _____
 Date Prepared: _____
 Prepared By: _____
 Notebook/page no.: _____

PREPARATION INFORMATION—Continued
 8. Fraction Reference Material in Standard (Line 7 ÷ Line 5) soln. _____, g/g
 9. Total Volume of Standard Solution. _____, ml
 10. Weight Reference Material per ml of Solution (Line 7 ÷ Line 9). _____, g/ml
 Laboratory ID No. for this Standard. _____
 Expiration Date for this Standard. _____

PREPARATION INFORMATION
 1. Weight Empty Flask ,g
 2. Weight Plus DMF ,g
 3. Weight Plus Reference Material. _____, g
 4. Weight After Made to Volume. _____, g
 5. Weight DMF (lines 2–1+3–4). _____, g
 6. Weight Ref. Material (lines 3–2). _____, g
 7. Corrected Weight of Reference Material (line 6 times purity). _____, g

CALIBRATION STANDARD
 Date Prepared: _____
 Date Expires: _____
 Prepared By: _____
 Notebook/page: _____
 Calibration Standard Identification No.: _____

PREPARATION INFORMATION
 Final Weight Flask Plus Reagents. _____, g
 Weight Empty Flask , g
 Total Weight Of Reagents _____, g

Analyte name ^a	Stock reference standard ID No.	Amount of stock reference standard added (by volume or by weight)				Calculated weight analyte added, g	Weight percent analyte in calibration standard ^b
		Volume added, ml	Amount in standard, g/ml	Weight added, g	Amount in standard, g/g soln		
.....	
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^a Include internal standard(s).
^b Weight percent = weight analyte added ÷ total weight of reagents.

PART 1.—RETENTION TIMES FOR INDIVIDUAL ANALYTES—Continued

Analyte	Stock stand- ard. ID No.	Recorder chart speed		Distance from injection point to peak maximum		Retention time, minutes ^a
		Inches/min.	cm/min.	Inches	Centimeters	
.....
.....

^aRetention time=distance to peak maxima÷chart speed.

CALIBRATION OF GAS CHROMATOGRAPH Calibrated By: _____

Calibration Date: _____

PART 2.—ANALYSIS OF CALIBRATION STANDARDS

Analyte	Calib. STD ID No.	Calib. STD ID No.	Calib. STD ID No.
Name:			
Conc. in STD
Area Response
RT
Name:			
Conc. in STD
Area Response
RT
Name:			
Conc. in STD
Area Response
RT
Name:			
Conc. in STD
Area Response
RT
Name:			
Conc. in STD
Area Response
RT
Name:			
Conc. in STD
Area Response
RT
Name:			
Conc. in STD
Area Response
RT
Internal Standard Name:			
Conc. in STD
Area Response
RT

Calibration of Gas Chromatograph Calibrated By: _____

Calibration Date: _____

PART 3.—DATA ANALYSIS FOR CALIBRATION STANDARDS

Analyte	Calib. STD ID	Calib. STD ID	Calib. STD ID	Mean	percent RSD of RF	Is RT within ±0.05 min of RT for stock? (Y/N)	Is percent RSD <30% (Y/N)
Name:							
RT
RF
Name:							
RT

PART 3.—DATA ANALYSIS FOR CALIBRATION STANDARDS—Continued

Analyte	Calib. STD ID	Calib. STD ID	Calib. STD ID	Mean	percent RSD of RF	Is RT within ±0.05 min of RT for stock? (Y/N)	Is percent RSD <30% (Y/N)
Name: RF
Name: RT
Name: RF
Name: RT
Name: RF
Name: RT
Name: RF
Name: RT
Name: RF
Name: RT
Name: RF
Name: RT
Name: RF
Name: RT
Name: RF

Daily Calibration Check

Date: _____ Analyst: _____
 Calibration Check Standard ID No.: _____
 Expiration Date: _____

Analyte	Retention Time (RT)			Response Factor (RF)		
	Last	This	Difference ^a	Last	This	Difference ^b
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^a Retention time (RT) change (difference) must be less than ±0.10 minutes.
^b Response factor (RF) change (difference) must be less than 20 percent for each analyte and for the internal standard.

Sample Analysis

Vial A ID No.: _____ Vial B ID No.: _____
 Analyzed By: _____
 Date: _____

Sample preparation information	Vial A (g)	Vial B (g)
Measured:		
wt empty vial		
wt plus DMF		
wt plus sample		
wt plus internal standard		
Calculated:		
wt DMF		
wt sample		
wt internal standard		

ANALYSIS RESULTS: DUPLICATE SAMPLES

Analyte	Area response		RF	Wt percent in sample		
	Vial A	Vial B		Vial A	Vial B	Average
.....						

ANALYSIS RESULTS: DUPLICATE SAMPLES—Continued

Analyte	Area response		RF	Wt percent in sample		
	Vial A	Vial B		Vial A	Vial B	Average
.....						
.....						
.....						
.....						
.....						
.....						
.....						
.....						
.....						
.....						
Internal Standard						

METHOD 312A—DETERMINATION OF STYRENE IN LATEX STYRENE-BUTADIENE RUBBER, THROUGH GAS CHROMATOGRAPHY

1. Scope and Application

1.1 This method describes a procedure for determining parts per million (ppm) styrene monomer (CAS No. 100-42-5) in aqueous samples, including latex samples and styrene stripper water.

1.2 The sample is separated in a gas chromatograph equipped with a packed column and a flame ionization detector.

2.0 Summary of Method

2.1 This method utilizes a packed column gas chromatograph with a flame ionization detector to determine the concentration of residual styrene in styrene butadiene rubber (SBR) latex samples.

3.0 Definitions

3.1 The definitions are included in the text as needed.

4.0 Interferences

4.1 In order to reduce matrix effects and emulsify the styrene, similar styrene free latex is added to the internal standard. There are no known interferences.

4.2 The operating parameters are selected to obtain resolution necessary to determine styrene monomer concentrations in latex.

5.0 Safety

5.1 It is the responsibility of the user of this procedure to establish appropriate safety and health practices.

6.0 Equipment and Supplies

6.1 Adjustable bottle-top dispenser, set to deliver 3 ml. (for internal standard), Brinkmann Dispensette, or equivalent.

6.2 Pipettor, set to 10 ml., Oxford Macroset, or equivalent.

6.3 Volumetric flask, 100-ml, with stopper.

6.4 Hewlett Packard Model 5710A dual channel gas chromatograph equipped with flame ionization detector.

6.4.1 11 ft. x ¼ in. stainless steel column packed with 10% TCEP on 100/120 mesh Chromosorb P, or equivalent.

6.4.2 Perkin Elmer Model 023 strip chart recorder, or equivalent.

6.5 Helium carrier gas, zero grade.

6.6 Liquid syringe, 25-µl.

6.7 Digital MicroVAX 3100 computer with VG Multichrom software, or equivalent data handling system.

6.6 Wire Screens, circular, 70-mm, 80-mesh diamond weave.

6.7 DEHA—(N,N-Diethyl hydroxylamine), 97+% purity, CAS No. 3710-84-7

6.8 p-Dioxane, CAS No. 123-91-1

7.0 Reagents and Standards

7.1 Internal standard preparation.

7.1.1 Pipette 5 ml p-dioxane into a 1000-ml volumetric flask and fill to the mark with distilled water and mix thoroughly.

7.2 Calibration solution preparation.

7.2.1 Pipette 10 ml styrene-free latex (eg: NBR latex) into a 100-ml volumetric flask.

7.2.2 Add 3 ml internal standard (section 7.1.1 of this method).

7.2.3 Weigh exactly 10µl fresh styrene and record the weight.

7.2.4 Inject the styrene into the flask and mix well.

7.2.5 Add 2 drops of DEHA, fill to the mark with water and mix well again.

7.2.6 Calculate concentration of the calibration solution as follows:

$$\text{mg/l styrene} = (\text{mg styrene added})/0.1 \text{ L}$$

8.0 Sample Collection, Preservation, and Storage

8.1 A representative SBR emulsion sample should be caught in a clean, dry 6-oz. teflon lined glass container. Close it properly to assure no sample leakage.

8.2 The container should be labeled with sample identification, date and time.

9.0 Quality Control

9.1 The instrument is calibrated by injecting calibration solution (Section 7.2 of this method) five times.

9.2 The retention time for components of interest and relative response of monomer to the internal standard is determined.

9.3 Recovery efficiency must be determined once for each sample type and whenever modifications are made to the method.

9.3.1 A set of six latex samples shall be collected. Two samples shall be prepared for analysis from each sample. Each sample shall be analyzed in duplicate.

9.3.2 The second set of six latex samples shall be analyzed in duplicate before spiking each sample with approximately 1000 ppm styrene. The spiked samples shall be analyzed in duplicate.

9.3.3 For each hydrocarbon, calculate the average recovery efficiency (R) using the following equations:

where:

$$R = \Sigma(R_n)/6$$

where:

$$R_n = (C_{ns} - C_u)/S_n$$

n=sample number

C_{ns} =concentration of compound measured in spiked sample number n.

C_u = concentration of compound measured in unspiked sample number n.

S_n =theoretical concentration of compound spiked into sample n.

9.3.4 A value of R between 0.70 and 1.30 is acceptable.

9.3.5 R is used to correct all reported results for each compound by dividing the measured results of each compound by the R for that compound for the same sample type.

10.0 Calibration and Instrument Settings

10.1 Injection port temperature, 250 °C.

10.2 Oven temperature, 110 °C, isothermal.

10.3 Carrier gas flow, 25 cc/min.

10.4 Detector temperature, 250 °C.

10.5 Range, 1X.

11.0 Procedure

11.1 Turn on recorder and adjust baseline to zero.

11.2 Prepare sample.

11.2.1 For latex samples, add 3 ml Internal Standard (section 7.1 of this method) to a 100-ml volumetric flask. Pipet 10 ml sample into the flask using the Oxford pipettor, dilute to the 100-ml mark with water, and shake well.

11.2.2 For water samples, add 3 ml Internal Standard (section 7.1 of this method) to a 100-ml volumetric flask and fill to the mark with sample. Shake well.

11.3 Flush syringe with sample.

11.4 Carefully inject 2 µl of sample into the gas chromatograph column injection port and press the start button.

11.5 When the run is complete the computer will print a report of the analysis.

12.0 Data Analysis and Calculation

12.1 For samples that are prepared as in section 11.2.1 of this method:

$$\text{ppm styrene} = A \times D$$

Where:

A = "ppm" readout from computer

D = dilution factor (10 for latex samples)

12.2 For samples that are prepared as in section 11.2.2 of this method, ppm styrene is read directly from the computer.

13.0 Method Performance

13.1 This test has a standard deviation (1) of 3.3 ppm at 100 ppm styrene. The average Spike Recovery from six samples at 1000 ppm Styrene was 96.7 percent. The test method was validated using 926 ppm styrene standard. Six analysis of the same standard provided average 97.7 percent recovery. Note: These are example recoveries and do not replace quality assurance procedures in this method.

14.0 Pollution Prevention

14.1 Waste generation should be minimized where possible. Sample size should be an amount necessary to adequately run the analysis.

15.0 Waste Management

15.1 All waste shall be handled in accordance with Federal and State environmental regulations.

16.0 References and Publications

16.1 40 CFR 63 Appendix A—Method 301 Test Methods Field Validation of Pollutant Measurement

16.2 DSM Copolymer Test Method T-3060, dated October 19, 1995, entitled: *Determination of Residual Styrene in Latex*, Leonard, C.D., Vora, N.M. et al

METHOD 312B—DETERMINATION OF RESIDUAL STYRENE IN STYRENE-BUTADIENE (SBR) RUBBER LATEX BY CAPILLARY GAS CHROMATOGRAPHY

1.0 Scope

1.1 This method is applicable to SBR latex solutions.

1.2 This method quantitatively determines residual styrene concentrations in SBR latex solutions at levels from 80 to 1200 ppm.

2.0 Principle of Method

2.1 A weighed sample of a latex solution is coagulated with an ethyl alcohol (EtOH) solution containing a specific amount of alpha-methyl styrene (AMS) as the internal standard. The extract of this coagulation is then

injected into a gas chromatograph and separated into individual components. Quantification is achieved by the method of internal standardization.

3.0 Definitions

3.1 The definitions are included in the text as needed.

4.0 Interferences

[Reserved]

5.0 Safety

5.1 This method may involve hazardous materials, operations, and equipment. This method does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

6.0 Equipment and Supplies

6.1 Analytical balance, 160 g capacity, and 0.1 mg resolution

6.2 Bottles, 2-oz capacity, with poly-cap screw lids

6.3 Mechanical shaker

6.4 Syringe, 10- μ l capacity

6.5 Gas chromatograph, Hewlett Packard model 5890A, or equivalent, configured with FID with a megabore jet, splitless injector packed with silanized glass wool.

6.5.1 Establish the following gas chromatographic conditions, and allow the system to thoroughly equilibrate before use.

Injection technique = Splitless

Injector temperature = 225 deg C

Oven temperature = 70 deg C (isothermal)

Detector: temperature = 300 deg C

range = 5

attenuation = 0

Carrier gas: helium = 47 ml/min

Detector gases: hydrogen = 30 ml/min

air = 270 ml/min

make-up = 0 ml/min

Analysis time: = 3.2 min at the specified carrier gas flow rate and column temperature.

6.6 Gas chromatographic column, DB-1, 30 M X 0.53 ID, or equivalent, with a 1.5 micron film thickness.

6.7 Data collection system, Perkin-Elmer/Nelson Series Turbochrom 4 Series 900 Interface, or equivalent.

6.8 Pipet, automatic dispensing, 50-ml capacity, and 2-liter reservoir.

6.9 Flasks, volumetric, class A, 100-ml and 1000-ml capacity.

6.10 Pipet, volumetric delivery, 10-ml capacity, class A.

7.0 Chemicals and Reagents

CHEMICALS:

7.1 Styrene, C₈H₈, 99+%, CAS 100-42-5

7.2 Alpha methyl styrene, C₉H₁₀, 99%, CAS 98-83-9

7.3 Ethyl alcohol, C₂H₅OH, denatured formula 2B, CAS 64-17-5

REAGENTS:

7.4 Internal Standard Stock Solution: 5.0 mg/ml AMS in ethyl alcohol.

7.4.1 Into a 100-ml volumetric flask, weigh 0.50 g of AMS to the nearest 0.1 mg.

7.4.2 Dilute to the mark with ethyl alcohol. This solution will contain 5.0 mg/ml AMS in ethyl alcohol and will be labeled the AMS STOCK SOLUTION.

7.5 Internal Standard Working Solution: 2500 ug/50 ml of AMS in ethyl alcohol.

7.5.1 Using a 10 ml volumetric pipet, quantitatively transfer 10.0 ml of the AMS STOCK SOLUTION into a 1000-ml volumetric flask.

7.5.2 Dilute to the mark with ethyl alcohol. This solution will contain 2500 ug/50ml of AMS in ethyl alcohol and will be labeled the AMS WORKING SOLUTION.

7.5.3 Transfer the AMS WORKING SOLUTION to the automatic dispensing pipet reservoir.

7.6 Styrene Stock Solution: 5.0 mg/ml styrene in ethyl alcohol.

7.6.1 Into a 100-ml volumetric flask, weigh 0.50 g of styrene to the nearest 0.1 mg.

7.6.2 Dilute to the mark with ethyl alcohol. This solution will contain 5.0 mg/ml styrene in ethyl alcohol and will be labeled the STYRENE STOCK SOLUTION.

7.7 Styrene Working Solution: 5000 ug/10 ml of styrene in ethyl alcohol.

7.7.1 Using a 10-ml volumetric pipet, quantitatively transfer 10.0 ml of the STYRENE STOCK SOLUTION into a 100-ml volumetric flask.

7.7.2 Dilute to the mark with ethyl alcohol. This solution will contain 5000 ug/10 ml of styrene in ethyl alcohol and will be labeled the STYRENE WORKING SOLUTION.

8.0 Sample Collection, Preservation and Storage

8.1 Label a 2-oz sample poly-cap lid with the identity, date and time of the sample to be obtained.

8.2 At the sample location, open sample valve for at least 15 seconds to ensure that the sampling pipe has been properly flushed with fresh sample.

8.3 Fill the sample jar to the top (no headspace) with sample, then cap it tightly.

8.4 Deliver sample to the Laboratory for testing within one hour of sampling.

8.5 Laboratory testing will be done within two hours of the sampling time.

8.6 No special storage conditions are required unless the storage time exceeds 2 hours in which case refrigeration of the sample is recommended.

9.0 Quality Control

9.1 For each sample type, 12 samples of SBR latex shall be obtained from the process for the recovery study. Half the vials and caps shall be tared, labeled "spiked", and numbered 1 through 6. The other vials are labeled "unspiked" and need not be tared, but are also numbered 1 through 6.

9.2 The six vials labeled "spiked" shall be spiked with an amount of styrene to approximate 50% of the solution's expected residual styrene level.

9.3 The spiked samples shall be shaken for several hours and allowed to cool to room temperature before analysis.

9.4 The six samples of unspiked solution shall be coagulated and a mean styrene value shall be determined, along with the standard deviation, and the percent relative standard deviation.

9.5 The six samples of the spiked solution shall be coagulated and the results of the analyses shall be determined using the following equations:

$$M_i = M_s - M_u$$

$$R = M_i / S$$

where:

M_u = Mean value of styrene in the unspiked sample

M_s = Measured amount of styrene in the spiked sample

M_i = Measured amount of the spiked compound

S = Amount of styrene added to the spiked sample

R = Fraction of spiked styrene recovered

9.6 A value of R between 0.70 and 1.30 is acceptable.

9.7 R is used to correct all reported results for each compound by dividing the measured results of each compound by the R for that compound for the same sample type.

10.0 Calibration

10.1 Using a 10-ml volumetric pipet, quantitatively transfer 10.0 ml of the STYRENE WORKING SOLUTION (section 7.7.2 of this method) into a 2-oz bottle.

10.2 Using the AMS WORKING SOLUTION equipped with the automatic dispensing pipet (section 7.5.3 of this method), transfer 50.0 ml of the internal standard solution into the 2-oz bottle.

10.3 Cap the 2-oz bottle and swirl. This is the calibration standard, which contains 5000 μg of styrene and 2500 μg of AMS.

10.4 Using the conditions prescribed (section 6.5 of this method), chromatograph 1 μl of the calibration standard.

10.5 Obtain the peak areas and calculate the relative response factor as described in the calculations section (section 12.1 of this method).

11.0 Procedure

11.1 Into a tared 2-oz bottle, weigh 10.0 g of latex to the nearest 0.1 g.

11.2 Using the AMS WORKING SOLUTION equipped with the automatic dispensing pipet (section 7.5.3 of this method), transfer 50.0 ml of the internal standard solution into the 2-oz bottle.

11.3 Cap the bottle. Using a mechanical shaker, shake the bottle for at least one minute or until coagulation of the latex is complete as indicated by a clear solvent.

11.4 Using the conditions prescribed (section 6.5 of this method), chromatograph 1 μl of the liquor.

11.5 Obtain the peak areas and calculate the concentration of styrene in the latex as described in the calculations section (Section 12.2 of this method).

12.0 Calculations

12.1 Calibration:

$$RF = (W_x \times A_{is}) / (W_{is} \times A_x)$$

where:

RF = the relative response factor for styrene

W_x = the weight (μg) of styrene

A_{is} = the area of AMS

W_{is} = the weight (μg) of AMS

A_x = the area of styrene

12.2 Procedure:

$$\text{ppm}_{\text{styrene}} = (A_x \text{ RF} \times W_{is}) / (A_{is} \times W_s)$$

where:

$\text{ppm}_{\text{styrene}}$ = parts per million of styrene in the latex

A_x = the area of styrene

RF = the response factor for styrene

W_{is} = the weight (μg) of AMS

A_{is} = the area of AMS

W_s = the weight (g) of the latex sample

12.3 Correct for recovery (R) as determined by section 9.0 of this method.

13.0 Precision

13.1 Precision for the method was determined at the 80, 144, 590, and 1160 ppm levels. The standard deviations were 0.8, 1.5, 5 and 9 ppm respectively. The percent relative standard deviations (%RSD) were 1% or less at all levels. Five degrees of freedom were used for all precision data except at the 80 ppm level, where nine degrees of freedom were used. Note: These are example results and do not replace quality assurance procedures in this method.

14.0 Pollution Prevention

14.1 Waste generation should be minimized where possible. Sample size should be an amount necessary to adequately run the analysis.

15.0 Waste Management

15.1 Discard liquid chemical waste into the chemical waste drum.

15.2 Discard latex sample waste into the latex waste drum.

15.3 Discard polymer waste into the polymer waste container.

16.0 References

16.1 This method is based on Goodyear Chemical Division Test Method E-889.

METHOD 312C—DETERMINATION OF RESIDUAL STYRENE IN SBR LATEX PRODUCED BY EMULSION POLYMERIZATION

1.0 Scope

1.1 This method is applicable for determining the amount of residual styrene in SBR latex as produced in the emulsion polymerization process.

2.0 Principle of Method

2.1 A weighed sample of latex is coagulated in 2-propanol which contains alpha-methyl styrene as an Internal Standard. The extract from the coagulation will contain the alpha-methyl styrene as the Internal Standard and the residual styrene from the latex. The extract is analyzed by a Gas Chromatograph. Percent styrene is calculated by relating the area of the styrene peak to the area of the Internal Standard peak of known concentration.

3.0 Definitions

3.1 The definitions are included in the text as needed.

4.0 Interferences

[Reserved]

5.0 Safety

5.1 When using solvents, avoid contact with skin and eyes. Wear hand and eye protection. Wash thoroughly after use.

5.2 Avoid overexposure to solvent vapors. Handle only in well ventilated areas.

6.0 Equipment and Supplies

6.1 *Gas Chromatograph*—Hewlett Packard 5890, Series II with flame ionization detector, or equivalent.

Column—HP 19095F-123, 30m × 0.53mm, or equivalent. Substrate HP FFAP (cross-linked) film thickness 1 micrometer. Glass injector port liners with silanized glass wool plug.

Integrator—HP 3396, Series II, or equivalent.

6.2 Wrist action shaker

6.3 Automatic dispenser

6.4 Automatic pipet, calibrated to deliver 5.0 ± 0.01 grams of latex

6.5 Four-ounce wide-mouth bottles with foil lined lids

6.6 Crimp cap vials, 2ml, teflon lined septa

6.7 Disposable pipets

6.8 Qualitative filter paper

6.9 Cap crimper

6.10 Analytical balance

6.11 10ml pipette

6.12 Two-inch funnel

7.0 Reagents and Standards

7.1 2-Propanol (HP2C grade)

7.2 Alpha methyl styrene (99+% purity)

7.3 Styrene (99+% purity)

7.4 Zero air

7.5 Hydrogen (chromatographic grade)

7.6 Helium

7.7 Internal Standard preparation

7.7.1 Weigh 5.000–5.005 grams of alpha-methyl styrene into a 100ml volumetric flask and bring to mark with 2-propanol to make Stock "A" Solution.

NOTE: Shelf life—6 months.

7.7.2 Pipette 10ml of Stock "A" Solution into a 100ml volumetric flask and bring to mark with 2-propanol to prepare Stock "B" Solution.

7.7.3 Pipette 10ml of the Stock "B" solution to a 1000ml volumetric flask and bring to the mark with 2-propanol. This will be the Internal Standard Solution (0.00005 grams/ml).

7.8 Certification of Internal Standard—Each batch of Stock "B" Solution will be certified to confirm concentration.

7.8.1 Prepare a Standard Styrene Control Solution in 2-propanol by the following method:

7.8.1.1 Weigh 5.000 ± 0.005g of styrene to a 100ml volumetric flask and fill to mark with 2-propanol to make Styrene Stock "A" Solution.

7.8.1.2 Pipette 10ml of Styrene Stock "A" Solution to a 100ml volumetric flask and fill to mark with 2-propanol to make Styrene Stock "B" Solution.

7.8.1.3 Pipette 10ml of Styrene Stock "B" solution to a 250ml volumetric flask and fill to mark with 2-propanol to make the Certification Solution.

7.8.2 Certify Alpha-Methyl Styrene Stock "B" Solution.

7.8.2.1 Pipette 5ml of the Certification Solution and 25ml of the Alpha Methyl Styrene Internal Standard Solution to a 4-oz. bottle, cap and shake well.

7.8.2.2 Analyze the resulting mixture by GC using the residual styrene method. (11.4–11.6 of this method)

7.8.2.3 Calculate the weight of alpha methyl styrene present in the 25ml aliquot of the new Alpha Methyl Styrene Standard by the following equation:

$$W_x = F_x \times W_{is} (A_x/A_{is})$$

Where

A_x = Peak area of alpha methyl styrene

A_{is} = Peak area of styrene

W_x = Weight of alpha methyl styrene

W_{is} = Weight of styrene (.00100)

F_x = Analyzed response factor = 1

The Alpha Methyl Styrene Stock Solution used to prepare the Internal Standard Solution may be considered certified if the weight of alpha methyl styrene analyzed by this method is within the range of .00121g to .00129g.

8.0 Sampling

8.1 Collect a latex sample in a capped container. Cap the bottle and identify the sample as to location and time.

8.2 Deliver sample to Laboratory for testing within one hour.

8.3 Laboratory will test within two hours.

8.4 No special storage conditions are required.

9.0 Quality Control

9.1 The laboratory is required to operate a formal quality control program. This consists of an initial demonstration of the capability of the method as well as ongoing analysis of standards, blanks, and spiked samples to demonstrate continued performance.

9.1.1 When the method is first set up, a calibration is run and the recovery efficiency for each type of sample must be determined.

9.1.2 If new types of samples are being analyzed, then recovery efficiency for each new type of sample must be determined. New type includes any change, such as polymer type, physical form or a significant change in the composition of the matrix.

9.2 Recovery efficiency must be determined once for each sample type and whenever modifications are made to the method.

9.2.1 In determining the recovery efficiency, the quadruplet sampling system shall be used. Six sets of samples (for a total of 24) shall be taken. In each quadruplet set, half of the samples (two out of the four) shall be spiked with styrene.

9.2.2 Prepare the samples as described in section 8 of this method. To the vials labeled "spiked", add a known amount of styrene that is expected to be present in the latex.

9.2.3 Run the spiked and unspiked samples in the normal manner. Record the concentrations of styrene reported for each pair of spiked and unspiked samples with the same vial number.

9.2.4 For each hydrocarbon, calculate the average recovery efficiency (R) using the following equation:

$$R = \Sigma(R_n)/12$$

Where: n = sample number

$$R_n = (M_s - M_u)/S$$

M_s = total mass of compound (styrene) measured in spiked sample (µg)

M_u = total mass of compound (styrene) measured in unspiked sample (µg)

S = theoretical mass of compound (styrene) spiked into sample (µg)

R = fraction of spiked compound (styrene) recovered

9.2.5 A different R value should be obtained for each sample type. A value of R between 0.70 and 1.30 is acceptable.

9.2.6 R is used to correct all reported results for each compound by dividing the measured results of each compound by the R for that compound for the same sample type.

10.0 Calibration

A styrene control sample will be tested weekly to confirm the FID response and calibration.

10.1 Using the Styrene Certification Solution prepared in 7.8.1, perform test analysis as described in 7.8.2 using the equation in 7.8.2.3 to calculate results.

10.2 Calculate the weight of styrene in the styrene control sample using the following equation:

$$W_{sty} = (F_x \times A_{sty} \times W_{is}) / A_{is}$$

The instrument can be considered calibrated if the weight of the styrene analyzed is within range of 0.00097—0.00103gms.

11.0 Procedure

11.1 Using an auto pipet, add 25ml of Internal Standard Solution to a 4 oz. wide-mouth bottle.

11.2 Using a calibrated auto pipet, add 5.0 ± 0.01g latex to the bottle containing the 25ml of Internal Standard Solution.

11.3 Cap the bottle and place on the wrist action shaker. Shake the sample for a minimum of five minutes using the timer on the shaker. Remove from shaker.

11.4 Using a disposable pipet, fill the 2ml sample vial with the clear alcohol extract. (If the extract is not clear, it should be filtered using a funnel and filter paper.) Cap and seal the vial.

11.5 Place the sample in the autosampler tray and start the GC and Integrator. The sample will be injected into the GC by the auto-injector, and the Integrator will print the results.

11.6 Gas Chromatograph Conditions

Oven Temp—70 °C

Injector Temp—225 °C

Detector Temp—275 °C

Helium Pressure—500 KPA

Column Head Pressure—70 KPA

Makeup Gas—30 ml/min.

Column—HP 19095F—123, 30m x 0.53mm

Substrate: HP—FFAP (cross-linked) 1 micrometer film thickness

12.0 Calculations

12.1 The integrator is programmed to do the following calculation at the end of the analysis:

$$\% \text{Residual Styrene} = (A_x \times XW_{is}) / (A_{is} \times XW_x) \times F_x \times X100$$

Where:

A_x = Peak area of styrene

A_{is} = Peak area of internal standard

W_x = Weight of sample = 5g
 W_{is} = Weight of internal std. = 0.00125g
 F_x = Analyzed response factor = 1.0

12.2 The response factor is determined by analyzing a solution of 0.02g of styrene and 0.02g of alpha methyl styrene in 100ml of 2-propanol. Calculate the factor by the following equation:

$$F_x = (W_x \times A_{is}) / (W_{is} \times A_x)$$

Where:

W_x = Weight of styrene
 A_x = Peak area of styrene
 W_{is} = Weight of alpha methyl styrene
 A_{is} = Peak area of alpha methyl styrene

13.0 Method Performance

13.1 Performance must be determined for each sample type by following the procedures in section 9 of this method.

14.0 Waste Generation

14.1 Waste generation should be minimized where possible.

15.0 Waste Management

15.1 All waste shall be handled in accordance with Federal and State environmental regulations.

16.0 References
[Reserved]

METHOD 313A—DETERMINATION OF RESIDUAL HYDROCARBONS IN RUBBER CRUMB

1.0 Scope and Application

1.1 This method determines residual toluene and styrene in stripper crumb of the of the following types of rubber: polybutadiene (PBR) and styrene/butadiene rubber (SBR), both derived from solution polymerization processes that utilize toluene as the polymerization solvent.

1.2 The method is applicable to a wide range of concentrations of toluene and styrene provided that calibration standards cover the desired range. It is applicable at least over the range of 0.01 to 10.0 % residual toluene and from 0.1 to 3.0 % residual styrene. It is probably applicable over a wider range, but this must be verified prior to use.

1.3 The method may also be applicable to other process samples as long as they are of a similar composition to stripper crumb. See section 3.1 of this method for a description of stripper crumb.

2.0 Summary of Method

2.1 The wet crumb is placed in a sealed vial and run on a headspace sampler which heats the vial to a specified temperature for a specific time and then injects a known volume of vapor into a capillary GC. The concentration of each component in the vapor is proportional to the level of that component

in the crumb sample and does not depend on water content of the crumb.

2.2 Identification of each component is performed by comparing the retention times to those of known standards.

2.3 Results are calculated by the external standard method since injections are all performed in an identical manner. The response for each component is compared with that obtained from dosed samples of crumb.

2.4 Measured results of each compound are corrected by dividing each by the average recovery efficiency determined for the same compound in the same sample type.

3.0 Definitions

3.1 Stripper crumb refers to pieces of rubber resulting from the steam stripping of a toluene solution of the same polymer in a water slurry. The primary component of this will be polymer with lesser amounts of entrained water and residual toluene and other hydrocarbons. The amounts of hydrocarbons present must be such that the crumb is a solid material, generally less than 10 % of the dry rubber weight.

4.0 Interferences

4.1 Contamination is not normally a problem since samples are sealed into vials immediately on sampling.

4.2 Cross contamination in the headspace sampler should not be a problem if the correct sampler settings are used. This should be verified by running a blank sample immediately following a normal or high sample. Settings may be modified if necessary if this proves to be a problem, or a blank sample may be inserted between samples.

4.3 Interferences may occur if volatile hydrocarbons are present which have retention times close to that of the components of interest. Since the solvent makeup of the processes involved are normally fairly well defined this should not be a problem. If it is found to be the case, switching to a different chromatographic column will probably resolve the situation.

5.0 Safety

5.1 The chemicals specified in this method should all be handled according to standard laboratory practices as well as any special precautions that may be listed in the MSDS for that compound.

5.2 Sampling of strippers or other process streams may involve high pressures and temperatures or may have the potential for exposure to chemical fumes. Only personnel who have been trained in the specific sampling procedures required for that process should perform this operation. An understanding of the process involved is necessary. Proper personal protective equipment should be worn. Any sampling devices should be inspected prior to use. A detailed sampling

procedure which specifies exactly how to obtain the sample must be written and followed.

6.0 Equipment and Supplies

6.1 Hewlett Packard (HP) 7694 Headspace sampler, or equivalent, with the following conditions:

Times (min.): GC cycle time 6.0 , vial equilibration 30.0 , pressurization 0.25 , loop fill 0.25, loop equilibration 0.05 , inject 0.25

Temperatures (deg C): oven 70, loop 80, transfer line 90

Pressurization gas: He @ 16 psi

6.2 HP 5890 Series II capillary gas chromatograph, or equivalent, with the following conditions:

Column: Supelco SPB-1, or equivalent, 15m × .25mm × .25μ film

Carrier: He @ 6 psi

Run time: 4 minutes

Oven: 70 deg C isothermal

Injector: 200 deg C split ratio 50:1

Detector: FID @ 220 deg C

6.3 HP Chemstation consisting of computer, printer and Chemstation software, or an equivalent chromatographic data system.

6.4 20 ml headspace vials with caps and septa.

6.5 Headspace vial crimper.

6.6 Microliter pipetting syringes.

6.7 Drying oven at 100 deg C vented into cold trap or other means of trapping hydrocarbons released.

6.8 Laboratory shaker or tumbler suitable for the headspace vials.

6.9 Personal protective equipment required for sampling the process such as rubber gloves and face and eye protection.

7.0 Reagents and Standards

7.1 Toluene, 99.9+% purity, HPLC grade.

7.2 Styrene, 99.9+% purity, HPLC grade.

7.3 Dry rubber of same type as the strip-crumb samples.

8.0 Sample Collection, Preservation and Storage

8.1 Collect a sample of crumb in a manner appropriate for the process equipment being sampled.

8.1.1 If conditions permit, this may be done by passing a stream of the crumb slurry through a strainer, thus separating the crumb from the water. Allow the water to drain freely, do not attempt to squeeze any water from the crumb. Results will not depend on the exact water content of the samples. Immediately place several pieces of crumb directly into a headspace vial. This should be done with rubber gloves to protect the hands from both the heat and from contact with residual hydrocarbons. The vial should be between ¼ and ½ full. Results do

not depend on sample size as long as there is sufficient sample to reach an equilibrium vapor pressure in the headspace of the vial. Cap and seal the vial. Prepare each sample at least in duplicate. This is to minimize the effect of the variation that naturally occurs in the composition of non homogeneous crumb. The free water is not analyzed by this method and should be disposed of appropriately along with any unused rubber crumb.

8.1.2 Alternatively the process can be sampled in a specially constructed sealed bomb which can then be transported to the laboratory. The bomb is then cooled to ambient temperature by applying a stream of running water. The bomb can then be opened and the crumb separated from the water and the vials filled as described in section 8.1.1 of this method. The bomb may be stored up to 8 hours prior to transferring the crumb into vials.

8.2 The sealed headspace vials may be run immediately or may be stored up to 72 hours prior to running. It is possible that even longer storage times may be acceptable, but this must be verified for the particular type of sample being analyzed (see section 9.2.3 of this method). The main concern here is that some types of rubber eventually may flow, thus compacting the crumb so that the surface area is reduced. This may have some effect on the headspace equilibration.

9.0 Quality Control

9.1 The laboratory is required to operate a formal quality control program. This consists of an initial demonstration of the capability of the method as well as ongoing analysis of standards, blanks and spiked samples to demonstrate continued performance.

9.1.1 When the method is first set up a calibration is run (described in section 10 of this method) and an initial demonstration of method capability is performed (described in section 9.2 of this method). Also recovery efficiency for each type of sample must be determined (see section 9.4 of this method).

9.1.2 It is permissible to modify this method in order to improve separations or make other improvements, provided that all performance specifications are met. Each time a modification to the method is made it is necessary to repeat the calibration (section 10 of this method), the demonstration of method performance (section 9.2 of this method) and the recovery efficiency for each type of sample (section 9.4 of this method).

9.1.3 Ongoing performance should be monitored by running a spiked rubber standard. If this test fails to demonstrate that the analysis is in control, then corrective action must be taken. This method is described in section 9.3 of this method.

9.1.4 If new types of samples are being analyzed then recovery efficiency for each new type of sample must be determined. New type includes any change, such as polymer

type, physical form or a significant change in the composition of the matrix.

9.2 Initial demonstration of method capability to establish the accuracy and precision of the method. This is to be run following the calibration described in section 10 of this method.

9.2.1 Prepare a series of identical spiked rubber standards as described in section 9.3 of this method. A sufficient number to determine statistical information on the test should be run. Ten may be a suitable number, depending on the quality control methodology used at the laboratory running the tests. These are run in the same manner as unknown samples (see section 11 of this method).

9.2.2 Determine mean and standard deviation for the results. Use these to determine the capability of the method and to calculate suitable control limits for the ongoing performance check which will utilize the same standards.

9.2.3 Prepare several additional spiked rubber standards and run 2 each day to determine the suitability of storage of the samples for 24, 48 and 72 hours or longer if longer storage times are desired.

9.3 A spiked rubber standard should be run on a regular basis to verify system performance. This would probably be done daily if samples are run daily. This is prepared in the same manner as the calibration standards (section 10.1 of this method), except that only one concentration of toluene and styrene is prepared. Choose concentrations of toluene and styrene that fall in the middle of the range expected in the stripper crumb and then do not change these unless there is a major change in the composition of the unknowns. If it becomes necessary to change the composition of this standard the initial performance demonstration must be repeated with the new standard (section 9.2 of this method).

9.3.1 Each day prepare one spiked rubber standard to be run the following day. The dry rubber may be prepared in bulk and stored for any length of time consistent with the shelf life of the product. The addition of water and hydrocarbons must be performed daily and all the steps described under section 10.1 of this method must be followed.

9.3.2 Run the spiked rubber standard prepared the previous day. Record the results and plot on an appropriate control chart or other means of determining statistical control.

9.3.3 If the results for the standard indicate that the test is out of control then corrective action must be taken. This may include a check on procedures, instrument settings, maintenance or recalibration. Samples may be stored (see section 8.2 of this method) until compliance is demonstrated.

9.4 Recovery efficiency must be determined once for each sample type and whenever modifications are made to the method.

9.4.1 For each sample type collect 12 samples from the process (section 8.1 of this method). This should be done when the process is operating in a normal manner and residual hydrocarbon levels are in the normal range. Half the vials and caps should be tared, labeled "spiked" and numbered 1 through 6. The other vials are labeled "unspiked" and need not be tared but are also numbered 1 through 6. Immediately on sampling, the vials should be capped to prevent loss of volatiles. Allow all the samples to cool completely to ambient temperature. Reweigh each of the vials labeled "spiked" to determine the weight of wet crumb inside.

9.4.2 The dry weight of rubber present in the wet crumb is estimated by multiplying the weight of wet crumb by the fraction of nonvolatiles typical for the sample. If this is not known, an additional quantity of crumb may be sampled, weighed, dried in an oven and reweighed to determine the fraction of volatiles and nonvolatiles prior to starting this procedure.

9.4.3 To the vials labeled "spiked" add an amount of a mixture of toluene and styrene that is between 40 and 60 % of the amount expected in the crumb. This is done by removing the cap, adding the mixture by syringe, touching the tip of the needle to the sample in order to remove the drop and then immediately recapping the vials. The mixture is not added through the septum, because a punctured septum may leak and vent vapors as the vial is heated. The weights of toluene and styrene added may be calculated from the volumes of the mixture added, its composition and density, or may be determined by the weight of the vials and caps prior to and after addition. The exact dry weight of rubber present and the concentration of residual toluene and styrene are not known at this time so an exact calculation of the concentration of hydrocarbons is not possible until the test is completed.

9.4.4 Place all the vials onto a shaker or tumbler for 24 ± 2 hours. This is essential in order for the hydrocarbons to be evenly distributed and completely absorbed into the rubber. If this is not followed the toluene and styrene will be mostly at the surface of the rubber and high results will be obtained.

9.4.5 Remove the vials from the shaker and tap them so that all the crumb settles to the bottom of the vials. Allow them to stand for 1 hour prior to analysis to allow any liquid to drain fully to the bottom.

9.4.6 Run the spiked and unspiked samples in the normal manner. Record the concentrations of toluene and styrene reported for each pair of spiked and unspiked samples with the same vial number.

9.4.7 Open each of the vials labeled "spiked", remove all the rubber crumb and

place it into a tarred drying pan. Place in a 100 deg C oven for two hours, cool and re-weigh. Subtract the weight of the tare to give the dry weight of rubber in each spiked vial. Calculate the concentration of toluene and styrene spiked into each vial as percent of dry rubber weight. This will be slightly different for each vial since the weights of dry rubber will be different.

9.4.8 For each hydrocarbon calculate the average recovery efficiency (R) using the following equations:

$$R = R \frac{\sum(P_n)}{6} \text{ (average of the 6 individual } R_n \text{ values)}$$

Where:

$$R_n = (C_{ns} - C_{nu}) / S_n$$

Where:

n=vial number

Cns=concentration of compound measured in spiked sample number n.

Cnu=concentration of compound measured in unspiked sample number n.

Sn=theoretical concentration of compound spiked into sample n calculated in step 9.4.7

9.4.9 A different R value should be obtained for each compound (styrene and toluene) and for each sample type.

9.4.10 A value of R between 0.70 and 1.30 is acceptable.

9.4.11 R is used to correct all reported results for each compound by dividing the measured results of each compound by the R for that compound for the same sample type (see section 12.2 of this method.)

10.0 Calibration

10.1 Calibration standards are prepared by dosing known amounts of the hydrocarbons of interest into vials containing known amounts of rubber and water.

10.1.1 Cut a sufficient quantity of dry rubber of the same type as will be analyzed into pieces about the same size as that of the crumb. Place these in a single layer on a piece of aluminum foil or other suitable surface and place into a forced air oven at 100 °C for four hours. This is to remove any residual hydrocarbons that may be present. This step may be performed in advance.

10.1.2 Into each of a series of vials add 3.0 g of the dry rubber.

10.1.3 Into each vial add 1.0 ml distilled water or an amount that is close to the amount that will be present in the unknowns. The exact amount of water present does not have much effect on the analysis, but it is necessary to have a saturated environment. The water will also aid in the uniform distribution of the spiked hydrocarbons over the surface of the rubber after the vials are placed on the shaker (in step 10.1.5 of this method).

10.1.4 Into each vial add varying amounts of toluene and styrene by microliter syringe and cap the vials immediately to prevent

loss. The tip of the needle should be carefully touched to the rubber in order to transfer the last drop to the rubber. Toluene and styrene may first be mixed together in suitable proportions and added together if desired. The weights of toluene and styrene added may be calculated from the volumes of the mixture added, its composition and density, or may be determined by the weight of the vials and caps prior to and after addition. Concentrations of added hydrocarbons are calculated as percent of the dry rubber weight. At least 5 standards should be prepared with the amounts of hydrocarbons added being calculated to cover the entire range possible in the unknowns. Retain two samples with no added hydrocarbons as blanks.

10.1.5 Place all the vials onto a shaker or tumbler for 24 ± 2 hours. This is essential in order for the hydrocarbons to be evenly distributed and completely absorbed into the rubber. If this is not followed the toluene and styrene will be mostly at the surface of the rubber and high results will be obtained.

10.1.6 Remove the vials from the shaker and tap them so that all the crumb settles to the bottom of the vials. Allow them to stand for 1 hour prior to analysis to allow any liquid to drain fully to the bottom.

10.2 Run the standards and blanks in the same manner as described for unknowns (section 11 of this method), starting with a blank, then in order of increasing hydrocarbon content and ending with the other blank.

10.3 Verify that the blanks are sufficiently free from toluene and styrene or any interfering hydrocarbons.

10.3.1 It is possible that trace levels may be present even in dry product. If levels are high enough that they will interfere with the calibration then the drying procedure in section 10.1.1 of this method should be reviewed and modified as needed to ensure that suitable standards can be prepared.

10.3.2 It is possible that the final blank is contaminated by the previous standard. If this is the case review and modify the sampler parameters as needed to eliminate this problem. If necessary it is possible to run blank samples between regular samples in order to reduce this problem, though it should not be necessary if the sampler is properly set up.

10.4 Enter the amounts of toluene and styrene added to each of the samples (as calculated in section 10.1.4 of this method) into the calibration table and perform a calibration utilizing the external standard method of analysis.

10.5 At low concentrations the calibration should be close to linear. If a wide range of levels are to be determined it may be desirable to apply a nonlinear calibration to get the best fit.

11.0 Procedure

11.1 Place the vials in the tray of the headspace sampler. Enter the starting and ending positions through the console of the sampler. For unknown samples each is run in duplicate to minimize the effect of variations in crumb composition. If excessive variation is noted it may be desirable to run more than two of each sample.

11.2 Make sure the correct method is loaded on the Chemstation. Turn on the gas flows and light the FID flame.

11.3 Start the sequence on the Chemstation. Press the START button on the headspace unit. The samples will be automatically injected after equilibrating for 30 minutes in the oven. As each sample is completed the Chemstation will calculate and print out the results as percent toluene and styrene in the crumb based on the dry weight of rubber.

12.0 Data Analysis and Calculations

12.1 For each set of duplicate samples calculate the average of the measured concentration of toluene and styrene. If more than two replicates of each sample are run calculate the average over all replicates.

12.2 For each sample correct the measured amounts of toluene and styrene using the following equation:

$$\text{Corrected Result} = C_m/R$$

Where:

C_m = Average measured concentration for that compound.

R = Recovery efficiency for that compound in the same sample type (see section 9.4 of this method)

12.3 Report the recovery efficiency (R) and the corrected results of toluene and styrene for each sample.

13.0 Method Performance

13.1 This method can be very sensitive and reproducible. The actual performance depends largely on the exact nature of the samples being analyzed. Actual performance must be determined by each laboratory for each sample type.

13.2 The main source of variation is the actual variation in the composition of non homogeneous crumb in a stripping system and the small sample sizes employed here. It therefore is the responsibility of each laboratory to determine the optimum number of replicates of each sample required to obtain accurate results.

14.0 Pollution Prevention

14.1 Samples should be kept sealed when possible in order to prevent evaporation of hydrocarbons.

14.2 When drying of samples is required it should be done in an oven which vents into

a suitable device that can trap the hydrocarbons released.

14.3 Dispose of samples as described in section 15.

15.0 Waste Management

15.1 Excess stripper crumb and water as well as the contents of the used sample vials should be properly disposed of in accordance with local and federal regulations.

15.2 Preferably this will be accomplished by having a system of returning unused and spent samples to the process.

16.0 References

16.1 "HP 7694 Headspace Sampler—Operating and Service Manual", Hewlett-Packard Company, publication number G1290-90310, June 1993.

METHOD 313B—THE DETERMINATION OF RESIDUAL HYDROCARBON IN SOLUTION POLYMERS BY CAPILLARY GAS CHROMATOGRAPHY

1.0 Scope

1.1 This method is applicable to solution polymerized polybutadiene (PBD).

1.2 This method quantitatively determines n-hexane in wet crumb polymer at levels from 0.08 to 0.15% by weight.

1.3 This method may be extended to the determination of other hydrocarbons in solution produced polymers with proper experimentation and documentation.

2.0 Principle of Method

2.1 A weighed sample of polymer is dissolved in chloroform and the cement is coagulated with an isopropyl alcohol solution containing a specific amount of alpha-methyl styrene (AMS) as the internal standard. The extract of this coagulation is then injected into a gas chromatograph and separated into individual components. Quantification is achieved by the method of internal standardization.

3.0 Definitions

3.1 The definitions are included in the text as needed.

4.0 Interferences

[Reserved]

5.0 Safety

5.1 This method may involve hazardous materials, operations, and equipment. This method does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

6.0 *Equipment and Supplies*

6.1 Analytical balance, 160 g capacity, 0.1 mg resolution

6.2 Bottles, 2-oz capacity with poly-cap screw lids

6.3 Mechanical shaker

6.4 Syringe, 10- μ l capacity

6.5 Syringe, 2.5-ml capacity, with 22 gauge 1.25 inch needle, PP/PE material, disposable

6.6 Gas chromatograph, Hewlett-Packard model 5890, or equivalent, configured with FID, split injector packed with silanized glass wool.

6.6.1 Establish the following gas chromatographic conditions, and allow the system to thoroughly equilibrate before use.

6.6.2 Injector parameters:

Injection technique=Split

Injector split flow=86 ml/min

Injector temperature=225 deg C

6.6.3 Oven temperature program:

Initial temperature=40 deg C

Initial time=6 min

Program rate=10 deg C/min

Upper limit temperature=175 deg C

Upper limit interval=10 min

6.6.4 Detector parameters:

Detector temperature=300 deg C

Hydrogen flow=30 ml/min

Air flow=350 ml/min

Nitrogen make up=26 ml/min

6.7 Gas chromatographic columns: SE-54 (5%-phenyl) (1%-vinyl)-methylpolysiloxane, 15 M \times 0.53 mm ID with a 1.2 micron film thickness, and a Carbowax 20M (polyethylene glycol), 15 M \times 0.53 mm ID with a 1.2 micron film thickness.

6.7.1 Column assembly: using a 0.53 mm ID butt connector union, join the 15 M \times 0.53 mm SE-54 column to the 15 M \times 0.53 mm Carbowax 20M. The SE-54 column will be inserted into the injector and the Carbowax 20M inserted into the detector after they have been joined.

6.7.2 Column parameters:

Helium flow=2.8 ml/min

Helium headpressure=2 psig

6.8 Centrifuge

6.9 Data collection system, Hewlett-Packard Model 3396, or equivalent

6.10 Pipet, 25-ml capacity, automatic dispensing, and 2 liter reservoir

6.11 Pipet, 2-ml capacity, volumetric delivery, class A

6.12 Flasks, 100 and 1000-ml capacity, volumetric, class A

6.13 Vial, serum, 50-ml capacity, red rubber septa and crimp ring seals

6.14 Sample collection basket fabricated out of wire mesh to allow for drainage

7.0 *Chemicals and Reagents*

CHEMICALS:

7.1 alpha-Methyl Styrene, C₉H₁₀, 99+% purity, CAS 98-83-9

7.2 n-Hexane, C₆H₁₄, 99+% purity, CAS 110-54-3

7.3 Isopropyl alcohol, C₃H₈O 99.5+% purity, reagent grade, CAS 67-63-0

7.4 Chloroform, CHCl₃, 99% min., CAS 67-66-3

REAGENTS:

7.5 Internal Standard Stock Solution: 10 mg/25 ml AMS in isopropyl alcohol.

7.5.1 Into a 25-ml beaker, weigh 0.4 g of AMS to the nearest 0.1 mg.

7.5.2 Quantitatively transfer this AMS into a 1-L volumetric flask. Dilute to the mark with isopropyl alcohol.

7.5.3 Transfer this solution to the automatic dispensing pipet reservoir. This will be labeled the AMS STOCK SOLUTION.

7.6 n-Hexane Stock Solution: 13mg/2ml hexane in isopropyl alcohol.

7.6.1 Into a 100-ml volumetric flask, weigh 0.65 g of n-hexane to the nearest 0.1 mg.

7.6.2 Dilute to the mark with isopropyl alcohol. This solution will be labeled the n-HEXANE STOCK SOLUTION.

8.0 *Sample Collection, Preservation and Storage*

8.1 A sampling device similar to Figure 1 is used to collect a non-vented crumb rubber sample at a location that is after the stripping operation but before the sample is exposed to the atmosphere.

8.2 The crumb rubber is allowed to cool before opening the sampling device and removing the sample.

8.3 The sampling device is opened and the crumb rubber sample is collected in the sampling basket.

8.4 One pound of crumb rubber sample is placed into a polyethylene bag. The bag is labeled with the time, date and sample location.

8.5 The sample should be delivered to the laboratory for testing within one hour of sampling.

8.6 Laboratory testing will be done within 3 hours of the sampling time.

8.7 No special storage conditions are required unless the storage time exceeds 3 hours in which case refrigeration of the samples is recommended.

9.0 *Quality Control*

9.1 For each sample type, 12 samples shall be obtained from the process for the recovery study. Half of the vials and caps shall be tared, labeled "spiked", and numbered 1 through 6. The other vials shall be labeled "unspiked" and need not be tared, but are also numbered 1 through 6.

9.2 Determine the % moisture content of the crumb sample. After determining the % moisture content, the correction factor for

calculating the dry crumb weight can be determined by using the equation in section 12.2 of this method.

9.3 Run the spiked and unspiked samples in the normal manner. Record the concentrations of the n-hexane content of the mixed hexane reported for each pair of spiked and unspiked samples.

9.4 For the recovery study, each sample of crumb shall be dissolved in chloroform containing a known amount of mixed hexane solvent.

9.5 For each hydrocarbon, calculate the recovery efficiency (R) using the following equations:

$$M_i = M_s - M_u$$

$$R = M_i / S$$

Where:

M_u = Measured amount of compound in the unspiked sample

M_s = Measured amount of compound in the spiked sample

M_i = Measured amount of the spiked compound

S = Amount of compound added to the spiked sample

R = Fraction of spiked compound recovered

9.6 Normally a value of R between 0.70 and 1.30 is acceptable.

9.7 R is used to correct all reported results for each compound by dividing the measured results of each compound by the R for that compound for the same sample type.

10.0 Calibration

10.1 Using the AMS STOCK SOLUTION equipped with the automatic dispensing pipet (7.5.3 of this method), transfer 25.0 ml of the internal standard solution into an uncapped 50-ml serum vial.

10.2 Using a 2.0 ml volumetric pipet, quantitatively transfer 2.0 ml of the n-HEXANE STOCK SOLUTION (7.6.2 of this method) into the 50-ml serum vial and cap. This solution will be labeled the CALIBRATION SOLUTION.

10.3 Using the conditions prescribed (6.6 of this method), inject 1 μ l of the supernate.

10.4 Obtain the peak areas and calculate the response factor as described in the calculations section (12.1 of this method).

11.0 Procedure

11.1 Determination of Dry Polymer Weight

11.1.1 Remove wet crumb from the polyethylene bag and place on paper towels to absorb excess surface moisture.

11.1.2 Cut small slices or cubes from the center of the crumb sample to improve sample uniformity and further eliminate surface moisture.

11.1.3 A suitable gravimetric measurement should be made on a sample of this wet crumb to determine the correction factor needed to calculate the dry polymer weight.

11.2 Determination of n-Hexane in Wet Crumb

11.2.1 Remove wet crumb from the polyethylene bag and place on paper towels to absorb excess surface moisture.

11.2.2 Cut small slices or cubes from the center of the crumb sample to improve sample uniformity and further eliminate surface moisture.

11.2.3 Into a tared 2 oz bottle, weigh 1.5 g of wet polymer to the nearest 0.1 mg.

11.2.4 Add 25 ml of chloroform to the 2 oz bottle and cap.

11.2.5 Using a mechanical shaker, shake the bottle until the polymer dissolves.

11.2.6 Using the autodispensing pipet, add 25.0 ml of the AMS STOCK SOLUTION (7.5.3 of this method) to the dissolved polymer solution and cap.

11.2.7 Using a mechanical shaker, shake the bottle for 10 minutes to coagulate the dissolved polymer.

11.2.8 Centrifuge the sample for 3 minutes at 2000 rpm.

11.2.9 Using the conditions prescribed (6.6 of this method), chromatograph 1 μ l of the supernate.

11.2.10 Obtain the peak areas and calculate the concentration of the component of interest as described in the calculations (12.2 of this method).

12.0 Calculations

12.1 Calibration:

$$RF_x = (W_x \times A_{is}) / (W_{is} \times A_x)$$

Where:

RF_x = the relative response factor for n-hexane

W_x = the weight (g) of n-hexane in the CALIBRATION SOLUTION

A_{is} = the area of AMS

W_{is} = the weight (g) of AMS in the CALIBRATION SOLUTION

A_x = the area of n-hexane

12.2 Procedure:

12.2.1 Correction Factor for calculating dry crumb weight.

$$F = 1 - (\% \text{ moisture} / 100)$$

Where:

F = Correction factor for calculating dry crumb weight

% moisture determined by appropriate method

12.2.2 Moisture adjustment for chromatographic determination.

$$W_s = F \times W_c$$

Where:

W_s = the weight (g) of the dry polymer corrected for moisture

F = Correction factor for calculating dry crumb weight

W_c = the weight (g) of the wet crumb in section 9.6

12.2.3 Concentration (ppm) of hexane in the wet crumb.

$$\text{ppm}_x = (A_x * \text{RF}_x * W_{is} * 10000) / (A_{is} * W_s)$$

Where:

ppm_x =parts per million of n-hexane in the polymer

A_x =the area of n-hexane

RF_x =the relative response factor for n-hexane

W_{is} =the weight (g) of AMS in the sample solution

A_{is} =the area of AMS

W_s =the weight (g) of the dry polymer corrected for moisture

13.0 Method Performance

13.1 Precision for the method was determined at the 0.08% level.

The standard deviation was 0.01 and the percent relative standard deviation (RSD) was 16.3 % with five degrees of freedom.

14.0 Waste Generation

14.1 Waste generation should be minimized where possible.

15.0 Waste Management

15.1 Discard liquid chemical waste into the chemical waste drum.

15.2 Discard polymer waste into the polymer waste container.

16.0 References

16.1 This method is based on Goodyear Chemical Division Test Method E-964.

METHOD 315—DETERMINATION OF PARTICULATE AND METHYLENE CHLORIDE EXTRACTABLE MATTER (MCEM) FROM SELECTED SOURCES AT PRIMARY ALUMINUM PRODUCTION FACILITIES

NOTE: This method does not include all of the specifications (e.g., equipment and supplies) and procedures (e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, and Method 5 of 40 CFR part 60, appendix A.

1.0 Scope and Application.

1.1 Analytes. Particulate matter (PM). No CAS number assigned. Methylene chloride extractable matter (MCEM). No CAS number assigned.

1.2 Applicability. This method is applicable for the simultaneous determination of PM and MCEM when specified in an applicable regulation. This method was developed by consensus with the Aluminum Association and the U.S. Environmental Protection

Agency (EPA) and has limited precision estimates for MCEM; it should have similar precision to Method 5 for PM in 40 CFR part 60, appendix A since the procedures are similar for PM.

1.3 Data quality objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method.

Particulate matter and MCEM are withdrawn isokinetically from the source. PM is collected on a glass fiber filter maintained at a temperature in the range of 120 ± 14 °C (248 ± 25 °F) or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application. The PM mass, which includes any material that condenses on the probe and is subsequently removed in an acetone rinse or on the filter at or above the filtration temperature, is determined gravimetrically after removal of uncombined water. MCEM is then determined by adding a methylene chloride rinse of the probe and filter holder, extracting the condensable hydrocarbons collected in the impinger water, adding an acetone rinse followed by a methylene chloride rinse of the sampling train components after the filter and before the silica gel impinger, and determining residue gravimetrically after evaporating the solvents.

3.0 Definitions. [Reserved]

4.0 Interferences. [Reserved]

5.0 Safety.

This method may involve hazardous materials, operations, and equipment. This method does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

6.0 Equipment and Supplies.

NOTE: Mention of trade names or specific products does not constitute endorsement by the EPA.

6.1 Sample collection. The following items are required for sample collection:

6.1.1 Sampling train. A schematic of the sampling train used in this method is shown in Figure 5-1, Method 5, 40 CFR part 60, appendix A. Complete construction details are given in APTD-0581 (Reference 2 in section 17.0 of this method); commercial models of this train are also available. For changes from APTD-0581 and for allowable modifications of the train shown in Figure 5-1, Method 5, 40 CFR part 60, appendix A, see the following subsections.

NOTE: The operating and maintenance procedures for the sampling train are described in APTD-0576 (Reference 3 in section 17.0 of this method). Since correct usage is important in obtaining valid results, all users should read APTD-0576 and adopt the operating and maintenance procedures outlined in it, unless otherwise specified herein. The use of grease for sealing sampling train components is not recommended because many greases are soluble in methylene chloride. The sampling train consists of the following components:

6.1.1.1 Probe nozzle. Glass or glass lined with sharp, tapered leading edge. The angle of taper shall be $\leq 30^\circ$, and the taper shall be on the outside to preserve a constant internal diameter. The probe nozzle shall be of the button-hook or elbow design, unless otherwise specified by the Administrator. Other materials of construction may be used, subject to the approval of the Administrator. A range of nozzle sizes suitable for isokinetic sampling should be available. Typical nozzle sizes range from 0.32 to 1.27 cm ($\frac{1}{8}$ to $\frac{1}{2}$ in.) inside diameter (ID) in increments of 0.16 cm ($\frac{1}{16}$ in.). Larger nozzle sizes are also available if higher volume sampling trains are used. Each nozzle shall be calibrated according to the procedures outlined in section 10.0 of this method.

6.1.1.2 Probe liner. Borosilicate or quartz glass tubing with a heating system capable of maintaining a probe gas temperature at the exit end during sampling of $120 \pm 14^\circ\text{C}$ ($248 \pm 25^\circ\text{F}$), or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application. Because the actual temperature at the outlet of the probe is not usually monitored during sampling, probes constructed according to APTD-0581 and using the calibration curves of APTD-0576 (or calibrated according to the procedure outlined in APTD-0576) will be considered acceptable. Either borosilicate or quartz glass probe liners may be used for stack temperatures up to about 480°C (900°F); quartz liners shall be used for temperatures between 480 and 900°C (900 and $1,650^\circ\text{F}$). Both types of liners may be used at higher temperatures than specified for short periods of time, subject to the approval of the Administrator. The softening temperature for borosilicate glass is 820°C ($1,500^\circ\text{F}$) and for quartz glass it is $1,500^\circ\text{C}$ ($2,700^\circ\text{F}$).

6.1.1.3 Pitot tube. Type S, as described in section 6.1 of Method 2, 40 CFR part 60, appendix A, or other device approved by the Administrator. The pitot tube shall be attached to the probe (as shown in Figure 5-1 of Method 5, 40 CFR part 60, appendix A) to allow constant monitoring of the stack gas velocity. The impact (high pressure) opening plane of the pitot tube shall be even with or above the nozzle entry plane (see Method 2,

Figure 2-6b, 40 CFR part 60, appendix A) during sampling. The Type S pitot tube assembly shall have a known coefficient, determined as outlined in section 10.0 of Method 2, 40 CFR part 60, appendix A.

6.1.1.4 Differential pressure gauge. Inclined manometer or equivalent device (two), as described in section 6.2 of Method 2, 40 CFR part 60, appendix A. One manometer shall be used for velocity head (D_p) readings, and the other, for orifice differential pressure readings.

6.1.1.5 Filter holder. Borosilicate glass, with a glass frit filter support and a silicone rubber gasket. The holder design shall provide a positive seal against leakage from the outside or around the filter. The holder shall be attached immediately at the outlet of the probe (or cyclone, if used).

6.1.1.6 Filter heating system. Any heating system capable of maintaining a temperature around the filter holder of $120 \pm 14^\circ\text{C}$ ($248 \pm 25^\circ\text{F}$) during sampling, or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application. Alternatively, the tester may opt to operate the equipment at a temperature lower than that specified. A temperature gauge capable of measuring temperature to within 3°C (5.4°F) shall be installed so that the temperature around the filter holder can be regulated and monitored during sampling. Heating systems other than the one shown in APTD-0581 may be used.

6.1.1.7 Temperature sensor. A temperature sensor capable of measuring temperature to within $\pm 3^\circ\text{C}$ (5.4°F) shall be installed so that the sensing tip of the temperature sensor is in direct contact with the sample gas, and the temperature around the filter holder can be regulated and monitored during sampling.

6.1.1.8 Condenser. The following system shall be used to determine the stack gas moisture content: four glass impingers connected in series with leak-free ground glass fittings. The first, third, and fourth impingers shall be of the Greenburg-Smith design, modified by replacing the tip with a 1.3 cm ($\frac{1}{2}$ in.) ID glass tube extending to about 1.3 cm ($\frac{1}{2}$ in.) from the bottom of the flask. The second impinger shall be of the Greenburg-Smith design with the standard tip. The first and second impingers shall contain known quantities of water (section 8.3.1 of this method), the third shall be empty, and the fourth shall contain a known weight of silica gel or equivalent desiccant. A temperature sensor capable of measuring temperature to within 1°C (2°F) shall be placed at the outlet of the fourth impinger for monitoring.

6.1.1.9 Metering system. Vacuum gauge, leak-free pump, temperature sensors capable of measuring temperature to within 3°C (5.4

°F), dry gas meter (DGM) capable of measuring volume to within 2 percent, and related equipment, as shown in Figure 5-1 of Method 5, 40 CFR part 60, appendix A. Other metering systems capable of maintaining sampling rates within 10 percent of isokinetic and of determining sample volumes to within 2 percent may be used, subject to the approval of the Administrator. When the metering system is used in conjunction with a pitot tube, the system shall allow periodic checks of isokinetic rates.

6.1.1.10 Sampling trains using metering systems designed for higher flow rates than that described in APTD-0581 or APTD-0576 may be used provided that the specifications of this method are met.

6.1.2 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm (0.1 in.) Hg.

NOTE: The barometric reading may be obtained from a nearby National Weather Service station. In this case, the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and sampling point shall be made at a rate of minus 2.5 mm (0.1 in) Hg per 30 m (100 ft) elevation increase or plus 2.5 mm (0.1 in) Hg per 30 m (100 ft) elevation decrease.

6.1.3 Gas density determination equipment. Temperature sensor and pressure gauge, as described in sections 6.3 and 6.4 of Method 2, 40 CFR part 60, appendix A, and gas analyzer, if necessary, as described in Method 3, 40 CFR part 60, appendix A. The temperature sensor shall, preferably, be permanently attached to the pitot tube or sampling probe in a fixed configuration, such that the tip of the sensor extends beyond the leading edge of the probe sheath and does not touch any metal. Alternatively, the sensor may be attached just prior to use in the field. Note, however, that if the temperature sensor is attached in the field, the sensor must be placed in an interference-free arrangement with respect to the Type S pitot tube openings (see Method 2, Figure 2-4, 40 CFR part 60, appendix A). As a second alternative, if a difference of not more than 1 percent in the average velocity measurement is to be introduced, the temperature sensor need not be attached to the probe or pitot tube. (This alternative is subject to the approval of the Administrator.)

6.2 Sample recovery. The following items are required for sample recovery:

6.2.1 Probe-liner and probe-nozzle brushes. Nylon or Teflon® bristle brushes with stainless steel wire handles. The probe brush shall have extensions (at least as long as the probe) constructed of stainless steel, nylon, Teflon®, or similarly inert material. The brushes shall be properly sized and shaped to brush out the probe liner and nozzle.

6.2.2 Wash bottles. Glass wash bottles are recommended. Polyethylene or tetrafluoroethylene (TFE) wash bottles may be used, but they may introduce a positive bias due to contamination from the bottle. It is recommended that acetone not be stored in polyethylene or TFE bottles for longer than a month.

6.2.3 Glass sample storage containers. Chemically resistant, borosilicate glass bottles, for acetone and methylene chloride washes and impinger water, 500 ml or 1,000 ml. Screw-cap liners shall either be rubber-backed Teflon® or shall be constructed so as to be leak-free and resistant to chemical attack by acetone or methylene chloride. (Narrow-mouth glass bottles have been found to be less prone to leakage.) Alternatively, polyethylene bottles may be used.

6.2.4 Petri dishes. For filter samples, glass, unless otherwise specified by the Administrator.

6.2.5 Graduated cylinder and/or balance. To measure condensed water, acetone wash and methylene chloride wash used during field recovery of the samples, to within 1 ml or 1 g. Graduated cylinders shall have subdivisions no greater than 2 ml. Most laboratory balances are capable of weighing to the nearest 0.5 g or less. Any such balance is suitable for use here and in section 6.3.4 of this method.

6.2.6 Plastic storage containers. Air-tight containers to store silica gel.

6.2.7 Funnel and rubber policeman. To aid in transfer of silica gel to container; not necessary if silica gel is weighed in the field.

6.2.8 Funnel. Glass or polyethylene, to aid in sample recovery.

6.3 Sample analysis. The following equipment is required for sample analysis:

6.3.1 Glass or Teflon® weighing dishes.

6.3.2 Desiccator. It is recommended that fresh desiccant be used to minimize the chance for positive bias due to absorption of organic material during drying.

6.3.3 Analytical balance. To measure to within 0.1 mg.

6.3.4 Balance. To measure to within 0.5 g.

6.3.5 Beakers. 250 ml.

6.3.6 Hygrometer. To measure the relative humidity of the laboratory environment.

6.3.7 Temperature sensor. To measure the temperature of the laboratory environment.

6.3.8 Buchner fritted funnel. 30 ml size, fine (<50 micron)-porosity fritted glass.

6.3.9 Pressure filtration apparatus.

6.3.10 Aluminum dish. Flat bottom, smooth sides, and flanged top, 18 mm deep and with an inside diameter of approximately 60 mm.

7.0 Reagents and Standards.

7.1 Sample collection. The following reagents are required for sample collection:

7.1.1 Filters. Glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3 micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM Method D 2986-95A (incorporated by reference in §63.841 of this part). Test data from the supplier's quality control program are sufficient for this purpose. In sources containing SO₂ or SO₃, the filter material must be of a type that is unreactive to SO₂ or SO₃. Reference 10 in section 17.0 of this method may be used to select the appropriate filter.

7.1.2 Silica gel. Indicating type, 6 to 16 mesh. If previously used, dry at 175 °C (350 °F) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used, subject to the approval of the Administrator.

7.1.3 Water. When analysis of the material caught in the impingers is required, deionized distilled water shall be used. Run blanks prior to field use to eliminate a high blank on test samples.

7.1.4 Crushed ice.

7.1.5 Stopcock grease. Acetone-insoluble, heat-stable silicone grease. This is not necessary if screw-on connectors with Teflon sleeves, or similar, are used. Alternatively, other types of stopcock grease may be used, subject to the approval of the Administrator. [Caution: Many stopcock greases are methylene chloride-soluble. Use sparingly and carefully remove prior to recovery to prevent contamination of the MCEM analysis.]

7.2 Sample recovery. The following reagents are required for sample recovery:

7.2.1 Acetone. Acetone with blank values < 1 ppm, by weight residue, is required. Acetone blanks may be run prior to field use, and only acetone with low blank values may be used. In no case shall a blank value of greater than 1E-06 of the weight of acetone used be subtracted from the sample weight.

NOTE: This is more restrictive than Method 5, 40 CFR part 60, appendix A. At least one vendor (Supelco Incorporated located in Bellefonte, Pennsylvania) lists <1 mg/l as residue for its Environmental Analysis Solvents.

7.2.2 Methylene chloride. Methylene chloride with a blank value <1.5 ppm, by weight, residue. Methylene chloride blanks may be run prior to field use, and only methylene chloride with low blank values may be used. In no case shall a blank value of greater than 1.6E-06 of the weight of methylene chloride used be subtracted from the sample weight.

NOTE: A least one vendor quotes <1 mg/l for Environmental Analysis Solvents-grade methylene chloride.

7.3 Sample analysis. The following reagents are required for sample analysis:

7.3.1 Acetone. Same as in section 7.2.1 of this method.

7.3.2 Desiccant. Anhydrous calcium sulfate, indicating type. Alternatively, other types of desiccants may be used, subject to the approval of the Administrator.

7.3.3 Methylene chloride. Same as in section 7.2.2 of this method.

8.0 Sample Collection, Preservation, Storage, and Transport.

NOTE: The complexity of this method is such that, in order to obtain reliable results, testers should be trained and experienced with the test procedures.

8.1.1 Pretest preparation. It is suggested that sampling equipment be maintained according to the procedures described in APTD-0576.

8.1.1 Weigh several 200 g to 300 g portions of silica gel in airtight containers to the nearest 0.5 g. Record on each container the total weight of the silica gel plus container. As an alternative, the silica gel need not be preweighed but may be weighed directly in its impinger or sampling holder just prior to train assembly.

8.1.2 A batch of glass fiber filters, no more than 50 at a time, should be placed in a Soxhlet extraction apparatus and extracted using methylene chloride for at least 16 hours. After extraction, check filters visually against light for irregularities, flaws, or pinhole leaks. Label the shipping containers (glass or plastic petri dishes), and keep the filters in these containers at all times except during sampling and weighing.

8.1.3 Desiccate the filters at 20 ±5.6 °C (68 ±10 °F) and ambient pressure for at least 24 hours and weigh at intervals of at least 6 hours to a constant weight, i.e., <0.5 mg change from previous weighing; record results to the nearest 0.1 mg. During each weighing the filter must not be exposed to the laboratory atmosphere for longer than 2 minutes and a relative humidity above 50 percent. Alternatively (unless otherwise specified by the Administrator), the filters may be oven-dried at 104 °C (220 °F) for 2 to 3 hours, desiccated for 2 hours, and weighed. Procedures other than those described, which account for relative humidity effects, may be used, subject to the approval of the Administrator.

8.2 Preliminary determinations.

8.2.1 Select the sampling site and the minimum number of sampling points according to Method 1, 40 CFR part 60, appendix A or as specified by the Administrator. Determine the stack pressure, temperature, and the range of velocity heads using Method 2, 40 CFR part 60, appendix A; it is recommended that a leak check of the pitot lines (see section 8.1 of Method 2, 40 CFR part 60, appendix A) be performed. Determine the moisture content using Approximation

Method 4 (section 1.2 of Method 4, 40 CFR part 60, appendix A) or its alternatives to make isokinetic sampling rate settings. Determine the stack gas dry molecular weight, as described in section 8.6 of Method 2, 40 CFR part 60, appendix A; if integrated Method 3 sampling is used for molecular weight determination, the integrated bag sample shall be taken simultaneously with, and for the same total length of time as, the particulate sample run.

8.2.2 Select a nozzle size based on the range of velocity heads such that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates. During the run, do not change the nozzle size. Ensure that the proper differential pressure gauge is chosen for the range of velocity heads encountered (see section 8.2 of Method 2, 40 CFR part 60, appendix A).

8.2.3 Select a suitable probe liner and probe length such that all traverse points can be sampled. For large stacks, consider sampling from opposite sides of the stack to reduce the required probe length.

8.2.4 Select a total sampling time greater than or equal to the minimum total sampling time specified in the test procedures for the specific industry such that: (1) The sampling time per point is not less than 2 minutes (or some greater time interval as specified by the Administrator); and (2) the sample volume taken (corrected to standard conditions) will exceed the required minimum total gas sample volume. The latter is based on an approximate average sampling rate.

8.2.5 The sampling time at each point shall be the same. It is recommended that the number of minutes sampled at each point be an integer or an integer plus one-half minute, in order to eliminate timekeeping errors.

8.2.6 In some circumstances (e.g., batch cycles), it may be necessary to sample for shorter times at the traverse points and to obtain smaller gas sample volumes. In these cases, the Administrator's approval must first be obtained.

8.3 Preparation of sampling train.

8.3.1 During preparation and assembly of the sampling train, keep all openings where contamination can occur covered until just prior to assembly or until sampling is about to begin. Place 100 ml of water in each of the first two impingers, leave the third impinger empty, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the fourth impinger. More silica gel may be used, but care should be taken to ensure that it is not entrained and carried out from the impinger during sampling. Place the container in a clean place for later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest 0.5 g and recorded.

8.3.2 Using a tweezer or clean disposable surgical gloves, place a labeled (identified) and weighed filter in the filter holder. Be sure that the filter is properly centered and the gasket properly placed so as to prevent the sample gas stream from circumventing the filter. Check the filter for tears after assembly is completed.

8.3.3 When glass liners are used, install the selected nozzle using a Viton A O-ring when stack temperatures are less than 260 °C (500 °F) and an asbestos string gasket when temperatures are higher. See APTD-0576 for details. Mark the probe with heat-resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.

8.3.4 Set up the train as in Figure 5-1 of Method 5, 40 CFR part 60, appendix A, using (if necessary) a very light coat of silicone grease on all ground glass joints, greasing only the outer portion (see APTD-0576) to avoid possibility of contamination by the silicone grease. Subject to the approval of the Administrator, a glass cyclone may be used between the probe and filter holder when the total particulate catch is expected to exceed 100 mg or when water droplets are present in the stack gas.

8.3.5 Place crushed ice around the impingers.

8.4 Leak-check procedures.

8.4.1 Leak check of metering system shown in Figure 5-1 of Method 5, 40 CFR part 60, appendix A. That portion of the sampling train from the pump to the orifice meter should be leak-checked prior to initial use and after each shipment. Leakage after the pump will result in less volume being recorded than is actually sampled. The following procedure is suggested (see Figure 5-2 of Method 5, 40 CFR part 60, appendix A): Close the main valve on the meter box. Insert a one-hole rubber stopper with rubber tubing attached into the orifice exhaust pipe. Disconnect and vent the low side of the orifice manometer. Close off the low side orifice tap. Pressurize the system to 13 to 18 cm (5 to 7 in.) water column by blowing into the rubber tubing. Pinch off the tubing, and observe the manometer for 1 minute. A loss of pressure on the manometer indicates a leak in the meter box; leaks, if present, must be corrected.

8.4.2 Pretest leak check. A pretest leak-check is recommended but not required. If the pretest leak-check is conducted, the following procedure should be used.

8.4.2.1 After the sampling train has been assembled, turn on and set the filter and probe heating systems to the desired operating temperatures. Allow time for the temperatures to stabilize. If a Viton A O-ring or other leak-free connection is used in assembling the probe nozzle to the probe liner, leak-check the train at the sampling site by

plugging the nozzle and pulling a 380 mm (15 in.) Hg vacuum.

NOTE: A lower vacuum may be used, provided that it is not exceeded during the test.

8.4.2.2 If an asbestos string is used, do not connect the probe to the train during the leak check. Instead, leak-check the train by first plugging the inlet to the filter holder (cyclone, if applicable) and pulling a 380 mm (15 in.) Hg vacuum. (See NOTE in section 8.4.2.1 of this method). Then connect the probe to the train and perform the leak check at approximately 25 mm (1 in.) Hg vacuum; alternatively, the probe may be leak-checked with the rest of the sampling train, in one step, at 380 mm (15 in.) Hg vacuum. Leakage rates in excess of 4 percent of the average sampling rate or 0.00057 m³/min (0.02 cfm), whichever is less, are unacceptable.

8.4.2.3 The following leak check instructions for the sampling train described in APTD-0576 and APTD-0581 may be helpful. Start the pump with the bypass valve fully open and the coarse adjust valve completely closed. Partially open the coarse adjust valve and slowly close the bypass valve until the desired vacuum is reached. *Do not* reverse the direction of the bypass valve, as this will cause water to back up into the filter holder. If the desired vacuum is exceeded, either leak-check at this higher vacuum or end the leak check as shown below and start over.

8.4.2.4 When the leak check is completed, first slowly remove the plug from the inlet to the probe, filter holder, or cyclone (if applicable) and immediately turn off the vacuum pump. This prevents the water in the impingers from being forced backward into the filter holder and the silica gel from being entrained backward into the third impinger.

8.4.3 Leak checks during sample run. If, during the sampling run, a component (e.g., filter assembly or impinger) change becomes necessary, a leak check shall be conducted immediately before the change is made. The leak check shall be done according to the procedure outlined in section 8.4.2 of this method, except that it shall be done at a vacuum equal to or greater than the maximum value recorded up to that point in the test. If the leakage rate is found to be no greater than 0.00057 m³/min (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction will need to be applied to the total volume of dry gas metered; if, however, a higher leakage rate is obtained, either record the leakage rate and plan to correct the sample volume as shown in section 12.3 of this method or void the sample run.

NOTE: Immediately after component changes, leak checks are optional; if such leak checks are done, the procedure outlined in section 8.4.2 of this method should be used.

8.4.4 Post-test leak check. A leak check is mandatory at the conclusion of each sampling run. The leak check shall be performed in accordance with the procedures outlined in section 8.4.2 of this method, except that it shall be conducted at a vacuum equal to or greater than the maximum value reached during the sampling run. If the leakage rate is found to be no greater than 0.00057 m³/min (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction need be applied to the total volume of dry gas metered. If, however, a higher leakage rate is obtained, either record the leakage rate and correct the sample volume, as shown in section 12.4 of this method, or void the sampling run.

8.5 Sampling train operation. During the sampling run, maintain an isokinetic sampling rate (within 10 percent of true isokinetic unless otherwise specified by the Administrator) and a temperature around the filter of 120 ± 14 °C (248 ± 25 °F), or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator.

8.5.1 For each run, record the data required on a data sheet such as the one shown in Figure 5-2 of Method 5, 40 CFR part 60, appendix A. Be sure to record the initial reading. Record the DGM readings at the beginning and end of each sampling time increment, when changes in flow rates are made, before and after each leak-check, and when sampling is halted. Take other readings indicated by Figure 5-2 of Method 5, 40 CFR part 60, appendix A at least once at each sample point during each time increment and additional readings when significant changes (20 percent variation in velocity head readings) necessitate additional adjustments in flow rate. Level and zero the manometer. Because the manometer level and zero may drift due to vibrations and temperature changes, make periodic checks during the traverse.

8.5.2 Clean the portholes prior to the test run to minimize the chance of sampling deposited material. To begin sampling, remove the nozzle cap and verify that the filter and probe heating systems are up to temperature and that the pitot tube and probe are properly positioned. Position the nozzle at the first traverse point with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions. Nomographs are available, which aid in the rapid adjustment of the isokinetic sampling rate without excessive computations. These nomographs are designed for use when the Type S pitot tube coefficient (C_p) is 0.85 ± 0.02 and the stack gas equivalent density (dry molecular weight) is 29 ± 4. APTD-0576 details the procedure for using the nomographs. If C_p and M_d are outside the above-stated ranges, do not use the nomographs unless appropriate steps (see

Reference 7 in section 17.0 of this method) are taken to compensate for the deviations.

8.5.3 When the stack is under significant negative pressure (height of impinger stem), close the coarse adjust valve before inserting the probe into the stack to prevent water from backing into the filter holder. If necessary, the pump may be turned on with the coarse adjust valve closed.

8.5.4 When the probe is in position, block off the openings around the probe and port-hole to prevent unrepresentative dilution of the gas stream.

8.5.5 Traverse the stack cross-section, as required by Method 1, 40 CFR part 60, appendix A or as specified by the Administrator, being careful not to bump the probe nozzle into the stack walls when sampling near the walls or when removing or inserting the probe through the portholes; this minimizes the chance of extracting deposited material.

8.5.6 During the test run, make periodic adjustments to keep the temperature around the filter holder at the proper level; add more ice and, if necessary, salt to maintain a temperature of less than 20 °C (68 °F) at the condenser/silica gel outlet. Also, periodically check the level and zero of the manometer.

8.5.7 If the pressure drop across the filter becomes too high, making isokinetic sampling difficult to maintain, the filter may be replaced in the midst of the sample run. It is recommended that another complete filter assembly be used rather than attempting to change the filter itself. Before a new filter assembly is installed, conduct a leak check (see section 8.4.3 of this method). The total PM weight shall include the summation of the filter assembly catches.

8.5.8 A single train shall be used for the entire sample run, except in cases where simultaneous sampling is required in two or more separate ducts or at two or more different locations within the same duct, or in cases where equipment failure necessitates a change of trains. In all other situations, the use of two or more trains will be subject to the approval of the Administrator.

NOTE: When two or more trains are used, separate analyses of the front-half and (if applicable) impinger catches from each train shall be performed, unless identical nozzle sizes were used in all trains, in which case the front-half catches from the individual trains may be combined (as may the impinger catches) and one analysis of the front-half catch and one analysis of the impinger catch may be performed.

8.5.9 At the end of the sample run, turn off the coarse adjust valve, remove the probe and nozzle from the stack, turn off the pump, record the final DGM reading, and then conduct a post-test leak check, as outlined in section 8.4.4 of this method. Also leak-check the pitot lines as described in section 8.1 of Method 2, 40 CFR part 60, appendix A. The

lines must pass this leak check in order to validate the velocity head data.

8.6 Calculation of percent isokinetic. Calculate percent isokinetic (see Calculations, section 12.12 of this method) to determine whether a run was valid or another test run should be made. If there was difficulty in maintaining isokinetic rates because of source conditions, consult the Administrator for possible variance on the isokinetic rates.

8.7 Sample recovery.

8.7.1 Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool.

8.7.2 When the probe can be safely handled, wipe off all external PM near the tip of the probe nozzle and place a cap over it to prevent losing or gaining PM. Do not cap off the probe tip tightly while the sampling train is cooling down. This would create a vacuum in the filter holder, thus drawing water from the impingers into the filter holder.

8.7.3 Before moving the sample train to the cleanup site, remove the probe from the sample train, wipe off the silicone grease, and cap the open outlet of the probe. Be careful not to lose any condensate that might be present. Wipe off the silicone grease from the filter inlet where the probe was fastened and cap it. Remove the umbilical cord from the last impinger and cap the impinger. If a flexible line is used between the first impinger or condenser and the filter holder, disconnect the line at the filter holder and let any condensed water or liquid drain into the impingers or condenser. After wiping off the silicone grease, cap off the filter holder outlet and impinger inlet. Ground-glass stoppers, plastic caps, or serum caps may be used to close these openings.

8.7.4 Transfer the probe and filter-impinger assembly to the cleanup area. This area should be clean and protected from the wind so that the chances of contaminating or losing the sample will be minimized.

8.7.5 Save a portion of the acetone and methylene chloride used for cleanup as blanks. Take 200 ml of each solvent directly from the wash bottle being used and place it in glass sample containers labeled "acetone blank" and "methylene chloride blank," respectively.

8.7.6 Inspect the train prior to and during disassembly and note any abnormal conditions. Treat the samples as follows:

8.7.6.1 Container No. 1. Carefully remove the filter from the filter holder, and place it in its identified petri dish container. Use a pair of tweezers and/or clean disposable surgical gloves to handle the filter. If it is necessary to fold the filter, do so such that the PM cake is inside the fold. Using a dry nylon bristle brush and/or a sharp-edged blade, carefully transfer to the petri dish any PM

and/or filter fibers that adhere to the filter holder gasket. Seal the container.

8.7.6.2 Container No. 2. Taking care to see that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover PM or any condensate from the probe nozzle, probe fitting, probe liner, and front half of the filter holder by washing these components with acetone and placing the wash in a glass container. Perform the acetone rinse as follows:

8.7.6.2.1 Carefully remove the probe nozzle and clean the inside surface by rinsing with acetone from a wash bottle and brushing with a nylon bristle brush. Brush until the acetone rinse shows no visible particles, after which make a final rinse of the inside surface with acetone.

8.7.6.2.2 Brush and rinse the inside parts of the Swagelok fitting with acetone in a similar way until no visible particles remain.

8.7.6.2.3 Rinse the probe liner with acetone by tilting and rotating the probe while squirting acetone into its upper end so that all inside surfaces are wetted with acetone. Let the acetone drain from the lower end into the sample container. A funnel (glass or polyethylene) may be used to aid in transferring liquid washes to the container. Follow the acetone rinse with a probe brush. Hold the probe in an inclined position, squirt acetone into the upper end as the probe brush is being pushed with a twisting action through the probe, hold a sample container under the lower end of the probe, and catch any acetone and PM that is brushed from the probe. Run the brush through the probe three times or more until no visible PM is carried out with the acetone or until none remains in the probe liner on visual inspection. With stainless steel or other metal probes, run the brush through in the above-described manner at least six times, since metal probes have small crevices in which PM can be entrapped. Rinse the brush with acetone and quantitatively collect these washings in the sample container. After the brushing, make a final acetone rinse of the probe as described above.

8.7.6.2.4 It is recommended that two people clean the probe to minimize sample losses. Between sampling runs, keep brushes clean and protected from contamination.

8.7.6.2.5 After ensuring that all joints have been wiped clean of silicone grease, clean the inside of the front half of the filter holder by rubbing the surfaces with a nylon bristle brush and rinsing with acetone. Rinse each surface three times or more if needed to remove visible particulate. Make a final rinse of the brush and filter holder. Carefully rinse out the glass cyclone also (if applicable).

8.7.6.2.6 After rinsing the nozzle, probe, and front half of the filter holder with acetone, repeat the entire procedure with meth-

ylene chloride and save in a separate No. 2M container.

8.7.6.2.7 After acetone and methylene chloride washings and PM have been collected in the proper sample containers, tighten the lid on the sample containers so that acetone and methylene chloride will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to determine whether leakage occurs during transport. Label each container to identify clearly its contents.

8.7.6.3 Container No. 3. Note the color of the indicating silica gel to determine whether it has been completely spent, and make a notation of its condition. Transfer the silica gel from the fourth impinger to its original container and seal the container. A funnel may make it easier to pour the silica gel without spilling. A rubber policeman may be used as an aid in removing the silica gel from the impinger. It is not necessary to remove the small amount of dust particles that may adhere to the impinger wall and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If a balance is available in the field, follow the procedure for Container No. 3 in section 11.2.3 of this method.

8.7.6.4 Impinger water. Treat the impingers as follows:

8.7.6.4.1 Make a notation of any color or film in the liquid catch. Measure the liquid that is in the first three impingers to within 1 ml by using a graduated cylinder or by weighing it to within 0.5 g by using a balance (if one is available). Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas.

8.7.6.4.2 Following the determination of the volume of liquid present, rinse the back half of the train with water, add it to the impinger catch, and store it in a container labeled 3W (water).

8.7.6.4.3 Following the water rinse, rinse the back half of the train with acetone to remove the excess water to enhance subsequent organic recovery with methylene chloride and quantitatively recover to a container labeled 3S (solvent) followed by at least three sequential rinsings with aliquots of methylene chloride. Quantitatively recover to the same container labeled 3S. Record separately the amount of both acetone and methylene chloride used to the nearest 1 ml or 0.5g.

NOTE: Because the subsequent analytical finish is gravimetric, it is okay to recover both solvents to the same container. This would not be recommended if other analytical finishes were required.

8.8 Sample transport. Whenever possible, containers should be shipped in such a way that they remain upright at all times.

9.0 Quality Control.

9.1 Miscellaneous quality control measures.

Section	Quality control measure	Effect
8.4, 10.1-10.6.	Sampling and equipment leak check and calibration.	Ensure accurate measurement of stack gas flow rate, sample volume.

9.2 Volume metering system checks. The following quality control procedures are suggested to check the volume metering system calibration values at the field test site prior to sample collection. These procedures are optional.

9.2.1 Meter orifice check. Using the calibration data obtained during the calibration procedure described in section 10.3 of this method, determine the ΔH_a for the metering system orifice. The ΔH_a is the orifice pressure differential in units of in. H₂O that correlates to 0.75 cfm of air at 528 °R and 29.92 in. Hg. The ΔH_a is calculated as follows:

$$\Delta H_a = 0.0319 \Delta H \frac{T_m \Theta^2}{P_{bar} Y^2 V_m^2}$$

Where

- 0.0319 = (0.0567 in. Hg/ °R)(0.75 cfm)²;
- ΔH = Average pressure differential across the orifice meter, in. H₂O;
- T_m = Absolute average DGM temperature, °R;
- Θ = Total sampling time, min;
- P_{bar} = Barometric pressure, in. Hg;
- Y = DGM calibration factor, dimensionless;
- V_m = Volume of gas sample as measured by DGM, dcf.

9.2.1.1 Before beginning the field test (a set of three runs usually constitutes a field test), operate the metering system (i.e., pump, volume meter, and orifice) at the ΔH_a pressure differential for 10 minutes. Record the volume collected, the DGM temperature, and the barometric pressure. Calculate a DGM calibration check value, Y_c , as follows:

$$Y_c = \frac{10}{V_m} \left[\frac{0.0319 T_m}{P_{bar}} \right]^{\frac{1}{2}}$$

Where

- Y_c = DGM calibration check value, dimensionless;
- 10 = Run time, min.

9.2.1.2 Compare the Y_c value with the dry gas meter calibration factor Y to determine that: $0.97 Y < Y_c < 1.03Y$. If the Y_c value is not within this range, the volume metering system should be investigated before beginning the test.

9.2.2 Calibrated critical orifice. A calibrated critical orifice, calibrated against a wet test meter or spirometer and designed to be inserted at the inlet of the sampling meter box, may be used as a quality control check by following the procedure of section 16.2 of this method.

10.0 Calibration and Standardization.

NOTE: Maintain a laboratory log of all calibrations.

10.1 Probe nozzle. Probe nozzles shall be calibrated before their initial use in the field. Using a micrometer, measure the ID of the nozzle to the nearest 0.025 mm (0.001 in.). Make three separate measurements using different diameters each time, and obtain the average of the measurements. The difference between the high and low numbers shall not exceed 0.1 mm (0.004 in.). When nozzles become nicked, dented, or corroded, they shall be reshaped, sharpened, and recalibrated before use. Each nozzle shall be permanently and uniquely identified.

10.2 Pitot tube assembly. The Type S pitot tube assembly shall be calibrated according to the procedure outlined in section 10.1 of Method 2, 40 CFR part 60, appendix A.

10.3 Metering system.

10.3.1 Calibration prior to use. Before its initial use in the field, the metering system shall be calibrated as follows: Connect the metering system inlet to the outlet of a wet test meter that is accurate to within 1 percent. Refer to Figure 5-5 of Method 5, 40 CFR part 60, appendix A. The wet test meter should have a capacity of 30 liters/revolution (1 ft³/rev). A spirometer of 400 liters (14 ft³) or more capacity, or equivalent, may be used for this calibration, although a wet test meter is usually more practical. The wet test meter should be periodically calibrated with a spirometer or a liquid displacement meter to ensure the accuracy of the wet test meter. Spirometers or wet test meters of other sizes may be used, provided that the specified accuracies of the procedure are maintained. Run the metering system pump for about 15 minutes with the orifice manometer indicating a median reading, as expected in field

use, to allow the pump to warm up and to permit the interior surface of the wet test meter to be thoroughly wetted. Then, at each of a minimum of three orifice manometer settings, pass an exact quantity of gas through the wet test meter and note the gas volume indicated by the DGM. Also note the barometric pressure and the temperatures of the wet test meter, the inlet of the DGM, and the outlet of the DGM. Select the highest and lowest orifice settings to bracket the expected field operating range of the orifice. Use a minimum volume of 0.15 m³ (5 cf) at all orifice settings. Record all the data on a form similar to Figure 5-6 of Method 5, 40 CFR part 60, appendix A, and calculate Y (the DGM calibration factor) and ΔH_a (the orifice calibration factor) at each orifice setting, as shown on Figure 5-6 of Method 5, 40 CFR part 60, appendix A. Allowable tolerances for individual Y and ΔH_a values are given in Figure 5-6 of Method 5, 40 CFR part 60, appendix A. Use the average of the Y values in the calculations in section 12 of this method.

10.3.1.1 Before calibrating the metering system, it is suggested that a leak check be conducted. For metering systems having diaphragm pumps, the normal leak check procedure will not detect leakages within the pump. For these cases the following leak check procedure is suggested: make a 10-minute calibration run at 0.00057 m³/min (0.02 cfm); at the end of the run, take the difference of the measured wet test meter and DGM volumes; divide the difference by 10 to get the leak rate. The leak rate should not exceed 0.00057 m³/min (0.02 cfm).

10.3.2 Calibration after use. After each field use, the calibration of the metering system shall be checked by performing three calibration runs at a single, intermediate orifice setting (based on the previous field test) with the vacuum set at the maximum value reached during the test series. To adjust the vacuum, insert a valve between the wet test meter and the inlet of the metering system. Calculate the average value of the DGM calibration factor. If the value has changed by more than 5 percent, recalibrate the meter over the full range of orifice settings, as previously detailed.

NOTE: Alternative procedures, e.g., rechecking the orifice meter coefficient, may be used, subject to the approval of the Administrator.

10.3.3 Acceptable variation in calibration. If the DGM coefficient values obtained before and after a test series differ by more than 5 percent, either the test series shall be voided or calculations for the test series shall be performed using whichever meter coefficient value (i.e., before or after) gives the lower value of total sample volume.

10.4 Probe heater calibration. Use a heat source to generate air heated to selected

temperatures that approximate those expected to occur in the sources to be sampled. Pass this air through the probe at a typical sample flow rate while measuring the probe inlet and outlet temperatures at various probe heater settings. For each air temperature generated, construct a graph of probe heating system setting versus probe outlet temperature. The procedure outlined in APTD-0576 can also be used. Probes constructed according to APTD-0581 need not be calibrated if the calibration curves in APTD-0576 are used. Also, probes with outlet temperature monitoring capabilities do not require calibration.

NOTE: The probe heating system shall be calibrated before its initial use in the field.

10.5 Temperature sensors. Use the procedure in section 10.3 of Method 2, 40 CFR part 60, appendix A to calibrate in-stack temperature sensors. Dial thermometers, such as are used for the DGM and condenser outlet, shall be calibrated against mercury-in-glass thermometers.

10.6 Barometer. Calibrate against a mercury barometer.

11.0 Analytical Procedure.

11.1 Record the data required on a sheet such as the one shown in Figure 315-1 of this method.

11.2 Handle each sample container as follows:

11.2.1 Container No. 1.

11.2.1.1 PM analysis. Leave the contents in the shipping container or transfer the filter and any loose PM from the sample container to a tared glass weighing dish. Desiccate for 24 hours in a desiccator containing anhydrous calcium sulfate. Weigh to a constant weight and report the results to the nearest 0.1 mg. For purposes of this section, the term "constant weight" means a difference of no more than 0.5 mg or 1 percent of total weight less tare weight, whichever is greater, between two consecutive weighings, with no less than 6 hours of desiccation time between weighings (overnight desiccation is a common practice). If a third weighing is required and it agrees within ± 0.5 mg, then the results of the second weighing should be used. For quality assurance purposes, record and report each individual weighing; if more than three weighings are required, note this in the results for the subsequent MCEM results.

11.2.1.2 MCEM analysis. Transfer the filter and contents quantitatively into a beaker. Add 100 ml of methylene chloride and cover with aluminum foil. Sonicate for 3 minutes then allow to stand for 20 minutes. Set up the filtration apparatus. Decant the solution into a clean Buchner fritted funnel. Immediately pressure filter the solution through the tube into another clean, dry

beaker. Continue decanting and pressure filtration until all the solvent is transferred. Rinse the beaker and filter with 10 to 20 ml methylene chloride, decant into the Buchner fritted funnel and pressure filter. Place the beaker on a low-temperature hot plate (maximum 40 °C) and slowly evaporate almost to dryness. Transfer the remaining last few milliliters of solution quantitatively from the beaker (using at least three aliquots of methylene chloride rinse) to a tared clean dry aluminum dish and evaporate to complete dryness. Remove from heat once solvent is evaporated. Reweigh the dish after a 30-minute equilibrium in the balance room and determine the weight to the nearest 0.1 mg. Conduct a methylene chloride blank run in an identical fashion.

11.2.2 Container No. 2.

11.2.2.1 PM analysis. Note the level of liquid in the container, and confirm on the analysis sheet whether leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Measure the liquid in this container either volumetrically to ± 1 ml or gravimetrically to 1 ± 0.5 g. Transfer the contents to a tared 250 ml beaker and evaporate to dryness at ambient temperature and pressure. Desiccate for 24 hours, and weigh to a constant weight. Report the results to the nearest 0.1 mg.

11.2.2.2 MCEM analysis. Add 25 ml methylene chloride to the beaker and cover with aluminum foil. Sonicate for 3 minutes then allow to stand for 20 minutes; combine with contents of Container No. 2M and pressure filter and evaporate as described for Container 1 in section 11.2.1.2 of this method.

Notes for MCEM Analysis

1. Light finger pressure only is necessary on 24/40 adaptor. A Chemplast adapter #15055-240 has been found satisfactory.

2. Avoid aluminum dishes made with fluted sides, as these may promote solvent "creep," resulting in possible sample loss.

3. If multiple samples are being run, rinse the Buchner fritted funnel twice between samples with 5 ml solvent using pressure filtration. After the second rinse, continue the flow of air until the glass frit is completely dry. Clean the Buchner fritted funnels thoroughly after filtering five or six samples.

11.2.3 Container No. 3. Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance. This step may be conducted in the field.

11.2.4 Container 3W (impinger water).

11.2.4.1 MCEM analysis. Transfer the solution into a 1,000 ml separatory funnel quantitatively with methylene chloride washes. Add enough solvent to total approximately 50 ml, if necessary. Shake the funnel for 1

minute, allow the phases to separate, and drain the solvent layer into a 250 ml beaker. Repeat the extraction twice. Evaporate with low heat (less than 40 °C) until near dryness. Transfer the remaining few milliliters of solvent quantitatively with small solvent washes into a clean, dry, tared aluminum dish and evaporate to dryness. Remove from heat once solvent is evaporated. Reweigh the dish after a 30-minute equilibration in the balance room and determine the weight to the nearest 0.1 mg.

11.2.5 Container 3S (solvent).

11.2.5.1 MCEM analysis. Transfer the mixed solvent to 250 ml beaker(s). Evaporate and weigh following the procedures detailed for container 3W in section 11.2.4 of this method.

11.2.6 Blank containers. Measure the distilled water, acetone, or methylene chloride in each container either volumetrically or gravimetrically. Transfer the "solvent" to a tared 250 ml beaker, and evaporate to dryness at ambient temperature and pressure. (Conduct a solvent blank on the distilled deionized water blank in an identical fashion to that described in section 11.2.4.1 of this method.) Desiccate for 24 hours, and weigh to a constant weight. Report the results to the nearest 0.1 mg.

NOTE: The contents of Containers No. 2, 3W, and 3M as well as the blank containers may be evaporated at temperatures higher than ambient. If evaporation is done at an elevated temperature, the temperature must be below the boiling point of the solvent; also, to prevent "bumping," the evaporation process must be closely supervised, and the contents of the beaker must be swirled occasionally to maintain an even temperature. Use extreme care, as acetone and methylene chloride are highly flammable and have a low flash point.

12.0 Data Analysis and Calculations.

12.1 Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after the final calculation. Other forms of the equations may be used as long as they give equivalent results.

12.2 Nomenclature.

A_n = Cross-sectional area of nozzle, m^3 (ft^3).

B_{ws} = Water vapor in the gas stream, proportion by volume.

C_a = Acetone blank residue concentration, mg/g.

C_s = Concentration of particulate matter in stack gas, dry basis, corrected to standard conditions, g/dscm (g/dscf).

I = Percent of isokinetic sampling.

L_a = Maximum acceptable leakage rate for either a pretest leak check or for a leak check following a component change;

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equal to 0.00057 m³/min (0.02 cfm) or 4 percent of the average sampling rate, whichever is less.

L_i = Individual leakage rate observed during the leak check conducted prior to the "ith" component change (I = 1, 2, 3...n), m³/min (cfm).

L_p = Leakage rate observed during the post-test leak check, m³/min (cfm).

m_a = Mass of residue of acetone after evaporation, mg.

m_n = Total amount of particulate matter collected, mg.

M_w = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).

P_{bar} = Barometric pressure at the sampling site, mm Hg (in Hg).

P_s = Absolute stack gas pressure, mm Hg (in Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

R = Ideal gas constant, 0.06236 [(mm Hg)(m³)/[(°K) (g-mole)] '61' 21.85 [(in. Hg)(ft³)/[(°R)(lb-mole)'61']].

T_m = Absolute average dry gas meter (DGM) temperature (see Figure 5-2 of Method 5, 40 CFR part 60, appendix A), °K (°R).

T_s = Absolute average stack gas temperature (see Figure 5-2 of Method 5, 40 CFR part 60, appendix A), °K (°R).

T_{std} = Standard absolute temperature, 293 °K (528 °R).

V_a = Volume of acetone blank, ml.

V_{aw} = Volume of acetone used in wash, ml.

V_t = Volume of methylene chloride blank, ml.

V_{tw} = Volume of methylene chloride used in wash, ml.

V_{lc} = Total volume liquid collected in impingers and silica gel (see Figure 5-3 of Method 5, 40 CFR part 60, appendix A), ml.

V_m = Volume of gas sample as measured by dry gas meter, dcm (dcf).

$V_{m(std)}$ = Volume of gas sample measured by the dry gas meter, corrected to standard conditions, dscm (dscf).

$V_{w(std)}$ = Volume of water vapor in the gas sample, corrected to standard conditions, scm (scf).

V_s = Stack gas velocity, calculated by Equation 2-9 in Method 2, 40 CFR part 60, appendix A, using data obtained from Method 5, 40 CFR part 60, appendix A, m/sec (ft/sec).

W_a = Weight of residue in acetone wash, mg.

Y = Dry gas meter calibration factor.

ΔH = Average pressure differential across the orifice meter (see Figure 5-2 of Method 5, 40 CFR part 60, appendix A), mm H₂O (in H₂O).

ρ_a = Density of acetone, 785.1 mg/ml (or see label on bottle).

ρ_w = Density of water, 0.9982 g/ml (0.002201 lb/ml).

ρ_t = Density of methylene chloride, 1316.8 mg/ml (or see label on bottle).

θ = Total sampling time, min.

θ_1 = Sampling time interval, from the beginning of a run until the first component change, min.

θ_2 = Sampling time interval, between two successive component changes, beginning with the interval between the first and second changes, min.

θ_p = Sampling time interval, from the final (nth) component change until the end of the sampling run, min.

13.6 = Specific gravity of mercury.

60 = Sec/min.

100 = Conversion to percent.

12.3 Average dry gas meter temperature and average orifice pressure drop. See data sheet (Figure 5-2 of Method 5, 40 CFR part 60, appendix A).

12.4 Dry gas volume. Correct the sample volume measured by the dry gas meter to standard conditions (20 °C, 760 mm Hg or 68 °F, 29.92 in Hg) by using Equation 315-1.

$$V = V_m Y \frac{T_{std} \left(P_{bar} + \frac{\Delta H}{13.6} \right)}{T_m P_{std}} = V = K_1 V_m Y \frac{P_{bar} + \left(\frac{\Delta H}{13.6} \right)}{T_m} \quad \text{Eq. 315-1}$$

Where

K_1 = 0.3858 °K/mm Hg for metric units, = 17.64 °R/in Hg for English units.

NOTE: Equation 315-1 can be used as written unless the leakage rate observed during any of the mandatory leak checks (i.e., the post-test leak check or leak checks conducted prior to component changes) exceeds L_a . If L_p or L_i exceeds L_a , Equation 315-1 must be modified as follows:

(a) Case I. No component changes made during sampling run. In this case, replace V_m in Equation 315-1 with the expression:

$$[V_m - (L_p - L_a) \theta]$$

(b) Case II. One or more component changes made during the sampling run. In this case, replace V_m in Equation 315-1 by the expression:

$$\left[V_m - (L_1 - L_a) \Theta_1 - \sum_{i=2}^n (L_i - L_a) \Theta_i - (L_p - L_a) \Theta_p \right]$$

and substitute only for those leakage rates (L_i or L_p) which exceed L_a. 12.5 Volume of water vapor condensed.

$$V_{w(std)} = V_{lc} \frac{\rho_w RT_{std}}{M_w P_{std}} = K_2 V_{lc} \quad \text{Eq. 315-2}$$

Where
 K₂ = 0.001333 m³/ml for metric units;
 = 0.04706 ft³/ml for English units.

12.6 Moisture content.

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}} \quad \text{Eq. 315-3}$$

NOTE: In saturated or water droplet-laden gas streams, two calculations of the moisture content of the stack gas shall be made, one from the impinger analysis (Equation 315-3), and a second from the assumption of saturated conditions. The lower of the two values of B_{ws} shall be considered correct. The procedure for determining the moisture content based upon assumption of saturated conditions is given in section 4.0 of Method 4, 40 CFR part 60, appendix A. For the purposes of this method, the average stack gas temperature from Figure 5-2 of Method 5, 40 CFR part 60, appendix A may be used to make this determination, provided that the accuracy of the in-stack temperature sensor is ±1 °C (2 °F).

12.7 Acetone blank concentration.

$$C_a = \frac{M_a}{V_a \rho_a} \quad \text{Eq. 315-4}$$

12.8 Acetone wash blank.

$$W_a = C_a V_{aw} \rho_a \quad \text{Eq. 315-5}$$

12.9 Total particulate weight. Determine the total PM catch from the sum of the weights obtained from Containers 1 and 2 less the acetone blank associated with these two containers (see Figure 315-1).

NOTE: Refer to section 8.5.8 of this method to assist in calculation of results involving two or more filter assemblies or two or more sampling trains.

12.10 Particulate concentration.

$$C_s = K_3 m_n / V_{m(std)} \quad \text{Eq. 315-6}$$

where

K = 0.001 g/mg for metric units;
 = 0.0154 gr/mg for English units.

12.11 Conversion factors.

From	To	Multiply by
ft ³	m ³	0.02832
gr	mg	64.80004
gr/ft ³	mg/m ³	2288.4
mg	g	0.001
gr	lb	1.429×10 ⁻⁴

12.12 Isokinetic variation.

12.12.1 Calculation from raw data.

$$I = \frac{100 T_s \left[K_4 V_{lc} + \left(\frac{V_m Y}{T_m} \right) \left(P_{bar} + \frac{\Delta H}{13.6} \right) \right]}{60 \Theta V_s P_s A_n} \quad \text{Eq. 315-7}$$

where
 K₄ = 0.003454 [(mm Hg)(m³)]/[(ml)(°K)] for metric units;

= 0.002669 [(in Hg)(ft³)]/[(ml)(°R)] for English units.

12.12.2 Calculation from intermediate values.

$$I = \frac{T_s V_m(\text{std}) P_{\text{std}} 100}{T_{\text{std}} V_s \Theta A_n P_s 60 (1 - B_{\text{ws}})} = K_5 \frac{T_s V_m(\text{std})}{P_s V_s A_n \Theta (1 - B_{\text{ws}})} \quad \text{Eq. 315-8}$$

where

$K_5 = 4.320$ for metric units;
 $= 0.09450$ for English units.

12.12.3 Acceptable results. If 90 percent $\leq I \leq 110$ percent, the results are acceptable. If the PM or MCEM results are low in comparison to the standard, and ‘I’ is over 110 percent or less than 90 percent, the Administrator may opt to accept the results. Reference 4 in the Bibliography may be used to make acceptability judgments. If ‘I’ is judged to be unacceptable, reject the results, and repeat the test.

12.13 Stack gas velocity and volumetric flow rate. Calculate the average stack gas velocity and volumetric flow rate, if needed, using data obtained in this method and the equations in sections 5.2 and 5.3 of Method 2, 40 CFR part 60, appendix A.

12.14 MCEM results. Determine the MCEM concentration from the results from Containers 1, 2, 2M, 3W, and 3S less the acetone, methylene chloride, and filter blanks value as determined in the following equation:

$$m_{\text{mcecm}} = S m_{\text{total}} - w_a - w_t - f_b$$

13.0 Method Performance. [Reserved]

14.0 Pollution Prevention. [Reserved]

15.0 Waste Management. [Reserved]

16.0 Alternative Procedures.

16.1 Dry gas meter as a calibration standard. A DGM may be used as a calibration standard for volume measurements in place of the wet test meter specified in section 16.1 of this method, provided that it is calibrated initially and recalibrated periodically as follows:

16.1.1 Standard dry gas meter calibration.

16.1.1.1. The DGM to be calibrated and used as a secondary reference meter should be of high quality and have an appropriately sized

capacity, e.g., 3 liters/rev (0.1 ft³/rev). A spirometer (400 liters or more capacity), or equivalent, may be used for this calibration, although a wet test meter is usually more practical. The wet test meter should have a capacity of 30 liters/rev (1 ft³/rev) and be capable of measuring volume to within 1.0 percent; wet test meters should be checked against a spirometer or a liquid displacement meter to ensure the accuracy of the wet test meter. Spirometers or wet test meters of other sizes may be used, provided that the specified accuracies of the procedure are maintained.

16.1.1.2 Set up the components as shown in Figure 5-7 of Method 5, 40 CFR part 60, appendix A. A spirometer, or equivalent, may be used in place of the wet test meter in the system. Run the pump for at least 5 minutes at a flow rate of about 10 liters/min (0.35 cfm) to condition the interior surface of the wet test meter. The pressure drop indicated by the manometer at the inlet side of the DGM should be minimized (no greater than 100 mm H₂O [4 in. H₂O] at a flow rate of 30 liters/min [1 cfm]). This can be accomplished by using large-diameter tubing connections and straight pipe fittings.

16.1.1.3 Collect the data as shown in the example data sheet (see Figure 5-8 of Method 5, 40 CFR part 60, appendix A). Make triplicate runs at each of the flow rates and at no less than five different flow rates. The range of flow rates should be between 10 and 34 liters/min (0.35 and 1.2 cfm) or over the expected operating range.

16.1.1.4 Calculate flow rate, Q, for each run using the wet test meter volume, V_w, and the run time, q. Calculate the DGM coefficient, Y_{ds}, for each run. These calculations are as follows:

$$Q = K_1 \frac{P_{\text{bar}} V_w}{(t_w + t_{\text{std}}) \Theta} \quad \text{Eq. 315-9}$$

$$Y_{\text{ds}} = \frac{V_w (T_{\text{ds}} + T_{\text{std}}) P_{\text{bar}}}{V_{\text{ds}} (T_w + T_{\text{std}}) \left(P_{\text{bar}} + \frac{\Delta p}{13.6} \right)} \quad \text{Eq. 315-10}$$

Where

$K_1 = 0.3858$ for international system of units (SI); 17.64 for English units;

P_{bar} = Barometric pressure, mm Hg (in Hg);

V_w = Wet test meter volume, liter (ft³);

t_w = Average wet test meter temperature, °C (°F);

t_{std} = 273 °C for SI units; 460°F for English units;

θ = Run time, min;

t_{ds} = Average dry gas meter temperature, °C (°F);

V_{ds} = Dry gas meter volume, liter (ft³);

Δp = Dry gas meter inlet differential pressure, mm H₂O (in H₂O).

16.1.1.5 Compare the three Y_{ds} values at each of the flow rates and determine the maximum and minimum values. The difference between the maximum and minimum values at each flow rate should be no greater than 0.030. Extra sets of triplicate runs may be made in order to complete this requirement. In addition, the meter coefficients should be between 0.95 and 1.05. If these specifications cannot be met in three sets of successive triplicate runs, the meter is not suitable as a calibration standard and should not be used as such. If these specifications are met, average the three Y_{ds} values at each flow rate resulting in five average meter coefficients, Y_{ds} .

16.1.1.6 Prepare a curve of meter coefficient, Y_{ds} , versus flow rate, Q , for the DGM. This curve shall be used as a reference when the meter is used to calibrate other DGMs and to determine whether recalibration is required.

16.1.2 Standard dry gas meter recalibration.

16.1.2.1 Recalibrate the standard DGM against a wet test meter or spirometer annually or after every 200 hours of operation, whichever comes first. This requirement is valid provided the standard DGM is kept in a laboratory and, if transported, cared for as any other laboratory instrument. Abuse to the standard meter may cause a change in the calibration and will require more frequent recalibrations.

16.1.2.2 As an alternative to full recalibration, a two-point calibration check may be made. Follow the same procedure and equipment arrangement as for a full recalibration, but run the meter at only two flow rates (suggested rates are 14 and 28 liters/min [0.5 and 1.0 cfm]). Calculate the meter coefficients for these two points, and compare the values with the meter calibration curve. If the two coefficients are within 1.5 percent of the calibration curve values at the same flow rates, the meter need not be recalibrated until the next date for a recalibration check.

6.2 Critical orifices as calibration standards. Critical orifices may be used as calibration standards in place of the wet test meter specified in section 10.3 of this method, provided that they are selected, calibrated, and used as follows:

16.2.1 Selection of critical orifices.

16.2.1.1 The procedure that follows describes the use of hypodermic needles or stainless steel needle tubing that has been found suitable for use as critical orifices. Other materials and critical orifice designs

may be used provided the orifices act as true critical orifices; i.e., a critical vacuum can be obtained, as described in section 7.2.2.2.3 of Method 5, 40 CFR part 60, appendix A. Select five critical orifices that are appropriately sized to cover the range of flow rates between 10 and 34 liters/min or the expected operating range. Two of the critical orifices should bracket the expected operating range. A minimum of three critical orifices will be needed to calibrate a Method 5 DGM; the other two critical orifices can serve as spares and provide better selection for bracketing the range of operating flow rates. The needle sizes and tubing lengths shown in Table 315-1 give the approximate flow rates indicated in the table.

16.2.1.2 These needles can be adapted to a Method 5 type sampling train as follows: Insert a serum bottle stopper, 13 x 20 mm sleeve type, into a 0.5 in Swagelok quick connect. Insert the needle into the stopper as shown in Figure 5-9 of Method 5, 40 CFR part 60, appendix A.

16.2.2 Critical orifice calibration. The procedure described in this section uses the Method 5 meter box configuration with a DGM as described in section 6.1.1.9 of this method to calibrate the critical orifices. Other schemes may be used, subject to the approval of the Administrator.

16.2.2.1 Calibration of meter box. The critical orifices must be calibrated in the same configuration as they will be used; i.e., there should be no connections to the inlet of the orifice.

16.2.2.1.1 Before calibrating the meter box, leak-check the system as follows: Fully open the coarse adjust valve and completely close the bypass valve. Plug the inlet. Then turn on the pump and determine whether there is any leakage. The leakage rate shall be zero; i.e., no detectable movement of the DGM dial shall be seen for 1 minute.

16.2.2.1.2 Check also for leakages in that portion of the sampling train between the pump and the orifice meter. See section 5.6 of Method 5, 40 CFR part 60, appendix A for the procedure; make any corrections, if necessary. If leakage is detected, check for cracked gaskets, loose fittings, worn O-rings, etc. and make the necessary repairs.

16.2.2.1.3 After determining that the meter box is leakless, calibrate the meter box according to the procedure given in section 5.3 of Method 5, 40 CFR part 60, appendix A. Make sure that the wet test meter meets the requirements stated in section 7.1.1.1 of Method 5, 40 CFR part 60, appendix A. Check the water level in the wet test meter. Record the DGM calibration factor, Y .

16.2.2.2 Calibration of critical orifices. Set up the apparatus as shown in Figure 5-10 of Method 5, 40 CFR part 60, appendix A.

16.2.2.2.1 Allow a warm-up time of 15 minutes. This step is important to equilibrate

the temperature conditions through the DGM.

16.2.2.2.2 Leak-check the system as in section 7.2.2.1.1 of Method 5, 40 CFR part 60, appendix A. The leakage rate shall be zero.

16.2.2.2.3 Before calibrating the critical orifice, determine its suitability and the appropriate operating vacuum as follows: turn on the pump, fully open the coarse adjust valve, and adjust the bypass valve to give a vacuum reading corresponding to about half of atmospheric pressure. Observe the meter box orifice manometer reading, DH. Slowly increase the vacuum reading until a stable reading is obtained on the meter box orifice manometer. Record the critical vacuum for each orifice. Orifices that do not reach a critical value shall not be used.

16.2.2.2.4 Obtain the barometric pressure using a barometer as described in section 6.1.2 of this method. Record the barometric pressure, P_{bar} , in mm Hg (in. Hg).

16.2.2.2.5 Conduct duplicate runs at a vacuum of 25 to 50 mm Hg (1 to 2 in. Hg) above the critical vacuum. The runs shall be at least 5 minutes each. The DGM volume readings shall be in increments of complete revolutions of the DGM. As a guideline, the times should not differ by more than 3.0 seconds (this includes allowance for changes in the DGM temperatures) to achieve ± 0.5 percent in K' . Record the information listed in Figure 5-11 of Method 5, 40 CFR part 60, appendix A.

16.2.2.2.6 Calculate K' using Equation 315-11.

$$K' = \frac{K_1 V_m Y \left(P_{\text{bar}} + \frac{\Delta H}{13.6} \right) T_{\text{amb}}^{\frac{1}{2}}}{P_{\text{bar}} T_m \Theta} \quad \text{Eq. 315-11}$$

where

K' = Critical orifice coefficient, $[\text{m}^3(\text{ }^\circ\text{K})^{1/2}]/[(\text{mm Hg})(\text{min})]^{-1} [\text{ft}^3(\text{ }^\circ\text{R})^{1/2}]/[(\text{in. Hg})(\text{min})]^{-1}$

T_{amb} = Absolute ambient temperature, $^\circ\text{K}$ ($^\circ\text{R}$).

16.2.2.2.7 Average the K' values. The individual K' values should not differ by more than ± 0.5 percent from the average.

16.2.3 Using the critical orifices as calibration standards.

16.2.3.1 Record the barometric pressure.

16.2.3.2 Calibrate the metering system according to the procedure outlined in sections 7.2.2.2.1 to 7.2.2.2.5 of Method 5, 40 CFR part 60, appendix A. Record the information listed in Figure 5-12 of Method 5, 40 CFR part 60, appendix A.

16.2.3.3 Calculate the standard volumes of air passed through the DGM and the critical orifices, and calculate the DGM calibration factor, Y , using the equations below:

$V_{\text{m(std)}} = K_1 V_m [P_{\text{bar}} + (\Delta H/13.6)]/T_m$ Eq. 315-12

$V_{\text{cr(std)}} = K' (P_{\text{bar}} \Theta)/T_{\text{amb}}^{1/2}$ Eq. 315-13

$Y = V_{\text{cr(std)}}/V_{\text{m(std)}}$ Eq. 315-14

where

$V_{\text{cr(std)}}$ = Volume of gas sample passed through the critical orifice, corrected to standard conditions, dscm (dscf).

$K' = 0.3858$ $^\circ\text{K}/\text{mm Hg}$ for metric units
 $= 17.64$ $^\circ\text{R}/\text{in Hg}$ for English units.

16.2.3.4 Average the DGM calibration values for each of the flow rates. The calibration factor, Y , at each of the flow rates should not differ by more than ± 2 percent from the average.

16.2.3.5 To determine the need for recalibrating the critical orifices, compare the DGM Y factors obtained from two adjacent orifices each time a DGM is calibrated; for example, when checking orifice 13/2.5, use orifices 12/10.2 and 13/5.1. If any critical orifice yields a DGM Y factor differing by more than 2 percent from the others, recalibrate the critical orifice according to section 7.2.2.2 of Method 5, 40 CFR part 60, appendix A.

17.0 References.

1. Addendum to Specifications for Incinerator Testing at Federal Facilities. PHS, NCAPC, December 6, 1967.
2. Martin, Robert M. Construction Details of Isokinetic Source-Sampling Equipment. Environmental Protection Agency, Research Triangle Park, NC. APTD-0581. April 1971.
3. Rom, Jerome J. Maintenance, Calibration, and Operation of Isokinetic Source Sampling Equipment. Environmental Protection Agency, Research Triangle Park, NC. APTD-0576. March 1972.
4. Smith, W.S., R.T. Shigehara, and W.F. Todd. A Method of Interpreting Stack Sampling Data. Paper Presented at the 63rd Annual Meeting of the Air Pollution Control Association, St. Louis, MO. June 14-19, 1970.
5. Smith, W.S., et al. Stack Gas Sampling Improved and Simplified With New Equipment. APCA Paper No. 67-119. 1967.
6. Specifications for Incinerator Testing at Federal Facilities. PHS, NCAPC. 1967.
7. Shigehara, R.T. Adjustment in the EPA Nomograph for Different Pitot Tube Coefficients and Dry Molecular Weights. Stack Sampling News 2:4-11. October 1974.

8. Vollaro, R.F. A Survey of Commercially Available Instrumentation for the Measurement of Low-Range Gas Velocities. U.S. Environmental Protection Agency, Emission Measurement Branch. Research Triangle Park, NC. November 1976 (unpublished paper).

9. Annual Book of ASTM Standards. Part 26. Gaseous Fuels; Coal and Coke; Atmospheric Analysis. American Society for Testing and Materials. Philadelphia, PA. 1974. pp. 617-622.

10. Felix, L.G., G.I. Clinard, G.E. Lacy, and J.D. McCain. Inertial Cascade Impactor Substrate Media for Flue Gas Sampling. U.S. En-

vironmental Protection Agency. Research Triangle Park, NC 27711. Publication No. EPA-600/7-77-060. June 1977. 83 p.

11. Westlin, P.R., and R.T. Shigehara. Procedure for Calibrating and Using Dry Gas Volume Meters as Calibration Standards. Source Evaluation Society Newsletter. 3(1):17-30. February 1978.

12. Lodge, J.P., Jr., J.B. Pate, B.E. Ammons, and G.A. Swanson. The Use of Hypodermic Needles as Critical Orifices in Air Sampling. J. Air Pollution Control Association. 16:197-200. 1966.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

TABLE 315-1. FLOW RATES FOR VARIOUS NEEDLE SIZES AND TUBE LENGTHS.

Gauge/length (cm)	Flow rate (liters/min)	Gauge/length (cm)	Flow rate (liters/min)
12/7.6	32.56	14/2.5	19.54
12/10.2	30.02	14/5.1	17.27
13/2.5	25.77	14/7.6	16.14
13/5.1	23.50	15/3.2	14.16
13/7.6	22.37	15/7.6	11.61
13/10.2	20.67	115/10.2	10.48

FIGURE 315-1. PARTICULATE AND MCEM ANALYSES

Particulate Analysis					
Plant					
Date					
Run No.					
Filter No.					
Amount liquid lost during transport					
Acetone blank volume (ml)					
Acetone blank concentration (Eq. 315-4) (mg/mg)					
Acetone wash blank (Eq. 315-5) (mg)					
		Final weight (mg)	Tare weight (mg)	Weight gain (mg)	
Container No. 1					
Container No. 2					
Total					
Less Acetone blank					
Weight of particulate matter					
		Final volume (mg)	Initial volume (mg)	Liquid collected (mg)	
Moisture Analysis					
Impingers	Note 1	Note 1			
Silica gel					
Total					
Note 1: Convert volume of water to weight by multiplying by the density of water (1 g/ml).					
Container No.	Final weight (mg)	Tare of aluminum dish (mg)	Weight gain	Acetone wash volume (ml)	Methylene chloride wash volume (ml)
MCEM Analysis					
1					

Container No.	Final weight (mg)	Tare of aluminum dish (mg)	Weight gain	Acetone wash volume (ml)	Methylene chloride wash volume (ml)
2+2M					
3W					
3S					
Total			$\sum m_{total}$	$\sum V_{aw}$	$\sum V_{tw}$
Less acetone wash blank (mg) (not to exceed 1 mg/l of acetone used).			$w_a = c_a \rho_a \sum V_{aw}$		
Less methylene chloride wash blank (mg) (not to exceed 1.5 mg/l of methylene chloride used).			$w_t = c_t \rho_t \sum V_{tw}$		
Less filter blank (mg) (not to exceed . . . (mg/filter)			f_b		
MCEM weight (mg)			$m_{MCEOM} = \sum m_{total} - w_a - w_t - f_b$		

METHOD 316—SAMPLING AND ANALYSIS FOR FORMALDEHYDE EMISSIONS FROM STATIONARY SOURCES IN THE MINERAL WOOL AND WOOL FIBERGLASS INDUSTRIES

1.0 Introduction

This method is applicable to the determination of formaldehyde, CAS Registry number 50-00-0, from stationary sources in the mineral wool and wool fiber glass industries. High purity water is used to collect the formaldehyde. The formaldehyde concentrations in the stack samples are determined using the modified pararosaniline method. Formaldehyde can be detected as low as 8.8×10^{10} lbs/cu ft (11.3 ppbv) or as high as 1.8×10^3 lbs/cu ft (23,000,000 ppbv), at standard conditions over a 1 hour sampling period, sampling approximately 30 cu ft.

2.0 Summary of Method

Gaseous and particulate pollutants are withdrawn isokinetically from an emission source and are collected in high purity water. Formaldehyde present in the emissions is highly soluble in high purity water. The high purity water containing formalde-

hyde is then analyzed using the modified pararosaniline method. Formaldehyde in the sample reacts with acidic pararosaniline, and the sodium sulfite, forming a purple chromophore. The intensity of the purple color, measured spectrophotometrically, provides an accurate and precise measure of the formaldehyde concentration in the sample.

3.0 Definitions

See the definitions in the General Provisions of this Subpart.

4.0 Interferences

Sulfite and cyanide in solution interfere with the pararosaniline method. A procedure to overcome the interference by each compound has been described by Miksch, et al.

5.0 Safety. (Reserved)

6.0 Apparatus and Materials

6.1 A schematic of the sampling train is shown in Figure 1. This sampling train configuration is adapted from EPA Method 5, 40 CFR part 60, appendix A, procedures.

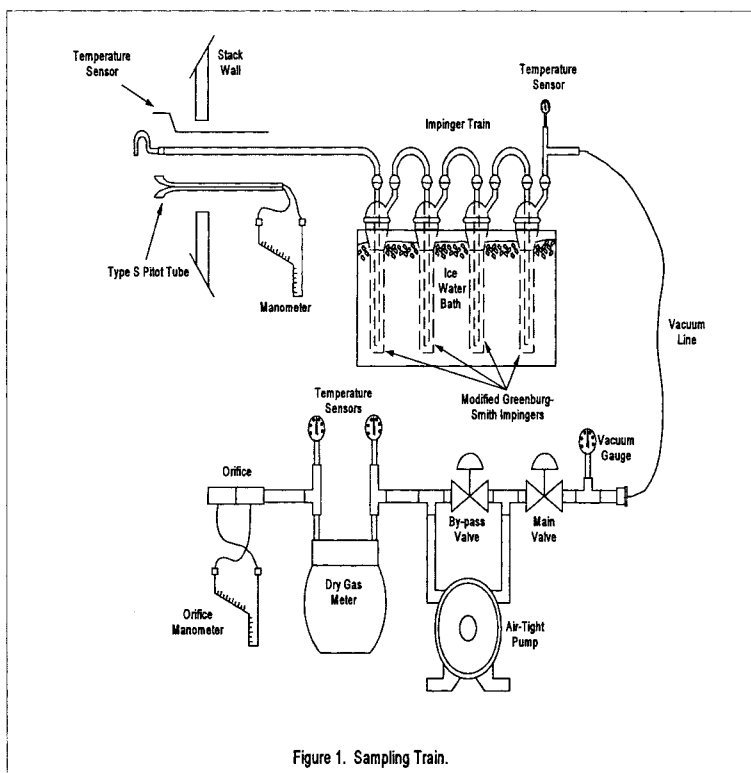


Figure 1. Sampling Train.

The sampling train consists of the following components: probe nozzle, probe liner, pitot tube, differential pressure gauge, impingers, metering system, barometer, and gas density determination equipment.

6.1.1 Probe Nozzle: Quartz, glass, or stainless steel with sharp, tapered (30° angle) leading edge. The taper shall be on the outside to preserve a constant inner diameter. The nozzle shall be buttonhook or elbow design. A range of nozzle sizes suitable for isokinetic sampling should be available in increments of 0.15 cm (1/16 in), e.g., 0.32 to 1.27 cm (1/8 to 1/2 in), or larger if higher volume sampling trains are used. Each nozzle shall be calibrated according to the procedure outlined in Section 10.1.

6.1.2 Probe Liner: Borosilicate glass or quartz shall be used for the probe liner. The probe shall be maintained at a temperature of 120 °C ± 14 °C (248 °F ± 25 °F).

6.1.3 Pitot Tube: The pitot tube shall be Type S, as described in Section 2.1 of EPA Method 2, 40 CFR part 60, appendix A, or any other appropriate device. The pitot tube

shall be attached to the probe to allow constant monitoring of the stack gas velocity. The impact (high pressure) opening plane of the pitot tube shall be even with or above the nozzle entry plane (see Figure 2-6b, EPA Method 2, 40 CFR part 60, appendix A) during sampling. The Type S pitot tube assembly shall have a known coefficient, determined as outlined in Section 4 of EPA Method 2, 40 CFR part 60, appendix A.

6.1.4 Differential Pressure Gauge: The differential pressure gauge shall be an inclined manometer or equivalent device as described in Section 2.2 of EPA Method 2, 40 CFR part 60, appendix A. One manometer shall be used for velocity-head reading and the other for orifice differential pressure readings.

6.1.5 Impingers: The sampling train requires a minimum of four impingers, connected as shown in Figure 1, with ground glass (or equivalent) vacuum-tight fittings. For the first, third, and fourth impingers, use the Greenburg-Smith design, modified by replacing the tip with a 1.3 cm inside diameter (1/2 in) glass tube extending to 1.3 cm (1/2

in) from the bottom of the flask. For the second impinger, use a Greenburg-Smith impinger with the standard tip. Place a thermometer capable of measuring temperature to within 1 °C (2 °F) at the outlet of the fourth impinger for monitoring purposes.

6.1.6 Metering System: The necessary components are a vacuum gauge, leak-free pump, thermometers capable of measuring temperatures within 3 °C (5.4 °F), dry-gas meter capable of measuring volume to within 1 percent, and related equipment as shown in Figure 1. At a minimum, the pump should be capable of 4 cfm free flow, and the dry gas meter should have a recording capacity of 0–999.9 cu ft with a resolution of 0.005 cu ft. Other metering systems may be used which are capable of maintaining sample volumes to within 2 percent. The metering system may be used in conjunction with a pitot tube to enable checks of isokinetic sampling rates.

6.1.7 Barometer: The barometer may be mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in Hg). In many cases, the barometric reading may be obtained from a nearby National Weather Service Station, in which case the station value (which is the absolute barometric pressure) is requested and an adjustment for elevation differences between the weather station and sampling point is applied at a rate of minus 2.5 mm Hg (0.1 in Hg) per 30 m (100 ft) elevation increase (rate is plus 2.5 mm Hg per 30 m (100 ft) of elevation decrease).

6.1.8 Gas Density Determination Equipment: Temperature sensor and pressure gauge (as described in Sections 2.3 and 2.3 of EPA Method 2, 40 CFR part 60, appendix A), and gas analyzer, if necessary (as described in EPA Method 3, 40 CFR part 60, appendix A). The temperature sensor ideally should be permanently attached to the pitot tube or sampling probe in a fixed configuration such that the top of the sensor extends beyond the leading edge of the probe sheath and does not touch any metal. Alternatively, the sensor may be attached just prior to use in the field. Note, however, that if the temperature sensor is attached in the field, the sensor must be placed in an interference-free arrangement with respect to the Type S pitot openings (see Figure 2-7, EPA Method 2, 40 CFR part 60, appendix A). As a second alternative, if a difference of no more than 1 percent in the average velocity measurement is to be introduced, the temperature gauge need not be attached to the probe or pitot tube.

6.2 Sample Recovery

6.2.1 Probe Liner: Probe nozzle and brushes; bristle brushes with stainless steel wire handles are required. The probe brush shall have extensions of stainless steel, Teflon™, or inert material at least as long as the

probe. The brushes shall be properly sized and shaped to brush out the probe liner, the probe nozzle, and the impingers.

6.2.2 Wash Bottles: One wash bottle is required. Polyethylene, Teflon™, or glass wash bottles may be used for sample recovery.

6.2.3 Graduated Cylinder and/or Balance: A graduated cylinder or balance is required to measure condensed water to the nearest 1 ml or 1 g. Graduated cylinders shall have division not >2 ml. Laboratory balances capable of weighing to ± 0.5 g are required.

6.2.4 Polyethylene Storage Containers: 500 ml wide-mouth polyethylene bottles are required to store impinger water samples.

6.2.5 Rubber Policeman and Funnel: A rubber policeman and funnel are required to aid the transfer of material into and out of containers in the field.

6.3 Sample Analysis

6.3.1 Spectrophotometer—B&L 70, 710, 2000, etc., or equivalent; 1 cm pathlength cuvette holder.

6.3.2 Disposable polystyrene cuvettes, pathlength 1 cm, volume of about 4.5 ml.

6.3.3 Pipettors—Fixed-volume Oxford pipet (250 µl; 500 µl; 1000 µl); adjustable volume Oxford or equivalent pipettor 1–5 ml model, set to 2.50 ml.

6.3.4 Pipet tips for pipettors above.

6.3.5 Parafilm, 2 ° wide; cut into about 1" squares.

7.0 Reagents

7.1 High purity water: All references to water in this method refer to high purity water (ASTM Type I water or equivalent). The water purity will dictate the lower limits of formaldehyde quantification.

7.2 Silica Gel: Silica gel shall be indicting type, 6–16 mesh. If the silica gel has been used previously, dry at 175 °C (350 °F) for 2 hours before using. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used.

7.3 Crushed Ice: Quantities ranging from 10–50 lbs may be necessary during a sampling run, depending upon ambient temperature. Samples which have been taken must be stored and shipped cold; sufficient ice for this purpose must be allowed.

7.4 Quaternary ammonium compound stock solution: Prepare a stock solution of dodecyltrimethylammonium chloride (98 percent minimum assay, reagent grade) by dissolving 1.0 gram in 1000 ml water. This solution contains nominally 1000 µg/ml quaternary ammonium compound, and is used as a biocide for some sources which are prone to microbial contamination.

7.5 Pararosaniline: Weigh 0.16 grams pararosaniline (free base; assay of 95 percent or greater, C.I. 42500; Sigma P7632 has been

found to be acceptable) into a 100 ml flask. Exercise care, since pararosaniline is a dye and will stain. Using a wash bottle with high-purity water, rinse the walls of the flask. Add no more than 25 ml water. Then, carefully add 20 ml of concentrated hydrochloric acid to the flask. The flask will become warm after the addition of acid. Add a magnetic stir bar to the flask, cap, and place on a magnetic stirrer for approximately 4 hours. Then, add additional water so the total volume is 100 ml. This solution is stable for several months when stored tightly capped at room temperature.

7.6 Sodium sulfite: Weigh 0.10 grams anhydrous sodium sulfite into a 100 ml flask. Dilute to the mark with high purity water. Invert 15-20 times to mix and dissolve the sodium sulfite. This solution must be prepared fresh every day.

7.7 Formaldehyde standard solution: Pipet exactly 2.70 ml of 37 percent formaldehyde solution into a 1000 ml volumetric flask which contains about 500 ml of high-purity water. Dilute to the mark with high-purity water. This solution contains nominally 1000 µg/ml of formaldehyde, and is used to prepare the working formaldehyde standards. The exact formaldehyde concentration may be determined if needed by suitable modification of the sodium sulfite method (Reference: J.F. Walker, Formaldehyde (Third Edition), 1964.). The 1000 µg/ml formaldehyde stock solution is stable for at least a year if kept tightly closed, with the neck of the flask sealed with Parafilm. Store at room temperature.

7.8 Working formaldehyde standards: Pipet exactly 10.0 ml of the 1000 µg/ml formaldehyde stock solution into a 100 ml volumetric flask which is about half full of high-purity water. Dilute to the mark with high-purity water, and invert 15-20 times to mix thoroughly. This solution contains nominally 100 µg/ml formaldehyde. Prepare the working standards from this 100 µg/ml standard solution and using the Oxford pipets:

Working standard, µ/mL	µL or 100 µg/mL solution	Volumetric flask volume (dilute to mark with water)
0.250	250	100
0.500	500	100
1.00	1000	100
2.00	2000	100
3.00	1500	50

The 100 µg/ml stock solution is stable for 4 weeks if kept refrigerated between analyses. The working standards (0.25-3.00 µg/ml) should be prepared fresh every day, consistent with good laboratory practice for trace analysis. If the laboratory water is not of sufficient purity, it may be necessary to prepare the working standards every day. The laboratory must establish that the

working standards are stable—DO NOT assume that your working standards are stable for more than a day unless you have verified this by actual testing for several series of working standards.

8.0 Sample Collection

8.1 Because of the complexity of this method, field personnel should be trained in and experienced with the test procedures in order to obtain reliable results.

8.2 Laboratory Preparation

8.2.1 All the components shall be maintained and calibrated according to the procedure described in APTD-0576, unless otherwise specified.

8.2.2 Weigh several 200 to 300 g portions of silica gel in airtight containers to the nearest 0.5 g. Record on each container the total weight of the silica gel plus containers. As an alternative to preweighing the silica gel, it may instead be weighed directly in the impinger or sampling holder just prior to train assembly.

8.3 Preliminary Field Determinations

8.3.1 Select the sampling site and the minimum number of sampling points according to EPA Method 1, 40 CFR part 60, appendix A, or other relevant criteria. Determine the stack pressure, temperature, and range of velocity heads using EPA Method 2, 40 CFR part 60, appendix A. A leak-check of the pitot lines according to Section 3.1 of EPA Method 2, 40 CFR part 60, appendix A, must be performed. Determine the stack gas moisture content using EPA Approximation Method 4, 40 CFR part 60, appendix A, or its alternatives to establish estimates of isokinetic sampling rate settings. Determine the stack gas dry molecular weight, as described in EPA Method 2, 40 CFR part 60, appendix A, Section 3.6. If integrated EPA Method 3, 40 CFR part 60, appendix A, sampling is used for molecular weight determination, the integrated bag sample shall be taken simultaneously with, and for the same total length of time as, the sample run.

8.3.2 Select a nozzle size based on the range of velocity heads so that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates below 28 l/min (1.0 cfm). During the run do not change the nozzle. Ensure that the proper differential pressure gauge is chosen for the range of velocity heads encountered (see Section 2.2 of EPA Method 2, 40 CFR part 60, appendix A).

8.3.3 Select a suitable probe liner and probe length so that all traverse points can be sampled. For large stacks, to reduce the length of the probe, consider sampling from opposite sides of the stack.

8.3.4 A minimum of 30 cu ft of sample volume is suggested for emission sources with

stack concentrations not greater than 23,000,000 ppbv. Additional sample volume shall be collected as necessitated by the capacity of the water reagent and analytical detection limit constraint. Reduced sample volume may be collected as long as the final concentration of formaldehyde in the stack sample is greater than 10 (ten) times the detection limit.

8.3.5 Determine the total length of sampling time needed to obtain the identified minimum volume by comparing the anticipated average sampling rate with the volume requirement. Allocate the same time to all traverse points defined by EPA Method 1, 40 CFR part 60, appendix A. To avoid timekeeping errors, the length of time sampled at each traverse point should be an integer or an integer plus 0.5 min.

8.3.6 In some circumstances (e.g., batch cycles) it may be necessary to sample for shorter times at the traverse points and to obtain smaller gas-volume samples. In these cases, careful documentation must be maintained in order to allow accurate calculations of concentrations.

8.4 Preparation of Collection Train

8.4.1 During preparation and assembly of the sampling train, keep all openings where contamination can occur covered with Teflon™ film or aluminum foil until just prior to assembly or until sampling is about to begin.

8.4.2 Place 100 ml of water in each of the first two impingers, and leave the third impinger empty. If additional capacity is required for high expected concentrations of formaldehyde in the stack gas, 200 ml of water per impinger may be used or additional impingers may be used for sampling. Transfer approximately 200 to 300 g of pre-weighed silica gel from its container to the fourth impinger. Care should be taken to ensure that the silica gel is not entrained and carried out from the impinger during sampling. Place the silica gel container in a clean place for later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest 0.5 g and recorded.

8.4.3 With a glass or quartz liner, install the selected nozzle using a Viton-A O-ring when stack temperatures are <260 °C (500 °F) and a woven glass-fiber gasket when temperatures are higher. See APTD-0576 for details. Other connection systems utilizing either 316 stainless steel or Teflon™ ferrules may be used. Mark the probe with heat-resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.

8.4.4 Assemble the train as shown in Figure 1. During assembly, a very light coating of silicone grease may be used on ground-glass joints of the impingers, but the silicone grease should be limited to the outer portion

(see APTD-0576) of the ground-glass joints to minimize silicone grease contamination. If necessary, Teflon™ tape may be used to seal leaks. Connect all temperature sensors to an appropriate potentiometer/display unit. Check all temperature sensors at ambient temperatures.

8.4.5 Place crushed ice all around the impingers.

8.4.6 Turn on and set the probe heating system at the desired operating temperature. Allow time for the temperature to stabilize.

8.5 Leak-Check Procedures

8.5.1 Pre-test Leak-check: Recommended, but not required. If the tester elects to conduct the pre-test leak-check, the following procedure shall be used.

8.5.1.1 After the sampling train has been assembled, turn on and set probe heating system at the desired operating temperature. Allow time for the temperature to stabilize. If a Viton-a O-ring or other leak-free connection is used in assembling the probe nozzle to the probe liner, leak-check the train at the sampling site by plugging the nozzle and pulling a 381 mm Hg (15 in Hg) vacuum.

NOTE: A lower vacuum may be used, provided that the lower vacuum is not exceeded during the test.

If a woven glass fiber gasket is used, do not connect the probe to the train during the leak-check. Instead, leak-check the train by first attaching a carbon-filled leak-check impinger to the inlet and then plugging the inlet and pulling a 381 mm Hg (15 in Hg) vacuum. (A lower vacuum may be used if this lower vacuum is not exceeded during the test.) Next connect the probe to the train and leak-check at about 25 mm Hg (1 in Hg) vacuum. Alternatively, leak-check the probe with the rest of the sampling train in one step at 381 mm Hg (15 in Hg) vacuum. Leakage rates in excess of (a) 4 percent of the average sampling rate or (b) 0.00057 m³/min (0.02 cfm), whichever is less, are unacceptable.

8.5.1.2 The following leak-check instructions for the sampling train described in APTD-0576 and APTD-0581 may be helpful. Start the pump with the fine-adjust valve fully open and coarse-valve completely closed. Partially open the coarse-adjust valve and slowly close the fine-adjust valve until the desired vacuum is reached. Do not reverse direction of the fine-adjust valve, as liquid will back up into the train. If the desired vacuum is exceeded, either perform the leak-check at this higher vacuum or end the leak-check, as described below, and start over.

8.5.1.3 When the leak-check is completed, first slowly remove the plug from the inlet to the probe. When the vacuum drops to 127 mm (5 in) Hg or less, immediately close the coarse-adjust valve. Switch off the pumping system and reopen the fine-adjust valve. Do

not reopen the fine-adjust valve until the coarse-adjust valve has been closed to prevent the liquid in the impingers from being forced backward in the sampling line and silica gel from being entrained backward into the third impinger.

8.5.2 Leak-checks During Sampling Run:

8.5.2.1 If, during the sampling run, a component change (e.g., impinger) becomes necessary, a leak-check shall be conducted immediately after the interruption of sampling and before the change is made. The leak-check shall be done according to the procedure described in Section 10.3.3, except that it shall be done at a vacuum greater than or equal to the maximum value recorded up to that point in the test. If the leakage rate is found to be no greater than 0.0057 m³/min (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable. If a higher leakage rate is obtained, the tester must void the sampling run.

NOTE: Any correction of the sample volume by calculation reduces the integrity of the pollutant concentration data generated and must be avoided.

8.5.2.2 Immediately after component changes, leak-checks are optional. If performed, the procedure described in section 8.5.1.1 shall be used.

8.5.3 Post-test Leak-check:

8.5.3.1 A leak-check is mandatory at the conclusion of each sampling run. The leak-check shall be done with the same procedure

as the pre-test leak-check, except that the post-test leak-check shall be conducted at a vacuum greater than or equal to the maximum value reached during the sampling run. If the leakage rate is found to be no greater than 0.0057 m³/min (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable. If, however, a higher leakage rate is obtained, the tester shall record the leakage rate and void the sampling run.

8.6 Sampling Train Operation

8.6.1 During the sampling run, maintain an isokinetic sampling rate to within 10 percent of true isokinetic, below 28 l/min (1.0 cfm). Maintain a temperature around the probe of 120 °C ± 14 °C (248 ° ± 25 °F).

8.6.2 For each run, record the data on a data sheet such as the one shown in Figure 2. Be sure to record the initial dry-gas meter reading. Record the dry-gas meter readings at the beginning and end of each sampling time increment, when changes in flow rates are made, before and after each leak-check, and when sampling is halted. Take other readings required by Figure 2 at least once at each sample point during each time increment and additional readings when significant adjustments (20 percent variation in velocity head readings) necessitate additional adjustments in flow rate. Level and zero the manometer. Because the manometer level and zero may drift due to vibrations and temperature changes, make periodic checks during the traverse.

Figure 2 - Formaldehyde Field Data

Plant	Ambient temperature
Location	Barometric pressure
Operator	Assumed moisture, percent
Date	Probe length, m (ft)
Run No	Nozzle Identification No
Sample box No	Average calibrated nozzle diameter, cm (in.)
Meter box No	Probe heater setting
Meter ΔH	Leak rate, m ³ /min (cfm)
C Factor	Probe liner material
Pitot tube coefficient, Op	Static pressure, mm Hg (in. Hg)
	Filter No.

SCHEMATIC OF STACK CROSS SECTION

Traverse point number	Sampling time (e) min.	Vacuum mm Hg (in. Hg)	Stack temperature (T) °C (°F)	Velocity head (ΔP) mm (in) H ₂ O	Pressure differential across orifice meter mm H ₂ O (in. H ₂ O)	Gas sample volume m ³ (ft. ³)	Gas sample temperature at dry gas meter		Filter holder temperature °C (°F)	Temperature of gas leaving condenser or last impinger °C (°F)
							Inlet °C (°F)	Outlet °C (°F)		

Total	Avg.	Avg.
Average	Avg.

8.6.3 Clean the stack access ports prior to the test run to eliminate the chance of sampling deposited material. To begin sampling, remove the nozzle cap, verify that the probe heating system are at the specified temperature, and verify that the pitot tube and probe are properly positioned. Position the nozzle at the first traverse point, with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions. Nomographs, which aid in the rapid adjustment of the isokinetic sampling rate without excessive computations, are available. These nomographs are designed for use when the Type S pitot tube coefficient is 0.84 ± 0.02 and the stack gas equivalent density (dry molecular weight) is equal to 29 ± 4 . APTD-0576 details the procedure for using the nomographs. If the stack gas molecular weight and the pitot tube coefficient are outside the above ranges, do not use the nomographs unless appropriate steps are taken to compensate for the deviations.

8.6.4 When the stack is under significant negative pressure (equivalent to the height of the impinger stem), take care to close the coarse-adjust valve before inserting the probe into the stack in order to prevent liquid from backing up through the train. If necessary, a low vacuum on the train may have to be started prior to entering the stack.

8.6.5 When the probe is in position, block off the openings around the probe and stack access port to prevent unrepresentative dilution of the gas stream.

8.6.6 Traverse the stack cross section, as required by EPA Method 1, 40 CFR part 60, appendix A, being careful not to bump the probe nozzle into the stack walls when sampling near the walls or when removing or inserting the probe through the access port, in order to minimize the chance of extracting deposited material.

8.6.7 During the test run, make periodic adjustments to keep the temperature around the probe at the proper levels. Add more ice and, if necessary, salt, to maintain a temperature of <20 °C (68 °F) at the silica gel outlet.

8.6.8 A single train shall be used for the entire sampling run, except in cases where simultaneous sampling is required in two or more separate ducts or at two or more different locations within the same duct, or in cases where equipment failure necessitates a change of trains. An additional train or trains may also be used for sampling when the capacity of a single train is exceeded.

8.6.9 When two or more trains are used, separate analyses of components from each train shall be performed. If multiple trains have been used because the capacity of a single train would be exceeded, first impingers from each train may be combined, and second impingers from each train may be combined.

8.6.10 At the end of the sampling run, turn off the coarse-adjust valve, remove the probe and nozzle from the stack, turn off the pump, record the final dry gas meter reading, and conduct a post-test leak-check. Also, check the pitot lines as described in EPA Method 2, 40 CFR part 60, appendix A. The lines must pass this leak-check in order to validate the velocity-head data.

8.6.11 Calculate percent isokineticity (see Method 2) to determine whether the run was valid or another test should be made.

8.7 Sample Preservation and Handling

8.7.1 Samples from most sources applicable to this method have acceptable holding times using normal handling practices (shipping samples iced, storing in refrigerator at 2 °C until analysis). However, forming section stacks and other sources using waste water sprays may be subject to microbial contamination. For these sources, a biocide (quaternary ammonium compound solution) may be added to collected samples to improve sample stability and method ruggedness.

8.7.2 Sample holding time: Samples should be analyzed within 14 days of collection. Samples must be refrigerated/kept cold for the entire period preceding analysis. After the samples have been brought to room temperature for analysis, any analyses needed should be performed on the same day. Repeated cycles of warming the samples to room temperature/refrigerating/rewarming, then analyzing again, etc., have not been investigated in depth to evaluate if analyte levels remain stable for all sources.

8.7.3 Additional studies will be performed to evaluate whether longer sample holding times are feasible for this method.

8.8 Sample Recovery

8.8.1 Preparation:

8.8.1.1 Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool. When the probe can be handled safely, wipe off all external particulate matter near the tip of the probe nozzle and place a cap over the tip to prevent losing or gaining particulate matter. Do not cap the probe tightly while the sampling train is cooling because a vacuum will be created, drawing liquid from the impingers back through the sampling train.

8.8.1.2 Before moving the sampling train to the cleanup site, remove the probe from the sampling train and cap the open outlet, being careful not to lose any condensate that might be present. Remove the umbilical cord from the last impinger and cap the impinger. If a flexible line is used, let any condensed water or liquid drain into the impingers. Cap off any open impinger inlets and outlets. Ground glass stoppers, Teflon™ caps, or

caps of other inert materials may be used to seal all openings.

8.8.1.3 Transfer the probe and impinger assembly to an area that is clean and protected from wind so that the chances of contaminating or losing the sample are minimized.

8.8.1.4 Inspect the train before and during disassembly, and note any abnormal conditions.

8.8.1.5 Save a portion of the washing solution (high purity water) used for cleanup as a blank.

8.8.2 Sample Containers:

8.8.2.1 Container 1: Probe and Impinger Catches. Using a graduated cylinder, measure to the nearest ml, and record the volume of the solution in the first three impingers. Alternatively, the solution may be weighed to the nearest 0.5 g. Include any condensate in the probe in this determination. Transfer the combined impinger solution from the graduated cylinder into the polyethylene bottle. Taking care that dust on the outside of the probe or other exterior surfaces does not get into the sample, clean all surfaces to which the sample is exposed (including the probe nozzle, probe fitting, probe liner, first three impingers, and impinger connectors) with water. Use less than 400 ml for the entire waste (250 ml would be better, if possible). Add the rinse water to the sample container.

8.8.2.1.1 Carefully remove the probe nozzle and rinse the inside surface with water from a wash bottle. Brush with a bristle brush and rinse until the rinse shows no visible particles, after which make a final rinse of the inside surface. Brush and rinse the inside parts of the Swagelok (or equivalent) fitting with water in a similar way.

8.8.2.1.2 Rinse the probe liner with water. While squirting the water into the upper end of the probe, tilt and rotate the probe so that all inside surfaces will be wetted with water. Let the water drain from the lower end into the sample container. The tester may use a funnel (glass or polyethylene) to aid in transferring the liquid washes to the container. Follow the rinse with a bristle brush. Hold the probe in an inclined position, and squirt water into the upper end as the probe brush is being pushed with a twisting action through the probe. Hold the sample container underneath the lower end of the probe, and catch any water and particulate matter that is brushed from the probe. Run the brush through the probe three times or more. Rinse the brush with water and quantitatively collect these washings in the sample container. After the brushing, make a final rinse of the probe as describe above.

NOTE: Two people should clean the probe in order to minimize sample losses. Between sampling runs, brushes must be kept clean and free from contamination.

8.8.2.1.3 Rinse the inside surface of each of the first three impingers (and connecting tubing) three separate times. Use a small portion of water for each rinse, and brush each surface to which the sample is exposed with a bristle brush to ensure recovery of fine particulate matter. Make a final rinse of each surface and of the brush, using water.

8.8.2.1.4 After all water washing and particulate matter have been collected in the sample container, tighten the lid so the sample will not leak out when the container is shipped to the laboratory. Mark the height of the fluid level to determine whether leakage occurs during transport. Label the container clearly to identify its contents.

8.8.2.1.5 If the first two impingers are to be analyzed separately to check for breakthrough, separate the contents and rinses of the two impingers into individual containers. Care must be taken to avoid physical carryover from the first impinger to the second. Any physical carryover of collected moisture into the second impinger will invalidate a breakthrough assessment.

8.8.2.2 Container 2: Sample Blank. Prepare a blank by using a polyethylene container and adding a volume of water equal to the total volume in Container 1. Process the blank in the same manner as Container 1.

8.8.2.3 Container 3: Silica Gel. Note the color of the indicating silica gel to determine whether it has been completely spent and make a notation of its condition. The impinger containing the silica gel may be used as a sample transport container with both ends sealed with tightly fitting caps or plugs. Ground-glass stoppers or Teflon™ caps maybe used. The silica gel impinger should then be labeled, covered with aluminum foil, and packaged on ice for transport to the laboratory. If the silica gel is removed from the impinger, the tester may use a funnel to pour the silica gel and a rubber policeman to remove the silica gel from the impinger. It is not necessary to remove the small amount of dust particles that may adhere to the impinger wall and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use water or other liquids to transfer the silica gel. If a balance is available in the field, the spent silica gel (or silica gel plus impinger) may be weighed to the nearest 0.5 g.

8.8.2.4 Sample containers should be placed in a cooler, cooled by (although not in contact with) ice. Putting sample bottles in Zip-Lock™ bags can aid in maintaining the integrity of the sample labels. Sample containers should be placed vertically to avoid leakage during shipment. Samples should be cooled during shipment so they will be received cold at the laboratory. It is critical that samples be chilled immediately after recovery. If the source is susceptible to microbial contamination from wash water (e.g.

forming section stack), add biocide as directed in section 8.2.5.

8.8.2.5 A quaternary ammonium compound can be used as a biocide to stabilize samples against microbial degradation following collection. Using the stock quaternary ammonium compound (QAC) solution; add 2.5 ml QAC solution for every 100 ml of recovered sample volume (estimate of volume is satisfactory) immediately after collection. The total volume of QAC solution must be accurately known and recorded, to correct for any dilution caused by the QAC solution addition.

8.8.3 Sample Preparation for Analysis
8.8.3.1 The sample should be refrigerated if the analysis will not be performed on the day of sampling. Allow the sample to warm at room temperature for about two hours (if it has been refrigerated) prior to analyzing.

8.8.3.2 Analyze the sample by the pararosaniline method, as described in Section 11. If the color-developed sample has an absorbance above the highest standard, a suitable dilution in high purity water should be prepared and analyzed.

9.0 Quality Control

9.1 Sampling: See EPA Manual 600/4-77-02b for Method 5 quality control.

9.2 Analysis: The quality assurance program required for this method includes the analysis of the field and method blanks, and procedure validations. The positive identification and quantitation of formaldehyde are dependent on the integrity of the samples received and the precision and accuracy of the analytical methodology. Quality assurance procedures for this method are designed to monitor the performance of the analytical methodology and to provide the required information to take corrective action if problems are observed in laboratory operations or in field sampling activities.

9.2.1 Field Blanks: Field blanks must be submitted with the samples collected at each sampling site. The field blanks include the sample bottles containing aliquots of sample recover water, and water reagent. At a minimum, one complete sampling train will be assembled in the field staging area, taken to the sampling area, and leak-checked at the beginning and end of the testing (or for the same total number of times as the actual sampling train). The probe of the blank train must be heated during the sample test. The train will be recovered as if it were an actual test sample. No gaseous sample will be passed through the blank sampling train.

9.2.2 Blank Correction: The field blank formaldehyde concentrations will be subtracted from the appropriate sample formaldehyde concentrations. Blank formaldehyde concentrations above 0.25 µg/ml should be considered suspect, and subtraction from the sample formaldehyde concentrations

should be performed in a manner acceptable to the Administrator.

9.2.3 Method Blanks: A method blank must be prepared for each set of analytical operations, to evaluate contamination and artifacts that can be derived from glassware, reagents, and sample handling in the laboratory.

10 Calibration

10.1 Probe Nozzle: Probe nozzles shall be calibrated before their initial use in the field. Using a micrometer, measure the inside diameter of the nozzle to the nearest 0.025 mm (0.001 in). Make measurements at three separate places across the diameter and obtain the average of the measurements. The difference between the high and low numbers shall not exceed 0.1 mm (0.004 in). When the nozzle becomes nicked or corroded, it shall be repaired and calibrated, or replaced with a calibrated nozzle before use. Each nozzle must be permanently and uniquely identified.

10.2 Pitot Tube: The Type S pitot tube assembly shall be calibrated according to the procedure outlined in Section 4 of EPA Method 2, or assigned a nominal coefficient of 0.84 if it is not visibly nicked or corroded and if it meets design and intercomponent spacing specifications.

10.3 Metering System

10.3.1 Before its initial use in the field, the metering system shall be calibrated according to the procedure outlined in APTD-0576. Instead of physically adjusting the dry-gas meter dial readings to correspond to the wet-test meter readings, calibration factors may be used to correct the gas meter dial readings mathematically to the proper values. Before calibrating the metering system, it is suggested that a leak-check be conducted. For metering systems having diaphragm pumps, the normal leak-check procedure will not delete leakages with the pump. For these cases, the following leak-check procedure will apply: Make a ten-minute calibration run at 0.00057 m³/min (0.02 cfm). At the end of the run, take the difference of the measured wet-test and dry-gas meter volumes and divide the difference by 10 to get the leak rate. The leak rate should not exceed 0.00057 m³/min (0.02 cfm).

10.3.2 After each field use, check the calibration of the metering system by performing three calibration runs at a single intermediate orifice setting (based on the previous field test). Set the vacuum at the maximum value reached during the test series. To adjust the vacuum, insert a valve between the wet-test meter and the inlet of the metering system. Calculate the average

value of the calibration factor. If the calibration has changed by more than 5 percent, recalibrate the meter over the full range of orifice settings, as outlined in APTD-0576.

10.3.3 Leak-check of metering system: The portion of the sampling train from the pump to the orifice meter (see Figure 1) should be leak-checked prior to initial use and after each shipment. Leakage after the pump will result in less volume being recorded than is actually sampled. Use the following procedure: Close the main valve on the meter box. Insert a one-hole rubber stopper with rubber tubing attached into the orifice exhaust pipe. Disconnect and vent the low side of the orifice manometer. Close off the low side orifice tap. Pressurize the system to 13-18 cm (5-7 in) water column by blowing into the rubber tubing. Pinch off the tubing and observe the manometer for 1 min. A loss of pressure on the manometer indicates a leak in the meter box. Leaks must be corrected.

NOTE: If the dry-gas meter coefficient values obtained before and after a test series differ by >5 percent, either the test series must be voided or calculations for test series must be performed using whichever meter coefficient value (i.e., before or after) gives the lower value of total sample volume.

10.4 Probe Heater: The probe heating system must be calibrated before its initial use in the field according to the procedure outlined in APTD-0576. Probes constructed according to APTD-0581 need not be calibrated if the calibration curves in APTD-0576 are used.

10.5 Temperature gauges: Use the procedure in section 4.3 of USEPA Method 2 to calibrate in-stack temperature gauges. Dial thermometers such as are used for the dry gas meter and condenser outlet, shall be calibrated against mercury-in-glass thermometers.

10.6 Barometer: Adjust the barometer initially and before each test series to agree to within ± 2.5 mm Hg (0.1 in Hg) of the mercury barometer. Alternately, if a National Weather Service Station (NWSS) is located at the same altitude above sea level as the test site, the barometric pressure reported by the NWSS may be used.

10.7 Balance: Calibrate the balance before each test series, using Class S standard weights. The weights must be within ± 0.5 percent of the standards, or the balance must be adjusted to meet these limits.

11.0 Procedure for Analysis.

The working formaldehyde standards (0.25, 0.50, 1.0, 2.0, and 3.0 $\mu\text{g/ml}$) are analyzed and a calibration curve is calculated for each day's analysis. The standards should be analyzed first to ensure that the method is working properly prior to analyzing the samples. In addition, a sample of the high-purity

water should also be analyzed and used as a "0" formaldehyde standard.

The procedure for analysis of samples and standards is identical: Using the pipet set to 2.50 ml, pipet 2.50 ml of the solution to be analyzed into a polystyrene cuvette. Using the 250 μl pipet, pipet 250 μl of the pararosaniline reagent solution into the cuvette. Seal the top of the cuvette with a Parafilm square and shake at least 30 seconds to ensure the solution in the cuvette is well-mixed. Peel back a corner of the Parafilm so the next reagent can be added. Using the 250 μl pipet, pipet 250 μl of the sodium sulfite reagent solution into the cuvette. Reseal the cuvette with the Parafilm, and again shake for about 30 seconds to mix the solution in the cuvette. Record the time of addition of the sodium sulfite and let the color develop at room temperature for 60 minutes. Set the spectrophotometer to 570 nm and set to read in Absorbance Units. The spectrophotometer should be equipped with a holder for the 1-cm pathlength cuvettes. Place cuvette(s) containing high-purity water in the spectrophotometer and adjust to read 0.000 AU.

After the 60 minutes color development period, read the standard and samples in the spectrophotometer. Record the absorbance reading for each cuvette. The calibration curve is calculated by linear regression, with the formaldehyde concentration as the "x" coordinate of the pair, and the absorbance reading as the "y" coordinate. The procedure is very reproducible, and typically will yield values similar to these for the calibration curve:

Correlation Coefficient: 0.9999

Slope: 0.50

Y-Intercept: 0.090

The formaldehyde concentration of the samples can be found by using the trend-line feature of the calculator or computer program used for the linear regression. For example, the TI-55 calculators use the "X" key (this gives the predicted formaldehyde concentration for the value of the absorbance you key in for the sample). Multiply the formaldehyde concentration from the sample by the dilution factor, if any, for the sample to give the formaldehyde concentration of the original, undiluted, sample (units will be micrograms/ml).

11.1 Notes on the Pararosaniline Procedure

11.1.1 The pararosaniline method is temperature-sensitive. However, the small fluctuations typical of a laboratory will not significantly affect the results.

11.1.2 The calibration curve is linear to beyond 4 " $\mu\text{g/ml}$ " formaldehyde, however, a

research-grade spectrophotometer is required to reproducibly read the high absorbance values. Consult your instrument manual to evaluate the capability of the spectrophotometer.

11.1.3 The quality of the laboratory water used to prepare standards and make dilutions is critical. It is important that the cautions given in the Reagents section be observed. This procedure allows quantitation of formaldehyde at very low levels, and thus it is imperative to avoid contamination from other sources of formaldehyde and to exercise the degree of care required for trace analyses.

11.1.4 The analyst should become familiar with the operation of the Oxford or equivalent pipettors before using them for an analysis. Follow the instructions of the manufacturer; one can pipet water into a tared container on any analytical balance to check pipet accuracy and precision. This will also establish if the proper technique is being used. Always use a new tip for each pipetting operation.

11.1.5 This procedure follows the recommendations of ASTM Standard Guide D 3614, reading all solutions versus water in the reference cell. This allows the absorbance of the blank to be tracked on a daily basis. Refer to ASTM D 3614 for more information.

12.0 Calculations

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculations.

12.1 Calculations of Total Formaldehyde

12.1.1 To determine the total formaldehyde in mg, use the following equation if biocide was not used:

Total mg formaldehyde=

$$C_d \times V \times DF \times 0.001 \text{ mg}/\mu\text{g}$$

Where:

C_d = measured conc. formaldehyde, $\mu\text{g}/\text{ml}$
 V = total volume of stack sample, ml
 DF = dilution factor

12.1.2 To determine the total formaldehyde in mg, use the following equation if biocide was used:

Total mg formaldehyde=

$$\frac{C_d \times V}{(V - B) \times DF \times 0.001} \text{ mg}/\mu\text{g}$$

Where:

C_d = measured conc. formaldehyde, $\mu\text{g}/\text{ml}$
 V = total volume of stack sample, ml
 B = total volume of biocide added to sample, ml
 DF = dilution factor

12.2 Formaldehyde concentration (mg/m^3) in stack gas. Determine the formaldehyde

concentration (mg/m^3) in the stack gas using the following equation: Formaldehyde concentration (mg/m^3) =

$$\frac{K \times [\text{total formaldehyde, mg}]}{V_m(\text{std})}$$

Where:

$K = 35.31 \text{ cu ft}/\text{m}^3$ for $V_m(\text{std})$ in English units, or

$K = 1.00 \text{ m}^3/\text{m}^3$ for $V_m(\text{std})$ in metric units

$V_m(\text{std})$ = volume of gas sample measured by a dry gas meter, corrected to standard conditions, dscm (dscf)

12.3 Average dry gas meter temperature and average orifice pressure drop are obtained from the data sheet.

12.4 Dry Gas Volume: Calculate $V_m(\text{std})$ and adjust for leakage, if necessary, using the equation in Section 6.3 of EPA Method 5, 40 CFR part 60, appendix A.

12.5 Volume of Water Vapor and Moisture Content: Calculated the volume of water vapor and moisture content from equations 5-2 and 5-3 of EPA Method 5.

13.0 Method Performance

The precision of this method is estimated to be better than ± 5 percent, expressed as \pm the percent relative standard deviation.

14.0 *Pollution Prevention.* (Reserved)

15.0 *Waste Management.* (Reserved)

16.0 References

R.R. Miksch, et al., Analytical Chemistry, November 1981, 53 pp. 2118-2123.

J.F. Walker, Formaldehyde, Third Edition, 1964.

US EPA 40 CFR, part 60, Appendix A, Test Methods 1-5

METHOD 318—EXTRACTIVE FTIR METHOD FOR THE MEASUREMENT OF EMISSIONS FROM THE MINERAL WOOL AND WOOL FIBERGLASS INDUSTRIES

1.0 Scope and Application

This method has been validated and approved for mineral wool and wool fiberglass sources. This method may not be applied to other source categories without validation and approval by the Administrator according to the procedures in Test Method 301, 40 CFR part 63, appendix A. For sources seeking to apply FTIR to other source categories, Test Method 320 (40 CFR part 63, appendix A) may be utilized.

1.1 Scope. The analytes measured by this method and their CAS numbers are:

Carbon Monoxide 630-08-0
 Carbonyl Sulfide 463-58-1
 Formaldehyde 50-00-0
 Methanol 1455-13-6
 Phenol 108-95-2

1.2 Applicability

1.2.1 This method is applicable for the determination of formaldehyde, phenol, methanol, carbonyl sulfide (COS) and carbon monoxide (CO) concentrations in controlled and uncontrolled emissions from manufacturing processes using phenolic resins. The com-

pounds are analyzed in the mid-infrared spectral region (about 400 to 4000 cm⁻¹ or 2.5 to 2.5 μm). Suggested analytical regions are given below (Table 1). Slight deviations from these recommended regions may be necessary due to variations in moisture content and ammonia concentration from source to source.

TABLE 1.—EXAMPLE ANALYTICAL REGIONS

Compound	Analytical region (cm ⁻¹) FL _m – FU _m	Potential interferants
Formaldehyde	2840.93 – 2679.83	Water, Methane.
Phenol	1231.32 – 1131.47	Water, Ammonia, Methane.
Methanol	1041.56 – 1019.95	Water, Ammonia.
COS ^a	2028.4 – 2091.9	Water, CO ₂ , CO.
CO ^a	2092.1 – 2191.8	Water, CO ₂ , COS.

^a Suggested analytical regions assume about 15 percent moisture and CO₂, and that COS and CO have about the same absorbance (in the range of 10 to 50 ppm). If CO and COS are hundreds of ppm or higher, then CO₂ and moisture interference is reduced. If CO or COS is present at high concentration and the other at low concentration, then a shorter cell pathlength may be necessary to measure the high concentration component.

1.2.2 This method does not apply when: (a) Polymerization of formaldehyde occurs, (b) moisture condenses in either the sampling system or the instrumentation, and (c) when moisture content of the gas stream is so high relative to the analyte concentrations that it causes severe spectral interference.

1.3 Method Range and Sensitivity

1.3.1 The analytical range is a function of instrumental design and composition of the gas stream. Theoretical detection limits depend, in part, on (a) the absorption coefficient of the compound in the analytical frequency region, (b) the spectral resolution, (c) interferometer sampling time, (d) detector sensitivity and response, and (e) absorption pathlength.

1.3.2 Practically, there is no upper limit to the range. The practical lower detection limit is usually higher than the theoretical value, and depends on (a) moisture content of the flue gas, (b) presence of interferants, and (c) losses in the sampling system. In general, a 22 meter pathlength cell in a suitable sampling system can achieve practical detection limits of 1.5 ppm for three compounds (formaldehyde, phenol, and methanol) at moisture levels up to 15 percent by volume. Sources with uncontrolled emissions of CO and COS may require a 4 meter pathlength cell due to high concentration levels. For

these two compounds, make sure absorbance of highest concentration component is <1.0.

1.4 Data Quality Objectives

1.4.1 In designing or configuring the system, the analyst first sets the data quality objectives, i.e., the desired lower detection limit (DL_i) and the desired analytical uncertainty (AU_i) for each compound. The instrumental parameters (factors b, c, d, and e in Section 1.3.1) are then chosen to meet these requirements, using Appendix D of the FTIR Protocol.

1.4.2 Data quality for each application is determined, in part, by measuring the RMS (Root Mean Square) noise level in each analytical spectral region (Appendix C of the FTIR Protocol). The RMS noise is defined as the RMSD (Root Mean Square Deviation) of the absorbance values in an analytical region from the mean absorbance value of the region. Appendix D of the FTIR Protocol defines the MAU_m (minimum analyte uncertainty of the ith analyte in the mth analytical region). The MAU is the minimum analyte concentration for which the analytical uncertainty limit (AU_i) can be maintained: if the measured analyte concentration is less than MAU_i, then data quality is unacceptable. Table 2 gives some example DL and AU values along with calculated areas and MAU values using the protocol procedures.

TABLE 2.—EXAMPLE PRE-TEST PROTOCOL CALCULATIONS

Protocol value	Form	Phenol	Methanol	Protocol appendix
Reference concentration ^a (ppm-meters)/K	3.016	3.017	5.064	
Reference Band Area	8.2544	16.6417	4.9416	B
DL (ppm-meters)/K	0.1117	0.1117	0.1117	B
AU	0.2	0.2	0.2	B
CL	0.02234	0.02234	0.02234	B
FL	2679.83	1131.47	1019.95	B

TABLE 2.—EXAMPLE PRE-TEST PROTOCOL CALCULATIONS—Continued

Protocol value	Form	Phenol	Methanol	Protocol appendix
FU	2840.93	1231.32	1041.56	B
FC	2760.38	1181.395	1030.755	B
AAI (ppm-meters)/K	0.18440	0.01201	0.00132	B
RMSD	2.28E-03	1.21E-03	1.07E-03	C
MAU (ppm-meters)/K	4.45E-02	7.26E-03	4.68E-03	D
MAU (ppm at 22)	0.0797	0.0130	0.0084	D

^a Concentration units are: ppm concentration of the reference sample (ASC), times the path length of the FTIR cell used when the reference spectrum was measured (meters), divided by the absolute temperature of the reference sample in Kelvin (K), or (ppm-meters)/K.

2.0 Summary of Method

2.1 Principle

2.1.1 Molecules are composed of chemically bonded atoms, which are in constant motion. The atomic motions result in bond deformations (bond stretching and bond-angle bending). The number of fundamental (or independent) vibrational motions depends on the number of atoms (N) in the molecule. At typical testing temperatures, most molecules are in the ground-state vibrational state for most of their fundamental vibrational motions. A molecule can undergo a transition from its ground state (for a particular vibration) to the first excited state by absorbing a quantum of light at a frequency characteristic of the molecule and the molecular motion. Molecules also undergo rotational transitions by absorbing energies in the far-infrared or microwave spectral regions. Rotational transition absorbencies are superimposed on the vibrational absorbencies to give a characteristic shape to each rotational-vibrational absorbance "band."

2.1.2 Most molecules exhibit more than one absorbance band in several frequency regions to produce an infrared spectrum (a characteristic pattern of bands or a "fingerprint") that is unique to each molecule. The infrared spectrum of a molecule depends on its structure (bond lengths, bond angles, bond strengths, and atomic masses). Even small differences in structure can produce significantly different spectra.

2.1.3 Spectral band intensities vary with the concentration of the absorbing compound. Within constraints, the relationship between absorbance and sample concentration is linear. Sample spectra are compared to reference spectra to determine the species and their concentrations.

2.2 Sampling and Analysis

2.2.1 Flue gas is continuously extracted from the source, and the gas or a portion of the gas is conveyed to the FTIR gas cell, where a spectrum of the flue gas is recorded. Absorbance band intensities are related to sample concentrations by Beer's Law.

Where:

$$A_v = \sum a_i b c_i \quad (6)$$

A_v = absorbance of the i^{th} component at the given frequency, #.

a = absorption coefficient of the i^{th} component at the frequency, #.

b = path length of the cell.

c = concentration of the i^{th} compound in the sample at frequency #.

2.2.2 After identifying a compound from the infrared spectrum, its concentration is determined by comparing band intensities in the sample spectrum to band intensities in "reference spectra" of the formaldehyde, phenol, methanol, COS and CO. These reference spectra are available in a permanent soft copy from the EPA spectral library on the EMTIC bulletin board. The source may also prepare reference spectra according to Section 4.5 of the FTIR Protocol.

NOTE: Reference spectra not prepared according to the FTIR Protocol are not acceptable for use in this test method. Documentation detailing the FTIR Protocol steps used in preparing any non-EPA reference spectra shall be included in each test report submitted by the source.

2.3 Operator Requirements. The analyst must have some knowledge of source sampling and of infrared spectral patterns to operate the sampling system and to choose a suitable instrument configuration. The analyst should also understand FTIR instrument operation well enough to choose an instrument configuration consistent with the data quality objectives.

3.0 Definitions

See Appendix A of the FTIR Protocol.

4.0 Interferences

4.1 Analytical (or Spectral) Interferences. Water vapor. High concentrations of ammonia (hundreds of ppm) may interfere with the analysis of low concentrations of methanol (1 to 5 ppm). For CO, carbon dioxide and water may be interferants. In cases where COS levels are low relative to CO levels, CO and water may be interferants.

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4.2 Sampling System Interferences. Water, if it condenses, and ammonia, which reacts with formaldehyde.

5.0 Safety

5.1 Formaldehyde is a suspected carcinogen; therefore, exposure to this compound must be limited. Proper monitoring and safety precautions must be practiced in any atmosphere with potentially high concentrations of CO.

5.2 This method may involve sampling at locations having high positive or negative pressures, high temperatures, elevated heights, high concentrations of hazardous or toxic pollutants, or other diverse sampling conditions. It is the responsibility of the tester(s) to ensure proper safety and health practices, and to determine the applicability of regulatory limitations before performing this test method.

6.0 Equipment and Supplies

The equipment and supplies are based on the schematic of a sampling train shown in

Figure 1. Either the evacuated or purged sampling technique may be used with this sampling train. Alternatives may be used, provided that the data quality objectives of this method are met.

6.1 Sampling Probe. Glass, stainless steel, or other appropriate material of sufficient length and physical integrity to sustain heating, prevent adsorption of analytes, and to reach gas sampling point.

6.2 Particulate Filters. A glass wool plug (optional) inserted at the probe tip (for large particulate removal) and a filter rated at 1-micron (e.g., Balston™) for fine particulate removal, placed immediately after the heated probe.

6.3 Sampling Line/Heating System. Heated (maintained at 250 ± 25 degrees F) stainless steel, Teflon™, or other inert material that does not adsorb the analytes, to transport the sample to analytical system.

6.4 Stainless Steel Tubing. Type 316, e.g., $\frac{3}{8}$ in. diameter, and appropriate length for heated connections.

6.5 Gas Regulators. Appropriate for individual gas cylinders.

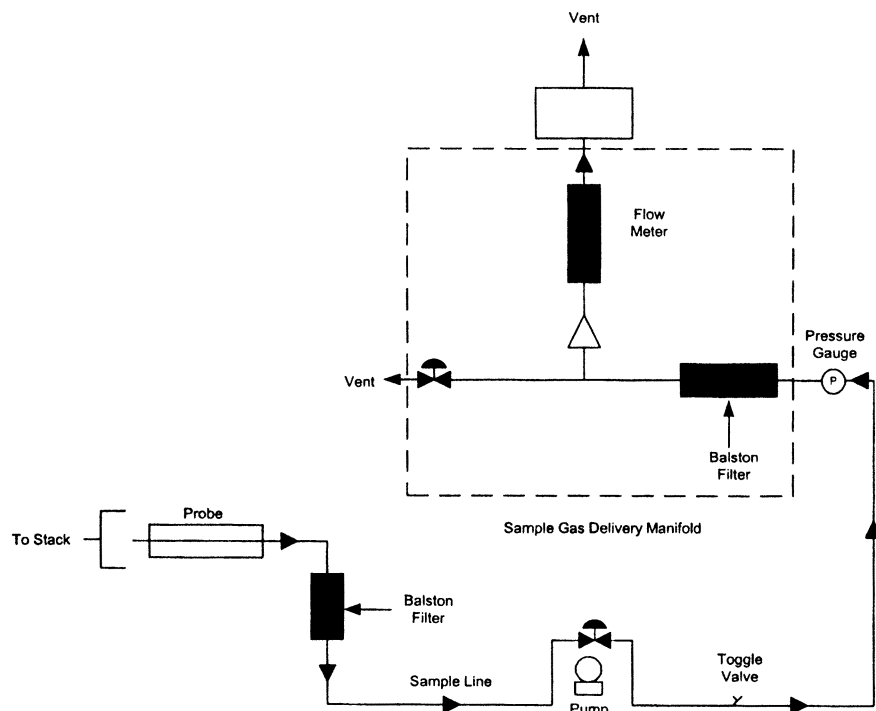


Figure 1. The extractive FTIR sampling system.

6.6 Teflon™ Tubing. Diameter (e.g., 3/8 in.) and length suitable to connect cylinder regulators.

6.7 Sample Pump. A leak-free pump (e.g., KNF™), with by-pass valve, capable of pulling sample through entire sampling system at a rate of about 10 to 20 L/min. If placed before the analytical system, heat the pump and use a pump fabricated from materials non-reactive to the target pollutants. If the pump is located after the instrument, systematically record the sample pressure in the gas cell.

6.8 Gas Sample Manifold. A heated manifold that diverts part of the sample stream to the analyzer, and the rest to the by-pass discharge vent or other analytical instrumentation.

6.9 Rotameter. A calibrated 0 to 20 L/min range rotameter.

6.10 FTIR Analytical System. Spectrometer and detector, capable of measuring formaldehyde, phenol, methanol, COS and CO to the predetermined minimum detectable level. The system shall include a personal computer with compatible software that provides real-time updates of the spectral profile during sample collection and spectral collection.

6.11 FTIR Cell Pump. Required for the evacuated sampling technique, capable of evacuating the FTIR cell volume within 2 minutes. The FTIR cell pump should allow the operator to obtain at least 8 sample spectra in 1 hour.

6.12 Absolute Pressure Gauge. Heatable and capable of measuring pressure from 0 to 1000 mmHg to within ± 2.5 mmHg (e.g., Baratron™).

6.13 Temperature Gauge. Capable of measuring the cell temperature to within ± 2 °C.

7.0 Reagents and Standards

7.1 Ethylene (Calibration Transfer Standard). Obtain NIST traceable (or Protocol) cylinder gas.

7.2 Nitrogen. Ultra high purity (UHP) grade.

7.3 Reference Spectra. Obtain reference spectra for the target pollutants at concentrations that bracket (in ppm-meter/K) the emission source levels. Also, obtain reference spectra for SF₆ and ethylene. Suitable concentrations are 0.0112 to 0.112 (ppm-meter)/K for SF₆ and 5.61 (ppm-meter)/K or less for ethylene. The reference spectra shall meet the criteria for acceptance outlined in Section 2.2.2. The optical density (ppm-meters/K) of the reference spectrum must match the optical density of the sample spectrum within (less than) 25 percent.

8.0 Sample Collection, Preservation, and Storage

Sampling should be performed in the following sequence: Collect background, collect CTS spectrum, collect samples, collect post-test CTS spectrum, verify that two copies of all data were stored on separate computer media.

8.1 Pretest Preparations and Evaluations. Using the procedure in Section 4.0 of the *FTIR Protocol*, determine the optimum sampling system configuration for sampling the target pollutants. Table 2 gives some example values for AU, DL, and MAU. Based on a study (Reference 1), an FTIR system using 1 cm⁻¹ resolution, 22 meter path length, and a broad band MCT detector was suitable for meeting the requirements in Table 2. Other factors that must be determined are:

a. Test requirements: AU_i, CMAX_i, DL_i, OFU_i, and t_{AN} for each.

b. Interferants: See Table 1.

c. Sampling system: L_{S'}, P_{min}, P_{S'}, T_{S'}, t_{SS}, V_{SS}; fractional error, MIL.

d. Analytical regions: 1 through N_m, FL_m, FC_m, and FU_m, plus interferants, FFU_m, FFL_m, wavenumber range FNU to FNL. See Tables 1 and 2.

8.1.1 If necessary, sample and acquire an initial spectrum. Then determine the proper operational pathlength of the instrument to obtain non-saturated absorbances of the target analytes.

8.1.2 Set up the sampling train as shown in Figure 1.

8.2 Sampling System Leak-check. Leak-check from the probe tip to pump outlet as follows: Connect a 0- to 250-mL/min rate meter (rotameter or bubble meter) to the outlet of the pump. Close off the inlet to the probe, and note the leakage rate. The leakage rate shall be ≤200 mL/min.

8.3 Analytical System Leak-check.

8.3.1 For the evacuated sample technique, close the valve to the FTIR cell, and evacuate the absorption cell to the minimum ab-

solute pressure P_{min}. Close the valve to the pump, and determine the change in pressure ΔP_v after 2 minutes.

8.3.2 For both the evacuated sample and purging techniques, pressurize the system to about 100 mmHg above atmospheric pressure. Isolate the pump and determine the change in pressure ΔP_p after 2 minutes.

8.3.3 Measure the barometric pressure, P_b in mmHg.

8.3.4 Determine the percent leak volume %V_L for the signal integration time t_{SS} and for ΔP_{max}, i.e., the larger of ΔP_v or ΔP_p, as follows:

$$\%V_L = 50 t_{SS} \frac{\Delta P_{\max}}{P_{SS}} \quad (2)$$

Where:

50 = 100% divided by the leak-check time of 2 minutes.

8.3.5 Leak volumes in excess of 4 percent of the sample system volume V_{SS} are unacceptable.

8.4 Background Spectrum. Evacuate the gas cell to ≤5 mmHg, and fill with dry nitrogen gas to ambient pressure. Verify that no significant amounts of absorbing species (for example water vapor and CO₂) are present. Collect a background spectrum, using a signal averaging period equal to or greater than the averaging period for the sample spectra. Assign a unique file name to the background spectrum. Store the spectra of the background interferogram and processed single-beam background spectrum on two separate computer media (one is used as the back-up). If continuous sampling will be used during sample collection, collect the background spectrum with nitrogen gas flowing through the cell at the same pressure and temperature as will be used during sampling.

8.5 Pre-Test Calibration Transfer Standard. Evacuate the gas cell to ≤5 mmHg absolute pressure, and fill the FTIR cell to atmospheric pressure with the CTS gas. Or, purge the cell with 10 cell volumes of CTS gas. Record the spectrum. If continuous sampling will be used during sample collection, collect the CTS spectrum with CTS gas flowing through the cell at the same pressure and temperature as will be used during sampling.

8.6 Samples

8.6.1 Evacuated Samples. Evacuate the absorbance cell to ≤5 mmHg absolute pressure. Fill the cell with flue gas to ambient pressure and record the spectrum. Before taking the next sample, evacuate the cell until no further evidence of absorption exists. Repeat this procedure to collect at least 8 separate spectra (samples) in 1 hour.

8.6.2 Purge Sampling. Purge the FTIR cell with 10 cell volumes of flue gas and at least for about 10 minutes. Discontinue the gas

cell purge, isolate the cell, and record the sample spectrum and the pressure. Before taking the next sample, purge the cell with 10 cell volumes of flue gas.

8.6.3 Continuous Sampling. Spectra can be collected continuously while the FTIR cell is being purged. The sample integration time, t_{ss} , the sample flow rate through the FTIR gas cell, and the total run time must be chosen so that the collected data consist of at least 10 spectra with each spectrum being of a separate cell volume of flue gas. More spectra can be collected over the run time and the total run time (and number of spectra) can be extended as well.

8.7 Sampling QA, Data Storage and Reporting

8.7.1 Sample integration times should be sufficient to achieve the required signal-to-noise ratios. Obtain an absorbance spectrum by filling the cell with nitrogen. Measure the RMSD in each analytical region in this absorbance spectrum. Verify that the number of scans is sufficient to achieve the target MAU (Table 2).

8.7.2 Identify all sample spectra with unique file names.

8.7.3 Store on two separate computer media a copy of sample interferograms and processed spectra. The data shall be available to the Administrator on request for the length of time specified in the applicable regulation.

8.7.4 For each sample spectrum, document the sampling conditions, the sampling time (while the cell was being filled), the time the spectrum was recorded, the instrumental conditions (path length, temperature, pressure, resolution, integration time), and the spectral file name. Keep a hard copy of these data sheets.

8.8 Signal Transmittance. While sampling, monitor the signal transmittance through the instrumental system. If signal transmittance (relative to the background) drops below 95 percent in any spectral region where the sample does not absorb infrared energy, obtain a new background spectrum.

8.9 Post-run CTS. After each sampling run, record another CTS spectrum.

8.10 Post-test QA

8.10.1 Inspect the sample spectra immediately after the run to verify that the gas matrix composition was close to the expected (assumed) gas matrix.

8.10.2 Verify that the sampling and instrumental parameters were appropriate for the conditions encountered. For example, if the moisture is much greater than anticipated, it will be necessary to use a shorter path length or dilute the sample.

8.10.3 Compare the pre and post-run CTS spectra. They shall agree to within -5 percent. See FTIR Protocol, Appendix E.

9.0 Quality Control

Follow the quality assurance procedures in the method, including the analysis of pre and post-run calibration transfer standards (Sections 8.5 and 8.9) and the post-test quality assurance procedures in Section 8.10.

10.0 Calibration and Standardization

10.1 Signal-to-Noise Ratio (S/N). The S/N shall be sufficient to meet the MAU in each analytical region.

10.2 Absorbance Pathlength. Verify the absorbance path length by comparing CTS spectra to reference spectra of the calibration gas(es). See FTIR Protocol, Appendix E.

10.3 Instrument Resolution. Measure the line width of appropriate CTS band(s) and compare to reference CTS spectra to verify instrumental resolution.

10.4 Apodization Function. Choose appropriate apodization function. Determine any appropriate mathematical transformations that are required to correct instrumental errors by measuring the CTS. Any mathematical transformations must be documented and reproducible.

10.5 FTIR Cell Volume. Evacuate the cell to ≤ 5 mmHg. Measure the initial absolute temperature (T_i) and absolute pressure (P_i). Connect a wet test meter (or a calibrated dry gas meter), and slowly draw room air into the cell. Measure the meter volume (V_m), meter absolute temperature (T_m), and meter absolute pressure (P_m), and the cell final absolute temperature (T_f) and absolute pressure (P_f). Calculate the FTIR cell volume V_{ss} , including that of the connecting tubing, as follows:

$$V_{ss} = \frac{V_m \frac{P_m}{T_m}}{\left[\frac{P_f}{T_f} - \frac{P_i}{T_i} \right]} \quad (8)$$

As an alternative to the wet test meter/calibrated dry gas meter procedure, measure the inside dimensions of the cell cylinder and calculate its volume.

11.0 Procedure

Refer to Sections 4.6-4.11, Sections 5, 6, and 7, and the appendices of the FTIR Protocol.

12.0 Data Analysis and Calculations

a. Data analysis is performed using appropriate reference spectra whose concentrations can be verified using CTS spectra. Various analytical programs are available to relate sample absorbance to a concentration standard. Calculated concentrations should be verified by analyzing spectral baselines after mathematically subtracting scaled reference spectra from the sample spectra. A

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full description of the data analysis and calculations may be found in the FTIR Protocol (Sections 4.0, 5.0, 6.0 and appendices).

b. Correct the calculated concentrations in sample spectra for differences in absorption pathlength between the reference and sample spectra by:

$$C_{\text{corr}} = \left[\frac{L_r}{L_s} \right] \left[\frac{T_s}{T_r} \right] C_{\text{calc}} \quad (9)$$

Where:

C_{corr} = The pathlength corrected concentration.

C_{calc} = The initial calculated concentration (output of the Multicomp program designed for the compound).

L_r = The pathlength associated with the reference spectra.

L_s = The pathlength associated with the sample spectra.

T_s = The absolute temperature (K) of the sample gas.

T_r = The absolute gas temperature (K) at which reference spectra were recorded.

13.0 Reporting and Recordkeeping

All interferograms used in determining source concentration shall be stored for the period of time required in the applicable regulation. The Administrator has the option of requesting the interferograms recorded during the test in electronic form as part of the test report.

14.0 Method Performance

Refer to the FTIR Protocol.

15.0 Pollution Prevention. [Reserved]

16.0 Waste Management

Laboratory standards prepared from the formaldehyde and phenol are handled according to the instructions in the materials safety data sheets (MSDS).

17.0 References

(1) "Field Validation Test Using Fourier Transform Infrared (FTIR) Spectrometry To Measure Formaldehyde, Phenol and Methanol at a Wool Fiberglass Production Facility." Draft. U.S. Environmental Protection Agency Report, Entropy, Inc., EPA Contract No. 68D20163, Work Assignment I-32, December 1994 (docket item II-A-13).

(2) "Method 301—Field Validation of Pollutant Measurement Methods from Various Waste Media," 40 CFR part 63, appendix A.

METHOD 319—DETERMINATION OF FILTRATION EFFICIENCY FOR PAINT OVERSPRAY ARRESTORS

1.0 Scope and Application.

1.1 This method applies to the determination of the initial, particle size dependent, filtration efficiency for paint arrestors over the particle diameter range from 0.3 to 10 μm . The method applies to single and multiple stage paint arrestors or paint arrestor media. The method is applicable to efficiency determinations from 0 to 99 percent. Two test aerosols are used—one liquid phase and one solid phase. Oleic acid, a low-volatility liquid (CAS Number 112-80-1), is used to simulate the behavior of wet paint overspray. The solid-phase aerosol is potassium chloride salt (KCl, CAS Number 7447-40-7) and is used to simulate the behavior of a dry overspray. The method is limited to determination of the initial, clean filtration efficiency of the arrestor. Changes in efficiency (either increase or decrease) due to the accumulation of paint overspray on and within the arrestor are not evaluated.

1.2 Efficiency is defined as 1—Penetration (e.g., 70 percent efficiency is equal to 0.30 penetration). Penetration is based on the ratio of the downstream particle concentration to the upstream concentration. It is often more useful, from a mathematical or statistical point of view, to discuss the upstream and downstream counts in terms of penetration rather than the derived efficiency value. Thus, this document uses both penetration and efficiency as appropriate.

1.3 For a paint arrestor system or subsystem which has been tested by this method, adding additional filtration devices to the system or subsystem shall be assumed to result in an efficiency of at least that of the original system without the requirement for additional testing. (For example, if the final stage of a three-stage paint arrestor system has been tested by itself, then the addition of the other two stages shall be assumed to maintain, as a minimum, the filtration efficiency provided by the final stage alone. Thus, in this example, if the final stage has been shown to meet the filtration requirements of Table 1 of §63.745 of subpart GG, then the final stage in combination with any additional paint arrestor stages also passes the filtration requirements.)

2.0 Summary of Method.

2.1 This method applies to the determination of the fractional (i.e., particle-size dependent) aerosol penetration of several types of paint arrestors. Fractional penetration is

computed from aerosol concentrations measured upstream and downstream of an arrestor installed in a laboratory test rig. The aerosol concentrations upstream and downstream of the arrestors are measured with an aerosol analyzer that simultaneously counts and sizes the particles in the aerosol stream. The aerosol analyzer covers the particle diameter size range from 0.3 to 10 μm in a minimum of 12 contiguous sizing channels. Each sizing channel covers a narrow range of particle diameters. For example, Channel 1 may cover from 0.3 to 0.4 μm , Channel 2 from 0.4 to 0.5 μm , * * * By taking the ratio of the downstream to upstream counts on a channel by channel basis, the penetration is computed for each of the sizing channels.

2.2 The upstream and downstream aerosol measurements are made while injecting the test aerosol into the air stream upstream of the arrestor (ambient aerosol is removed with HEPA filters on the inlet of the test rig). This test aerosol spans the particle size range from 0.3 to 10 μm and provides sufficient upstream concentration in each of the optical particle counter (OPC) sizing channels to allow accurate calculation of penetration, down to penetrations of approximately 0.01 (i.e., 1 percent penetration; 99 percent efficiency). Results are presented as a graph and a data table showing the aerodynamic particle diameter and the corresponding fractional efficiency.

3.0 Definitions.

Aerodynamic Diameter—diameter of a unit density sphere having the same aerodynamic properties as the particle in question.

Efficiency is defined as equal to 1—Penetration.

Optical Particle Counter (OPC)—an instrument that counts particles by size using light scattering. An OPC gives particle diameters based on size, index of refraction, and shape.

Penetration—the fraction of the aerosol that penetrates the filter at a given particle diameter. Penetration equals the downstream concentration divided by the upstream concentration.

4.0 Interferences.

4.1 The influence of the known interferences (particle losses) are negated by correction of the data using blanks.

5.0 Safety.

5.1 There are no specific safety precautions for this method above those of good laboratory practice. This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user of this method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

6.0 Equipment and Supplies.

6.1 Test Facility. A schematic diagram of a test duct used in the development of the method is shown in Figure 319-1.

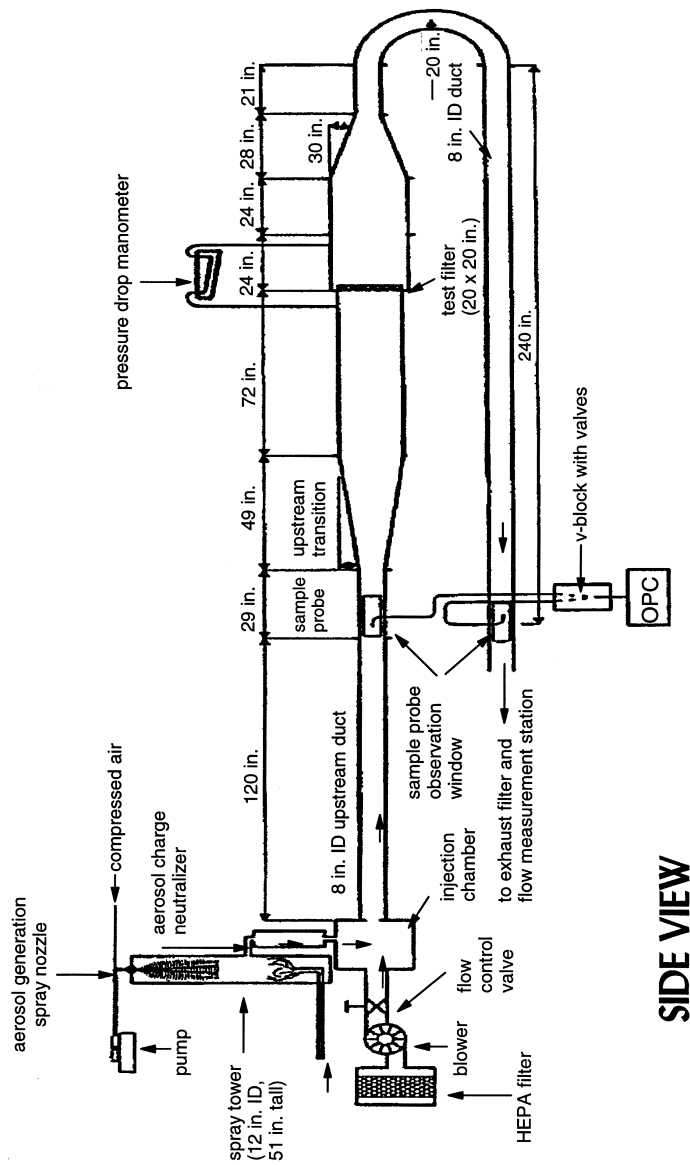


Figure 319-1. Schematic illustration of the fractional efficiency test rig.

6.1.1 The test section, paint spray section, and attached transitions are constructed of stainless and galvanized steel. The upstream and downstream ducting is 20 cm diameter polyvinyl chloride (PVC). The upstream transition provides a 7° angle of expansion to provide a uniform air flow distribution to the paint arrestors. Aerosol concentration is measured upstream and downstream of the

test section to obtain the challenge and penetrating aerosol concentrations, respectively. Because the downstream ducting runs back under the test section, the challenge and penetrating aerosol taps are located physically near each other, thereby facilitating aerosol sampling and reducing sample-line length. The inlet nozzles of the upstream and downstream aerosol probes are

designed to yield isokinetic sampling conditions.

6.1.2 The configuration and dimensions of the test duct can deviate from those of Figure 319-1 provided that the following key elements are maintained: the test duct must meet the criteria specified in Table 319-1; the inlet air is HEPA filtered; the blower is on the upstream side of the duct thereby creating a positive pressure in the duct relative to the surrounding room; the challenge air has a temperature between 50 ° and 100 °F and a relative humidity of less than 65 percent; the angle of the upstream transition (if used) to the paint arrestor must not exceed

7 °; the angle of the downstream transition (if used) from the paint arrestor must not exceed 30 °; the test duct must provide a means for mixing the challenge aerosol with the upstream flow (in lieu of any mixing device, a duct length of 15 duct diameters fulfills this requirement); the test duct must provide a means for mixing any penetrating aerosol with the downstream flow (in lieu of any mixing device, a duct length of 15 duct diameters fulfills this requirement); the test section must provide a secure and leak-free mounting for single and multiple stage arrestors; and the test duct may utilize a 180 ° bend in the downstream duct.

TABLE 319-1.—QC CONTROL LIMITS

	Frequency and description	Control limits
OPC zero count	Each Test. OPC samples HEPA-filtered air.	<50 counts per minute.
OPC sizing accuracy check	Daily. Sample aerosolized PSL spheres	Peak of distribution should be in correct OPC channel.
Minimum counts per channel for challenge aerosol.	Each Test	Minimum total of 500 particle counts per channel.
Maximum particle concentration	Each Test. Needed to ensure OPC is not overloaded.	<10% of manufacturer's claimed upper limit corresponding to a 10% count error.
Standard Deviation of Penetration	Computed for each test based on the CV of the upstream and downstream counts.	<0.10 for 0.3 to 3 μm diameter. <0.30 for >3 μm diameter.
0% Penetration	Monthly	<0.01.
100% Penetration—KCl	Triplicate tests performed immediately before, during, or after triplicate arrestor tests.	0.3 to 1 μm: 0.90 to 1.10. 1 to 3 μm: 0.75 to 1.25. 3 to 10 μm: 0.50 to 1.50.
100% Penetration—Oleic Acid	Triplicate tests performed immediately before, during, or after triplicate arrestor tests.	0.3 to 1 μm: 0.90 to 1.10. 1 to 3 μm: 0.75 to 1.25. 3 to 10 μm: 0.50 to 1.50.

6.2 Aerosol Generator. The aerosol generator is used to produce a stable aerosol covering the particle size range from 0.3 to 10 μm diameter. The generator used in the development of this method consists of an air atomizing nozzle positioned at the top of a 0.30-m (12-in.) diameter, 1.3-m (51-in.) tall, acrylic, transparent, spray tower. This tower allows larger sized particles, which would otherwise foul the test duct and sample lines, to fall out of the aerosol. It also adds drying air to ensure that the KCl droplets dry to solid salt particles. After generation, the aerosol passes through an aerosol neutralizer (Kr85 radioactive source) to neutralize any electrostatic charge on the aerosol (electrostatic charge is an unavoidable consequence of most aerosol generation methods). To improve the mixing of the aerosol with the air stream, the aerosol is injected counter to the airflow. Generators of other designs may be used, but they must produce a stable aerosol concentration over the 0.3 to 10 μm diameter size range; provide a means of ensuring the complete drying of the KCl aerosol; and utilize a charge neutralizer to neutralize any electrostatic charge on the aerosol. The resultant challenge aerosol

must meet the minimum count per channel and maximum concentration criteria of Table 319-1.

6.3 Installation of Paint Arrestor. The paint arrestor is to be installed in the test duct in a manner that precludes air bypassing the arrestor. Since arrestor media are often sold unmounted, a mounting frame may be used to provide back support for the media in addition to sealing it into the duct. The mounting frame for 20 in. x 20 in. arrestors will have minimum open internal dimensions of 18 in. square. Mounting frames for 24 in. x 24 in. arrestors will have minimum open internal dimensions of 22 in. square. The open internal dimensions of the mounting frame shall not be less than 75 percent of the approach duct dimensions.

6.4 Optical Particle Counter. The upstream and downstream aerosol concentrations are measured with a high-resolution optical particle counter (OPC). To ensure comparability of test results, the OPC shall utilize an optical design based on wide-angle light scattering and provided a minimum of 12 contiguous particle sizing channels from 0.3 to 10μm diameter (based on response to PSL) where, for each channel, the ratio of

the diameter corresponding to the upper channel bound to the lower channel bound must not exceed 1.5.

6.5 Aerosol Sampling System. The upstream and downstream sample lines must be made of rigid electrically-grounded metallic tubing having a smooth inside surface, and they must be rigidly secured to prevent movement during testing. The upstream and downstream sample lines are to be nominally identical in geometry. The use of a short length (100 mm maximum) of straight flexible tubing to make the final connection to the OPC is acceptable. The inlet nozzles of the upstream and downstream probes must be sharp-edged and of appropriate entrance diameter to maintain isokinetic sampling within 20 percent of the air velocity.

6.5.1 The sampling system may be designed to acquire the upstream and downstream samples using (a) sequential upstream-downstream sampling with a single OPC, (b) simultaneous upstream and down-

stream sampling with two OPC's, or (c) sequential upstream-downstream sampling with two OPC's.

6.5.2 When two particle counters are used to acquire the upstream and downstream counts, they must be closely matched in flowrate and optical design.

6.6 Airflow Monitor. The volumetric airflow through the system shall be measured with a calibrated orifice plate, flow nozzle, or laminar flow element. The measurement device must have an accuracy of 5 percent or better.

7.0 Reagents and Standards.

7.1 The liquid test aerosol is reagent grade, 98 percent pure, oleic acid (Table 319-2). The solid test aerosol is KCl aerosolized from a solution of KCl in water. In addition to the test aerosol, a calibration aerosol of monodisperse polystyrene latex (PSL) spheres is used to verify the calibration of the OPC.

TABLE 319-2.—PROPERTIES OF THE TEST AND CALIBRATION AEROSOLS

	Refractive index	Density, g/cm ³	Shape
Oleic Acid (liquid-phase challenge aerosol).	1.46 nonabsorbing	0.89	Spherical.
KCl (solid-phase challenge aerosol).	1.49	1.98	Cubic or agglomerated cubes.
PSL (calibration aerosol)	1.59 nonabsorbing	1.05	Spherical.

8.0 Sample Collection, Preservation, and Storage.

8.1 In this test, all sampling occurs in real-time, thus no samples are collected that require preservation or storage during the test. The paint arrestors are shipped and stored to avoid structural damage or soiling. Each arrestor may be shipped in its original box from the manufacturer or similar cardboard box. Arrestors are stored at the test site in a location that keeps them clean and

dry. Each arrestor is clearly labeled for tracking purposes.

9.0 Quality Control.

9.1 Table 319-1 lists the QC control limits.

9.2 The standard deviation (σ) of the penetration (P) for a given test at each of the 15 OPC sizing channels is computed from the coefficient of variation (CV), the standard deviation divided by the mean) of the upstream and downstream measurements as:

$$\sigma_P = P \sqrt{(CV_{\text{upstream}}^2 + CV_{\text{downstream}}^2)} \quad (\text{Eq. 319-1})$$

For a properly operating system, the standard deviation of the penetration is < 0.10 at particle diameters from 0.3 to 3 μm and less than 0.30 at diameters > 3 μm .

9.3 Data Quality Objectives (DQO).

9.3.1 Fractional Penetration. From the triplicate tests of each paint arrestor model, the standard deviation for the penetration measurements at each particle size (i.e., for each sizing channel of the OPC) is computed as:

$$s = \left[\sum (P_i - \bar{P})^2 / (n-1) \right]^{1/2} \quad (\text{Eq. 319-2})$$

where P_i represents an individual penetration measurement, and \bar{P} the average of the 3 ($n = 3$) individual measurements.

9.3.2 Bias of the fractional penetration values is determined from triplicate no-filter and HEPA filter tests. These tests determine the measurement bias at 100 percent penetration and 0 percent penetration, respectively.

9.3.3 PSL-Equivalent Light Scattering Diameter. The precision and bias of the OPC sizing determination are based on sampling a known diameter of PSL and noting whether the particle counts peak in the correct channel of the OPC. This is a pass/fail measurement with no calculations involved.

9.3.4 Airflow. The precision of the measurement must be within 5 percent of the set point.

10.0 Calibration and Standardization.

10.1 Optical Particle Counter. The OPC must have an up-to-date factory calibration. Check the OPC zero at the beginning and end of each test by sampling HEPA-filtered air. Verify the sizing accuracy on a daily basis (for days when tests are performed) with 1-size PSL spheres.

10.2 Airflow Measurement. Airflow measurement devices must have an accuracy of 5 percent or better. Manometers used in conjunction with the orifice plate must be inspected prior to use for proper level, zero, and mechanical integrity. Tubing connections to the manometer must be free from kinks and have secure connections.

10.3 Pressure Drop. Measure pressure drop across the paint arrestor with an inclined manometer readable to within 0.01 in. H₂O. Prior to use, the level and zero of the manometer, and all tubing connections, must be inspected and adjusted as needed.

11.0 Procedure.

11.1 Filtration Efficiency. For both the oleic acid and KCl challenges, this procedure is performed in triplicate using a new arrestor for each test.

11.1.1 General Information and Test Duct Preparation

11.1.1.1 Use the "Test Run Sheet" form (Figure 319-2) to record the test information.

RUN SHEET

Part 1. General Information

Date and Time: _____
 Test Operator: _____
 Test #: _____
 Paint Arrestor: _____

Brand/Model _____
 Arrestor Assigned ID # _____
 Condition of arrestor (i.e., is there any damage? Must be new condition to proceed): _____

Manometer zero and level confirmed? _____

Part 2. Clean Efficiency Test

Date and Time: _____
 Optical Particle Counter: _____
 20 min. warm up _____
 Zero count (< 50 counts/min) _____
 Daily PSL check _____
 PSL Diam: _____ μm
 File name for OPC data: _____

Test Conditions:
 Air Flow: _____
 Temp & RH: Temp _____ °F RH _____ %
 Atm. Pressure: _____ in. Hg
 (From mercury barometer)
 Aerosol Generator: (record all operating parameters)

Test Aerosol:
 (Oleic acid or KCl) _____
 Arrestor:
 Pressure drop: at start _____ in. H₂O
 at end _____ in. H₂O
 Condition of arrestor at end of test (note any physical deterioration): _____

FIGURE 319-2. TEST RUN SHEET

Other report formats which contain the same information are acceptable.

11.1.1.2 Record the date, time, test operator, Test #, paint arrestor brand/model and its assigned ID number. For tests with no arrestor, record none.

11.1.1.3 Ensure that the arrestor is undamaged and is in "new" condition.

11.1.1.4 Mount the arrestor in the appropriate frame. Inspect for any airflow leak paths.

11.1.1.5 Install frame-mounted arrestor in the test duct. Examine the installed arrestor to verify that it is sealed in the duct. For tests with no arrestor, install the empty frame.

11.1.1.6 Visually confirm the manometer zero and level. Adjust as needed.

11.1.2 Clean Efficiency Test.

11.1.2.1 Record the date and time upon beginning this section.

11.1.2.2 Optical Particle Counter.

11.1.2.2.1 General: Operate the OPC per the manufacturer's instructions allowing a minimum of 20 minutes warm up before making any measurements.

11.1.2.2.2 Overload: The OPC will yield inaccurate data if the aerosol concentration it is attempting to measure exceeds its operating limit. To ensure reliable measurements, the maximum aerosol concentration will not exceed 10 percent of the manufacturer's claimed upper concentration limit corresponding to a 10 percent count error. If this value is exceeded, reduce the aerosol concentration until the acceptable conditions are met.

11.1.2.2.3 Zero Count: Connect a HEPA capsule to the inlet of the OPC and obtain printouts for three samples (each a minimum of 1-minute each). Record maximum cumulative zero count. If the count rate exceeds 50 counts per minute, the OPC requires servicing before continuing.

11.1.2.2.4 PSL Check of OPC Calibration: Confirm the calibration of the OPC by sampling a known size PSL aerosol. Aerosolize the PSL using an appropriate nebulizer. Record whether the peak count is observed in the proper channel. If the peak is not seen in the appropriate channel, have the OPC recalibrated.

11.1.2.3 Test Conditions:

11.1.2.3.1 Airflow: The test airflow corresponds to a nominal face velocity of 120 FPM through the arrestor. For arrestors having nominal 20 in. x 20 in. face dimensions, this measurement corresponds to an airflow of 333 cfm. For arrestors having nominal face dimensions of 24 in. x 24 in., this measurement corresponds to an airflow of 480 cfm.

11.1.2.3.2 Temperature and Relative Humidity: The temperature and relative humidity of the challenge air stream will be measured to within an accuracy of ± 2 °F and ± 10 percent RH. To protect the probe from fouling, it may be removed during periods of aerosol generation.

11.1.2.3.3 Barometric Pressure: Use a mercury barometer. Record the atmospheric pressure.

11.1.2.4 Upstream and Downstream Background Counts.

11.1.2.4.1 With the arrestor installed in the test duct and the airflow set at the proper value, turn on the data acquisition computer and bring up the data acquisition program.

11.1.2.4.2 Set the OPC settings for the appropriate test sample duration with output for both printer and computer data collection.

11.1.2.4.3 Obtain one set of upstream-downstream background measurements.

11.1.2.4.4 After obtaining the upstream-downstream measurements, stop data acquisition.

11.1.2.5 Efficiency Measurements:

11.1.2.5.1 Record the arrestor pressure drop.

11.1.2.5.2 Turn on the Aerosol Generator. Begin aerosol generation and record the operating parameters.

11.1.2.5.3 Monitor the particle counts. Allow a minimum of 5 minutes for the generator to stabilize.

11.1.2.5.4 Confirm that the total particle count does not exceed the predetermined upper limit. Adjust generator as needed.

11.1.2.5.5 Confirm that a minimum of 50 particle counts are measured in the upstream sample in each of the OPC channels per sample. (A minimum of 50 counts per channel per sample will yield the required minimum 500 counts per channel total for the 10 upstream samples as specified in Table 319-1.) Adjust generator or sample time as needed.

11.1.2.5.6 If you are unable to obtain a stable concentration within the concentration limit and with the 50 count minimum per channel, adjust the aerosol generator.

11.1.2.5.7 When the counts are stable, perform repeated upstream-downstream sampling until 10 upstream-downstream measurements are obtained.

11.1.2.5.8 After collection of the 10 upstream-downstream samples, stop data acquisition and allow 2 more minutes for final purging of generator.

11.1.2.5.9 Obtain one additional set of upstream-downstream background samples.

11.1.2.5.10 After obtaining the upstream-downstream background samples, stop data acquisition.

11.1.2.5.11 Record the arrestor pressure drop.

11.1.2.5.12 Turn off blower.

11.1.2.5.13 Remove the paint arrestor assembly from the test duct. Note any signs of physical deterioration.

11.1.2.5.14 Remove the arrestor from the frame and place the arrestor in an appropriate storage bag.

11.2 Control Test: 100 Percent Penetration Test. A 100 percent penetration test must be performed immediately before each individual paint arrestor test using the same challenge aerosol substance (i.e., oleic acid or KCl) as to be used in the arrestor test. These tests are performed with no arrestor installed in the test housing. This test is a relatively stringent test of the adequacy of the overall duct, sampling, measurement, and aerosol generation system. The test is performed as a normal penetration test except the paint arrestor is not used. A perfect system would yield a measured penetration of 1 at all particle sizes. Deviations from 1

can occur due to particle losses in the duct, differences in the degree of aerosol uniformity (i.e., mixing) at the upstream and downstream probes, and differences in particle transport efficiency in the upstream and downstream sampling lines.

11.3 Control Test: 0 Percent Penetration. One 0 percent penetration test must be performed at least monthly during testing. The test is performed by using a HEPA filter rather than a paint arrestor. This test assesses the adequacy of the instrument response time and sample line lag.

12.0 Data Analysis and Calculations.

12.1 Analysis. The analytical procedures for the fractional penetration and flow velocity measurements are described in Section 11. Note that the primary measurements, those of the upstream and downstream aerosol concentrations, are performed with the OPC which acquires the sample and analyzes it in real time. Because all the test data are collected in real time, there are no analytical procedures performed subsequent to the actual test, only data analysis.

12.2 Calculations.

12.2.1 Penetration.

Nomenclature

- U = Upstream particle count
- D = Downstream particle count
- U_b = Upstream background count
- D_b = Downstream background count
- P₁₀₀ = 100 percent penetration value determined immediately prior to the arrestor test computed for each channel as:

$$P_{100} = \frac{(\bar{D} - \bar{D}_b)}{(\bar{U} - \bar{U}_b)}$$

- P = Penetration of the arrestor corrected for P₁₀₀
- ρ = sample standard deviation
- CV = coefficient of variation = ρ/mean
- E = Efficiency.

Overbar denotes arithmetic mean of quantity.

Analysis of each test involves the following quantities:

- P₁₀₀ value for each sizing channel from the 100 percent penetration control test,
- 2 upstream background values,
- 2 downstream background values,
- 10 upstream values with aerosol generator on, and
- 10 downstream values with aerosol generator on.

Using the values associated with each sizing channel, the penetration associated with each particle-sizing channel is calculated as:

$$P = \left\{ \frac{(\bar{D} - \bar{D}_b)}{(\bar{U} - \bar{U}_b)} \right\} / P_{100} \quad (\text{Eq. 319-3})$$

$$E = 1 - P \quad (\text{Eq. 319-4})$$

Most often, the background levels are small compared to the values when the aerosol generator is on.

12.3 The relationship between the physical diameter (D_{Physical}) as measured by the OPC to the aerodynamic diameter (D_{Aero}) is given by:

$$D_{Aero} = D_{Physical} \sqrt{\frac{\rho_{Particle}}{\rho_o} \frac{CCF_{Physical}}{CCF_{Aero}}} \quad (\text{Eq. 319-5})$$

Where:

- ρ_o = unit density of 1 g/cm³.
- ρ_{Particle} = the density of the particle, 0.89 g/cm³ for oleic acid.
- CCF_{Physical} = the Cunningham Correction Factor at D_{Physical}.
- CCF_{Aero} = the Cunningham Correction Factor at D_{Aero}.

12.4 Presentation of Results. For a given arrestor, results will be presented for:

- Triplicate arrestor tests with the liquid-phase challenge aerosol,
 - ; Triplicate arrestor tests with the solid-phase challenge aerosol,

•••; Triplicate 100 percent penetration tests with the liquid-phase challenge aerosol,

- ; Triplicate 100 percent penetration tests with the solid-phase challenge aerosol, and

•••; One 0 percent filter test (using either the liquid-phase or solid-phase aerosol and performed at least monthly).

12.4.1 Results for the paint arrestor test must be presented in both graphical and tabular form. The X-axis of the graph will be a logarithmic scale of aerodynamic diameter from 0.1 to 100 μm. The Y-axis will be efficiency (%) on a linear scale from 0 to 100. Plots for each individual run and a plot of

the average of triplicate solid-phase and of the average triplicate liquid-phase tests must be prepared. All plots are to be based on point-to-point plotting (i.e., no curve fitting is to be used). The data are to be plotted based on the geometric mean diameter of each of the OPC's sizing channels.

12.4.2 Tabulated data from each test must be provided. The data must include the upper and lower diameter bound and geometric mean diameter of each of the OPC sizing channels, the background particle counts for each channel for each sample, the upstream particle counts for each channel for each sample, the downstream particle counts for each channel for each sample, the 100 percent penetration values computed for each channel, and the 0 percent penetration values computed for each channel.

13.0 Pollution Prevention.

13.1 The quantities of materials to be aerosolized should be prepared in accord with the amount needed for the current tests so as to prevent wasteful excess.

14.0 Waste Management.

14.1 Paint arrestors may be returned to originator, if requested, or disposed of with regular laboratory waste.

15.0 References.

1. Hanley, J.T., D.D. Smith and L. Cox. "Fractional Penetration of Paint Overspray Arrestors, Draft Final Report," EPA Cooperative Agreement CR-817083-01-0, January 1994.
2. Hanley, J.T., D.D. Smith, and D.S. Ensor. "Define a Fractional Efficiency Test Method that is Compatible with Particulate Removal Air Cleaners Used in General Ventilation," Final Report, 671-RP, American Society of Heating, Refrigerating, and Air-Conditioning Engineers, Inc., December 1993.
3. "Project Work and Quality Assurance Plan: Fractional Penetration of Paint Overspray Arrestors, Category II," EPA Cooperative Agreement No. CR-817083, July 1994.

TEST METHOD 320—MEASUREMENT OF VAPOR PHASE ORGANIC AND INORGANIC EMISSIONS BY EXTRACTIVE FOURIER TRANSFORM INFRARED (FTIR) SPECTROSCOPY

1.0 Introduction.

Persons unfamiliar with basic elements of FTIR spectroscopy should not attempt to use this method. This method describes sampling and analytical procedures for extractive emission measurements using Fourier transform infrared (FTIR) spectroscopy. Detailed analytical procedures for interpreting infrared spectra are described in the "Protocol for the Use of Extractive Fourier Transform Infrared (FTIR) Spectrometry in

Analyses of Gaseous Emissions from Stationary Sources," hereafter referred to as the "Protocol." Definitions not given in this method are given in appendix A of the Protocol. References to specific sections in the Protocol are made throughout this Method. For additional information refer to references 1 and 2, and other EPA reports, which describe the use of FTIR spectrometry in specific field measurement applications and validation tests. The sampling procedure described here is extractive. Flue gas is extracted through a heated gas transport and handling system. For some sources, sample conditioning systems may be applicable. Some examples are given in this method.

NOTE: sample conditioning systems may be used providing the method validation requirements in Sections 9.2 and 13.0 of this method are met.

1.1 Scope and Applicability.

1.1.1 *Analytes.* Analytes include hazardous air pollutants (HAPs) for which EPA reference spectra have been developed. Other compounds can also be measured with this method if reference spectra are prepared according to section 4.6 of the protocol.

1.1.2 *Applicability.* This method applies to the analysis of vapor phase organic or inorganic compounds which absorb energy in the mid-infrared spectral region, about 400 to 4000 cm^{-1} (25 to 2.5 μm). This method is used to determine compound-specific concentrations in a multi-component vapor phase sample, which is contained in a closed-path gas cell. Spectra of samples are collected using double beam infrared absorption spectroscopy. A computer program is used to analyze spectra and report compound concentrations.

1.2 *Method Range and Sensitivity.* Analytical range and sensitivity depend on the frequency-dependent analyte absorptivity, instrument configuration, data collection parameters, and gas stream composition. Instrument factors include: (a) spectral resolution, (b) interferometer signal averaging time, (c) detector sensitivity and response, and (d) absorption path length.

1.2.1 For any optical configuration the analytical range is between the absorbance values of about .01 (infrared transmittance relative to the background = 0.98) and 1.0 ($T = 0.1$). (For absorbance > 1.0 the relation between absorbance and concentration may not be linear.)

1.2.2 The concentrations associated with this absorbance range depend primarily on the cell path length and the sample temperature. An analyte absorbance greater than 1.0, can be lowered by decreasing the optical path length. Analyte absorbance increases with a longer path length. Analyte detection also depends on the presence of other species exhibiting absorbance in the same analytical

region. Additionally, the estimated lower absorbance (A) limit

($A = 0.01$) depends on the root mean square deviation (RMSD) noise in the analytical region.

1.2.3 The concentration range of this method is determined by the choice of optical configuration.

1.2.3.1 The absorbance for a given concentration can be decreased by decreasing the path length or by diluting the sample. There is no practical upper limit to the measurement range.

1.2.3.2 The analyte absorbance for a given concentration may be increased by increasing the cell path length or (to some extent) using a higher resolution. Both modifications also cause a corresponding increased absorbance for all compounds in the sample, and a decrease in the signal throughput. For this reason the practical lower detection range (quantitation limit) usually depends on sample characteristics such as moisture content of the gas, the presence of other interferants, and losses in the sampling system.

1.3 *Sensitivity.* The limit of sensitivity for an optical configuration and integration time is determined using appendix D of the Protocol: Minimum Analyte Uncertainty, (MAU). The MAU depends on the RMSD noise in an analytical region, and on the absorptivity of the analyte in the same region.

1.4 *Data Quality.* Data quality shall be determined by executing Protocol pre-test procedures in appendices B to H of the protocol and post-test procedures in appendices I and J of the protocol.

1.4.1 Measurement objectives shall be established by the choice of detection limit (DL_i) and analytical uncertainty (AU_i) for each analyte.

1.4.2 An instrumental configuration shall be selected. An estimate of gas composition shall be made based on previous test data, data from a similar source or information gathered in a pre-test site survey. Spectral interferants shall be identified using the selected DL_i and AU_i and band areas from reference spectra and interferant spectra. The baseline noise of the system shall be measured in each analytical region to determine the MAU of the instrument configuration for each analyte and interferant (MIU_i).

1.4.3 Data quality for the application shall be determined, in part, by measuring the RMS (root mean square) noise level in each analytical spectral region (appendix C of the Protocol). The RMS noise is defined as the RMSD of the absorbance values in an analytical region from the mean absorbance value in the region.

1.4.4 The MAU is the minimum analyte concentration for which the AU_i can be maintained; if the measured analyte concentration is less than MAU_i, then data quality are unacceptable.

2.0 Summary of Method

2.1 *Principle.* References 4 through 7 provide background material on infrared spectroscopy and quantitative analysis. A summary is given in this section.

2.1.1 Infrared absorption spectroscopy is performed by directing an infrared beam through a sample to a detector. The frequency-dependent infrared absorbance of the sample is measured by comparing this detector signal (single beam spectrum) to a signal obtained without a sample in the beam path (background).

2.1.2 Most molecules absorb infrared radiation and the absorbance occurs in a characteristic and reproducible pattern. The infrared spectrum measures fundamental molecular properties and a compound can be identified from its infrared spectrum alone.

2.1.3 Within constraints, there is a linear relationship between infrared absorption and compound concentration. If this frequency dependent relationship (absorptivity) is known (measured), it can be used to determine compound concentration in a sample mixture.

2.1.4 Absorptivity is measured by preparing, in the laboratory, standard samples of compounds at known concentrations and measuring the FTIR "reference spectra" of these standard samples. These "reference spectra" are then used in sample analysis: (1) Compounds are detected by matching sample absorbance bands with bands in reference spectra, and (2) concentrations are measured by comparing sample band intensities with reference band intensities.

2.1.5 This method is self-validating provided that the results meet the performance requirement of the QA spike in sections 8.6.2 and 9.0 of this method, and results from a previous method validation study support the use of this method in the application.

2.2 *Sampling and Analysis.* In extractive sampling a probe assembly and pump are used to extract gas from the exhaust of the affected source and transport the sample to the FTIR gas cell. Typically, the sampling apparatus is similar to that used for single-component continuous emission monitor (CEM) measurements.

2.2.1 The digitized infrared spectrum of the sample in the FTIR gas cell is measured and stored on a computer. Absorbance band intensities in the spectrum are related to sample concentrations by what is commonly referred to as Beer's Law.

$$A_i = a_i b c_i \quad (1)$$

Where:

A_i = absorbance at a given frequency of the i th sample component.

a_i = absorption coefficient (absorptivity) of the i th sample component.

b = path length of the cell.

c_i = concentration of the i th sample component.

2.2.2 Analyte spiking is used for quality assurance (QA). In this procedure (section 8.6.2 of this method) an analyte is spiked into the gas stream at the back end of the sample probe. Analyte concentrations in the spiked samples are compared to analyte concentrations in unspiked samples. Since the concentration of the spike is known, this procedure can be used to determine if the sampling system is removing the spiked analyte(s) from the sample stream.

2.3 *Reference Spectra Availability.* Reference spectra of over 100 HAPs are available in the EPA FTIR spectral library on the EMTIC (Emission Measurement Technical Information Center) computer bulletin board service and at internet address <http://info.arnold.af.mil/epa/welcome.htm>. Reference spectra for HAPs, or other analytes, may also be prepared according to section 4.6 of the Protocol.

2.4 *Operator Requirements.* The FTIR analyst shall be trained in setting up the instrumentation, verifying the instrument is functioning properly, and performing routine maintenance. The analyst must evaluate the initial sample spectra to determine if the sample matrix is consistent with pre-test assumptions and if the instrument configuration is suitable. The analyst must be able to modify the instrument configuration, if necessary.

2.4.1 The spectral analysis shall be supervised by someone familiar with EPA FTIR Protocol procedures.

2.4.2 A technician trained in instrumental test methods is qualified to install and operate the sampling system. This includes installing the probe and heated line assembly, operating the analyte spike system, and performing moisture and flow measurements.

3.0 Definitions

See appendix A of the Protocol for definitions relating to infrared spectroscopy. Additional definitions are given in sections 3.1 through 3.29.

3.1 *Analyte.* A compound that this method is used to measure. The term "target analyte" is also used. This method is multi-component and a number of analytes can be targeted for a test.

3.2 *Reference Spectrum.* Infrared spectrum of an analyte prepared under controlled, documented, and reproducible laboratory conditions according to procedures in section 4.6 of the Protocol. A library of reference spectra is used to measure analytes in gas samples.

3.3 *Standard Spectrum.* A spectrum that has been prepared from a reference spectrum through a (documented) mathematical operation. A common example is de-resolving of reference spectra to lower-resolution stand-

ard spectra (Protocol, appendix K to the addendum of this method). Standard spectra, prepared by approved, and documented, procedures can be used as reference spectra for analysis.

3.4 *Concentration.* In this method concentration is expressed as a molar concentration, in ppm-meters, or in (ppm-meters)/K, where K is the absolute temperature (Kelvin). The latter units allow the direct comparison of concentrations from systems using different optical configurations or sampling temperatures.

3.5 *Interferant.* A compound in the sample matrix whose infrared spectrum overlaps with part of an analyte spectrum. The most accurate analyte measurements are achieved when reference spectra of interferants are used in the quantitative analysis with the analyte reference spectra. The presence of an interferant can increase the analytical uncertainty in the measured analyte concentration.

3.6 *Gas Cell.* A gas containment cell that can be evacuated. It is equipped with the optical components to pass the infrared beam through the sample to the detector. Important cell features include: path length (or range if variable), temperature range, materials of construction, and total gas volume.

3.7 *Sampling System.* Equipment used to extract the sample from the test location and transport the sample gas to the FTIR analyzer. This includes sample conditioning systems.

3.8 *Sample Analysis.* The process of interpreting the infrared spectra to obtain sample analyte concentrations. This process is usually automated using a software routine employing a classical least squares (cls), partial least squares (pls), or K- or P-matrix method.

3.9 *One hundred percent line.* A double beam transmittance spectrum obtained by combining two background single beam spectra. Ideally, this line is equal to 100 percent transmittance (or zero absorbance) at every frequency in the spectrum. Practically, a zero absorbance line is used to measure the baseline noise in the spectrum.

3.10 *Background Deviation.* A deviation from 100 percent transmittance in any region of the 100 percent line. Deviations greater than ± 5 percent in an analytical region are unacceptable (absorbance of 0.021 to -0.022). Such deviations indicate a change in the instrument throughput relative to the background single beam.

3.11 *Batch Sampling.* A procedure where spectra of discreet, static samples are collected. The gas cell is filled with sample and the cell is isolated. The spectrum is collected. Finally, the cell is evacuated to prepare for the next sample.

3.12 *Continuous Sampling.* A procedure where spectra are collected while sample gas

is flowing through the cell at a measured rate.

3.13 *Sampling resolution.* The spectral resolution used to collect sample spectra.

3.14 *Truncation.* Limiting the number of interferogram data points by deleting points farthest from the center burst (zero path difference, ZPD).

3.15 *Zero filling.* The addition of points to the interferogram. The position of each added point is interpolated from neighboring real data points. Zero filling adds no information to the interferogram, but affects line shapes in the absorbance spectrum (and possibly analytical results).

3.16 *Reference CTS.* Calibration Transfer Standard spectra that were collected with reference spectra.

3.17 *CTS Standard.* CTS spectrum produced by applying a de-resolution procedure to a reference CTS.

3.18 *Test CTS.* CTS spectra collected at the sampling resolution using the same optical configuration as for sample spectra. Test spectra help verify the resolution, temperature and path length of the FTIR system.

3.19 *RMSD.* Root Mean Square Difference, defined in EPA FTIR Protocol, appendix A.

3.20 *Sensitivity.* The noise-limited compound-dependent detection limit for the FTIR system configuration. This is estimated by the MAU. It depends on the RMSD in an analytical region of a zero absorbance line.

3.21 *Quantitation Limit.* The lower limit of detection for the FTIR system configuration in the sample spectra. This is estimated by mathematically subtracting scaled reference spectra of analytes and interferences from sample spectra, then measuring the RMSD in an analytical region of the subtracted spectrum. Since the noise in subtracted sample spectra may be much greater than in a zero absorbance spectrum, the quantitation limit is generally much higher than the sensitivity. Removing spectral interferences from the sample or improving the spectral subtraction can lower the quantitation limit toward (but not below) the sensitivity.

3.22 *Independent Sample.* A unique volume of sample gas; there is no mixing of gas between two consecutive independent samples. In continuous sampling two independent samples are separated by at least 5 cell volumes. The interval between independent measurements depends on the cell volume and the sample flow rate (through the cell).

3.23 *Measurement.* A single spectrum of flue gas contained in the FTIR cell.

3.24 *Run.* A run consists of a series of measurements. At a minimum a run includes 8 independent measurements spaced over 1 hour.

3.25 *Validation.* Validation of FTIR measurements is described in sections 13.0 through 13.4 of this method. Validation is used to verify the test procedures for meas-

uring specific analytes at a source. Validation provides proof that the method works under certain test conditions.

3.26 *Validation Run.* A validation run consists of at least 24 measurements of independent samples. Half of the samples are spiked and half are not spiked. The length of the run is determined by the interval between independent samples.

3.27 *ning.* Screening is used when there is little or no available information about a source. The purpose of screening is to determine what analytes are emitted and to obtain information about important sample characteristics such as moisture, temperature, and interferences. Screening results are semi-quantitative (estimated concentrations) or qualitative (identification only). Various optical and sampling configurations may be used. Sample conditioning systems may be evaluated for their effectiveness in removing interferences. It is unnecessary to perform a complete run under any set of sampling conditions. Spiking is not necessary, but spiking can be a useful screening tool for evaluating the sampling system, especially if a reactive or soluble analyte is used for the spike.

3.28 *Emissions Test.* An FTIR emissions test is performed according specific sampling and analytical procedures. These procedures, for the target analytes and the source, are based on previous screening and validation results. Emission results are quantitative. A QA spike (sections 8.6.2 and 9.2 of this method) is performed under each set of sampling conditions using a representative analyte. Flow, gas temperature and diluent data are recorded concurrently with the FTIR measurements to provide mass emission rates for detected compounds.

3.29 *Surrogate.* A surrogate is a compound that is used in a QA spike procedure (section 8.6.2 of this method) to represent other compounds. The chemical and physical properties of a surrogate shall be similar to the compounds it is chosen to represent. Under given sampling conditions, usually a single sampling factor is of primary concern for measuring the target analytes: for example, the surrogate spike results can be representative for analytes that are more reactive, more soluble, have a lower absorptivity, or have a lower vapor pressure than the surrogate itself.

4.0 Interferences

Interferences are divided into two classifications: analytical and sampling.

4.1 *Analytical Interferences.* An analytical interference is a spectral feature that complicates (in extreme cases may prevent) the analysis of an analyte. Analytical interferences are classified as background or spectral interference.

4.1.1 *Background Interference.* This results from a change in throughput relative to the

single beam background. It is corrected by collecting a new background and proceeding with the test. In severe instances the cause must be identified and corrected. Potential causes include: (1) Deposits on reflective surfaces or transmitting windows, (2) changes in detector sensitivity, (3) a change in the infrared source output, or (4) failure in the instrument electronics. In routine sampling throughput may degrade over several hours. Periodically a new background must be collected, but no other corrective action will be required.

4.1.2 *Spectral Interference.* This results from the presence of interfering compound(s) (interferant) in the sample. Interferant spectral features overlap analyte spectral features. Any compound with an infrared spectrum, including analytes, can potentially be an interferant. The Protocol measures absorbance band overlap in each analytical region to determine if potential interferants shall be classified as known interferants (FTIR Protocol, section 4.9 and appendix B). Water vapor and CO₂ are common spectral interferants. Both of these compounds have strong infrared spectra and are present in many sample matrices at high concentrations relative to analytes. The extent of interference depends on the (1) interferant concentration, (2) analyte concentration, and (3) the degree of band overlap. Choosing an alternate analytical region can minimize or avoid the spectral interference. For example, CO₂ interferes with the analysis of the 670 cm⁻¹ benzene band. However, benzene can also be measured near 3000 cm⁻¹ (with less sensitivity).

4.2 *Sampling System Interferences.* These prevent analytes from reaching the instrument. The analyte spike procedure is designed to measure sampling system interference, if any.

4.2.1 *Temperature.* A temperature that is too low causes condensation of analytes or water vapor. The materials of the sampling system and the FTIR gas cell usually set the upper limit of temperature.

4.2.2 *Reactive Species.* Anything that reacts with analytes. Some analytes, like formaldehyde, polymerize at lower temperatures.

4.2.3 *Materials.* Poor choice of material for probe, or sampling line may remove some analytes. For example, HF reacts with glass components.

4.2.4 *Moisture.* In addition to being a spectral interferant, condensed moisture removes soluble compounds.

5.0 Safety

The hazards of performing this method are those associated with any stack sampling method and the same precautions shall be followed. Many HAPs are suspected carcinogens or present other serious health risks. Exposure to these compounds should be

avoided in all circumstances. For instructions on the safe handling of any particular compound, refer to its material safety data sheet. When using analyte standards, always ensure that gases are properly vented and that the gas handling system is leak free. (Always perform a leak check with the system under maximum vacuum and, again, with the system at greater than ambient pressure.) Refer to section 8.2 of this method for leak check procedures. This method does not address all of the potential safety risks associated with its use. Anyone performing this method must follow safety and health practices consistent with applicable legal requirements and with prudent practice for each application.

6.0 Equipment and Supplies

NOTE: Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

The equipment and supplies are based on the schematic of a sampling system shown in Figure 1. Either the batch or continuous sampling procedures may be used with this sampling system. Alternative sampling configurations may also be used, provided that the data quality objectives are met as determined in the post-analysis evaluation. Other equipment or supplies may be necessary, depending on the design of the sampling system or the specific target analytes.

6.1 *Sampling Probe.* Glass, stainless steel, or other appropriate material of sufficient length and physical integrity to sustain heating, prevent adsorption of analytes, and to transport analytes to the infrared gas cell. Special materials or configurations may be required in some applications. For instance, high stack sample temperatures may require special steel or cooling the probe. For very high moisture sources it may be desirable to use a dilution probe.

6.2 *Particulate Filters.* A glass wool plug (optional) inserted at the probe tip (for large particulate removal) and a filter (required) rated for 99 percent removal efficiency at 1-micron (e.g., Balston™) connected at the outlet of the heated probe.

6.3 *Sampling Line/Heating System.* Heated (sufficient to prevent condensation) stainless steel, polytetrafluoroethane, or other material inert to the analytes.

6.4 *Gas Distribution Manifold.* A heated manifold allowing the operator to control flows of gas standards and samples directly to the FTIR system or through sample conditioning systems. Usually includes heated flow meter, heated valve for selecting and sending sample to the analyzer, and a bypass vent. This is typically constructed of stainless steel tubing and fittings, and high-temperature valves.

6.5 *Stainless Steel Tubing.* Type 316, appropriate diameter (e.g., 3/8 in.) and length for

heated connections. Higher grade stainless may be desirable in some applications.

6.6 *Calibration/Analyte Spike Assembly.* A three way valve assembly (or equivalent) to introduce analyte or surrogate spikes into the sampling system at the outlet of the probe upstream of the out-of-stack particulate filter and the FTIR analytical system.

6.7 *Mass Flow Meter (MFM).* These are used for measuring analyte spike flow. The MFM shall be calibrated in the range of 0 to 5 L/min and be accurate to ± 2 percent (or better) of the flow meter span.

6.8 *Gas Regulators.* Appropriate for individual gas standards.

6.9 *Polytetrafluoroethane Tubing.* Diameter (e.g., $\frac{3}{8}$ in.) and length suitable to connect cylinder regulators to gas standard manifold.

6.10 *Sample Pump.* A leak-free pump (e.g., KNF™), with by-pass valve, capable of producing a sample flow rate of at least 10 L/min through 100 ft of sample line. If the pump is positioned upstream of the distribution manifold and FTIR system, use a heated pump that is constructed from materials non-reactive to the analytes. If the pump is located downstream of the FTIR system, the gas cell sample pressure will be lower than ambient pressure and it must be recorded at regular intervals.

6.11 *Gas Sample Manifold.* Secondary manifold to control sample flow at the inlet to the FTIR manifold. This is optional, but includes a by-pass vent and heated rotameter.

6.12 *Rotameter.* A 0 to 20 L/min rotameter. This meter need not be calibrated.

6.13 *FTIR Analytical System.* Spectrometer and detector, capable of measuring the analytes to the chosen detection limit. The system shall include a personal computer with compatible software allowing automated collection of spectra.

6.14 *FTIR Cell Pump.* Required for the batch sampling technique, capable of evacuating the FTIR cell volume within 2 minutes. The pumping speed shall allow the operator to obtain 8 sample spectra in 1 hour.

6.15 *Absolute Pressure Gauge.* Capable of measuring pressure from 0 to 1000 mmHg to within ± 2.5 mmHg (e.g., Baratron™).

6.16 *Temperature Gauge.* Capable of measuring the cell temperature to within ± 2 °C.

6.17 *Sample Conditioning.* One option is a condenser system, which is used for moisture removal. This can be helpful in the measurement of some analytes. Other sample conditioning procedures may be devised for the removal of moisture or other interfering species.

6.17.1 The analyte spike procedure of section 9.2 of this method, the QA spike procedure of section 8.6.2 of this method, and the validation procedure of section 13 of this method demonstrate whether the sample conditioning affects analyte concentrations. Alternatively, measurements can be made with two parallel FTIR systems; one meas-

uring conditioned sample, the other measuring unconditioned sample.

6.17.2 Another option is sample dilution. The dilution factor measurement must be documented and accounted for in the reported concentrations. An alternative to dilution is to lower the sensitivity of the FTIR system by decreasing the cell path length, or to use a short-path cell in conjunction with a long path cell to measure more than one concentration range.

7.0 Reagents and Standards

7.1 *Analyte(s) and Tracer Gas.* Obtain a certified gas cylinder mixture containing all of the analyte(s) at concentrations within ± 2 percent of the emission source levels (expressed in ppm-meter/K). If practical, the analyte standard cylinder shall also contain the tracer gas at a concentration which gives a measurable absorbance at a dilution factor of at least 10:1. Two ppm SF₆ is sufficient for a path length of 22 meters at 250 °F.

7.2 *Calibration Transfer Standard(s).* Select the calibration transfer standards (CTS) according to section 4.5 of the FTIR Protocol. Obtain a National Institute of Standards and Technology (NIST) traceable gravimetric standard of the CTS (± 2 percent).

7.3 *Reference Spectra.* Obtain reference spectra for each analyte, interferant, surrogate, CTS, and tracer. If EPA reference spectra are not available, use reference spectra prepared according to procedures in section 4.6 of the EPA FTIR Protocol.

8.0 Sampling and Analysis Procedure

Three types of testing can be performed: (1) Screening, (2) emissions test, and (3) validation. Each is defined in section 3 of this method. Determine the purpose(s) of the FTIR test. Test requirements include: (a) AU_i, DL_i, overall fractional uncertainty, OFU_i, maximum expected concentration (CMAX_i), and t_{AN} for each, (b) potential interferants, (c) sampling system factors, e.g., minimum absolute cell pressure, (P_{min}), FTIR cell volume (V_{SS}), estimated sample absorption pathlength, L_s', estimated sample pressure, P_s', T_s', signal integration time (t_{SS}), minimum instrumental linewidth, MIL, fractional error, and (d) analytical regions, e.g., m=1 to M, lower wavenumber position, FL_m, center wavenumber position, FC_m, and upper wavenumber position, FU_m, plus interferants, upper wavenumber position of the CTS absorption band, FFU_m, lower wavenumber position of the CTS absorption band, FFL_m, wavenumber range FNU to FNL. If necessary, sample and acquire an initial spectrum. From analysis of this preliminary spectrum determine a suitable operational path length. Set up the sampling train as shown in Figure 1 or use an appropriate alternative configuration. Sections 8.1 through 8.11 of this method provide guidance on pre-

test calculations in the EPA protocol, sampling and analytical procedures, and post-test protocol calculations.

8.1 *Pretest Preparations and Evaluations.* Using the procedure in section 4.0 of the FTIR Protocol, determine the optimum sampling system configuration for measuring the target analytes. Use available information to make reasonable assumptions about moisture content and other interferences.

8.1.1 *Analytes.* Select the required detection limit (DL_i) and the maximum permissible analytical uncertainty (AU_i) for each analyte (labeled from 1 to i). Estimate, if possible, the maximum expected concentration for each analyte, C_{MAX_i} . The expected measurement range is fixed by DL_i and C_{MAX_i} for each analyte (i).

8.1.2 *Potential Interferants.* List the potential interferants. This usually includes water vapor and CO_2 , but may also include some analytes and other compounds.

8.1.3 *Optical Configuration.* Choose an optical configuration that can measure all of the analytes within the absorbance range of .01 to 1.0 (this may require more than one path length). Use Protocol sections 4.3 to 4.8 for guidance in choosing a configuration and measuring CTS.

8.1.4 *Fractional Reproducibility Uncertainty (FRU).* The FRU is determined for each analyte by comparing CTS spectra taken before and after the reference spectra were measured. The EPA para-xylene reference spectra were collected on 10/31/91 and 11/01/91 with corresponding CTS spectra "cts1031a," and "cts1101b." The CTS spectra are used to estimate the reproducibility (FRU) in the system that was used to collect the references. The FRU must be $< AU$. Appendix E of the protocol is used to calculate the FRU from CTS spectra. Figure 2 plots results for 0.25 cm^{-1} CTS spectra in EPA reference library: S_3 (cts1101b-cts1031a), and S_4 [(cts1101b+cts1031a)/2]. The RMSD (SRMS) is calculated in the subtracted baseline, S_3 , in the corresponding CTS region from 850 to 1065 cm^{-1} . The area (BAV) is calculated in the same region of the averaged CTS spectrum, S_4 .

8.1.5 *Known Interferants.* Use appendix B of the EPA FTIR Protocol.

8.1.6 Calculate the Minimum Analyte Uncertainty, MAU (section 1.3 of this method discusses MAU and protocol appendix D gives the MAU procedure). The MAU for each analyte, i, and each analytical region, m, depends on the RMS noise.

8.1.7 *Analytical Program.* See FTIR Protocol, section 4.10. Prepare computer program based on the chosen analytical technique. Use as input reference spectra of all target analytes and expected interferants. Reference spectra of additional compounds shall also be included in the program if their presence (even if transient) in the samples is considered possible. The program output

shall be in ppm (or ppb) and shall be corrected for differences between the reference path length, L_R , temperature, T_R , and pressure, P_R , and the conditions used for collecting the sample spectra. If sampling is performed at ambient pressure, then any pressure correction is usually small relative to corrections for path length and temperature, and may be neglected.

8.2 Leak-Check

8.2.1 *Sampling System.* A typical FTIR extractive sampling train is shown in Figure 1. Leak check from the probe tip to pump outlet as follows: Connect a 0-to 250-mL/min rate meter (rotameter or bubble meter) to the outlet of the pump. Close off the inlet to the probe, and record the leak rate. The leak rate shall be ≤ 200 mL/min.

8.2.2 *Analytical System Leak check.* Leak check the FTIR cell under vacuum and under pressure (greater than ambient). Leak check connecting tubing and inlet manifold under pressure.

8.2.2.1 For the evacuated sample technique, close the valve to the FTIR cell, and evacuate the absorption cell to the minimum absolute pressure P_{min} . Close the valve to the pump, and determine the change in pressure ΔP_v after 2 minutes.

8.2.2.2 For both the evacuated sample and purging techniques, pressurize the system to about 100 mmHg above atmospheric pressure. Isolate the pump and determine the change in pressure ΔP_p after 2 minutes.

8.2.2.3 Measure the barometric pressure, P_b in mmHg.

8.2.2.4 Determine the percent leak volume $\%V_L$ for the signal integration time t_{SS} and for ΔP_{max} , i.e., the larger of ΔP_v or ΔP_p , as follows:

$$\%V_L = 50t_{SS} \frac{\Delta P_{max}}{P_{SS}} \quad (2)$$

where 50=100% divided by the leak-check time of 2 minutes. 8.2.2.5 Leak volumes in excess of 4 percent of the FTIR system volume V_{SS} are unacceptable.

8.3 *Detector Linearity.* Once an optical configuration is chosen, use one of the procedures of sections 8.3.1 through 8.3.3 to verify that the detector response is linear. If the detector response is not linear, decrease the aperture, or attenuate the infrared beam. After a change in the instrument configuration perform a linearity check until it is demonstrated that the detector response is linear.

8.3.1 Vary the power incident on the detector by modifying the aperture setting. Measure the background and CTS at three instrument aperture settings: (1) at the aperture setting to be used in the testing, (2) at one half this aperture and (3) at twice the proposed testing aperture. Compare the

three CTS spectra. CTS band areas shall agree to within the uncertainty of the cylinder standard and the RMSD noise in the system. If test aperture is the maximum aperture, collect CTS spectrum at maximum aperture, then close the aperture to reduce the IR throughput by half. Collect a second background and CTS at the smaller aperture setting and compare the spectra again.

8.3.2 Use neutral density filters to attenuate the infrared beam. Set up the FTIR system as it will be used in the test measurements. Collect a CTS spectrum. Use a neutral density filter to attenuate the infrared beam (either immediately after the source or the interferometer) to approximately $\frac{1}{2}$ its original intensity. Collect a second CTS spectrum. Use another filter to attenuate the infrared beam to approximately $\frac{1}{4}$ its original intensity. Collect a third background and CTS spectrum. Compare the CTS spectra. CTS band areas shall agree to within the uncertainty of the cylinder standard and the RMSD noise in the system.

8.3.3 Observe the single beam instrument response in a frequency region where the detector response is known to be zero. Verify that the detector response is "flat" and equal to zero in these regions.

8.4 *Data Storage Requirements.* All field test spectra shall be stored on a computer disk and a second backup copy must be stored on a separate disk. The stored information includes sample interferograms, processed absorbance spectra, background interferograms, CTS sample interferograms and CTS absorbance spectra. Additionally, documentation of all sample conditions, instrument settings, and test records must be recorded on hard copy or on computer medium. Table 1 gives a sample presentation of documentation.

8.5 *Background Spectrum.* Evacuate the gas cell to ≤ 5 mmHg, and fill with dry nitrogen gas to ambient pressure (or purge the cell with 10 volumes of dry nitrogen). Verify that no significant amounts of absorbing species (for example water vapor and CO_2) are present. Collect a background spectrum, using a signal averaging period equal to or greater than the averaging period for the sample spectra. Assign a unique file name to the background spectrum. Store two copies of the background interferogram and processed single-beam spectrum on separate computer disks (one copy is the back-up).

8.5.1 *Interference Spectra.* If possible, collect spectra of known and suspected major interferences using the same optical system that will be used in the field measurements. This can be done on-site or earlier. A number of gases, e.g. CO_2 , SO_2 , CO , NH_3 , are readily available from cylinder gas suppliers.

8.5.2 Water vapor spectra can be prepared by the following procedure. Fill a sample tube with distilled water. Evacuate above the sample and remove dissolved gasses by

alternately freezing and thawing the water while evacuating. Allow water vapor into the FTIR cell, then dilute to atmospheric pressure with nitrogen or dry air. If quantitative water spectra are required, follow the reference spectrum procedure for neat samples (protocol, section 4.6). Often, interference spectra need not be quantitative, but for best results the absorbance must be comparable to the interference absorbance in the sample spectra.

8.6 Pre-Test Calibrations

8.6.1 *Calibration Transfer Standard.* Evacuate the gas cell to ≤ 5 mmHg absolute pressure, and fill the FTIR cell to atmospheric pressure with the CTS gas. Alternatively, purge the cell with 10 cell volumes of CTS gas. (If purge is used, verify that the CTS concentration in the cell is stable by collecting two spectra 2 minutes apart as the CTS gas continues to flow. If the absorbance in the second spectrum is no greater than in the first, within the uncertainty of the gas standard, then this can be used as the CTS spectrum.) Record the spectrum.

8.6.2 *QA Spike.* This procedure assumes that the method has been validated for at least some of the target analytes at the source. For emissions testing perform a QA spike. Use a certified standard, if possible, of an analyte, which has been validated at the source. One analyte standard can serve as a QA surrogate for other analytes which are less reactive or less soluble than the standard. Perform the spike procedure of section 9.2 of this method. Record spectra of at least three independent (section 3.22 of this method) spiked samples. Calculate the spiked component of the analyte concentration. If the average spiked concentration is within 0.7 to 1.3 times the expected concentration, then proceed with the testing. If applicable, apply the correction factor from the Method 301 of this appendix validation test (not the result from the QA spike).

8.7 *Sampling.* If analyte concentrations vary rapidly with time, continuous sampling is preferable using the smallest cell volume, fastest sampling rate and fastest spectra collection rate possible. Continuous sampling requires the least operator intervention even without an automated sampling system. For continuous monitoring at one location over long periods, Continuous sampling is preferred. Batch sampling and continuous static sampling are used for screening and performing test runs of finite duration. Either technique is preferred for sampling several locations in a matter of days. Batch sampling gives reasonably good time resolution and ensures that each spectrum measures a discreet (and unique) sample volume. Continuous static (and continuous) sampling provide a very stable background over long periods. Like batch sampling, continuous static

sampling also ensures that each spectrum measures a unique sample volume. It is essential that the leak check procedure under vacuum (section 8.2 of this method) is passed if the batch sampling procedure is used. It is essential that the leak check procedure under positive pressure is passed if the continuous static or continuous sampling procedures are used. The sampling techniques are described in sections 8.7.1 through 8.7.2 of this method.

8.7.1 *Batch Sampling.* Evacuate the absorbance cell to ≤ 5 mmHg absolute pressure. Fill the cell with exhaust gas to ambient pressure, isolate the cell, and record the spectrum. Before taking the next sample, evacuate the cell until no spectral evidence of sample absorption remains. Repeat this procedure to collect eight spectra of separate samples in 1 hour.

8.7.2 *Continuous Static Sampling.* Purge the FTIR cell with 10 cell volumes of sample gas. Isolate the cell, collect the spectrum of the static sample and record the pressure. Before measuring the next sample, purge the cell with 10 more cell volumes of sample gas.

8.8 Sampling QA and Reporting

8.8.1 Sample integration times shall be sufficient to achieve the required signal-to-noise ratio. Obtain an absorbance spectrum by filling the cell with N₂. Measure the RMSD in each analytical region in this absorbance spectrum. Verify that the number of scans used is sufficient to achieve the target MAU.

8.8.2 Assign a unique file name to each spectrum.

8.8.3 Store two copies of sample interferograms and processed spectra on separate computer disks.

8.8.4 For each sample spectrum, document the sampling conditions, the sampling time (while the cell was being filled), the time the spectrum was recorded, the instrumental conditions (path length, temperature, pressure, resolution, signal integration time), and the spectral file name. Keep a hard copy of these data sheets.

8.9 *Signal Transmittance.* While sampling, monitor the signal transmittance. If signal transmittance (relative to the background) changes by 5 percent or more (absorbance = $-.02$ to $.02$) in any analytical spectral region, obtain a new background spectrum.

8.10 *Post-test CTS.* After the sampling run, record another CTS spectrum.

8.11 Post-test QA

8.11.1 Inspect the sample spectra immediately after the run to verify that the gas matrix composition was close to the expected (assumed) gas matrix.

8.11.2 Verify that the sampling and instrumental parameters were appropriate for the conditions encountered. For example, if the moisture is much greater than antici-

pated, it may be necessary to use a shorter path length or dilute the sample.

8.11.3 Compare the pre- and post-test CTS spectra. The peak absorbance in pre- and post-test CTS must be ± 5 percent of the mean value. See appendix E of the FTIR Protocol.

9.0 Quality Control

Use analyte spiking (sections 8.6.2, 9.2 and 13.0 of this method) to verify that the sampling system can transport the analytes from the probe to the FTIR system.

9.1 *Spike Materials.* Use a certified standard (accurate to ± 2 percent) of the target analyte, if one can be obtained. If a certified standard cannot be obtained, follow the procedures in section 4.6.2.2 of the FTIR Protocol.

9.2 *Spiking Procedure.* QA spiking (section 8.6.2 of this method) is a calibration procedure used before testing. QA spiking involves following the spike procedure of sections 9.2.1 through 9.2.3 of this method to obtain at least three spiked samples. The analyte concentrations in the spiked samples shall be compared to the expected spike concentration to verify that the sampling/analytical system is working properly. Usually, when QA spiking is used, the method has already been validated at a similar source for the analyte in question. The QA spike demonstrates that the validated sampling/analytical conditions are being duplicated. If the QA spike fails then the sampling/analytical system shall be repaired before testing proceeds. The method validation procedure (section 13.0 of this method) involves a more extensive use of the analyte spike procedure of sections 9.2.1 through 9.2.3 of this method. Spectra of at least 12 independent spiked and 12 independent unspiked samples are recorded. The concentration results are analyzed statistically to determine if there is a systematic bias in the method for measuring a particular analyte. If there is a systematic bias, within the limits allowed by Method 301 of this appendix, then a correction factor shall be applied to the analytical results. If the systematic bias is greater than the allowed limits, this method is not valid and cannot be used.

9.2.1 Introduce the spike/tracer gas at a constant flow rate of ≤ 10 percent of the total sample flow, when possible.

NOTE: Use the rotameter at the end of the sampling train to estimate the required spike/tracer gas flow rate.

Use a flow device, e.g., mass flow meter (± 2 percent), to monitor the spike flow rate. Record the spike flow rate every 10 minutes.

9.2.2 Determine the response time (RT) of the system by continuously collecting spectra of the spiked effluent until the spectrum of the spiked component is constant for 5 minutes. The RT is the interval from the

first measurement until the spike becomes constant. Wait for twice the duration of the RT, then collect spectra of two independent spiked gas samples. Duplicate analyses of the spiked concentration shall be within 5 percent of the mean of the two measurements.

9.2.3 Calculate the dilution ratio using the tracer gas as follows: where:

$$DF = \frac{SF_{6(\text{spk})}}{SF_{6(\text{dir})}} \quad (3)$$

Where:

$$CS = DF * \text{Spike}_{\text{dir}} + \text{Unspike} (1 - DF) \quad (4)$$

DF=Dilution factor of the spike gas; this value shall be ≥ 10 .

$SF_{6(\text{dir})}$ = SF_6 (or tracer gas) concentration measured directly in undiluted spike gas.

$SF_{6(\text{spk})}$ =Diluted SF_6 (or tracer gas) concentration measured in a spiked sample.

$\text{Spike}_{\text{dir}}$ =Concentration of the analyte in the spike standard measured by filling the FTIR cell directly.

CS=Expected concentration of the spiked samples.

Unspike=Native concentration of analytes in unspiked samples.

10.0 Calibration and Standardization

10.1 *Signal-to-Noise Ratio (S/N)*. The RMSD in the noise must be less than one tenth of the minimum analyte peak absorbance in each analytical region. For example if the minimum peak absorbance is 0.01 at the required DL, then RMSD measured over the entire analytical region must be ≤ 0.001 .

10.2 *Absorbance Path length*. Verify the absorbance path length by comparing reference CTS spectra to test CTS spectra. See appendix E of the FTIR Protocol.

10.3 *Instrument Resolution*. Measure the line width of appropriate test CTS band(s) to verify instrument resolution. Alternatively, compare CTS spectra to a reference CTS spectrum, if available, measured at the nominal resolution.

10.4 *Apodization Function*. In transforming the sample interferograms to absorbance spectra use the same apodization function that was used in transforming the reference spectra.

10.5 *FTIR Cell Volume*. Evacuate the cell to ≤ 5 mmHg. Measure the initial absolute temperature (T_i) and absolute pressure (P_i). Connect a wet test meter (or a calibrated dry gas meter), and slowly draw room air into the cell. Measure the meter volume (V_m), meter absolute temperature (T_m), and meter absolute pressure (P_m); and the cell final absolute temperature (T_f) and absolute pressure (P_f). Calculate the FTIR cell volume VSS, including that of the connecting tubing, as follows:

$$V_{SS} = \frac{V_m \frac{P_m}{T_m}}{\left[\frac{P_f}{T_f} - \frac{P_i}{T_i} \right]} \quad (5)$$

11.0 Data Analysis and Calculations

Analyte concentrations shall be measured using reference spectra from the EPA FTIR spectral library. When EPA library spectra are not available, the procedures in section 4.6 of the Protocol shall be followed to prepare reference spectra of all the target analytes.

11.1 *Spectral De-resolution*. Reference spectra can be converted to lower resolution standard spectra (section 3.3 of this method) by truncating the original reference sample and background interferograms. Appendix K of the FTIR Protocol gives specific deresolution procedures. Deresolved spectra shall be transformed using the same apodization function and level of zero filling as the sample spectra. Additionally, pre-test FTIR protocol calculations (e.g., FRU, MAU, FCU) shall be performed using the deresolved standard spectra.

11.2 *Data Analysis*. Various analytical programs are available for relating sample absorbance to a concentration standard. Calculated concentrations shall be verified by analyzing residual baselines after mathematically subtracting scaled reference spectra from the sample spectra. A full description of the data analysis and calculations is contained in the FTIR Protocol (sections 4.0, 5.0, 6.0 and appendices). Correct the calculated concentrations in the sample spectra for differences in absorption path length and temperature between the reference and sample spectra using equation 6,

$$C_{\text{corr}} = \left(\frac{L_r}{L_s} \right) \left(\frac{T_s}{T_r} \right) \left(\frac{P_r}{P_s} \right) C_{\text{calc}} \quad (6)$$

Where:

C_{corr} =Concentration, corrected for path length.

C_{calc} =Concentration, initial calculation (output of the analytical program designed for the compound).

L_r =Reference spectra path length.

L_s =Sample spectra path length.

T_s =Absolute temperature of the sample gas, K.

T_r =Absolute gas temperature of reference spectra, K.

P_s =Sample cell pressure.

P_r =Reference spectrum sample pressure.

12.0 Method Performance

12.1 *Spectral Quality.* Refer to the FTIR Protocol appendices for analytical requirements, evaluation of data quality, and analysis of uncertainty.

12.2 *Sampling QA/QC.* The analyte spike procedure of section 9 of this method, the QA spike of section 8.6.2 of this method, and the validation procedure of section 13 of this method are used to evaluate the performance of the sampling system and to quantify sampling system effects, if any, on the measured concentrations. This method is self-validating provided that the results meet the performance requirement of the QA spike in sections 9.0 and 8.6.2 of this method and results from a previous method validation study support the use of this method in the application. Several factors can contribute to uncertainty in the measurement of spiked samples. Factors which can be controlled to provide better accuracy in the spiking procedure are listed in sections 12.2.1 through 12.2.4 of this method.

12.2.1 *Flow meter.* An accurate mass flow meter is accurate to ± 1 percent of its span. If a flow of 1 L/min is monitored with such a MFM, which is calibrated in the range of 0–5 L/min, the flow measurement has an uncertainty of 5 percent. This may be improved by re-calibrating the meter at the specific flow rate to be used.

12.2.2 *Calibration gas.* Usually the calibration standard is certified to within ± 2 percent. With reactive analytes, such as HCl, the certified accuracy in a commercially available standard may be no better than ± 5 percent.

12.2.3 *Temperature.* Temperature measurements of the cell shall be quite accurate. If practical, it is preferable to measure sample temperature directly, by inserting a thermocouple into the cell chamber instead of monitoring the cell outer wall temperature.

12.2.4 *Pressure.* Accuracy depends on the accuracy of the barometer, but fluctuations in pressure throughout a day may be as much as 2.5 percent due to weather variations.

13.0 Method Validation Procedure

This validation procedure, which is based on EPA Method 301 (40 CFR part 63, appendix (A)), may be used to validate this method for

the analytes in a gas matrix. Validation at one source may also apply to another type of source, if it can be shown that the exhaust gas characteristics are similar at both sources.

13.1 Section 5.3 of Method 301 (40 CFR part 63, appendix A), the Analyte Spike procedure, is used with these modifications. The statistical analysis of the results follows section 6.3 of EPA Method 301. Section 3 of this method defines terms that are not defined in Method 301.

13.1.1 The analyte spike is performed dynamically. This means the spike flow is continuous and constant as spiked samples are measured.

13.1.2 The spike gas is introduced at the back of the sample probe.

13.1.3 Spiked effluent is carried through all sampling components downstream of the probe.

13.1.4 A single FTIR system (or more) may be used to collect and analyze spectra (not quadruplicate integrated sampling trains).

13.1.5 All of the validation measurements are performed sequentially in a single "run" (section 3.26 of this method).

13.1.6 The measurements analyzed statistically are each independent (section 3.22 of this method).

13.1.7 A validation data set can consist of more than 12 spiked and 12 unspiked measurements.

13.2 *Batch Sampling.* The procedure in sections 13.2.1 through 13.2.2 may be used for stable processes. If process emissions are highly variable, the procedure in section 13.2.3 shall be used.

13.2.1 With a single FTIR instrument and sampling system, begin by collecting spectra of two unspiked samples. Introduce the spike flow into the sampling system and allow 10 cell volumes to purge the sampling system and FTIR cell. Collect spectra of two spiked samples. Turn off the spike and allow 10 cell volumes of unspiked sample to purge the FTIR cell. Repeat this procedure until the 24 (or more) samples are collected.

13.2.2 In batch sampling, collect spectra of 24 distinct samples. (Each distinct sample consists of filling the cell to ambient pressure after the cell has been evacuated.)

13.2.3 Alternatively, a separate probe assembly, line, and sample pump can be used for spiked sample. Verify and document that sampling conditions are the same in both the spiked and the unspiked sampling systems. This can be done by wrapping both sample lines in the same heated bundle. Keep the same flow rate in both sample lines. Measure samples in sequence in pairs. After two spiked samples are measured, evacuate the FTIR cell, and turn the manifold valve so that spiked sample flows to the FTIR cell. Allow the connecting line from the manifold to the FTIR cell to purge thoroughly (the

time depends on the line length and flow rate). Collect a pair of spiked samples. Repeat the procedure until at least 24 measurements are completed.

13.3 Simultaneous Measurements With Two FTIR Systems. If unspiked effluent concentrations of the target analyte(s) vary significantly with time, it may be desirable to perform synchronized measurements of spiked and unspiked sample. Use two FTIR systems, each with its own cell and sampling system to perform simultaneous spiked and unspiked measurements. The optical configurations shall be similar, if possible. The sampling configurations shall be the same. One sampling system and FTIR analyzer shall be used to measure spiked effluent. The other sampling system and FTIR analyzer shall be used to measure unspiked flue gas. Both systems shall use the same sampling procedure (i.e., batch or continuous).

13.3.1 If batch sampling is used, synchronize the cell evacuation, cell filling, and collection of spectra. Fill both cells at the same rate (in cell volumes per unit time).

13.3.2 If continuous sampling is used, adjust the sample flow through each gas cell so that the same number of cell volumes pass through each cell in a given time (i.e. $TC_1 = TC_2$).

13.4 *Statistical Treatment.* The statistical procedure of EPA Method 301 of this appendix, section 6.3 is used to evaluate the bias and precision. For FTIR testing a validation "run" is defined as spectra of 24 independent samples, 12 of which are spiked with the analyte(s) and 12 of which are not spiked.

13.4.1 *Bias.* Determine the bias (defined by EPA Method 301 of this appendix, section 6.3.2) using equation 7:

$$B = S_m - CS \quad (7)$$

Where:

B = Bias at spike level.

S_m = Mean concentration of the analyte spiked samples.

CS = Expected concentration of the spiked samples.

13.4.2 *Correction Factor.* Use section 6.3.2.2 of Method 301 of this appendix to evaluate the statistical significance of the bias. If it is determined that the bias is significant, then use section 6.3.3 of Method 301 to calculate a correction factor (CF). Analytical results of the test method are multiplied by the correction factor, if $0.7 \leq CF \leq 1.3$. If it is determined that the bias is significant and $CF > \pm 30$ percent, then the test method is considered to "not valid."

13.4.3 If measurements do not pass validation, evaluate the sampling system, instrument configuration, and analytical system to determine if improper set-up or a malfunction was the cause. If so, repair the system and repeat the validation.

14.0 *Pollution Prevention.*

The extracted sample gas is vented outside the enclosure containing the FTIR system and gas manifold after the analysis. In typical method applications the vented sample volume is a small fraction of the source volumetric flow and its composition is identical to that emitted from the source. When analyte spiking is used, spiked pollutants are vented with the extracted sample gas. Approximately 1.6×10^{-4} to 3.2×10^{-4} lbs of a single HAP may be vented to the atmosphere in a typical validation run of 3 hours. (This assumes a molar mass of 50 to 100g, spike rate of 1.0 L/min, and a standard concentration of 100 ppm). Minimize emissions by keeping the spike flow off when not in use.

15.0 *Waste Management.*

Small volumes of laboratory gas standards can be vented through a laboratory hood. Neat samples must be packed and disposed according to applicable regulations. Surplus materials may be returned to supplier for disposal.

16.0 *References.*

1. "Field Validation Test Using Fourier Transform Infrared (FTIR) Spectrometry To Measure Formaldehyde, Phenol and Methanol at a Wool Fiberglass Production Facility." Draft. U.S. Environmental Protection Agency Report, EPA Contract No. 68D20163, Work Assignment I-32, September 1994.
2. "FTIR Method Validation at a Coal-Fired Boiler". Prepared for U.S. Environmental Protection Agency, Research Triangle Park, NC. Publication No.: EPA-454/R95-004, NTIS No.: PB95-193199. July, 1993.
3. "Method 301—Field Validation of Pollutant Measurement Methods from Various Waste Media," 40 CFR part 63, appendix A.
4. "Molecular Vibrations; The Theory of Infrared and Raman Vibrational Spectra," E. Bright Wilson, J.C. Decius, and P.C. Cross, Dover Publications, Inc., 1980. For a less intensive treatment of molecular rotational-vibrational spectra see, for example, "Physical Chemistry," G.M. Barrow, chapters 12, 13, and 14, McGraw Hill, Inc., 1979.
5. "Fourier Transform Infrared Spectrometry," Peter R. Griffiths and James de Haseth, Chemical Analysis, 83, 16-25.(1986), P.J. Elving, J.D. Winefordner and I.M. Kolthoff (ed.), John Wiley and Sons.
6. "Computer-Assisted Quantitative Infrared Spectroscopy," Gregory L. McClure (ed.), ASTM Special Publication 934 (ASTM), 1987.
7. "Multivariate Least-Squares Methods Applied to the Quantitative Spectral Analysis of Multicomponent Mixtures," Applied Spectroscopy, 39(10), 73-84, 1985.

TABLE 1.—EXAMPLE PRESENTATION OF SAMPLING DOCUMENTATION

Sample time	Spectrum file name	Background file name	Sample conditioning			Process condition	
Sample time	Spectrum file	Interferogram	Resolution	Scans	Apodization	Gain	CTS Spectrum

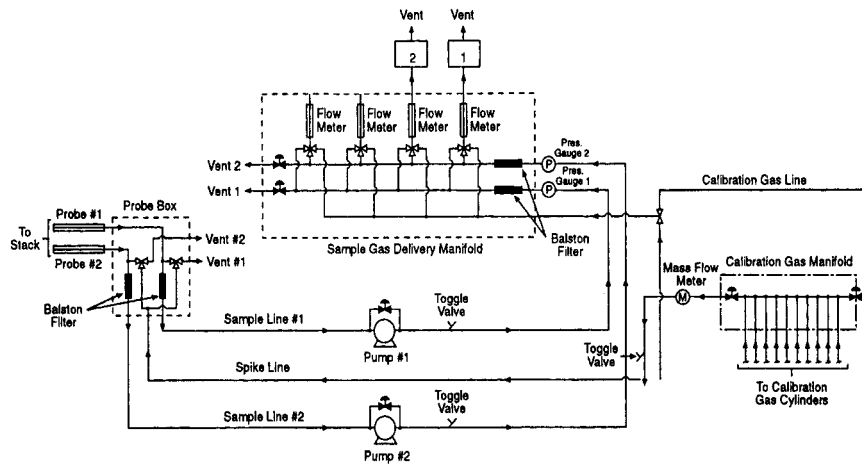


Figure 1. Extractive FTIR sampling system.

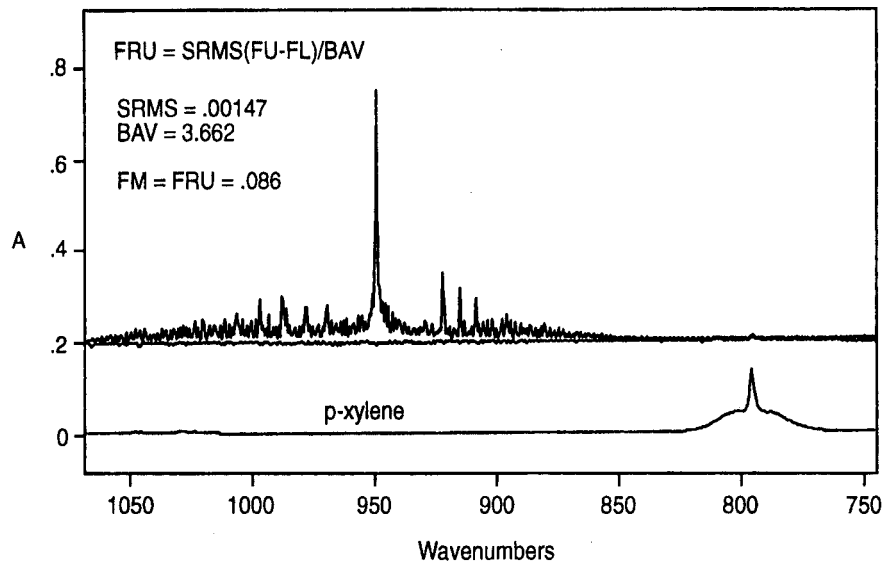


Figure 2. Fractional Reproducibility. Top: average of cts1031a and cts1101b. Bottom: Reference spectrum of p-xylene.

ADDENDUM TO TEST METHOD 320—PROTOCOL FOR THE USE OF EXTRACTIVE FOURIER TRANSFORM INFRARED (FTIR) SPECTROMETRY FOR THE ANALYSES OF GASEOUS EMISSIONS FROM STATIONARY SOURCES

1.0 Introduction

The purpose of this addendum is to set general guidelines for the use of modern FTIR spectroscopic methods for the analysis of gas samples extracted from the effluent of stationary emission sources. This addendum outlines techniques for developing and evaluating such methods and sets basic requirements for reporting and quality assurance procedures.

1.1 Nomenclature

1.1.1 Appendix A to this addendum lists definitions of the symbols and terms used in this Protocol, many of which have been taken directly from American Society for Testing and Materials (ASTM) publication E 131-90a, entitled "Terminology Relating to Molecular Spectroscopy."

1.1.2 Except in the case of background spectra or where otherwise noted, the term "spectrum" refers to a double-beam spectrum in units of absorbance vs. wavenumber (cm^{-1}).

1.1.3 The term "Study" in this addendum refers to a publication that has been subjected to EPA- or peer-review.

2.0 Applicability and Analytical Principle

2.1 *Applicability.* This Protocol applies to the determination of compound-specific concentrations in single- and multiple-component gas phase samples using double-beam absorption spectroscopy in the mid-infrared band. It does not specifically address other FTIR applications, such as single-beam spectroscopy, analysis of open-path (non-enclosed) samples, and continuous measurement techniques. If multiple spectrometers, absorption cells, or instrumental linewidths are used in such analyses, each distinct operational configuration of the system must be evaluated separately according to this Protocol.

2.2 Analytical Principle

2.2.1 In the mid-infrared band, most molecules exhibit characteristic gas phase absorption spectra that may be recorded by FTIR systems. Such systems consist of a source of mid-infrared radiation, an interferometer, an enclosed sample cell of known absorption pathlength, an infrared detector, optical elements for the transfer of infrared radiation between components, and gas flow control and measurement components. Adjunct and integral computer systems are used for controlling the instrument, processing the signal, and for performing both

Fourier transforms and quantitative analyses of spectral data.

2.2.2 The absorption spectra of pure gases and of mixtures of gases are described by a linear absorbance theory referred to as Beer's Law. Using this law, modern FTIR systems use computerized analytical programs to quantify compounds by comparing the absorption spectra of known (reference) gas samples to the absorption spectrum of the sample gas. Some standard mathematical techniques used for comparisons are classical least squares, inverse least squares, cross-correlation, factor analysis, and partial least squares. Reference A describes several of these techniques, as well as additional techniques, such as differentiation methods, linear baseline corrections, and non-linear absorbance corrections.

3.0 General Principles of Protocol Requirements

The characteristics that distinguish FTIR systems from gas analyzers used in instrumental gas analysis methods (e.g., Methods 6C and 7E of appendix A to part 60 of this chapter) are: (1) Computers are necessary to obtain and analyze data; (2) chemical concentrations can be quantified using previously recorded infrared reference spectra; and (3) analytical assumptions and results, including possible effects of interfering compounds, can be evaluated after the quantitative analysis. The following general principles and requirements of this Protocol are based on these characteristics.

3.1 *Verifiability and Reproducibility of Results.* Store all data and document data analysis techniques sufficient to allow an independent agent to reproduce the analytical results from the raw interferometric data.

3.2 *Transfer of Reference Spectra.* To determine whether reference spectra recorded under one set of conditions (e.g., optical bench, instrumental linewidth, absorption pathlength, detector performance, pressure, and temperature) can be used to analyze sample spectra taken under a different set of conditions, quantitatively compare "calibration transfer standards" (CTS) and reference spectra as described in this Protocol.

NOTE: The CTS may, but need not, include analytes of interest). To effect this, record the absorption spectra of the CTS (a) immediately before and immediately after recording reference spectra and (b) immediately after recording sample spectra.

3.3 *Evaluation of FTIR Analyses.* The applicability, accuracy, and precision of FTIR measurements are influenced by a number of interrelated factors, which may be divided into two classes:

3.3.1 *Sample-Independent Factors.* Examples are system configuration and performance (e.g., detector sensitivity and infrared source output), quality and applicability of reference absorption spectra, and type of

mathematical analyses of the spectra. These factors define the fundamental limitations of FTIR measurements for a given system configuration. These limitations may be estimated from evaluations of the system before samples are available. For example, the detection limit for the absorbing compound under a given set of conditions may be estimated from the system noise level and the strength of a particular absorption band. Similarly, the accuracy of measurements may be estimated from the analysis of the reference spectra.

3.3.2 Sample-Dependent Factors. Examples are spectral interferants (e.g., water vapor and CO₂) or the overlap of spectral features of different compounds and contamination deposits on reflective surfaces or transmitting windows. To maximize the effectiveness of the mathematical techniques used in spectral analysis, identification of interferants (a standard initial step) and analysis of samples (includes effect of other analytical errors) are necessary. Thus, the Protocol requires post-analysis calculation of measurement concentration uncertainties for the detection of these potential sources of measurement error.

4.0 Pre-Test Preparations and Evaluations

Before testing, demonstrate the suitability of FTIR spectrometry for the desired application according to the procedures of this section.

4.1 Identify Test Requirements. Identify and record the test requirements described in sections 4.1.1 through 4.1.4 of this addendum. These values set the desired or required goals of the proposed analysis; the description of methods for determining whether these goals are actually met during the analysis comprises the majority of this Protocol.

4.1.1 Analytes (specific chemical species) of interest. Label the analytes from $i = 1$ to I .

4.1.2 Analytical uncertainty limit (AU_{*i*}). The AU_{*i*} is the maximum permissible fractional uncertainty of analysis for the i^{th} analyte concentration, expressed as a fraction of the analyte concentration in the sample.

4.1.3 Required detection limit for each analyte (DL_{*i*}, ppm). The detection limit is the lowest concentration of an analyte for which its overall fractional uncertainty (OFU_{*i*}) is required to be less than its analytical uncertainty limit (AU_{*i*}).

4.1.4 Maximum expected concentration of each analyte (CMAX_{*i*}, ppm).

4.2 Identify Potential Interferants. Considering the chemistry of the process or results of previous studies, identify potential interferants, i.e., the major effluent constituents and any relatively minor effluent constituents that possess either strong absorption characteristics or strong structural similarities to any analyte of interest. Label

them 1 through N_j , where the subscript "j" pertains to potential interferants. Estimate the concentrations of these compounds in the effluent (CPOT_{*j*}, ppm).

4.3 Select and Evaluate the Sampling System. Considering the source, e.g., temperature and pressure profiles, moisture content, analyte characteristics, and particulate concentration), select the equipment for extracting gas samples. Recommended are a particulate filter, heating system to maintain sample temperature above the dew point for all sample constituents at all points within the sampling system (including the filter), and sample conditioning system (e.g., coolers, water-permeable membranes that remove water or other compounds from the sample, and dilution devices) to remove spectral interferants or to protect the sampling and analytical components. Determine the minimum absolute sample system pressure (P_{min}, mmHg) and the infrared absorption cell volume (V_{SS}, liter). Select the techniques and/or equipment for the measurement of sample pressures and temperatures.

4.4 Select Spectroscopic System. Select a spectroscopic configuration for the application. Approximate the absorption pathlength (L_s', meter), sample pressure (P_s', kPa), absolute sample temperature T_s', and signal integration period (t_{SS}, seconds) for the analysis. Specify the nominal minimum instrumental linewidth (MIL) of the system. Verify that the fractional error at the approximate values P_s' and T_s' is less than one half the smallest value AU_{*i*} (see section 4.1.2 of this addendum).

4.5 Select Calibration Transfer Standards (CTS's). Select CTS's that meet the criteria listed in sections 4.5.1, 4.5.2, and 4.5.3 of this addendum.

NOTE: It may be necessary to choose preliminary analytical regions (see section 4.7 of this addendum), identify the minimum analyte linewidths, or estimate the system noise level (see section 4.12 of this addendum) before selecting the CTS. More than one compound may be needed to meet the criteria; if so, obtain separate cylinders for each compound.

4.5.1 The central wavenumber position of each analytical region shall lie within 25 percent of the wavenumber position of at least one CTS absorption band.

4.5.2 The absorption bands in section 4.5.1 of this addendum shall exhibit peak absorbances greater than ten times the value RMS_{EST} (see section 4.12 of this addendum) but less than 1.5 absorbance units.

4.5.3 At least one absorption CTS band within the operating range of the FTIR instrument shall have an instrument-independent linewidth no greater than the narrowest analyte absorption band. Perform and document measurements or cite Studies to determine analyte and CTS compound linewidths.

4.5.4 For each analytical region, specify the upper and lower wavenumber positions (FFU_m and FFL_m , respectively) that bracket the CTS absorption band or bands for the associated analytical region. Specify the wavenumber range, FNU to FNL, containing the absorption band that meets the criterion of section 4.5.3 of this addendum.

4.5.5 Associate, whenever possible, a single set of CTS gas cylinders with a set of reference spectra. Replacement CTS gas cylinders shall contain the same compounds at concentrations within 5 percent of that of the original CTS cylinders; the entire absorption spectra (not individual spectral segments) of the replacement gas shall be scaled by a factor between 0.95 and 1.05 to match the original CTS spectra.

4.6 Prepare Reference Spectra

NOTE: Reference spectra are available in a permanent soft copy from the EPA spectral library on the EMTIC (Emission Measurement Technical Information Center) computer bulletin board; they may be used if applicable.

4.6.1 Select the reference absorption pathlength (L_R) of the cell.

4.6.2 Obtain or prepare a set of chemical standards for each analyte, potential and known spectral interferants, and CTS. Select the concentrations of the chemical standards to correspond to the top of the desired range.

4.6.2.1 *Commercially-Prepared Chemical Standards.* Chemical standards for many compounds may be obtained from independent sources, such as a specialty gas manufacturer, chemical company, or commercial laboratory. These standards (accurate to within ± 2 percent) shall be prepared according to EPA Traceability Protocol (see Reference D) or shall be traceable to NIST standards. Obtain from the supplier an estimate of the stability of the analyte concentration. Obtain and follow all of the supplier's recommendations for recertifying the analyte concentration.

4.6.2.2 *Self-Prepared Chemical Standards.* Chemical standards may be prepared by diluting certified commercially prepared chemical gases or pure analytes with ultra-pure carrier (UPC) grade nitrogen according to the barometric and volumetric techniques generally described in Reference A, section A4.6.

4.6.3 Record a set of the absorption spectra of the CTS {R1}, then a set of the reference spectra at two or more concentrations in duplicate over the desired range (the top of the range must be less than 10 times that of the bottom), followed by a second set of CTS spectra {R2}. (If self-prepared standards are used, see section 4.6.5 of this addendum before disposing of any of the standards.) The maximum accepted standard concentration-pathlength product (ASCP) for each compound shall be higher than the

maximum estimated concentration-pathlength products for both analytes and known interferants in the effluent gas. For each analyte, the minimum ASCPP shall be no greater than ten times the concentration-pathlength product of that analyte at its required detection limit.

4.6.4 Permanently store the background and interferograms in digitized form. Document details of the mathematical process for generating the spectra from these interferograms. Record the sample pressure (P_R), sample temperature (T_R), reference absorption pathlength (L_R), and interferogram signal integration period (t_{SR}). Signal integration periods for the background interferograms shall be $\geq t_{SR}$. Values of P_R , L_R , and t_{SR} shall not deviate by more than ± 1 percent from the time of recording [R1] to that of recording [R2].

4.6.5 If self-prepared chemical standards are employed and spectra of only two concentrations are recorded for one or more compounds, verify the accuracy of the dilution technique by analyzing the prepared standards for those compounds with a secondary (non-FTIR) technique in accordance with sections 4.6.5.1 through 4.6.5.4 of this addendum.

4.6.5.1 Record the response of the secondary technique to each of the four standards prepared.

4.6.5.2 Perform a linear regression of the response values (dependant variable) versus the accepted standard concentration (ASC) values (independent variable), with the regression constrained to pass through the zero-response, zero ASC point.

4.6.5.3 Calculate the average fractional difference between the actual response values and the regression-predicted values (those calculated from the regression line using the four ASC values as the independent variable).

4.6.5.4 If the average fractional difference value calculated in section 4.6.5.3 of this addendum is larger for any compound than the corresponding AU_i , the dilution technique is not sufficiently accurate and the reference spectra prepared are not valid for the analysis.

4.7 *Select Analytical Regions.* Using the general considerations in section 7 of Reference A and the spectral characteristics of the analytes and interferants, select the analytical regions for the application. Label them $m = 1$ to M . Specify the lower, center and upper wavenumber positions of each analytical region (FL_m , FC_m , and FU_m , respectively). Specify the analytes and interferants which exhibit absorption in each region.

4.8 *Determine Fractional Reproducibility Uncertainties.* Using appendix E of this addendum, calculate the fractional reproducibility uncertainty for each analyte (FRU_i) from a comparison of [R1] and [R2]. If $FRU_i > AU_i$,

for any analyte, the reference spectra generated in accordance with section 4.6 of this addendum are not valid for the application.

4.9 *Identify Known Interferants.* Using appendix B of this addendum, determine which potential interferants affect the analyte concentration determinations. Relabel these potential interferant as "known" interferants, and designate these compounds from $k = 1$ to K . Appendix B to this addendum also provides criteria for determining whether the selected analytical regions are suitable.

4.10 *Prepare Computerized Analytical Programs*

4.10.1 Choose or devise mathematical techniques (e.g., classical least squares, inverse least squares, cross-correlation, and factor analysis) based on equation 4 of Reference A that are appropriate for analyzing spectral data by comparison with reference spectra.

4.10.2 Following the general recommendations of Reference A, prepare a computer program or set of programs that analyzes all of the analytes and known interferants, based on the selected analytical regions (section 4.7 of this addendum) and the prepared reference spectra (section 4.6 of this addendum). Specify the baseline correction technique (e.g., determining the slope and intercept of a linear baseline contribution in each analytical region) for each analytical region, including all relevant wavenumber positions.

4.10.3 Use programs that provide as output [at the reference absorption pathlength (L_R), reference gas temperature (T_R), and reference gas pressure (P_R)] the analyte concentrations, the known interferant concentrations, and the baseline slope and intercept values. If the sample absorption pathlength (L_S), sample gas temperature (T_S), or sample gas pressure (P_S) during the actual sample analyses differ from L_R , T_R , and P_R , use a program or set of programs that applies multiplicative corrections to the derived concentrations to account for these variations, and that provides as output both the corrected and uncorrected values. Include in the report of the analysis (see section 7.0 of this addendum) the details of any transformations applied to the original reference spectra (e.g., differentiation), in such a fashion that all analytical results may be verified by an independent agent from the reference spectra and data spectra alone.

4.11 *Determine the Fractional Calibration Uncertainty.* Calculate the fractional calibration uncertainty for each analyte (FCU_i) according to appendix F of this addendum, and compare these values to the fractional uncertainty limits (AU_i; see section 4.1.2 of this addendum). If FCU_i > AU_i, either the reference spectra or analytical programs for that analyte are unsuitable.

4.12 *Verify System Configuration Suitability.* Using appendix C of this addendum, measure

or obtain estimates of the noise level (RMS_{EST}, absorbance) of the FTIR system. Alternatively, construct the complete spectrometer system and determine the values RMS_{Sm} using appendix G of this addendum. Estimate the minimum measurement uncertainty for each analyte (MAU_i, ppm) and known interferant (MIU_k, ppm) using appendix D of this addendum. Verify that (a) MAU_i < (AU_i)(DL_i), FRU_i < AU_i, and FCU_i < AU_i for each analyte and that (b) the CTS chosen meets the requirements listed in sections 4.5.1 through 4.5.5 of this addendum.

5.0 *Sampling and Analysis Procedure*

5.1 *Analysis System Assembly and Leak-Test.* Assemble the analysis system. Allow sufficient time for all system components to reach the desired temperature. Then, determine the leak-rate (L_R) and leak volume (V_L), where $V_L = L_R t_{SS}$. Leak volumes shall be ≤4 percent of V_{SS} .

5.2 *Verify Instrumental Performance.* Measure the noise level of the system in each analytical region using the procedure of appendix G of this addendum. If any noise level is higher than that estimated for the system in section 4.12 of this addendum, repeat the calculations of appendix D of this addendum and verify that the requirements of section 4.12 of this addendum are met; if they are not, adjust or repair the instrument and repeat this section.

5.3 *Determine the Sample Absorption Pathlength*

Record a background spectrum. Then, fill the absorption cell with CTS at the pressure P_R and record a set of CTS spectra [R3]. Store the background and unscaled CTS single beam interferograms and spectra. Using appendix H of this addendum, calculate the sample absorption pathlength (L_S) for each analytical region. The values L_S shall not differ from the approximated sample pathlength L_S' (see section 4.4 of this addendum) by more than 5 percent.

5.4 *Record Sample Spectrum.* Connect the sample line to the source. Either evacuate the absorption cell to an absolute pressure below 5 mmHg before extracting a sample from the effluent stream into the absorption cell, or pump at least ten cell volumes of sample through the cell before obtaining a sample. Record the sample pressure P_S . Generate the absorbance spectrum of the sample. Store the background and sample single beam interferograms, and document the process by which the absorbance spectra are generated from these data. (If necessary, apply the spectral transformations developed in section 5.6.2 of this addendum). The resulting sample spectrum is referred to below as S_S .

NOTE: Multiple sample spectra may be recorded according to the procedures of section

5.4 of this addendum before performing sections 5.5 and 5.6 of this addendum.

5.5 *Quantify Analyte Concentrations.* Calculate the unscaled analyte concentrations RUA_i and unscaled interferant concentrations RUI_k using the programs developed in section 4 of this addendum. To correct for pathlength and pressure variations between the reference and sample spectra, calculate the scaling factor, R_{LPS} using equation A.1,

$$R_{LPS} = (L_R P_R T_S) / (L_S P_S T_R) \quad (A.1)$$

Calculate the final analyte and interferant concentrations RSA_i and RSI_k using equations A.2 and A.3,

$$RSA_i = R_{LPS} RUA_i \quad (A.2)$$

$$RSI_k = R_{LPS} RUI_k \quad (A.3)$$

5.6 *Determine Fractional Analysis Uncertainty.* Fill the absorption cell with CTS at the pressure P_S . Record a set of CTS spectra [R4]. Store the background and CTS single beam interferograms. Using appendix H of this addendum, calculate the fractional analysis uncertainty (FAU) for each analytical region. If the FAU indicated for any analytical region is greater than the required accuracy requirements determined in sections 4.1.1 through 4.1.4 of this addendum, then comparisons to previously recorded reference spectra are invalid in that analytical region, and the analyst shall perform one or both of the procedures of sections 5.6.1 through 5.6.2 of this addendum.

5.6.1 Perform instrumental checks and adjust the instrument to restore its performance to acceptable levels. If adjustments are made, repeat sections 5.3, 5.4 (except for the recording of a sample spectrum), and 5.5 of this addendum to demonstrate that acceptable uncertainties are obtained in all analytical regions.

5.6.2 Apply appropriate mathematical transformations (e.g., frequency shifting, zero-filling, apodization, smoothing) to the spectra (or to the interferograms upon which the spectra are based) generated during the performance of the procedures of section 5.3 of this addendum. Document these transformations and their reproducibility. Do not apply multiplicative scaling of the spectra, or any set of transformations that is mathematically equivalent to multiplicative scaling. Different transformations may be applied to different analytical regions. Frequency shifts shall be less than one-half the minimum instrumental linewidth, and must be applied to all spectral data points in an analytical region. The mathematical transformations may be retained for the analysis if they are also applied to the appropriate analytical regions of all sample spectra recorded, and if all original sample spectra are digitally stored. Repeat sections 5.3, 5.4 (ex-

cept the recording of a sample spectrum), and 5.5 of this addendum to demonstrate that these transformations lead to acceptable calculated concentration uncertainties in all analytical regions.

6.0 Post-Analysis Evaluations

Estimate the overall accuracy of the analyses performed in accordance with sections 5.1 through 5.6 of this addendum using the procedures of sections 6.1 through 6.3 of this addendum.

6.1 *Qualitatively Confirm the Assumed Matrix.* Examine each analytical region of the sample spectrum for spectral evidence of unexpected or unidentified interferants. If found, identify the interfering compounds (see Reference C for guidance) and add them to the list of known interferants. Repeat the procedures of section 4 of this addendum to include the interferants in the uncertainty calculations and analysis procedures. Verify that the MAU and FCU values do not increase beyond acceptable levels for the application requirements. Re-calculate the analyte concentrations (section 5.5 of this addendum) in the affected analytical regions.

6.2 *Quantitatively Evaluate Fractional Model Uncertainty (FMU).* Perform the procedures of either section 6.2.1 or 6.2.2 of this addendum:

6.2.1 Using appendix I of this addendum, determine the fractional model error (FMU) for each analyte.

6.2.2 Provide statistically determined uncertainties FMU for each analyte which are equivalent to two standard deviations at the 95 percent confidence level. Such determinations, if employed, must be based on mathematical examinations of the pertinent sample spectra (not the reference spectra alone). Include in the report of the analysis (see section 7.0 of this addendum) a complete description of the determination of the concentration uncertainties.

6.3 *Estimate Overall Concentration Uncertainty (OCU).* Using appendix J of this addendum, determine the overall concentration uncertainty (OCU) for each analyte. If the OCU is larger than the required accuracy for any analyte, repeat sections 4 and 6 of this addendum.

7.0 Reporting Requirements

[Documentation pertaining to virtually all the procedures of sections 4, 5, and 6 will be required. Software copies of reference spectra and sample spectra will be retained for some minimum time following the actual testing.]

8.0 References

(A) Standard Practices for General Techniques of Infrared Quantitative Analysis

(American Society for Testing and Materials, Designation E 168-88).

(B) The Coblenz Society Specifications for Evaluation of Research Quality Analytical Infrared Reference Spectra (Class II); Anal. Chemistry 47, 945A (1975); Appl. Spectroscopy 44, pp. 211-215, 1990.

(C) Standard Practices for General Techniques for Qualitative Infrared Analysis, American Society for Testing and Materials, Designation E 1252-88.

(D) "EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards," U.S. Environmental Protection Agency Publication No. EPA/600/R-93/224, December 1993.

APPENDIX A TO ADDENDUM TO METHOD 320—
DEFINITIONS OF TERMS AND SYMBOLS

A.1 *Definitions of Terms.* All terms used in this method that are not defined below have the meaning given to them in the CAA and in subpart A of this part.

Absorption band means a contiguous wavenumber region of a spectrum (equivalently, a contiguous set of absorbance spectrum data points) in which the absorbance passes through a maximum or a series of maxima.

Absorption pathlength means the distance in a spectrophotometer, measured in the direction of propagation of the beam of radiant energy, between the surface of the specimen on which the radiant energy is incident and the surface of the specimen from which it is emergent.

Analytical region means a contiguous wavenumber region (equivalently, a contiguous set of absorbance spectrum data points) used in the quantitative analysis for one or more analytes.

NOTE: The quantitative result for a single analyte may be based on data from more than one analytical region.

Apodization means modification of the ILS function by multiplying the interferogram by a weighing function whose magnitude varies with retardation.

Background spectrum means the single beam spectrum obtained with all system components without sample present.

Baseline means any line drawn on an absorption spectrum to establish a reference point that represents a function of the radiant power incident on a sample at a given wavelength.

Beer's law means the direct proportionality of the absorbance of a compound in a homogeneous sample to its concentration.

Calibration transfer standard (CTS) gas means a gas standard of a compound used to achieve and/or demonstrate suitable quantitative agreement between sample spectra and the reference spectra; see section 4.5.1 of this addendum.

Compound means a substance possessing a distinct, unique molecular structure.

Concentration (c) means the quantity of a compound contained in a unit quantity of sample. The unit "ppm" (number, or mole, basis) is recommended.

Concentration-pathlength product means the mathematical product of concentration of the species and absorption pathlength. For reference spectra, this is a known quantity; for sample spectra, it is the quantity directly determined from Beer's law. The units "centimeters-ppm" or "meters-ppm" are recommended.

Derivative absorption spectrum means a plot of rate of change of absorbance or of any function of absorbance with respect to wavelength or any function of wavelength.

Double beam spectrum means a transmission or absorbance spectrum derived by dividing the sample single beam spectrum by the background spectrum.

NOTE: The term "double-beam" is used elsewhere to denote a spectrum in which the sample and background interferograms are collected simultaneously along physically distinct absorption paths. Here, the term denotes a spectrum in which the sample and background interferograms are collected at different times along the same absorption path.

Fast Fourier transform (FFT) means a method of speeding up the computation of a discrete FT by factoring the data into sparse matrices containing mostly zeros.

Flyback means interferometer motion during which no data are recorded.

Fourier transform (FT) means the mathematical process for converting an amplitude-time spectrum to an amplitude-frequency spectrum, or vice versa.

Fourier transform infrared (FTIR) spectrometer means an analytical system that employs a source of mid-infrared radiation, an interferometer, an enclosed sample cell of known absorption pathlength, an infrared detector, optical elements that transfer infrared radiation between components, and a computer system. The time-domain detector response (interferogram) is processed by a Fourier transform to yield a representation of the detector response vs. infrared frequency.

NOTE: When FTIR spectrometers are interfaced with other instruments, a slash should be used to denote the interface; e.g., GC/FTIR; HPCL/FTIR, and the use of FTIR should be explicit; i.e., FTIR not IR.

Frequency, ν means the number of cycles per unit time.

Infrared means the portion of the electromagnetic spectrum containing wavelengths from approximately 0.78 to 800 microns.

Interferogram, $I(\sigma)$ means record of the modulated component of the interference

signal measured as a function of retardation by the detector.

Interferometer means device that divides a beam of radiant energy into two or more paths, generates an optical path difference between the beams, and recombines them in order to produce repetitive interference maxima and minima as the optical retardation is varied.

Linewidth means the full width at half maximum of an absorption band in units of wavenumbers (cm^{-1}).

Mid-infrared means the region of the electromagnetic spectrum from approximately 400 to 5000 cm^{-1} .

Reference spectra means absorption spectra of gases with known chemical compositions, recorded at a known absorption pathlength, which are used in the quantitative analysis of gas samples.

Retardation, σ means optical path difference between two beams in an interferometer; also known as "optical path difference" or "optical retardation."

Scan means digital representation of the detector output obtained during one complete motion of the interferometer's moving assembly or assemblies.

Scaling means application of a multiplicative factor to the absorbance values in a spectrum.

Single beam spectrum means Fourier-transformed interferogram, representing the detector response vs. wavenumber.

NOTE: The term "single-beam" is used elsewhere to denote any spectrum in which the sample and background interferograms are recorded on the same physical absorption path; such usage differentiates such spectra from those generated using interferograms recorded along two physically distinct absorption paths (see "double-beam spectrum" above). Here, the term applies (for example) to the two spectra used directly in the calculation of transmission and absorbance spectra of a sample.

Standard reference material means a reference material, the composition or properties of which are certified by a recognized standardizing agency or group.

NOTE: The equivalent ISO term is "certified reference material."

Transmittance, T means the ratio of radiant power transmitted by the sample to the radiant power incident on the sample. Estimated in FTIR spectroscopy by forming the ratio of the single-beam sample and background spectra.

Wavenumber, $\bar{\nu}$ means the number of waves per unit length.

NOTE: The usual unit of wavenumber is the reciprocal centimeter, cm^{-1} . The wavenumber is the reciprocal of the wavelength, λ , when λ is expressed in centimeters.

Zero-filling means the addition of zero-valued points to the end of a measured interferogram.

NOTE: Performing the FT of a zero-filled interferogram results in correctly interpolated points in the computed spectrum.

A.2 *Definitions of Mathematical Symbols.* The symbols used in equations in this protocol are defined as follows:

(1) A , absorbance = the logarithm to the base 10 of the reciprocal of the transmittance (T).

$$A = \log_{10} \left(\frac{1}{T} \right) = -\log_{10} T$$

(2) AAI_{im} = band area of the i^{th} analyte in the m^{th} analytical region, at the concentration (CL_i) corresponding to the product of its required detection limit (DL_i) and analytical uncertainty limit (AU_i).

(3) AAV_{im} = average absorbance of the i^{th} analyte in the m^{th} analytical region, at the concentration (CL_i) corresponding to the product of its required detection limit (DL_i) and analytical uncertainty limit (AU_i).

(4) ASC , accepted standard concentration = the concentration value assigned to a chemical standard.

(5) $ASCPP$, accepted standard concentration-pathlength product = for a chemical standard, the product of the ASC and the sample absorption pathlength. The units "centimeters-ppm" or "meters-ppm" are recommended.

(6) AU_i , analytical uncertainty limit = the maximum permissible fractional uncertainty of analysis for the i^{th} analyte concentration, expressed as a fraction of the analyte concentration determined in the analysis.

(7) AVT_m = average estimated total absorbance in the m^{th} analytical region.

(8) $CKWN_k$ = estimated concentration of the k^{th} known interferant.

(9) $CMAX_i$ = estimated maximum concentration of the i^{th} analyte.

(10) $CPOT_j$ = estimated concentration of the j^{th} potential interferant.

(11) $DL_{i,r}$, required detection limit = for the i^{th} analyte, the lowest concentration of the analyte for which its overall fractional uncertainty (OFU_i) is required to be less than the analytical uncertainty limit (AU_i).

(12) FC_m = center wavenumber position of the m^{th} analytical region.

(13) FAU_i , fractional analytical uncertainty = calculated uncertainty in the measured concentration of the i^{th} analyte because of errors in the mathematical comparison of reference and sample spectra.

(14) FCU_i , fractional calibration uncertainty = calculated uncertainty in the measured concentration of the i^{th} analyte because of errors in Beer's law modeling of the reference spectra concentrations.

(15) FFL_m = lower wavenumber position of the CTS absorption band associated with the m^{th} analytical region.

(16) FFU_m = upper wavenumber position of the CTS absorption band associated with the m^{th} analytical region.

(17) FL_m = lower wavenumber position of the m^{th} analytical region.

(18) FMU_i , fractional model uncertainty = calculated uncertainty in the measured concentration of the i^{th} analyte because of errors in the absorption model employed.

(19) FN_L = lower wavenumber position of the CTS spectrum containing an absorption band at least as narrow as the analyte absorption bands.

(20) FN_U = upper wavenumber position of the CTS spectrum containing an absorption band at least as narrow as the analyte absorption bands.

(21) FRU_i , fractional reproducibility uncertainty = calculated uncertainty in the measured concentration of the i^{th} analyte because of errors in the reproducibility of spectra from the FTIR system.

(22) FU_m = upper wavenumber position of the m^{th} analytical region.

(23) IAI_{jm} = band area of the j^{th} potential interferant in the m^{th} analytical region, at its expected concentration (CPOT_j).

(24) IAV_{im} = average absorbance of the i^{th} analyte in the m^{th} analytical region, at its expected concentration (CPOT_j).

(25) ISC_i or k , indicated standard concentration = the concentration from the computerized analytical program for a single-compound reference spectrum for the i^{th} analyte or k^{th} known interferant.

(26) kPa = kilo-Pascal (see Pascal).

(27) L_S' = estimated sample absorption pathlength.

(28) L_R = reference absorption pathlength.

(29) L_S = actual sample absorption pathlength.

(30) MAU_i = mean of the MAU_{im} over the appropriate analytical regions.

(31) MAU_{im} , minimum analyte uncertainty = the calculated minimum concentration for which the analytical uncertainty limit (AU_i) in the measurement of the i^{th} analyte, based on spectral data in the m^{th} analytical region, can be maintained.

(32) MIU_j = mean of the MIU_{jm} over the appropriate analytical regions.

(33) MIU_{jm} , minimum interferant uncertainty = the calculated minimum concentration for which the analytical uncertainty limit CPOT_j/20 in the measurement of the j^{th} interferant, based on spectral data in the m^{th} analytical region, can be maintained.

(34) MIL, minimum instrumental linewidth = the minimum linewidth from the FTIR system, in wavenumbers.

NOTE: The MIL of a system may be determined by observing an absorption band known (through higher resolution examinations) to be narrower than indicated by the

system. The MIL is fundamentally limited by the retardation of the interferometer, but is also affected by other operational parameters (e.g., the choice of apodization).

(35) N_i = number of analytes.

(36) N_i = number of potential interferants.

(37) N_k = number of known interferants.

(38) N_{scan} = the number of scans averaged to obtain an interferogram.

(39) OFU_i = the overall fractional uncertainty in an analyte concentration determined in the analysis ($OFU_i = \text{MAX}[FRU_i, FCU_i, FAU_i, FMU_i]$).

(40) Pascal (Pa) = metric unit of static pressure, equal to one Newton per square meter; one atmosphere is equal to 101,325 Pa; 1/760 atmosphere (one Torr, or one millimeter Hg) is equal to 133.322 Pa.

(41) P_{min} = minimum pressure of the sampling system during the sampling procedure.

(42) P_S' = estimated sample pressure.

(43) P_R = reference pressure.

(44) P_S = actual sample pressure.

(45) RMS_{sm} = measured noise level of the FTIR system in the m^{th} analytical region.

(46) RMSD, root mean square difference = a measure of accuracy determined by the following equation:

$$RMSD = \sqrt{\left(\frac{1}{n}\right) \sum_{i=1}^n e_i^2}$$

Where:

n = the number of observations for which the accuracy is determined.

e_i = the difference between a measured value of a property and its mean value over the n observations.

NOTE: The RMSD value "between a set of n contiguous absorbance values (A_i) and the mean of the values" (A_M) is defined as

$$RMSD = \sqrt{\left(\frac{1}{n}\right) \sum_{i=1}^n (A_i - A_M)^2}$$

(47) RSA_i = the (calculated) final concentration of the i^{th} analyte.

(48) RSI_k = the (calculated) final concentration of the k^{th} known interferant.

(49) t_{scan} , scan time = time used to acquire a single scan, not including flyback.

(50) t_S , signal integration period = the period of time over which an interferogram is averaged by addition and scaling of individual scans. In terms of the number of scans N_{scan} and scan time t_{scan} , $t_S = N_{scan} t_{scan}$.

(51) t_{SR} = signal integration period used in recording reference spectra.

(52) t_{SS} = signal integration period used in recording sample spectra.

(53) T_R = absolute temperature of gases used in recording reference spectra.

(54) T_S = absolute temperature of sample gas as sample spectra are recorded.

(55) TP, Throughput = manufacturer's estimate of the fraction of the total infrared power transmitted by the absorption cell and transfer optics from the interferometer to the detector.

(56) V_{SS} = volume of the infrared absorption cell, including parts of attached tubing.

(57) W_{ik} = weight used to average over analytical regions k for quantities related to the analyte i ; see appendix D of this addendum.

APPENDIX B TO ADDENDUM TO METHOD 320—
IDENTIFYING SPECTRAL INTERFERENTS

B.1 General

B.1.1 Assume a fixed absorption pathlength equal to the value L_S' .

B.1.2 Use band area calculations to compare the relative absorption strengths of the analytes and potential interferents. In the m^{th} analytical region (FL_m to FU_m), use either rectangular or trapezoidal approximations to determine the band areas described below (see Reference A, sections A.3.1 through A.3.3). Document any baseline corrections applied to the spectra.

B.1.3 Use the average total absorbance of the analytes and potential interferents in each analytical region to determine whether the analytical region is suitable for analyte concentration determinations.

NOTE: The average absorbance in an analytical region is the band area divided by the width of the analytical region in wavenumbers. The average total absorbance in an analytical region is the sum of the av-

erage absorbances of all analytes and potential interferents.

B.2 Calculations

B.2.1 Prepare spectral representations of each analyte at the concentration $CL_i = (DL_i)(AU_i)$, where DL_i is the required detection limit and AU_i is the maximum permissible analytical uncertainty. For the m^{th} analytical region, calculate the band area (AAI_{im}) and average absorbance (AAV_{im}) from these scaled analyte spectra.

B.2.2 Prepare spectral representations of each potential interferent at its expected concentration (CPOT_{*i*}). For the m^{th} analytical region, calculate the band area (IAI_{jm}) and average absorbance (IAV_{jm}) from these scaled potential interferent spectra.

B.2.3 Repeat the calculation for each analytical region, and record the band area results in matrix form as indicated in Figure B.1.

B.2.4 If the band area of any potential interferent in an analytical region is greater than the one-half the band area of any analyte (i.e., $IAI_{jm} > 0.5 AAI_{im}$ for any pair ij and any m), classify the potential interferent as a known interferent. Label the known interferents $k = 1$ to K . Record the results in matrix form as indicated in Figure B.2.

B.2.5 Calculate the average total absorbance (AVT_m) for each analytical region and record the values in the last row of the matrix described in Figure B.2. Any analytical region where $AVT_m > 2.0$ is unsuitable.

FIGURE B.1 Presentation of Potential Interferant Calculations.

		Analytical Regions			
		1	M	
		Analyte Labels			
1	AAI ₁₁	AAI _{1M}		
.	.				
I	AAI _{I1}	AAI _{IM}		
		Potential Interferant Labels			
1	IAI ₁₁	IAI _{1M}		
.	.				
J	IAI _{J1}	IAI _{JM}		

FIGURE B.2 Presentation of Known Interferant Calculations

		Analytical Regions			
		1	M	
		Analyte Labels			
1	AAI ₁₁	AAI _{1M}		
.	.				
I	AAI _{I1}	AAI _{IM}		
		Known Interferant Labels			
1	IAI ₁₁	IAI _{1M}		
.	.				
K	IAI _{K1}	IAI _{KM}		
		323			
		Total Average Absorbance			
		AVT ₁		AVT _M	

APPENDIX C TO ADDENDUM TO METHOD 320—
ESTIMATING NOISE LEVELS

C.1 General

C.1.1 The root-mean-square (RMS) noise level is the standard measure of noise in this addendum. The RMS noise level of a contiguous segment of a spectrum is defined as the

RMS difference (RMSD) between the absorbance values which form the segment and the mean value of that segment (see appendix A of this addendum).

C.1.2 The RMS noise value in double-beam absorbance spectra is assumed to be inversely proportional to: (a) the square root of the signal integration period of the sample single beam spectra from which it is formed,

and (b) the total infrared power transmitted through the interferometer and absorption cell.

C.1.3 Practically, the assumption of C.1.2 allows the RMS noise level of a complete system to be estimated from the quantities described in sections C.1.3.1 through C.1.3.4:

C.1.3.1 RMS_{MAN} , the noise level of the system (in absorbance units), without the absorption cell and transfer optics, under those conditions necessary to yield the specified minimum instrumental linewidth, e.g., Jacquinot stop size.

C.1.3.2 t_{MAN} , the manufacturer's signal integration time used to determine RMS_{MAN} .

C.1.3.3 t_{SS} , the signal integration time for the analyses.

C.1.3.4 TP, the manufacturer's estimate of the fraction of the total infrared power transmitted by the absorption cell and transfer optics from the interferometer to the detector.

C.2 Calculations

C.2.1 Obtain the values of RMS_{MAN} , t_{MAN} , and TP from the manufacturers of the equipment, or determine the noise level by direct measurements with the completely constructed system proposed in section 4 of this addendum.

C.2.2 Calculate the noise value of the system (RMS_{EST}) using equation C.1.

$$RMS_{EST} = RMS_{MAN} TP \sqrt{\frac{t_{SS}}{t_{MAN}}} \quad (C.1)$$

APPENDIX D TO ADDENDUM TO METHOD 320—ESTIMATING MINIMUM CONCENTRATION MEASUREMENT UNCERTAINTIES (MAU AND MIU)

D.1 General

Estimate the minimum concentration measurement uncertainties for the i^{th} analyte (MAU_i) and j^{th} interferant (MIU_j) based on the spectral data in the m^{th} analytical region by comparing the analyte band area in the analytical region (AAI_{im}) and estimating or measuring the noise level of the system (RMS_{EST} or RMS_{SM}).

NOTE: For a single analytical region, the MAU or MIU value is the concentration of the analyte or interferant for which the band

area is equal to the product of the analytical region width (in wavenumbers) and the noise level of the system (in absorbance units). If data from more than one analytical region are used in the determination of an analyte concentration, the MAU or MIU is the mean of the separate MAU or MIU values calculated for each analytical region.

D.2 Calculations

D.2.1 For each analytical region, set $RMS = RMS_{SM}$ if measured (appendix G of this addendum), or set $RMS = RMS_{EST}$ if estimated (appendix C of this addendum).

D.2.2 For each analyte associated with the analytical region, calculate MAU_{im} using equation D.1.

$$MAU_{im} = (RMS) (DL_i) (AU_i) \frac{(FU_m - FL_m)}{AAI_{im}} \quad (D.1)$$

D.2.3 If only the m^{th} analytical region is used to calculate the concentration of the i^{th} analyte, set $MAU_i = MAU_{im}$.

D.2.4 If more than one analytical region is used to calculate the concentration of the i^{th} analyte, set MAU_i equal to the weighted mean of the appropriate MAU_{im} values calculated above; the weight for each term in the mean is equal to the fraction of the total wavenumber range used for the calculation

represented by each analytical region. Mathematically, if the set of analytical regions employed is $\{m'\}$, then the MAU for each analytical region is given by equation D.2.

$$MAU_i = \sum_{k \in \{m'\}} W_k MAU_{ik} \quad (D.2)$$

where the weight W_{ik} is defined for each term in the sum as

$$W_{ik} = (FM_k - FL_k) \left(\sum_{p \in \{m'\}} [FM_p - FL_p] \right)^{-1} \quad (D.3)$$

D.2.5 Repeat sections D.2.1 through D.2.4 of this appendix to calculate the analogous values MIU_j for the interferants $j = 1$ to J . Replace the value (AU_i) (DL_i) in equation D.1 with $CPOT/20$; replace the value AAI_m in equation D.1 with IAI_{jm} .

APPENDIX E TO ADDENDUM TO METHOD 320—
DETERMINING FRACTIONAL REPRODUCIBILITY
UNCERTAINTIES (FRU)

E.1 General

To estimate the reproducibility of the spectroscopic results of the system, compare the CTS spectra recorded before and after preparing the reference spectra. Compare the difference between the spectra to their average band area. Perform the calculation for each analytical region on the portions of the CTS spectra associated with that analytical region.

E.2 Calculations

E.2.1 The CTS spectra $\{R1\}$ consist of N spectra, denoted by S_{1i} , $i=1, N$. Similarly, the CTS spectra $\{R2\}$ consist of N spectra, de-

noted by S_{2i} , $i=1, N$. Each S_{ki} is the spectrum of a single compound, where i denotes the compound and k denotes the set $\{Rk\}$ of which S_{ki} is a member. Form the spectra S_3 according to $S_{3i} = S_{2i} - S_{1i}$ for each i . Form the spectra S_4 according to $S_{4i} = [S_{2i} + S_{1i}]/2$ for each i .

E.2.2 Each analytical region m is associated with a portion of the CTS spectra S_{2i} and S_{1i} , for a particular i , with lower and upper wavenumber limits FFL_m and FFU_m , respectively.

E.2.3 For each m and the associated i , calculate the band area of S_{4i} in the wavenumber range FFU_m to FFL_m . Follow the guidelines of section B.1.2 of this addendum for this band area calculation. Denote the result by BAV_m .

E.2.4 For each m and the associated i , calculate the RMSD of S_{3i} between the absorbance values and their mean in the wavenumber range FFU_m to FFL_m . Denote the result by $SRMS_m$.

E.2.5 For each analytical region m , calculate FM_m using equation E.1,

$$FM_m = SRMS_m (FFU_m - FFL_m) / BAV_m \quad (E.1)$$

E.2.6 If only the m^{th} analytical region is used to calculate the concentration of the i^{th} analyte, set $FRU_i = FM_m$.

E.2.7 If a number p_i of analytical regions are used to calculate the concentration of the i^{th} analyte, set FRU_i equal to the weighted mean of the appropriate FM_m values calculated according to section E.2.5. Mathematically, if the set of analytical regions employed is $\{m'\}$, then FRU_i is given by equation E.2,

$$FRU_i = \sum_{k \in \{m'\}} W_{ik} FM_k \quad (E.2)$$

where the W_{ik} are calculated as described in appendix D of this addendum.

APPENDIX F OF ADDENDUM TO METHOD 320—
DETERMINING FRACTIONAL CALIBRATION UN-
CERTAINTIES (FCU)

F.1 General

F.1.1 The concentrations yielded by the computerized analytical program applied to

each single-compound reference spectrum are defined as the indicated standard concentrations (ISC's). The ISC values for a single compound spectrum should ideally equal the accepted standard concentration (ASC) for one analyte or interferant, and should ideally be zero for all other compounds. Variations from these results are caused by errors in the ASC values, variations from the Beer's law (or modified Beer's law) model used to determine the concentrations, and noise in the spectra. When the first two effects dominate, the systematic nature of the errors is often apparent and the analyst shall take steps to correct them.

F.1.2 When the calibration error appears non-systematic, apply the procedures of sections F.2.1 through F.2.3 of this appendix to estimate the fractional calibration uncertainty (FCU) for each compound. The FCU is defined as the mean fractional error between the ASC and the ISC for all reference spectra with non-zero ASC for that compound. The FCU for each compound shall be less than the required fractional uncertainty specified in section 4.1 of this addendum.

F.1.3 The computerized analytical programs shall also be required to yield acceptably low concentrations for compounds with $ISC = 0$ when applied to the reference spectra. The ISC of each reference spectrum for each analyte or interferant shall not exceed that compound's minimum measurement uncertainty (MAU or MIU).

F.2 Calculations

F.2.1 Apply each analytical program to each reference spectrum. Prepare a similar table to that in Figure F.1 to present the ISC and ASC values for each analyte and interferant in each reference spectrum.

Maintain the order of reference file names and compounds employed in preparing Figure F.1.

F.2.2 For all reference spectra in Figure F.1, verify that the absolute values of the ISC's are less than the compound's MAU (for analytes) or MIU (for interferants).

F.2.3 For each analyte reference spectrum, calculate the quantity $(ASC - ISC)/ASC$. For each analyte, calculate the mean of these values (the FCU_i for the ith analyte) over all reference spectra. Prepare a similar table to that in Figure F.2 to present the FCU_i and analytical uncertainty limit (AU_i) for each analyte.

FIGURE F.1.—PRESENTATION OF ACCEPTED STANDARD CONCENTRATIONS (ASC'S) AND INDICATED STANDARD CONCENTRATIONS (ISC'S)

Compound name	Reference spectrum file name	ASC (ppm)	ISC (ppm)								
			Analytes			Interferants					
			i=1	j=1		I	J				

FIGURE F.2.—PRESENTATION OF FRACTIONAL CALIBRATION UNCERTAINTIES (FCU'S) AND ANALYTICAL UNCERTAINTIES (AU'S)

Analyte name	FCU (%)	AU (%)

APPENDIX G TO ADDENDUM TO METHOD 320—MEASURING NOISE LEVELS

G.1 General

The root-mean-square (RMS) noise level is the standard measure of noise. The RMS noise level of a contiguous segment of a spectrum is the RMSD between the absorbance values that form the segment and the mean value of the segment (see appendix A of this addendum).

G.2 Calculations

G.2.1 Evacuate the absorption cell or fill it with UPC grade nitrogen at approximately one atmosphere total pressure.

G.2.2 Record two single beam spectra of signal integration period t_{ss} .

G.2.3 Form the double beam absorption spectrum from these two single beam spectra, and calculate the noise level RMS_{sm} in the M analytical regions.

APPENDIX H OF ADDENDUM TO METHOD 320—DETERMINING SAMPLE ABSORPTION PATHLENGTH (L_s) AND FRACTIONAL ANALYTICAL UNCERTAINTY (FAU)

H.1 General

Reference spectra recorded at absorption pathlength (L_R), gas pressure (P_R), and gas absolute temperature (T_R) may be used to determine analyte concentrations in samples whose spectra are recorded at conditions different from that of the reference spectra, i.e., at absorption pathlength (L_s), absolute

temperature (T_S), and pressure (P_S). This appendix describes the calculations for estimating the fractional uncertainty (FAU) of this practice. It also describes the calculations for determining the sample absorption pathlength from comparison of CTS spectra, and for preparing spectra for further instrumental and procedural checks.

H.1.1 Before sampling, determine the sample absorption pathlength using least squares analysis. Determine the ratio L_S/L_R by comparing the spectral sets {R1□ and {R3□, which are recorded using the same CTS at L_S and L_R , and T_S and T_R , but both at P_R .

H.1.2 Determine the fractional analysis uncertainty (FAU) for each analyte by comparing a scaled CTS spectral set, recorded at L_S , T_S , and P_S , to the CTS reference spectra of the same gas, recorded at L_R , T_R , and P_R . Perform the quantitative comparison after recording the sample spectra, based on band areas of the spectra in the CTS absorbance band associated with each analyte.

H.2 Calculations

H.2.1 *Absorption Pathlength Determination.* Perform and document separate linear base-

line corrections to each analytical region in the spectral sets {R1□ and {R3□. Form a one-dimensional array A_R containing the absorbance values from all segments of {R1□ that are associated with the analytical regions; the members of the array are A_{Ri} , $i = 1, n$. Form a similar one-dimensional array A_S from the absorbance values in the spectral set {R3□; the members of the array are A_{Si} , $i = 1, n$. Based on the model $A_S = rA_R + E$, determine the least-squares estimate of r , the value of r which minimizes the square error E^2 . Calculate the sample absorption pathlength, L_S , using equation H.1,

$$L_S = r'(T_S/T_R)L_R \quad (\text{H.1})$$

H.2.2 *Fractional Analysis Uncertainty.* Perform and document separate linear baseline corrections to each analytical region in the spectral sets {R1□ and {R4□. Form the arrays A_S and A_R as described in section H.2.1 of this appendix, using values from {R1□ to form A_R , and values from {R4□ to form A_S . Calculate $NRMS_E$ and IA_{AV} using equations H.2 and H.3,

$$NRMS_E = \sqrt{\sum_{i=1}^n \left[A_{Si} - \left(\frac{T_R}{T_S} \right) \left(\frac{L_S}{L_R} \right) \left(\frac{P_S}{P_R} \right) A_{Ri} \right]^2} \quad (\text{H.2})$$

$$IA_{AV} = \frac{1}{2} \sum_{i=1}^n \left[A_{Si} + \left(\frac{T_R}{T_S} \right) \left(\frac{L_S}{L_R} \right) \left(\frac{P_S}{P_R} \right) A_{Ri} \right] \quad (\text{H.3})$$

The fractional analytical uncertainty, FAU, is given by equation H.4,

$$FAU = \frac{NRMS_E}{IA_{AV}} \quad (\text{H.4})$$

APPENDIX I TO ADDENDUM TO METHOD 320— DETERMINING FRACTIONAL MODEL UNCERTAINTIES (FMU)

I.1 General

To prepare analytical programs for FTIR analyses, the sample constituents must first be assumed. The calculations in this appendix, based upon a simulation of the sample spectrum, shall be used to verify the appropriateness of these assumptions. The simulated spectra consist of the sum of single compound reference spectra scaled to represent their contributions to the sample absorbance spectrum; scaling factors are based on the indicated standard concentrations

(ISC) and measured (sample) analyte and interferant concentrations, the sample and reference absorption pathlengths, and the sample and reference gas pressures. No bandshape correction for differences in the temperature of the sample and reference spectra gases is made; such errors are included in the FMU estimate. The actual and simulated sample spectra are quantitatively compared to determine the fractional model uncertainty; this comparison uses the reference spectra band areas and residuals in the difference spectrum formed from the actual and simulated sample spectra.

I.2 Calculations

I.2.1 For each analyte (with scaled concentration RSA_i), select a reference spectrum SA_i with indicated standard concentration ISC_i . Calculate the scaling factors, RA_i , using equation I.1,

$$RA_i = \frac{T_R L_S P_S RSA_i}{T_S L_R P_R ISC_i} \quad (I.1)$$

Form the spectra SAC_i by scaling each SA_i by the factor RA_i .

I.2.2 For each interferant, select a reference spectrum SI_k with indicated standard concentration ISC_k . Calculate the scaling factors, RI_k , using equation I.2.

$$RI_k = \frac{T_R L_S P_S RSI_k}{T_S L_R P_R ISC_k} \quad (I.2)$$

Form the spectra SIC_k by scaling each SI_k by the factor RI_k .

I.2.3 For each analytical region, determine by visual inspection which of the spec-

tra SAC_i and SIC_k exhibit absorbance bands within the analytical region. Subtract each spectrum SAC_i and SIC_k exhibiting absorbance from the sample spectrum S_s to form the spectrum SUB_s . To save analysis time and to avoid the introduction of unwanted noise into the subtracted spectrum, it is recommended that the calculation be made (1) only for those spectral data points within the analytical regions, and (2) for each analytical region separately using the original spectrum S_s .

I.2.4 For each analytical region m , calculate the RMSD of SUB_s between the absorbance values and their mean in the region FFU_m to FFL_m . Denote the result by $RMSS_m$.

I.2.5 For each analyte i , calculate FM_m , using equation I.3.

$$FM_m = \frac{RMSS_m (FFU_m - FFL_m) AU_i DL_i}{AAI_i RSA_i} \quad (I.3)$$

for each analytical region associated with the analyte.

I.2.6 If only the m^{th} analytical region is used to calculate the concentration of the i^{th} analyte, set $FMU_i = FM_m$.

I.2.7 If a number of analytical regions are used to calculate the concentration of the i^{th} analyte, set FM_i equal to the weighted mean of the appropriate FM_m values calculated using equation I-3. Mathematically, if the set of analytical regions employed is $\{m\}$, then the fractional model uncertainty, FMU_i , is given by equation I.4.

$$FMU_i = \sum_{k \in \{m\}} W_{ik} FM_k \quad (I.4)$$

where W_{ik} is calculated as described in appendix D of this addendum.

APPENDIX J OF ADDENDUM TO METHOD 320—DETERMINING OVERALL CONCENTRATION UNCERTAINTIES (OCU)

The calculations in this addendum estimate the measurement uncertainties for various FTIR measurements. The lowest possible overall concentration uncertainty (OCU) for an analyte is its MAU value, which is an estimate of the absolute concentration uncertainty when spectral noise dominates the measurement error. However, if the product of the largest fractional concentration uncertainty (FRU, FCU, FAU, or FMU) and the measured concentration of an analyte exceeds the MAU for the analyte, then the OCU is this product. In mathematical terms, set $OFU_i = \text{MAX}\{FRU_i, FCU_i, FAU_i, FMU_i\}$ and $OCU_i = \text{MAX}\{RSA_i * OFU_i, MAU_i\}$.

TEST METHOD 321—MEASUREMENT OF GASEOUS HYDROGEN CHLORIDE EMISSIONS AT PORTLAND CEMENT KILNS BY FOURIER TRANSFORM INFRARED (FTIR) SPECTROSCOPY

1.0 Introduction

This method should be performed by those persons familiar with the operation of Fourier Transform Infrared (FTIR) instrumentation in the application to source sampling. This document describes the sampling procedures for use in the application of FTIR spectrometry for the determination of vapor phase hydrogen chloride (HCl) concentrations both before and after particulate matter control devices installed at portland cement kilns. A procedure for analyte spiking is included for quality assurance. This method is considered to be self validating provided that the requirements listed in section 9 of this method are followed. The analytical procedures for interpreting infrared spectra from emission measurements are described in the "Protocol For The Use of Extractive Fourier Transform Infrared (FTIR) Spectrometry in Analyses of Gaseous Emissions From Stationary Industrial Sources", included as an addendum to proposed Method 320 of this appendix (hereafter referred to as the "FTIR Protocol"). References 1 and 2 describe the use of FTIR spectrometry in field measurements. Sample transport presents the principal difficulty in directly measuring HCl emissions. This identical problem must be overcome by any extractive measurement method. HCl is reactive and water soluble.

The sampling system must be adequately designed to prevent sample condensation in the system.

1.1 Scope and Application

This method is specifically designed for the application of FTIR Spectrometry in extractive measurements of gaseous HCl concentrations in portland cement kiln emissions.

1.2 Applicability

This method applies to the measurement of HCl [CAS No. 7647-01-0]. This method can be

applied to the determination of HCl concentrations both before and after particulate matter control devices installed at portland cement manufacturing facilities. This method applies to either continuous flow through measurement (with isolated sample analysis) or grab sampling (batch analysis). HCl is measured using the mid-infrared spectral region for analysis (about 400 to 4000 cm⁻¹ or 25 to 2.5 μm). Table 1 lists the suggested analytical region for quantification of HCl taking the interference from water vapor into consideration.

TABLE 1.—EXAMPLE ANALYTICAL REGION FOR HCL

Compound	Analytical region (cm ⁻¹)	Potential interferants
Hydrogen chloride	2679–2840	Water.

1.3 Method Range and Sensitivity

1.3.1 The analytical range is determined by the instrumental design and the composition of the gas stream. For practical purposes there is no upper limit to the range because the pathlength may be reduced or the sample may be diluted. The lower detection range depends on (1) the absorption coefficient of the compound in the analytical frequency region, (2) the spectral resolution, (3) the interferometer sampling time, (4) the detector sensitivity and response, and (5) the absorption pathlength.

1.3.2 The practical lower quantification range is usually higher than the instrument sensitivity allows and is dependent upon (1) the presence of interfering species in the exhaust gas including H₂O, CO₂, and SO₂, (2) analyte losses in the sampling system, (3) the optical alignment of the gas cell and transfer optics, and (4) the quality of the reflective surfaces in the cell (cell throughput). Under typical test conditions (moisture content of up to 30% and CO₂ concentrations from 1 to 15 percent), a 22 meter path length cell with a suitable sampling system may achieve a lower quantification range of from 1 to 5 ppm for HCl.

1.4 Data Quality Objectives

1.4.1 In designing or configuring the analytical system, data quality is determined by measuring of the root mean square deviation (RMSD) of the absorbance values within a chosen spectral (analytical) region. The RMSD provides an indication of the signal-to-noise ratio (S/N) of the spectral baseline. Appendix D of the FTIR Protocol (the addendum to Method 320 of this appendix) presents a discussion of the relationship between the RMSD, lower detection limit, DL_i, and analytical uncertainty, AU_i. It is important to

consider the target analyte quantification limit when performing testing with FTIR instrumentation, and to optimize the system to achieve the desired detection limit.

1.4.2 Data quality is determined by measuring the root mean square (RMS) noise level in each analytical spectral region (appendix C of the FTIR Protocol). The RMS noise is defined as the root mean square deviation (RMSD) of the absorbance values in an analytical region from the mean absorbance value in the same region. Appendix D of the FTIR Protocol defines the minimum analyte uncertainty (MAU), and how the RMSD is used to calculate the MAU. The MAU_{im} is the minimum concentration of the ith analyte in the mth analytical region for which the analytical uncertainty limit can be maintained. Table 2 presents example values of AU and MAU using the analytical region presented in Table 1.

TABLE 2.—EXAMPLE PRE-TEST PROTOCOL CALCULATIONS FOR HYDROGEN CHLORIDE

	HCl
Reference concentration (ppm-meters)/K	11.2
Reference Band area	2.881
DL (ppm-meters)/K	0.1117
AU	0.2
CL (DL × AU)	0.02234
FL (cm ⁻¹)	2679.83
FU (cm ⁻¹)	2840.93
FC (cm ⁻¹)	2760.38
AAI (ppm-meters)/K	0.06435
RMSD	2.28E-03
MAU (ppm-meters)/K	1.28E-01
MAU ppm at 22 meters and 250 °F02284

2.0 Summary of Method

2.1 Principle

See Method 320 of this appendix. HCl can also undergo rotation transitions by absorbing energy in the far-infrared spectral region. The rotational transitions are superimposed on the vibrational fundamental to give a series of lines centered at the fundamental vibrational frequency, 2885 cm^{-1} . The frequencies of absorbance and the pattern of rotational/vibrational lines are unique to HCl. When this distinct pattern is observed in an infrared spectrum of an unknown sample, it unequivocally identifies HCl as a component of the mixture. The infrared spectrum of HCl is very distinctive and cannot be confused with the spectrum of any other compound. See Reference 6.

2.2 *Sampling and Analysis.* See Method 320 of this appendix.

2.3 *Operator Requirements.* The analyst must have knowledge of spectral patterns to choose an appropriate absorption path length or determine if sample dilution is necessary. The analyst should also understand FTIR instrument operation well enough to choose instrument settings that are consistent with the objectives of the analysis.

3.0 Definitions

See appendix A of the FTIR Protocol.

4.0 Interferences

This method will not measure HCl under conditions: (1) where the sample gas stream can condense in the sampling system or the instrumentation, or (2) where a high moisture content sample relative to the analyte concentrations imparts spectral interference due to the water vapor absorbance bands. For measuring HCl the first (sampling) consideration is more critical. Spectral interference from water vapor is not a significant problem except at very high moisture levels and low HCl concentrations.

4.1 *Analytical Interferences.* See Method 320 of this appendix.

4.1.1 *Background Interferences.* See Method 320 of this appendix.

4.1.2 *Spectral interferences.* Water vapor can present spectral interference for FTIR gas analysis of HCl. Therefore, the water vapor in the spectra of kiln gas samples must be accounted for. This means preparing at least one spectrum of a water vapor sample where the moisture concentration is close to that in the kiln gas.

4.2 *Sampling System Interferences.* The principal sampling system interferant for measuring HCl is water vapor. Steps must be taken to ensure that no condensation forms anywhere in the probe assembly, sample lines, or analytical instrumentation. Cold spots anywhere in the sampling system must

be avoided. The extent of sampling system bias in the FTIR analysis of HCl depends on concentrations of potential interferants, moisture content of the gas stream, temperature of the gas stream, temperature of sampling system components, sample flow rate, and reactivity of HCl with other species in the gas stream (e.g., ammonia). For measuring HCl in a wet gas stream the temperatures of the gas stream, sampling components, and the sample flow rate are of primary importance. Analyte spiking with HCl is performed to demonstrate the integrity of the sampling system for transporting HCl vapor in the flue gas to the FTIR instrument. See section 9 of this method for a complete description of analyte spiking.

5.0 Safety

5.1 Hydrogen chloride vapor is corrosive and can cause irritation or severe damage to respiratory system, eyes and skin. Exposure to this compound should be avoided.

5.2 This method may involve sampling at locations having high positive or negative pressures, or high concentrations of hazardous or toxic pollutants, and can not address all safety problems encountered under these diverse sampling conditions. It is the responsibility of the tester(s) to ensure proper safety and health practices, and to determine the applicability of regulatory limitations before performing this test method. Leak-check procedures are outlined in section 8.2 of Method 320 of this appendix.

6.0 Equipment and Supplies

NOTE: Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

6.1 *FTIR Spectrometer and Detector.* An FTIR Spectrometer system (interferometer, transfer optics, gas cell and detector) having the capability of measuring HCl to the predetermined minimum detectable level required (see section 4.1.3 of the FTIR Protocol). The system must also include an accurate means to control and/or measure the temperature of the FTIR gas analysis cell, and a personal computer with compatible software that provides real-time updates of the spectral profile during sample and spectral collection.

6.2 *Pump.* Capable of evacuating the FTIR cell volume to 1 Torr (133.3 Pascals) within two minutes (for batch sample analysis).

6.3 *Mass Flow Meters/Controllers.* To accurately measure analyte spike flow rate, having the appropriate calibrated range and a stated accuracy of ± 2 percent of the absolute measurement value. This device must be calibrated with the major component of the calibration/spike gas (e.g., nitrogen) using an NIST traceable bubble meter or equivalent. Single point calibration checks should be performed daily in the field. When spiking

HCl, the mass flow meter/controller should be thoroughly purged before and after introduction of the gas to prevent corrosion of the interior parts.

6.4 *Polytetrafluoroethane tubing.* Diameter and length suitable to connect cylinder regulators.

6.5 *Stainless Steel tubing.* Type 316 of appropriate length and diameter for heated connections.

6.6 *Gas Regulators.* Purgeable HCl regulator.

6.7 *Pressure Gauge.* Capable of measuring pressure from 0 to 1000 Torr (133.3 Pa=1 Torr) within ± 5 percent.

6.8 *Sampling Probe.* Glass, stainless steel or other appropriate material of sufficient length and physical integrity to sustain heating, prevent adsorption of analytes and capable of reaching gas sampling point.

6.9 *Sampling Line.* Heated 180 °C (360 °F) and fabricated of either stainless steel, polytetrafluoroethane or other material that prevents adsorption of HCl and transports effluent to analytical instrumentation. The extractive sample line must have the capability to transport sample gas to the analytical components as well as direct heated calibration spike gas to the calibration assembly located at the sample probe. It is important to minimize the length of heated sample line.

6.10 *Particulate Filters.* A sintered stainless steel filter rated at 20 microns or greater may be placed at the inlet of the probe (for removal of large particulate matter). A heated filter (Balston or equivalent) rated at 1 micron is necessary for primary particulate matter removal, and shall be placed immediately after the heated probe. The filter/filter holder temperature should be maintained at 180 °C (360 °F).

6.11 *Calibration/Analyte Spike Assembly.* A heated three-way valve assembly (or equivalent) to introduce surrogate spikes into the sampling system at the outlet of the probe before the primary particulate filter.

6.12 *Sample Extraction Pump.* A leak-free heated head pump (KNF Neuberger or equivalent) capable of extracting sample effluent through entire sampling system at a rate which prevents analyte losses and minimizes analyzer response time. The pump should have a heated by-pass and may be placed either before the FTIR instrument or after. If the sample pump is located upstream of the FTIR instrument, it must be fabricated from materials non-reactive to HCl. The sampling system and FTIR measurement system shall allow the operator to obtain at least six sample spectra during a one-hour period.

6.13 *Barometer.* For measurement of barometric pressure.

6.14 *Gas Sample Manifold.* A distribution manifold having the capabilities listed in sections 6.14.1 through 6.14.4;

6.14.1 Delivery of calibration gas directly to the analytical instrumentation;

6.14.2 Delivery of calibration gas to the sample probe (system calibration or analyte spike) via a heated traced sample line;

6.14.3 Delivery of sample gas (kiln gas, spiked kiln gas, or system calibrations) to the analytical instrumentation;

6.14.4 Delivery (optional) of a humidified nitrogen sample stream.

6.15 *Flow Measurement Device.* Type S Pitot tube (or equivalent) and Magnahelic set for measurement of volumetric flow rate.

7.0 Reagents and Standards

HCl can be purchased in a standard compressed gas cylinder. The most stable HCl cylinder mixture available has a concentration certified at ± 5 percent. Such a cylinder is suitable for performing analyte spiking because it will provide reproducible samples. The stability of the cylinder can be monitored over time by periodically performing direct FTIR analysis of cylinder samples. It is recommended that a 10-50 ppm cylinder of HCl be prepared having from 2-5 ppm SF₆ as a tracer compound. (See sections 7.1 through 7.3 of Method 320 of this appendix for a complete description of the use of existing HCl reference spectra. See section 9.1 of Method 320 of this appendix for a complete discussion of standard concentration selection.)

8.0 Sample Collection, Preservation and Storage

See also Method 320 of this appendix.

8.1 *Pretest.* A screening test is ideal for obtaining proper data that can be used for preparing analytical program files. Information from literature surveys and source personnel is also acceptable. Information about the sampling location and gas stream composition is required to determine the optimum sampling system configuration for measuring HCl. Determine the percent moisture of the kiln gas by Method 4 of appendix A to part 60 of this chapter or by performing a wet bulb/dry bulb measurement. Perform a preliminary traverse of the sample duct or stack and select the sampling point(s). Acquire an initial spectrum and determine the optimum operational pathlength of the instrument.

8.2 *Leak-Check.* See Method 320 of this appendix, section 8.2 for direction on performing leak-checks.

8.3 *Background Spectrum.* See Method 320 of this appendix, section 8.5 for direction in background spectral acquisition.

8.4 *Pre-Test Calibration Transfer Standard (Direct Instrument Calibration).* See Method 320 of this appendix, section 8.3 for direction in CTS spectral acquisition.

8.5 *Pre-Test System Calibration.* See Method 320 of this appendix, sections 8.6.1 through

8.6.2 for direction in performing system calibration.

8.6 Sampling

8.6.1 *Extractive System.* An extractive system maintained at 180 °C (360 °F) or higher which is capable of directing a total flow of at least 12 L/min to the sample cell is required (References 1 and 2). Insert the probe into the duct or stack at a point representing the average volumetric flow rate and 25 percent of the cross sectional area. Co-locate an appropriate flow monitoring device with the sample probe so that the flow rate is recorded at specified time intervals during emission testing (e.g., differential pressure measurements taken every 10 minutes during each run).

8.6.2 *Batch Samples.* Evacuate the absorbance cell to 5 Torr (or less) absolute pressure before taking first sample. Fill the cell with kiln gas to ambient pressure and record the infrared spectrum, then evacuate the cell until there is no further evidence of infrared absorption. Repeat this procedure, collecting a total of six separate sample spectra within a 1-hour period.

8.6.3 *Continuous Flow Through Sampling.* Purge the FTIR cell with kiln gas for a time period sufficient to equilibrate the entire sampling system and FTIR gas cell. The time required is a function of the mechanical response time of the system (determined by performing the system calibration with the CTS gas or equivalent), and by the chemical reactivity of the target analytes. If the effluent target analyte concentration is not variable, observation of the spectral up-date of the flowing gas sample should be performed until equilibration of the sample is achieved. Isolate the gas cell from the sample flow by directing the purge flow to vent. Record the spectrum and pressure of the sample gas. After spectral acquisition, allow the sample gas to purge the cell with at least three volumes of kiln gas. The time required to adequately purge the cell with the required volume of gas is a function of (1) cell volume, (2) flow rate through the cell, and (3) cell design. It is important that the gas introduction and vent for the FTIR cell provides a complete purge through the cell.

8.6.4 *Continuous Sampling.* In some cases it is possible to collect spectra continuously while the FTIR cell is purged with sample gas. The sample integration time, t_{ss} , the sample flow rate through the gas cell, and the sample integration time must be chosen so that the collected data consist of at least 10 spectra with each spectrum being of a separate cell volume of flue gas. Sampling in this manner may only be performed if the native source analyte concentrations do not affect the test results.

8.7 Sample Conditioning

8.7.1 *High Moisture Sampling.* Kiln gas emitted from wet process cement kilns may contain 3- to 40 percent moisture. Zinc selenide windows or the equivalent should be used when attempting to analyze hot/wet kiln gas under these conditions to prevent dissolution of water soluble window materials (e.g., KBr).

8.7.2 *Sample Dilution.* The sample may be diluted using an in-stack dilution probe, or an external dilution device provided that the sample is not diluted below the instrument's quantification range. As an alternative to using a dilution probe, nitrogen may be dynamically spiked into the effluent stream in the same manner as analyte spiking. A constant dilution rate shall be maintained throughout the measurement process. It is critical to measure and verify the exact dilution ratio when using a dilution probe or the nitrogen spiking approach. Calibrating the system with a calibration gas containing an appropriate tracer compound will allow determination of the dilution ratio for most measurement systems. The tester shall specify the procedures used to determine the dilution ratio, and include these calibration results in the report.

8.8 *Sampling QA, Data Storage and Reporting.* See the FTIR Protocol. Sample integration times shall be sufficient to achieve the required signal-to-noise ratio, and all sample spectra should have unique file names. Two copies of sample interferograms and processed spectra will be stored on separate computer media. For each sample spectrum the analyst must document the sampling conditions, the sampling time (while the cell was being filled), the time the spectrum was recorded, the instrumental conditions (path length, temperature, pressure, resolution, integration time), and the spectral file name. A hard copy of these data must be maintained until the test results are accepted.

8.9 *Signal Transmittance.* Monitor the signal transmittance through the instrumental system. If signal transmittance (relative to the background) drops below 95 percent in any spectral region where the sample does not absorb infrared energy, then a new background spectrum must be obtained.

8.10 *Post-test CTS.* After the sampling run completion, record the CTS spectrum. Analysis of the spectral band area used for quantification from pre- and post-test CTS spectra should agree to within ± 5 percent or corrective action must be taken.

8.11 *Post-test QA.* The sample spectra shall be inspected immediately after the run to verify that the gas matrix composition was close to the assumed gas matrix, (this is necessary to account for the concentrations of the interferants for use in the analytical analysis programs), and to confirm that the

sampling and instrumental parameters were appropriate for the conditions encountered.

9.0 Quality Control

Use analyte spiking to verify the effectiveness of the sampling system for the target compounds in the actual kiln gas matrix. QA spiking shall be performed before and after each sample run. QA spiking shall be performed after the pre- and post-test CTS direct and system calibrations. The system biases calculated from the pre- and post-test dynamic analyte spiking shall be within ± 30 percent for the spiked surrogate analytes for the measurements to be considered valid. See sections 9.3.1 through 9.3.2 for the requisite calculations. Measurement of the undiluted spike (direct-to-cell measurement) involves sending dry, spike gas to the FTIR cell, filling the cell to 1 atmosphere and obtaining the spectrum of this sample. The direct-to-cell measurement should be performed before each analyte spike so that the recovery of the dynamically spiked analytes may be calculated. Analyte spiking is only effective for assessing the integrity of the sampling system when the concentration of HCl in the source does not vary substantially. Any attempt to quantify an analyte recovery in a variable concentration matrix will result in errors in the expected concentration of the spiked sample. If the kiln gas target analyte concentrations vary by more than ± 5 percent (or 5 ppm, whichever is greater) in the time required to acquire a sample spectrum, it may be necessary to: (1) Use a dual sample probe approach, (2) use two independent FTIR measurement systems, (3) use alternate QA/QC procedures, or (4) postpone testing until stable emission concentrations are achieved. (See section 9.2.3 of this method). It is recommended that a laboratory evaluation be performed before attempting to employ this method under actual field conditions. The laboratory evaluation shall include (1) performance of all applicable calculations in section 4 of the FTIR Protocol; (2) simulated analyte spiking experiments in dry (ambient) and humidified sample matrices using HCl; and (3) performance of bias (recovery) calculations from analyte spiking experiments. It is not necessary to perform a laboratory evaluation before every field test. The purpose of the laboratory study is to demonstrate that the actual instrument and sampling system configuration used in field testing meets the requirements set forth in this method.

9.1 *Spike Materials.* Perform analyte spiking with an HCl standard to demonstrate the integrity of the sampling system.

9.1.1 An HCl standard of approximately 50 ppm in a balance of ultra pure nitrogen is recommended. The SF₆ (tracer) concentration shall be 2 to 5 ppm depending upon the measurement pathlength. The spike ratio

(spike flow/total flow) shall be no greater than 1:10, and an ideal spike concentration should approximate the native effluent concentration.

9.1.2 The ideal spike concentration may not be achieved because the target concentration cannot be accurately predicted prior to the field test, and limited calibration standards will be available during testing. Therefore, practical constraints must be applied that allow the tester to spike at an anticipated concentration. For these tests, the analyte concentration contributed by the HCl standard spike should be 1 to 5 ppm or should more closely approximate the native concentration if it is greater.

9.2 Spike Procedure

9.2.1 A spiking/sampling apparatus is shown in Figure 2. Introduce the spike/tracer gas mixture at a constant flow (± 2 percent) rate at approximately 10 percent of the total sample flow. (For example, introduce the surrogate spike at 1 L/min 20 cc/min, into a total sample flow rate of 10 L/min). The spike must be pre-heated before introduction into the sample matrix to prevent a localized condensation of the gas stream at the spike introduction point. A heated sample transport line(s) containing multiple transport tubes within the heated bundle may be used to spike gas up through the sampling system to the spike introduction point. Use a calibrated flow device (e.g., mass flow meter/controller), to monitor the spike flow as indicated by a calibrated flow meter or controller, or alternately, the SF₆ tracer ratio may be calculated from the direct measurement and the diluted measurement. It is often desirable to use the tracer approach in calculating the spike/total flow ratio because of the difficulty in accurately measuring hot/wet total flow. The tracer technique has been successfully used in past validation efforts (Reference 1).

9.2.2 Perform a direct-to-cell measurement of the dry, undiluted spike gas. Introduce the spike directly to the FTIR cell, bypassing the sampling system. Fill cell to 1 atmosphere and collect the spectrum of this sample. Ensure that the spike gas has equilibrated to the temperature of the measurement cell before acquisition of the spectra. Inspect the spectrum and verify that the gas is dry and contains negligible CO₂. Repeat the process to obtain a second direct-to-cell measurement. Analysis of spectral band areas for HCl from these duplicate measurements should agree to within ± 5 percent of the mean.

9.2.3 *Analyte Spiking.* Determine whether the kiln gas contains native concentrations of HCl by examination of preliminary spectra. Determine whether the concentration varies significantly with time by observing a continuously up-dated spectrum of sample gas in the flow-through sampling mode. If

the concentration varies by more than ± 5 percent during the period of time required to acquire a spectra, then an alternate approach should be used. One alternate approach uses two sampling lines to convey sample to the gas distribution manifold. One of the sample lines is used to continuously extract unspiked kiln gas from the source. The other sample line serves as the analyte spike line. One FTIR system can be used in this arrangement. Spiked or unspiked sample gas may be directed to the FTIR system from the gas distribution manifold, with the need to purge only the components between the manifold and the FTIR system. This approach minimizes the time required to acquire an equilibrated sample of spiked or unspiked kiln gas. If the source varies by more than ± 5 percent (or 5 ppm, whichever is greater) in the time it takes to switch from the unspiked sample line to the spiked sample line, then analyte spiking may not be a feasible means to determine the effectiveness of the sampling system for the HCl in the sample matrix. A second alternative is to use two completely independent FTIR measurement systems. One system would measure unspiked samples while the other system would measure the spiked samples. As a last option, (where no other alternatives can be used) a humidified nitrogen stream may be generated in the field which approximates the moisture content of the kiln gas. Analyte spiking into this humidified stream can be employed to assure that the sampling system is adequate for transporting the HCl to the FTIR instrumentation.

9.2.3.1 Adjust the spike flow rate to approximately 10 percent of the total flow by metering spike gas through a calibrated mass flowmeter or controller. Allow spike flow to equilibrate within the sampling system before analyzing the first spiked kiln gas samples. A minimum of two consecutive spikes are required. Analysis of the spectral band area used for quantification should agree to within ± 5 percent or corrective action must be taken.

9.2.3.2 After QA spiking is completed, the sampling system components shall be purged with nitrogen or dry air to eliminate traces of the HCl compound from the sampling system components. Acquire a sample spectra of the nitrogen purge to verify the absence of the calibration mixture.

9.2.3.3 Analyte spiking procedures must be carefully executed to ensure that meaningful measurements are achieved. The requirements of sections 9.2.3.3.1 through 9.2.3.3.4 shall be met.

9.2.3.3.1 The spike must be in the vapor phase, dry, and heated to (or above) the kiln gas temperature before it is introduced to the kiln gas stream.

9.2.3.3.2 The spike flow rate must be constant and accurately measured.

9.2.3.3.3 The total flow must also be measured continuously and reliably or the dilution ratio must otherwise be verified before and after a run by introducing a spike of a non-reactive, stable compound (i.e., tracer).

9.2.3.3.4 The tracer must be inert to the sampling system components, not contained in the effluent gas, and readily detected by the analytical instrumentation. Sulfur hexafluoride (SF_6) has been used successfully (References 1 and 2) for this purpose.

9.3 Calculations

9.3.1 *Recovery.* Calculate the percent recovery of the spiked analytes using equations 1 and 2.

$$\%R = 100 \times \frac{S_m - S_u(1 - DF)}{DF \times C_s} \quad (1)$$

S_m = Mean concentration of the analyte spiked effluent samples (observed).

$$C_e = DF \times C_s + S_u(1 - DF) \quad (2)$$

C_e = Expected concentration of the spiked samples (theoretical).

D_f = dilution Factor (Total flow/Spike flow).
total flow = spike flow plus effluent flow.

C_s = cylinder concentration of spike gas.

S_u = native concentration of analytes in unspiked samples.

The spike dilution factor may be confirmed by measuring the total flow and the spike flow directly. Alternately, the spike dilution can be verified by comparing the concentration of the tracer compound in the spiked samples (diluted) to the tracer concentration in the direct (undiluted) measurement of the spike gas.

If SF_6 is the tracer gas, then

$$D_f = [\text{SF}_6]_{\text{spike}} / [\text{SF}_6]_{\text{direct}} \quad (3)$$

$[\text{SF}_6]_{\text{spike}}$ = the diluted SF_6 concentration measured in a spiked sample.

$[\text{SF}_6]_{\text{direct}}$ = the SF_6 concentration measured directly.

9.3.2 *Bias.* The bias may be determined by the difference between the observed spike value and the expected response (i.e., the equivalent concentration of the spiked material plus the analyte concentration adjusted for spike dilution). Bias is defined by section 6.3.1 of EPA Method 301 of this appendix (Reference 8) as,

$$B = S_m - C_e \quad (4)$$

Where:

B = Bias at spike level.

S_m = Mean concentration of the analyte spiked samples.

C_e = Expected concentration of the analyte in spiked samples.

Acceptable recoveries for analyte spiking are ± 30 percent. Application of correction factors

to the data based upon bias and recovery calculations is subject to the approval of the Administrator.

10.0 Calibration and Standardization

10.1 *Calibration transfer standards (CTS).* The EPA Traceability Protocol gases or NIST traceable standards, with a minimum accuracy of ± 2 percent shall be used. For other requirements of the CTS, see the FTIR Protocol section 4.5.

10.2 *Signal-to-Noise Ratio (S/N).* The S/N shall be less than the minimum acceptable measurement uncertainty in the analytical regions to be used for measuring HCl.

10.3 *Absorbance Pathlength.* Verify the absorbance path length by comparing CTS spectra to reference spectra of the calibration gas(es).

10.4 *Instrument Resolution.* Measure the line width of appropriate CTS band(s) to verify instrumental resolution.

10.5 *Apodization Function.* Choose the appropriate apodization function. Determine any appropriate mathematical transformations that are required to correct instrumental errors by measuring the CTS. Any mathematical transformations must be documented and reproducible. Reference 9

provides additional information about FTIR instrumentation.

11.0 Analytical Procedure

A full description of the analytical procedures is given in sections 4.6–4.11, sections 5, 6, and 7, and the appendices of the FTIR Protocol. Additional description of quantitative spectral analysis is provided in References 10 and 11.

12.0 Data Analysis and Calculations

Data analysis is performed using appropriate reference spectra whose concentrations can be verified using CTS spectra. Various analytical programs (References 10 and 11) are available to relate sample absorbance to a concentration standard. Calculated concentrations should be verified by analyzing spectral baselines after mathematically subtracting scaled reference spectra from the sample spectra. A full description of the data analysis and calculations may be found in the FTIR Protocol (sections 4.0, 5.0, 6.0 and appendices).

12.1 Calculated concentrations in sample spectra are corrected for differences in absorption pathlength between the reference and sample spectra by

$$C_{\text{corr}} = (L_r/L_s) \times (T_s/T_r) \times (C_{\text{calc}}) \quad (5)$$

Where:

C_{corr} = The pathlength corrected concentration.

C_{calc} = The initial calculated concentration (output of the multicomponent analysis program designed for the compound).

L_r = The pathlength associated with the reference spectra.

L_s = The pathlength associated with the sample spectra.

T_s = The absolute temperature (K) of the sample gas.

T_r = The absolute temperature (K) at which reference spectra were recorded.

12.2 The temperature correction in equation 5 is a volumetric correction. It does not account for temperature dependence of rotational-vibrational relative line intensities. Whenever possible, the reference spectra used in the analysis should be collected at a temperature near the temperature of the FTIR cell used in the test to minimize the calculated error in the measurement (FTIR Protocol, appendix D). Additionally, the analytical region chosen for the analysis should be sufficiently broad to minimize errors caused by small differences in relative line intensities between reference spectra and the sample spectra.

13.0 Method Performance

A description of the method performance may be found in the FTIR Protocol. This method is self validating provided the results meet the performance specification of the QA spike in sections 9.0 through 9.3 of this method.

14.0 Pollution Prevention

This is a gas phase measurement. Gas is extracted from the source, analyzed by the instrumentation, and discharged through the instrument vent.

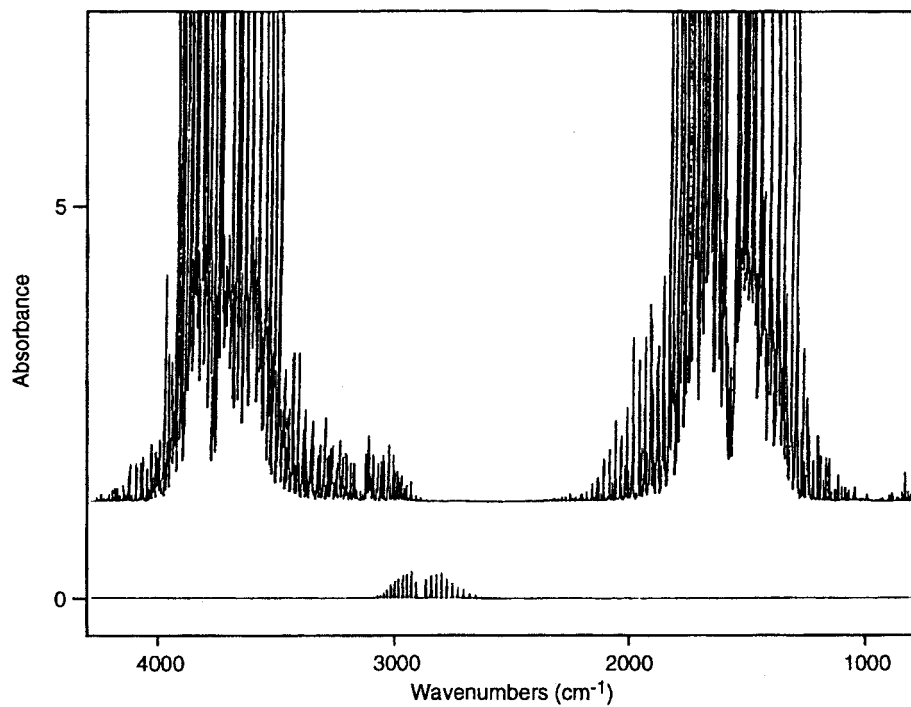
15.0 Waste Management

Gas standards of HCl are handled according to the instructions enclosed with the material safety data sheet.

16.0 References

1. "Laboratory and Field Evaluation of a Methodology for Determination of Hydrogen Chloride Emissions From Municipal and Hazardous Waste Incinerators," S.C. Steinsberger and J.H. Margeson. Prepared for U.S. Environmental Protection Agency, Research Triangle Park, NC. NTIS Report No. PB89-220586. (1989).

2. "Evaluation of HCl Measurement Techniques at Municipal and Hazardous Waste Incinerators," S.A. Shanklin, S.C. Steinsberger, and L. Cone, Entropy, Inc. Prepared for U.S. Environmental Protection Agency, Research Triangle Park, NC. NTIS Report No. PB90-221896. (1989).
3. "Fourier Transform Infrared (FTIR) Method Validation at a Coal Fired-Boiler," Entropy, Inc. Prepared for U.S. Environmental Protection Agency, Research Triangle Park, NC. EPA Publication No. EPA-454/R95-004. NTIS Report No. PB95-193199. (1993).
4. "Field Validation Test Using Fourier Transform Infrared (FTIR) Spectrometry To Measure Formaldehyde, Phenol and Methanol at a Wool Fiberglass Production Facility." Draft. U.S. Environmental Protection Agency Report, Entropy, Inc., EPA Contract No. 68D20163, Work Assignment I-32.
5. Kinner, L.L., Geyer, T.G., Plummer, G.W., Dunder, T.A., Entropy, Inc. "Application of FTIR as a Continuous Emission Monitoring System." Presentation at 1994 International Incineration Conference, Houston, TX. May 10, 1994.
6. "Molecular Vibrations; The Theory of Infrared and Raman Vibrational Spectra," E. Bright Wilson, J.C. Decius, and P.C. Cross, Dover Publications, Inc., 1980. For a less intensive treatment of molecular rotational-vibrational spectra see, for example, "Physical Chemistry," G.M. Barrow, chapters 12, 13, and 14, McGraw Hill, Inc., 1979.
7. "Laboratory and Field Evaluations of Ammonium Chloride Interference in Method 26," U.S. Environmental Protection Agency Report, Entropy, Inc., EPA Contract No. 68D20163, Work Assignment No. I-45.
8. 40 CFR 63, appendix A. Method 301—Field Validation of Pollutant Measurement Methods from Various Waste Media.
9. "Fourier Transform Infrared Spectrometry," Peter R. Griffiths and James de Haseth, Chemical Analysis, 83, 16-25, (1986), P.J. Elving, J.D. Winefordner and I.M. Kolthoff (ed.), John Wiley and Sons.
10. "Computer-Assisted Quantitative Infrared Spectroscopy," Gregory L. McClure (ed.), ASTM Special Publication 934 (ASTM), 1987.
11. "Multivariate Least-Squares Methods Applied to the Quantitative Spectral Analysis of Multicomponent Mixtures," Applied Spectroscopy, 39(10), 73-84, 1985.



Top, water vapor (194hsub); Bottom, HCl at 11.4 (ppm-M)/K.

Figure 1. FTIR Spectra of HCl and Water.

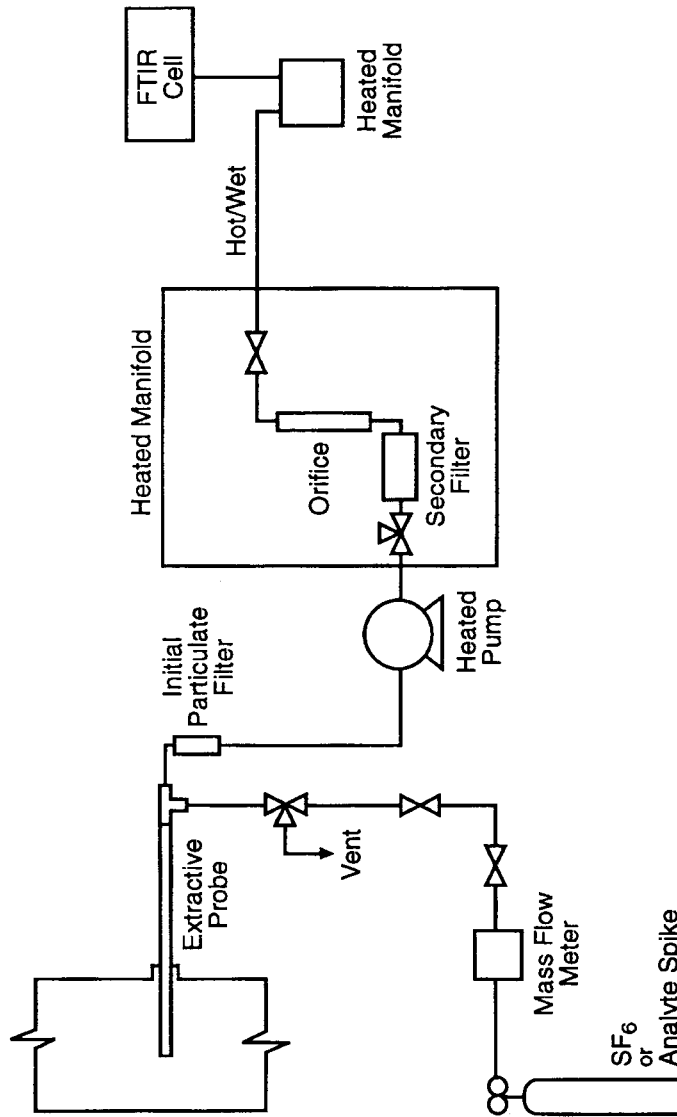


Figure 2. FTIR Sampling/Spiking System.

[57 FR 61992, Dec. 29, 1992, as amended at 58 FR 57924, Oct. 27, 1993; 59 FR 1992, Jan. 13, 1994; 59 FR 19590, Apr. 22, 1994; 59 FR 61816, Dec. 2, 1994; 60 FR 4979, Jan. 25, 1995; 60 FR 33122, 33123, June 27, 1995; 60 FR 62952, Dec. 7, 1995; 62 FR 2793, Jan. 17, 1997; 62 FR 12549, Mar. 17, 1997; 62 FR 52418, Oct. 7, 1997; 63 FR 15027, Mar. 27, 1998; 63 FR 18630, Apr. 15, 1998; 63 FR 46535, Sept. 1, 1998; 64 FR 31718, 31937, June 14, 1999; 65 FR 62216, Oct. 17, 2000]

APPENDIX B TO PART 63—SOURCES DEFINED FOR EARLY REDUCTION PROVISIONS

Source	Location of definition
1. Organic Process Equipment in Volatile Hazardous Air Pollutant Service at Chemical Plants and Other Designated Facilities.	56 FR 9315, March 6, 1991, Announcement of Negotiated Rulemaking
<ul style="list-style-type: none"> a. All valves in gas or light liquid service within a process unit b. All pumps in light liquid service within a process unit c. All connectors in gas or light liquid service within a process unit d. Each compressor e. Each product accumulator vessel f. Each agitator g. Each pressure relief device h. Each open-ended valve or line i. Each sampling connection system j. Each instrumentation system k. Each pump, valve, or connector in heavy liquid service l. Each closed vent system and control device 	

APPENDIX C TO PART 63—DETERMINATION OF THE FRACTION BIODEGRADED (F_{bio}) IN A BIOLOGICAL TREATMENT UNIT

I. Purpose

The purpose of this appendix is to define the procedures for an owner or operator to use to calculate the site specific fraction of organic compounds biodegraded (F_{bio}) in a biological treatment unit. If an acceptable level of organic compounds is destroyed rather than emitted to the air or remaining in the effluent, the biological treatment unit may be used to comply with the applicable treatment requirements without the unit being covered and vented through a closed vent system to an air pollution control device.

The determination of F_{bio} shall be made on a system as it would exist under the rule. The owner or operator should anticipate changes that would occur to the wastewater flow and concentration of organics, to be treated by the biological treatment unit, as

a result of enclosing the collection and treatment system as required by the rule.

Unless otherwise specified, the procedures presented in this appendix are designed to be applied to thoroughly mixed treatment units. A thoroughly mixed treatment unit is a unit that is designed and operated to approach or achieve uniform biomass distribution and organic compound concentration throughout the aeration unit by quickly dispersing the recycled biomass and the wastewater entering the unit. Detailed discussion on how to determine if a biological treatment unit is thoroughly mixed can be found in reference 7. Systems that are not thoroughly mixed treatment units should be subdivided into a series of zones that have uniform characteristics within each zone. The number of zones required to characterize a biological treatment system will depend on the design and operation of the treatment system. Detailed discussion on how to determine the number of zones in a biological treatment unit and examples of determination of f_{bio} can be found in reference 8. Each zone should then be modeled as a separate unit. The amount of air emissions and biodegradation from the modeling of these separate zones can then be added to reflect the entire system.

II. Definitions

Biological treatment unit = wastewater treatment unit designed and operated to promote the growth of bacteria to destroy organic materials in wastewater.

f_{bio} = The fraction of individual applicable organic compounds in the wastewater biodegraded in a biological treatment unit.

F_{bio} = The fraction of total applicable organic compounds in the wastewater biodegraded in a biological treatment unit.

F_e = The fraction of applicable organic compounds emitted from the wastewater to the atmosphere.

K1 = First order biodegradation rate constant, L/g MLVSS-hr

KL = liquid-phase mass transfer coefficient, m/s

M = compound specific mass flow weighted average of organic compounds in the wastewater, Mg/Yr

III. Procedures for Determination of f_{bio}

The first step in the analysis to determine if a biological treatment unit may be used without being covered and vented through a closed-vent system to an air pollution control device is to determine the compound-specific f_{bio} . The following procedures may be used to determine f_{bio} :

- (1) The EPA Test Method 304A or 304B (appendix A, part 63)—Method for the Determination of Biodegradation Rates of Organic Compounds,

- (2) Performance data with and without biodegradation,
- (3) Inlet and outlet concentration measurements,
- (4) Batch tests,
- (5) Multiple zone concentration measurements.

All procedures must be executed so that the resulting f_{bio} is based on the collection system and waste management units being in compliance with the rule. If the collection system and waste management units meet the suppression requirements at the time of the test, any of the procedures may be chosen. If the collection system and waste management units are not in compliance at the time of the performance test, then only Method 304A, B, or the batch test shall be chosen. If Method 304A, B, or the batch test is used, any anticipated changes to the influent of the full-scale biological treatment unit that will occur after the facility has enclosed the collection system must be represented in the influent feed to the benchtop bioreactor unit, or test unit.

Select one or more appropriate procedures from the five listed above based on the availability of site specific data and the type of mixing that occurs in the unit (thoroughly mixed or multiple mixing zone). If the facility does not have site-specific data on the removal efficiency of its biological treatment unit, then Procedure 1 or Procedure 4 may be used. Procedure 1 allows the use of a benchtop bioreactor to determine the first-order biodegradation rate constant. An owner or operator may elect to assume the first order biodegradation rate constant is zero for any regulated compound(s) present in the wastewater. Procedure 4 explains two types of batch tests which may be used to estimate the first order biodegradation rate constant. An owner or operator may elect to assume the first order biodegradation rate constant is zero for any regulated compound(s) present in the wastewater. Procedure 3 would be used if the facility has, or measures to determine, data on the inlet and outlet individual organic compound concentration for the biological treatment unit. Procedure 3 may only be used on a thoroughly mixed treatment unit. Procedure 5 is the concentration measurement test that can be used for units with multiple mixing zones. Procedure 2 is used if a facility has or obtains performance data on a biotreatment unit prior to and after addition of the microbial mass. An example where Procedure 2 could be used is an activated sludge unit where measurements have been taken on inlet and exit concentration of organic compounds in the wastewater prior to seeding with the microbial mass and startup of the unit. The flow chart in figure 1 outlines the steps to use for each of the procedures.

A. Method 304A or 304B (Procedure 1)

If the first procedure is selected, follow the instructions in appendix A of part 63 Method 304A "Method for the Determination of Biodegradation Rates of Organic Compounds (Vented Option)" or Method 304B "Method for the Determination of Biodegradation Rates of Organic Compounds (Scrubber Option)." Method 304A or 304B provides instruction on setting up and operating a self-contained benchtop bioreactor system which is operated under conditions representative of the target full-scale system. Method 304A uses a benchtop bioreactor system with a vent, and uses modeling to estimate any air emissions. Method 304B uses a benchtop bioreactor system which is equipped with a scrubber and is not vented.

There are some restrictions on which method a source may use. If the facility is measuring the rate of biodegradation of compounds that may tend to react or hydrolyze in the scrubber of Method 304B, this method shall not be used and Method 304A is the required method. If a Henry's law value is not available to use with Form V, then Method 304A shall not be used and Method 304B is the required method. When using either method, the feed flow to the benchtop bioreactor shall be representative of the flow and concentration of the wastewater that will be treated by the full-scale biological treatment unit after the collection and treatment system has been enclosed as required under the applicable subpart.

The conditions under which the full-scale biological treatment unit is run establish the operating parameters of Method 304A or 304B. If the biological treatment unit is operated under abnormal operating conditions (conditions outside the range of critical parameters examined and confirmed in the laboratory), the EPA believes this will adversely affect the biodegradation rate and is an unacceptable treatment option. The facility would be making multiple runs of the test method to simulate the operating range for its biological treatment unit. For wide ranges of variation in operating parameters, the facility shall demonstrate the biological treatment unit is achieving an acceptable level of control, as required by the regulation, across the ranges and not only at the endpoints.

If Method 304A is used, complete Form V initially. Form V is used to calculate K1 from the Method 304A results. Form V uses the Henry's law constant to estimate the fraction lost from the benchtop reactor vent. The owner or operator shall use the Henry's law values in Table I. Form V also gives direction for calculating an equivalent KL. Note on Form V if the calculated number for line 11 is greater than the calculated value for line 13, this procedure shall not be used

to demonstrate the compound is biodegradable. If line 11 is greater than line 13, this is an indication the fraction emitted from the vent is greater than the fraction biodegraded. The equivalent KL determined on Form V is used in Form II (line 6). Estimation of the Fe and f_{bio} must be done following the steps in Form III. Form III uses the previously calculated values of K1 and KL (equivalent KL), and site-specific parameters of the full-scale bioreactor as input to the calculations. Forms II, III, and V must be completed for each organic compound in the wastewater to determine Fe and f_{bio} .

If Method 304B is used, perform the method and use the measurements to determine K1, which is the first-order biodegradation rate constant. Form I lists the sequence of steps in the procedure for calculating K1 from the Method 304B results. Once K1 is determined, KL must be calculated by use of mass transfer equations. Form II outlines the procedure to follow for use of mass transfer equations to determine KL. A computer program which incorporates these mass transfer equations may be used. Water7 is a program that incorporates these mass transfer equations and may be used to determine KL. Refer to Form II-A to determine KL, if Water7 or the most recent update to this model is used. In addition, the Bay Area Sewage Toxics Emission (BASTE) model version 3.0 or equivalent upgrade and the TOXCHEM (Environment Canada's Wastewater Technology Centre and Environmega, Ltd.) model version 1.10 or equivalent upgrade may also be used to determine KL for the biological treatment unit with several stipulations. The programs must be altered to output a KL value which is based on the site-specific parameters of the unit modeled, and the Henry's law values listed in Table I must be substituted for the existing Henry's law values in the programs. Input values used in the model and corresponding output values shall become documentation of the f_{bio} determination. The owner or operator should be aware these programs do not allow modeling of certain units. To model these units, the owner or operator shall use one of the other appropriate procedures as outlined in this appendix. The owner or operator shall not use a default value for KL. The KL value determined by use of these models shall be based on the site-specific parameters of the specific unit. This KL value shall be inserted in Form II (line 6). Estimation of the Fe and f_{bio} must be done following the steps in Form III. Form III uses the previously calculated values of K1 and KL, and site-specific parameters of the full-scale bioreactor as input to the calculations. Forms I, II, and III must be completed for each organic compound in the wastewater to determine Fe and f_{bio} .

B. Performance Data With and Without Biodegradation (Procedure 2)

Procedure 2 uses site-specific performance data that represents or characterizes operation of the unit both with and without biodegradation. As previously mentioned, proper determination of f_{bio} must be made on a system as it would exist under the rule. Using Form IV, calculate KL and K1. After KL and K1 are determined, Form III is used to calculate Fe and f_{bio} for each organic compound present in the wastewater.

C. Inlet and Outlet Concentration Measurements (Procedure 3)

Procedure 3 uses measured inlet and outlet organic compound concentrations for the unit. This procedure may only be used on a thoroughly mixed treatment unit. Again, proper determination of f_{bio} must be made on a system as it would exist under the rule. The first step in using this procedure is to calculate KL using Form II. A computer model may be used. If the Water7 model or the most recent update to this model is used, then use Form II-A to calculate KL. After KL is determined using field data, complete Form VI to calculate K1. The TOXCHEM or BASTE model may also be used to calculate KL for the biological treatment unit, with the stipulations listed in procedure 304B. After KL and K1 are determined, Form III is used to calculate Fe and f_{bio} for each organic compound.

D. Batch Tests (Procedure 4)

Two types of batch tests which may be used to determine kinetic parameters are: (1) The aerated reactor test and (2) the sealed reactor test. The aerated reactor test is also known as the BOX test (batch test with oxygen addition). The sealed reactor test is also known as the serum bottle test. These batch tests should be conducted only by persons familiar with procedures for determining biodegradation kinetics. Detailed discussions of batch procedures for determining biodegradation kinetic parameters can be found in references 1-4.

For both batch test approaches, a biomass sample from the activated sludge unit of interest is collected, aerated, and stored for no more than 4 hours prior to testing. To collect sufficient data when biodegradation is rapid, it may be necessary to dilute the biomass sample. If the sample is to be diluted, the biomass sample shall be diluted using treated effluent from the activated sludge unit of interest to a concentration such that the biodegradation test will last long enough to make at least six concentration measurements. It is recommended that the tests not be terminated until the compound concentration falls below the limit of quantitation (LOQ). Measurements that are below the LOQ should not be used in the data analysis.

Biomass concentrations shall be determined using standard methods for measurement of mixed liquor volatile suspended solids (MLVSS) (reference 5).

The change in concentration of a test compound may be monitored by either measuring the concentration in the liquid or in the reactor headspace. The analytical technique chosen for the test should be as sensitive as possible. For the batch test procedures described in this section, equilibrium conditions must exist between the liquid and gas phases of the experiments because the data analysis procedures are based on this premise. To use the headspace sampling approach, the reactor headspace must be in equilibrium with the liquid so that the headspace concentrations can be correlated with the liquid concentrations. Before the biodegradation testing is conducted, the equilibrium assumption must be verified. A discussion of the equilibrium assumption verification is given below in sections D.1 and D.2 since different approaches are required for the two types of batch tests.

To determine biodegradation kinetic parameters in a batch test, it is important to choose an appropriate initial substrate (compound(s) of interest) concentration for the test. The outcome of the batch experiment may be influenced by the initial substrate (S_0) to biomass (X_0) ratio (see references 3, 4, and 6). This ratio is typically measured in chemical oxygen demand (COD) units. When the S_0/X_0 ratio is low, cell multiplication and growth in the batch test is negligible and the kinetics measured by the test are representative of the kinetics in the activated sludge unit of interest. The S_0/X_0 ratio for a batch test is determined with the following equation:

$$\frac{S_0}{X_0} = \frac{S_i}{1.42 X} \quad (\text{Eqn App. C-1})$$

Where:

S_0/X_0 =initial substrate to biomass ratio on a COD basis

S_i =initial substrate concentration in COD units (g COD/L)

X =biomass concentration in the batch test (g MLVSS/L)

1.42 = Conversion factor to convert to COD units

For the batch tests described in this section, the S_0/X_0 ratio (on a COD basis) must be initially less than 0.5.

1. *Aerated Reactor Test.* An aerated draft tube reactor may be used for the biokinetics testing (as an example see Figure 2 of appendix C). Other aerated reactor configurations may also be used. Air is bubbled through a porous frit at a rate sufficient to aerate and keep the reactor uniformly mixed. Aeration rates typically vary from 50 to 200 ml/min for a 1 liter system. A mass flow rate controller is used to carefully control the air flow rate because it is important to have an accurate measure of this rate. The dissolved oxygen (DO) concentration in the system must not fall below 2 mg/liter so that the biodegradation observed will not be DO-limited. Once the air flow rate is established, the test mixture (or compound) of interest is then injected into the reactor and the concentration of the compound(s) is monitored over time. Concentrations may be monitored in the liquid or in the headspace. A minimum of six samples shall be taken over the period of the test. However, it is necessary to collect samples until the compound concentration falls below the LOQ. If liquid samples are collected, they must be small enough such that the liquid volume in the batch reactor does not change by more than 10%.

Before conducting experiments with biomass, it is necessary to verify the equilibrium assumption. The equilibrium assumption can be verified by conducting a stripping experiment using the effluent (no biomass) from the activated sludge unit of interest. Effluent is filtered with a 0.45 um or smaller filter and placed in the draft tube reactor. Air is sparged into the system and the compound concentration in the liquid or headspace is monitored over time. This test with no biomass may provide an estimate of the Henry's law constant. If the system is at equilibrium, the Henry's law constant may be estimated with the following equation:

$$-\ln(C/C_0) = (GK_{eq}/V)t \quad (\text{Eqn App. C-2})$$

Where:

C =concentration at time, t (min)

C_0 =concentration at $t=0$

G =volumetric gas flow rate (ml/min)

V =liquid volume in the batch reactor (ml)

K_{eq} =Henry's law constant (mg/L-gas)/(mg/L-liquid)

t =time (min)

A plot of $-\ln(C/C_0)$ as a function of t will have a slope equal to GK_{eq}/V . The equilibrium assumption can be verified by comparing the experimentally determined K_{eq} for the system to literature values of the Henry's Law constant (including those listed in this appendix). If K_{eq} does not match the

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Henry's law constant, K_{eq} shall be determined from analysis of the headspace and liquid concentration in a batch system.

The concentration of a compound decreases in the bioreactor due to both bio-

degradation and stripping. Biodegradation processes are typically described with a Monod model. This model and a stripping expression are combined to give a mass balance for the aerated draft tube reactor):

$$-\frac{ds}{dt} = \left(\frac{GK_{eq}}{V} \right) s + \left(\frac{Q_m X}{K_s + s} \right) s \quad (\text{Eqn App. C-3})$$

Where:

s =test compound concentration, mg/liter
 G =volumetric gas flow rate, liters/hr
 K_{eq} =Henry's Law constant measured in the system, (mg/liter gas)/(mg/liter liquid)
 V =volume of liquid in the reactor, liters
 X =biomass concentration (g MLVSS/liter)

Q_m =maximum rate of substrate removal, mg/g MLVSS/hr

K_s =Monod biorate constant at half the maximum rate, mg/liter

Equation App. C-3 can be integrated to obtain the following equation:

$$-t = \frac{VK_s}{A} \ln \left(\frac{s}{s_0} \right) + \frac{Q_m XV^2}{AB} \ln \left(\frac{A + Bs}{A + Bs_0} \right) \quad (\text{Eqn App. C-4})$$

Where:

$A = GK_{eq}K_s + Q_m VX$
 $B = GK_{eq}$
 S_0 =test compound concentration at $t=0$

This equation is used along with the substrate concentration versus time data to determine the best fit parameters (Q_m and K_s) to describe the biodegradation process in the aerated reactor. If the aerated reactor test is used, the following procedure is used to analyze the data. Evaluate K_{eq} for the compound of interest with Form XI. The concentration in the vented headspace or liquid is measured as a function of time and the data is entered on Form XI. A plot is made from the data and attached to the Form XI. K_{eq} is calculated on Form XI and the results are contrasted with the expected value of Henry's law obtained from Form IX. If the comparison is satisfactory, the stripping constant is calculated from K_{eq} , completing Form XI. The values of K_{eq} may differ because the theoretical value of K_{eq} may not be applicable to the system of interest. If the comparison of the calculated K_{eq} from the form and the expected value of Henry's law is unsatisfactory, Form X can alternatively be used to validate K_{eq} . If the aerated reactor is demonstrated to not be at equilibrium, either modify the reactor design and/or operation, or use another type of batch test.

The compound-specific biorate constants are then measured using Form XII. The stripping constant that was determined from Form XI and a headspace correction factor of 1 are entered on Form XII. The aerated reac-

tor biotest may then be run, measuring concentrations of each compound of interest as a function of time. If headspace concentrations are measured instead of liquid concentrations, then the corresponding liquid concentrations are calculated from the headspace measurements using the K_{eq} determined on Form XI and entered on Form XII.

The concentration data on Form XII may contain scatter that can adversely influence the data interpretation. It is possible to curve fit the concentration data and enter the concentrations on the fitted curve instead of the actual data. If curve fitting is used, the curve-fitting procedure must be based upon the Equation App. C-4. When curve fitting is used, it is necessary to attach a plot of the actual data and the fitted curve to Form XII.

If the stripping rate constant is relatively large when compared to the biorate at low concentrations, it may be difficult to obtain accurate evaluations of the first-order biorate constant. In these cases, either reducing the stripping rate constant by lowering the aeration rate, or increasing the biomass concentrations should be considered.

The final result of the batch testing is the measurement of a biorate that can be used to estimate the fraction biodegraded, f_{bio} . The

number transferred to Form III is obtained from Form XII, line 9.

2. *Sealed Reactor Test.* This test uses a closed system to prevent losses of the test compound by volatilization. This test may be conducted using a serum bottle or a sealed draft tube reactor (for an example see Figure 3 of appendix C). Since no air is supplied, it is necessary to ensure that sufficient oxygen is present in the system. The DO concentration in the system must not fall below 2 mg/liter so that the biodegradation observed will not be DO-limited. As an alternative, oxygen may be supplied by electrolysis as needed to maintain the DO concentration above 2 mg/liter. The reactor contents must be uniformly mixed, by stirring or agitation using a shaker or similar apparatus. The test mixture (or compound) of interest is injected into the reactor and the concentration is monitored over time. A minimum of six samples shall be taken over the period of the test. However, it is nec-

essary to monitor the concentration until it falls below the LOQ.

The equilibrium assumption must be verified for the batch reactor system. In this case, K_{eq} may be determined by simultaneously measuring gas and liquid phase concentrations at different times within a given experiment. A constant ratio of gas/liquid concentrations indicates that equilibrium conditions are present and K_{eq} is not a function of concentration. This ratio is then taken as the K_{eq} for the specific compound in the test. It is not necessary to measure K_{eq} for each experiment. If the ratio is not constant, the equilibrium assumption is not valid and it is necessary to (1) increase mixing energy for the system and retest for the equilibrium assumption, or (2) use a different type of test (for example, a collapsible volume reactor).

The concentration of a compound decreases in the bioreactor due to biodegradation according to Equation App. C-5:

$$\frac{ds}{dt} = \left[\frac{-V_1}{V_g K_{eq} + V_1} \right] \left[\left(\frac{Q_m X}{K_s + s} \right) s \right] \quad (\text{Eqn App. C-5})$$

Where:

s =test compound concentration (mg/liters)
 V_1 =the average liquid volume in the reactor (liters)
 V_g =the average gas volume in the reactor (liters)
 Q_m =maximum rate of substrate removal (mg/g ML VSS/hr)

K_{eq} =Henry's Law constant determined for the test, (mg/liter gas)/(mg/liter liquid)
 K_s =Monod biorate constant at one-half the maximum rate (mg/liter)
 t =time (hours)
 X =biomass concentration (g ML VSS/liter)
 s_0 =test compound concentration at time $t=0$
 Equation App. C-5 can be solved analytically to give:

$$t = \frac{-(V_g K_{eq} + V_1)}{V_1 Q_m X} \left[(s - s_0) + K_s \ln \left(\frac{s}{s_0} \right) \right] \quad (\text{Eqn App. C-6})$$

This equation is used along with the substrate concentration versus time data to determine the best fit parameters (Q_m and K_s) to describe the biodegradation process in the sealed reactor.

If the sealed reactor test is used, Form X is used to determine the headspace correction factor. The disappearance of a compound in the sealed reactor test is slowed because a fraction of the compound is not available for biodegradation because it is present in the headspace. If the compound is almost entirely in the liquid phase, the headspace correction factor is approximately one. If the headspace correction factor is

substantially less than one, improved mass transfer or reduced headspace may improve the accuracy of the sealed reactor test. A preliminary sealed reactor test must be conducted to test the equilibrium assumption. As the compound of interest is degraded, simultaneous headspace and liquid samples should be collected and Form X should be used to evaluate K_{eq} . The ratio of headspace to liquid concentrations must be constant in order to confirm that equilibrium conditions exist. If equilibrium conditions are not present, additional mixing or an alternate reactor configuration may be required.

The compound-specific biorate constants are then calculated using Form XII. For the sealed reactor test, a stripping rate constant of zero and the headspace correction factor that was determined from Form X are entered on Form XII. The sealed reactor test may then be run, measuring the concentrations of each compound of interest as a function of time. If headspace concentrations are measured instead of liquid concentrations, then the corresponding liquid concentrations are calculated from the headspace measurements using K_{eq} from Form X and entered on Form XII.

The concentration data on Form XII may contain scatter that can adversely influence the data interpretation. It is possible to curve fit the concentration data and enter the concentrations on the fitted curve instead of the actual data. If curve fitting is used, the curve-fitting procedure must be based upon Equation App. C-6. When curve fitting is used, it is necessary to attach a plot of the actual data and the fitted curve to Form XII.

If a sealed collapsible reactor is used that has no headspace, the headspace correction factor will equal 1, but the stripping rate constant may not equal 0 due to diffusion losses through the reactor wall. The ratio of the rate of loss of compound to the concentration of the compound in the reactor (units of per hour) must be evaluated. This loss ratio has the same units as the stripping rate constant and may be entered as the stripping rate constant on line 1 of Form XII.

If the loss due to diffusion through the walls of the collapsible reactor is relatively large when compared to the biorate at low concentrations, it may be difficult to obtain accurate evaluations of the first-order biorate constant. In these cases, either replacing the materials used to construct the reactor with materials of low permeability or increasing the biomass concentration should be considered.

The final result of the batch testing is the measurement of a biorate that can be used to estimate the fraction biodegraded, f_{bio} . The number transferred to Form III is obtained from Form XII, line 9.

The number on Form XII line 9 will equal the Monod first-order biorate constant if the full-scale system is operated in the first-order range. If the full-scale system is operated at concentrations above that of the Monod first-order range, the value of the number on line 9 will be somewhat lower than the Monod first-order biorate constant. With supporting biorate data, the Monod model used in Form XII may be used to estimate the effective biorate constant K_1 for use in Form III.

If a reactor with headspace is used, analysis of the data using equation App. C-6 is valid only if V_l and V_g do not change more

than 10% (i.e., they can be approximated as constant for the duration of the test). Since biodegradation is occurring only in the liquid, as the liquid concentration decreases it is necessary for mass to transfer from the gas to the liquid phase. This may require vigorous mixing and/or reducing the volume in the headspace of the reactor.

If there is no headspace (e.g., a collapsible reactor), equation App. C-6 is independent of V_l and there are no restrictions on the liquid volume. If a membrane or bag is used as the collapsible-volume reactor, it may be important to monitor for diffusion losses in the system. To determine if there are losses, the bag should be used without biomass and spiked with the compound(s) of interest. The concentration of the compound(s) in the reactor should be monitored over time. The data are analyzed as described above for the sealed reactor test.

3. *Quality Control/Quality Assurance (QA/QC)*. A QA/QC plan outlining the procedures used to determine the biodegradation rate constants shall be prepared and a copy maintained at the source. The plan should include, but may not be limited to:

1. A description of the apparatus used (e.g., size, volume, method of supplying air or oxygen, mixing, and sampling procedures) including a simplified schematic drawing.

2. A description of how biomass was sampled from the activated sludge unit.

3. A description of how biomass was held prior to testing (age, etc.).

4. A description of what conditions (DO, gas-liquid equilibrium, temperature, etc.) are important, what the target values are, how the factors were controlled, and how well they were controlled.

5. A description of how the experiment was conducted, including preparation of solutions, dilution procedures, sampling procedures, monitoring of conditions, etc.

6. A description of the analytical instrumentation used, how the instruments were calibrated, and a summary of the precision for that equipment.

7. A description of the analytical procedures used. If appropriate, reference to an ASTM, EPA or other procedure may be used. Otherwise, describe how the procedure is done, what is done to measure precision, accuracy, recovery, etc., as appropriate.

8. A description of how data are captured, recorded, and stored.

9. A description of the equations used and their solutions, including a reference to any software used for calculations and/or curve-fitting.

E. Multiple Zone Concentration Measurements (Procedure 5)

Procedure 5 is the concentration measurement method that can be used to determine the f_{bio} for units that are not thoroughly

mixed and thus have multiple zones of mixing. As with the other procedures, proper determination of f_{bio} must be made on a system as it would exist under the rule. For purposes of this calculation, the biological unit must be divided¹ into zones with uniform characteristics within each zone. The number of zones that is used depends on the complexity of the unit. Reference 8, "Technical Support Document for the Evaluation of Aerobic Biological Treatment Units with Multiple Mixing Zones," is a source for further information concerning how to determine the number of zones that should be used for evaluating your unit. The following information on the biological unit must be available to use this procedure: basic unit variables such as inlet and recycle wastewater flow rates, type of agitation, and operating conditions; measured representative organic compound concentrations in each zone and the inlet and outlet; and estimated mass transfer coefficients for each zone.

Reference 8 "Technical Support Document for the Evaluation of Aerobic Biological Treatment Units with Multiple Mixing Zones," is a source for further information concerning how to interpolate the biorates for multiple zones. In units with well-characterized concentration measurements obtained in an initial evaluation of the unit, it may be possible to demonstrate that there is a good correlation of the component concentrations with the locations in the multiple-zone unit. With this good correlation, it may be possible to accurately predict the concentrations in selected zones without actually testing each selected zone. This correlation method may be used for units that have many zones (greater than 5) or where one of the interior zones is not readily accessible for sampling. To use this correlation method of estimating zone concentrations, it is necessary to measure the concentrations

in the inlet unit, the exit unit, and sufficient interior units to obtain a correlation of component concentrations with the locations. You cannot use this correlation method of estimating selected zone concentrations if monitoring of each zone is required, or if the accuracy and precision of the correlation is inferior to actual individual sampling error. The accuracy and precision of the correlation may be improved by increasing the number of locations tested. Because the correlation is based on many samples, it should provide an accurate representation of a stable operating system.

The estimated mass transfer coefficient for each compound in each zone is obtained from Form II using the characteristics of each zone. A computer model may be used. If the Water7 model or the most recent update to this model is used, then use Form II-A to calculate KL. The TOXCHEM or BASTE model may also be used to calculate KL for the biological treatment unit, with the stipulations listed in Procedure 304B. Compound concentration measurements for each zone are used in Form XIII to calculate the f_{bio} . A copy of Form XIII is completed for each of the compounds of concern treated in the biological unit.

IV. Calculation of F_{bio}

At this point, the individual f_{bios} determined by the previously explained procedures must be summed to obtain the total F_{bio} . To determine the F_{bio} multiply each compound specific f_{bio} by the compound-specific average mass flow rate of the organic compound in the wastewater stream (see regulation for instruction on calculation of average mass flow rate). Sum these products and divide by the total wastewater stream average mass flow rate of organic compounds.

$$F_{bio} = \frac{\sum_{i=1}^N (f_{bio\ i} \times M_i)}{\sum_{i=1}^n M_i} \quad (\text{Eqn App. C - 7})$$

M=compound specific average mass flow rate of the organic compounds in the wastewater (Mg/Yr)
n=number of organic compounds in the wastewater

The F_{bio} is then used in the applicable compliance equations in the regulation to determine if biodegradation may be used to comply with the treatment standard without covering and venting to an air pollution control device.

¹This is a mathematical division of the actual unit; not addition of physical barriers.

References

1. Rajagopalan, S. et al. "Comparison of Methods for Determining Biodegradation Kinetics of Volatile Organic Compounds." Proceedings of Water Environment Federation, 67th Annual Conference, October 15-19, 1994.
2. Ellis, T.G. et al. "Determination of Toxic Organic Chemical Biodegradation Kinetics Using Novel Respirometric Technique". Proceedings Water Environment Federation, 67th Annual Conference, October 15-19, 1994.
3. Pitter, P. and J. Chudoba. Biodegradability of Organic Substances in the Aquatic Environment. CRC Press, Boca Raton, FL, 1990.

4. Grady, C.P.L., B. Smets, and D. Barbeau. Variability in kinetic parameter estimates: A review of possible causes and a proposed terminology. *Wat. Res.* 30 (3), 742-748, 1996.
5. Eaton, A.D., et al. eds., *Standard Methods for the Examination of Water and Wastewater*, 19th Edition, American Public Health Association, Washington, DC, 1995.
6. Chudoba P., B. Capdeville, and J. Chudoba. Explanation of biological meaning of the So/Xo ratio in batch cultivation. *Wat. Sci. Tech.* 26 (3/4), 743-751, 1992.
7. Technical Support Document for Evaluation of Thoroughly Mixed Biological Treatment Units. November 1998.
8. Technical Support Document for the Evaluation of Aerobic Biological Treatment Units with Multiple Mixing Zones. July 1999.

TABLE I

Compound	H _L @ 25 °C (atm/mole frac)	H _L @ 100 °C (atm/mole frac)
1 Acetaldehyde	4.87e+00	5.64e+01
3 Acetonitrile	1.11e+00	1.78e+01
4 Acetophenone	5.09e-01	2.25e+01
5 Acrolein	4.57e+00	6.61e+01
8 Acrylonitrile	5.45e+00	6.67e+01
9 Allyl chloride	5.15e+02	2.26e+03
10 Aniline	9.78e-02	1.42e+00
12 Benzene	3.08e+02	1.93e+03
14 Benzyl chloride	1.77e+01	2.88e+02
15 Biphenyl	2.27e+01	1.27e+03
17 Bromoform	2.96e+01	3.98e+02
18 1,3-Butadiene	3.96e+03	1.56e+04
20 Carbon disulfide	1.06e+03	3.60e+03
21 Carbon tetrachloride	1.68e+03	1.69e+04
23 2-Chloroacetophenone	4.84e-02	1.43e+01
24 Chlorobenzene	2.09e+02	3.12e+03
25 Chloroform	2.21e+02	1.34e+03
26 Chloroprene	5.16e+01	1.74e+02
29 o-Cresol	9.12e-02	2.44e+01
31 Cumene	7.28e+02	7.15e+03
32 1,4-Dichlorobenzene(p)	1.76e+02	1.95e+03
33 Dichloroethyl ether	1.14e+00	3.57e+01
34 1,3-Dichloropropene	1.97e+02	1.44e+03
36 N,N-Dimethylaniline	7.70e-01	5.67e+02
37 Diethyl sulfate	3.41e-01	4.22e+01
38 3,3'-Dimethylbenzidine	7.51e-05	5.09e-01
40 1,1-Dimethylhydrazine	9.11e-02	1.57e+01
42 Dimethyl sulfate	2.23e-01	1.43e+01
43 2,4-Dinitrophenol	2.84e-01	1.50e+02
44 2,4-Dinitrotoluene	4.00e-01	9.62e+00
45 1,4-Dioxane	3.08e-01	9.53e+00
47 Epichlorohydrin	1.86e+00	4.34e+01
48 Ethyl acrylate	1.41e+01	3.01e+02
49 Ethylbenzene	4.38e+02	4.27e+03
50 Ethyl chloride (chloroethane)	6.72e+02	3.10e+03
51 Ethylene dibromide	3.61e+01	5.15e+02
52 Ethylene dichloride (1,2-Dichloroethane)	6.54e+01	5.06e+02
54 Ethylene oxide	1.32e+01	9.09e+01
55 Ethylidene dichloride (1,1-Dichloroethane)	3.12e+02	2.92e+03
57 Ethylene glycol dimethyl ether	1.95e+00	4.12e+01
60 Ethylene glycol monoethyl ether acetate	9.86e-02	6.03e+00
62 Ethylene glycol monomethyl ether acetate	1.22e-01	6.93e+00
64 Diethylene glycol dimethyl ether	8.38e-02	4.69e+00
69 Diethylene glycol diethyl ether	1.19e-01	7.71e+00
72 Ethylene glycol monobutyl ether acetate	2.75e-01	2.50e+01
73 Hexachlorobenzene	9.45e+01	2.57e+04
74 Hexachlorobutadiene	5.72e+02	6.92e+03
75 Hexachloroethane	4.64e+02	7.49e+04
76 Hexane	4.27e+04	9.44e+04

TABLE I—Continued

Compound	H _L @ 25 °C (atm/ mole frac)	H _L @ 100 °C (atm/mole frac)
78 Isophorone	3.68e-01	1.68e+01
80 Methanol	2.89e-01	7.73e+00
81 Methyl bromide (Bromomethane)	3.81e+02	2.12e+03
82 Methyl chloride (Chloromethane)	4.90e+02	2.84e+03
83 Methyl chloroform (1,1,1-Trichloroethane)	9.67e+02	5.73e+03
84 Methyl ethyl ketone (2-Butanone)	7.22e+00	5.92e+01
86 Methyl isobutyl ketone (Hexone)	2.17e+01	3.72e+02
88 Methyl methacrylate	7.83e+00	9.15e+01
89 Methyl tert-butyl ether	3.08e+01	2.67e+02
90 Methylene chloride (Dichloromethane)	1.64e+02	9.15e+02
93 Naphthalene	2.68e+01	7.10e+02
94 Nitrobenzene	1.33e+00	2.80e+01
96 2-Nitropropane	6.61e+00	8.76e+01
99 Phosgene	7.80e+02	3.51e+03
102 Propionaldehyde	3.32e+00	1.42e+02
103 Propylene dichloride	1.59e+02	1.27e+03
104 Propylene oxide	1.98e+01	1.84e+02
106 Styrene	1.45e+02	1.72e+03
107 1,1,2,2-Tetrachloroethane	1.39e+01	1.99e+02
108 Tetrachloroethylene (Perchloroethylene)	9.83e+02	1.84e+04
109 Toluene	3.57e+02	2.10e+03
112 o-Toluidine	1.34e-01	1.15e+01
113 1,2,4-Trichlorobenzene	1.07e+02	1.04e+03
114 1,1,2-Trichloroethane	4.58e+01	5.86e+02
115 Trichloroethylene	5.67e+02	7.66e+03
116 2,4,5-Trichlorophenol	4.84e-01	6.27e+01
117 Triethylamine	6.94e+00	2.57e+02
118 2,2,4-Trimethylpentane	1.85e+05	9.74e+05
119 Vinyl acetate	2.82e+01	2.80e+02
120 Vinyl chloride	1.47e+03	6.45e+03
121 Vinylidene chloride (1,1-Dichloroethylene)	1.44e+03	1.40e+04
123 m-Xylene	4.13e+02	3.25e+03
124 o-Xylene	2.71e+02	2.55e+03
125 p-Xylene	4.13e+02	3.20e+03

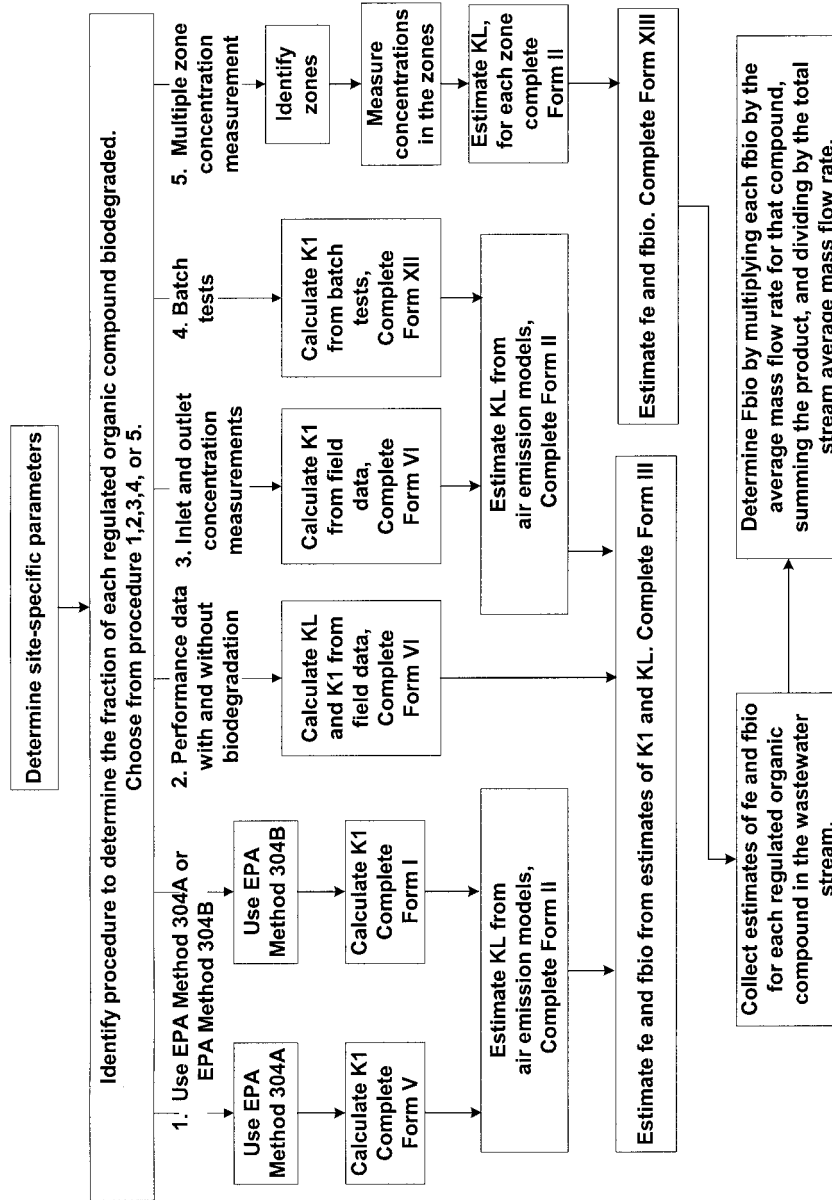


Figure 1. ALTERNATIVE EXPERIMENTAL METHODS FOR DETERMINING THE FRACTION OF ORGANIC COMPOUND BIODEGRADED (Fbio) IN A BIOLOGICAL TREATMENT UNIT

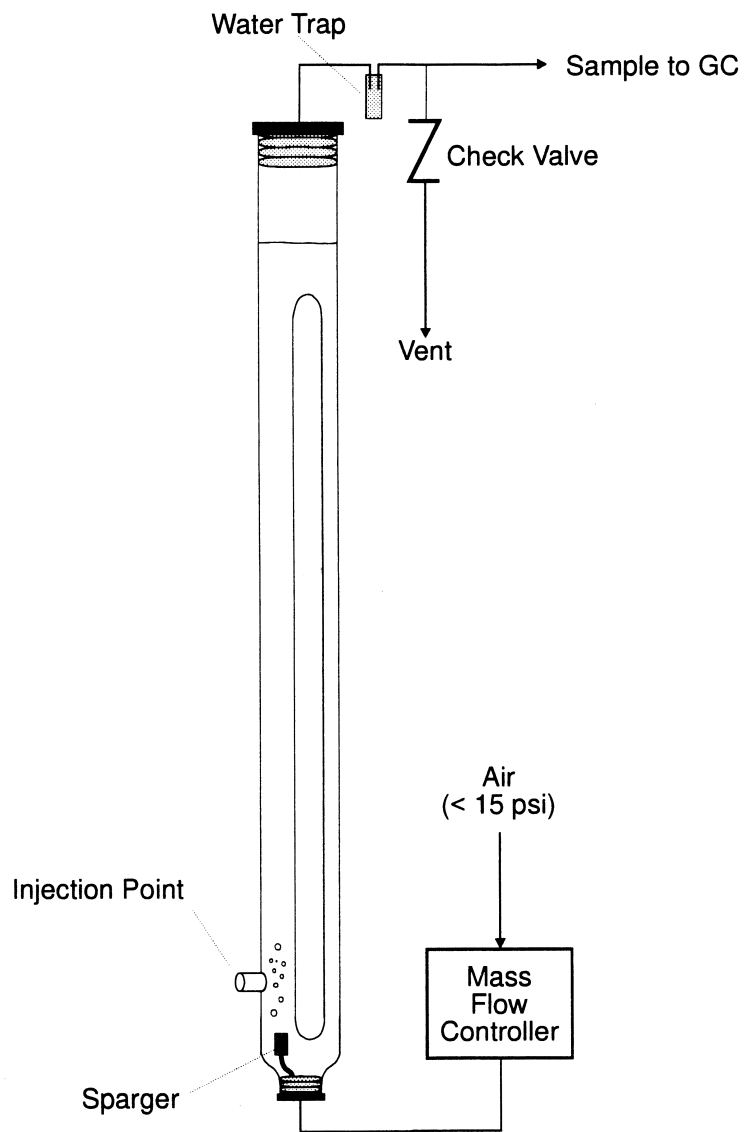


Figure 2. Example Aerated Draft Tube Reactor

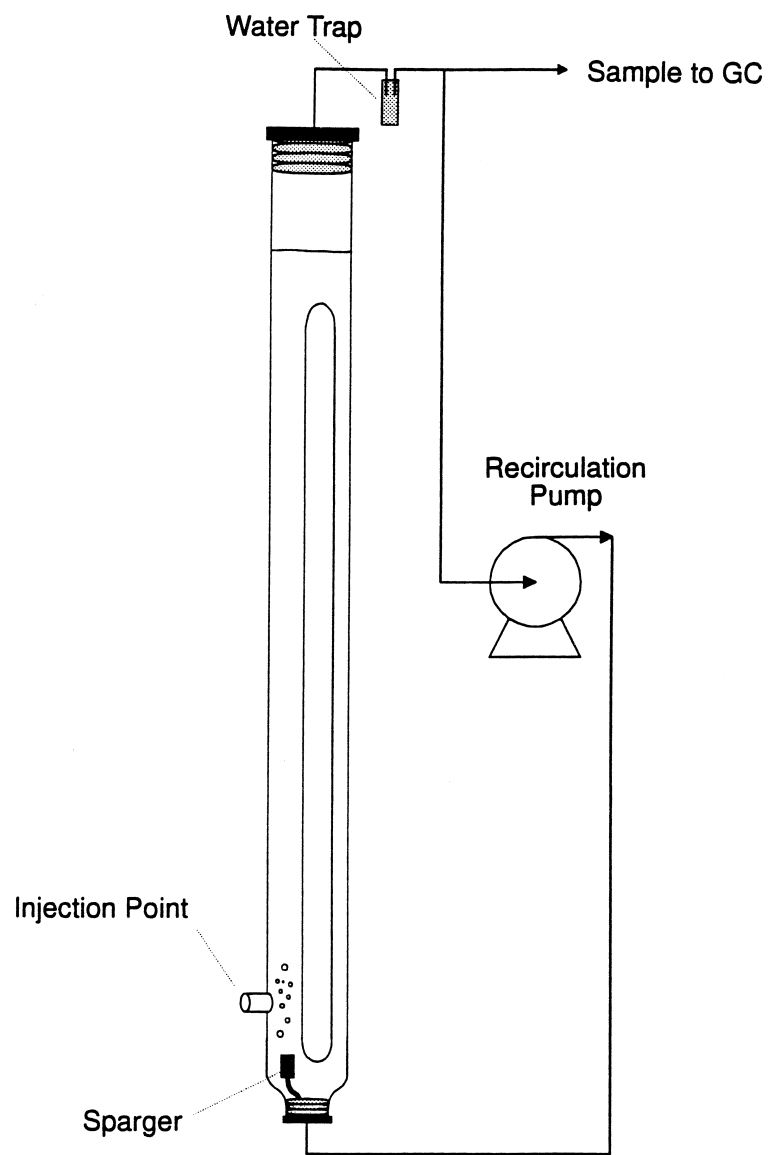


Figure 3. Example Sealed Draft Tube Reactor

Form I DATA FORM FOR THE ESTIMATION OF THE EPA METHOD 304B FIRST ORDER BIORATE CONSTANT			
NAME OF THE FACILITY for site specific biorate determination			Example
COMPOUND for site specific biorate determination			METHANOL
INLET CONCENTRATION used in EPA METHOD 304B	1		78
EXIT CONCENTRATION measured by EPA METHOD 304B	2		6
BIOMASS (g/L) This is the dried solids that are obtained from the mixed liquor suspended solids in the bench scale bioreactor.	3		0.075
TEMPERATURE OF BIOREACTOR (deg. C)	4		35
VOLUME of EPA METHOD 304B bench scale bioreactor (L)	5		6
FLOW RATE of waste treated in the bench scale bioreactor (L/hr)	6		0.146
CALCULATIONS FROM EPA METHOD 304B DATA MEASUREMENTS			
RESIDENCE TIME (hr) Divide the number on line 5 by the number on line 6 and enter the results here.	7		41.10
Concentration Decrease (g/m ³). Subtract the number on line 2 from the number on line 1 and enter the results here.	8		72.00
BIORATE (g/m ³ -hr). Divide the number on line 8 by the number on line 7 and enter the results here.	9		1.75
Product of concentration and biomass. Multiply the number on line 2 by the number on line 3 and enter the results here.	10		0.45
BIORATE K1 (L/g bio-hr) Divide the number on line 9 by the number on line 10 and enter the results here.	11		3.89
Temperature adjustment. Subtract 25 deg. C from the number on line 4 and enter the results here.	12		10
Temperature adjustment factor. 1.046 is the default temperature adjustment factor. Enter the temperature adjustment factor here.	13		1.046
Biorate temperature ratio. Raise the number on line 13 to the power of the number on line 12.	14		1.567
BIORATE K1 at 25 deg. C (L/g MLVSS-hr) Divide the number on line 11 by the number on line 14 and enter the results here.	15		2.48

Note: With Monod kinetics, use $K_{max}=1000$ to convert the Monod kinetics to first order. If a different temperature adjustment factor than the default is entered on line 13, make sure that the adjustment factor used in the calculations agrees with the value entered on line 13.

Form II		PROCEDURES FORM FOR THE ESTIMATION OF THE KL FROM UNIT SPECIFICATIONS	
NAME OF THE FACILITY for site specific biorate determination			
NAME OF UNIT for site specific biorate determination			
NAME OF COMPOUND			
HENRY'S LAW constant for the compound (mole fraction in gas per mole fraction in water at 25 degrees Celsius)			
IDENTIFY THE TYPE OF UNIT (check one box below)			
	Quiescent impoundment	1	
	Surface agitated impoundment	2	
	Surface agitated impoundment with submerged air	3	
	Unit agitated by submerged aeration gas	4	
	EPA Method 304A, Covered unit, UNOX system, or bench scale reactor	5	
PROCEDURES BASED UPON THE TYPE OF UNIT			
UNIT	PROCEDURE TO FOLLOW		
1	Use the quiescent impoundment model to determine KL. Use Kq as KL as determined from Form VII.		
2	Use the quiescent impoundment model to determine KL for the quiescent zone, Form VII. Use the aerated impoundment model to determine KL for the agitated surface, Form VIII.		
3	Use the quiescent impoundment model to determine Kq for the quiescent zone, Form VII. Use the aerated impoundment model to determine KL for the agitated surface, Form VIII. The total system KL is the sum of the KL from Form VIII and the equivalent KL from Form V. Use the submerged air rate as the vent rate in form V.		
4	Use the aerated impoundment model to determine KL if the surface is agitated. Use the quiescent impoundment model if the surface is not agitated. KL includes the effect of volatilization in the air discharge. See section 5.6.1 in AIR EMISSIONS MODELS FOR WASTE AND WASTEWATER (EPA-453/R-94-080A). The total system KL is the sum of the KL from Form VIII and the equivalent KL from Form V. Use the submerged air rate as the vent rate in Form V.		
5	KL for the surface is assumed to be equal zero. Determine equivalent KL based upon air discharge. Use Form V for EPA Method 304A or if the concentration in the vent is not measured. Use Form V-A if the concentration in the vent is measured.		
Estimate of KL obtained from above procedures (m/s)		6	

Form II-A		PROCEDURES FORM FOR THE ESTIMATION OF THE KL FROM WATER 7	
NAME OF THE FACILITY for site specific biorate determination			
NAME OF UNIT for site specific biorate determination			
NAME OF COMPOUND			
HENRY'S LAW COMPOUND			
IDENTIFY THE TYPE OF UNIT		(check one box below)	
	Quiescent impoundment	1	
	Surface agitated impoundment	2	
	Surface agitated impoundment with submerged air	3	
	Unit agitated by submerged aeration gas	4	
	Covered unit, UNOX system, bench scale reactor	5	
PROCEDURES BASED UPON THE TYPE OF UNIT			
unit	procedure to follow		
1	Use the quiescent impoundment model to determine KL.		
2	Use the aerated impoundment model to determine KL for the combined agitated surfaces and quiescent surfaces.		
3	Use the aerated impoundment model to determine KL for the combined agitated surfaces and quiescent surfaces.		
4	Use the aerated impoundment model to determine KL if the surface is agitated. Use the quiescent impoundment model if the surface is not agitated. KL includes the effect of volatilization in the air discharge. See section 5.6.1 in AIR EMISSIONS MODELS FOR WASTE AND WASTEWATER (EPA-453/R-94-080A).		
5	KL for the surface is assumed to equal zero. Select the covered unit option with the aerated impoundment model.		

Form III DATA FORM FOR THE ESTIMATION OF THE COMPOUND FRACTION BIODEGRADED AND AIR EMISSIONS			
NAME OF THE FACILITY for site specific biorate determination			example
COMPOUND for site specific biorate determination			<i>methanol</i>
ESTIMATE OF K ₁ from Form I line 11, Form V line 15, Form V-A line 15, Form IV line 14, Form VI line 13, or Form XII line 9. (L/g MLVSS-hr)	1		3.89
BIOMASS (g/L) This is the dried solids that are obtained from the mixed liquor suspended solids in the full-scale bioreactor.	2		2.4
VOLUME of full-scale system (cubic meters)	3		2700
AREA of the liquid surface of the full-scale system (square meters)	4		1500
ESTIMATE OF K _L from Form II, II-A, IV, V, V-A, or V-B (m/s)	5		0.0000036
FLOW RATE of waste treated in full-scale bioreactor (m ³ /s)	6		0.1565
CALCULATIONS FROM ESTIMATES OF K ₁ AND K _L			
BIORATE (m ³ /s) Multiply the numbers on lines 1, 2, and 3 together and divide the results by 3600. Enter the results here.	7		7.0020000
AIR STRIPPING (m ³ /s). Multiply the numbers on lines 4 and 5 together. Enter the results here.	8		0.0054000
EFFLUENT DISCHARGE (m ³ /s). Enter the number on line 6 here.	9		0.1565000
TOTAL of the three loss mechanisms. Add the numbers on lines 7, 8, and 9. Enter the results here.	10		7.1639000
Fraction biodegraded: Divide the number on line 7 by the number on line 10 and enter the results here.	11		0.9774006
Fraction air emissions: Divide the number on line 8 by the number on line 10 and enter the results here.	12		0.0007538
Fraction remaining in unit effluent: Divide the number on line 9 by the number on line 10 and enter the results here.	13		0.0218456
Total: add the numbers on lines 11, 12, and 13. The sum should equal 1.0	14		1.0000000

Form IV DATA FORM FOR THE ESTIMATION OF K1 AND KL FROM FULL SCALE UNIT DATA WITH AND WITHOUT BIODEGRADATION			
For a general discussion of this approach, see Air Emissions Models for Waste and Wastewater, EPA-453/R-94-080A, Chapter 5, November 1994.			
NAME OF THE FACILITY for site specific biorate determination			example
COMPOUND for site specific biorate determination			methanol
BIOMASS (g/L) This is the dried solids that are obtained from the mixed liquor suspended solids in the full-scale bioreactor.	1		2.4
VOLUME of full-scale system (cubic meters)	2		2700
AREA of the liquid surface of the full-scale system (square meters)	3		1500
INLET CONCENTRATION of compound (g/m ³ or ppmw)	4		133.5
EXIT CONCENTRATION of compound (g/m ³ or ppmw)	5		10.57
EXIT CONCENTRATION (NO BIODEGRADATION) of compound (g/m ³ or ppmw)	6		133
FLOW RATE of waste treated in the full-scale bioreactor (m ³ /s)	7		0.1565
ESTIMATES OF K1 AND KL FROM FIELD DATA WITH AND WITHOUT BIODEGRADATION			
REMOVAL WITH BIODEGRADATION (g/s) Subtract the number on line 5 from the number on line 4 and multiply the results by the number on line 7. Enter the results here.	8		19.238545
REMOVAL WITHOUT BIODEGRADATION (g/s) Subtract the number on line 6 from the number on line 4 and multiply the results by the number on line 7. Enter the results here.	9		0.078250
KL A ESTIMATE (m ³ /s) Divide the number on line 9 by the number on line 6. Enter the results here.	10		0.000588
K1 B V + KL A ESTIMATE (m ³ /s) Divide the number on line 8 by the number on line 5. Enter the results here.	11		1.820108
K1 B V ESTIMATE (m ³ /s) Subtract the number on line 10 from the number on line 11. Enter the results here.	12		1.819520
Product of B and V. Multiply the number on line 1 by the number on line 2 and enter the results here.	13		6480
K1 ESTIMATE (L/gMLVSS-hr) Divide the number on line 12 by the number on line 13 and multiply by 3600 s/hr. Enter the results here.	14		1.010844
KL ESTIMATE (m/s) Divide the number on line 10 by the number on line 3. Enter the results here.	15		0.0000004

Form V DATA FORM FOR THE ESTIMATION OF K1 FOR EPA METHOD 304A OR FROM A COVERED, VENTED BIODEGRADATION UNIT.			
For a general discussion of this approach, see Air Emissions Models for Waste and Wastewater, EPA-453/R-94-080A, Chapter 5, November 1994			
NAME OF THE FACILITY for site specific biorate determination			example
COMPOUND for site specific biorate determination			<i>methanol</i>
BIOMASS (g/L) This is the dried solids that are obtained from the mixed liquor suspended solids in the unit.	1		0.075
VENT RATE of total gas leaving the unit (G, m ³ /s)	2		1
TEMPERATURE of the liquid in the unit (deg. C)	3		25
INLET CONCENTRATION of compound (g/m ³ or ppmw)	4		100
EXIT CONCENTRATION of compound (g/m ³ or ppmw)	5		5
ESTIMATE OF Henry's law constant (H, g/m ³ in gas / g/m ³ in liquid). Obtained from Form IX	6		0.00021
AREA OF REACTOR (m ²)	7		3400
VOLUME OF REACTOR (m ³)	8		10000
FLOW RATE of waste treated in the unit (m ³ /s)	9		0.146
CALCULATION OF THE ESTIMATE OF K1			
TOTAL REMOVAL (g/s) Subtract the number on line 5 from the number on line 4 and multiply the result by the number on line 9. Enter the results here.	10		13.870000
[H G] ESTIMATE (m ³ /s) Multiply the number on line 2 by the number on line 6. Enter the results here.	11		0.000021
[K1 B V + H G] (m ³ /s) Divide the number on line 10 by the number on line 5. Enter the results here.	12		2.774000
[K1 B V] ESTIMATE (m ³ /s) Subtract the number on line 11 from the number on line 12. Enter the results here.	13		2.773979
If the number on line 11 is greater than the number on line 13, this procedure cannot be used to demonstrate that the compound is biodegradable. Do not complete lines 14 and 15.			
Product of B and V. Multiply the number on line 1 by the number on line 8 and enter the results here.	14		750.000000
K1 ESTIMATE (L/g MLVSS-hr) Divide the number on line 13 by the number on line 14 and multiply by 3600 s/hr. Enter the results here.	15		13.315099
EQUIVALENT KL. Divide the number on line 11 by the number on line 7. Enter the results on line 16.	16		6.18e-09

This form may be used to estimate the Equivalent KL with input data for lines 2, 6, and 7.

Form V-A DATA FORM FOR THE CALCULATION OF K1 FROM A COVERED, VENTED BIODEGRADABLE UNIT. THE VENT CONCENTRATION IS MEASURED.			
For a general discussion of this approach, see Air Emissions Models for Waste and Wastewater, EPA-453/R-94-080A, Chapter 5, November 1994.			
NAME OF THE FACILITY for site specific biorate determination			example
COMPOUND for site specific biorate determination			<i>methanol</i>
BIOMASS (g/L) This is the dried solids that are obtained from the mixed liquor suspended solids in the unit.	1		0.075
VENT RATE of total gas leaving the unit (G, m ³ /s)	2		.1
TEMPERATURE of the liquid in the unit (deg. C)	3		25
INLET CONCENTRATION of compound (Ci, g/m ³ or ppmw)	4		100
EXIT CONCENTRATION of compound (Ce, g/m ³ or ppmw)	5		5
VENT CONCENTRATION of compound (Cv, g/m ³)	6		0.001
AREA OF REACTOR SURFACE (m ²)	7		3400
VOLUME OF REACTOR (m ³)	8		10000
FLOW RATE of waste treated in the unit (m ³ /s)	9		0.146
CALCULATION OF THE ESTIMATE OF K1			
TOTAL REMOVAL (g/s) Subtract the number on line 5 from the number on line 4 and multiply the results by the number on line 9. Enter the results here.	10		13.87
[G Cv/Ce] ESTIMATE (m ³ /s) Multiply the number on line 2 by the number on line 6 and divide by the number on line 5. Enter the results here.	11		0.000020
[K1 B V + G Cv/Ce] (m ³ /s) Divide the number on line 10 by the number on line 5. Enter the results here.	12		2.77
[K1 B V] ESTIMATE (m ³ /s) Subtract the number on line 11 from the number on line 12. Enter the results here.	13		2.77
If the number on line 11 is greater than the number on line 13, this procedure cannot be used to demonstrate that the compound is biodegradable. Do not complete lines 14 and 15.			
Product of B and V. Multiply the number on line 1 by the number on line 8 and enter the results here.	14		750.00
K1 ESTIMATE (L/g MLVSS-hr) Divide the number on line 13 by the number on line 14 and multiply by 3600 s/hr. Enter the results here.	15		13.30
EQUIVALENT KL. Divide the number on line 11 by the number on line 7. Enter the results here.	16		5.9e-09

This form may be used to calculate the Equivalent KL with input data for lines 2, 5, 6, and 7.

Form V-B DATA FORM FOR THE CALCULATION OF EQUIVALENT KL FROM A VENTED BIODEGRADATION UNIT WITH AN AIR SUPPORTED COVER. THE VENT CONCENTRATION IS MEASURED.			
NAME OF THE FACILITY for site specific biorate determination			example
COMPOUND for site specific biorate determination			<i>methanol</i>
Vent rate of total gas entering the cover (m ³ /s)	1		120
Vent rate of total gas leaving the cover transferred to a control device (m ³ /s)	2		100
TEMPERATURE of the liquid in the unit (deg. C)	3		25
Area of air supported cover (m ²)	4		1950
Permeability through the cover (cm/s)	5		5E-6
VENT CONCENTRATION of compound (g/m ³)	6		0.0022
EXIT CONCENTRATION of compound (g/m ³ or ppmw)	7		10.57
AREA OF REACTOR SURFACE (m ²)	8		1500
Performance of vent control device (% control)	9		95
CALCULATION OF THE ESTIMATE OF EQUIVALENT KL			
Loss of forced air in the cover due to leakage. (m ³ /s) Subtract the number on line 2 from the number on line 1. Enter the results here.	10		20
Loss of compound in forced air (g/s) Multiply the number on line 10 by the number on line 6. Enter the results here.	11		0.044
Loss of compound by permeation through cover (g/s). Line 4 times line 5, line 6, and divide by 100. Enter the results here.	12		0
Loss of compound by permeation through vent (g/s). Line 2 times line 6. Enter the results here.	13		0.22
Treatment of compound in control device (g/s). Line 13 times line 9, divided by 100. Enter the results here.	14		0.209
Total removal from air phase (g/s). Sum of 11, 12, and 13.	15		0.264
Total treatment effectiveness (%) Line 14 divided by 15 times 100.	16		79.1666
[G Cv/Ce] ESTIMATE (m ³ /s) Divide line 15 by line 7.	17		0.025
EQUIVALENT KL. Divide the number on line 17 by line 8.	18		1.67e-05

The permeability is the ratio of the flux (g/cm²) to the gas concentration (g/cm³).
If the gas is generated by the unit, the gas entering the cover may be estimated from an estimate of the cover leak rate and the total gas transferred to the control device.

Form VI DATA FORM FOR THE ESTIMATION OF K1 FROM FULL SCALE UNIT DATA WITH BIODEGRADATION			
NAME OF THE FACILITY for site specific biorate determination			example
COMPOUND for site specific biorate determination			<i>methanol</i>
BIOMASS (g/L) This is the dried solids that are obtained from the mixed liquor suspended solids in the full-scale bioreactor.	1		0.075
VOLUME of full-scale system (cubic meters)	2		100000
AREA of the liquid surface of the full-scale system (square meters)	3		10000
INLET CONCENTRATION of compound (g/m ³ or ppmw)	4		100
EXIT CONCENTRATION of compound (g/m ³ or ppmw)	5		5
ESTIMATE OF KL from Form II (m/s)	6		0.00001
FLOW RATE of waste treated in the full-scale bioreactor (m ³ /s)	7		0.146
CALCULATION OF THE ESTIMATE OF K1 FROM FIELD DATA			
REMOVAL WITH BIODEGRADATION (g/s) Subtract the number on line 5 from the number on line 4 and multiply the results by the number on line 7. Enter the results here.	8		13.87
[KL A] ESTIMATE (m ³ /s) Multiply the number on line 3 by the number on line 6. Enter the results here.	9		0.10
[K1 B V + KL A] (m ³ /s) Divide the number on line 8 by the number on line 5. Enter the results here.	10		2.774
[K1 B V] ESTIMATE (m ³ /s) Subtract the number on line 9 from the number on line 10. Enter the results here.	11		2.674
Product of B and V. Multiply the number on line 1 by the number on line 2 and enter the results here.	12		7500
K1 ESTIMATE (L/g MLVSS-hr) Divide the number on line 11 by the number on line 12 and multiply by 3600 s/hr. Enter the results here.	13		1.28352

FORM VII

DATA FORM FOR CALCULATING THE
MASS TRANSFER COEFFICIENT FOR A QUIESCENT SURFACE IMPOUNDMENT

Facility Name: _____

Waste Stream Compound: _____

Enter the following:

- F - Impoundment fetch (m) _____
- D - Impoundment depth (m) _____
- U_{10} - Windspeed 10 m above liquid surface (m/s) _____
- D_w - Diffusivity of compound in water (cm²/s) _____
- D_{ether} - Diffusivity of ether in water (cm²/s) _____
- μ_G - Viscosity of air, (g/cm-s) _____
- ρ_G - Density of air, (g/cm³) _____
- D_a - Diffusivity of compound in air, (cm²/s) _____
- A - Area of impoundment, (m²) _____
- H - Henry's law constant, (atm-m³/g mol) _____
- R - Universal gas constant, (atm-m³/g mol. °K) _____
- μ_L - Viscosity of water, (g/cm-s) _____
- ρ_L - Density of liquid, (g/cm³) _____
- T - Impoundment temperature, (°C) _____

Calculate the following:

Calculate F/D: _____

A. Calculate the liquid phase mass transfer coefficient, k_L , using one of the following procedures, (m/s)

1. Where $F/D < 14$ and $U_{10} > 3.25$ m/s, use the following procedure from MacKay and Yeun:

Calculate the Schmidt number on the liquid side, Sc_L , as follows:

$$Sc_L = \mu_L / \rho_L D_w \quad \underline{\hspace{2cm}}$$

Calculate the friction velocity, U^* , as follows, (m/s):

$$U^* = 0.01 \times U_{10} (6.1 + 0.63 U_{10})^{0.5} \quad \underline{\hspace{2cm}}$$

Where U^* is > 0.3 , calculate k_L as follows:

$$k_L = (1.0 \times 10^{-6}) + (34.1 \times 10^{-6}) U^* \times Sc_L^{-0.5} \quad \underline{\hspace{2cm}}$$

Where U^* is < 0.3 , calculate k_L as follows:

$$k_L = (1.0 \times 10^{-9}) + (144 \times 10^{-4}) (U^*)^{2.2} \times Sc_L^{-0.5} \quad \underline{\hspace{2cm}}$$

2. For all other values of F/D and U_{10} , calculate k_L using the following procedure from Springer:¹

¹Springer, C., P. D. Lunney, and K. T. Valsaraj. Emission of Hazardous Chemicals from Surface and Near Surface Impoundments to Air. U.S. Environmental Protection Agency, Solid and Hazardous Waste Research Division. Cincinnati, OH. Project Number 808161-02. December 1984.

Where U_{10} is < 3.25 m/s, calculate k_L as follows:

$$k_L = 2.78 \times 10^{-6} (D_w/D_{ether})^{2/3}$$

Where U_{10} is > 3.25 and $14 < F/D < 51.2$, Calculate k_L as follows:

$$k_L = [2.605 \times 10^{-9} (F/D) + 1.277 \times 10^{-7}] U_{10}^2 (D_w/D_{ether})^{2/3}$$

Where $U_{10} > 3.25$ m/s and $F/D > 51.2$, calculate k_L as follows:

$$k_L = (2.611 \times 10^{-7}) U_{10}^2 (D_w/D_{ether})^{2/3}$$

- B. Calculate the gas phase mass transfer coefficient, k_G , using the following procedure from MacKay and Matsasugu, (m/s):²

Calculate the Schmidt number on the gas side, Sc_G , as follows: $Sc_G = \mu_g/\rho_g D_a$

Calculate the effective diameter of the impoundment, d_e , as follows, (m):

$$d_e = (4A/\pi)^{0.5}$$

Calculate k_{G1} as follows, (m/s): $k_{G1} = 4.82 \times 10^{-3} U_{10}^{0.78} Sc_G^{-0.67} d_e^{-0.11}$

- C. Calculate the partition coefficient, Keq , as follows: $Keq = H/[R(T+273)]$

- D. Calculate the overall mass transfer coefficient, K_q , as follows, (m/s):

$$1/K_q = 1/k_L + 1/Keq - k_G$$

Where the total impoundment surface is quiescent:

$$KL = K_q$$

Where a portion of the impoundment surface is turbulent, continue with Form VIII.

²Hwang, S. T. Toxic Emissions from Land Disposal Facilities. Environmental Progress. 1:46-52. February 1982.

FORM VIII

DATA FORM FOR CALCULATING THE
MASS TRANSFER COEFFICIENT FOR AN AERATED SURFACE IMPOUNDMENT

Facility Name: _____

Waste Stream Compound: _____

Enter the following:

- J - Oxygen transfer rating of surface aerator, (lb O₂/hr-hp) _____
- POWR - Total power to aerators, (hp) _____
- T - Water temperature, (°C) _____
- O_t - Oxygen transfer correction factor _____
- MW_L - Molecular weight of liquid _____
- A_t - Turbulent surface area of impoundment, (ft²) _____
(If unknown, use values from Table 1)
- A - Total surface area of impoundment, (ft²) _____
- ρ_L - Density of liquid, (lb/ft³) _____
- D_w - Diffusivity of constituent in water, (cm²/s) _____
- D_{O₂,w} - Diffusivity of oxygen in water, (cm²/s) _____

- d - Impeller diameter, (cm) _____
- w - Rotational speed of impeller, (rad/s) _____
- ρ_a - Density of air, (gm/cm³) _____
- N - Number of aerators _____
- g_c - Gravitation constant, (lb_m-ft/s²/lb_f) _____
- d' - Impeller diameter, (ft) _____
- D_a - Diffusivity of constituent in air, (cm²/s) _____
- MW_a - Molecular weight of air _____
- R - Universal gas constant, (atm-m³/g mol. °C) _____
- H = Henry's law constant, (atm-m³/g mol) _____

Calculate the following:

- A. Calculate the liquid phase mass transfer coefficient, k_L, using the following Equation from Thibodeaux:^{3,4}

$$k_L = [8.22 \times 10^{-9} J (POWR)(1.024)^{T-20} O_t 10^6 MW_L / (V_a \rho_L)] (D_w / D_{O_2,w})^{0.5}, (m/s)$$

³GCA Corporation. Emissions Data and Model Review for Wastewater Treatment Operations. Draft Technical Note. Prepared for U.S. Environmental Protection Agency. Contract No. 68-01-6871, Assignment 49. August 1985. p. 4-2.

⁴Hwang, S. T. Toxic Emissions from Land Disposal Facilities. Environmental Progress. 1:46-52. February 1982.

B. Calculate the gas phase mass transfer coefficient, k_G , using the following procedure from Reinhardt:^{5,6}

Calculate the viscosity of air, μ_a , as follows, (g/cm.s):
 $\mu_a = 4.568 \times 10^{-7} T + 1.7209 \times 10^{-4}$ _____

Calculate the Reynold's number as follows:
 $R_e = d^2 w \rho_a / \mu_a$ _____

Calculate power to impeller, P_i , as follows, (ft.lb/s):
 $P_i = 0.85 (\text{POWR}) 550/N$ _____

Calculate the power number, p , as follows:
 $p = P_i g_c / (\rho_L d^5 w^3)$ _____

Calculate the Schmidt number, Sc_G , as follows:
 $Sc_G = \mu_a / \rho_a D_a$ _____

Calculate the Fronde number, F_r , as follows:
 $F_r = d^3 w^2 / g_c$ _____

Calculate k_G as follows:
 $k_G = 1.35 \times 10^{-7} R_e^{1.42} p^{0.4} Sc_G^{0.5} F_r^{-0.21} D_a \text{MW}_g / d$, (m/s) _____

C. Calculate the partition coefficient, K_{eq} , as follows:
 $K_{eq} = H/[R(T+273)]$ _____

D. Calculate the overall turbulent mass transfer coefficient, K_t , as follows, (m/s):
 $1/K_t = 1/k_L + 1/K_{eq} k_G$ _____

E. Calculate the quiescent mass transfer coefficient, K_q , for the impoundment using Form VII.

F. Calculate the overall mass transfer coefficient, KL , for the impoundment as follows:
 $KL = \frac{K_q (A - A_t) + K_t A_t}{A}$ _____

⁵GCA Corporation. Emissions Data and Model Review for Wastewater Treatment Operations. Draft Technical Note. Prepared for U.S. Environmental Protection Agency. Contract No. 68-01-6871, Assignment 49. August 1985. p. 4-3.

⁶Reinhardt, J. R. Gas-Side Mass-Transfer Coefficient and Interfacial Phenomena of Flat-Bladed Surface Agitators. Ph.D. dissertation, University of Arkansas, Fayetteville, Ar. 1977. p. 48.

Table 1. Turbulent Areas and Volumes for Surface Agitators^a

ω , Motor horsepower, hp	A_t , Turbulent area,		Effective depth, ft	V , Agitated volume, ft ³	a_v , Area per volume ft ² /ft ³
	ft ²	m ²			
5	177	16.4	10	1,767	0.100
7.5	201	18.7	10	2,010	0.100
10	227	21	10.5	2,383	0.0952
15	284	26.4	11	3,119	0.0909
20	346	32.1	11.5	3,983	0.0870
25	415	38.6	12	4,986	0.0833
30	491	45.7	12	5,890	0.0833
40	661	61.4	13	8,587	0.0769
50	855	79.5	14	11,970	0.0714
60	1,075	100	15	16,130	0.0666
75	1,452	135	16	23,240	0.0625
100	2,206	205	18	39,710	0.0555

^aData for a high speed (1,200 rpm) aerator with 60 cm propeller diameter (d).

Form IX DATA FORM FOR THE ESTIMATION OF THE HENRY'S LAW CONSTANT FOR A COMPOUND IN THE BIOLOGICAL TREATMENT UNIT			
NAME OF THE FACILITY for site specific biorate determination			example
COMPOUND for site specific biorate determination			<i>methanol</i>
LISTED HENRY'S LAW VALUE AT 25 degrees Celsius. (Table 1, ratio of mol fraction in gas to mole fraction in water)	1		.2885
TEMPERATURE of the liquid in the unit (deg.C)	2		25
CALCULATION OF K			
Temperature adjusted Henry's law value (equals the value on line 1 if the temperature on line 2 is 25)	3		0.2885
Discuss basis of temperature adjustment			
Temperature in degrees Kelvin. Add 273.16 to the number on line 2. Enter the results here.	4		298.1600
Temperature ratio. Divide 273.16 by the number on line 4. Enter the results here.	5		0.9162
Henry's Law adjustment factor. Multiply the number on line 5 by 0.804 and enter the results here.	6		0.7366
Henry's Law value (g/m ³ gas per g/m ³ liquid) Multiply the number on line 3 by the number on line 6 and divide the results by 1000. Enter the results here and on Form V line 6.	7		0.000213
Henry's Law value (atm m ³ per mol) Divide the number on line 3 by 55555 and enter the results here.	8		0.000005

Form X DATA FORM FOR THE CALCULATION OF THE HENRY'S LAW CONSTANT FOR A COMPOUND IN A SEALED BATCH TEST					
NAME OF THE FACILITY for site specific biorate determination					example
COMPOUND for site specific biorate determination					methanol
REACTOR HEADSPACE VOLUME, (L)			1		1
REACTOR LIQUID VOLUME (L)			2		10
TEMPERATURE of the liquid in the unit (deg.C)			3		25
Wastewater compounds are biodegraded by biomass in a sealed batch test. For the compound listed above, a data set of liquid and gas concentrations is measured at four different times during the sealed batch test. The data are entered below, and the ratio of the concentrations for each data set is entered in column E.					
A	B	C	D	E	
Data set	Time (hr)	Liquid Conc. (mg/L)	Gas Conc. (mg/L)	K_{eq} D/C	.0002108
1					
2					
3					
4					
Temperature in degrees Kelvin. Add 273.16 to the number on line 3. Enter the results here			4		298.16
Molar ratio. Multiply the number on line 4 by 4.555. Enter the results on line 5.			5		1,358.12
Henry's law value (mg/L gas per mg/L liquid). Enter the average value in column E above on line 6.			6		0.000211
Henry's law value (mole fraction gas per mole fraction liquid) Multiply the number on line 6 by the number on line 5. Enter the results on line 7.			7		0.286563
Expected Henry's law value. Enter the number from Form IX line 3.			8		0.288500
Precision: Discuss any variability of the numbers in column E. Accuracy: Discuss any difference between the numbers on line 7 and line 8. Identify which value will be used for evaluating the biodegradation rate data. Divide the Henry's law value by the number on line 5 and enter the results on line 9.					
K_{eq} value (mg/L gas per mg/L liquid)			9		0.000211
HEADSPACE CORRECTION FACTOR. Divide the number on line 2 by the sum of the number on line 2 and the product of the numbers on line 9 and line 1. Enter the result on line 10.			10		0.999979
The headspace correction factor should equal approximately 1 if the headspace is relatively small. Reducing the headspace volume may improve the test data quality if the headspace correction factor is substantially less than one.					

Form XI DATA FORM FOR THE CALCULATION OF THE HENRY'S LAW CONSTANT AND THE STRIPPING CONSTANT FOR A COMPOUND IN AN AERATED BATCH TEST				
NAME OF THE FACILITY for site specific biorate determination				example
COMPOUND for site specific biorate determination				<i>methanol</i>
Concentration basis (liquid or gas)				gas
TEMPERATURE of the liquid in the unit (deg.C)		1		25
GAS FLOW RATE (L/hr)		2		1
LIQUID VOLUME (L)		3		10
Co concentration measurement at time=0 (mg/L)		4		
A	B	C	D	E
data point	time (hr)	Concentration, C (mg/L)	C/Co	-ln(C/Co)
1				
2				
3				
4				
5				
CALCULATIONS. Use additional lines as needed in an expansion of the above table. Plot the values in column E (y axis) vs the data in column B (x axis). Reject outliers. Curve fit with a straight line. Calculate the slope and enter the slope on line 7. Attach the plot and table to this form.				
Temperature in degrees Kelvin. Add 273.16 to the number on line 1. Enter the results here		5		298.16
MOLAR RATIO. Multiply the number on line 5 by 4.555. Enter the results on line 6.		6		1,358.12
Slope of the plot of -ln(C/Co) vs time (per hour)		7		2.10e-05
Calculated K_{eq} value (mg/L gas per mg/L liquid). Divide the number on line 7 by the number on line 2 and multiply the results by the number on line 3. Enter the results on line 8.		8		0.000210
Expected K_{eq} value. Divide the number from Form IX line 3 by the number on line 6 and enter the results on line 9.		9		0.000212
Discuss any differences between the numbers on line 8 and line 9. Identify which value will be used for the evaluation of the stripping constant (line 10). Problems can sometimes be resolved by system redesign, changing the bubble size, or confirming the experimental value of K_{eq} by using Form X.				
K_{eq} value (mg/L gas per mg/L liquid)		10		0.000210
STRIPPING CONSTANT(per hour). Divide the number on line 10 by number on line 3 and multiply by the number on line 2. Enter the final result on line 11.		11		0.000021
The headspace correction factor equals one for an aerated batch test.				

Form XII DATA FORM FOR THE CALCULATION OF BATCH RATES AND THE DETERMINATION OF THE MONOD CONSTANTS						
Complete this table with measured liquid concentrations from the batch test. If headspace concentrations were measured and equilibrium has been verified, convert them to liquid concentrations by using K_{eq} . If the data are scattered, plot the concentration vs. time data, and fit the data with a curve based on Equation Appendix C-4 for the Aerated Batch test or Equation Appendix C-6 for the Sealed Batch test. Complete this form with concentrations obtained from that fitted curve. If the curve fitting approach is used, attach a plot of the data and the associated fitted curve to this form. Note: If the initial results appear to be anomalous, do not use the initial results.						
COMPOUND for site specific biorate determination						Methanol
Stripping rate constant (/hr) Form XI, line 11					1	2.1e-5
Enter the batch test Biomass concentration (g/L) on line 2.					2	.258
Headspace correction factor. For a Sealed Batch test use Form X line 10 or 1.00 for an Aerated Batch test.					3	0.999979
A	B	C	D	E	F	G
concentration S (mg/L)	time (hr)	Rate for interval (mg/L-hr) $(a-a_{t+1}) / (b_{t+1}-b_t)$	Log Mean S for interval (mg/L) $(a-a_{t+1}) / \ln(a/a_{t+1})$	Ratio of rate to S (/hr) (C/D)	Adjusted rate (/hr) (E-line 1)	Reciprocal of adj. rate (hr) (1/F)
1.						
2.						
3.						
4.						
5.						
6.						
7.						
8.						
9.						
Continue table on attached sheet as needed. Plot values in column G on y axis, values in column D on x axis. Extrapolate the trend of data points to the y intercept (S=0). Attach the plot to the form.						
Slope of line near intercept (hr-L/mg)					4	.4845
Y intercept from plot (hr)					5	1.938
First order rate constant K1 (or Q_m/K_s , L/g-hr). The number 1.00 divided by the products of the values on line 5, line 2, and line 3.					6	2.000026
Zero order rate constant (Q_m , /hr). The number 1.00 divided by the products of the values on line 4, line 2, and line 3.					7	8.000104
Concentration applicable to full-scale unit. Enter on line 8.					8	5
Effective biorate K1 ESTIMATE (L/g MLVSS-hr)*					9	0.9606
*Match the concentration on line 8 to the values in Column D and look up the equivalent rate in Column F. Divide the result with both the biomass concentration (line 2) and the headspace correction factor (line 3). Enter this value on line 9. Do not use this method to estimate K1 for line 9 if the data quality is poor in Column F. The number on line 9 is multiplied by the biomass and the system concentration to estimate the full scale biorate. Alternatively, the Monod model parameters may be used.						

FORM XIII. DATA FORM FOR THE ESTIMATION OF MULTIPLE ZONE BIODEGRADATION FROM UNIT CONCENTRATIONS

NAME OF THE FACILITY for site specific biorate determination	
COMPOUND for site specific biorate determination	
Number of zones in the biological treatment unit	1
VOLUME of full-scale system (cubic meters)	2
Average DEPTH of the full-scale system (meters)	3
FLOW RATE of wastewater treated in the unit (m ³ /s)	4
Recycle flow of wastewater added to the unit, if any (m ³ /s)	5
Concentration in the wastewater treated in the unit (mg/L)	6
Concentration in the recycle flow, if any (mg/L)	7
Concentration in the effluent (mg/L).	8

TOTAL INLET FLOW (m ³ /s) line 4 plus the number on line 5	9
TOTAL RESIDENCE TIME (s) line 2 divided by line 9.	10
TOTAL AREA OF IMPOUNDMENT (m ²) line 2 divided by line 3	11

Zone number	Concentration for zone, C _i (mg/L)	Area of the zone, A (m ²)	Estimate of KL in the zone (m/s) from Form II		AIR STRIPPING KL A C _i (g/s)
1					
2					
3					
4					
5					
6					
7					
8					
9					
10					
TOTALS sum for each zone.	12		13		

Removal by air stripping (g/s). Line 13.	14
Loading in effluent (g/s). Line 8 times line 9.	15
Total loading (g/s). (Line 5 * line 7) + (line 4* line 6).	16
Removal by biodegradation (g/s) Line 16 minus (line 14 + line 15).	17
Fraction biodegraded: Divide line 17 by line 16..	18
Fraction air emissions: Divide line 14 by line 16.	19
Fraction remaining in unit effluent: Divide line 15 by line 16.	20

[62 FR 2801, Jan. 17, 1997, as amended at 63 FR 67794, Dec. 9, 1998; 66 FR 6935, Jan. 22, 2001]

APPENDIX D TO PART 63—ALTERNATIVE VALIDATION PROCEDURE FOR EPA WASTE AND WASTEWATER METHODS

Sections 5.1 and 5.3 of Test Method 301, 40 CFR Part 63, Appendix A. For the purposes of this appendix, "waste" means waste and wastewater.

1. Applicability

This procedure is to be applied exclusively to Environmental Protection Agency methods developed by the Office of Water and the Office of Solid Waste. Alternative methods developed by any other group or agency shall be validated according to the procedures in

2. Procedure

This procedure shall be applied once for each waste matrix. Waste matrix in the context of this procedure refers to the target compound mixture in the waste as well as the formulation of the medium in which the

target compounds are suspended. The owner or operator shall prepare a sampling plan. Wastewater samples shall be collected using sampling procedures which minimize loss of organic compounds during sample collection and analysis and maintain sample integrity. The sample plan shall include procedures for determining recovery efficiency of the relevant compounds regulated in the applicable subpart. An example of an acceptable sampling plan would be one that incorporates similar sampling and sample handling requirements to those of Method 25D of 40 CFR part 60, appendix A.

2.1. Sampling and Analysis

2.1.1. For each waste matrix, collect twice the number of samples required by the applicable regulation. Designate and label half the sample vials the "spiked" sample set, and the other half the "unspiked" sample set. Immediately before or immediately after sampling (immediately after in the context of this procedure means after placing the sample into the sample vial, but before the sample is capped, cooled, and shipped to the laboratory for analysis), inject, either individually or as a solution, all the target compounds into each spiked sample.

2.1.2. The mass of each spiked compound shall be 40 to 60 percent of the mass expected to be present in the waste matrix. If the concentration of the target compounds in the waste are not known, the mass of each spiked compound shall be 40 to 60 percent of the limit allowed in the applicable regula-

tion. Analyze both sets of samples (spiked and unspiked) with the chosen method.

3. Calculations

For each pair of spiked and unspiked samples, determine the fraction of spiked compound recovered (R) using the following equations.

where:

m_r = mass spiked compound measured (μ g).

m_s = total mass of compound measured in spiked sample (μ g).

m_u = total mass of compound measured in unspiked sample (μ g).

where:

S = theoretical mass of compound spiked into spiked sample (μ g).

3.1. Method Evaluation

In order for the chosen method to be acceptable for a compound, $0.70 \leq R \leq 1.30$ (R in this case is an average value of all the spiked and unspiked sample set R values). If the average R value does not meet this criterion for a target compound, the chosen method is not acceptable for that compound, and therefore another method shall be evaluated for acceptance (by repeating the procedures outlined above with another method).

3.2. Records and Reports

Report the average R value in the test report and correct all reported measurements made with the method with the calculated R value for that compound by using the following equation:

$$\text{Reported Result} = \frac{\text{Measured Mass of Compound}}{\text{R for that compound}}$$

3.3. Optional Correction Step

If the applicable regulation allows for correction of the mass of the compound in the waste by a published f_m value, multiply the reported result calculated above with the appropriate f_m value for that compound.

[61 FR 34200, July 1, 1996]

APPENDIX E TO PART 63—MONITORING PROCEDURE FOR NONTHOROUGHLY MIXED OPEN BIOLOGICAL TREATMENT SYSTEMS AT KRAFT PULP MILLS UNDER UNSAFE SAMPLING CONDITIONS

I. Purpose

This procedure is required to be performed in subpart S of this part, entitled National Emission Standards for Hazardous Air Pol-

lutants from the Pulp and Paper Industry. Subpart S requires this procedure in §63.453(p)(3) to be followed during unsafe sampling conditions when it is not practicable to obtain representative samples of hazardous air pollutants (HAP) concentrations from an open biological treatment unit. It is assumed that inlet and outlet HAP concentrations from the open biological treatment unit may be obtained during the unsafe sampling conditions. The purpose of this procedure is to estimate the concentration of HAP within the open biological treatment unit based on information obtained at inlet and outlet sampling locations in units that are not thoroughly mixed and, therefore, have different concentrations of HAP at different locations within the unit.

II. Definitions

Biological treatment unit = wastewater treatment unit designed and operated to promote the growth of bacteria to destroy organic materials in wastewater.

f_{bio} = The fraction of organic compounds in the wastewater biodegraded in a biological treatment unit.

F_e = The fraction of applicable organic compounds emitted from the wastewater to the atmosphere.

K_1 = First-order biodegradation rate constant, L/g mixed liquor volatile suspended solids (MLVSS)-hr

KL = Liquid-phase mass transfer coefficient, m/s

K_s = Monod biorate constant at half the maximum rate, g/m³

III. Test Procedure for Determination of f_{bio} for Nonthoroughly Mixed Open Biological Treatment Units Under Unsafe Sampling Conditions

This test procedure is used under unsafe sampling conditions that do not permit practicable sampling of open biological treatment units within the unit itself, but rather relies on sampling at the inlet and outlet locations of the unit. This procedure may be used only under unsafe sampling conditions to estimate f_{bio} . Once the unsafe conditions have passed, then the formal compliance demonstration procedures of f_{bio} based upon measurements within the open biological treatment unit must be completed.

A. Overview of Estimation Procedure

The steps in the estimation procedure include data collection, the estimation of concentrations within the unit, and the use of Form 1 to estimate f_{bio} . The data collection procedure consists of two separate components. The first data collection component demonstrates that the open biological treatment unit can be represented by Monod kinetics and characterizes the effectiveness of the open biological treatment unit as part of the initial performance test, and the second data collection component is used when there are unsafe sampling conditions. These two data collection components are used together in a data calculation procedure based on a Monod kinetic model to estimate the concentrations in each zone of the open biological treatment unit. After the first two components of data collection are completed, the calculation procedures are used to back estimate the zone concentrations, starting with the last zone in the series and ending with the first zone.

B. Data Collection Requirements

This method is based upon modeling the nonthoroughly mixed open biological treatment unit as a series of well-mixed zones

with internal recycling between the units and assuming that two Monod biological kinetic parameters can be used to characterize the biological removal rates in each unit. The data collection procedure consists of two separate components. The first data collection component is part of the initial performance test, and the second data collection component is used during unsafe sampling conditions.

1. Initial Performance Test

The objective of the first data collection component is to demonstrate that the open biological treatment unit can be represented by Monod kinetics and to characterize the performance of the open biological treatment unit. An appropriate value of the biorate constant, K_s , is determined using actual sampling data from the open biological treatment unit. This is done during the initial performance test when the open biological treatment unit is operating under normal conditions. This specific K_s value obtained during the initial performance test is used in the calculation procedure to characterize the open biological treatment unit during unsafe sampling conditions. The following open biological treatment unit characterization information is obtained from the first component of the data collection procedure:

- (1) The value of the biorate constant, K_s ;
- (2) The number and characteristics of each zone in the open biological treatment unit (depth, area, characterization parameters for surface aeration, submerged aeration rates, biomass concentration, concentrations of organic compounds, dissolved oxygen (DO), dissolved solids, temperature, and other relevant variables); and
- (3) The recycle ratio of internal recirculation between the zones. The number of zones and the above characterization of the zones are also used to determine the performance of the unit under the unsafe sampling conditions of concern.

2. Data Collected Under Unsafe Sampling Conditions

In the second data collection component obtained under unsafe sampling conditions, the measured inlet and outlet HAP concentrations and the biomass concentration are obtained for the open biological treatment unit. After the site specific data collection is completed on the day a parameter excursion occurs, the inlet and outlet concentrations are used with the prior open biological treatment unit characterization to estimate the concentrations of HAP in each zone. The following information on the open biological treatment unit must be available in the second data collection component:

- (1) Basic unit variables such as inlet and recycle wastewater flow rates, type of agitation, and operating conditions;

(2) The value of the inlet and outlet HAP concentrations; and

(3) The biomass concentration in the open biological treatment unit.

C. One Time Determination of a Single Value of Ks (Initial Performance Test)

A single value of Ks is calculated using Form 3 for each data set that is collected during the initial performance test. A single composite value of Ks, deemed to be representative of the biological unit, is subsequently selected so that the f_{bio} values calculated by the procedures in this appendix (using this single value of Ks) for the data sets collected during the initial performance test are within 10 percent of the f_{bio} value determined by using Form 1 with these same data sets. The value of Ks meeting these criteria is obtained by the following steps:

(1) Determine the median of the Ks values calculated for each data set;

(2) Estimate f_{bio} for each data set using the selected Ks value (Form 1 and Form 2);

(3) Calculate f_{bio} for each data set using Form 1; and

(4) Compare the f_{bio} values obtained in steps (2) and (3); if the f_{bio} value calculated using step (2) differs from that calculated using step (3) by more than 10 percent, adjust Ks (decrease Ks if the f_{bio} value is lower than that calculated by Form 1 and vice versa) and repeat this procedure starting at step (2). If a negative value is obtained for the values of Ks, then this negative kinetic constant may not be used with the Monod model. If a negative value of Ks is obtained, this test procedure cannot be used for evaluating the performance of the open biological treatment unit.

D. Confirmation of Monod Kinetics (Initial Performance Test)

(1) Confirmation that the unit can be represented by Monod kinetics is made by identifying the following two items:

(i) The zone methanol concentrations measured during the initial performance test; and

(ii) The zone methanol concentrations estimated by the Multiple Zone Concentrations Calculations Procedure based on inlet and outlet concentrations (Column A of Form 2). For each zone, the concentration in item 1 is compared to the concentration in item 2.

(2) For each zone, the estimated value of item 2 must be:

(i) Within 25 percent of item 1 when item 1 exceeds 8 mg/L; or

(ii) Within 2 mg/L of item 1 when item 1 is 8 mg/L or less.

(3) Successful demonstration that the calculated zone concentrations meet these criteria must be achieved for 80 percent of the performance test data sets.

(4) If negative values are obtained for the values of K1 and Ks, then these negative kinetic constants may not be used with the Monod model, even if the criteria are met. If negative values are obtained, this test procedure cannot be used for evaluating the performance of the open biological treatment unit.

E. Determination of KL for Each Zone (Unsafe Sampling Conditions)

(1) A site-specific liquid-phase mass transfer coefficient (KL) must be obtained for each zone during the unsafe sampling conditions. Do not use a default value for KL. The KL value for each zone must be based on the site-specific parameters of the specific unit. The first step in using this procedure is to calculate KL for each zone in the unit using Form 4. Form 4 outlines the procedure to follow for using mass transfer equations to determine KL. Form 4 identifies the appropriate form to use for providing the detailed calculations to support the estimate of the value of KL. Forms 5 and 6 are used to provide individual compound estimates of KL for quiescent and aerated impoundments, respectively. A computer model may be used to perform the calculations. If the WATER8 model or the most recent update to this model is used, then report the computer model input parameters that you used as an attachment to Form 4. In addition, the Bay Area Sewage Toxics Emission (BASTE) model, version 3.0, or equivalent upgrade and the TOXCHEM (Environment Canada's Wastewater Technology Centre and Environmega, Ltd.) model, version 1.10, or equivalent upgrade may also be used to determine KL for the open biological treatment unit with the following stipulations:

(i) The programs must be altered to output a KL value that is based on the site-specific parameters of the unit modeled; and

(ii) The Henry's law value listed in Form 4 must be substituted for the existing Henry's law values in the models.

(2) The Henry's law value listed in Form 4 may be obtained from the following sources:

(i) Values listed by EPA with temperature adjustment if needed;

(ii) Measured values for the system of concern with temperature adjustment; or

(iii) Literature values of Henry's law values for methanol, adjusted for temperature if needed.

(3) Input values used in the model and corresponding output values shall become part of the documentation of the f_{bio} determination. The owner or operator should be aware that these models may not provide equivalent KL values for some types of units. To obtain an equivalent KL value in this situation, the owner or operator shall either use the appropriate procedure on Form 4 or adjust the KL value from the model to the equivalent KL value as described on Form 4.

(4) Report the input parameters that you used in the computer model on Forms 5, 6, and 7 as an attachment to Form 4. If you have submerged air flow in your unit, you must add the value of KL estimated on Form 7 to the value of KL obtained with Forms 5 and 6 before using the value of KL with Form 2.

**F. Estimation of Zone Concentrations
(Unsafe Sampling Conditions)**

Form 2 is used to estimate the zone concentrations of HAP based on the inlet and outlet data. The value of Ks entered on the form is that single composite value of Ks discussed in section III.C of this appendix. This value of Ks is calculated during the Initial Performance Test (and subsequently updated, if necessary). A unique value of the biorate K1 is entered on line 5 of Form 2, and the inlet concentration is estimated in Column A of Form 2. The inlet concentration is located in the row of Form 2 corresponding to zone 0. If there are three zones in the system, n-3 equals 0 for the inlet concentration row. These estimated zone concentrations are then used in Form 1 to estimate f bio for the treatment unit.

**G. Quality Control/Quality Assurance (QA/
QC)**

A QA/QC plan outlining the procedures used to determine the measured inlet and outlet concentrations during unsafe conditions and how the zone characterization data were obtained during the initial performance test shall be prepared and submitted with the initial performance test report. The plan should include, but may not be limited to:

(1) A description of each of the sampling methods that were used (method, procedures, time, method to avoid losses during sampling and holding, and sampling procedures) including simplified schematic drawings;

(2) A description of how that biomass was sampled from the biotreatment unit, including methods, locations, and times;

(3) A description of what conditions (DO, temperature, etc.) are important, what the target values are in the zones, how the factors were controlled, and how they were monitored. These conditions are primarily used to establish that the conditions of the

initial performance test correspond to the conditions of the day in question;

(4) A description of how each analytical measurement was conducted, including preparation of solutions, dilution procedures, sampling procedures, monitoring of conditions, etc;

(5) A description of the analytical instrumentation used, how the instruments were calibrated, and a summary of the accuracy and precision for each instrument;

(6) A description of the test methods used to determine HAP concentrations and other measurements. Section 63.457(c)(3) specifies the test methods that must be used to determine HAP concentrations. During unsafe sampling conditions, you do not have to sample over an extended period of time or obtain more than one sample at each sample point.

(7) A description of how data are captured, recorded, and stored; and

(8) A description of the equations used and their solutions for sampling and analysis, including a reference to any software used for calculations and/or curve-fitting.

**IV. Calculation of Individual f_{bio} (Unsafe
Sampling Conditions)**

Use Form 1 with your zone concentration information to estimate the value of f bio under unsafe sampling conditions. Form 1 uses measured concentrations of HAP in the unit inlet and outlet, and Form 1 also uses the estimated concentrations in each zone of the unit obtained from Form 2. This procedure may be used on an open biological treatment unit that has defined zones within the unit. Use Form 1 to determine f_{bio} for each open biological treatment unit as it exists under subpart S of part 63. The first step in using Form 1 is to calculate KL for each zone in the unit using Form 4. Form 7 must also be used if submerged aeration is used. After KL is determined using field data, obtain the concentrations of the HAP in each zone. In this alternative procedure for unsafe sampling conditions, the actual measured concentrations of the HAP in each zone are replaced with the zone concentrations that are estimated with Form 2. After KL and the zone concentrations are determined, Form 1 is used to estimate the overall unit F_e and f_{bio} for methanol.

Form 1

DATA FORM FOR THE ESTIMATION OF MULTIPLE ZONE BIODEGRADATION FROM UNIT CONCENTRATIONS

NAME OF THE FACILITY for site specific biorate determination	
COMPOUND for site specific biorate determination	Methanol
Number of zones in the biological treatment unit	1
VOLUME of full-scale system (cubic meters)	2
Average DEPTH of the full-scale system (meters)	3
FLOW RATE of wastewater treated in the unit (m ³ /s)	4
Recycle flow of wastewater added to the unit, if any (m ³ /s)	5
Concentration in the wastewater treated in the unit (mg/L)	6
Concentration in the recycle flow, if any (mg/L)	7
Concentration in the effluent (mg/L).	8

TOTAL INLET FLOW (m ³ /s) line 4 plus the number on line 5	9
TOTAL RESIDENCE TIME (s) line 2 divided by line 9.	10
TOTAL AREA OF IMPOUNDMENT (m ²) line 2 divided by line 3	11

Zone number	Concentration for zone, C _i (mg/L)	Area of the zone, A (m ²)	Estimate of KL in the zone (m/s) from Form 4	AIR STRIPPING KL A C _i (g/s)
1				
2				
3				
4				
5				
6				
7				
8				
9				
10				
TOTALS sum for each zone.		12		13

Removal by air stripping (g/s). Line 13.	14
Loading in effluent (g/s). Line 8 times line 9.	15
Total loading (g/s). (Line 5 * line 7) + (line 4* line 6).	16
Removal by biodegradation (g/s) Line 16 minus (line 14 + line 15).	17
Fraction biodegraded: Divide line 17 by line 16.	18
Fraction air emissions: Divide line 14 by line 16.	19
Fraction remaining in unit effluent: Divide line 15 by line 16.	20

DATA FORM FOR THE DETERMINATION OF ZONE CONCENTRATIONS FROM KS AND INLET/OUTLET DATA								
COMPOUND for site specific biorates determination						Methanol		
Influent Flow (m ³ /s)						1		
Inlet Concentration (g/m ³)						2		
Outlet Concentration (g/m ³) - Use value from line 3 as Ci value in column A for final Zone (zone n) in table below						3		
Saturation Coefficient, Ks (g/m ³) From Form 3						4		
Biorate K1 (1/s) - Estimate						5		
Number of Zones						6		
<p>Adjust K1 value (line 5) until Column A, Row (n - line 6) is within +/- 5% of line 2.</p> <p>Instructions for completion of table: (1) Transfer value from line 3 into row n, column A. (2) Enter data for all zones into columns B, D, E, G, H, & K. (3) Beginning with row n, perform calculations for columns F, I, J, L, M, N, & O for that zone only. (4) Calculate row n-1, column A using results from previous row (i.e., J_{i-1}, M_{i-1}, N_{i-1}). (5) Repeat steps (3) and (4) until a row of calculations has been completed for each zone. (6) row n - line 6, column A is the calculated inlet concentration.</p>								
	A	B	C	D	E	F	G	H
Zone	Ci					line 5 * A*C*D		
Number	(J _{i-1} + N _{i-1})/O _{i-1}	Temp C	(1.045) ^(B-25)	biomass g/m ³	Volume m ³	*E/(line 4+ A) g/s	KL m/s	Area m ²
n								
n-1								
n-2								
n-3								
n-4								
	I	J	K	L	M	N	O	
Zone		Reaction		(1+BM _i +BM _{i+1})	BM _{i+1} * C _{i+1}	Flux	(1+BM _i) *	
Number	A*G*H	F+I	Backmix BM _i	*C _i *line 1 g/s	*line1 g/s	L-M g/s	line1 g/s	
n								
n-1								
n-2								
n-3								
n-4								
<p>The backmix ratio, Bmi, is the ratio of (the return flow from the zone back to the upstream zone) to (the total inlet flow into the unit). This approach assumes that the flow is sequential through the different zones.</p>								

DATA FORM FOR THE DETERMINATION OF MONOD CONSTANTS FROM ZONE CONCENTRATIONS WITH BACKMIXING								
COMPOUND for site specific biorates determination						Methanol		
Total Inlet Flow (m ³ /s)						1		
Inlet Concentration (g/m ³) - Use value from line 2 as C _{i-1} value in column D for Zone 1 in table below						2		
	A	B	C	D	E	F	G	H
Zone Number	C _i g/m ³	Backmix (B _{M_i})	(1+B _{M_i} +B _{M_{i-1}})*C _i g/m ³	(1+B _{M_i})*C _{i-1}	B _{M_{i-1}} * C _{i-1} g/m ³	KL m/s	Area m ²	A*F*G g/s
1								
2								
3								
4								
5								
	I	J	K	L	M	N	O	
Zone Number	Volume m ³	Temp C	(1.045) ^(J-25)	biomass g/m ³	I*K*L gm	M/[line 1*(D+E-C)-H] s	1/A m ³ /g	
1								
2								
3								
4								
5								
Plot values in column N on y axis, and values in column O on x axis, up to, and including first row where C _i is equal to MDL or to last zone.								
						3		
						4		
						5		
						6		
The backmix ratio, B _{M_i} , is the ratio of (the return flow from the zone back to the upstream zone) to (the total inlet flow into the unit). This approach assumes that the flow is sequential through the different zones.								

Form 4

PROCEDURES FORM FOR THE ESTIMATION OF THE KL FROM UNIT SPECIFICATIONS	
NAME OF THE FACILITY for site specific biorate determination	
NAME OF UNIT for site specific biorate determination	
NAME OF COMPOUND	Methanol
HENRY'S LAW constant for the compound (mole fraction in gas per mole fraction in water at 25 degrees Celsius)	
IDENTIFY THE TYPE OF UNIT (check one box below)	
Quiescent impoundment	1
Surface agitated impoundment	2
Surface agitated impoundment with submerged air present	3
Unit with submerged aeration gas	4
PROCEDURES BASED UPON THE TYPE OF UNIT	
<p>1. Use Form 5 to determine KL for the surface of the quiescent impoundment.</p> <p>2. Use Form 5 to determine KL for the surface of the quiescent part of the impoundment. Use Form 6 to determine KL for the part of the surface that is agitated, then complete Form 6 with Kq as determined from Form 5.</p> <p>3. Use Form 5 to determine KL for the surface of the quiescent part of the impoundment. Use Form 6 to determine KL for the part of the surface that is agitated, then complete Form 6 with Kq as determined from Form 5. The total system KL is the sum of the KL from the completed Form 6 and the equivalent KL from Form 7.</p> <p>4. Evaluate the fraction of the surface that is agitated and the extent of the aeration. Use Form 5 to determine KL for the quiescent part of the surface of the impoundment. Use Form 6 to determine KL for the part of the surface that is agitated, then complete Form 6 with Kq as determined from Form 5. The total system KL is the sum of the KL from the completed Form 6 and the equivalent KL from Form 7. See section 5.6.1 in the document Air Emission Models for Waste and Wastewater.</p>	
Estimate of surface KL obtained from above procedures (m/s)	5
If the submerged aeration is present, the equivalent KL from Form 7	6
The total KL is the sum of line 5 and line 6.	7

**FORM FOR CALCULATING THE MASS TRANSFER COEFFICIENT
FOR A QUIESCENT SURFACE IMPOUNDMENT**

FACILITY NAME for site specific biorate determination
COMPOUND for site specific biorate determination

Methanol

Input values

- Enter the following:
 F - Impoundment fetch (m)
 D - Impoundment depth (m)
 U10 - Windspeed 10 m above liquid surface (m/s)
 Dw - Diffusivity of compound in water (cm²/s)
 Dether - Diffusivity of ether in water (cm²/s)
 μG - Viscosity of air, (g/cm-s)
 G - Density of air, (g/cm³)
 Da - Diffusivity of compound in air, (cm²/s)
 A - Area of impoundment, (m²)
 H - Henry's law constant, (atm-m³/g mol)
 R - Universal gas constant, (atm-m³/g mol. K)
 μL - Viscosity of water, (g/cm-s)
 L - Density of liquid, (g/cm³)
 T - Impoundment temperature, (C)

Calculate the following:

Calculate F/D:

--

Calculate the liquid phase mass transfer coefficient, kL, using one of the following procedures, (m/s)

Where F/D < 14 and U10 > 3.25 m/s, use the following procedure from MacKay and Yeun:

Calculate the Schmidt number on the liquid side, ScL, as follows:
 $ScL = \mu L / LDw$

--

Calculate the friction velocity, U*, as follows, (m/s):
 $U^* = 0.01 \times U10(6.1 + 0.63 U10)^{0.5}$

--

Where U* is > 0.3, calculate kL as follows:
 $kL = (1.0 \times 10^{-6}) + (34.1 \times 10^{-4})U^* \times ScL^{-0.5}$

--

Where U* is < 0.3, calculate kL as follows:
 $kL = (1.0 \times 10^{-6}) + (144 \times 10^{-4})(U^*)^{2.2} \times ScL^{-0.5}$

--

For all other values of F/D and U10, calculate kL using the following procedure from Springer:

Where U10 is < 3.25 m/s, calculate kL as follows:

(identical to Form VII, Appendix C to Part 63)

Form 5

$k_L = 2.78 \times 10^{-6} (Dw/Dether)^{2/3}$

Where U_{10} is > 3.25 and $14 < F/D < 51.2$, Calculate k_L as follows:

$k_L = [2.605 \times 10^{-9} (F/D) + 1.277 \times 10^{-7}] U_{10}^2 (Dw/Dether)^{2/3}$

Where $U_{10} > 3.25$ m/s and $F/D > 51.2$, calculate k_L as follows:

$k_L = (2.611 \times 10^{-7}) U_{10}^2 (Dw/Dether)^{2/3}$

- B. Calculate the gas phase mass transfer coefficient, k_G , using the following procedure from MacKay and Matsasugu, (m/s):

Calculate the Schmidt number on the gas side, Sc_G , as follows: $Sc_G = \mu G / GDa$

Calculate the effective diameter of the impoundment, d_e , as follows, (m):

$d_e = (4A/3.14)^{0.5}$

Calculate k_G as follows, (m/s): $k_G = 4.82 \times 10^{-3} U_{10}^{0.78} Sc_G^{-0.67} d_e^{-0.11}$

- C. Calculate the partition coefficient, Keq , as follows: $Keq = H/[R(T+273)]$

- D. Calculate the overall mass transfer coefficient, Kq , as follows, (m/s):

$1/Kq = 1/k_L + 1/(Keq \cdot k_G)$

Where the total impoundment surface is quiescent:

$KL = Kq$

Where a portion of the impoundment surface is turbulent, continue with Form 6.

DATA FORM FOR CALCULATING THE MASS TRANSFER COEFFICIENT FOR AN AERATED SURFACE IMPOUNDMENT

Facility Name:
 Waste Stream Compound:

Enter the following:

J - Oxygen transfer rating of surface aerator, (lb O₂/hr-hp)
 POWR - Total power to aerators, (hp)
 T - Water temperature, (C)
 Ot - Oxygen transfer correction factor
 MWL - Molecular weight of liquid
 At - Turbulent surface area of impoundment, (ft²)
 (If unknown, use values from Table 1)
 A - Total surface area of impoundment, (ft²)
 rhoL - Density of liquid, (lb/ft³)
 Dw - Diffusivity of constituent in water, (cm²/s)
 Do - Diffusivity of oxygen in water, (cm²/s)
 d - Impeller diameter, (cm)
 w - Rotational speed of impeller, (rad/s)
 a - Density of air, (gm/cm³)
 N - Number of aerators
 gc - Gravitation constant, (lbm-ft/s²/lbf)
 d* - Impeller diameter, (ft)
 Da - Diffusivity of constituent in air, (cm²/s)
 MWa - Molecular weight of air
 R - Universal gas constant, (atm-m³/g mol. C)
 H = Henry's law constant, (atm-m³/g mol)

Calculate the following:

A. Calculate the liquid phase mass transfer coefficient, k_L, using the following Equation from Thibodeaux:

$k_L = [8.22 \times 10^{-9} J (POWR)(1.024)^{(T-20)} Ot 10^6 MWL / (At \times \rho L / 62.37)] (Dw/Do)^{0.5}$, (m/s)

B. Calculate the gas phase mass transfer coefficient, k_G, using the following procedure from Reinhardt:

Calculate the viscosity of air, μ_a, as follows, (g/cm.s):
 $\mu_a = 4.568 \times 10^{-7} T + 1.7209 \times 10^{-4}$

Calculate the Reynold's number as follows:
 $Re = d^2 w a / \mu_a$

Calculate power to impeller, P_I, as follows, (ft.lbf/s):
 $P_I = 0.85 (POWR) 550/N$

Form 6

- Calculate the power number, p , as follows:
 $p = \frac{P}{\rho L g c / (\rho L d^5 w^3)}$
- Calculate the Schmidt number, ScG , as follows:
 $ScG = \frac{\mu a}{a Da}$
- Calculate the Fronde number, Fr , as follows:
 $Fr = \frac{d w^2}{g c}$
- Calculate kG as follows:
 $kG = 1.35 \times 10^{-7} Re^{1.42} p^{0.4} ScG^{0.5} Fr^{-0.21} Da^{MWa/d}$, (m/s)
- C. Calculate the partition coefficient, Keq , as follows:
 $Keq = \frac{H}{R(T+273)}$
- D. Calculate the overall turbulent mass transfer coefficient, Kt , as follows, (m/s):
 $\frac{1}{Kt} = \frac{1}{kL} + \frac{1}{Keq kG}$
- E. Calculate the quiescent mass transfer coefficient, Kq , for the impoundment using Form 5.
- F. Calculate the overall mass transfer coefficient, KL , for the impoundment as follows:
 $KL = \frac{(A-At)}{A} Kq + At \frac{Kt}{A}$

Form 6 Table 1

PROCEDURES FORM FOR THE ESTIMATION OF THE KL FROM WATER⁸ a,b

Motor horsepower	At, Turbulent area,		Effective depth	V, Agitated volume	aV, Area per volume
	ft ²	m ²			
5	177	16.4	10	1,767	0.1002
7.5	201	18.7	10	2,010	0.1000
10	227	21	10.5	2,383	0.0953
15	284	26.4	11	3,119	0.0911
20	346	32.1	11.5	3,983	0.0869
25	415	38.6	12	4,986	0.0832
30	491	45.7	12	5,890	0.0834
40	661	61.4	13	8,587	0.0770
50	855	79.5	14	11,970	0.0714
60	1075	100	15	16,130	0.0666
75	1452	135	16	23,240	0.0625
100	2206	205	18	39,710	0.0556

a Data for a high speed (1,200 rpm) aerator with 60 cm propeller diameter (d).

b This table provides information potentially useful for the value of At.

Form 7

**DATA FORM FOR THE ESTIMATION OF THE EQUIVALENT KL
FROM AIR STRIPPING DUE TO SUBMERGED AERATION.**

NAME OF THE FACILITY for site specific biorate determination

COMPOUND for site specific biorate determination

VENT RATE of total gas leaving the unit (G, m³/s)

TEMPERATURE of the liquid in the unit (deg. C)

ESTIMATE OF Henry's law constant (H, g/m³ in gas / g/m³ in liquid).

Corrected for the temperature on line 2.

AREA OF REACTOR (m²)

CALCULATION OF THE ESTIMATE OF EQUIVALENT KL

[H G] ESTIMATE (m³/s) Multiply the number on line 1 by the number on line 3. Enter the results here.

EQUIVALENT KL. Divide the number on line 5 by the number on line 4. Enter the results on line 6.

	Methanol
1	
2	
3	
4	
5	
6	

[65 FR 80765, Dec. 22, 2000]

Environmental Protection Agency

§ 60.111b

(2) Each owner or operator of each storage vessel equipped with a vapor recovery and return or disposal system in accordance with the requirements of § 60.112a (a)(3) and (b).

[45 FR 23379, Apr. 4, 1980]

Subpart Kb—Standards of Performance for Volatile Organic Liquid Storage Vessels (Including Petroleum Liquid Storage Vessels) for Which Construction, Reconstruction, or Modification Commenced After July 23, 1984

SOURCE: 52 FR 11429, Apr. 8, 1987, unless otherwise noted.

§ 60.110b Applicability and designation of affected facility.

(a) Except as provided in paragraphs (b), (c), and (d) of this section, the affected facility to which this subpart applies is each storage vessel with a capacity greater than or equal to 40 cubic meters (m³) that is used to store volatile organic liquids (VOL's) for which construction, reconstruction, or modification is commenced after July 23, 1984.

(b) Except as specified in paragraphs (a) and (b) of § 60.116b, storage vessels with design capacity less than 75 m³ are exempt from the General Provisions (part 60, subpart A) and from the provisions of this subpart.

(c) Except as specified in paragraphs (a) and (b) of § 60.116b, vessels either with a capacity greater than or equal to 151 m³ storing a liquid with a maximum true vapor pressure less than 3.5 kPa or with a capacity greater than or equal to 75 m³ but less than 151 m³ storing a liquid with a maximum true vapor pressure less than 15.0 kPa are exempt from the General Provisions (part 60, subpart A) and from the provisions of this subpart.

(d) This subpart does not apply to the following:

(1) Vessels at coke oven by-product plants.

(2) Pressure vessels designed to operate in excess of 204.9 kPa and without emissions to the atmosphere.

(3) Vessels permanently attached to mobile vehicles such as trucks, rail-cars, barges, or ships.

(4) Vessels with a design capacity less than or equal to 1,589.874 m³ used for petroleum or condensate stored, processed, or treated prior to custody transfer.

(5) Vessels located at bulk gasoline plants.

(6) Storage vessels located at gasoline service stations.

(7) Vessels used to store beverage alcohol.

[52 FR 11429, Apr. 8, 1987, as amended at 54 FR 32973, Aug. 11, 1989]

§ 60.111b Definitions.

Terms used in this subpart are defined in the Act, in subpart A of this part, or in this subpart as follows:

(a) *Bulk gasoline plant* means any gasoline distribution facility that has a gasoline throughput less than or equal to 75,700 liters per day. Gasoline throughput shall be the maximum calculated design throughput as may be limited by compliance with an enforceable condition under Federal requirement or Federal, State or local law, and discoverable by the Administrator and any other person.

(b) *Condensate* means hydrocarbon liquid separated from natural gas that condenses due to changes in the temperature or pressure, or both, and remains liquid at standard conditions.

(c) *Custody transfer* means the transfer of produced petroleum and/or condensate, after processing and/or treatment in the producing operations, from storage vessels or automatic transfer facilities to pipelines or any other forms of transportation.

(d) *Fill* means the introduction of VOL into a storage vessel but not necessarily to complete capacity.

(e) *Gasoline service station* means any site where gasoline is dispensed to motor vehicle fuel tanks from stationary storage tanks.

(f) *Maximum true vapor pressure* means the equilibrium partial pressure exerted by the stored VOL at the temperature equal to the highest calendar-month average of the VOL storage temperature for VOL's stored above or below the ambient temperature or at the local maximum monthly average

§ 60.112b

temperature as reported by the National Weather Service for VOL's stored at the ambient temperature, as determined:

(1) In accordance with methods described in American Petroleum Institute Bulletin 2517, Evaporation Loss From External Floating Roof Tanks, (incorporated by reference—see § 60.17); or

(2) As obtained from standard reference texts; or

(3) As determined by ASTM Method D2879-83 (incorporated by reference—see § 60.17);

(4) Any other method approved by the Administrator.

(g) *Reid vapor pressure* means the absolute vapor pressure of volatile crude oil and volatile nonviscous petroleum liquids except liquified petroleum gases, as determined by ASTM D323-82 (incorporated by reference—see § 60.17).

(h) *Petroleum* means the crude oil removed from the earth and the oils derived from tar sands, shale, and coal.

(i) *Petroleum liquids* means petroleum, condensate, and any finished or intermediate products manufactured in a petroleum refinery.

(j) *Storage vessel* means each tank, reservoir, or container used for the storage of volatile organic liquids but does not include:

(1) Frames, housing, auxiliary supports, or other components that are not directly involved in the containment of liquids or vapors; or

(2) Subsurface caverns or porous rock reservoirs.

(k) *Volatile organic liquid (VOL)* means any organic liquid which can emit volatile organic compounds into the atmosphere except those VOL's that emit only those compounds which the Administrator has determined do not contribute appreciably to the formation of ozone. These compounds are identified in EPA statements on ozone abatement policy for SIP revisions (42 FR 35314, 44 FR 32042, 45 FR 32424, and 45 FR 48941).

(l) *Waste* means any liquid resulting from industrial, commercial, mining or agricultural operations, or from community activities that is discarded or is being accumulated, stored, or physically, chemically, or biologically

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treated prior to being discarded or recycled.

[52 FR 11429, Apr. 8, 1987, as amended at 54 FR 32973, Aug. 11, 1989]

§ 60.112b Standard for volatile organic compounds (VOC).

(a) The owner or operator of each storage vessel either with a design capacity greater than or equal to 151 m³ containing a VOL that, as stored, has a maximum true vapor pressure equal to or greater than 5.2 kPa but less than 76.6 kPa or with a design capacity greater than or equal to 75 m³ but less than 151 m³ containing a VOL that, as stored, has a maximum true vapor pressure equal to or greater than 27.6 kPa but less than 76.6 kPa, shall equip each storage vessel with one of the following:

(1) A fixed roof in combination with an internal floating roof meeting the following specifications:

(i) The internal floating roof shall rest or float on the liquid surface (but not necessarily in complete contact with it) inside a storage vessel that has a fixed roof. The internal floating roof shall be floating on the liquid surface at all times, except during initial fill and during those intervals when the storage vessel is completely emptied or subsequently emptied and refilled. When the roof is resting on the leg supports, the process of filling, emptying, or refilling shall be continuous and shall be accomplished as rapidly as possible.

(ii) Each internal floating roof shall be equipped with one of the following closure devices between the wall of the storage vessel and the edge of the internal floating roof:

(A) A foam- or liquid-filled seal mounted in contact with the liquid (liquid-mounted seal). A liquid-mounted seal means a foam- or liquid-filled seal mounted in contact with the liquid between the wall of the storage vessel and the floating roof continuously around the circumference of the tank.

(B) Two seals mounted one above the other so that each forms a continuous closure that completely covers the space between the wall of the storage vessel and the edge of the internal floating roof. The lower seal may be

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vapor-mounted, but both must be continuous.

(C) A mechanical shoe seal. A mechanical shoe seal is a metal sheet held vertically against the wall of the storage vessel by springs or weighted levers and is connected by braces to the floating roof. A flexible coated fabric (envelope) spans the annular space between the metal sheet and the floating roof.

(iii) Each opening in a noncontact internal floating roof except for automatic bleeder vents (vacuum breaker vents) and the rim space vents is to provide a projection below the liquid surface.

(iv) Each opening in the internal floating roof except for leg sleeves, automatic bleeder vents, rim space vents, column wells, ladder wells, sample wells, and stub drains is to be equipped with a cover or lid which is to be maintained in a closed position at all times (i.e., no visible gap) except when the device is in actual use. The cover or lid shall be equipped with a gasket. Covers on each access hatch and automatic gauge float well shall be bolted except when they are in use.

(v) Automatic bleeder vents shall be equipped with a gasket and are to be closed at all times when the roof is floating except when the roof is being floated off or is being landed on the roof leg supports.

(vi) Rim space vents shall be equipped with a gasket and are to be set to open only when the internal floating roof is not floating or at the manufacturer's recommended setting.

(vii) Each penetration of the internal floating roof for the purpose of sampling shall be a sample well. The sample well shall have a slit fabric cover that covers at least 90 percent of the opening.

(viii) Each penetration of the internal floating roof that allows for passage of a column supporting the fixed roof shall have a flexible fabric sleeve seal or a gasketed sliding cover.

(ix) Each penetration of the internal floating roof that allows for passage of a ladder shall have a gasketed sliding cover.

(2) An external floating roof. An external floating roof means a pontoon-type or double-deck type cover that rests on the liquid surface in a vessel

with no fixed roof. Each external floating roof must meet the following specifications:

(i) Each external floating roof shall be equipped with a closure device between the wall of the storage vessel and the roof edge. The closure device is to consist of two seals, one above the other. The lower seal is referred to as the primary seal, and the upper seal is referred to as the secondary seal.

(A) The primary seal shall be either a mechanical shoe seal or a liquid-mounted seal. Except as provided in § 60.113b(b)(4), the seal shall completely cover the annular space between the edge of the floating roof and tank wall.

(B) The secondary seal shall completely cover the annular space between the external floating roof and the wall of the storage vessel in a continuous fashion except as allowed in § 60.113b(b)(4).

(ii) Except for automatic bleeder vents and rim space vents, each opening in a noncontact external floating roof shall provide a projection below the liquid surface. Except for automatic bleeder vents, rim space vents, roof drains, and leg sleeves, each opening in the roof is to be equipped with a gasketed cover, seal, or lid that is to be maintained in a closed position at all times (i.e., no visible gap) except when the device is in actual use. Automatic bleeder vents are to be closed at all times when the roof is floating except when the roof is being floated off or is being landed on the roof leg supports. Rim vents are to be set to open when the roof is being floated off the roof legs supports or at the manufacturer's recommended setting. Automatic bleeder vents and rim space vents are to be gasketed. Each emergency roof drain is to be provided with a slotted membrane fabric cover that covers at least 90 percent of the area of the opening.

(iii) The roof shall be floating on the liquid at all times (i.e., off the roof leg supports) except during initial fill until the roof is lifted off leg supports and when the tank is completely emptied and subsequently refilled. The process of filling, emptying, or refilling when the roof is resting on the leg supports shall be continuous and shall be accomplished as rapidly as possible.

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(3) A closed vent system and control device meeting the following specifications:

(i) The closed vent system shall be designed to collect all VOC vapors and gases discharged from the storage vessel and operated with no detectable emissions as indicated by an instrument reading of less than 500 ppm above background and visual inspections, as determined in part 60, subpart VV, §60.485(b).

(ii) The control device shall be designed and operated to reduce inlet VOC emissions by 95 percent or greater. If a flare is used as the control device, it shall meet the specifications described in the general control device requirements (§60.18) of the General Provisions.

(4) A system equivalent to those described in paragraphs (a)(1), (a)(2), or (a)(3) of this section as provided in §60.114b of this subpart.

(b) The owner or operator of each storage vessel with a design capacity greater than or equal to 75 m³ which contains a VOL that, as stored, has a maximum true vapor pressure greater than or equal to 76.6 kPa shall equip each storage vessel with one of the following:

(1) A closed vent system and control device as specified in §60.112b(a)(3).

(2) A system equivalent to that described in paragraph (b)(1) as provided in §60.114b of this subpart.

(c) *Site-specific standard for Merck & Co., Inc.'s Stonewall Plant in Elkton, Virginia.* This paragraph applies only to the pharmaceutical manufacturing facility, commonly referred to as the Stonewall Plant, located at Route 340 South, in Elkton, Virginia ("site").

(1) For any storage vessel that otherwise would be subject to the control technology requirements of paragraphs (a) or (b) of this section, the site shall have the option of either complying directly with the requirements of this subpart, or reducing the site-wide total criteria pollutant emissions cap (total emissions cap) in accordance with the procedures set forth in a permit issued pursuant to 40 CFR 52.2454. If the site chooses the option of reducing the total emissions cap in accordance with the procedures set forth in such permit, the requirements of such permit

shall apply in lieu of the otherwise applicable requirements of this subpart for such storage vessel.

(2) For any storage vessel at the site not subject to the requirements of 40 CFR 60.112b (a) or (b), the requirements of 40 CFR 60.116b (b) and (c) and the General Provisions (subpart A of this part) shall not apply.

[52 FR 11429, Apr. 8, 1987, as amended at 62 FR 52641, Oct. 8, 1997]

§ 60.113b Testing and procedures.

The owner or operator of each storage vessel as specified in §60.112b(a) shall meet the requirements of paragraph (a), (b), or (c) of this section. The applicable paragraph for a particular storage vessel depends on the control equipment installed to meet the requirements of §60.112b.

(a) After installing the control equipment required to meet §60.112b(a)(1) (permanently affixed roof and internal floating roof), each owner or operator shall:

(1) Visually inspect the internal floating roof, the primary seal, and the secondary seal (if one is in service), prior to filling the storage vessel with VOL. If there are holes, tears, or other openings in the primary seal, the secondary seal, or the seal fabric or defects in the internal floating roof, or both, the owner or operator shall repair the items before filling the storage vessel.

(2) For Vessels equipped with a liquid-mounted or mechanical shoe primary seal, visually inspect the internal floating roof and the primary seal or the secondary seal (if one is in service) through manholes and roof hatches on the fixed roof at least once every 12 months after initial fill. If the internal floating roof is not resting on the surface of the VOL inside the storage vessel, or there is liquid accumulated on the roof, or the seal is detached, or there are holes or tears in the seal fabric, the owner or operator shall repair the items or empty and remove the storage vessel from service within 45 days. If a failure that is detected during inspections required in this paragraph cannot be repaired within 45 days and if the vessel cannot be

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emptied within 45 days, a 30-day extension may be requested from the Administrator in the inspection report required in §60.115b(a)(3). Such a request for an extension must document that alternate storage capacity is unavailable and specify a schedule of actions the company will take that will assure that the control equipment will be repaired or the vessel will be emptied as soon as possible.

(3) For vessels equipped with a double-seal system as specified in §60.112b(a)(1)(ii)(B):

(i) Visually inspect the vessel as specified in paragraph (a)(4) of this section at least every 5 years; or

(ii) Visually inspect the vessel as specified in paragraph (a)(2) of this section.

(4) Visually inspect the internal floating roof, the primary seal, the secondary seal (if one is in service), gaskets, slotted membranes and sleeve seals (if any) each time the storage vessel is emptied and degassed. If the internal floating roof has defects, the primary seal has holes, tears, or other openings in the seal or the seal fabric, or the secondary seal has holes, tears, or other openings in the seal or the seal fabric, or the gaskets no longer close off the liquid surfaces from the atmosphere, or the slotted membrane has more than 10 percent open area, the owner or operator shall repair the items as necessary so that none of the conditions specified in this paragraph exist before refilling the storage vessel with VOL. In no event shall inspections conducted in accordance with this provision occur at intervals greater than 10 years in the case of vessels conducting the annual visual inspection as specified in paragraphs (a)(2) and (a)(3)(ii) of this section and at intervals no greater than 5 years in the case of vessels specified in paragraph (a)(3)(i) of this section.

(5) Notify the Administrator in writing at least 30 days prior to the filling or refilling of each storage vessel for which an inspection is required by paragraphs (a)(1) and (a)(4) of this section to afford the Administrator the opportunity to have an observer present. If the inspection required by paragraph (a)(4) of this section is not planned and the owner or operator

could not have known about the inspection 30 days in advance or refilling the tank, the owner or operator shall notify the Administrator at least 7 days prior to the refilling of the storage vessel. Notification shall be made by telephone immediately followed by written documentation demonstrating why the inspection was unplanned. Alternatively, this notification including the written documentation may be made in writing and sent by express mail so that it is received by the Administrator at least 7 days prior to the refilling.

(b) After installing the control equipment required to meet §60.112b(a)(2) (external floating roof), the owner or operator shall:

(1) Determine the gap areas and maximum gap widths, between the primary seal and the wall of the storage vessel and between the secondary seal and the wall of the storage vessel according to the following frequency.

(i) Measurements of gaps between the tank wall and the primary seal (seal gaps) shall be performed during the hydrostatic testing of the vessel or within 60 days of the initial fill with VOL and at least once every 5 years thereafter.

(ii) Measurements of gaps between the tank wall and the secondary seal shall be performed within 60 days of the initial fill with VOL and at least once per year thereafter.

(iii) If any source ceases to store VOL for a period of 1 year or more, subsequent introduction of VOL into the vessel shall be considered an initial fill for the purposes of paragraphs (b)(1)(i) and (b)(1)(ii) of this section.

(2) Determine gap widths and areas in the primary and secondary seals individually by the following procedures:

(i) Measure seal gaps, if any, at one or more floating roof levels when the roof is floating off the roof leg supports.

(ii) Measure seal gaps around the entire circumference of the tank in each place where a 0.32-cm diameter uniform probe passes freely (without forcing or binding against seal) between the seal and the wall of the storage vessel and measure the circumferential distance of each such location.

(iii) The total surface area of each gap described in paragraph (b)(2)(ii) of

this section shall be determined by using probes of various widths to measure accurately the actual distance from the tank wall to the seal and multiplying each such width by its respective circumferential distance.

(3) Add the gap surface area of each gap location for the primary seal and the secondary seal individually and divide the sum for each seal by the nominal diameter of the tank and compare each ratio to the respective standards in paragraph (b)(4) of this section.

(4) Make necessary repairs or empty the storage vessel within 45 days of identification in any inspection for seals not meeting the requirements listed in (b)(4) (i) and (ii) of this section:

(i) The accumulated area of gaps between the tank wall and the mechanical shoe or liquid-mounted primary seal shall not exceed 212 Cm² per meter of tank diameter, and the width of any portion of any gap shall not exceed 3.81 cm.

(A) One end of the mechanical shoe is to extend into the stored liquid, and the other end is to extend a minimum vertical distance of 61 cm above the stored liquid surface.

(B) There are to be no holes, tears, or other openings in the shoe, seal fabric, or seal envelope.

(ii) The secondary seal is to meet the following requirements:

(A) The secondary seal is to be installed above the primary seal so that it completely covers the space between the roof edge and the tank wall except as provided in paragraph (b)(2)(iii) of this section.

(B) The accumulated area of gaps between the tank wall and the secondary seal shall not exceed 21.2 cm² per meter of tank diameter, and the width of any portion of any gap shall not exceed 1.27 cm.

(C) There are to be no holes, tears, or other openings in the seal or seal fabric.

(iii) If a failure that is detected during inspections required in paragraph (b)(1) of §60.113b(b) cannot be repaired within 45 days and if the vessel cannot be emptied within 45 days, a 30-day extension may be requested from the Administrator in the inspection report required in §60.115b(b)(4). Such extension

request must include a demonstration of unavailability of alternate storage capacity and a specification of a schedule that will assure that the control equipment will be repaired or the vessel will be emptied as soon as possible.

(5) Notify the Administrator 30 days in advance of any gap measurements required by paragraph (b)(1) of this section to afford the Administrator the opportunity to have an observer present.

(6) Visually inspect the external floating roof, the primary seal, secondary seal, and fittings each time the vessel is emptied and degassed.

(i) If the external floating roof has defects, the primary seal has holes, tears, or other openings in the seal or the seal fabric, or the secondary seal has holes, tears, or other openings in the seal or the seal fabric, the owner or operator shall repair the items as necessary so that none of the conditions specified in this paragraph exist before filling or refilling the storage vessel with VOL.

(ii) For all the inspections required by paragraph (b)(6) of this section, the owner or operator shall notify the Administrator in writing at least 30 days prior to the filling or refilling of each storage vessel to afford the Administrator the opportunity to inspect the storage vessel prior to refilling. If the inspection required by paragraph (b)(6) of this section is not planned and the owner or operator could not have known about the inspection 30 days in advance of refilling the tank, the owner or operator shall notify the Administrator at least 7 days prior to the refilling of the storage vessel. Notification shall be made by telephone immediately followed by written documentation demonstrating why the inspection was unplanned. Alternatively, this notification including the written documentation may be made in writing and sent by express mail so that it is received by the Administrator at least 7 days prior to the refilling.

(c) The owner or operator of each source that is equipped with a closed vent system and control device as required in §60.112b (a)(3) or (b)(2) (other than a flare) is exempt from §60.8 of the General Provisions and shall meet the following requirements.

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(1) Submit for approval by the Administrator as an attachment to the notification required by § 60.7(a)(1) or, if the facility is exempt from § 60.7(a)(1), as an attachment to the notification required by § 60.7(a)(2), an operating plan containing the information listed below.

(i) Documentation demonstrating that the control device will achieve the required control efficiency during maximum loading conditions. This documentation is to include a description of the gas stream which enters the control device, including flow and VOC content under varying liquid level conditions (dynamic and static) and manufacturer's design specifications for the control device. If the control device or the closed vent capture system receives vapors, gases, or liquids other than fuels from sources that are not designated sources under this subpart, the efficiency demonstration is to include consideration of all vapors, gases, and liquids received by the closed vent capture system and control device. If an enclosed combustion device with a minimum residence time of 0.75 seconds and a minimum temperature of 816 °C is used to meet the 95 percent requirement, documentation that those conditions will exist is sufficient to meet the requirements of this paragraph.

(ii) A description of the parameter or parameters to be monitored to ensure that the control device will be operated in conformance with its design and an explanation of the criteria used for selection of that parameter (or parameters).

(2) Operate the closed vent system and control device and monitor the parameters of the closed vent system and control device in accordance with the operating plan submitted to the Administrator in accordance with paragraph (c)(1) of this section, unless the plan was modified by the Administrator during the review process. In this case, the modified plan applies.

(d) The owner or operator of each source that is equipped with a closed vent system and a flare to meet the requirements in § 60.112b (a)(3) or (b)(2) shall meet the requirements as speci-

fied in the general control device requirements, § 60.18 (e) and (f).

[52 FR 11429, Apr. 8, 1987, as amended at 54 FR 32973, Aug. 11, 1989]

§ 60.114b Alternative means of emission limitation.

(a) If, in the Administrator's judgment, an alternative means of emission limitation will achieve a reduction in emissions at least equivalent to the reduction in emissions achieved by any requirement in § 60.112b, the Administrator will publish in the FEDERAL REGISTER a notice permitting the use of the alternative means for purposes of compliance with that requirement.

(b) Any notice under paragraph (a) of this section will be published only after notice and an opportunity for a hearing.

(c) Any person seeking permission under this section shall submit to the Administrator a written application including:

(1) An actual emissions test that uses a full-sized or scale-model storage vessel that accurately collects and measures all VOC emissions from a given control device and that accurately simulates wind and accounts for other emission variables such as temperature and barometric pressure.

(2) An engineering evaluation that the Administrator determines is an accurate method of determining equivalence.

(d) The Administrator may condition the permission on requirements that may be necessary to ensure operation and maintenance to achieve the same emissions reduction as specified in § 60.112b.

§ 60.115b Reporting and recordkeeping requirements.

The owner or operator of each storage vessel as specified in § 60.112b(a) shall keep records and furnish reports as required by paragraphs (a), (b), or (c) of this section depending upon the control equipment installed to meet the requirements of § 60.112b. The owner or operator shall keep copies of all reports and records required by this section, except for the record required by (c)(1), for at least 2 years. The record required by (c)(1) will be kept for the life of the control equipment.

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(a) After installing control equipment in accordance with § 60.112b(a)(1) (fixed roof and internal floating roof), the owner or operator shall meet the following requirements.

(1) Furnish the Administrator with a report that describes the control equipment and certifies that the control equipment meets the specifications of § 60.112b(a)(1) and § 60.113b(a)(1). This report shall be an attachment to the notification required by § 60.7(a)(3).

(2) Keep a record of each inspection performed as required by § 60.113b (a)(1), (a)(2), (a)(3), and (a)(4). Each record shall identify the storage vessel on which the inspection was performed and shall contain the date the vessel was inspected and the observed condition of each component of the control equipment (seals, internal floating roof, and fittings).

(3) If any of the conditions described in § 60.113b(a)(2) are detected during the annual visual inspection required by § 60.113b(a)(2), a report shall be furnished to the Administrator within 30 days of the inspection. Each report shall identify the storage vessel, the nature of the defects, and the date the storage vessel was emptied or the nature of and date the repair was made.

(4) After each inspection required by § 60.113b(a)(3) that finds holes or tears in the seal or seal fabric, or defects in the internal floating roof, or other control equipment defects listed in § 60.113b(a)(3)(ii), a report shall be furnished to the Administrator within 30 days of the inspection. The report shall identify the storage vessel and the reason it did not meet the specifications of § 60.112b(a)(1) or § 60.113b(a)(3) and list each repair made.

(b) After installing control equipment in accordance with § 60.112b(a)(2) (external floating roof), the owner or operator shall meet the following requirements.

(1) Furnish the Administrator with a report that describes the control equipment and certifies that the control equipment meets the specifications of § 60.112b(a)(2) and § 60.113b(b)(2), (b)(3), and (b)(4). This report shall be an attachment to the notification required by § 60.7(a)(3).

(2) Within 60 days of performing the seal gap measurements required by

§ 60.113b(b)(1), furnish the Administrator with a report that contains:

(i) The date of measurement.

(ii) The raw data obtained in the measurement.

(iii) The calculations described in § 60.113b (b)(2) and (b)(3).

(3) Keep a record of each gap measurement performed as required by § 60.113b(b). Each record shall identify the storage vessel in which the measurement was performed and shall contain:

(i) The date of measurement.

(ii) The raw data obtained in the measurement.

(iii) The calculations described in § 60.113b (b)(2) and (b)(3).

(4) After each seal gap measurement that detects gaps exceeding the limitations specified by § 60.113b(b)(4), submit a report to the Administrator within 30 days of the inspection. The report will identify the vessel and contain the information specified in paragraph (b)(2) of this section and the date the vessel was emptied or the repairs made and date of repair.

(c) After installing control equipment in accordance with § 60.112b (a)(3) or (b)(1) (closed vent system and control device other than a flare), the owner or operator shall keep the following records.

(1) A copy of the operating plan.

(2) A record of the measured values of the parameters monitored in accordance with § 60.113b(c)(2).

(d) After installing a closed vent system and flare to comply with § 60.112b, the owner or operator shall meet the following requirements.

(1) A report containing the measurements required by § 60.18(f) (1), (2), (3), (4), (5), and (6) shall be furnished to the Administrator as required by § 60.8 of the General Provisions. This report shall be submitted within 6 months of the initial start-up date.

(2) Records shall be kept of all periods of operation during which the flare pilot flame is absent.

(3) Semiannual reports of all periods recorded under § 60.115b(d)(2) in which the pilot flame was absent shall be furnished to the Administrator.

§ 60.116b Monitoring of operations.

(a) The owner or operator shall keep copies of all records required by this section, except for the record required by paragraph (b) of this section, for at least 2 years. The record required by paragraph (b) of this section will be kept for the life of the source.

(b) The owner or operator of each storage vessel as specified in § 60.110b(a) shall keep readily accessible records showing the dimension of the storage vessel and an analysis showing the capacity of the storage vessel. Each storage vessel with a design capacity less than 75 m³ is subject to no provision of this subpart other than those required by this paragraph.

(c) Except as provided in paragraphs (f) and (g) of this section, the owner or operator of each storage vessel either with a design capacity greater than or equal to 151 m³ storing a liquid with a maximum true vapor pressure greater than or equal to 3.5 kPa or with a design capacity greater than or equal to 75 m³ but less than 151 m³ storing a liquid with a maximum true vapor pressure greater than or equal to 15.0 kPa shall maintain a record of the VOL stored, the period of storage, and the maximum true vapor pressure of that VOL during the respective storage period.

(d) Except as provided in paragraph (g) of this section, the owner or operator of each storage vessel either with a design capacity greater than or equal to 151 m³ storing a liquid with a maximum true vapor pressure that is normally less than 5.2 kPa or with a design capacity greater than or equal to 75 m³ but less than 151 m³ storing a liquid with a maximum true vapor pressure that is normally less than 27.6 kPa shall notify the Administrator within 30 days when the maximum true vapor pressure of the liquid exceeds the respective maximum true vapor pressure values for each volume range.

(e) Available data on the storage temperature may be used to determine the maximum true vapor pressure as determined below.

(1) For vessels operated above or below ambient temperatures, the maximum true vapor pressure is calculated based upon the highest expected calendar-month average of the storage

temperature. For vessels operated at ambient temperatures, the maximum true vapor pressure is calculated based upon the maximum local monthly average ambient temperature as reported by the National Weather Service.

(2) For crude oil or refined petroleum products the vapor pressure may be obtained by the following:

(i) Available data on the Reid vapor pressure and the maximum expected storage temperature based on the highest expected calendar-month average temperature of the stored product may be used to determine the maximum true vapor pressure from nomographs contained in API Bulletin 2517 (incorporated by reference—see § 60.17), unless the Administrator specifically requests that the liquid be sampled, the actual storage temperature determined, and the Reid vapor pressure determined from the sample(s).

(ii) The true vapor pressure of each type of crude oil with a Reid vapor pressure less than 13.8 kPa or with physical properties that preclude determination by the recommended method is to be determined from available data and recorded if the estimated maximum true vapor pressure is greater than 3.5 kPa.

(3) For other liquids, the vapor pressure:

(i) May be obtained from standard reference texts, or

(ii) Determined by ASTM Method D2879-83 (incorporated by reference—see § 60.17); or

(iii) Measured by an appropriate method approved by the Administrator; or

(iv) Calculated by an appropriate method approved by the Administrator.

(f) The owner or operator of each vessel storing a waste mixture of indeterminate or variable composition shall be subject to the following requirements.

(1) Prior to the initial filling of the vessel, the highest maximum true vapor pressure for the range of anticipated liquid compositions to be stored will be determined using the methods described in paragraph (e) of this section.

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(2) For vessels in which the vapor pressure of the anticipated liquid composition is above the cutoff for monitoring but below the cutoff for controls as defined in §60.112b(a), an initial physical test of the vapor pressure is required; and a physical test at least once every 6 months thereafter is required as determined by the following methods:

- (i) ASTM Method D2879-83 (incorporated by reference—see §60.17); or
- (ii) ASTM Method D323-82 (incorporated by reference—see §60.17); or
- (iii) As measured by an appropriate method as approved by the Administrator.

(g) The owner or operator of each vessel equipped with a closed vent system and control device meeting the specifications of §60.112b is exempt from the requirements of paragraphs (c) and (d) of this section.

§ 60.117b Delegation of authority.

(a) In delegating implementation and enforcement authority to a State under section 111(c) of the Act, the authorities contained in paragraph (b) of this section shall be retained by the Administrator and not transferred to a State.

(b) Authorities which will not be delegated to States: §§ 60.111b(f)(4), 60.114b, 60.116b(e)(3)(iii), 60.116b(e)(3)(iv), and 60.116b(f)(2)(iii).

[52 FR 11429, Apr. 8, 1987, as amended at 52 FR 22780, June 16, 1987]

Subpart L—Standards of Performance for Secondary Lead Smelters

§ 60.120 Applicability and designation of affected facility.

(a) The provisions of this subpart are applicable to the following affected facilities in secondary lead smelters: Pot furnaces of more than 250 kg (550 lb) charging capacity, blast (cupola) furnaces, and reverberatory furnaces.

(b) Any facility under paragraph (a) of this section that commences construction or modification after June 11, 1973, is subject to the requirements of this subpart.

[42 FR 37937, July 25, 1977]

§ 60.121 Definitions.

As used in this subpart, all terms not defined herein shall have the meaning given them in the Act and in subpart A of this part.

(a) *Reverberatory furnace* includes the following types of reverberatory furnaces: stationary, rotating, rocking, and tilting.

(b) *Secondary lead smelter* means any facility producing lead from a leadbearing scrap material by smelting to the metallic form.

(c) *Lead* means elemental lead or alloys in which the predominant component is lead.

[39 FR 9317, Mar. 8, 1974; 39 FR 13776, Apr. 17, 1974]

§ 60.122 Standard for particulate matter.

(a) On and after the date on which the performance test required to be conducted by §60.8 is completed, no owner or operator subject to the provisions of this subpart shall discharge or cause the discharge into the atmosphere from a blast (cupola) or reverberatory furnace any gases which:

- (1) Contain particulate matter in excess of 50 mg/dscm (0.022 gr/dscf).
- (2) Exhibit 20 percent opacity or greater.

(b) On and after the date on which the performance test required to be conducted by §60.8 is completed, no owner or operator subject to the provisions of this subpart shall discharge or cause the discharge into the atmosphere from any pot furnace any gases which exhibit 10 percent opacity or greater.

[39 FR 9317, Mar. 8, 1974, as amended at 40 FR 46259, Oct. 6, 1975]

§ 60.123 Test methods and procedures.

(a) In conducting the performance tests required in §60.8, the owner or operator shall use as reference methods and procedures the test methods in Appendix A of this part or other methods and procedures as specified in this section, except as provided in §60.8(b).

(b) The owner or operator shall determine compliance with the particulate matter standards in §60.122 as follows:

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furnace, the owner or operator shall determine the applicable standard under § 60.292(a)(2) as follows:

(1) The ratio (Y) of liquid fuel heating value to total (gaseous and liquid) fuel heating value fired in the glass melting furnaces shall be computed for each run using the following equation:

$$Y = (H_l L) / (H_l L + H_g G)$$

where:

Y=decimal fraction of liquid fuel heating value to total fuel heating value.

H_l=gross calorific value of liquid fuel, J/kg.

H_g=gross calorific value of gaseous fuel, J/kg.

L=liquid flow rate, kg/hr.

G=gaseous flow rate, kg/hr.

(2) Suitable methods shall be used to determine the rates (L and G) of fuels burned during each test period and a material balance over the glass melting furnace shall be used to confirm the rates.

(3) American Society of Testing and Materials (ASTM) Method D 240-76 (liquid fuels) and D 1826-77 (gaseous fuels) (incorporated by reference—see § 60.17), as applicable, shall be used to determine the gross calorific values.

(c) In conducting the performance tests required in § 60.8, the owner or operator shall use as reference methods and procedures the test methods in appendix A of this part or other methods and procedures as specified in this section, except as provided in § 60.8(b).

(d) The owner or operator shall determine compliance with the particulate matter standards in §§ 60.292 and 60.293 as follows:

(1) The emission rate (E) of particulate matter shall be computed for each run using the following equation:

$$E = (c_s Q_{sd} - A) / P$$

where:

E=emission rate of particulate matter, g/kg.

c_s=concentration of particulate matter, g/dsm.

Q_{sd}=volumetric flow rate, dscm/hr.

A=zero production rate correction

=227 g/hr for container glass, pressed and blown (soda-lime and lead) glass, and

pressed and blown (other than borosilicate, soda-lime, and lead) glass.

=454 g/hr for pressed and blown (borosilicate) glass, wool fiberglass, and flat glass.

P=glass production rate, kg/hr.

(2) Method 5 shall be used to determine the particulate matter concentration (c_s) and volumetric flow rate (Q_{sd}) of the effluent gas. The sampling time and sample volume for each run shall

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be at least 60 minutes and 0.90 dscm (31.8 dscf). The probe and filter holder heating system may be set to provide a gas temperature no greater than 177±14 °C (350±25 °F), except under the conditions specified in § 60.293(e).

(3) Direct measurement or material balance using good engineering practice shall be used to determine the amount of glass pulled during the performance test. The rate of glass produced is defined as the weight of glass pulled from the affected facility during the performance test divided by the number of hours taken to perform the performance test.

(4) Method 9 and the procedures in § 60.11 shall be used to determine opacity.

[54 FR 6674, Feb. 14, 1989; 54 FR 21344, May 17, 1989]

Subpart DD—Standards of Performance for Grain Elevators

SOURCE: 43 FR 34347, Aug. 3, 1978, unless otherwise noted.

§ 60.300 Applicability and designation of affected facility.

(a) The provisions of this subpart apply to each affected facility at any grain terminal elevator or any grain storage elevator, except as provided under § 60.304(b). The affected facilities are each truck unloading station, truck loading station, barge and ship unloading station, barge and ship loading station, railcar loading station, railcar unloading station, grain dryer, and all grain handling operations.

(b) Any facility under paragraph (a) of this section which commences construction, modification, or reconstruction after August 3, 1978, is subject to the requirements of this part.

[43 FR 34347, Aug. 3, 1978, as amended at 52 FR 42434, Nov. 5, 1988]

§ 60.301 Definitions.

As used in this subpart, all terms not defined herein shall have the meaning given them in the act and in subpart A of this part.

(a) *Grain* means corn, wheat, sorghum, rice, rye, oats, barley, and soybeans.

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(b) *Grain elevator* means any plant or installation at which grain is unloaded, handled, cleaned, dried, stored, or loaded.

(c) *Grain terminal elevator* means any grain elevator which has a permanent storage capacity of more than 88,100 m³(ca. 2.5 million U.S. bushels), except those located at animal food manufacturers, pet food manufacturers, cereal manufacturers, breweries, and livestock feedlots.

(d) *Permanent storage capacity* means grain storage capacity which is inside a building, bin, or silo.

(e) *Railcar* means railroad hopper car or boxcar.

(f) *Grain storage elevator* means any grain elevator located at any wheat flour mill, wet corn mill, dry corn mill (human consumption), rice mill, or soybean oil extraction plant which has a permanent grain storage capacity of 35,200 m³(ca. 1 million bushels).

(g) *Process emission* means the particulate matter which is collected by a capture system.

(h) *Fugitive emission* means the particulate matter which is not collected by a capture system and is released directly into the atmosphere from an affected facility at a grain elevator.

(i) *Capture system* means the equipment such as sheds, hoods, ducts, fans, dampers, etc. used to collect particulate matter generated by an affected facility at a grain elevator.

(j) *Grain unloading station* means that portion of a grain elevator where the grain is transferred from a truck, railcar, barge, or ship to a receiving hopper.

(k) *Grain loading station* means that portion of a grain elevator where the grain is transferred from the elevator to a truck, railcar, barge, or ship.

(l) *Grain handling operations* include bucket elevators or legs (excluding legs used to unload barges or ships), scale hoppers and surge bins (garners), turn heads, scalpers, cleaners, trippers, and the headhouse and other such structures.

(m) *Column dryer* means any equipment used to reduce the moisture content of grain in which the grain flows from the top to the bottom in one or more continuous packed columns between two perforated metal sheets.

(n) *Rack dryer* means any equipment used to reduce the moisture content of grain in which the grain flows from the top to the bottom in a cascading flow around rows of baffles (racks).

(o) *Unloading leg* means a device which includes a bucket-type elevator which is used to remove grain from a barge or ship.

§ 60.302 Standard for particulate matter.

(a) On and after the 60th day of achieving the maximum production rate at which the affected facility will be operated, but no later than 180 days after initial startup, no owner or operator subject to the provisions of this subpart shall cause to be discharged into the atmosphere any gases which exhibit greater than 0 percent opacity from any:

(1) Column dryer with column plate perforation exceeding 2.4 mm diameter (ca. 0.094 inch).

(2) Rack dryer in which exhaust gases pass through a screen filter coarser than 50 mesh.

(b) On and after the date on which the performance test required to be conducted by §60.8 is completed, no owner or operator subject to the provisions of this subpart shall cause to be discharged into the atmosphere from any affected facility except a grain dryer any process emission which:

(1) Contains particulate matter in excess of 0.023 g/dscm (ca. 0.01 gr/dscf).

(2) Exhibits greater than 0 percent opacity.

(c) On and after the 60th day of achieving the maximum production rate at which the affected facility will be operated, but no later than 180 days after initial startup, no owner or operator subject to the provisions of this subpart shall cause to be discharged into the atmosphere any fugitive emission from:

(1) Any individual truck unloading station, railcar unloading station, or railcar loading station, which exhibits greater than 5 percent opacity.

(2) Any grain handling operation which exhibits greater than 0 percent opacity.

(3) Any truck loading station which exhibits greater than 10 percent opacity.

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(4) Any barge or ship loading station which exhibits greater than 20 percent opacity.

(d) The owner or operator of any barge or ship unloading station shall operate as follows:

(1) The unloading leg shall be enclosed from the top (including the receiving hopper) to the center line of the bottom pulley and ventilation to a control device shall be maintained on both sides of the leg and the grain receiving hopper.

(2) The total rate of air ventilated shall be at least 32.1 actual cubic meters per cubic meter of grain handling capacity (ca. 40 ft³/bu).

(3) Rather than meet the requirements of paragraphs (d)(1) and (2) of this section the owner or operator may use other methods of emission control if it is demonstrated to the Administrator's satisfaction that they would reduce emissions of particulate matter to the same level or less.

§ 60.303 Test methods and procedures.

(a) In conducting the performance tests required in §60.8, the owner or operator shall use as reference methods and procedures the test methods in appendix A of this part or other methods and procedures as specified in this section, except as provided in §60.8(b). Acceptable alternative methods and procedures are given in paragraph (c) of this section.

(b) The owner or operator shall determine compliance with the particulate matter standards in §60.302 as follows:

(1) Method 5 shall be used to determine the particulate matter concentration and the volumetric flow rate of the effluent gas. The sampling time and sample volume for each run shall be at least 60 minutes and 1.70 dscm (60 dscf). The probe and filter holder shall be operated without heaters.

(2) Method 2 shall be used to determine the ventilation volumetric flow rate.

(3) Method 9 and the procedures in §60.11 shall be used to determine opacity.

(c) The owner or operator may use the following as alternatives to the reference methods and procedures specified in this section:

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(1) For Method 5, Method 17 may be used.

[54 FR 6674, Feb. 14, 1989]

§ 60.304 Modifications.

(a) The factor 6.5 shall be used in place of "annual asset guidelines repair allowance percentage," to determine whether a capital expenditure as defined by §60.2 has been made to an existing facility.

(b) The following physical changes or changes in the method of operation shall not by themselves be considered a modification of any existing facility:

(1) The addition of gravity loadout spouts to existing grain storage or grain transfer bins.

(2) The installation of automatic grain weighing scales.

(3) Replacement of motor and drive units driving existing grain handling equipment.

(4) The installation of permanent storage capacity with no increase in hourly grain handling capacity.

Subpart EE—Standards of Performance for Surface Coating of Metal Furniture

SOURCE: 47 FR 49287, Oct. 29, 1982, unless otherwise noted.

§ 60.310 Applicability and designation of affected facility.

(a) The affected facility to which the provisions of this subpart apply is each metal furniture surface coating operation in which organic coatings are applied.

(b) This subpart applies to each affected facility identified in paragraph (a) of this section on which construction, modification, or reconstruction is commenced after November 28, 1980.

(c) Any owner or operator of a metal furniture surface coating operation that uses less than 3,842 liters of coating (as applied) per year and keeps purchase or inventory records or other data necessary to substantiate annual coating usage shall be exempt from all other provisions of this subpart. These records shall be maintained at the source for a period of at least 2 years.

[47 FR 49287, Oct. 29, 1982, as amended at 50 FR 18248, Apr. 30, 1985]