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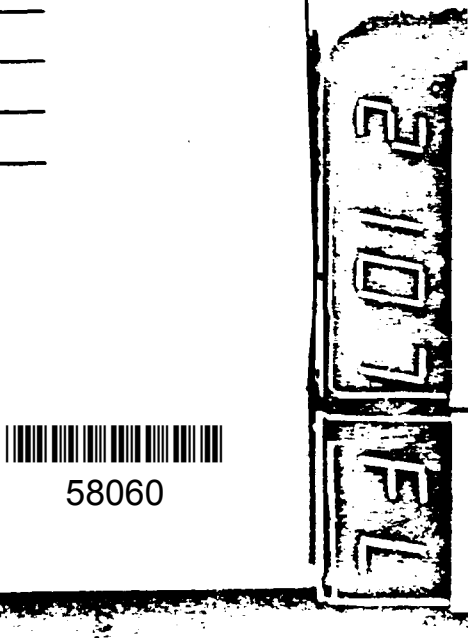

58060

WORK PLAN
FOR
80 LISTER AVENUE
ADDENDUM

JUNE 20, 1984

Diamond Shamrock

June 20, 1984

Mr. Michael Catania
Director, Office of Regulatory Services
New Jersey Department of Environmental Protection
CN-402
John Fitch Plaza
Labor and Industry Building - 8th Floor
Trenton, New Jersey 08625

Reference: Administrative Consent Order 40-18
Modification of Site Evaluation Plan

Dear Mr. Catania:

On behalf of Diamond Shamrock Chemicals Company and in response to your comments on the site evaluation plan which we submitted April 19, and in accordance with paragraph 6 (b) of the above named order, we are submitting the attached modifications. These modifications have been made in direct response to both your "General Comments/Concerns" and "Specific Comments/Concerns", and the format is patterned to answer each of your comments specifically.

Overall, we disagree with your suggestion that a grid system would be more effective for the 80 Lister Avenue site than the biased sampling approach. We believe quantification of the dioxin levels and amounts of other chemicals on this site could best be accomplished by our original plan, but we have modified the plan to accommodate your comments.

Additionally, we have reviewed the Sampling Parameters requesting that selected samples be analyzed for TCDF and OCDD.

Diamond Shamrock Corporation
World Headquarters 717 North Harwood Street Dallas, Texas 75201 Phone 214 922-2000

[redacted] though not required by the order, analysis of 10% of [redacted] near-surface samples borings and sediment samples have [redacted] included in the site evaluation plan modifications.

[redacted] have any questions, please let me know.

Very truly yours,

William C. Hutton, PE
Corporate Manager
Environmental Affairs

[redacted] ach.

[redacted] Mr. Ron Senna (12 copies)
Bureau Chief
New Jersey Department of Environmental Protection
Hazardous Site Mitigation Administration
8 Hanover Street
Trenton, New Jersey 08625

Response to Comments in NJDEP Transmittal Letter

Question: Paragraphs 4 and 5 - One of our major concerns is your statement in Section 4.0, Analytical Procedures page 4-3, as follows, "Therefore only samples having concentrations of dioxin less than 50 parts per billion will be evaluated for analysis of other parameters". This is unacceptable and in accordance with the Administrative Consent Order, soil samples both near-surface and borings, as well as sediment samples, require complete priority pollutant analysis plus 40 and 2,3,7,8-TCDD analysis.

The priority pollutants analysis plus 40 is required regardless of the 2,3,7,8-TCDD level. We are aware of the toxicological concerns of the 2,3,7,8-TCDD above the 50 ppb level, however, a high hazard substance laboratory should have the capability to perform the analytical preparation of these samples.

Response: The objective of the site evaluation is to obtain sufficient data through appropriate sampling and analysis to prepare feasibility plans for remedial activities. It has already been determined that dioxin is present at the site (the NUS site survey found concentrations of dioxin ranging from 60 ppb to 51,000 ppb in surface samples). Because of these levels at the surface, health and safety problems could be created in performing full analysis on all samples. While the sample preparations are performed under a controlled environment, two of the instrumental analyses, by their nature, are not as controllable. The cases in point are for the direct aspiration of the metals and VOC's. The aspiration of the extracts during metal analysis are not totally contained or destroyed. Second, the volatile organic analysis requires purging of the sample under positive pressure. This accepted method tends to mist and aerosol the sample. Therefore, in assessing the site, we will perform the following analyses on surface and near-surface soil samples:

- All samples analyzed for dioxin
- All samples taken from zero to six inches and 12 to 24 inches analyzed for semivolatile priority pollutants and herbicides
- All samples taken from zero to six and 12 to 24 inches below 50 ppb dioxin analyzed for volatiles and metals.

River sediment samples will be analyzed as discussed in Response 3-58 and Figure D-5.

RESPONSE TO GENERAL COMMENTS/CONCERNS

A. Analytical Procedures - Section 4

The Standard Operating Procedures (SOP's) for sampling, preparation, and analytical methodology by GC/MS for dioxin (2,3,7,8-TCDD) are inadequate. Specifically, the content of the SOP's and Section 4 of the Work Plan present the following problems.

Question: a. Omission of references to all sampling analytical SOP's.

Response: The purpose of the analytical section is to address the methods/procedures of analysis of samples collected. All references in the analytical sections to sampling are generic and intended solely for the purpose of identifying the applicability of the analytical method/procedure to a sample matrix type.

For purpose of clarification, the sampling section of the Work Plan (Section 3) contains the sampling SOP's. Attached is an expanded SOP for wipes which was the area of greatest concern (Appendix C.1).

Question: b. Variation of sample size from 50 grams for scrapes, 10 grams for soils, and 0.5 grams for drum liquids is a factor of 100x and consequently the sensitivity loss must be examined.

Response: Variation of the sample size as it relates to sensitivity is a function on the analytical methodology as it applies to the sample matrices and the required detection limit. For 80 Lister Avenue and the adjacent Passaic River, the detection limits will be related to the 1 ppb detection limit stated for the USEPA Dioxin in Soil Methods and Contracts. Therefore, the instances cited should be adjusted as follows:

Stated	Adjusted
50 grams for scrapes	10 grams for scrapes
10 grams for soils and sediments	10 grams for soils
0.5 gram for organic drum liquids	2 grams for organic drum liquids

These adjustments in sample volumes are expected to yield 1 ppb detection limits as requested in the EPA methods. Note: this detection limit is assumed sufficiently low for remedial action levels (to be defined by NJDEP) with a

sufficient safety factor, for which remediation must take place.

Question: c. Expected and deliverable detection limits are not stated in any of the SOP's except for scrapes.

Response: The expected detection limits for the methods with fixed volumes/weights of samples taken for analysis are:

Matrix	Expected Detection Limit
Soils and sediments (10 grams)	1 ppb
Scrape (10 grams)	1 ppb
Organic drum liquid (2 grams)	1 ppb
Water	10 ppt

Other samples (air and wipes) are collected on a media. The media is then totally extracted and prepared for analysis. Therefore, the method detection limit is dependent on the amount of matrix sampled by the media. For air samples, the detection limit is based on the volume of air sampled, as discussed below. The analysis will be reported as the amount of dioxin found per unit volume of air sampled. The wipe sample detection limit is based on the area wiped and will be reported as the amount of dioxin found per unit area wiped.

The delivered detection limit is based on a 2.5 to 1 signal to noise ratio for samples reported as nondetected. For samples with positive identifications, the response concentration is reported in lieu of a detection limit.

Question: d. Analytical error in 4.17 - wipes, wherein the solvent for the wipes is not stated to be used before taking a 100 square inch sampling surface wipe. Since in excess of ninety sampling events are wipes, the importance of having a correct SOP cannot be overstated.

Response: The analytical section's purpose is to address the methods/procedures of analysis of samples collected. All references in the analytical section to sampling are generic and intended solely for the purpose of identifying the applicability of the analytical method/procedure to a sample matrix type. However, for clarity, the wipe SOP is expanded as in Appendix C.1 (attached). The solvent specified is hexane.

Question: e. Analytical error in 4.13 - water, wherein the spiking solution is given as 100 ml. This is incorrect; the spike should be 100 µl. Again, the importance of having a correct SOP cannot be excused.

Response: The typographical error is so noted and will be corrected to read "100 µl.

Question: f. Missing the SOP's for the non-specific TCDD analysis with supporting references. The use of other than an isomer separable column for 2,3,7,8-TCDD is not recommended.

Response: The nonisomer specific TCDD analysis was "proposed" for utilization after an appropriate number of actual site analyses were completed and verified to contain only 2,3,7,8-TCDD or a high percentage thereof. Until this information is obtained, the analysis will be 2,3,7,8-TCDD isomer specific.

Question: g. QA/QC SOP's are incomplete as they relate to wipes wherein a blank surface of aluminum foil is to be processed spiked and unspiked to show the effectiveness by recoveries of wipe techniques employed.

Response: The wipe techniques referred to by the sampling plan have been utilized in a number of sampling campaigns under the auspices or scrutinization of state and federal agencies. These methods have been accepted as representative of surface contamination.

To fully evaluate the wipe procedure would require a uniform application of TCDD for a surface similar in texture and area as that to be wiped. We are not aware of a method that would be suitable for the application of TCDD in consideration of its toxicity.

Question: h. QA/QC SOP's are incomplete as they relate to wipes, wherein detailed techniques for taking wipes should be stated and referenced.

Response: The wipe sampling SOP is expanded and included as Appendix C.1.

Page 2 - General Paragraph

Our review of those portions of Section 4 concerning the organic priority pollutants indicates omissions and confusion. Specifically, the following areas are highlighted for your attention:

Question: a. Analyte lists, checking the volatiles in Appendix 4.0-1, p. 4-8 do not match with table 4.2-2, p. 4-110.

Response: The analyte lists in Appendix 4.0-1, Page 4-6, as addressing the priority pollutants was generated from the original listing of analytes as published by the USEPA. The analyte

list of Table 4.2-2, Page 4-110, is the analyte list of the analysis as requested by the USEPA under the Contract Laboratory program. It reflects the current listing of priority pollutants plus the hazardous substance list. The first list was presented as a reference to the requirements of the consent decree and the second list as to the analytes of the organic analysis.

For clarification purposes, Appendix 4.0-1 will be removed. The lists associated with the analytical methodologies are the analytes that will be analyzed for in this program.

Question: b. SOP's are inadequate in detail, are not referenced and cited sub-SOP's such as EMSL-LV Procedure No. 2 are stated without indicating where the document is located in the Work Plan.

Response: The analytical section of the Work Plan was prepared to present each major analysis type as a complete section (i.e., dioxin, organic priority pollutants, inorganic priority pollutants, asbestos, ambient air). Each section presents how the analysis will be performed by referencing the appropriate published methods that will be utilized. If standard methods were not available, prepared procedures that have been utilized in the laboratory are presented. For the situations utilizing standard EPA reference methods, the opening narrative is to summarize the methods and their application followed immediately by copies of the standard methods.

For the organic priority pollutants, the referenced methods are those required for performing contracted priority pollutant analysis for the USEPA. The Cerritos laboratory is currently under contract to the USEPA for these services and has been participating for the previous three years in the contract laboratory program. The methods and subsequent modifications of this program represent the most current collective EPA analytical techniques.

The analytical methods referenced are included in the analytical methods section of the referenced contract document included in the Work Plan (Page 4-271). However, for clarity, a narrative of the methods follows with the attachment of copies of the referenced methods (Appendix B). The Contract QC found in Exhibit E of the Work Plan document beginning on Page 4-344 is in effect as stated in the organic section of the Work Plan.

Response: (Cont'd.) Analytical Methods - Samples are prepared and analyzed according to the following EPA methods. Modifications to these methods have been noted in this text. Where inconsistencies occur between this text and references, this text has precedence. See references below:

Analyte Categories	Matrix	Method References
Volatile Organics	Water	EPA 624
	Soil	Modified 624, and Modified EMSL-Ci Procedure
Semivolatile Organics	Water	Revised EPA 625
	Soil	Modified EMSL-LV Procedure No. 2 and Revised EPA 625
Organochlorine Pesticides and PCBs	Water	Revised PA 608
	Soil	Modified EMSL-LV Procedure No. 2 and Revised EPA 608
Chlorinated Herbicides	Water	EPA 615
	Soil	Modified EPA 8150

Additional references not included in this submission:

EPA Method 625 has been revised by EPA to combine Base/Neutral and Acid extracts immediately prior to analysis, by Fused Silica Capillary column.

EPA Method 608 has been revised by EPA to include second column analysis on Fused Silica Capillary Column.

EPA, "Test Methods for Evaluating Solid Waste Physical/Chemical Methods."

EPA-600/4-82-029, "Handbook for Sampling and Sample Preservation of Water and Wastewater."

EPA-600/4-79-019, "Handbook for Analytical Quality Control in Water and Wastewater Laboratories."

Samples are initially assumed to be low concentration unless prescreening or observation of the sample indicates the presence of compounds at medium concentration. Observation includes odor, color, and any other physical properties. Solid samples are routinely screened for BNA and pesticide fractions. A low sample which requires dilution to medium level for good quantitation as a medium-level sample.

Response: (Cont'd.)

A. Volatile Organics

1. Water - Samples are prepared and analyzed by EPA Method 624. Samples requiring dilution are diluted with organic-free water and analyzed. Preparation for low- and medium-level samples is the same (Appendix B.6).

2. Soil - Samples are prepared and analyzed by EPA Method 624 modified for soil samples. The specific preparation depends on whether a sample contains volatile organic compounds at low or medium concentration (Modified EMSL-Ci Procedure, Appendix B.7).

   a. Low Concentration - One gram of samples is weighed into a soil VOA tube; 5 ml of organic-free water is added; the sample is spiked with the Internal Standard/Surrogate solution; and the sample is purged according to EPA Method 624.

   b. Medium Concentration - One gram of sample is weighed into a soil VOA tube; 5 ml of contamination-free methanol is added; the sample is extracted; 50 µl of methanol extract is added to 5 ml organic-free water in a water VOA tube; the sample is spiked with the Internal Standard/ Surrogate solution; and the sample is purged according to EPA Method 624.

B. Semivolatile Organics

1. Water - Samples are prepared and analyzed by EPA Method 625. The specific preparation depends on whether a sample contains semivolatile compounds at low and medium concentration (Appendix B.8).

   a. Low Concentration - One liter of sample is prepared and analyzed according to revised EPA Method 625.

   b. Medium Concentration - One ml of sample is extracted with methylene chloride at neutral pH; the extract is dried through sodium sulfate; concentrated; and analyzed according to revised EPA Method 625. This extraction yields one BNA extract and no combining of B/N and acid extract is needed.

Response: (Cont'd.)

2. Soil - Samples are prepared and analyzed according to Modified EMSL-LV Procedure No. 2. The specific preparation depends on whether a sample contains extractable compounds (BNAs or pesticide/PCBs) at low or medium concentration. Because the soil preparation method for extractables requires only one extraction for all fractions (BNA, pesticide/PCBs and TCDD), the soil samples for which one or both extractable fractions screened medium are prepared and analyzed as medium-level samples for all extractable fractions (Appendices B.9 and B.10).

C. Organochlorine Pesticides and PCBs

1. Water - Samples are analyzed by EPA Method 608. The specific preparation depends on whether a sample contains organochlorine pesticides and PCBs at low or medium concentration. If necessary, samples are cleaned with sulfuric acid and mercury to remove interferences with detecting and quantitating PCBs. (Appendices B.11 and B.12).

   a. Low Concentration - One liter of sample is prepared and analyzed according to EPA Method 608.

   b. Medium Concentration - One ml of sample is extracted with methylene chloride at neutral pH; the extract is dried through sodium sulfate; concentrated; preparation completed according to EPA Method 608; and analyzed according to EPA Method 608.

2. Soil - Samples are prepared and analyzed according to Modified EMSL-LV Procedure No. 2. The specific preparation depends on whether a sample contains extractable compounds (BNAs or pesticide/PCBs) at low or medium concentration. Because the soil preparation method for extractables requires only one extraction for all fractions (BNA, pesticide/PCBs, and TCDD) the soil samples for which one or both extractable fractions screened medium are prepared and analyzed as medium-level samples for all extractable fractions (Appendices B.9 and B.10).

D. Chlorinated Herbicides

1. Water - Samples are prepared and analyzed according to EPA Method 615. Low and medium samples are prepared the same way and the resulting extract is

Response: (Cont'd.) diluted as needed. EPA Method 615 does not address the subject of low or medium level (Appendix B.8).

2. Soil - Samples are prepared and analyzed according to EPA Method 8150. Low and medium samples are prepared the same way and the resulting extract is diluted as needed. EPA Method 8150 does not address the subject of low or medium level (Appendix B.13).

Question: c. EPA's Invitation for Bid (IFB) contract citations are not properly referenced and may not be satisfactory for all matrices especially water and wastewater. The July 1982, EPA 624, 625 methods are appropriate.

Response: The EPA Methods 624 and 625 are embodied in the methods utilized in the performance of the analytical procedures. The methods are included as references for the response to (b) above. The reference to the methods incorporated in preparing the analytical procedures is on Page 4-278 of the Work Plan.

Question: d. QC acceptance limits are not referenced for surrogates.

Response: The following is the current acceptance limits for surrogates as required by EPA. These limits are periodically updated by EPA as interlaboratory data are evaluated.

Volatiles	% Water Recovery	% Soil Recovery
1,2-Dichloroethane-d4	77-120	64-129
Toluene	86-119	69-127
4-Bromofluorobenzene	85-121	61-122
Base/Neutrals		
Nitrobenzene-d5	41-120	24-115
2-Fluorobiphenyl	44-119	37-120
p-Terphenyl-d14	33-128	28-133
Acids		
2-Fluorophenol	23-107	24-111
Phenol-d5	15-96	20-106
2,4,6-Tribromophenol	20-105	11-102
Pesticides		
Dibutyl chlorendate	64-114	0-205

Question: e. 1,2,3,4-TCDD is listed as an internal standard on p. 4-147 and as surrogate on 124-148 and on deliverables. This is unacceptable, since the deliverable surrogate shall be $^{37}Cl_4$-2,3,7,8-TCDD.

Response: As the isomer specific analysis is to be performed, no effort was intended to utilize the dioxin screen of the contract laboratory program. The dioxin section will only apply for the analysis of 2,3,7,8-TCDD and all implications of the organic section to analysis of dioxin will be deleted.

Question: f. Misspelled analytes

p. 4-111 - 2-propane = 2-propanone
p. 4-143 - phospene = phospine
BFP = PFB

Response: The typographical errors are so noted and will be corrected.

Question: g. SOP's for all criteria to be achieved must be stated including surrogates and analyte spikes.

Response: The QA/QC portion of the organic section (4.2.5, Page 4-114) summarizes the QC expressed in Exhibit E (Page 4-344) of the Work Plan. The summary presents the key items that are currently required and delivered to the USEPA.

The following is a list of the matrix spikes used and their currently anticipated recoveries according to the USEPA. The surrogates are listed with the current expected recoveries according to the USEPA.

Volatile Organics	% Water Recovery	% Soil Recovery
Analyte Spikes		
1,1-Dichloroethylene	61-145	59-177
Trichloroethylene	71-120	62-137
Benzene	76-127	66-142
Toluene	76-125	59-139
Chlorobenzene	75-130	60-133
Surrogates		
1,2-Dichloroethane-d4	77-120	64-129
Toluene-d8	86-119	69-127
4-Bromofluorobenzene	85-121	61-122

Response: (Cont'd.)

Base/Neutrals

Analyte Spikes		
1,2,4-Trichlorobenzene	39-98	38-107
Acenaphthene	46-118	31-137
2,6-Dinitrotoluene	24-96	28-89
Di-n-butylphthalate	11-117	29-135
Pyrene	26-127	35-142
N-Nitrosodi-n-propylamine	41-116	41-126
1,4-Dichlorobenzene	36-97	28-104
Surrogates		
Nitrobenzene-d5	41-120	24-115
2-Fluorobiphenyl	44-119	37-120
p-Terphenyl-d14	33-128	28-133

Acids

Analyte Spikes		
Pentachlorophenol	9-103	17-109
4-Chloro-3-methylphenol	23-97	26-103
Phenol	12-89	26-90
2-Chlorophenol	27-123	25-102
4-Nitrophenol	10-80	11-114
Surrogates		
2-Fluorophenol	23-107	24-111
Phenol-d5	15-96	20-106
2,4,6-Tribromophenol	20-105	11-102

Pesticides

Analyte Spikes		
Lindane (gamma-BHC)	56-123	46-127
Heptachlor	40-131	35-130
Aldrin	40-120	34-132
Dieldrin	52-126	31-134
Endrin	56-121	42-139
p,p'-DDT	38-127	23-134
Surrogate		
Dibutyl chlorendate	67-114	0-205

Question: Page 3 - General Paragraph: In summary, the presentation of the organic priority pollutants is not in a form that will allow further evaluation and is not acceptable to the NJDEP.

We are requiring that the Work Plan indicate that for each set of 20 samples collected that split samples be provided to the OSC to be analyzed independently by the NJDEP. The

specific samples to be split will be determined by the NJDEP's OSC or other representatives. In addition, for each set of 20 samples that you analyzed, a "spiked" sample as well as a blind duplicate must also be analyzed.

A. Duplicate Samples

One (1) of every twenty (20) samples should be taken in duplicate and analyzed separately for the appropriate matrix type of material sampled on site. (i.e., water, soil/hydrosoil/sediment, waste).

A complete set of Quality Assurance blanks must accompany each day's samples for each matrix collected.

B. Travel/Trip Blank

A travel blank consists of a set of sample containers filled with laboratory demonstrated analyte free water. (This water preferably should be of the same quality as the method blank water used by the laboratory performing the specific analysis.) These travel blanks should be handled, transported, and analyzed in the same manner as the samples acquired that day.

1. A set of travel blanks must accompany all soil, hydrosoil, sediment samples one each day of sampling. At a minimum, purgeable organic blanks are required. Additional parameter blanks may be required in specific cases. NJDEP will review the submitted QA Plan and determine applicability of blanks.

2. A set of travel blanks must accompany all waste samples on each day of waste sampling. At a minimum, purgeable organic blanks are required on waste samples. Additional parameter blanks may be required in specific cases. NJDEP will review the submitted QA Plan and determine applicability of blanks.

These requirements must be met for all matrices on each day of sampling and/or with each sample container shipment or suite of sampling.

Response: The Work Plan had specified a duplicate, spike and method blank as appropriate for the matrix and analytes of interest. The QA/QC plan will be modified to include a blind duplicate and sample spike per 20 analyses. These changes are reflected in the amended QC plan in Appendix B.15 (attached). Due to the possible eight analyses that can be

performed on a single sample, the blind duplicate and sample spike are initiated at the laboratory QC coordinator level. This approach allows the most thorough and controlled coverage of each analysis type. It will also generate a sufficient amount of data on each analysis type for valid statistical evaluation.

In accordance with the comments, the spike material that will be needed for NJDEP is for each matrix and analysis type (i.e., semivolatile priority pollutants, volatile priority polluants, pesticides, herbicides, dioxin, metals, cyanides, phenols) to adequately QC the analyses.

Question: B. Sampling

As presented in the Work Plan, a number of general sampling programs will be performed on the site and are:

1. chips, wipes and scrapes
2. near surface sampling
3. borings
4. monitoring wells (See Specific Comments/Concerns)
5. sediment sampling (See Specific Comments/Concerns)

The chips, wipes and scrapes are self-explanatory and are based upon a "bias sampling" approach. This approach is acceptable to the department realizing that you are willing to consider large areas i.e., one complete side of a building as being totally contaminated to the degree exhibited by those bias samples. However, results indicating nondetectable levels will require further sampling and verification of previous nondetectable levels.

Response: All analyzed results will be evaluated with respect to surrounding data. Based on this, appropriate actions will be proposed for implementation as part of the remedial action plan which may include additional sampling for verification of nondetectable results using different sampling matrices.

Question: The near surface sampling consists of sampling at a depth from 0 inches (grade) to 60 inches. Discrete samples are to be collected from 1) 0 to 6 inches, 2) 6 inches to 12 inches and 3) at one foot increments down to 60 inches deep. The samples collected should be representative of the depth range being sampled i.e., composite of the sample depth range.

Response: Samples will be representative of a given depth range (see response Item 3-39).

Question: Further, in general, samples should be collected at each significant change of geology/composition of soil, stained/discolored soil and/or the presence of organics.

Response: Samples will be taken continuously throughout the depth of each hole. Samples will be split if lithological changes or physical variations are observed (see response, Item 3-39).

Question: Analysis consisting of priority pollutants and dioxin (2,3,7,8-TCDD) must be performed on the samples from 0-6 inches, 6 inches to 12 inches and 12 inches to 24 inches. All samples taken below the 24 inch depth (24 inch to 60 inch) are to be held for analysis (dioxin) subject to the results of the upper increment sample ranges.

Response: See response below.

Question: With respect to the sampling plan for the near surface soil investigation, the NJDEP is concerned that the biased sampling approach that you have proposed will not be sufficient to adequately assess the extent and magnitude of contamination. We believe it is critical that the site investigation phase be able to accurately quantify the amount and degree of contamination. This is important from a public health perspective as well as in selecting the most appropriate remedial action. For these reasons the biased sampling approach is unacceptable.

Consequently, we are rejecting your proposed sampling plan and requesting that you revise the plan to include a systematic (grid system) sampling program. This systematic sampling plan may be supplemented by the biased sampling points that you have identified. It may also be desirable to choose biased locations based on the least likelihood of finding contamination.

At this time we are recommending that a grid system, such as the 50 by 50 grid stated in the ACO be utilized. We are also requesting that you quantify the statistical probability of measuring a concentration of greater than 1 ppb 2,3,7,8-TCDD within the area of a grid, given that the contamination at each node of that grid is less than 1 ppb. If the statistical probability of this event is sufficiently low, the NJDEP may consider the entire grid "clean" based on the four measurements made at the nodes of the grid. However, if the statistical probability is unacceptable or cannot be determined, NJDEP will require that an additional sample or samples be taken within the grid to verify that the grid is "clean".

Moreover, you should explicitly indicate that if any one data point collected at the nodes of grid is greater than 1 ppb that, in the absence of any additional sampling within the grid, the entire grid will be considered contaminated.

Response: NEAR-SURFACE SOIL SAMPLING PLAN

A near-surface soil sampling program will be performed on the project site to obtain soil samples for chemical analysis. The EPA (EPA, July 1982, Test Methods for Evaluating Solid Waste, SW-846, not attached) provides guidelines for developing a sampling program. The guidelines describe how to obtain representative samples and how to estimate an appropriate number of samples to be analyzed. The objective of the sampling plan is to estimate chemical characteristics for the purpose of comparing those characteristics to applicable regulatory thresholds and to selecting remedial actions if required. As the guidelines state, generally, high accuracy and high precision are required if contaminants are present at a concentration close to regulatory thresholds. Alternatively, relatively low precision can be adequate if contaminants occur at levels far below or far above their applicable thresholds. A well-designed sampling program makes use of preliminary information to estimate the approximate number of samples to collect. It also analyzes such samples in a phased manner to optimize the effort. This type of prudent procedure allows for analysis of the appropriate number of samples needed to evaluate remedial actions and avoids unnecessary expense. More samples can subsequently be obtained using this approach if necessary. The near-surface soil sampling program proposed uses a systematic random sampling plan to collect data from 20 locations on the site. These locations are shown in Figure D-4 (Appendix D). The number of locations and their method of selection are described below. The approach used follows the EPA guidelines and makes use of the 50- by 50-foot grid. The number of locations is anticipated to provide the precision required to within the confidence interval (i.e., 80 percent) suggested by the guidelines.

A total of 60 samples will be analyzed for dioxin from the systematic random sampling consisting of three samples for each location from zero to 6 inches, 6 to 12 inches, and from 12 to 24 inches. A total of 40 samples will be analyzed for priority pollutants plus 40 consisting of two samples for each location from zero to 6 inches and from 12 to 24 inches. Each sample will be a composite and split, if required, of the sample depth range. In addition to the systematic random sampling, other selected locations as shown in Figure D-4 (biased samples) will also be taken and analyzed for dioxin only.

SYSTEMATIC RANDOM SAMPLING PLAN FOR SURFACE SOIL SAMPLING

EPA (Test Methods for Evaluation of Solid Waste, Physical/ Chemical Methods, 1982) recommends using available data to help determine how many samples should be analyzed. For the surface soil sampling, samples from nine locations were analyzed by NJDEP with results as follows:

SAMPLES WITH CONCENTRATIONS 1 PPB OR GREATER ON SITE
5/27/83

SAMPLE NUMBER	SAMPLE LOCATION	TCDD CONCENTRATION (ppb) INITIAL	REPEAT
1	Adjacent to bulkhead along Passaic River at north end of site	69	
2	South side of Building No. 1	NG	100
3	Adjacent to bulkhead along Passaic River at north end of site	305	560 1,000 duplicate
4	Under storage tank at northwest corner of site	NG	>51,000
5	Near railroad siding, western edge of site	427	530
6	Adjacent to storm drain near tall stack northeast corner	NG	680
7	Adjacent to railroad tracks, southwest entrance	68	
8	Adjacent to railroad tracks, southeast entrance	88	100
9	Adjacent to railroad tracks, southern gate	60	

Notes: (a) Nine samples were collected.
(b) NG = Did not pass EPA Monitoring Management Branch QA/QC requirements.

Following the procedures described in the EPA methods book, the d a were first transformed using a $\log_{10}$ transformation. Levels for the same location were averaged to produce one number or each location. The resulting numbers were 1.84, 2.00, 2.75, 4.71, 2.68, 2.83, 1.83, 1.97, and 1.78. The mean of these numbers is 2.49 and the standard deviation is 0.937. Using the 0.937 estimate, if we desire to compare contaminant levels to within a factor of 2 of 1 ppb, we perform the EPA calculations as follows:

RT (Regulatory Threshold) = 1 ppb

$\hat{X}$ (Potential Concentration) = 2 ppb

$\log_{10}(1) = 0$; $\log_{10}(2) = 0.301$

$\Delta = 0.301 - 0 = 0.301$

n (number of samples) = $t^2_{.20}s^2/\Delta^2$

where s = 0.937; $t_{.20}$ = t-statistic for 80% confidence for n samples

$n = 9.689\ t^2_{.20}$

The solution from the t-tables is n = 18 samples. Twenty samples are anticipated to provide sufficient accuracy, if levels are above 2 ppb or below 0.5 ppb. Every third node beginning with 1A that was available for surface sampling was selected as per the systematic random sampling plan.

Question: The boring program, and subsequent monitoring well installation, require continuous split spoon sampling for the entire depth of all of the borings. The Phase I boring program will allow determination of the site stratigraphy to a depth of approximately 10 feet to 15 feet along with continuous sampling throughout this depth. The locations of the borings must not coincide with the near surface sampling locations. The Work Plan indicates that selected samples from these borings, based upon visual inspection, will be submitted for priority pollutant and dioxin analysis. It is recommended that, at a maximum, a composite sample (6 inch increment) be taken in the depth range of seven (7) to ten (10) feet from each boring location. This sample should be submitted for both priority pollutant and dioxin analysis.

Response: The design of the boring program is presented in response to Items 3-40 and 3-43. Composited six-inch samples from depths between seven and 10 feet will be analyzed for dioxin and priority pollutants.

Question: C. IT Laboratory Certification/VO Holding Times:

In accordance with your letter of May 14, 1984 to Mr. Michael Cantania it is our understanding that IT Corporation (Knoxville - Directors Drive) is an acceptable laboratory for the performance of 2,3,7,8-TCDD (dioxin) analysis. Further, it was indicated during our meeting that the seven day extraction time for semi-volatile organics, as required by the USEPA, will not be a problem with you. Samples must be collected, shipped, screened for dioxin and extracted for the organic parameters within seven (7) days of collected. No exceptions will be permitted.

Response: For soil samples with dioxin below 50 ppb, the seven-day holding period will be applied.

Question: D. Sampling Parameters

In accordance with the Administrative Consent Order, all wipe, scrapes and chip samples are to be analyzed for 2,3,7,8-TCDD. All other samples are to be analyzed for priority pollutant plus 40 and 2,3,7,8-TCDD. In addition we request that 10% of the near surface samples, boring samples and sediment samples be analyzed for 2,3,7,8-TCDF (tetrachlorodibenzofuran) and octachlorodibenzodioxin (OCDD) wherein appropriate SOP's for these compounds will be required - equal to the SOP's for 2,3,7,8-TCDD.

Response: The response to sample analyses for priority pollutants is answered elsewhere in the responses (Page 1). In regard to the requested analysis of 10 percent of the near-surface samples, borings, and sediment samples for 2,3,7,8-TCDF (tetrachlorodibenzofuran) and octachlorodibenzodioxin (OCDD), these additional analytes will be added at this level. The samples for the analysis will be selected prior to the analysis so that the appropriate surrogates may be added. Draft SOP's for these analyses are included in Appendices B.16 and B.17.

Question: E. Health/Safety

Item E.1 - We recommend that an occupational physician in the Newark area be identified for those situations involving an accident/injury causing potential contamination. Dr. Kenneth Rosenman, Occupational/Environmental Health Service Director, NJDOH can be called for assistance in this matter at 609-984-1863.

Response: An occupational physician in the Newark area has been identified for those situations involving accidents/injuries with contamination. This physician is:

Dr. Steve Marcus
201 Lyons Avenue
Newark, NJ 07112
201-926-7443

Question: Item E.2 - The broad scope of the Community Public Health Protection (2.0.2), Health and Safety Plan (2.0.4), Site Security (2.0.5), and Sampling (3.0) portions of the Work Plan require specific details. These details should be presented in "Standard Operating Procedures" which must be available on-site, be fully understood by all on-site personnel and be followed "by-the-numbers". During our meeting you indicated that these detailed documents exist. Please include these documents as an appendix to the Work Plan. See Specific Comments for further details.

Response: The Community Public Health Protection (2.0.2), Health and Safety Plan (2.0.4), Site Security (2.0.5), and Sampling (3.0) portions of the Work Plan have been expanded to include specific details. These procedures will be discussed during the training sessions and will be available on site. The specific details are discussed later as specific responses in Appendix A, with the exception of the site security plan. The site security plan will be amended to include that all persons entering the site must sign a "check in/check out" log.

Page 6 - Specific Comments/Concerns as related to Work Plan pages are responded to as follows:

Question: Item 1-4 - Indicate the boundaries of the 1.8 acre and 1.6 acre portions of the total site on Figure 1-2.

Response: The boundaries of the 1.8 and 1.6 acre portions of the total site are shown in Appendix D as Figure D-1. This figure is as transmitted in the June 10, 1983 submittal to Mr. Michael Catania of NJDEP from Mr. James Worthington of Diamond Shamrock. The submittal, entitled, "Report on Lister Avenue Facility," summarized and overviewed the history and operations at the former Diamond Shamrock site.

Question: Item 1-4 - Indicate the boundaries and location of the parking lot on Figure 1-2. Is this area the Sergeant property, east of the site?

Response: The location of the parking lot is shown in Figure D-1 (Appendix D). The lot, used by employees to park their vehicles, was located on the Sergeant property east of the site. This figure was also taken from the June 10, 1983 submittal to NJDEP.

Question: Item 1-6 - Indicate and present by a separate figure the chronology of the construction of structures/buildings from 1951 through the 1960 explosion to the 1967 plant expansion. This should also include a chronology of ground surface modifications/expansions.

Response: A layout of the site before the explosion in 1960 is shown in Figure D-2 (Appendix D). A chronological history of process and plant changes is presented in Table D-1. Both of these attachments were also taken from the June 10, 1983 submittal to NJDEP.

Question: Item 1-7 - Identify samples indicated in Table 1.2-1 on Figure 1.2-1. Additional samples taken by NJDEP, EPA or DSCC must also be included i.e., two samples taken by NJDEP (April 1983) and DSCC Sergeant property (parking lot?) samples, if appropriate.

Response: Samples taken on the site May 27, 1983 and summarized in the Work Plan Table 1.2-1 are keyed to the site plot plan in Appendix D as Work Plan Figure D-3. Additional NJDEP samples can be added if the results are made available to Diamond Shamrock. New samples have been taken from the parking lot on the Sergeant property site.

New samples in the area of the proposed decon area were taken on June 1 and are reported in the responses below.

Question: Items 2-1 and 2-19 - Zones of contamination i.e., contaminated, contamination/reduction, clean, should be determined based upon present site data and clearly indicated on Figure 1.2-1 or some other separate figure. Also, present discussion concerning adjustment of these zones considering the proposed use of the office as a command post and subsequent operations to allow use of this office.

Response: The zones of contamination have been determined and are outlined in Appendix A.3. Samples were taken in this area on June 1, 1984 and results show dioxin contamination to be nondetectable (at less than 1.2 nanograms per 100 centimeter squared wipe). During this assessment activity, the decontamination area outlined will not be adjusted. The office will not be utilized as a command post or decontamination area.

Question: Item 2-1 - Provide at a minimum, a desk, locking filing cabinet and keys and one separate telephone line for use by the NJDEP on-scene coordinator.

Response: An office trailer will be located at the entrance to the site and will be furnished with office equipment. Diamond Shamrock, Diamond Shamrock's contractors, and NJDEP will share the the facilities. A file drawer will be made available to NJDEP. Three phone lines will also be available for common use.

Question: Item 2-5 - Include USEPA and NJDEP 24-hour emergency response numbers.

Response: The USEPA and NJDEP 24-hour emergency response numbers will be included for those agencies to contact in the event of an emergency. The numbers are as follows:

NJDEP - (609) 292-7172
USEPA - (201) 548-8730

Question: Item 2-5 - The presentation on precautions for preventing contamination from leaving the site is inadequate and should be expanded, i.e., plan for runoff control should either be all inclusive (entire perimeter) or based upon actual surveyed elevations (runoff patterns). This section on health preservation should be a separate document (appendix), able to stand alone. The sampling teams must be specifically directed to avoid and/or minimize the generation of airborne contaminants. Describe in detail procedures/apparatus that will be used.

The preparation of a separate preliminary contingency plan document must be prepared in conjunction with the City of Newark and NJDEP. We will schedule a briefing for the City of Newark and subsequent preparation/fine-tuning of this contingency plan.

Response: The precautions for preventing contamination from leaving the site has been expanded and is now a separate document (Appendix A.3). Please contact us when the briefing has been scheduled with the City of Newark for the preparation/fine tuning of this contingency plan.

Question: Item 2-6 - In the event of an injury or accident which causes potential contamination, medical tests, such as central nervous system peripheral neuropathy tests or liver profile blood tests should be specified in addition to the "Supervisor Employee Injury Report".

Response: An occupational physician has been identified and made aware of the contaminants present. Page 2-6 of the Work Plan will be amended to include a procedure for notifying the physician of an accident/injury with potential contamination, and the suspected contaminant. The physician will make a professional decision as to the appropriate medical test to screen for. The amendment will read as follows: "If there is potential contamination of an employee, the occupational physician will be contacted by the health and safety representative on site to inform the physician of suspected contaminants." The occupational physician to contact is:

Dr. Steve Marcus
201-926-7443

The physician will coordinate emergency actions with the hospital.

Question: Item 2-16 - In addition to TCDD, all other suspected hazards should be identified and appropriate toxicological data presented (see paragraph B, page 2-17).

Response: The raw products and the finished products for this site while under the control of and operated by DSCC were:

Raw Products

Acetic acid	Sulfuric acid
Acetic anhydride	Dimethylamine (40%)
*Acetaldehyde	Triethylamine
*Benzene	Chlorine
*Monochlorobenzene	2-Ethylhexanol
Tetrachlorobenzene	Butyl alcohol
*Chlorosulfonic acid	Isopropyl alcohol
Methanol	Butoxyethoxypropanol
*Oleum (20%)	*Nicotine
Phenol	Sodium Hydroxide

Finished Products

2,4,5-trichlorophenoxy acetic acid
2,4-dichlorophenoxy acetic acid
2,4,5-trichlorophenol
2,4,6-trichlorophenol
2,4-dichlorophenol
Monochloroacetic acid
*Hexachlorobenzene
*Dichlorodiphenyl tricloroethane
*p-chlorophenyl-p-chlorobenzene sulfonate (Ovex)
*1,1,1-trichloroacetaldehyde

Finished Products
(Continued)

*Benzensulfonyl chloride
*p-chlorobenzenesulfonyl chloride
*p-chlorobenzenesulfonamide
*4,4'-dichlorodiphenylsulfone
*p-acetylaminobenzene sulfonyl chloride
*p-methoxybenzene sulfonyl chloride
*1,2,4,5-tetrachlorobenzene
Amine salts of 2,4-D (dimethyl and triethyl amines)
Amine salts of 2,4,5-T (dimethyl and triethyl amines)
Esters of 2,4-3 (butyl, 2-ethylhexyl, isopropyl, butoxyethoxypropyl)
Esters of 2,4,5-T (butyl, 2-ethylhexyl, isopropyl, butoxyethoxypropyl)
Amine salts of N-oleyl-1,3-propylenediamine
*Nicotine sulfates
Muriatic Acid
*2,5-dichlorophenyl-p-chlorobenzene sulfonate
*Products and raw materials made or used from 1951 to February 1960 and not produced after that period

Evaluating this information from an employee exposure standpoint, we are concerned with dioxin (2,3,7,8 TCDD), 2,4-D, 2,4,5-T, trichlorophenol (TCP), DDT, sulfuric acid, organic solvents, and alcohols. These chemicals are known to have been at the site during periods under DSCC ownership and still may be present on the site. They will be monitored and results used as indicators to control employee exposures. The list of chemicals is not all inclusive of what may be at the site as manufacturing by others took place before and after DSCC ownership. Materials used are unknown. The initial monitoring for the organic solvents and alcohols on this list will utilize sorbent tube collection and GC/MS or GC analysis, whichever is appropriate. Once contamination is known for specific compounds, analysis will be by GC or appropriate method. The Material Safety Data Sheets for selected materials, along with additional toxicological data, are attached in Appendix A.4. This information, along with the NJ hazardous substances fact sheets, will be kept on site and will be provided to employees during the training sessions.

Question: Item 2-17 - A Permissible Exposure Limit (PEL) for dioxin is presented, however, background discussion, references and rationale should be presented. The most recent risk assessment is available from the Center for Disease Control. PEL's are set by the U.S. Department of Labor - OSHA, and at this time there is no OSHA PEL for TCDD.

Response: We are aware that there is no OSHA permissible exposure limit (PEL) for dioxin, but other organizations such as the American Conference of Governmental Industrial Hygienists (ACGIH), establish PELs (or Threshold Limit Values). When none have been established, it is the responsibility of industry to use the most recent toxicological information to establish an internal PEL. IT Corporation has done this in order to arrive at a PEL of 0.5 nanograms per cubic meter for TCDD. The justification for the PEL is attached as part of Appendix A.2.

Question: Item 2-18 - The Material Safety Data Sheets (MSDS) are inaccurate and incomplete. Specifically, they should be site specific, i.e., delete EPA-OSC and replace with NJDEP-OSC, threshold limit value should not be specified since one has not yet been established.

Response: In clarification, we noted no inaccuracies on the MSDS for dioxin. This material safety data sheet has been amended to replace EPA-OSC with NJDEP-OSC. Also, additions have been made. As mentioned in the previous comment, the PEL will be included on this MSDS. The MSDS will not be the only source of toxicological information present for employee training or on-site information. The information included in the preceding response for Item 2-16 will also be included.

Question: Item 2-19 - All decontamination water must be stored on-site, sampled, and based upon results, discharge will be authorized by the NJDEP-OSC. Discharge location must be selected and all necessary permits obtained i.e., discharge to Passaic River (NJPDES permit) or to Passaic Valley Sewerage Commission. Parameters for testing effluent will be established. Characterization of the influent stream (de-con water) should be provided such that effluent parameters can be established.

Response: All hydrostatic test water and decontamination water will be collected and stored in tanks on the site. The collected water will be sampled and analyzed for dioxin and other appropriate parameters prior to and after activated carbon treatment. The results of this characterization will be submitted to NJDEP to enable discharge of the water to either the Passaic River (NJPDES permit) or to the local public-owned treatment works (Passaic Valley Sewerage Commission).

Question: Item 2-19, Paragraph 2 - The location of the decontamination pad, decontamination trailer, etc. may be inappropriate considering the documented TCDD contamination in that area. Initial sampling should be conducted in these areas, especially the driveway, to assure that these proposed areas are acceptable "clean" areas. A program to clean these areas should also be prepared and presented.

Response: A sampling campaign was conducted per your request on June 1, 1984 at the site to determine the extent, if any, of dioxin contamination in the proposed decontamination area. Samples taken included wipes of the plastic cover, the road surface, and samples of standing water, sand and dirt scrapings from the crack adjacent to the west side of the road. Initial analytical results indicate no detectable contamination of the top surface or "sandwich" layer. The specifics for the decon line installation refer to further precautionary steps via a PVC overlay.

Question: Item 2-19 - Specific procedures for the decontamination of all equipment and personnel exiting the site must be included. These procedures must be step-by-step and include, types of washes, rinses etc. What will be de-conned for reuse and what will be disposed of? Further, procedures for decontamination of all sampling equipment must also be included.

Response: The specific procedures for decontamination of equipment and personnel is attached as Appendix A.3.

Question: Items 2-20 and 2-24 - Where is the break area? What procedures must the sampling team follow before break? Will workers totally de-con before break? SOP's for these activities must be included.

Response: The specific procedures for employees taking a break are detailed in the attached Appendix A.3.

Question: Item 2-20 - The level of respiratory protection advised for the TCDD hazard is not in accordance with the most recent NIOSH Bulletin #40 (January 23, 1984), as follows:

> "For situations where TCDD contamination is low (e.g., exposure to dust contaminated with low levels of TCDD), air purifying respirators should provide sufficient protection..."
>
> "Where quantities of materials highly contaminated with TCDD have been released and have contaminated an area (e.g., production accidents), all workers who may be exposed to TCDD should wear respirators that consist of a self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode."

The level or levels of respiratory protection (based upon type of site activity) must be clearly presented along with

justification and rationale. A decision must be made as to which guidance/criteria will be used on-site.

Response: As stated in the Work Plan, air-purifying respirators will be used when doing all assessment activities except drum and tank opening and sampling. This decision is based on industrial hygiene data obtained on similar projects by both IT Corporation and other companies doing assessment activities and mitigation work. The industrial hygiene group of IT Corporation just completed sampling in Missouri where activities, such as bulldozer operation and excavation, would generate a higher level of exposure than this understanding, and results showed nondetectable exposures (at 0.15 to 0.35 ng/m^3). Since activities on this site are primarily assessment with procedures established to eliminate, or minimize, dust generation, we are confident that air-purifying respirators will be adequate. As mentioned in the Work Plan, employee exposures will be monitored and if levels of dioxin are detected at or near the permissible exposure limit, air-supplied respirators will be required. Also, if the industrial hygienist on site notes any operation where significant exposures could occur, air-supplied respirators will be required. We feel this procedure is consistent with NIOSH Intelligence Bulletin 40.

Question: Items 2-24 and 3-23 - The methodology for segregating drums, e.g., labeling or moving, procedures for automatic sampling and procedures for sampling bulged drums should be expanded and detailed, for example, preparation of staging area, etc. All activities regarding the drums, inside and outside of the buildings, must be performed in self contained breathing apparatus. Further, prior to and during these activities, HNU/PID monitoring must be conducted.

Response: The drum opening procedure has been amended per Appendix C.2.

Question: Item 2-31 - The New Jersey Department of Health will attempt to prioritize the writing of the hazardous substances fact sheets if Diamond Shamrock can provide the list of expected chemicals as soon as possible.

Response: The raw material and finished products are per Question 2-16 response.

Question: Items 2-37 and 2-38 - The spent carbon units will constitute a hazardous waste and on-site storage/control must be indicated.

Response: The activated carbon (CANSORB) units are approximately the size of a standard 55-gallon drum. The spent units will be

potentially contaminated and will be considered a hazardous waste. As these units are replaced, the spent units will be placed in H-size overpacks and stored on site for later remedial action.

Question: Item 2-38 - The elevation for the 100-year flood should be determined and appropriate protection be provided.

Response: The entire site lies within the 100-year tidal floodplain. Flooding at this level, however, has not been observed in this century. According to the Bureau of Floodplain Management, the 100-year tidal floodplain elevation was only established within the past five years. Occupancy of the site began long before that determination. As with all other properties in this district, no additional protection is planned.

Question: Item 2-38 - Prior to the use of the sump as a runoff collection point, the integrity, influent/effluent lines, etc., must be evaluated.

Response: Prior to the use of any sump or runoff collection point for the containment of water, the integrity of the system will be checked and sealed or grouted as necessary.

Question: Item 3-1 - The proposed sample identification system is acceptable for use by the on-site personnel and laboratories. However, a simpler identification system along with sample location figures should be developed for those not familiar with the previously stated identification system.

Response: To avoid possible cross referencing transcription and other errors that usually accompany having dual numbering systems, the single system will be utilized. However, as the number system is established for this site, a detailed guide will be available of the corresponding locations to facilitate understanding of the system and locations.

Question: 3-9 - Samples that require special handling should also include all unknown drum samples, tank samples, reactor/process vessel samples, etc.

Response: The drum and tank samples will be added to this section.

Question: Item 3-14 - It is indicated that..."On-site wind speed and direction data will also be used to design the air sampling program to be conducted during site cleanup activities." It should also be stated that on-site wind data and off-site wind data from the National Weather Service Office at Newark International Airport will be compared to assure that the

nearby physical obstructions at the 80 Lister Avenue site do not have a major effect on the wind flow patterns on-site. During large-scale synoptic flow patterns, the wind direction and wind speed at both sites should be comparable.

Response: Off-site wind speed and direction data from the National Weather Service Office at Newark International Airport will be obtained for the duration of the study. These data will be compared with on-site wind speed and direction data to correlate the area-wide air movements that affect background air pollution levels within the study area to the local air movements that affect the dispersion of air pollutants near the project.

Question: Item 3-14 - Based on historical records, consideration should be given to include sampling parameters for materials which were used or stored on-site, such as feedstock material, by-products, chemical process intermediates, support material, etc. Please specifically list these parameters in Section 3.1.

Response: The following table lists parameters to be sampled in ambient air. This list includes all pesticides and other chlorinated organics that were products at the Newark site.

AMBIENT AIR PARAMETERS
CHEMICAL COMPOUNDS AND METALS TO BE MEASURED

I. Metals

Lead	Cadmium
Manganese	Zinc
Copper	Iron
Vanadium	Nickel

II. Volatile Organic Compounds (VOC's)

Vinyl chloride	Tetrachloroethylene (PERC)
Vinylidene chloride	Chlorobenzene
Methylene chloride (ME chloride)	Ethylbenzene
Chloroform	m-Xylene
1,2-Dichloroethane	p-Xylene
Benzene	Styrene
Carbon tetrachloride	o-Xylene
Trichloroethylene (TRIC)	1,1,2,2-Tetrachloroethane
1,4-Dioxane	o-Chlorotoluene
1,1,2-Trichloroethane	p-Chlorotoluene
Toluene	p-Dichlorobenzene
1,2-Dibromoethane	o-Dichlorobenzene
	Nitrobenzene

III. Polycyclic Organic Compounds (PAH's)

Benzo(k)fluoranthene	Anthracene
Benzo(a)pyrene	Fluoranthene
Benzo(ghi)perylene	Pyrene
Indeno(1,2,3-cd)pyrene	Benz(a)anthracene
Coronene	Benz(ah)anthracene
Phenantrene	Chrysene
Tyiphenylene	Perylene
Benzo(b)fluoranthene	

IV. Pesticides and Other Chlorinated Organics

Hexachlorobenzene (HCB)
dichlorodiphenyl trichloroethane (DDT)
Ovex, Multicide
p-chlorophenyl-p-chlorobenzene sulfonate (K101)
2,5-dichlorophenyl-p-chlorobenzene sulfonate (Compound 923)
1,1,1-trichloroacetaldehyde (Chloral)
benzenesulfonyl chloride (BSC)
p-chlorobenzenesulfonyl chloride (BCBSC)
p-chlorobenzene sulfonamide (BCBSA)
4,4,-dichlorodiphenylsulfone (44-DDS)
p-acetylaminobenzene sulfonyl chloride (PAABSC)
p-methoxy benzenesulfonyl chloride (PMBSC)
2,4,5 trichlorophenoxyacetic acid (2,4,5-T)
sodium 2,4,5-trichlorophenate
sodium trichlorophenate (NaTCP)
Monochloroacetic Acid (MAC)
2,4-dichlorophenol (2,4 DCP)
dichlorophenol (DCP)
Trichlorophenol (TCP)
1,2,4,5 tetrachlorobenzene

V. Asbestos

VI. Tetrachlorodibenzo dioxin (2,3,7,8 TCDD)

Question: Item 3-14 - We are requesting that one of the samplers be modified by adding a 10um, 50% particle cut size, size selective inlet instead of 15 um as indicated in the Work Plan. The current sampling being conducted by the NJDEP at the Newark Boys Club uses the 10um cut-off to permit comparison with the propsoed new national ambient air quality standard for particulate matter.

Response: One high-volume sampler will be equipped with a PM-10 Hi-Vol Size Selective Inlet manufactured by Sierra-Andersen to collect particles smaller than 10 micron. Inhalable particulate matter and metals will be determined from this filter.

Question: Item 3-14 - The modification of the high volume sampler is unacceptable. The sampling procedures as outlined in Section 4.5 of the report should be followed. Modified sampling methods are not valid. Sample trains should not be modified and combined.

Response: Sample collection will be accomplished using one Model UV2H TSP high-volume air sampler, one Model UV-11H IPM-10 selective high-volume air sampler, one Model PS-1 PUF sampler, one Model 155 Hi Flo Asbestos Sampler, and individual Tenax and Spherocarb sampling trains.

Question: Item 3-14 - The extraction method and analytical method are not listed in Table 3.1-2, as stated in the text.

Response: The text should read, "Ten parameters are to be measured during the 30-day air sampling program. These are listed in Table 3.1-2 along with the sampling method, typical flow rate, typical sample size, and detection limit. Extraction and analytical procedures are described in detail in Section 4.5 (Pages 4-650 through 4-854) of this report."

Question: Item 3-18 - We are concerned that the proposed analytical methodology for collecting samples for PAH's, TCDD and pesticides will not provide an adequate sample size for analysis. Therefore, we are requesting that you consider taking individual samples for the PAH, TCDD and pesticide analysis. We are especially concerned about the TCDD analysis. The need for compositing can be assessed following the results of the initial TCDD concentration.

It is stated that within the 30 day sampling period, ten (10) of the samples will be subjected to a detailed chemical analysis. While the number of samples to be analyzed is acceptable, we have some concern for the methodology used for choosing the days to be sampled. First, it is important that the 10 samples that are subjected to the chemical analysis include the days that the NJDEP samples at the Newark Boys Club. These samples are collected on the national every-sixth-day schedule for particulate sampling.

Second, concentrations of TCDD may not be directly correlated to the highest total particulate concentrations. This is because fugitive emissions of soil contaminated with TCDD would most likely occur on days with moderate to strong winds which do not necessarily correlate with photochemical smog incidences or general poor dispersion conditions associated with atmospheric inversions. Therefore, we are requesting that each sample taken from the hi-volume sampler should then be ranked for their concentration of iron and manganese.

Response: The TSP sampler will sample a total volume of 2,000 cubic meters of air. The PUF sampler with prefilter will sample a total volume of 290 cubic meters of air. These sample volumes with the proposed analytical techniques will enable detection limits of (1) 10 pg of TCDD/cubic meter of air, (2) 0.1 ng of pesticides/cubic meter of air and other chlorinated organics, and (3) 0.1 ng of PAH/cubic meter of air.

The 10 samples subject to chemical analysis will include the five or six days samples as collected at the Newark Boys Club during this study. The remaining four samples subject to chemical analysis will be based on highest TSP levels.

Question: Item 3-18 - The top ten (10) days should then be used as the basis for conducting the detailed chemical analysis. If the top 10 days do not coincide with the every sixth-day sampling, modifications to this approach will be presented by NJDEP to ensure that the maximum number of samples requiring chemical analysis does not exceed 10.

Response: See previous response.

Question: Item 3-18 - Specific information on the instrumentation to be used for measuring and recording wind speed and wind direction should be provided. Also, the placement of the meteorological instrumentation and air sampling equipment on top of the office building require justification.

Response: A Climatronics Mark III wind measuring system will be used to measure wind speed and direction on site. The instrument will be placed on a 10-meter tower. Specific loation will be decided on site ensuring it is unobstructed and outside of building wakes.

Question: Item 3-19 - The procedure outlined for sampling VOC's is for flue gas from hazardous waste incinerators or other similar combustion sources. Revise sampling method to an EPA approved ambient air sampling method for VOC's.

Response: We are unaware of any EPA-approved method for ambient air sampling for VOC's, therefore, we have proposed to use the same sampling methods used during the ATEOS/New Jersey study.

Question: Item 3-19 - The text states, "phase contact microscopy" will be performed for asbestos analysis. This should read, "phase contrast microscopy."

Response: Text will be corrected to read, "phase contrast microscopy."

Question: Item 3-20 - Quality Assurance/Quality Control requirements for meteorological data needs to be presented. Guidelines are presented in an EPA document, "Ambient Monitoring Guidelines for Prevention of Significant Deterioration", EPA 450/4-80-12, November 1980. At a minimum, daily calibration of the wind speed and direction instrumentation should occur.

Response: Daily checks for alignment and electronic calibrations will be performed. Where applicable, EPA 450/4-80-12 will be used as a guideline.

Question: Item 3-22 - Reference should be specifically made for statistical calculation of precision and accuracy to the relevant section of Title 40, Part 58 of the Code of Federal Regulations. As part of the QA/QC, filters spiked with lead, PAH's and other metals are available from EPA and the National Bureau of Standards. A field blank, a duplicate, a spiked blank and a matrix blank should be included.

Response: Filters spiked with metals and PAH's will be obtained from EPA or NBS. At least one field blank, one duplicate, one spiked blank, and one matrix blank will be included for analysis.

Question: Item 3-25 - In Section 3.3 Buildings, it is stated that the extent of contamination must be documented ..... in order to provide the design basis for a decontamination program. This statement is premature and should be restated ....."potential decontamination or subsequent total remedial action".

Response: The statement in Section 3.3, Buildings, is acknowledged for rewrite to read, "The extent of contamination must be documented . . . . . in order to provide the design basis for a potential decontamination program or for total remedial action." Work plan reissue of this page and any other will be at one time only, after all comments and concerns are addressed and finalized between NJDEP and Diamond Shamrock.

Question: Item 3-25 - In all cases, where sufficient sample weight/volume is available, an actual sample should be taken in lieu of a wipe sample.

Response: This option will be field assessed on an individual basis and a bulk sample in lieu of a wipe sample will be taken when available and practical.

Question: Item 3-28 - Shallow channel chip samples must also be taken at the top of exterior walls (office building and warehouse).

Response: Four additional shallow chip samples will be taken at the top exterior walls of the office building and four additional wipe samples will be taken from the top exterior walls of the warehouse.

Question: Items 3-29 and 3-30 - Will the 24 inch long channel provide two samples, one being 0-6" (low sample) and the second 4 feet (high sample) in all cases?

Response: Two independent samples will be taken on the lower exterior --one from 0 to 24 inches from the ground, the other from 3 to 5 feet above the ground

Question: Item 3-30 - The roof of the warehouse must be sampled for 2,3,7,8-TCDD.

Response: One wipe sample will be taken from the roof of the warehouse and analyzed for 2,3,7,8-TCDD.

Question: Item 3-35 - Provisions should be made to check the tanks for leaks by pressure testing prior to their use. Test methods and results should be provided to NJDEP.

Response: Tanks to be used for the storage of potentially contaminated and decontamination water will be hydrostatically tested with water to ensure their integrity. Test methods and results will be supplied to NJDEP.

Question: Item 3-35 - Openings of tanks must be performed in self-contained breathing apparatus with volatile organic and LEL monitoring/with appropriate protective clothing.

Response: Self-contained breathing apparatus and medium to heavy weight PVC suits will be worn when opening tanks. Also, monitoring will be done with the HNU/PID and combustible gas indicator, with operations suspended if levels of 10 percent of the LEL or concentrations above 500 ppm are reached. Pages 2-20, 2-21, and 2-22 of the Work Plan will be corrected to read as follows:

> Page 2-20 - "The respirator to be worn during activities involving drum opening, relocation of pressurized or corroded drums, and opening of tanks in the tank farm will be self contained breathing apparatus."
>
> Page 2-21 - "The protective apparel to be worn during heavier work activities, such as core drilling, drum handling and sampling, and sampling of tanks, will be:

- Medium to heavy PVC suits with hoods
- Viton or equivalent gloves with a neoprene outer glove
- PVC boots
- Hard hat with 'chin strap'."

Page 2-22 - "Monitoring will be conducted prior to and during sampling of drums and when opening tanks in the tank farm. The instruments used will be a HNU/PID and combustible gas indicator (Gas Tech GX-3A). If concentrations of gas or vapor exceed 500 ppm, when using the HNU/PID, or 10 percent of the lower explosive limit, when using the combustible gas indicator, operations must be suspended and the health and safety coordinator contacted."

Question: Item 3-38 - What does pump packing glands mean in Table 3-5.1-1?

Response: In both the raw material and finished product tank farms, the most likely source of contaminants is the area beneath the transfer pump seals. Chemicals transferred by centrifugal pumps often leak at the point of contact between the moving shaft and the stationary casing of the pump. Two types of seals, packed and mechanical, are typically used on pumps. The reference referred to in Table 3-5.1-1 as "Pump Packing Gland" means that those two areas of the site would be sampled in an area directly beneath a pump's packing gland or mechanical seal.

Question: Item 3-39 - The soil sampling program should include limited sampling along buried drain/sewers to determine if subsurface contamination has occurred due to leakage.

Response: Proper sampling technique to determine if leakage has occurred from buried drain or sewer lines would require excavation of soil. Excavation as a means to obtain samples at this stage of the site investigation will not be performed because of the potential increased risk of contamination due to dust formation and the potential of disturbing a line with questionable material content. The proposed soil and ground water sampling program should identify potential leak areas and the proposed sewer sampling will assess sump and line content for the remedial plan.

Question: Item 3-39 - Indicate the criteria that will be used for compositing of soil samples. Detail exactly what will be composited.

Response: Due to the large volume of soil required for analysis (approximately 900 grams), it will be necessary to composite vertical intervals of the borehole. This will be accomplished by combining continuous samples to achieve the desired sample amount. It is anticipated that this composite sample length may be as much as 18 inches for samples to be split with NJDEP. In no case will samples be composited that include lithologic changes or appear visually to have distinctly different characteristics.

A portable bench will be brought to the location of the boring. The surface of this bench will be covered with heavy-duty aluminum foil that will be discarded after each composite has been performed. The samples will be placed on the foil, crumbled by hand to a coarse granular consistency, and combined into a single pile. This pile will be quartered with a clean knife and recombined by overlapping opposite corners. A second division into quarters will be performed with opposite (i.e., northeast-southwest quadrants combined and northwest-southeast quadrants combined) portions subsequently placed into separate sample jars.

The compositing method recommended by NJDEP (homogenation by blending) will excessively disrupt the sample. Large fractions of the volatile organic contaminants to be analyzed may be lost if they were present. The method IT proposes to use reduces air contact during the handling of the sample.

DSCC requires that a one-day notice be given prior to splitting samples. This will allow adequate time to prepare for the sampling procedure. This notice will include boring number and depth. The project geologist will be available to consult with the NJDEP geologist concerning sample location.

Question: Item 3-39 - The method as stated is inappropriate for compositing due to the unknown degree of homogenization achieved; consider the use of a stainless steel blender. The mixing and shaking of soil samples that will require volatile organic compound analysis is unacceptable.

Response: Answered Item 3-39 above.

Question: Item 3-39 - Clearly specify all sampling equipment to be used correlated with the particular type of sampling event, i.e. near surface, borings, etc.

Response: The shallow samples (0 to 24 inches) will be taken with a 6-inch-diameter post-hole digger, 3-inch-diameter bucket auger, or spoon. All samples deeper than 24 inches will be taken by

split-spoon or Shelby tube. River sediment samples will be taken with a Hvorslev sampler or dip sampler.

Question: Item 3-39 - Specify decontamination procedures for sampling equipment.

Response: Refer to Appendix A.3.

Question: Item 3-40 - What is meant by refusal considering the various types of drilling equipment?

Response: Refusal by any type of drilling equipment occurs when the hole is no longer able to be advanced. In the shallow subsurfce borings, refusal may be due to debris contained in the fill (e.g., bricks, wood, concrete). Refusal is not anticipated in deeper borings. Refusal will result in the movement and redrilling of a hole.

Question: Item 3-40 - What will the narrative description of the sample contain?

Response: The sample will be described using the Unified Soil Classification System. This contains a density/strength estimation, color, and grain-size estimation. This description will be made for each sample by the rig geologist at the time of drilling with periodic verification by the project geologist.

Question: Item 3-40 - The geotechnical evaluation, consisting of the soil sampling at depth, other than the near-surface soil sampling (0 inches is 60 inches), should consist of a three phase approach, as follows:

Phase I - Drilling of soil borings designed to delineate on-site stratigraphy to the top of the silt layer.

Phase II - The installation and sampling of shallow monitor wells, those wells set in the first water bearing zone, to define ground water flow direction(s) and quality. In addition to the five (5) shallow wells presented in the Work Plan, the following additional wells should be installed:

a. One located along the western boundary of the site between monitor wells No. 1 and No. 5.

b. One located along the eastern boundary between monitor wells No. 3 and No. 4.

c. One located along the southern boundary next to the office building.

Phases I and II can be combined i.e., allowing the conversion of a boring (hole) to a monitoring well.

Phase III - Following the completion of Phases I and II, and subsequent to the receipt of analytical data for soil/groundwater, determination of location(s) and specifications for deeper borings and/or monitoring wells (i.e., 25 ft., 35 ft. and 100 ft.) if needed, should be undertaken.

Response: Phase I will include drilling of soil borings at each of the locations proposed for shallow monitor wells to delineate on-site stratigraphy through the bottom of the silt layer. Physical characteristics of the silt layer will also be tested. This testing is necessary to evaluate the geotechnical concerns associated with certain remedial actions.

Phase I borings will be advanced to the top of the silt layer with hollow-stem augers. Continuous split-spoon samples will be taken as the boring advances. Upon reaching the top of the silt layer, hollow-stem augering will be terminated and mud rotary advancement will begin. The augers will be sealed into the top of the silt and the rotary drilling will take place through the auger string. Continuous split-spoon or Shelby tube samples will be taken for the entire thickness of the silt. These will be used primarily to study the physical properties of the silt. At the base of the silt, drilling will be halted and the boring will be filled with cement/bentonite grout to the ground surface.

The grout will be placed at the bottom of the boring by the use of a tremie through the hollow-stem augers. As the surface of the grout rises in the boring, the augers will be withdrawn at a rate that maintains a minimum of a two-foot head of grout within them. Any excess grout or ground water displaced by it will be collected and stored on site.

Upon completion of the grouting operation, the drill rig will be moved no more than 10 feet and a second hole will be advanced for installation of the Phase II monitor well. With accurate information about the stratigraphy overlying the silt, placement of the well at the top of the layer will be possible. This boring will be advanced with hollow-stem augers.

Additional Phase II monitor wells requested [(a) along the western boundary of the site between MW1 and MW5, (b) along the eastern boundary of the site between MW3 and MW4, and (c) along the southern boundary next to the office building] will be installed. Well locations will be selected in consultation with the NJDEP geologist and noted on the site map.

Subsequent phases of the investigation, if needed, will be determined following receipt of the analytical data for the soil/ground water samples tested.

Question: Item 3-40 - In order to determine the site's stratigraphy, split-spoon sampling should be taken for the total depth of all borings and wells.

Response: Continuous samples will be obtained for the total depth of the profile at each location for borings/wells within an approximately 15-foot-diameter circle. Samples will be obtained with split-spoon samplers or tube samplers.

Question: Item 3-43 - All well locations indicated in the Work Plan are within the site boundaries. Accordingly, there will be no data concerning upgradient groundwater quality. It is recommended that an additional well be installed to determine the background quality of groundwater entering the site.

Response: A background water quality well will be installed provided the location for that well is specified and the necessary access and permission are obtained by NJDEP.

Question: Item 3-43 - The installation of all soil borings and monitor wells should be conducted to minimize vertical cross-contamination. Specifically, the use of hollow-stem auger drilling is of concern to this department. In fill material, auger drilling can create a very unstable bore hole, particularly if debris entangles the equipment. This situation can cause the bore hole to be ripped apart, thereby setting off an uncontrollable collapse of material into the hole. Accordingly, "chop and wash" drilling is the department's preference for all soil borings and monitor wells at the site. However, we will allow the final selection of drilling methodology for the shallow wells (Phase I) to be determined by Diamond Shamrock in conjunction with the NJDEP geologist. During the drilling operations, a NJDEP geologist will be on-site verifying compliance with the Work Plan. We require that a experienced geologist representing Diamond Shamrock be present at each drill site providing strict assurance, in the form of a certification, as to the depth of well/borings and sample locations. If problems are encountered during the drilling operations, the department geologist may find it necessary to stop the operation and subsequently discuss the situation with your on-site personnel, making modifications/adjustments in the drilling methodology as necessary.

Response: The preferred method of drilling remains large-diameter, hollow-stem auger advancement. This method of drilling is

the only one practically available that will allow sampling without the use of drill fluids which provide the potential for cross contamination. The potential for encountering debris that could cause catastrophic collapse of the boring exists for all drilling methods. The additional risk created by the larger diameter of the hollow-stem augers is minimal compared to the potential loss of information and cross contamination that is likely to occur with "chop and wash" techniques.

An experienced geologist will be present with the drill rig at all times. It will be his responsibility to observe, describe, and log each sample. These logs will be reviewed and verified by the project geologist supervising the investigation. An experienced geologist will be present on the site at all times providing confirmation of subsurface conditions in the form of signed boring logs. If so desired by NJDEP, all logs will be approved at the time of drilling by their geologist. Should problems be encountered during drilling, the recommendations of the NJDEP geologist will be considered.

MISCELLANEOUS RECOMMENDATIONS

Question: Item i - All monitor wells should be 4 inches in diameter.

Response: No loss of drilling information, sampling convenience, or available sample quantity are anticipated due to the installation of two-inch-diameter monitor wells. A substantial reduction in the time required for the investigation and improvement in control of the borehole can be realized by the use of these smaller diameter wells. The wells will be gravel packed and slug tests can be performed in the two-inch-diameter well screens. The two-inch wells proposed also have a history of being used at other New Jersey sites. Additionally, the smaller wells will decrease exposure by minimizing volume of materials generated and stored on site during drilling (soils and waters) and purging waters during sampling. Thus, the Work Plan proposed remains. Two-inch-diameter screens and casings will be installed as monitoring wells.

Question: Item ii - All PVC well casings and screens should have threaded joints and should not be glued.

Response: As stated in the Work Plan submitted (Page 3-43), all well casings and screens will have threaded, flush joints and will not be glued.

Question: Item iii - Bentonite pellets should not be used above the gravel pack because of the possible high chloride content of the groundwater.

Response: Bentonite pellets remain the preferred method of sealing wells above the gravel pack. Work performed in the laboratory of Woodward-Clyde Consultants and information from bentontite suppliers shows that sufficient expansion will occur and be maintained to adequately seal the wells at the salinities expected. Should other methods be required (chemical grout, bentontite with additives), chemical interferences may be introduced that could offset or mask actual contamination.

Question: Item iv - All wells must be gravel packed.

Response: All wells will be gravel packed. The material used for the pack will consist of a gravel with particles no longer than 1/4 inch or smaller than .001 inch.

Question: Item v - Neat cement (5.2 gal. water/94 lb. bag) should be used for grouting.

Response: The neat cement mixture recommended for grouting will be very difficult to pump by ordinary means, making introduction at the appropriate location in the well difficult. Neat cement with no admixtures will shrink as it cures, precluding the possibility of an adequate seal between the grout and the side of the well casing and borehole. For these reasons, a cement/bentonite/water mixture is proposed for use. The grout composition, composed by weight, will be 10 parts cement to one-half part bentonite with a maximum of 10 gallons of water per 94-pound bag of cement (U.S. Army Toxic and Hazardous Materials Agency, 1983; not attached). This mixture will reduce the shrinkage problem associated with neat cement without compromising its structural integrity.

Question: Item vi - All shallow wells should be screened across the water table.

Response: All Phase II wells will be screened with the entire saturated thickness of the aquifer and above the water table when possible. Should the piezometric surface of the aquifer extend to within five feet of the ground surface, however, the screen and gravel pack zone will be shortened to allow for the seal and the cement collar at the ground surface.

Question: Item vii - The Work Plan must state the proposed lengths of all well screens.

Response: Based on previous stratigraphic information obtained at the site, the expected lengths of the Phase II well screens will range from five to eight feet. The wells will be screened over the entire saturated thickness and above the water table in the shallow aquifer when possible.

Question: Item viii - All outer protective casing should have vent openings.

Response: All protective casings will be fitted with vent holes, as stated in the Work Plan.

Question: Item ix - The drain hole on the outer protective casing should not be at ground level.

Response: The drain hole will be located approximately 0.5 foot above the surface of the ground in all protective casings.

Question: Item x - The outer casing for double-cased wells should be steel.

Response: The outer casing for double-cased wells should not be steel due to possible corrosion from the low soil pH conditions expected at this site. Metals and annealing/alloying contaminants can be mobilized in this situation, masking or interfering with chemical analyses. For this reason, PVC will be used for the outer casing in all wells. The PVC casing will be encased in grout to reduce exposure to the soil and ground water.

Question: Item xi - All wells must be developed upon completion for a minimum of one hour or to yield a turbid-free discharge.

Response: All wells will be developed for a period of a minimum of one hour or until a turbid-free discharge is obtained. The clarity of the discharge will be determined by the project geologist with consultation from the NJDEP geologist.

Question: Item xii - The two scheduled samplings of the monitor wells should be spaced further apart than one week. Wells should be resampled at three week intervals to evaluate/compare results on both spring and neap phases of the tidal cycle.

Response: The two scheduled samplings of the monitor wells will be separated by three weeks to evaluate/compare results on both spring and neap phases of the tidal cycle.

Question: Item xiii - The Work Plan should clarify what is meant by the collection of composite water samples from the monitor wells. This procedure is normally not acceptable.

Response: No composite water samples are proposed to be taken.

Question: Item xiv - The abandoned on site production well should be sampled for the same parameters as the monitor wells.

Response: The abandoned on-site production well will be sampled for the same parameters and at the same intervals as the monitor wells.

Question: Item xv - Attached to this letter are specifications for a) unconsolidated, b) rock and c) confined unconsolidated wells for your use and information.

Response: The unconsolidated, rock, and confined unconsolidated monitor well specifications have been received and considered in the development of the Work Plan.

Question: Item xvi - PVC boilers must not be used. Teflon or stainless steel only, dedicated, laboratory cleaned prior to sampling.

Response: Laboratory-cleaned PVC bailers will be dedicated for use in each well. The contact time with the water to be sampled will be minimal and no interference with analyses is anticipated. Analyses of water samples will be evaluated prior to completion of sampling.

Question: Item 3-58 -

1. A longitudinal transect on the southern bank of the river should be employed to approximate downstream nearshore migration of contaminaton (See Attachment 1). The stations on the transect shall be located at a fixed distance from the southern bank or break water.

2. Seven cross section transects should be employed to approximate longitudinal and crosssectional distribution of contaminants in upstream and down stream segments of the riverbed. Where crossectional transects and the longitudinal transect intersect only one sample will be collected. This sample will be representative of both transects.

Response: Analyses of the Passaic River sediments by the NJDEP and/or the USEPA have confirmed the presence of TCDD in the Passaic River in the vicinity of the project site. Based on these data, a river sediment sampling program has been developed to further assess off-site migration of TCDD, the extent of TCDD contamination in the Passaic River, and the presence of priority pollutants in the Passaic River sediments.

Thirty-five river sediment samples have been obtained and analyzed for TCDD by the NJDEP and/or the USEPA. Fifteen of these 35 samples were collected from five transects across the Passaic River. Based on a review of the analytical results from these samples, a supplementary sampling program has been developed (see Figure D-5, Appendix D). Sediment samples will be collected from a 4,800-foot stretch along the south bank of the Passaic River and from three additional transects near the site. Transects will be located at the west edge of the project site, 300 feet up river of the site, and 100 feet down river of the east edge of the site. The locations of these three transects should complement the data obtained from samples obtained from the five transects sampled by the NJDEP and/or the USEPA. Samples will be obtained from three locations along each of the three proposed transects. These locations are the north bank, center, and south bank of the Passaic River. Discrete samples from zero to 12 inches and 12 to 24 inches will be obtained from each of these sample locations.

Samples will also be collected along the south bank of the Passaic River at 200-foot increments for a distance of 1,200 feet, both up and down river, from the center of the project site. Additional samples will be collected at 400-foot intervals at a distance of 1,200 to 2,400 feet up and down river from the center of the site.

Each of the 27 sample locations described above will serve as a collection point for a sediment sample from zero to 12 inches in depth. At an additional 13 locations, sediment samples will be obtained from a depth of 12 to 24 inches. Seven of these deeper samples will be obtained from the south bank of the Passaic River, three will be obtained from the center of the Passaic River, and three will be obtained from the north bank of the Passaic River. Sediment samples obtained from locations previously sampled by the NJDEP and/or USEPA along the south bank of the Passaic River may be held for future analyses.

A total of 36 additional sediment samples will be obtained from the Passaic River and analyzed for TCDD during this supplementary sampling program. The analytical results from these 36 samples will be used with the results from the 35 samples previously collected by the NJDEP and/or USEPA (for a total of 71 samples) to evaluate the extent and migration of TCDD in the vicinity of the 80 Lister Avenue site and should provide a statistical assessment of TCDD contamination having an 80 percent confidence interval.

To provide information describing the presence of priority pollutants in Passaic River sediments, 15 of the 36 additional sediment samples will be submitted for analysis of the 129 priority pollutants plus 40 other identified constituents. The locations of these samples, shown in Figure D-5, have been selected based on knowledge of prior operations at the 80 Lister Avenue site and the nature of the Passaic River.

A biased sampling approach was selected to perform this assessment. Such an approach is expected to better assess the presence and levels of priority pollutants in Passaic River sediments as compared to random or systematic approaches. If the analytical results from these initial 15 sediment samples indicate the need to further characterize priority pollutants in the river sediments, a phased, supplemental sampling program will be developed based on the analytical results of the initial program, identified constituents of concern, and a statistical assessment of these data to the extent DSCC and NJDEP mutually agree on the need for assessment and expansion of the Passaic data based on DSCC's impact through 80 Lister Avenue operations.

APPENDIX A

APPENDIX A

HEALTH AND SAFETY PROTOCOL EXPANSION

APPENDIX A

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APPENDIX A

HEALTH AND SAFETY PROTOCOL EXPANSION

A.1 COMMUNITY PUBLIC HEALTH PRESERVATION

The health concerns for the community are of utmost concern. Precautions undertaken to prevent any contamination from leaving the site include:

- All equipment (mobile and portable) will be decontaminated before leaving the site contamination zone. See the following Sampling Equipment Decontamination Plan.
- Suspended solids in surface runoff will be prevented from migrating off site by the installation of a perimeter barrier. A silt fence (18 to 24 inches high) will be installed around the perimeter of the site wherever migration due to storm water or site work may occur. The entire north fence adjacent to the Passaic shall be so treated.
- Ambient air monitoring will be done. (Note: the Air Monitoring Plan will be attached when all changes per the prior comment text have been accepted.)
- A back-flow preventer (with air gap) will be installed on the water line in the mobile facilities to prevent any cross connection and subsequent contamination of the community's water line (i.e., decon trailer, decon wash station, etc.).
- Dust suppression techniques will be used at drilling operations to keep dust levels at a minimum. A Hudson Sprayer, filled with water, will be utilized to wet the ground before drilling and on an intermittent basis during the drilling activities.
- Once drilling is complete, the contaminated material (pavement, concrete, soil, rocks, etc.) will be sprayed with a water mist (utilizing the Hudson Sprayer) and the material loaded into a properly labeled 55-gallon salvage drum. The drum will be sealed when loading is complete. The area of drilling will be returned to stabilization, that is, recover the drilling area with the fabric membrane that was moved in order to drill.

- All drilling and sampling well bailed waters will be accumulated in 55-gallon drums and stored on site. Disposal will be addressed in the remedial plan.

In the unlikely event that there is an emergency which could affect the health of the community, the following agencies will be notified, as appropriate:

Police Department, Newark East District, Lt. Peake Newark, New Jersey	201-733-6007 or 201-773-6190
Fire Department, Newark Fifth Battalion Newark, New Jersey	201-733-7400
Sgt. John Ouweleen Office of Emergency Management State Highway Department Apt. 3B, 17 Riverview Drive Newark, New Jersey	201-465-8076 or 201-465-0891 or 201-465-0991 or 201-465-0995
New Jersey Department of Environmental Protection (NJDEP) CN402 Trenton, New Jersey	609-292-2885
U.S. Coast Guard	800-424-8802
Emergency Response Numbers NJDEP USEPA	 609-292-7172 201-548-8730

IT CORPORATION

June 15, 1984

TO: Mr. H. A. Pullum

FROM: Dr. T. C. Marshall TCM

SUBJECT: PERMISSIBLE EXPOSURE LIMIT TO CHLORINATED DIBENZO-P-DIOXIN AND DIBENZOFURAN DURING CLEANUP OPERATIONS

COPIES TO: J. Exner, D. R. Smith

INTRODUCTION

IT Corporation is committed to maintaining high standards of safety in the workplace for its employees. This is evidenced by IT's extensive safety and health training programs, the number of technical professionals in the IT Health and Safety Division, and the application of state-of-the-art safety technology during projects involving hazardous materials.

The setting of exposure criteria for internal use when no governmental regulatory standard exists is an important component of the safety and health program. This document discusses the rationale for establishing a proposed dioxin/dibenzofuran atmospheric exposure limit of 0.5 ng/m^3 in the workplace during cleanup operations. This is a guideline and is subject to change depending upon health and safety considerations on each individual cleanup project. Furthermore, the exposure limit is subject to refinement as new information on dioxin and the related dibenzofurans becomes available.

The term "dioxin" is widely used for the chemical family of 75 chlorinated dibenzo-p-dioxins, and quite often the term is meant to imply a single compound, 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). TCDD is the most toxic of this class of compounds, is a known animal carcinogen, and is the one with the most exisitng toxicological data. The chlorinated dibenzofurans are a very closely related group of chemicals as they differ by only one oxygen from their respective dioxin analogs. Much less is known about the toxicity of the dibenzofurans, but the information that is available indicates they may be about ten times less toxic than the dioxins. The 2,3,7,8-tetrachloro isomer (TCDF) is the most toxic of the dibenzofuran series. For these reasons, the dioxin/dibenzofuran exposure limit refers to TCDD equivalent exposures, and was determined using TCDD toxicity data.

Before discussing the rationale behind the PEL, it is important to clarify the manner in which IT Corporation uses the PEL. As stated in the health and safety plan, the PEL will be used only for downgrading respiratory protection from air-supplied respirators to air purifying, which absorb hydrocarbon vapors and filter 99.9% of airborne particulates. This is in keeping with the IT philosophy of always limiting occupational exposure to the greatest reasonable extent. This philosophy is based on the recognition that the interpretation of toxicology data and its extrapolation to man is a subjective process. Seldom do scientists agree on how a set of data should be used to establish an exposure limit. This is especially true with highly toxic materials, such as dioxin, that are also known to be carcinogens. The guideline of 0.5 ng dioxin/m^3 air for short data become available. In any event, IT employees and subcontractors will not be exposed to this level, but only be allowed to downgrade on the type of respiratory protection used.

RATIONALE

Four long-term graded-dose rodent studies conducted with TCDD are reported in the literature, all demonstrating carcinogenicity. Two were conducted in rats, the first being a two-year carcinogenicity study (Kociba et al., 1978), and the second being a three-generation reprodcution study (Murray et al., 1979). The National Toxicology Program (NTP) conducted two studies in mice, one by oral dosing, the other by dermal exposure (NTP 1982a, 1982b).

At least two federal agency documents discussing various estimates of risk to lifetime dioxin exposure have been prepared using the data cited above. These were prepared and are being reviewed to aid regulatory decision makers in establishing standards for acceptable levels of dioxin exposure for the general population. Obviously, this includes subpopulations, such as children and the elderly, which are usually recognized as more sensitive to toxic insults. The analyses result in dose ranges for a given cancer risk which cover more than two orders of magnitude, illustrating the imprecision associated with health risk assessments.

The Center for Disease Control (CDC; 1982) estimated that a daily intake of 0.002 to 0.1 ng TCDD/day for a 70 kg man was associated with a 10^{-6} cancer risk factor (that is, one excess cancer per one million population after a lifetime of exposure). This range represents the 95% confidence interval using the linear de-ived multistage model. The Environmental Protection Agency (EPA; 1983), using several different risk assessment models, produced a dose range for lifetime daily human TCDD intake of 0.02 to 0.6 ng/day to be associated with a 10^{-6} cancer risk factor.

Taking a value in the middle of this range of estimates yields lifetime daily intake levels of 0.05 ng TCDD/day for a 10^{-6} cancer risk and 0.5 ng/day for a 10^{-5} risk factor. A 10^{-5} risk is an appropriate level of consideration for the workplace, since the work force, on the whole, is more healthy than the general population, is not comprised of the very young or quite elderly age group, and is only subject to exposure for a fraction of the time relative to the general population should there be environmental contamination. For these reasons, regulatory agencies are leaning toward higher acceptable risk factors for occupational exposure.

The IT occupational exposure limit of 0.5 ng TCDD/m^3 converts to a daily human exposure of 5 ng, assuming a 10 m^3 breathing volume in an 8-hour workday. Assuming a respiratory tract deposition fraction of 75%, the TCDD dose would be 0.05 ng/kg/day for a 70 kg person. This is tenfold higher than the amount associated with a 10^{-5} cancer risk factor. However, the CDC and EPA risk estimates were conducted assuming lifetime exposure. Dioxin/dibenzofuran cleanup efforts are not a continuous daily activity. They are temporary assignments which are carefully planned to minimize personnel time in the contaminated area. The actual time spent in a contaminated area may be measured in hours, weeks, or at most several months, but certainly not in years that add up to a significant portion of a person's life span. Even if the same individuals are employed in the long term for dioxin/dibenzofuran cleanup, the occurence of these assignments to date are infrequent enough so that there are sufficient amounts of time between jobs to allow for significant decreases in any body burdens of these materials. Animal studies suggest that the TCDD elimination half-life is about 31 days (Rose et al., 1976).

Setting exposure limits for relatively short periods of exposure to suspected carcinogens is difficult because the cancer risk factors are derived from life span studies on animals. Application of such studies to the assessment of short-term human exposures may be entirely inappropriate, especially if the chemical, such as dioxin, is thought to act primarily as a promoter.

As with any suspected carcinogen, exposure of employees should be limited to the fullest extent reasonable regardless of the PEL. Furthermore, this PEL is proposed as a guideline for short-term dioxin/dibenzofuran cleanup operations. Its applicability to a specific project should be evaluated on a case-by-case basis. Under no circumstances should an employee be exposed to this PEL for more than 12 weeks over a 52 week period. If dioxin cleanup operations should become an on-going or much more frequent activity, this would be reason to consider lowering the permissble exposure limit. Similarly, a lower dioxin limit may be appropriate where multiple chemical exposures are probable, especially if liver toxicants having long residence times in the body are involved.

D143CDC-1

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D143 CDC-REF

A.3 DECONTAMINATION AREA PROTOCOLS

A. Personnel Decontamination Layout (Station Index Numbers)

B. Decon Area Diagram

C. Personnel Decontamination Sequence (Step by Step)

D. Sampling Equipment Decontamination

E. Protective Clothing for Decontamination Workers

F. Potential for Modification

A. PERSONNEL DECONTAMINATION LAYOUT
(STATION INDEX NUMBERS)

(Note: Heavily contaminated workers should be helped by decon assistant)

EXCLUSION ZONE

Station 1 Segregated Equipment Drop (to table or decon pad)

----X----X----Hotline Perimeter Boundary----X----X----X----X----X----

Station 2 Total wash (submersible pump/drums)

Station 3 Total Rinse (submersible pump/drums)

Station 4 Tape Removal (face, wrist, ankle, etc.)

Station 5 Outer Glove Removal (into bucket)

Station 6 Suit/Boot Removal (disposal of Tyvek into bucket)

Station 7 Tyvek Bootie Donning

Station 8 Respirator Removal (into bucket)

Station 9 Inner Glove Removal (in bucket for disposal)

Station 10 Inner White Tyvek Removal and Bootie Removal (in bucket for disposal)

Station 11 Shower

Station 12 Locker Room

Out

DAPPOLONIA
WASTE MANAGEMENT SERVICES

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Fig. A-1

C. PERSONNEL DECONTAMINATION SEQUENCE (STEP BY STEP)

Station 1: Segregated Equipment Drop

Task: Deposit all equipment used on site onto/into poly sheeting or poly lined containers. Place on table or pass to decon line personnel.

Equipment:
1. Various sized containers
2. Poly drum liners (4 to 6 mil)
3. Poly sheeting

Station 2: Total Outer Protective Clothing Wash

Task: Scrub suits, boots, and gloves thoroughly with solution and soft bristle scrub brushes.

Equipment:
1. Wash tubs
2. Decon solution or detergent/water (example: trisodium phosphate)
3. Hudson Sprayers
4. Garden hose and pressure reducing nozzles (minimize overspray contamination)
5. Long handled soft bristle scrub brushes
6. Submersible pump
7. Recovery drums (17C)

Station 3: Total Outer Protective Clothing Rinse

Task: Total rinse with large amounts of water. Repeat as necessary.

Equipment:
1. Wash tubs
2. Rinse water (garden hose and pressure reducing nozzles)
3. Hudson Sprayers
4. Submersible pump
5. Recovery drums (17C)

Station 4: Tape Removal

Task: Remove tape around boots, gloves, and face pieces and deposit in plastic-lined bucket.

Equipment:
1. Buckets
2. Poly drum liners (4 to 6 mil)

Station 5: Outer Glove Removal

Task: Remove outer gloves and deposit in container with plastic liner.

Equipment:
1. Buckets
2. Poly drum liners (4 to 6 mil)

Station 6: Suit/Boot Removal and/or Disposal (Tyvek)

Task: Remove suit inside out and deposit into a plastic-lined container. Remove pants and boots as one. Place in separate containers. Use bootjack to aid in boot removal. Keep liner white tyvek on.

Equipment:
1. Buckets
2. Small aluminum ladders (seats)
3. Poly drum liners (4 to 6 mil)
4. Bootjack

Station 7: Tyvek Bootie Donning

Task: Put on white Tyvek booties over socks.

Equipment:
1. Same aluminum ladder as in 6
2. Supply of Tyvek booties

Station 8: Respirator Removal

Task: Remove respirator and place in a plastic-lined container.

Equipment:
1. Buckets
2. Poly drum liners (4 to 6 mil)

Station 9: Inner Glove Removal

Task: Remove inner gloves (inside out) and dispose of in a plastic-lined container.

Equipment:
1. Buckets
2. Poly drum liners (4 to 6 mil)

Station 10: Inner White Tyvek Removal and Tyvek Bootie Removal

Task: Removal of Tyvek suit (inside out) and disposable booties.

Equipment:
1. Buckets
2. Poly drum liners (4 to 6 mil)

Station 11: Shower in Decon Trailer

Task: Thoroughly shower with soap.

Equipment:
1. Soap
2. Disposable and washable towels
3. Buckets
4. Poly drum liners (4 to 6 mil)

Station 12: Locker Room

Task: Don street clothes.

--Bagged disposal material will be trash compacted, drummed, and remain on site.

--Bagged reusable equipment will be taken to the decon pad where it will be washed, rinsed and hung on metal clothes hangers to drip-dry.

--Boots and gloves shall be washed, rinsed, the insides sprayed with disinfectant and hung on drying prong racks to drip-dry.

--After all protective equipment has been decontaminated, it will be brought to the drying building. Boots and gloves will be transferred to the drying racks within and the suits hung on poles.

--Cleaned respirators will be laid out neatly on the screen shelving to dry.

--During breaks all protective equipment other than outer/inner suits and boots will be removed. Suits will be unzipped to aid the cooling process.

D. SAMPLING EQUIPMENT DECONTAMINATION

1. Decontamination Pad

A specially constructed decontamination pad will function as a washdown area for all sampling equipment and vehicles used in the contaminated area. A diagram of the pad is shown in Figure 2. The location and overall arrangement of the pad is shown in the layout of the decon area (Figure 1).

The pad consists of interlocking steel pans with 3-inch by 12-inch wooden planks supported by 6-inch by 6-inch wooden cross members for vehicular load-bearing areas. The equipment/vehicles will be placed (driven) onto the planks and the wash/rinse procedures outlined in D.2 and D.3 shall be followed. All waters drain via a header to a collection basin.

The upper sections of the decontamination pad will be enclosed with a visqueen shield to control the spray from the pressure washer and hoses.

The contaminated wash material collected in the basin will be pumped to the temporary storage tanks, or the certified, pretested existing on-site tanks. The equipment/vehicles will be held for a short period of time to allow for the drippings to be retained in the collection basin. Equipment will then be placed on a poly-covered area on the decon pad to air dry.

2. Small Sampling Equipment Decontamination

a. Small equipment associated with sampling (split tube samplers, trowels, shovels, picks, chisels, hammers, other specific samplers, etc.) which are to be decontaminated prior to reuse or exit from the work site, will be bagged in plastic prior to crossing the hot line.

b. Equipment will be carried in plastic bags down the polyethylene corridor which is part of the

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Fig A-2

personnel decon shown in Figure 1, or straight to the decon pad.

c. At the decon pad this equipment will first be washed in a tub containing a phosphate-free soap (Bola® Phosphate Free Soap). A brush will be used to remove heavy contamination.

d. Equipment will then go to a freshwater rinse by submersion.

e. Equipment will then be sprayed (in a tub or container) with either spectrographic or pesticide grade methanol as a solvent rinse.

f. The final equipment rinse will be with distilled water. This will be done in the same manner as the methanol rinse.

g. Equipment will then be taken to a poly-covered area in the decon pad to air dry.

3. Large Sampling Equipment Decontamination

a. Large sampling equipment such as drill rigs, hollow-stem augers, etc., shall be driven or carted form the hot zone to the decon pad.

b. Equipment will first be washed with hot water pressure spray.

c. Equipment will then be scrubbed down with soapy water using brushes and a phosphate-free soap (Bola® Phosphate Free Soap).

d. Equipment will then be rinsed, by hose, with water.

e. Equipment will then be taken to the poly-covered area of the decon pad to air dry.

E. PROTECTIVE CLOTHING FOR DECONTAMINATION WORKERS

1. Decon Assistants (Aid Heavily Contaminated Workers)

   a. Two-piece medium weight PVC suits.

   b. Viton or equivalent gloves.

   c. PVC (polyvinyl chloride) boots (steel toe, steel shank).

   d. Full-face, air-purifying respirator with OV cartridges and dust/mist prefilters.

   e. Tearaways.

   f. Proper taping of gloves, chest coat closure and around face piece.

2. Suit, Boot, Glove Washer Personnel

   a. Two-piece, medium weight PVC suits.

   b. Viton or equivalent gloves (inner gloves).

   c. PVC (polyvinyl chloride) boots (steel toe, steel shank).

   d. Safety chemical goggles.

   e. Splash face shield (minimum 8 inches).

   f. Proper taping around gloves and chest coat closure.

   g. Half-face, air-purifying respirator with OV cartridges and dust/mist filters.

3. Decontaminating Large Equipment Such as Drill Rigs, Etc.

   a. Two-piece, medium weight PVC suits.

   b. Viton or equivalent gloves (inner gloves).

   c. PVC gloves (outer gloves).

d. PVC (polyvinyl chloride) boots (steel toe, steel shank).

e. Airline respirators (full face) supplied with Grade D breathing air.

f. Tearaways.

g. Proper taping of gloves, chest, coat closure, and around face piece.

4. Decontaminating Sampling Equipment such as Trowels, Shovels, Picks Chisels, Split-Tube Samplers, Etc. Protective Clothing will be the Same as in E.3

F. POTENTIAL FOR MODIFICATION

It must be understood that the decontamination system be flexible. Changes occur on site which can easily be overlooked during planning stages. Always be prepared to alter (add or delete a step or process) the decontamination sequence or equipment. Extra decon equipment (spares) as well as a local supplier need to be readily available for items such as brushes, rags, soap, buckets, hoses, etc.

The main thing to remember concerning modification of the decon sequence is to thoroughly and safely decontaminate regardless of the changes. Actions must be taken to minimize the contamination in the contamination reduction zone and eliminate any contamination in the clean zone and off-site areas. At all times, minimize contact between potentially contaminated material and clean material (e.g., do not touch yourself without thoroughly washing at the break area).

A.4 MATERIAL SAFETY DATA SHEETS AND TOXICOLOGICAL DATA

Material

- Dioxin (2,3,7,8-TCDD)
- 2,4,5-Trichlorophenol
- 2,4,5-T
- 2,4-D
- Sulfuric Acid
- DDT
- Hexachlorobenzene
- Asbestos

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

Form Approved
OMB No. 44-R138

MATERIAL SAFETY DATA SHEET

Required under USDL Safety and Health Regulations for Ship Repairing, Shipbuilding, and Shipbreaking (29 CFR 1915, 1916, 1917)

SECTION I

MANUFACTURER'S NAME: N/A	EMERGENCY TELEPHONE NO.: N/A
ADDRESS (Number, Street, City, State, and ZIP Code): N/A	
CHEMICAL NAME AND SYNONYMS: Dioxin, 2,3,7,8 tetrachlor-dibenzo-p-dioxin	TRADE NAME AND SYNONYMS: 2,3,7,8-TCDD, TCDD, TCDBD
CHEMICAL FAMILY: Chlorinated hydrocarbon	FORMULA: $C_{12} H_4 Cl_4 O_2$

SECTION II - HAZARDOUS INGREDIENTS

PAINTS, PRESERVATIVES, & SOLVENTS	%	TLV (Units)	ALLOYS AND METALLIC COATINGS	%	TLV (Units)
PIGMENTS			BASE METAL		
CATALYST			ALLOYS		
VEHICLE N/A			METALLIC COATINGS N/A		
SOLVENTS			FILLER METAL PLUS COATING OR CORE FLUX		
ADDITIVES			OTHERS		
OTHERS					

HAZARDOUS MIXTURES OF OTHER LIQUIDS, SOLIDS, OR GASES	%	TLV (Units)
An impurity in herbicide 2,4,5-T		
CAS Number 1746-01-6		
RTECS HP 3500000		

SECTION III - PHYSICAL DATA

BOILING POINT (°F) @ 1ATM >1292F	Decomposes	SPECIFIC GRAVITY (H_2O=1)	N/A
VAPOR PRESSURE (mm Hg) @ 77°F	$1.7X10^{-6}$mHg	PERCENT, VOLATILE BY VOLUME (%)	Unknown
VAPOR DENSITY (AIR=1)		EVAPORATION RATE (_____=1)	Unknown
SOLUBILITY IN WATER G/100 G water at 20°C 200ppm		Melting point	581°F
APPEARANCE AND ODOR Colorless, crystalline solid, Decomposes when exposed to UV			

SECTION IV - FIRE AND EXPLOSION HAZARD DATA

FLASH POINT (Method used) N/A	FLAMMABLE LIMITS	LEL N/A	UEL N/A

EXTINGUISHING MEDIA: Use alcohol foam, CO_2, dry chemical, or water fog on surrounding areas

SPECIAL FIRE FIGHTING PROCEDURES: Wear SCBA and full protective clothing

UNUSUAL FIRE AND EXPLOSION HAZARDS: N/A

N/A

DIA 002

THRESHOLD LIMIT VALUE
None established; LD50 IDLH (oral) 2250 NG/KG RAT IT CORP PEL = 0.5 ng/m3

EFFECTS OF OVEREXPOSURE
Chloracne, kidney/liver damage, skin/eye irritation, fatique, cough
CNS depression, cancer (lab animals)

EMERGENCY AND FIRST AID PROCEDURES
Wash eyes 15 minutes with copious amounts of water and skin with water and soap. After exposure by inhalation remove to fresh air immediately. Upon ingestion seek medical attention immediately. Seek medical attention after any exposure

SECTION VI - REACTIVITY DATA

STABILITY	UNSTABLE		CONDITIONS TO AVOID N/A
	STABLE	X	

INCOMPATABILITY (Materials to avoid)
Unknown

HAZARDOUS DECOMPOSITION PRODUCTS
None

HAZARDOUS POLYMERIZATION	MAY OCCUR		CONDITIONS TO AVOID
	WILL NOT OCCUR	X	

SECTION VII - SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN IN CASE MATERIAL IS RELEASED OR SPILLED
Contain drums, liquid material and keep from spreading poisonous solid N.O.S. or Poison B, Solid, N.O.S.

Reportable Quantities 2 lb

WASTE DISPOSAL METHOD
UN 2811

SECTION VIII - SPECIAL PROTECTION INFORMATION

RESPIRATORY PROTECTION (Specify type)
Fullface air purifying respirator with organic vapor cartridges with dust, fume, mist prefilte

VENTILATION	LOCAL EXHAUST Use whenever possible	*	SPECIAL Supplied air or SCBA
	MECHANICAL (General)		OTHER

PROTECTIVE GLOVES Viton gloves with PVC or Neoprene (OG) Outer Glove	EYE PROTECTION faceshield, goggles or FF Respirator

OTHER PROTECTIVE EQUIPMENT
PVC suits/poly Tyvek depending on the situation; PVC or Neoprene boots with disposable shoe coverlets. Taping necessary

SECTION IX - SPECIAL PRECAUTIONS

PRECAUTIONS TO BE TAKEN IN HANDLING AND STORING
Eyewash and shower in vicinity. Eating, smoking, drinking, etc prohibitied in the work area. Minimize contact at all times

OTHER PRECAUTIONS
Material is very persistent in the environment. Highly toxic. Carcinogen, mutagen, teratogen in animals

*with higher concentrations or greater potential per exposure

Send to Barry and Tim?

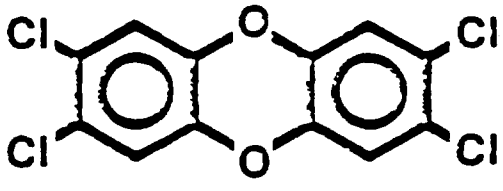
DB

NIOSH

Current Intelligence Bulletin 40

January 23, 1984

2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD, "dioxin")



U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control
National Institute for Occupational Safety and Health

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DHHS (NIOSH) Publication No. 84-104

FOREWORD

Current Intelligence Bulletins are reports issued by the National Institute for Occupational Safety and Health (NIOSH), Centers for Disease Control, Atlanta, Georgia, for the purpose of disseminating new scientific information about occupational hazards. A Current Intelligence Bulletin may draw attention to a hazard previously unrecognized or may report new data suggesting that a known hazard is either more or less dangerous than was previously thought.

Current Intelligence Bulletins are prepared by the staff of the Division of Standards Development and Technology Transfer, NIOSH, (Robert A. Taft Laboratories, 4676 Columbia Parkway, Cincinnati, Ohio, 45226) and are distributed to representatives of organized labor, industry, public health agencies, academic institutions, and public interest groups as well as to those federal agencies, such as the Department of Labor, which have responsibilities for protecting the health of workers. It is our intention that anyone with the need to know should have ready access to the information contained in these documents; we welcome suggestions concerning their content, style, and distribution.

Because of the recent attention given to human exposure to 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD, "dioxin") contaminated materials and published reports on the toxicity of TCDD, NIOSH staff consider it necessary to present a review of the pertinent data and a summary of findings related to the human hazard potential of TCDD. Because of the compression in this bulletin of the voluminous literature on TCDD, it is suggested that readers wanting to know more of the details of the reported studies consult the appended references.

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Centers for Disease Control

CURRENT INTELLIGENCE BULLETIN #40

2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD, "DIOXIN")

January 23, 1984

ABSTRACT

In animals, 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD, "dioxin") causes various systemic effects at a wide range of exposure concentrations, including tumorigenesis, immunological dysfunction, and teratogenesis. Studies of humans exposed to TCDD-contaminated materials suggest that TCDD is the cause of observed chloracne, metabolic disorders (porphyria), and other systemic problems and are suggestive of TCDD's ability to cause cancer.

TCDD occurs as a contaminant of materials such as 2,4,5-trichlorophenol (TCP), 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), and 2-(2,4,5-trichlorophenoxy)propionic acid (silvex). Occupational exposure may occur through contact with these materials during use or from the past contamination of worksites.

The National Institute for Occupational Safety and Health (NIOSH) recommends that TCDD be regarded as a potential occupational carcinogen, that occupational exposure to TCDD be controlled to the fullest extent feasible, and that decontamination measures be used for TCDD-contaminated work environments. This recommendation is based on a number of reliable studies demonstrating TCDD carcinogenicity in rats and mice.

BACKGROUND

Physical and Chemical Properties of 2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)

TCDD is one of a family of isomers known chemically as dibenzo-p-dioxins. The chemical and physical properties are summarized in Table I. TCDD is a colorless crystalline solid at room temperature. It is sparingly soluble in most organic solvents and essentially insoluble in water. TCDD is stable to heat, acids, and alkali and will decompose when exposed to ultraviolet light, including sunlight [1].

TABLE I

CHEMICAL AND PHYSICAL PROPERTIES OF TCDD [2,3]

CAS Registry No.:	1746-01-6	
Empirical formula		$C_{12}H_4Cl_4O_2$
Percent by weight	C	44.7
	O	9.95
	H	1.25
	Cl	44.1
Molecular weight		322
Vapor Pressure mm Hg at 25°C		1.7×10^{-6}
Melting point, °C		305
Decomposition temperature, °C		>700
Solubilities, g/liter		
o-Dichlorobenzene		1.4
Chlorobenzene		0.72
Benzene		0.57
Chloroform		0.37
n-Octanol		0.05
Methanol		0.01
Acetone		0.11
Water		2×10^{-7}

Formation and Use of TCDD

TCDD forms as a stable by-product or contaminant during the production of TCP. Run-away reactions at high temperature, in which excess TCDD was produced, have occurred at TCP production sites in the United States and elsewhere [4]. Normally, TCDD persists as a contaminant in TCP in relatively small, variable amounts (0.07-6.2 mg/kg) [5]. TCP has been utilized primarily as a feedstock for production of the phenoxy herbicides 2,4,5-T and silvex, resulting in the contamination of these products with TCDD. Production of 2,4,5-T and silvex ceased in the United States in 1979. However, stockpiles of both products are still being distributed and

used. TCP also is used in the production of hexachlorophene, a bactericide and fungicide.

The combustion of 2,4,5-T can result in its conversion to small amounts (0.6 ppt TCDD/1 ppm 2,4,5-T burned) of TCDD. Also, the burning or heating of commercial and purified chlorophenates and pyrolysis of polychlorinated biphenyls (PCBs) contaminated with trichlorobenzenes have resulted in the production of TCDD [6,7]. The formation of TCDD from trace chemical reactions in fires has been postulated but has not been verified [8,9].

Existing Regulations and Guides

No occupational exposure standard exists for TCDD. The United States Environmental Protection Agency (U.S. EPA) temporarily suspended or banned most uses of 2,4,5-T and silvex in 1979, although their use was allowed on sugarcane, orchards and for miscellaneous non-crop uses [10]. On October 18, 1983 EPA published its intent to cancel registration of pesticide products containing 2,4,5-T and silvex and to prohibit the transfer, distribution, sale or importation of any unregistered pesticide product containing 2,4,5-T or silvex or their derivatives [11].

Nature of Occupational Exposure to TCDD

It is not possible to estimate accurately the number of U.S. workers currently at risk of exposure to TCDD. Occupational exposure to TCDD may occur during production of TCP; in decontamination of worksites from prior production or use of TCP, 2,4,5-T, or silvex; from waste materials (such as reclaimed oil) contaminated with TCDD; or from cleanup after fires in transformers containing polychlorinated aromatics.

Dust or soil particles contaminated with TCDD can remain airborne or accumulate on indoor or outdoor work surfaces and may present a potential exposure hazard. Exposure to TCDD as a vapor will normally be negligible because of its low vapor pressure. Contact with TCDD-contaminated liquids is possible through the handling of drums or tanks containing the liquid or through dispersion of the liquid.

TOXICITY

Results of Studies of TCDD in Animals

Acute and Chronic Toxicity

There is wide variation in the dosage of TCDD required to cause death among animal species (oral LD_{50} 0.6-5,000 ug TCDD/kg body weight (bw)) [12,13]. Progressive weight loss with death several weeks later is reported to characterize the response in experimental animals after administration of a lethal dosage of TCDD [12,14,15]. Animals given single or repeated oral dosages of TCDD of 0.1 to 25 ug/kg bw demonstrated increased liver weights and lipid accumulation, thymic atrophy, and histopathological changes in liver and thymus [12,16-18].

TCDD is reported to be at least three times more potent than any other known compound in stimulating production of aminolevulinic acid synthetase (ALA), the rate-limiting enzyme in porphyrin and heme synthesis [19,20]. Varied effects on hematological functions have been reported in rats and mice dosed with TCDD: increased numbers of erythrocytes and leucocytes, increased hemoglobin concentration, decreased blood platelets in rats [21,22], and decreased hemoglobin concentration in mice [23].

Effects on Reproductive Function

TCDD administered at dosages of 0.125-3.0 ug TCDD/g bw to mice and rats induced fetotoxicity that included cleft palates and kidney anomalies [24-26], intestinal hemorrhages and excessive tissue/organ fluid (edema), and prenatal mortality [27,28].

Impairment of reproduction has been reported for rats ingesting 0.01 ug TCDD/kg bw/day. Significant decreased fertility, litter size, number of pups alive at birth, postnatal survival, and postnatal body weight of pups were evident in two successive generations delivered from male and female rats that ingested TCDD 90 days prior to first mating, during pregnancies, and for the durations of time between pregnancies [29]. No significant dose-related reproductive effects were observed in male mice treated with up to 2.4 ug TCDD/kg bw/day and mated with untreated female mice [30,31].

Immunological Effects

TCDD induced immunological function alterations, expressed by decreased thymus-to-body weight ratios, in nursing newborn rats exposed through dosing of the lactating mother [32]. Other reports have shown that pre- and post-natal maternal dosing of rats and mice with TCDD caused thymic atrophy

and suppression of cellular immunity in the offspring [33]. TCDD administered intraperitoneally or orally to mice induced a strong immunosuppressive effect on antibody production and cell-acquired immune responses [34].

Mutagenic Effects

Results of mutagenicity tests are inconclusive. In two studies TCDD was mutagenic in Salmonella typhimurium TA 1532 without activation [35,36]. In another study, which used a more sensitive mutant strain, Salmonella typhimurium TA 1537, TCDD was not a mutagen [37]. There is weak evidence of chromosomal aberrations in bone marrow of rats given dosages of 0.25 to 4 ug TCDD/kg bw [38,39].

Carcinogenic Effects

Male rats fed dosages of 0.001 ug TCDD/kg bw/week for 78 weeks and sacrificed at week 95 of the study showed a variety of neoplastic tumors (ear duct carcinoma; lymphocytic leukemia; kidney adenocarcinoma; malignant peritoneal histiocytoma; skin angiosarcoma; hard palate, tongue and nasal turbinate carcinoma) [40]. Female rats that had ingested TCDD for two years at a dosage of 0.1 ug/kg bw/day developed carcinomas of the liver and squamous cell carcinomas of the lung, hard palate, nasal turbinates, or tongue [41]. Male and female rats orally dosed with 0.5 ug TCDD/kg bw/week for two years demonstrated neoplastic nodules of the liver and thyroid adenomas [42].

Male mice fed dosages of TCDD of 0.05 or 0.5 ug/kg/week for two years developed liver cancer; female mice fed 0.2 or 2.0 ug/kg/week for the same duration developed liver cancer and thyroid follicular cell adenomas [42]. TCDD applied to the skin of female mice for two years (0.005 ug/kg bw/application; 3 days/week) resulted in a significantly higher incidence ($p=0.007$) of skin cancers (fibrosarcomas) when compared to untreated controls. An increase in the same tumor type, although not statistically significant ($p=0.084$), was also observed in the male mice that received a maximum dosage of 0.001 ug TCDD per application [43].

Human Health Effects

The only information on the health effects in humans from exposure to TCDD is from clinical or epidemiological studies of populations who were occupationally and non-occupationally exposed to 2,4,5-T and TCP contaminated with TCDD. Because of the coincidental exposure to 2,4,5-T and TCP and to other herbicides as well as to TCDD, it is not possible to

attribute the observed health effects solely to TCDD exposure. To date, no studies of humans include a quantitation of exposure to TCDD.

Chloracne and Other Systemic Effects

Chloracne is a chronic and sometimes disfiguring skin eruption caused by exposure to halogenated aromatic compounds including TCDD. Chloracne is possibly a result of systemic effects of these compounds, although it also may occur as a contact dermatitis [44,45].

There are numerous cases of chloracne reported following accidental exposure to chlorinated aromatic chemicals which were probably contaminated with TCDD [46-48]. The most notable recent exposure occurred in Seveso, Italy in 1976 [49]. In most incidences of chloracne, there are a variety of signs and symptoms (ranging from gastrointestinal disturbances to metabolic disorders) which accompany the appearance of the skin eruptions and persist for varying lengths of time [50-54].

Reproductive Effects In Humans

Reproductive effects resulting from possible human exposure to TCDD are inconclusive. Data on male workers who applied agricultural sprays of 2,4,5-T or who produced TCDD-contaminated materials are consistent with the animal data which suggest no reproductive effects in males from TCDD exposure [55-57]. To date, no study of reproductive effects in women or in offspring of males or females with defined exposure to TCDD has been reported.

Studies of birth defects in populations that may have been exposed non-occupationally to TCDD have been conducted in Australia where a correlation was observed between 2,4,5-T use and seasonal variation in the rate of spinal cord and spine formation defects; no causal association could be drawn [58]. In a similar study in Hungary, an increased incidence of congenital malformations including spine formation defects could not be correlated with increased use of 2,4,5-T [59]. A study based on incomplete fetal tissue samples from the Seveso, Italy population found no mutagenic, teratogenic, or fetotoxic effects in 30 interrupted pregnancies and four spontaneous abortions in women believed to have been exposed to TCDD [60]. A U.S. EPA study found a positive relationship between spontaneous abortions and 2,4,5-T use in the Alsea, Oregon area [61]. The study, however, has been severely criticized because of its numerous limitations: inaccurate comparisons of the study and control areas; inaccuracies in the collection of data on spontaneous abortions; incomplete and inaccurate data on 2,4,5-T usage; and failure to recognize that the rate of spontaneous abortions was not greater than would be expected [62].

[70]: a case control study with 169 malignant lymphoma cases found a significantly higher occupational exposure to phenoxyacetic acids (primarily 2,4,5-T, and 2,4-D) associated with the sarcoma cases than did the 338 controls. Analysis by individual herbicide exposure was not possible [71].

Two additional studies conducted in Sweden for colon cancer and nasal and nasopharyngeal cancer did not demonstrate an elevated risk for occupational exposure to phenoxyacetic acids [72,73].

Among four small groups of U.S. production workers exposed to TCP and 2,4,5-T a total of 105 deaths were observed [74-76]. In these, three deaths were attributed to soft tissue sarcoma (43 times the number expected for this age group of U.S. white males) [77]. Later, four additional cases were reported to have soft tissue sarcomas [78-81]. However, a detailed review of work records and expert review of pathological tissue specimens have shown only two of the seven cases with both confirmed exposure to TCP or 2,4,5-T and diagnosis of soft tissue sarcoma [82].

Summary of Toxicity in Animals and Humans

TCDD causes a variety of systemic and immunological effects in animals with wide variation among species in the dosage required to cause death. Studies using rats and mice have demonstrated that TCDD is an animal teratogen and carcinogen. Results of tests for mutagenicity are inconclusive.

Humans exposed to materials reported to be contaminated with TCDD have developed chloracne and other signs of systemic poisoning. Soft tissue sarcoma has been observed in excess among workers exposed to phenoxy herbicides. These data are inconclusive regarding TCDD toxicity in humans because the populations studied had mixed exposures making causal relationships between exposure and effect unclear. The data are, however, suggestive of an association between exposure to phenoxyacetic herbicides contaminated with TCDD and excess lymphoma and stomach cancer. Attempts to associate reproductive effects with TCDD exposure are inconclusive because of the inadequately defined populations studied and the difficulties of defining exposure.

RECOMMENDATIONS

There are several classifications for identifying a substance as a carcinogen. Such classifications have been developed by the U.S. National Institute of Environmental Health Sciences, National Toxicology Program [83], the International Agency for Research on Cancer [84], and OSHA [85]. NIOSH considers the OSHA classification the most appropriate for use in identifying carcinogens in the workplace. This classification is outlined

in 29 CFR 1990.103.* Since TCDD has been shown to carcinogenic in experimental studies with rats and mice, and studies are suggestive of an association between human exposure to TCDD-contaminated materials and carcinogenicity, NIOSH recommends that TCDD be considered as a potential occupational carcinogen and exposure to TCDD in all occupational settings should be controlled to the fullest extent feasible. While observations to date do not confirm a causal relationship between TCDD exposure and soft tissue sarcoma, they suggest a need for continued investigations.

Because of the variety of situations likely to be encountered in TCDD-contaminated worksites, it is not possible to offer in this bulletin detailed procedures for assessing exposures or decontamination. Based on NIOSH hazard evaluations of TCDD-contaminated sites, the following general guidelines are recommended until more specific procedures can be developed [86,87].

Assessment of Exposure

Workers may be exposed to TCDD derived from a variety of sources: the production of TCP, residues from prior production or use of 2,4,5-T or silvex, waste materials contaminated by TCDD, or contamination resulting from transformer fires. The first step in assessing workplace contamination should be environmental sampling to determine the presence of TCDD contamination, keeping in mind the possible routes of exposure, with later sampling conducted to define the quantity of TCDD in the environment. The assessment may include sampling of soil and settled dust for TCDD, air sampling for TCDD-contaminated particles, and wipe sampling of surfaces [86,87].

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*"'Potential occupational carcinogen' means any substance, or combination or mixture of substances, which causes an increased incidence of benign and/or malignant neoplasms, or a substantial decrease in the latency period between exposure and onset of neoplasms in humans or in one or more experimental mammalian species as the result of any oral, respiratory or dermal exposure, or any other exposure which results in the induction of tumors at a site other than the site of administration. This definition also includes any substance which is metabolized into one or more potential occupational carcinogens by mammals."

Decontamination and Worker Protection Programs

In general, decontamination procedures must provide an organized process in which levels of contamination are reduced. This requires containment, collection, and disposal of contaminated solutions and residues generated during the cleanup. Separate facilities should be provided for decontamination of large equipment.

Each stage of decontamination, such as gross decontamination and repetitive wash/rinse cycles, should be conducted separately, either by using different locations or by spacing in time. Personnel decontamination locations used should be physically separated to prevent cross-contact and should be arranged in order of decreasing level of contamination. Separate entry/exit routes and locations should be provided for workers when it is necessary to isolate them from different contamination areas containing incompatible waste. Entry and exit points to these areas should be well marked and controlled. Access to the decontamination area should be separate from the path between the contaminated and clean areas. Dressing stations for entry should be separate from re-dressing areas for exit.

Protective Clothing and Equipment

All workers who may be exposed to TCDD should be equipped with adequate chemical protective clothing and equipment to ensure their protection. In the selection of protective clothing, consideration should be given to the utilization of disposable apparel due to the uncertainty of decontamination of clothing.

The protective apparel should consist of both outer and inner garments. The outer garments should consist of a zippered coverall with attached hood and draw string or elastic sleeves, gloves and closure boots. If exposure is to particulate or dust, the coveralls should be made of a non-woven fabric such as spunbonded polyethylene, Tyvek®. In cases of exposure to liquids, the coveralls, gloves and boots should be made of chemically resistant materials such as disposable laminates, e.g., Saranax® coated Tyvek®, or synthetic elastomers such as butyl, nitrile or neoprene rubber. The inner garments should consist of cotton coveralls, undershirts, undershorts, gloves, and socks and should be disposed of after use. The effectiveness of the protective clothing should be evaluated under simulated use conditions, regardless of the type of clothing used. All disposable clothing should be placed in marked and approved containers and disposed of appropriately. All reusable clothing and equipment should be thoroughly cleaned and checked for residual contamination before reuse or storage.

Respiratory Protection

The use of respiratory protection requires that a respiratory protection program be instituted according to the requirements of 29 CFR 1910.134 [88] and that the respirators have been approved by the Mine Safety and Health Administration (MSHA) and by NIOSH. This program should include training on proper fit testing and use and procedures for respirator maintenance, inspection, cleaning and evaluation.

For situations where TCDD contamination is low (e.g., exposure to dust contaminated with low levels of TCDD), air purifying respirators should provide sufficient protection until the extent and characterization of the exposure can be determined. Where quantities of materials highly contaminated with TCDD have been released and have contaminated an area (e.g., production accidents), all workers who may be exposed to TCDD should wear respirators that consist of a self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. An alternate method utilizes a combination Type C supplied air respirator, with full facepiece, operated in pressure-demand mode and equipped with auxiliary positive pressure self-contained air supply.

Post-Decontamination Testing

The adequacy of the decontamination effort should be determined by conducting follow-up sampling and analysis of the contaminated areas and protective equipment. This testing should be conducted as each area is decontaminated and after the entire facility has been cleaned.

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CUMULATIVE LIST OF NIOSH CURRENT INTELLIGENCE BULLETINS

1.	Chloroprene	- January 20, 1975
2.	Trichloroethylene (TCE)	- June 6, 1975
3.	Ethylene Dibromide (EDB)	- July 7, 1975
4.	Chrome Pigment	- June 24, 1975 - October 7, 1975 - October 8, 1976
5.	Asbestos - Asbestos Exposure during Servicing of Motor Vehicle Brake and Clutch Assemblies	- August 8, 1975
6.	Hexamethylphosphoric Triamide (HMPA)	- October 24, 1975
7.	Polychlorinated Biphenyls (PCB's)	- November 3, 1975 - August 20, 1976
8.	4,4'-Diaminodiphenylmethane (DDM)	- January 30, 1976
9.	Chloroform	- March 15, 1976
10.	Radon Daughters	- May 11, 1976
11.	Dimethylcarbamoyl Chloride (DMCC) Revised	- July 7, 1976
12.	Diethylcarbamoyl Chloride (DECC)	- July 7, 1976
13.	Explosive Azide Hazard	- August 16, 1976
14.	Inorganic Arsenic - Respiratory Protection	- September 27, 1976
15.	Nitrosamines in Cutting Fluids	- October 6, 1976
16.	Metabolic Precursors of a Known Human Carcinogen, Beta-Naphthylamine	- December 17, 1976
17.	2-Nitropropane	- April 25, 1977
18.	Acrylonitrile	- July 1, 1977
19.	2,4-Diaminoanisole in Hair and Fur Dyes	- January 13, 1978
20.	Tetrachloroethylene (Perchloroethylene)	- January 20, 1978
21.	Trimellitic Anhydride (TMA)	- February 3, 1978
22.	Ethylene Thiourea (ETU)	- April 11, 1978
23.	Ethylene Dibromide and Disulfiram Toxic Interaction	- April 11, 1978
24.	Direct Black 38, Direct Blue 6, and Direct Brown 95 Benzidine Derived Dyes	- April 17, 1978
25.	Ethylene Dichloride (1,2-Dichloroethane)	- April 19, 1978
26.	NIAX Catalyst ESN	- May 22, 1978
27.	Chloroethanes - Review of Toxicity	- August 21, 1978
28.	Vinyl Halides - Carcinogenicity	- September 21, 1978
29.	Glycidyl Ethers	- October 12, 1978
30.	Epichlorohydrin	- October 12, 1978
31.	Adverse Health Effects of Smoking and the Occupational Environment	- February 5, 1979
32.	Arsine (Arsenic Hydride) Poisoning in the Workplace	- August 3, 1979
33.	Radiofrequency (RF) Sealers and Heaters: Potential Health Hazards and Their Prevention	- December 4, 1979
34.	Formaldehyde: Evidence of Carcinogenicity	- April 15, 1981

DEPARTMENT OF HEALTH AND HUMAN SERVICES
PUBLIC HEALTH SERVICE
CENTERS FOR DISEASE CONTROL
NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH
ROBERT A. TAFT LABORATORIES
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Occupational Safety and Health Administration

Form Approved
OMB No. 44-R138

MATERIAL SAFETY DATA SHEET

245TCPi

Required under USDL Safety and Health Regulations for Ship Repairing, Shipbuilding, and Shipbreaking (29 CFR 1915, 1916, 1917)

SECTION I

MANUFACTURER'S NAME	EMERGENCY TELEPHONE NO.
N/A	N/A

ADDRESS (Number, Street, City, State, and ZIP Code)
N/A

CHEMICAL NAME AND SYNONYMS	TRADE NAME AND SYNONYMS
2,4,5-Trichlorophenol 0.2,4,5-TCP	Collinosol, Dowicide 2

CHEMICAL FAMILY: Chlorinated hydrocarbon (Fungicide, bactericide)
FORMULA: $C_6H_3Cl_3O$

SECTION II - HAZARDOUS INGREDIENTS

PAINTS, PRESERVATIVES, & SOLVENTS	%	TLV (Units)	ALLOYS AND METALLIC COATINGS	%	TLV (Units)
PIGMENTS			BASE METAL		
CATALYST			ALLOYS		
VEHICLE			METALLIC COATINGS		
SOLVENTS			FILLER METAL PLUS COATING OR CORE FLUX		
ADDITIVES			OTHERS		
OTHERS					

HAZARDOUS MIXTURES OF OTHER LIQUIDS, SOLIDS, OR GASES	%	TLV (Units)
Heat Strong Alkalies, Caustics		
EPAHAZ U230		
CAS Number 95-95-4		
RTECS SN1400000		

SECTION III - PHYSICAL DATA

BOILING POINT (°F) @1 ATM °F	485.6	SPECIFIC GRAVITY (H_2O=1)	1.678
VAPOR PRESSURE (mm Hg.) @161.6°F	1 mmHG	PERCENT, VOLATILE BY VOLUME (%)	
VAPOR DENSITY (AIR=1)		EVAPORATION RATE (_____=1)	
SOLUBILITY IN WATER G/100 G water @20°C	<0.2G	Melting Point °F	154.4-
APPEARANCE AND ODOR	Colorless needles or gray flakes, strong phenolic odor		

SECTION IV - FIRE AND EXPLOSION HAZARD DATA

FLASH POINT (Method Used)	FLAMMABLE LIMITS	LEL (Combust)	UEL (Comb)
Nonflammable (None)			

EXTINGUISHING MEDIA

SPECIAL FIRE FIGHTING PROCEDURES
Wear SCBA and adequate protective clothing

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SECTION V - HEALTH HAZARD DATA

THRESHOLD LIMIT VALUE
None established, oral LD 50 TDLH (oral) 820 mg/kg - (RAT)

EFFECTS OF OVEREXPOSURE
Skin,eye, respiratory irritation, kidney damage, liver damage, CNS depression

chloraine, pharyngitis, fatique, lightheadedness, sweating, fibrination, abdominal

EMERGENCY AND FIRST AID PROCEDURES pain, vomiting, diarrhea
Wash eyes 15 min with copious amounts of water and skin with water and soap. After exposure

by inhalation remove to fresh air immediately. Upon ingestion seek medical help

immediately. Seek medical attention after any exposure

SECTION VI - REACTIVITY DATA

STABILITY	UNSTABLE		CONDITIONS TO AVOID
	STABLE		

INCOMPATABILITY (Materials to avoid)
Heat. strong Alkalies, caustics

HAZARDOUS DECOMPOSITION PRODUCTS
Toxic and /or Hazardous gases (Phosgene, HCl)

HAZARDOUS POLYMERIZATION	MAY OCCUR		CONDITIONS TO AVOID
	WILL NOT OCCUR		

SECTION VII - SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN IN CASE MATERIAL IS RELEASED OR SPILLED
Contact site supervisor immediately. Notify the proper authorities listed in the site

safety plan. Land spill (dig a pit, pond, lagoon or holding area to Reportable Quantity

1 lb/contain liquid or solid material. Cover solids with a plastic sheet to prevent

WASTE DISPOSAL METHOD
runoff. Water spill (Use natural deep water pockets, excavated lagoons or sandbags to

trap material at bottom. If dissolved apply activated charcoal at 10 times spilled amour

Remove trapped (ORM-A/NA 20201) material with suction hoses. Use dredges or lifts to remo
immobilizer masses

SECTION VIII - SPECIAL PROTECTION INFORMATION

RESPIRATORY PROTECTION (Specify type)
Fullface air purifying respirator with organic vapor cartridge with dust, mist, fume,prefi

VENTILATION	LOCAL EXHAUST	SPECIAL	
	Use whenever possible *	Supplied air or SCBA	
	MECHANICAL (General)	OTHER	

PROTECTIVE GLOVES	EYE PROTECTION
Neoprene (EX-G) natural rubber, nitrile, PVC(G-F)	Faceshield, goggles or FF Respirator

OTHER PROTECTIVE EQUIPMENT
Similar materials for boots, suits, etc. Taping necessary

SECTION IX - SPECIAL PRECAUTIONS

PRECAUTIONS TO BE TAKEN IN HANDLING AND STORING
Eyewash and shower in vicinity. Eating, smoking, drinking etc, prohibited in work area.
Minimize contact at all times

OTHER PRECAUTIONS
Material is very persistent in the environment

TPH | TRICHLOROPHENOL

Fire

Exposure

DUST OR SOLID

Water Pollution

HARMFUL TO AQUATIC LIFE IN LOW CONCENTRATIONS

1. RESPONSE TO DISCHARGE

2. LABELS

Code of Federal Regulations

3. CHEMICAL DESIGNATIONS

4. OBSERVABLE CHARACTERISTICS

5. HEALTH HAZARDS

6. FIRE HAZARDS

6.1 Flash Point

6.2 Flammable Limits in Air

6.3 Fire Extinguishing Agents

6.4 Fire Extinguishing Agents Not to be Used

6.5 Special Hazards of Combustion Products

6.6 Behavior in Fire

6.7 Ignition Temperature

6.8 Electrical Hazard

6.9 Burning Rate

7. CHEMICAL REACTIVITY

7.1 Reactivity with Water

7.2 Reactivity with Common Materials

7.3 Stability During Transport

7.4 Neutralizing Agents for Acids and Caustics

7.5 Polymerization

7.6 Inhibitor of Polymerization

8. WATER POLLUTION

8.1 Aquatic Toxicity

8.2 Waterfowl Toxicity

8.3 Biological Oxygen Demand (BOD)

8.4 Food Chain Concentration Potential

9. SELECTED MANUFACTURERS

10. SHIPPING INFORMATION

10.1 Grades of Purity

10.2 Storage Temperature

10.3 Inert Atmosphere

10.4 Vent Closure

11. HAZARD ASSESSMENT CODE

12. HAZARD CLASSIFICATIONS

12.1 Code of Federal Regulations

12.2 NAS Hazard Rating for Bulk Water Transportation

12.3 NFPA Hazard Classification

13. PHYSICAL AND CHEMICAL PROPERTIES

13.1 Physical State at 15°C and 1 atm

13.2 Molecular Weight

13.3 Boiling Point at 1 atm

13.4 Freezing Point

13.5 Critical Temperature

13.6 Critical Pressure

13.7 Specific Gravity

13.8 Liquid Surface Tension

13.9 Liquid-Water Interfacial Tension

13.10 Vapor (Gas) Specific Gravity

13.11 Ratio of Specific Heats of Vapor (Gas)

13.12 Latent Heat of Vaporization

13.13 Heat of Combustion

13.14 Heat of Decomposition

13.15 Heat of Solution

13.16 Heat of Polymerization

NOTES

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U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

Form Approved OMB No. 44-R131

MATERIAL SAFETY DATA SHEET

Required under USDL Safety and Health Regulations for Ship Repairing, Shipbuilding, and Shipbreaking (29 CFR 1915, 1916, 1917)

SECTION I

MANUFACTURER'S NAME: N/A	EMERGENCY TELEPHONE NO.: N/A
ADDRESS (Number, Street, City, State, and ZIP Code): N/A	
CHEMICAL NAME AND SYNONYMS: 2,4,5-Trichloronnenoxyacetic acid; 2,4,5-T	TRADE NAME AND SYNONYMS: Trinoxol, Verton 2 T, DED-Weed Brush
CHEMICAL FAMILY: Organochlorine Herbicide	FORMULA: $C_8H_5Cl_3O_3$

SECTION II - HAZARDOUS INGREDIENTS

PAINTS, PRESERVATIVES, & SOLVENTS	%	TLV (Units)	ALLOYS AND METALLIC COATINGS	%	TL (U
PIGMENTS			BASE METAL		
CATALYST			ALLOYS		
VEHICLE			METALLIC COATINGS		
SOLVENT			FILLER METAL PLUS COATING OR CORE FLUX		
ADDITIVES			OTHERS		
OTHERS					

HAZARDOUS MIXTURES OF OTHER LIQUIDS, SOLIDS, OR GASES	%	TL (U
Incompatible with strong oxidizers		
Suspected that 2,4,5-T is contaminated with dioxin (or TCDD)		
CAS Number 93-76-5		
RTECS - AJ8400000		
EPAHW# U232		

SECTION III - PHYSICAL DATA

BOILING POINT (°F) At 1ATM	decomposes	SPECIFIC GRAVITY (H_2O=1)	
VAPOR PRESSURE (mm Hg.) @ 20°C	0mm hg	PERCENT, VOLATILE BY VOLUME (%)	
VAPOR DENSITY (AIR=1)		EVAPORATION RATE (_____ =1)	
SOLUBILITY IN WATER G/100 G water at 20°C 0.03%		Melting Point	316°F
APPEARANCE AND ODOR Colorless to tan, Odorless solid used as a liquid mix for herbicide			

SECTION IV - FIRE AND EXPLOSION HAZARD DATA

FLASH POINT (Method used) Incombustible		FLAMMABLE LIMITS	Lel / U: Incombustible

EXTINGUISHING MEDIA
(Material does not burn)Water fog, alcohol foam or CO_2 or dry chemical or other suitable fo

SPECIAL FIRE FIGHTING PROCEDURES surrounding material
Wear SCBA in fire situation as well as full protective clothing. Potential for dioxin/fu

UNUSUAL FIRE AND EXPLOSION HAZARDS generation from incomplete combustion

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SECTION V - HEALTH HAZARD DATA

THRESHOLD LIMIT VALUE
10 mg/M3 OSHA PEL - 10 mg/M3-ACGIH - 20 mg/M3 STEL IDLH = 5000 mg/M3

EFFECTS OF OVEREXPOSURE
Abdominal pain, nausea, vomitting, diarrhea, skin irritation, blood in stool
ataxia dermatitis

EMERGENCY AND FIRST AID PROCEDURES
Wash eye 15 minutes with copious amounts of water and skin with water and mild detergent.
After severe inhalation removed to fresh air immediately. Upon ingestion seek medical hel
immediately. If not available induce vomiting. Seek medical help immediately after any
exposure

SECTION VI - REACTIVITY DATA

STABILITY	UNSTABLE		CONDITIONS TO AVOID
	STABLE	X	

INCOMPATABILITY (Materials to avoid)
Strong oxidizers.

HAZARDOUS DECOMPOSITION PRODUCTS
Potential Dioxin, furans, HCl, phosgene from incomplete combustion

HAZARDOUS POLYMERIZATION	MAY OCCUR		CONDITIONS TO AVOID
	WILL NOT OCCUR	X	

SECTION VII - SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN IN CASE MATERIAL IS RELEASED OR SPILLED
Contact site supervisor immediately. Notify the proper authorities listed in the
site safety plan. Minimize dust release. Reportable quantity 100 lb. Land spill
(Dig pit, pond to hold material, cover solids with a plastic sheet to prevent runoff

WASTE DISPOSAL METHOD
Water spill (~~if dissolved apply activated carbon~~ - remove trapped material with
suction hose
NA - 2765/ORM-A

SECTION VIII - SPECIAL PROTECTION INFORMATION

RESPIRATORY PROTECTION (Specify type)
Fullface Air Purifying respirator with OV or OA cartridges and dust, mist, fume prefilter

VENTILATION	LOCAL EXHAUST	*	SPECIAL
	Use whenever possible		Supplied air or SCBA if nec
	MECHANICAL (General)		OTHER

PROTECTIVE GLOVES
Neoprene (EX-GD)Nitrile, Natural Rubber PVC(F-GD)

EYE PROTECTION
Faceshield, Goggles-FF respirator

OTHER PROTECTIVE EQUIPMENT
Similar materials for suits, boots (Aromatic halogens) Taping necessary

SECTION IX - SPECIAL PRECAUTIONS

PRECAUTIONS TO BE TAKEN IN HANDLING AND STORING
Eyewash and shower in vicinity. Eating, smoking, drinking, etc. prohibited in work
area. Minimize contact at all times

OTHER PRECAUTIONS
Material extremely persistent in the environment. Keep drinking water out of
the work area.

TCA	2,4,5-TRICHLOROPHENOXYACETIC ACID

2,4,5-T | Solid | White | Odorless

Solid in water

Keep people away
Consult specialist
Isolate and remove discharged material
Notify local health and pollution control agencies

Fire

Combustible
POISONOUS GASES MAY BE PRODUCED IN FIRE
Extinguish with water, dry chemical, foam, or carbon dioxide

Exposure

CALL FOR MEDICAL AID
SOLID
POISONOUS IF SWALLOWED
Spreading on skin and eyes.
Remove contaminated clothing and shoes
Flush affected areas with plenty of water
IF IN EYES, hold eyelids open and flush with plenty of water
IF SWALLOWED and victim is CONSCIOUS, have victim drink water or milk and have victim induce vomiting
IF SWALLOWED and victim is UNCONSCIOUS OR HAVING CONVULSIONS, do nothing except keep victim warm

Water Pollution

HARMFUL TO AQUATIC LIFE IN VERY LOW CONCENTRATIONS
May be dangerous if it enters water intakes.
Notify local health and wildlife officials.
Notify operators of nearby water intakes.

1. RESPONSE TO DISCHARGE

Use respiratory protection (SCBA).
Wear protective clothing.
Stop discharge, if safe.
Isolate.
Ventilate.
Keep material out of water sources and sewers.
Build dikes to contain flow as necessary.
Recover free liquid and recycle, if possible.
Absorb remainder on vermiculite, dry sand, earth, or similar material.
Dispose of properly.
Contact fire department and pollution control agencies.
Water spray may reduce vapor; but may not prevent ignition in closed spaces.

2. LABEL

POISON

3. CHEMICAL DESIGNATIONS

3.1 Synonyms: 2,4,5-T
3.2 Coast Guard Compatibility Classification: Not applicable
3.3 Chemical Formula: $C_8H_5Cl_3O_3$
3.4 NAERG/United Nations Numerical Designation: 2765

4. OBSERVABLE CHARACTERISTICS

4.1 Physical State (at ambient temperature and pressure): Solid
4.2 Color: White
4.3 Odor: None

5. HEALTH HAZARDS

5.1 Personal Protective Equipment: Dust mask and rubber gloves.
5.2 Symptoms Following Exposure: Ingestion causes nausea, vomiting, severe bodily irritation, confusion, coma. Dust may irritate eyes and skin.
5.3 Treatment for Exposure: INHALATION: remove victim to fresh air; if necessary, give artificial respiration. EYES: flush with water gently for 15 minutes. SKIN: wash with soap and water. INGESTION: induce vomiting or drink copious quantities of water and administer gastric lavage.
5.4 Toxicity by Inhalation (Threshold Limit Value): 10 mg/m³
5.5 Short-Term Inhalation Limits: Data not available
5.6 Toxicity by Ingestion: Grade 3; oral LD_{50} = 100 mg/kg (rat)
5.7 Late Toxicity: Some cancers of skin and mice. Causes an abnormal fetal condition among laboratory animals.
5.8 Vapor (Gas) Irritant Characteristics: Not applicable
5.9 Liquid or Solid Irritant Characteristics: Data not available
5.10 Odor Threshold: Not applicable

6. FIRE HAZARDS

6.1 Flash Point: Not applicable (solid)
6.2 Flammable Limits in Air: Not applicable
6.3 Fire Extinguishing Agents: Water spray, dry chemical, carbon dioxide
6.4 Fire Extinguishing Agents Not to be Used: Not applicable
6.5 Special Hazards of Combustion Products: Toxic chlorine, phenols, and phosgene gases may be formed
6.6 Behavior in Fire: Not applicable
6.7 Ignition Temperature: Data not available
6.8 Electrical Hazard: Not applicable
6.9 Burning Rate: Not applicable

7. CHEMICAL REACTIVITY

7.1 Reactivity with Water: No reaction
7.2 Reactivity with Common Materials: Can be corrosive to aluminum metals
7.3 Stability During Transport: Stable
7.4 Neutralizing Agents for Acids and Caustics: Not applicable
7.5 Polymerization: Not applicable
7.6 Inhibitor of Polymerization: Not applicable

8. WATER POLLUTION

8.1 Aquatic Toxicity: [illegible]
8.2 Waterfowl Toxicity: [illegible]
8.3 Biological Oxygen Demand (BOD): Data not available
8.4 Food Chain Concentration Potential: Will not bioconcentrate

9. SELECTED MANUFACTURERS

Dow Chemical Co.
Midland, Mich. 48640

[illegible] Inc.
P.O. Box 69
[illegible], Ark. 72076

[illegible] Co.
[illegible] Lakeview Boulevard
[illegible], Mo. 63166

10. SHIPPING INFORMATION

10.1 Grades of Purity: Commercial
10.2 Storage Temperature: Ambient
10.3 Inert Atmosphere: Not required
10.4 Limited Quantity: Does not apply

11. HAZARD ASSESSMENT CODE

[illegible]
II

12. HAZARD CLASSIFICATIONS

12.1 Code of Federal Regulations: Poison, Label B
12.2 NFPA Hazard Rating for Bulk Water Transportation: Not rated
12.3 NFPA Hazard Classification: Not rated

13. PHYSICAL AND CHEMICAL PROPERTIES

13.1 Physical State at 15°C and 1 atm: Solid
13.2 Molecular Weight: 255.5
13.3 Boiling Point at 1 atm: Not applicable (solid at this temperature)
13.4 Freezing Point: 154 °C (309 °F)
13.5 Critical Temperature: Not applicable
13.6 Critical Pressure: Not applicable
13.7 Specific Gravity: [illegible]
13.8 Liquid Surface Tension: Not applicable
13.9 Liquid-Water Interfacial Tension: Not applicable
13.10 Vapor (Gas) Specific Gravity: Not applicable
13.11 Ratio of Specific Heats of Vapor (Gas): Not applicable
13.12 Latent Heat of Vaporization: Not applicable
13.13 Heat of Combustion: [illegible]
13.14 Heat of Decomposition: Not applicable
13.15 Heat of Solution: Not applicable
13.16 Heat of Polymerization: Not applicable

NOTES

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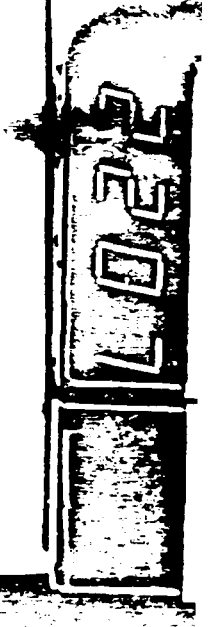

Occupational Health Guideline for 2,4,5-T *

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $Cl_3C_6H_2OCH_2COOH$
- Synonyms: 2,4,5-Trichlorophenoxyacetic acid
- Appearance and odor: Colorless to tan odorless solid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for 2,4,5-T is 10 milligrams of 2,4,5-T per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

2,4,5-T can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

Exposure to 2,4,5-T may cause abdominal pain, nausea, vomiting, diarrhea, and blood in the stool. It may also cause irritation of the skin. Common contaminants of commercial preparations of 2,4,5-T may cause acne and liver damage. Animal experiments have shown that these contaminants may produce damage in unborn rats.

- **Reporting signs and symptoms:**

A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to 2,4,5-T.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to 2,4,5-T at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the liver and attention to gastrointestinal complaints should be stressed. The skin should be examined for evidence of chronic disorders.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis.

- **Summary of toxicology**

2,4,5-T (2,4,5-trichlorophenoxyacetic acid) is of low toxicity. The oral LD50 for dogs is in the range of 100 mg/kg or higher; effects are limited to a slight or moderate stiffness in the hind legs with development of ataxia. Contaminants of commercial preparations of 2,4,5-T have been 2,3,7,8-tetrachlorodibenzo-p-dioxin, a potent animal teratogen, and 2,3,6,7-tetrachlorodibenzo-p-dioxin (TCDD), a potent acnegenic agent which is hepatotoxic in animals; they are present as unwanted side products of synthesis of 2,4,5-T. In a study of 73 workers in a 2,4,5-T manufacturing plant, 13 had moderate to severe acneform dermatitis (chloracne) and 22 had gastrointestinal complaints such as nausea, vomiting, diarrhea, abdominal pain, or blood in the stool; no significant liver dysfunction was found; although no air sample results were reported, the chloracne was thought to be a result of exposure to TCDD. 2,4,5-T dust is a slight irritant of the skin.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 255.5
2. Boiling point (760 mm Hg): Decomposes above melting point
3. Specific gravity (water = 1): Greater than 1
4. Vapor density (air = 1 at boiling point of 2,4,5-T): Not applicable
5. Melting point: 158 C (316 F) (decomposition)

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

September 1978

6. Vapor pressure at 20 C (68 F): Essentially zero
7. Solubility in water, g/100 g water at 20 C (68 F): 0.03
8. Evaporation rate (butyl acetate = 1): Not applicable

• **Reactivity**

1. Conditions contributing to instability: Temperatures above 158 C (316 F) may cause sealed metal containers to burst.
2. Incompatibilities: None.
3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride and carbon monoxide) may be released when 2,4,5-T decomposes.
4. Special precautions: None.

• **Flammability**

1. Not combustible

• **Warning properties**

2,4,5-T is not known to be an eye irritant.

MONITORING AND MEASUREMENT PROCEDURES

• **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• **Method**

An analytical method for 2,4,5-T is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1).

RESPIRATORS

• Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

• In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

SANITATION

• Eating and smoking should not be permitted in areas where 2,4,5-T is handled, processed, or stored.

• Employees who handle 2,4,5-T should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to 2,4,5-T may occur and control methods which may be effective in each case:

Operation	Controls
Formulation of herbicides and plant hormones	Process enclosure; local exhaust ventilation; personal protective equipment
Application as herbicide, defoliant, and plant hormone	Personal protective equipment
Manufacture of 2,4,5-T	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• **Eye Exposure**

If 2,4,5-T gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

• **Skin Exposure**

If 2,4,5-T or liquids containing 2,4,5-T get on the skin, wash the contaminated skin using soap or mild detergent and water. If 2,4,5-T or liquids containing 2,4,5-T soak through the clothing, remove the clothing and wash the skin using soap or mild detergent and water. If irritation is present after washing, get medical attention.

• **Breathing**

If a person breathes in large amounts of 2,4,5-T, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• **Swallowing**

When 2,4,5-T or bounds containing 2,4,5-T have been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical

attention immediately.

• **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.

• If 2,4,5-T is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation, or for disposal in a secured sanitary landfill. Liquid containing 2,4,5-T should be absorbed in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

2,4,5-T may be disposed of in sealed containers in a secured sanitary landfill.

REFERENCES

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* SPECIAL NOTE

The International Agency for Research on Cancer (IARC) has evaluated the data on this chemical and has concluded that it causes cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 15, 197[illegible]

RESPIRATORY PROTECTION FOR 2,4,5-T

Condition	Minimum Respiratory Protection* Required Above 10 mg/m³
Particulate Concentration	
50 mg/m³ or less	Any dust and mist respirator, except single-use.
100 mg/m³ or less	Any dust and mist respirator, except single-use or quarter-mask respirator. Any fume respirator or high efficiency particulate filter respirator. Any supplied-air respirator. Any self-contained breathing apparatus.
500 mg/m³ or less	A high efficiency particulate filter respirator with a full facepiece. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
5000 mg/m³ or less	A powered air-purifying respirator with a high efficiency particulate filter. A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 5000 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any dust and mist respirator, except single-use. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

Form Approved OMB No. 44-R138

MATERIAL SAFETY DATA SHEET

Required under USDL Safety and Health Regulations for Ship Repairing, Shipbuilding, and Shipbreaking (29 CFR 1915, 1916, 1917)

SECTION I

MANUFACTURER'S NAME	EMERGENCY TELEPHONE NO.
N/A	N/A

ADDRESS (Number, Street, City, State, and ZIP Code) N/A

CHEMICAL NAME AND SYNONYMS	TRADE NAME AND SYNONYMS
2,4-Dichlorophenoxy acetic acid	2,4-D, Weedar 64, Dormone, Agratect
CHEMICAL FAMILY: Chlorinated hydrocarbon(Herbicide)	FORMULA: $C_8 Cl_2 H_6 O_3$ Agent Orange

SECTION II - HAZARDOUS INGREDIENTS

PAINTS, PRESERVATIVES, & SOLVENTS	%	TLV (Units)	ALLOYS AND METALLIC COATINGS	%	TL (Un
PIGMENTS			BASE METAL		
CATALYST			ALLOYS		
VEHICLE			METALLIC COATINGS		
SOLVENTS			FILLER METAL PLUS COATING OR CORE FLUX		
ADDITIVES			OTHERS		
OTHERS					

HAZARDOUS MIXTURES OF OTHER LIQUIDS, SOLIDS, OR GASES	%	TL (Un
Incompatible with strong oxidizers		
Dioxin found as impurity or breakdown substance in 2,4D		Tra
CAS Number 94-75-7		
RTECS AG682500 EPA HWH P03S		

SECTION III - PHYSICAL DATA

BOILING POINT (°F.) at 1 ATM	Decomposes	SPECIFIC GRAVITY (H_2O=1)	
VAPOR PRESSURE (mm Hg.) @20C	7.63mm Hg	PERCENT, VOLATILE BY VOLUME (%)	
VAPOR DENSITY (AIR=1)		EVAPORATION RATE (_____ =1)	
SOLUBILITY IN WATER slight ~~G/100 G water at 20°C~~	0.07PPM	Melting Point	284°F
APPEARANCE AND ODOR Colorless, odorless solid; white to yellow crystalline powder			

SECTION IV - FIRE AND EXPLOSION HAZARD DATA

FLASH POINT (Method used)	FLAMMABLE LIMITS	Lel	U
Unknown		N/A	N/

EXTINGUISHING MEDIA
Extinguish using suitable material to surround the fire (water fog, CO_2, Dry Chem

SPECIAL FIRE FIGHTING PROCEDURES
Wear SCBA in fire situations as well as full protective clothing. Potential for dioxin/furon/phosgene etc. from incomplete combustion

SECTION V - HEALTH HAZARD DATA

THRESHOLD LIMIT VALUE
10 mg/m^3 OSHA PEL, 10 mg/m^3 ACGIH TWA-20 mg/m^3 STEL IDLH = 500 mg/m^3

EFFECTS OF OVEREXPOSURE
Liver damage, kidney damage, poison, itch, pupil, tremors, peripheral neuropathy, convulsions, icterus, incoordination, ventricular fibrillation, cardiac arrhythmia, CNS depressi

EMERGENCY AND FIRST AID PROCEDURES
Wash eyes 15 min with copious amounts of water and skin with water and soap. After exposur by inhalation remove to fresh air immediately. Upon ingestion seek medical help immediatel Induce vomiting if medical help unavailable. Seek medical attention after any exposure

SECTION VI - REACTIVITY DATA

STABILITY	UNSTABLE		CONDITIONS TO AVOID
	STABLE	X	

INCOMPATABILITY (Materials to avoid)
Strong oxidizers

HAZARDOUS DECOMPOSITION PRODUCTS
Potential Dioxin, furans, phosgene, HCl from incomplete combustion

HAZARDOUS POLYMERIZATION	MAY OCCUR		CONDITIONS TO AVOID
	WILL NOT OCCUR	X	

SECTION VII - SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN IN CASE MATERIAL IS RELEASED OR SPILLED
Contact site supervisor immediately Notify the proper authorities listed in the site safety plan. Minimize dust release. Reportable quantity 100 lbs. ORM-E or A (Hazardous substance, liquid or solid, N.O.S.) Land Spill (Dig pit/pond to hold material - cover solids with a plastic sheet to prevent runoff.. Water Spill(if dissolved apply activatec carbon at 10 times spilled amount - remove trapped material with suction hoses - use mechanical dredges or lifts to remove immobilized masses of pollutren and precipitates.

WASTE DISPOSAL METHOD
EPA HW# P035 NA #2765

SECTION VIII - SPECIAL PROTECTION INFORMATION

RESPIRATORY PROTECTION (Specify type)
Full face airpurifying respirator with OV or OA cartridge with dust, mist, fume prefilte

VENTILATION	LOCAL EXHAUST Use whenever possible *	SPECIAL Supplied-air or SCBA if need
	MECHANICAL (General)	OTHER

PROTECTIVE GLOVES
Neoprene(FX-6) Nitrite, natural rubber PVC(GO-F)

EYE PROTECTION
Faceshield, goggles, or FF respirator

OTHER PROTECTIVE EQUIPMENT
Similar materials for suits, boots, etc. (Aromatic halogen) Taping necessary

SECTION IX - SPECIAL PRECAUTIONS

PRECAUTIONS TO BE TAKEN IN HANDLING AND STORING
Eye wash and shower in vicinity, eating, smoking, drinking etc prohibited in work area. Minimize contact at all times.

OTHER PRECAUTIONS
Material is extremely persistent in the environment

*with higher concentrations in greater potential for exposure

Occupational Health Guideline for 2,4-D *

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $Cl_2C_6H_3OCH_2COOH$
- Synonyms: 2,4-Dichlorophenoxyacetic acid
- Appearance and odor: Colorless, odorless solid

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for 2,4-D is 10 milligrams of 2,4-D per cubic meter of air (mg/m^3) averaged over an eight-hour work shift.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

2,4-D can affect the body if it is inhaled, if it comes in contact with the eyes or skin, or if it is swallowed. It may enter the body through the skin.

- **Effects of overexposure**

1. Short-term Exposure: Massive exposure to 2,4-D may cause weakness, stupor, muscle twitching, and convulsions. Contact of the material with the skin may cause a rash. It has caused minor liver and kidney damage in animals.

2. Long-term Exposure: Not known.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to 2,4-D.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to 2,4-D at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from 2,4-D exposure.

—Liver disease: 2,4-D causes liver damage in animals. The importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: 2,4-D causes kidney damage in animals. The importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Cardiovascular disease: 2,4-D causes ventricular fibrillation in animals. In persons with impaired cardiovascular function, the inhalation of 2,4-D might cause exacerbation of pre-existing disorder.

—Skin disease: 2,4-D can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Convulsive disorder or neuropathy: 2,4-D may cause convulsions in humans. Persons with a history of such disorders may be more susceptible to the effects of this agent. 2,4-D may also produce neuropathy by analogy to effects observed in experimental animals.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

2,4-D dust causes signs of both hypo- and hyperexcitation of the central nervous system in animals. In several species of animals given massive oral doses, sudden death has been ascribed to ventricular fibrillation. If death is delayed, myotonia, stiffness of the extremities, ataxia, paralysis, and coma are seen; autopsy findings have included minor liver and kidney injury. The myotonia characteristic of intoxication by 2,4-D in animals has not been reported in humans. Possibly the only recognized fatal case of poisoning involved a suicidal person who ingested not less than 6500 mg; the

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

September 1978

person apparently experienced violent convulsions, although they were not actually observed; there were no significant findings at autopsy. A single dose of 3.6 g of 2,4-D administered intravenously to a patient for treatment of disseminated coccidiomycosis caused stupor, hyporeflexia, fibrillary twitching of some muscles, and urinary incontinence; 24 hours after the dose, the patient still complained of profound muscular weakness, which subsided after an additional 24 hours. Contact of the material with the skin may cause dermatitis; skin absorption is slight.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 221
  2. Boiling point (760 mm Hg): Decomposes
  3. Specific gravity (water = 1): 1.1 (estimated)
  4. Vapor density (air = 1 at boiling point of 2,4-D): 7.63
  5. Melting point: 140 C (284 F)
  6. Vapor pressure at 20 C (68 F): Essentially zero
  7. Solubility in water, at 20 C (68 F): 0.07 ppm
  8. Evaporation rate (butyl acetate = 1): Not applicable
- **Reactivity**
  1. Conditions contributing to instability: None
  2. Incompatibilities: Contact with strong oxidizers may cause fires and explosions.
  3. Hazardous decomposition products: Toxic gases and vapors (such as hydrogen chloride and carbon monoxide) may be released in a fire involving 2,4-D.
  4. Special precautions: None
- **Flammability**
  1. Flash point: Data not available
  2. Autoignition temperature: Data not available
  3. Flammable limits in air, % by volume: Data not available
  4. Extinguishant: Carbon dioxide, dry chemical, foam, water
- **Warning properties**

Since 2,4-D has a negligible vapor pressure, warning properties are not considered.

Grant states that "2,4-dichlorophenoxyacetic acid (2,4-D) is a herbicide for weed control, often used in the form of its salts or esters. Parenteral administration to dogs has caused sneezing, lacrimation, and rubbing of the eyes, along with gastrointestinal disturbances. In three human beings, absorption of an unspecified ester of dichlorophenoxyacetic acid through the skin caused polyneuritis, but with no disturbance of the eyes or vision." The above do not appear to be local effects on the eye. However, Stolman and Stecher note that this substance can cause irritation of the eyes.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

An analytical method for 2,4-D is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with 2,4-D or liquids containing 2,4-D.
- If employees' clothing may have become contaminated with 2,4-D, employees should change into uncontaminated clothing before leaving the work premises.
- Clothing contaminated with 2,4-D should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of 2,4-D from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the 2,4-D, the person performing the operation should be informed of 2,4-D's hazardous properties.
- Non-impervious clothing which becomes contami-

nated with 2,4-D should be removed promptly and not reworn until the 2,4-D is removed from the clothing.

• Employees should be provided with and required to use dust- and splash-proof safety goggles where 2,4-D or liquids containing 2,4-D may contact the eyes.

SANITATION

• Skin that becomes contaminated with 2,4-D should be promptly washed or showered with soap or mild detergent and water to remove any 2,4-D.

• Eating and smoking should not be permitted in areas where solid 2,4-D is handled, processed, or stored.

• Employees who handle 2,4-D or liquids containing 2,4-D should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to 2,4-D may occur and control methods which may be effective in each case:

Operation	Controls
Formulation of herbicides	Process enclosure; local exhaust ventilation; personal protective equipment; washing facilities
Manufacture of 2,4-D	Process enclosure; local exhaust ventilation; personal protective equipment; washing facilities
Application on cereal crops, corn, sorghum, milo, sugar cane, pastures, range land, and lawns for use as an herbicide; use as a plant hormone on agricultural crops	Personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• **Eye Exposure**

If 2,4-D or liquids containing 2,4-D get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

• **Skin Exposure**

If 2,4-D or liquids containing 2,4-D get on the skin, promptly wash the contaminated skin using soap or mild detergent and water. If 2,4-D or liquids containing 2,4-D penetrate through the clothing, remove the clothing promptly and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

• **Breathing**

If a person breathes in large amounts of 2,4-D, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• **Swallowing**

When 2,4-D has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

• **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills until cleanup has been completed.

• If 2,4-D is spilled, the following steps should be taken:

1. Ventilate area of spill.
2. For small quantities, sweep onto paper or other suitable material, place in an appropriate container and burn in a safe place (such as a fume hood). Large quantities may be reclaimed; however, if this is not practical, dispose of by burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device, as in below or deposit in a secured sanitary landfill.

• Waste disposal methods:

2,4-D may be disposed of:

1. By making packages of 2,4-D in paper or other flammable material and burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
2. By dissolving 2,4-D in a flammable solvent (such as alcohol) and atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.
3. By disposal in a secured sanitary landfill.

REFERENCES

• American Conference of Governmental Industrial Hygienists: "2,4-D (2,4-Dichlorophenoxyacetic Acid)," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

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• Spencer, E. Y.: *Guide to the Chemicals Used in Crop Protection* (6th ed.), Publication 1093, Research Branch Agriculture, Canada, 1973.

• Stecher, P. G. (ed.): *The Merck Index* (8th ed.), Merck & Co., Inc., Rahway, New Jersey, 1968.

• Stolman, A. (ed.): *Progress in Chemical Toxicology*, Academic Press, New York, 1965-1969.

* SPECIAL NOTE

The International Agency for Research on Cancer (IARC) has evaluated the data on this chemical and has concluded that it causes cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 15, 1977.

RESPIRATORY PROTECTION FOR 2,4-D

Condition	Minimum Respiratory Protection* Required Above 10 mg/m³
Particulate Concentration	
100 mg/m³ or less	Any chemical cartridge respirator with an organic vapor cartridge(s) and dust filter(s), including pesticide respirators which meet the requirements of this class.
	Any supplied-air respirator.
	Any self-contained breathing apparatus.
500 mg/m³ or less	A chemical cartridge respirator with a full facepiece and an organic vapor cartridge(s), and dust filter(s), including pesticide respirators which meet the requirements of this class.
	A gas mask with a chin-style or a front- or back-mounted organic vapor canister and dust and mist filter, including pesticide respirators which meet the requirements of this class.
	Any supplied-air respirator with a full facepiece, helmet, or hood.
	Any self-contained breathing apparatus with a full facepiece.
	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 500 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
	A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors and particulates, including pesticide respirators which meet the requirements of this class.
	Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

Form Approved OMB No. 44R13

MATERIAL SAFETY DATA SHEET

Required under USDL Safety and Health Regulations for Ship Repairing, Shipbuilding, and Shipbreaking (29 CFR 1915, 1916, 1917)

SECTION I

MANUFACTURER'S NAME	EMERGENCY TELEPHONE NO.
N/A	N/A

ADDRESS (Number, Street, City, State, and ZIP Code)
N/A

CHEMICAL NAME AND SYNONYMS	TRADE NAME AND SYNONYMS
Sulfuric Acid - Battery Electrolyte (Acid)	Qual Brand & Private Label Brands
CHEMICAL FAMILY: Inorganic Acid - Sulfuric Acid	FORMULA: H_2SO_4

SECTION II - HAZARDOUS INGREDIENTS

PAINTS, PRESERVATIVES, & SOLVENTS	%	TLV (Units)	ALLOYS AND METALLIC COATINGS	%	TLV
PIGMENTS			BASE METAL		
CATALYST			ALLOYS		
VEHICLE			METALLIC COATINGS		
SOLVENTS			FILLER METAL PLUS COATING OR CORE FLUX		
ADDITIVES			OTHERS		
OTHERS					

HAZARDOUS MIXTURES OF OTHER LIQUIDS, SOLIDS, OR GASES	%	TLV
BATTERY ELECTROLYTE (Acid): Battery Fluid is a highly corrosive mixture of sulfuric acid (H_2SO_4) and pure water (H_2O), possessing a specific gravity ranging from 1.200 ± 0.005 to 1.300 ± 0.005 at 80°F. (25%-40% H_2SO_4)		
the threshold limit value of sulfuric acid per eight (8) hour day is		1mg

SECTION III - PHYSICAL DATA

BOILING POINT (°F.)	203°F	SPECIFIC GRAVITY (H_2O=1)	1.200 to 1.300 @ 80°F
VAPOR PRESSURE (mm Hg.)	10@18°F	PERCENT, VOLATILE BY VOLUME (%)	
VAPOR DENSITY (AIR=1)	+ 1	EVAPORATION RATE (_____=1)	Water (H_2O) 1
SOLUBILITY IN WATER	100%	READ ATTACHED SPECIFICATIONS CAREFULLY	

APPEARANCE AND ODOR: Colorless, oily fluid, to slightly cloudy - Odorless

SECTION IV - FIRE AND EXPLOSION HAZARD DATA

FLASH POINT (Method used)	FLAMMABLE LIMITS	LEL	UEL
Non-Flammable			

EXTINGUISHING MEDIA
If this material is involved in a fire, use large quantities of water.

SPECIAL FIRE FIGHTING PROCEDURES
Dilute any spilled or leaking batter electrolyte with large amounts of water

DIA 002

SECTION V - HEALTH HAZARD DATA

THRESHOLD LIMIT VALUE: 1mg/M^3 per eight (8) hour day

EFFECTS OF OVEREXPOSURE: Extremely corrosive. Causes severe burns. Repeated contact may cause skin and eye irritation. Repeated innalation of mist may cuase inflammation of lungs.

EMERGENCY AND FIRST AID PROCEDURES: SEE ATTACHED INFORMATION! Immediate washing with large amounts of water for at least 15 minutes is recommended. Contact a physician immediately.

Battery electrolyte does not contain Poly Chlorinated Biphenyls.

SECTION VI - REACTIVITY DATA

STABILITY	UNSTABLE		CONDITIONS TO AVOID: All contact with all organic substances.
	STABLE	100%	

INCOMPATABILITY (Materials to avoid): Incompatible with all metals and all organic substances

HAZARDOUS DECOMPOSITION PRODUCTS

HAZARDOUS POLYMERIZATION	MAY OCCUR		CONDITIONS TO AVOID
	WILL NOT OCCUR	X	

SECTION VII - SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN IN CASE MATERIAL IS RELEASED OR SPILLED: Wash entire affected area with plenty of water. If water is not available, use sand or ashes. Do not use cloth, sawdust, or any other combustibles.

WASTE DISPOSAL METHOD: Neutralize with bicarbonate of soda and dilute with water.

SECTION VIII - SPECIAL PROTECTION INFORMATION

RESPIRATORY PROTECTION (Specify type): Full-face respirators with OA or Acid Gas Cartridges with dust, mist, fume prefilters

VENTILATION	LOCAL EXHAUST	SPECIAL: Supplied air or SCBA*
	MECHANICAL (General)	OTHER

PROTECTIVE GLOVES: Rubber Gloves	EYE PROTECTION: Chemical Safety Goggles

OTHER PROTECTIVE EQUIPMENT: Rubber Apron, Face Shield, Chemical Safety Goggles, Rubber Gloves

SECTION IX - SPECIAL PRECAUTIONS

PRECAUTIONS TO BE TAKEN IN HANDLING AND STORING: Store in cool, dry place, fully protected from moisture and severe weather. Avoid all handling and storage procedures that may result in spills, leaks, punctures.

OTHER PRECAUTIONS: Only handle and /or store in areas where an unlimited water supply is available.

*with higher concentrations or greater potential for exposure

Form

Occupational Health Guideline for Sulfuric Acid

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: H_2SO_4
- Synonyms: *Oil of vitriol*
- Appearance and odor: Colorless to dark brown, oily, odorless liquid.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for sulfuric acid is 1 milligram of sulfuric acid per cubic meter of air (mg/m³) averaged over an eight-hour work shift. NIOSH has recommended a permissible exposure limit of 1 mg/m³ averaged over a work shift of up to 10 hours per day, 40 hours per week. The NIOSH Criteria Document for Sulfuric Acid should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Sulfuric acid can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- *Effects of overexposure*

1. Short-term Exposure: Sulfuric acid may cause irritation of the eyes, nose, and throat. Breathing in the mist or vapor may cause teeth erosion or the mouth to become sore and also difficulty in breathing. Splashes in the eyes or on the skin will cause severe skin burns. *2. Long-term Exposure:* Repeated or prolonged exposure to dilute solutions of sulfuric acid may cause irritation of the skin. Repeated or prolonged exposure to mists or vapors of sulfuric acid may cause erosion of the teeth, chronic irritation of the eyes, or chronic inflammation of the nose, throat, and bronchial tubes. *3. Reporting Signs and Symptoms:* A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to sulfuric acid.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to sulfuric acid at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the respiratory system, eyes, and teeth should be stressed. The skin should be examined for evidence of chronic disorders.

—14" x 17" chest roentgenogram: Sulfuric acid may cause acute lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Sulfuric acid is reported to cause pulmonary function impairment. Periodic surveillance is indicated.

2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is considered necessary only when indicated by the results of pulmonary function testing.

- **Summary of toxicology**

Sulfuric acid mist severely irritates the eyes, respiratory tract, and skin. Concentrated sulfuric acid destroys tissue due to its severe dehydrating action, whereas the dilute form acts as a milder irritant due to acid properties. The LC50 of mist of 1-micron particle size for an 8 hour exposure was 50 mg/m³ for adult guinea pigs and 18 mg/m³ for young animals. Continuous exposure of guinea pigs to 2 mg/m³ for 5 days caused pulmonary edema and thickening of the alveolar walls; exposure of guinea pigs to 2 mg/m³ for 1 hour caused an increase in

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

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pulmonary airway resistance from reflex bronchoconstriction. A worker sprayed in the face with liquid fuming sulfuric acid suffered skin burns of the face and body, as well as pulmonary edema from inhalation. Sequelae were pulmonary fibrosis, residual bronchitis, and pulmonary emphysema; in addition, necrosis of the skin resulted in marked scarring. In human subjects, concentrations of about 5 mg/m³ were objectionable, usually causing cough, an increase in respiratory rate, and impairment of ventilatory capacity. Workers exposed to concentrations of 12.6 to 35 mg/m³ had a markedly higher incidence of erosion and discoloration of teeth than was noted in unexposed individuals. Splashed in the eye, the concentrated acid causes extremely severe damage, often leading to blindness, whereas dilute acid produces more transient effects from which recovery may be complete. Repeated exposure of workers to the mist causes chronic conjunctivitis, tracheobronchitis, stomatitis, and dermatitis, as well as dental erosion. While ingestion of the liquid is unlikely in ordinary industrial use, the highly corrosive nature of the substance may be expected to produce serious mucous membrane burns of the mouth and esophagus.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
  1. Molecular weight: 98
  2. Boiling point (760 mm Hg): 270 C (518 F)
  3. Specific gravity (water = 1): 1.84
  4. Vapor density (air = 1 at boiling point of sulfuric acid): 3.4
  5. Melting point: 3 C (37 F)
  6. Vapor pressure at 20 C (68 F): Less than 0.001 mm Hg
  7. Solubility in water, g/100 g water at 20 C (68 F): Miscible in all proportions
  8. Evaporation rate (butyl acetate = 1): Data not available
- **Reactivity**
  1. Conditions contributing to instability: None
  2. Incompatibilities: Contact of acid with organic materials (such as chlorates, carbides, fulminates, and picrates) may cause fires and explosions. Contact of acid with metals may form toxic sulfur dioxide fumes and flammable hydrogen gas.
  3. Hazardous decomposition products: Toxic gases and vapors (such as sulfuric acid fume, sulfur dioxide, and carbon monoxide) may be released when sulfuric acid decomposes.
  4. Special precautions: Liquid sulfuric acid will attack some forms of plastics, rubber, and coatings.
- **Flammability**
  1. Sulfuric acid is not combustible by itself, but is highly reactive and capable of igniting finely divided combustible materials on contact. Fires involving small amounts of combustibles may be smothered with dry chemical. Water applied directly to sulfuric acid causes evolution of heat and splattering.
- **Warning properties**

The International Labour Office (ILO) reports that sulfuric acid, in liquid or vapor form, can cause eye irritation, but no quantitative information is given. The NIOSH criteria document for sulfuric acid states that Bushtueva exposed 10 human subjects to different concentrations of sulfuric acid aerosol. At a concentration of 1.1 to 2.4 mg/m³, 40% of the subjects experienced eye irritation.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of sulfuric acid on a cellulose membrane filter, followed by extraction with distilled water and isopropyl alcohol, treatment with perchloric acid, and titration with barium perchlorate. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure sulfuric acid may be used. An analytical method for sulfuric acid is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

• Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquid sulfuric acid or solutions containing more than 1% sulfuric acid by weight.

• Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with solutions containing 1% or less sulfuric acid by weight.

• Where there is any possibility of exposure of an employee's body to liquid sulfuric acid or solutions containingmore than 1% sulfuric acid by weight, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

• Non-impervious clothing which becomes contaminated with sulfuric acid should be removed immediately and not reworn until the sulfuric acid is removed from the clothing.

• Clothing contaminated with sulfuric acid should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of sulfuric acid from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the sulfuric acid, the person performing the operation should be informed of sulfuric acid's hazardous properties.

• Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid sulfuric acid or solutions containing sulfuric acid contacting the eyes.

• Where there is any possibility that employees' eyes may be exposed to liquid sulfuric acid or solutions containmore than 1% sulfuric acid by weight, an eye-wash fountain should be provided within the immediate work area for emergency use.

SANITATION

• Skin that becomes contaminated with sulfuric acid should be immediately washed or showered to remove any sulfuric acid.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to sulfuric acid may occur and control methods which may be effective in each case:

Operation	Controls
Use in manufacture of phosphoric acid and fertilizers	Process enclosure; local exhaust ventilation; personal protective equipment
Use in petroleum refining as an alkylation catalyst for production of high-octane gasoline, production of jet fuels, kerosene, lube and white oils, oil additives, and preparation of cracking catalysts	Process enclosure; local exhaust ventilation; personal protective equipment
Use during manufacture of pigments and dyes, and dyestuff intermediates	Process enclosure; local exhaust ventilation; personal protective equipment
Use in manufacture of industrial and military explosives	Process enclosure; local exhaust ventilation; personal protective equipment
Use in production of alcohols, phenols, and inorganic sulfates	Process enclosure; local exhaust ventilation; personal protective equipment
Use in ore leaching and processing; use in metal cleaning and plating; manufacture of electrogalvanized wire; anodizing of metal; electroplating	Process enclosure; local exhaust ventilation; personal protective equipment
Use in manufacture of detergents	Process enclosure; local exhaust ventilation; personal protective equipment
Use in coke-oven gas refining; use in plastics industry for manufacture of rayon, cellophane, cellulose acetate, caprolactam, and others; use in lead storage batteries as electrolyte	Process enclosure; local exhaust ventilation; personal protective equipment
Use in food processing in manufacture of brewing sugars for beer, manufacture of glucose, refining of mineral and vegetable oils	Process enclosure; local exhaust ventilation; personal protective equipment

Operation	Controls
Use for preparation of insecticides; use in manufacture of natural and synthetic rubber	Process enclosure; local exhaust ventilation; personal protective equipment
Use for gas drying to dry acid and corrosive gases; use in treatment of industrial water for pH control	Process enclosure; local exhaust ventilation; personal protective equipment
Use in manufacture of textiles and leather for treatment of wool, pickling leather, as a dye assist, as a solvent for vat dyes, and in fabric finishing	Process enclosure; local exhaust ventilation; personal protective equipment
Use as a laboratory reagent as a solvent and for chemical analysis; use in chemical synthesis in preparation of acids, intermediates for medicinals, gas, esters, and fatty acids	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• **Eye Exposure**

If liquid sulfuric acid or solutions containing sulfuric acid get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with this chemical.

• **Skin Exposure**

If liquid sulfuric acid or solutions containing sulfuric acid get on the skin, immediately flush the contaminated skin with water. If liquid sulfuric acid or solutions containing sulfuric acid penetrate through the clothing, remove the clothing immediately and flush the skin with water. Get medical attention immediately.

• **Breathing**

If a person breathes in large amounts of sulfuric acid, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• **Swallowing**

If liquid sulfuric acid or solutions containing sulfuric acid have been swallowed and the person is conscious, give him large quantities of water immediately to dilute the sulfuric acid. Do not attempt to make the exposed person vomit. Get medical attention immediately.

• **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

• If sulfuric acid is spilled or leaked, the following steps should be taken:

1. Ventilate area of spill or leak.
2. Collect spilled or leaked material in the most convenient and safe manner for reclamation or for disposal in a secured sanitary landfill. Sulfuric acid should be absorbed in vermiculite, dry sand, earth, or a similar material. It may also be diluted and neutralized.

• Waste disposal method:

Sulfuric acid may be placed in sealed containers or absorbed in vermiculite, dry sand, earth, or a similar material and disposed of in a secured sanitary landfill. It may also be diluted and neutralized.

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RESPIRATORY PROTECTION FOR SULFURIC ACID

Condition	Minimum Respiratory Protection* Required Above 1 mg/m³
Particulate Concentration	
50 mg/m³ or less	A gas mask with a chin-style or a front- or back-mounted acid gas canister with a high efficiency particulate filter.
	A high efficiency particulate filter respirator with a full facepiece.
	Any supplied-air respirator with a full facepiece, helmet, or hood.
	Any self-contained breathing apparatus with a full facepiece.
100 mg/m³ or less	A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.
Greater than 100 mg/m³ or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
	A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	A gas mask with a chin-style or a front- or back-mounted acid gas canister with a high efficiency particulate filter.
	Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

DDT	DDT

Solid Colorless Odorless

Soluble in water.

Avoid contact with solid.
Cab fire department.
Isolate and remove discharged material.
Notify local health and pollution control agencies.

Fire

Combustible.
POISONOUS GASES ARE PRODUCED IN FIRE.
Wear goggles and self-contained breathing apparatus.
Extinguish with water, dry chemical, foam, or carbon dioxide.

Exposure

CALL FOR MEDICAL AID.
INHALED
Irritating to skin and eyes.
If unconscious, not breathing, or in distress, give artificial respiration.
Remove contaminated clothing and shoes.
Wash affected areas with plenty of water.
IF IN EYES, hold eyelids open and flush with plenty of water.
IF SWALLOWED and victim is CONSCIOUS, have victim drink water or milk.

Water Pollution

HARMFUL TO AQUATIC LIFE IN VERY LOW CONCENTRATIONS.
May be dangerous if in water intake streams.
Notify local health and wildlife officials.
Notify operators of nearby water intakes.

1. RESPONSE TO DISCHARGE

Wear recommended protective clothing, including self-contained breathing apparatus.
Isolate and remove discharged material.
Notify local health and pollution control agencies.
Should be removed.

2. LABELS

The hazard label required by Code of Federal Regulations.

3. CHEMICAL DESIGNATIONS

3.1 Synonyms: Dichlorodiphenyltrichloroethane; p,p'-DDT; 1,1,1-Trichloro-2,2-bis(p-chlorophenyl) ethane

3.2 Coast Guard Compatibility Classification: Not applicable

3.3 Chemical Formula: $(p\text{-}ClC_6H_4)_2CHCCl_3$

3.4 CAS Registry Number: Not found

4. OBSERVABLE CHARACTERISTICS

4.1 Physical State (as shipped): Solid

4.2 Color: White

4.3 Odor: None

5. HEALTH HAZARDS

5.1 Personal Protective Equipment: Does not apply

5.2 Symptoms Following Exposure: Very large doses are followed promptly by vomiting, due to gastric irritation, delayed nausea or diarrhea may occur. In an acutely toxic, irritable victim 2-3 hours after exposure. These include tingling of lips, tongue, and face, muscle tremor 2-3 hours after exposure. These include tingling of lips, tongue, and face, muscle tremor, hyperactive, sore throat, fatigue, anorexia, weakness of neck, head, and eyelids, apprehension, nausea, headache, sore throat, fatigue, anorexia, weakness of neck, head, and eyelids, apprehension, nausea, and convulsions. Convulsions may alternate with periods of coma and partial paralysis. Convulsions may alternate with periods of coma and partial paralysis. Tremor may be continuously expressed, but in severe poisoning the pulse may be irregular and irregular and abnormally slow; respiration fibrillation and sudden death may occur at any time during acute phase. Pulmonary edema usually advances without stimulation. Pulmonary edema usually advances without stimulation.

5.3 Treatment for Exposure: INGESTION: treatment should be done by a physician. It usually includes gastric lavage and administration of some carbonic physiochemical and symptomatic fluids. Person should be kept quiet and under observation for at least 24 hours. Fluids. Person should be kept quiet and under observation for at least 24 hours.

5.4 Toxicity by Inhalation (Threshold Limit Value): Not pertinent

5.5 Short Term Inhalation Limits: Not pertinent

5.6 Toxicity by Ingestion: Grade 3. LD$_{50}$ 30 to 300 mg/kg rats

5.7 Late Toxicity: Does not apply

5.8 Vapor (Not Irritant) Characteristics: Not pertinent

5.9 Liquid or Solid (Irritant) Characteristics: Moderate hazard. If spilled on clothing and allowed to remain, may cause smarting and reddening of the skin.

5.10 Odor Threshold: Not pertinent

6. FIRE HAZARDS

6.1 Flash Point: 162°F (77°F C.C.)

6.2 Flammable Limits in Air: Not pertinent

6.3 Fire Extinguishing Agents: Water, foam, dry chemical, or carbon dioxide

6.4 Fire Extinguishing Agents Not to be Used: Not pertinent

6.5 Special Hazards of Combustion Products: Toxic and irritating gases may be generated

6.6 Behavior in Fire: Melts and burns

6.7 Ignition Temperature: Does not apply

6.8 Electrical Hazard: Not pertinent

6.9 Burning Rate: Does not apply

7. CHEMICAL REACTIVITY

7.1 Reactivity with Water: No reaction

7.2 Reactivity with Common Materials: No reaction

7.3 Stability During Transport: Stable

7.4 Neutralizing Agents for Acids and Caustics: Not pertinent

7.5 Polymerization: Not pertinent

7.6 Inhibitor of Polymerization: Not pertinent

8. WATER POLLUTION

8.1 Aquatic Toxicity: 0.001 ppm/24 hr/Bass/TL$_m$/fresh water; 0.1 ppm/48 hr/Trout/TL$_m$/fresh water; 0.3-0.5 ppm/48 hr/Goldfish/30% kill/salt water

8.2 Waterfowl Toxicity: 2240 mg/kg

8.3 Biological Oxygen Demand (BOD): Not pertinent

8.4 Food Chain Concentration Potential: High

9. SELECTED MANUFACTURERS

1. Lebanon Chemical Corp, Lebanon, Pa. 17042
2. Westbrook Chemical Corp of Calif, 3000 South Vogel Ave, Los Angeles, Calif. 90005

10. SHIPPING INFORMATION

10.1 Grades of Purity: Technical

10.2 Storage Temperature: Does not apply

10.3 Inert Atmosphere: Does not apply

10.4 Venting: Does not apply

11. HAZARD ASSESSMENT CODE

Shipping regulations reference: 09-Mode

H

12. HAZARD CLASSIFICATIONS

12.1 Code of Federal Regulations: Other-A

12.2 NAS Hazard Rating for Bulk Water Transportation: Not listed

12.3 NFPA Hazard Classification: Not listed

13. PHYSICAL AND CHEMICAL PROPERTIES

13.1 Physical State at 15°C and 1 atm: Solid

13.2 Molecular Weight: 354.5

13.3 Boiling Point at 1 atm: Not pertinent

13.4 Freezing Point: 234°F = 108°C = 381°K

13.5 Critical Temperature: Not pertinent

13.6 Critical Pressure: Not pertinent

13.7 Specific Gravity: 1.56 at 77°C (solid)

13.8 Liquid Surface Tension: Not pertinent

13.9 Liquid-Water Interfacial Tension: Not pertinent

13.10 Vapor (Gas) Specific Gravity: Not pertinent

13.11 Ratio of Specific Heats of Vapor (Gas): Not pertinent

13.12 Latent Heat of Vaporization: Not pertinent

13.13 Heat of Combustion: Not pertinent

13.14 Heat of Decomposition: Not pertinent

13.15 Heat of Solution: Not pertinent

13.16 Heat of Polymerization: Not pertinent

(Continued on page 3 inside)

NOTES

DDT ♦ (Cont.)

BP: All India Medical Corp. (India) (*Diemar*)
"Atanor" Sociedad Anonima Mixta (Argentina)
Diamond Shamrock de Mexico, S.A. de C.V. (Mexico) (*DDT 35% °, Diamekte 50% °, Tech DDT °*)
Guanor y Fertilizantes, S.A. (Mexico)
Hindustan Insecticides Ltd. (India) (*Huldit °, Huldit 50 ° WP*)
Montrose Chemical Corp. of California (*DDT Technical, DDT 75% WDP*)
Produits Chimiques Ugine Kuhlmann (France)
Rumianca S.p.A. (Italy) (*DDT 75% WDP* and *Technical Granular DDT* for export; *Micro DDT 75 °* and *R50 °*, domestic)
Ugimica, S.A. (Spain) (*DDT Technical, DDT 75% WDP*)
F: Devidayal (Sales) Private Ltd. (India)

DDT 35% ° — see DDT ♦

DDT, Antiresistant — see Antiresistant DDT.

DDT Technical — see DDT ♦.

DDT 75% WDP — see DDT ♦.

DDVF — see DDVP.

DDVP

CHEMICAL NAME: 2,2-Dichlorovinyl dimethyl phosphate.

COMMON NAMES: *DDVP* (USA); *dichlorvos* (ISO, BSI) (USA-pharmaceutical grade); *UDVF* (USSR).

OTHER NAMES: *Benfos °, Cekusan °, Cypona °, Dedevap °, Derriban °, Derribante °, Diclorvos °* (discontinued by Quimica Estrella), *Divipan °, Duo-Kill °, Fly-Die °, Herkol °, Mafu °, Marvex °, Nogos °, No-Pest °, Nuvan °, Oko °, Phosvit °, Vapona °, Vaponite °.*

ACTION: Insecticide.

CHEMICAL PROPERTIES: Colorless to amber liquid, specific gravity 1.44 (60° 60° F.). Slightly soluble in water (about 1%); in kerosene 2-3%. Readily soluble in most organic solvents.

TOXICITY: Acute oral LD_{50} (rat), 56-80 mg/kg; acute dermal LD_{50} (rat), 75 mg/kg; (rabbit), 107 mg/kg.

SIGNAL WORD: DANGER; POISON.

ANTIDOTE: Atropine is the emergency antidote for *DDVP* poisoning. 2-PAM is also antidotal and may be used in conjunction with atropine.

HANDLING AND STORAGE CAUTIONS: Poisonous if swallowed, inhaled, or absorbed through skin. Do not contaminate feed or foodstuffs.

APPLICATION: A contact and stomach poison, it acts also as a fumigant. Controls household and public health pests, stored product insects, horn flies, house flies, face flies, stable flies, gnats, and mosquitoes on lactating dairy animals and beef cattle.

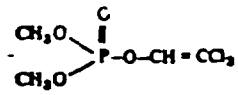
Control of mushroom flies; also aphids, spider mites, caterpillars, thrips, white flies in glasshouse crops, and outdoor fruit and vegetables.

FORMULATIONS: Emulsifiable concentrations, soluble concentrate, wettable powder, ready-to-use sprays, aerosols, space sprays, resin strips (*Mafu ° Strip, No-Pest ° Strip Insecticide*), flea collars, baits. Concentrates sold under the name of *Vaponite °* are for professional pest control use only.

Formulated as an anthelmintic for swine (*Atgard °*), horses (*Equigard °*), and dogs (*Task °*).

Benfos ° is used for control of weevils in stored grain.

COMBINATIONS: A mixture for use on lactating dairy animals is *Ciodrin °* (see *Ciodrin °*). A mixture for use as a residual premise spray and poultry larvicide is *Ravap °* (see *Rabon °*). Attractant mixture for fly control (*Golden Decoy °*). A mixture with *propoxur* as pressured spray for use in households.



DDVP

BP: All India Medical Corp. (India)
Amvac Chemical Corp.
Bayer AG (Federal Republic of Germany) (*Dedevap °, Mafu °, Oko °*)
Cequisa (Spain) (*Cekusan °*)
Ciba-Geigy Ltd. (Switzerland) (*Nogos °, Nuvan °*)
Makhteshim-Agan (Israel) (*Divipan °*)
Nippon Soda Co., Ltd. (Japan) (*Phosvit °*)
Quimica Estrella (Argentina) (*Benfos °, Derriban °, Derribante °*)
Shell Chemical Co. (*Vapona °, Vaponite °*)
Shell International Chemical Co. (Great Britain) (*Vapona °*)
Ugimica, S.A. (Spain)
F: Devidayal (Sales) Private Ltd. (India)
Diamond Shamrock (*Atgard °, Ciovap °, Equigard °, Farmstrip °, Stable Strip °, Ravap °, Task °*)
Hopkins Agricultural Chemical Co. (*Cypona ° E.C., Duo-Kill °, Fly-Die °, Vapona °, Vapona ° Plus*)
Texize, Division Morton-Norwich (*No-Pest ° Strip Insecticide*)

Deactivator

Some chlorinated hydrocarbon insecticides such as *aldrin, chlordane, endrin* and *toxaphene* are susceptible to breakdown when combined with certain carriers or diluents in dust formulations. The action is caused by catalytic action of acidic centers on the surface of some diluents and carriers.

Such diluents must be avoided or the acidic sites on the active carriers must be neutralized with deactivators. Urea and hexamethylene tetramine have been found satisfactory for this purpose.

2,4-DEB

CHEMICAL NAME: 2,4-Dichlorophenoxyethyl benzoate.

ACTION: Herbicide.

Débroussaillant 600 ° — see 2,4-D.

Débroussaillant Concentré ° — see 2,4,5-T.

Débroussaillant Super Concentré ° — see 2,4,5-T.

Decafentin — see Stannoram °.

Decamethrin — see Decis °; Pyrethroids.

Decanol — see Amtak °; Fair-Tac °; Off-Shoot-T °; Royal-tac °; Sprout-Off °; Sucker Plucker °.

Decarbofuran

CHEMICAL NAME: 2,3-Dihydro-2-methylbenzofuran-7-yl methylcarbamate.

SIGNAL WORD: DANGER.

ANTIDOTE: No specific antidote is known. See product label for practical treatment following ingestion, inhalation, or skin or eye contact.

HANDLING AND STORAGE CAUTIONS: Flammable. Hazardous by ingestion, inhalation, or by skin absorption. Although toxic to warm-blooded animals, the vapors provide a warning of the presence of *D-D* °. NIOSH or MESA approved respiratory equipment should be worn when liquid *D-D* ° is exposed to the atmosphere. When handling or working with *D-D* ° wear clean body covering including polyethylene or neoprene gloves and and heavy (greater than 3 mil thickness) polyethylene, neoprene, or rubber footwear; wear eye protection such as chemical workers' goggles. Store in cool place away from dwellings. Do not cut or weld container. Do not store in or use containers or equipment made of aluminum, magnesium, or their alloys. For further information regarding the safe handling of *D-D*, please refer to the *D-D Handling and Safety Manual*. Does not require Class B poison label.

APPLICATIONS: Controlled dosages are injected into the soil where *D-D* ° provides fumigant action against plant parasitic nematodes, symphylids, and wireworms on a broad range of crops; also preplant treatment to control bacterial canker and decline of peach trees, for suppression of verticillium wilt, and to control quackgrass in fields to be planted to white potatoes in northwestern states, for reduction of damaging effects of verticillium wilt in disease-infected land to be used for mint production in northwestern states, and as treatment to aid in control of field bindweed (perennial morninggiory) on bare ground.

For every 10 gallons of *D-D* ° applied broadcast per acre, at least one week must elapse before any planting can be done and the period must be lengthened in the event of low temperatures or excessive rain. Pineapple land can be treated at time of planting.

See also *Dichloropropane-dichloropropene, Nemex* °.

BP: Shell Chemical Co.
Shell International Chemical Co. (Great Britain)

DDA

CHEMICAL NAME: Bis(chlorophenyl) acetic acid.

CHEMICAL PROPERTIES: Degradation product of *DDT*♦.

See *DDT* ♦.

DDD — see TDE ♦.

DDE

CHEMICAL NAME: Dichlorodiphenyldichloroethylene.

CHEMICAL PROPERTIES: Product of degradation of *DDT*♦ by loss of one molecule of hydrochloric acid (dehydrohalogenation). *DDE* further degrades to *DDA* by loss of two more molecules *HCl*.

DDT ♦

CHEMICAL NAME: Dichloro diphenyl trichloroethane.

PRINCIPAL ISOMER PRESENT: 1,1,1-Trichloro-2,2-bis-(p-chlorophenyl) ethane (not less than 70%).

MEDICAL AND PHARMACEUTICAL NAME: *Chlorophenothane*.

OTHER COMMON NAMES: *DDT* (BSI, CSA, ESA, ESJ, MAFJ), *Zeidane* (France), *pp' Zeidane*.

TRADE NAMES: *Anofex* °, *Arkotine* ° (Shell Chemical U.K.), *DDT 35%* °, *DDT Technical*, *DDT 75% WDP*, *Dedelo* °, *Diamekta 50%* °, *Didimac* ° (ICI), *Digmar*, *Genitox* °, (*Gesapon* °, *Gesarex* °, *Gesarol* ° are obsolete trade names of Ciba-Geigy Ltd.), *Gyron* °, *Hildit* °, *Isodex* °, *Kopsol* °, *Micro DDT 75* °, *Neocid* ° (Ciba-Geigy Ltd.), *Pentachlorin* °, *R50* °, *Rukseam* °, *Tech DDT* °, *Zerdane* °.

HISTORY: First described in 1874 by Othmar Zeidler, German chemist, its insecticidal value was not uncovered until 1939 through the work of Paul Müller in Switzerland. Brought into the United States for testing in September 1942, it was later imported in quantity and by early 1944, domestic production for military use was under way.

DDT gained rapidly in popularity because of its very high toxicity to insects, relatively low hazard to warm-blooded animals and due to the fact that discovery came when rotenone and pyrethrum supplies were very low due to WW II. Later it was found that *DDT* is accumulative in the fatty tissue of warm-blooded animals and that special care was required for application to dairy cattle and animals raised for their food value. In further action to prevent contamination of food and the environment in general, all uses in the United States except emergency public health uses, and a very few other uses permitted on a case basis, have been canceled as of January 1, 1973.

ACTION: Insecticide.

CHEMICAL PROPERTIES: *DDT* is extremely non-volatile, almost insoluble in water, has limited solubility in aliphatic oils and is soluble in apolar organic solvents. Crystallization point min. 90° C; acidity (as sulfuric acid) max. 0.3% in weight; water: Max. 1.0% in weight.

DDT is unstable in the presence of alkalies and therefore is incompatible with alkaloid nicotine and dolomite, Bordeaux mixture, *ferbam*, and some clays may cause a slight decomposition.

TOXICITY: The acute oral toxicity for man has been established at 250 mg kg. Acute oral LD_{50} (rat), for technical *DDT*, 113 mg·kg. Toxicity varies widely according to the formulation. Cucurbits, young tomato plants, and beans are injured by normal dosages and *DDT* may accumulate in the top soil layer where heavy applications are made annually to crops such as apples.

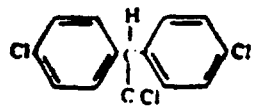
SIGNAL WORD: CAUTION.

APPLICATIONS: Build-up of red spider mites often occurs after application of *DDT* and this plus the fact that a number of major insect pests have shown their capacity to develop a hereditary resistance to *DDT* has resulted in some displacement by other chemicals. Also used as mosquito vector control for the eradication of malaria in many countries.

FORMULATIONS: A contact poison, it is formulated in aerosols, dusts, solutions, wettable powders, emulsifiable concentrates, granular.

Space sprays for home use usually are formulated with kerosene and a small amount of methylnaphthalene or xylene to produce 5% solutions. Methylnaphthalene, xylene, cyclohexanone, isophorone, tetralin, or cumene are used as solvents for emulsion concentrates.

There is a tendency to cake either before or after grinding so it is often mixed with an equal amount of pyrophyllite or talc before grinding. Addition of a wetting agent to this forms a wettable powder or it can be further diluted and used as a dust.



DDT ♦

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

Form Approved
OMB No. 44R1333

MATERIAL SAFETY DATA SHEET

Required under USDL Safety and Health Regulations for Ship Repairing, Shipbuilding, and Shipbreaking (29 CFR 1915, 1916, 1917)

SECTION I

MANUFACTURER'S NAME: N/A	EMERGENCY TELEPHONE NO.: N/A
ADDRESS (Number, Street, City, State, and ZIP Code): N/A	
CHEMICAL NAME AND SYNONYMS: Hexachlorobenzene (HCB)	TRADE NAME AND SYNONYMS: Perchlorobenzene, Sanocide
CHEMICAL FAMILY: Halogenated pesticide	FORMULA: C_6Cl_6

SECTION II - HAZARDOUS INGREDIENTS

PAINTS, PRESERVATIVES, & SOLVENTS	%	TLV (Units)	ALLOYS AND METALLIC COATINGS	%	
PIGMENTS			BASE METAL		
CATALYST			ALLOYS		
VEHICLE			METALLIC COATINGS		
SOLVENTS			FILLER METAL PLUS COATING OR CORE FLUX		
ADDITIVES			OTHERS		
OTHERS					

HAZARDOUS MIXTURES OF OTHER LIQUIDS, SOLIDS, OR GASES	%	
EPA HAZWASTE # U127		
CAS - 118-74-1		
RTEC - DA2975000		

SECTION III - PHYSICAL DATA

BOILING POINT (°F)	Sublimes (1ATM)	613F	SPECIFIC GRAVITY (H_2O=1)	2.04
VAPOR PRESSURE (mm Hg)	20C	1mm Hg	PERCENT, VOLATILE BY VOLUME (%)	N/A
VAPOR DENSITY (AIR=1)		N/A	EVAPORATION RATE (_____=1)	N/A
SOLUBILITY IN WATER	(Sol in benzene, alcohol)	Insoluable	Melting Point	229°C
APPEARANCE AND ODOR	Solid White crystal needles			

SECTION IV - FIRE AND EXPLOSION HAZARD DATA

FLASH POINT (Method used) 468°F	FLAMMABLE LIMITS: Combustible
EXTINGUISHING MEDIA: Use suitable material to surround fire	
SPECIAL FIRE FIGHTING PROCEDURES: Wear SCBA with full protective clothing	

DIA 002

SECTION V - HEALTH HAZARD DATA

THRESHOLD LIMIT VALUE
N/A — LD 50 10,000 mg/kg (oral)

EFFECTS OF OVEREXPOSURE
Chloracne liver damage, eye/skin irritation, abdominal pain, convulsions tremors, dizziness, headache, CNS depression, respiratory irritation

EMERGENCY AND FIRST AID PROCEDURES
Wash eyes with copious amounts of water and skin with soap and water/rubbing alcohol. After exposure by inhalation remove to fresh air immediately. Upon ingestion seek medical help, immediately. Seek medical attention after any exposure.

SECTION VI - REACTIVITY DATA

STABILITY	UNSTABLE		CONDITIONS TO AVOID
	STABLE	XX	

INCOMPATABILITY (Materials to avoid)
Dimethyl formamide, Heat

HAZARDOUS DECOMPOSITION PRODUCTS
Thermal decomposition releases toxic gases (phosgene, HCl)

HAZARDOUS POLYMERIZATION	MAY OCCUR		CONDITIONS TO AVOID
	WILL NOT OCCUR	X	

SECTION VII - SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN IN CASE MATERIAL IS RELEASED OR SPILLED
Notify site supervisor immediately. Notified the proper authorities listed in the site safety plan. Land spill (Dig pit, pond to hold material - cover solids with a plastic sheet to prevent run off). Water spill (If dissolved apply activated carbon

WASTE DISPOSAL METHOD
remove trapped material with suction hoses. Use mechanical dredges or lifts to remove immobilized masses UN-2729, Reportable quantity - 1 lb., ORM-E

SECTION VIII - SPECIAL PROTECTION INFORMATION

RESPIRATORY PROTECTION (Specify type)
Fullface air purifying respirator with OV cartridges with dust, mist, fume, prefilte

VENTILATION	LOCAL EXHAUST	*	SPECIAL Supplied air or SCBA
	MECHANICAL (General)		OTHER

PROTECTIVE GLOVES
Polyethylene (G-F) Rubber, Neoprene PVC (F-P)

EYE PROTECTION
Faceshield goggles or FF Respirator

OTHER PROTECTIVE EQUIPMENT
Polyethylene (G-F) Butyl Rubber (F-G) for boots, suits etc

SECTION IX - SPECIAL PRECAUTIONS

PRECAUTIONS TO BE TAKEN IN HANDLING AND STORING

OTHER PRECAUTIONS
Eye wash and shower in vicinity. Smoking, drinking, eating, etc. prohibited in work area. Minimize contact at all times.

*with higher concentrations or greater potential for exposure

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

Form Approved
OMB No. 44-R1331

MATERIAL SAFETY DATA SHEET

Required under USDL Safety and Health Regulations for Ship Repairing, Shipbuilding, and Shipbreaking (29 CFR 1915, 1916, 1917)

SECTION I

MANUFACTURER'S NAME: N/A	EMERGENCY TELEPHONE NO.: N/A
ADDRESS (Number, Street, City, State, and ZIP Code): N/A	
CHEMICAL NAME AND SYNONYMS: Asbestos	TRADE NAME AND SYNONYMS: Chrysotile, Amosite, Crocidolite
CHEMICAL FAMILY: Mineral Fiber	FORMULA: Variable

SECTION II - HAZARDOUS INGREDIENTS

PAINTS, PRESERVATIVES, & SOLVENTS	%	TLV (Units)	ALLOYS AND METALLIC COATINGS	%	TL (Uni
PIGMENTS			BASE METAL		
CATALYST			ALLOYS		
VEHICLE			METALLIC COATINGS		
SOLVENTS			FILLER METAL PLUS COATING OR CORE FLUX		
ADDITIVES			OTHERS		
OTHERS					

HAZARDOUS MIXTURES OF OTHER LIQUIDS, SOLIDS, OR GASES	%	TL (Un
CAS Number 1332-21-4		
RETECS - CI 6475000		

SECTION III - PHYSICAL DATA

BOILING POINT (°F) at 1 ATM	4046F	SPECIFIC GRAVITY (H_2O=1)	2.5
VAPOR PRESSURE (mm Hg.)	0.00	PERCENT, VOLATILE BY VOLUME (%)	N/A
VAPOR DENSITY (AIR=1)	N/A	EVAPORATION RATE (=1)	N/A
SOLUBILITY IN WATER	INSOL	Melting Point	3134F

APPEARANCE AND ODOR: Variable mineral, white to other colors (brown)

SECTION IV - FIRE AND EXPLOSION HAZARD DATA

FLASH POINT (Method used)	Nonflammable	FLAMMABLE LIMITS	Lel / Uel: Nonflammable

EXTINGUISHING MEDIA: Agent suitable for type of surrounding fire

SPECIAL FIRE FIGHTING PROCEDURES: N/A

SECTION V - HEALTH HAZARD DATA

THRESHOLD LIMIT VALUE
0.5 fibers >5u/cc IDLH = TDLO Inhalation 2.8 fibers/cc 5 yrs.

EFFECTS OF OVEREXPOSURE
Skin irritation, respiratory irritation, dermatitis, dyspnea, cough, cyanosis finger clubbing, pneumoconiosis

EMERGENCY AND FIRST AID PROCEDURES
Wash eyes 15 minutes with plenty of water. Wash skin with soap and water. Prohibit inhalation exposure

SECTION VI - REACTIVITY DATA

STABILITY	UNSTABLE		CONDITIONS TO AVOID
	STABLE	X	

INCOMPATABILITY (Materials to avoid)
None

HAZARDOUS DECOMPOSITION PRODUCTS
N/A

HAZARDOUS POLYMERIZATION	MAY OCCUR		CONDITIONS TO AVOID
	WILL NOT OCCUR	X	

SECTION VII - SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN IN CASE MATERIAL IS RELEASED OR SPILLED
Keep material wet and contain runoff
Keep dry material from becoming airborne

WASTE DISPOSAL METHOD
Place in appropriately labeled container and dispose of in a secure landfill
ORM-C. EPA HZD Waste Number U013

SECTION VIII - SPECIAL PROTECTION INFORMATION

RESPIRATORY PROTECTION (Specify type)
Half or full face air purifying respirator with HEPA cartridge

VENTILATION	LOCAL EXHAUST	Use whenever possible	SPECIAL: Supplied air or SCBA
	MECHANICAL (General)		OTHER

PROTECTIVE GLOVES
PVC/Latex/Natural Rubber

EYE PROTECTION
Faceshield, goggles, FF respirator

OTHER PROTECTIVE EQUIPMENT
Hooded Tyvek coverall with Tyvek booties, PVC boots (steel toed) Taping necessary

SECTION IX - SPECIAL PRECAUTIONS

PRECAUTIONS TO BE TAKEN IN HANDLING AND STORING
Store in airtight, waterright containers

OTHER PRECAUTIONS

with higher concentrations or greater potential for.

APPENDIX B

APPENDIX B
ANALYTICAL PROTOCOL EXPANSION

APPENDIX B

TABLE OF CONTENTS

APPENDIX B.5

Expected Detection Limits for HSL
Excerpt From Contract and Modification Dated 12/83

EXHIBIT C

HAZARDOUS SUBSTANCES LIST (HSL)* AND METHOD DETECTION LIMITS**

	Parameter (ug/l)	Method No.	CAS #	Detection Limit: Medium Level ug/g or ug/ml	Detection Limit: Low Level ug/L
1.	acenaphthene	625	83-32-9	10	10
2.	acrolein	603,624	107-02-8	10	100
3.	acrylonitrile	603,624	107-13-1	10	100
4.	benzene	624	71-43-2	1	5
5.	benzidine	625	92-87-5	25	40
6.	carbon tetrachloride	624	56-23-5	1	5
7.	chlorobenzene	624	108-90-7	1	5
8.	1,2,4-trichlorobenzene	625	120-82-1	10	10
9.	hexachlorobenzene	625	118-74-1	10	10
10.	1,2-dichloroethane	624	107-06-2	1	1
11.	1,1,1-trichloroethane	624	71-55-6	1	5
12.	hexachloroethane	625	67-72-1	10	10
13.	1,1-dichloroethane	624	75-34-3	1	5
14.	1,1,2-trichloroethane	624	79-00-5	1	5
15.	1,1,2,2-tetrachloroethane	624	79-34-5	1	10
16.	chloroethane	624	75-00-3	1	10
17.	bis(2-chloroethyl)ether	625	111-44-4	10	10
18.	2-chloroethyl vinyl ether	624	110-75-8	1	10
19.	2-chloronaphthalene	625	91-58-7	10	10

*NOTE: Wherever the term "priority pollutant(s)" is used in this contract and in any references cited in this contract, it is intended to mean "Hazardous Substances List (HSL) Compound(s)," which include all compounds listed in this Exhibit.

**NOTE: Specific detection limits are highly matrix dependent. The detection limits listed herein are provided for guidance and may not always be achievable.

	Parameter (ug/l)	Method No.	CAS #	Detection Limit Medium Level ug/g or ug/ml	Low Level ug/l
43.	bis(2-chloroethoxy)-methane	625	111-91-1	10	20
44.	methylene chloride	624	75-09-2	1	5
45.	chloromethane	624	74-87-3	1	10
46.	bromomethane	624	74-83-9	1	10
47.	bromoform	624	75-25-2	1	10
48.	bromodichloromethane	624	75-27-4	1	5
51.	chlorodibromomethane	624	124-48-1	1	5
52.	hexachlorobutadiene	625	87-68-3	10	10
53.	hexachlorocyclopentadiene	625	77-47-4	10	10
54.	isophorone	625	78-59-1	10	10
55.	naphthalene	625	91-20-3	10	10
56.	nitrobenzene	625	98-95-3	10	10
57.	2-nitrophenol	625	88-75-5	10	20
58.	4-nitrophenol	625	100-02-7	90	50
59.	2,4-dinitrophenol	625	51-28-5	40	50
60.	4,6-dinitro-2-methylphenol	625	534-52-1	20	20
61.	N-nitrosodimethylamine	625	62-75-9		
62.	N-nitrosodiphenylamine	625	86-30-6	10	10
63.	N-nitrosodipropylamine	625	621-64-7	10	10
64.	pentachlorophenol	625	87-86-5	25	10
65.	phenol	625	108-95-2	10	10
66.	bis(2-ethylhexyl)phthalate	625	117-81-7	10	10
67.	benzyl butyl phthalate	625	85-68-7	10	10

	Parameter (ug/l)	Method No.	CAS #	Detection Limit Medium Level ug/g or ug/ml	Detection Limit Low Level ug/L
68.	di-n-butyl phthalate	625	84-74-2	10	10
69.	di-n-octyl phthalate	625	117-84-0	10	10
70.	diethyl phthalate	625	84-66-2	10	10
71.	dimethyl phthalate	625	131-11-3	10	10
72.	benzo(a)anthracene	625	56-55-3	10	10
73.	benzo(a)pyrene	625	50-32-8	10	20
74.	benzo (b) fluoranthene	625	205-99-2	25	20
75.	benzo(k)fluoranthene	625	207-08-9	10	20
76.	chrysene	625	218-01-9	10	20
77.	acenaphthylene	625	208-96-8	10	10
78.	anthracene	625	120-12-7	10	10
79.	benzo(ghi)perylene	625	191-24-2	25	20
80.	fluorene	625	86-73-7	10	10
81.	phenanthrene	625	85-01-8	25	10
82.	dibenzo(ah)anthracene	625	53-70-3	25	20
83.	indeno(1,2,3-cd)pyrene	625	193-39-5	25	20
84.	pyrene	625	129-00-0	25	10
85.	tetrachloroethene	624	127-18-4	1	5
86.	toluene	624	108-88-3	1	5
87.	trichloroethene	624	79-01-6	1	5
88.	vinyl chloride	624	75-01-4	1	10
89.	2,3,7,8-tetrachlorodibenzo -p-dioxin	613	1746-01-6	0.1	.005
90.	aldrin	608,625*	309-00-2	0.1	.005

*Pesticides and PCB's are verified by Method 625 if detected at levels adequate for analysis by that method.

Revised 12/83

	Parameter (ug/l)	Method No.	CAS #	Detection Limit Medium Level ug/g or ug/m.	Low Level ug/L
91.	dieldrin	608,625*	60-57-1	0.1	.005
92.	chlordane	608,625*	57-74-9	0.1	.050
93.	4,4'-DDT	608,625*	50-29-3	0.1	.010
94.	4,4'-DDE	608,625*	72-55-9	0.1	.005
95.	4,4'-DDD	608,625*	72-54-8	0.1	.010
96.	endosulfan I	608,625*	115-29-7	0.1	.005
97.	endosulfan II	608,625*	115-29-7	0.1	.005
98.	endosulfan sulfate	608,625*	1031-07-8	0.1	.010
99.	endrin	608,625*	72-20-8	0.1	.005
100.	endrin aldehyd	608,625*	7421-93-4	0.1	.010
101.	heptachlor	608,625*	76-44-8	0.1	.005
102.	heptachlor epoxide	608,625*	1024-57-3	0.1	.005
103.	a-BHC	608,625*	319-84-6	0.1	.005
104.	b-BHC	608,625*	319-85-7	0.1	.005
105.	d-BHC	608,625*	319-86-8	0.1	.005
106.	g-BHC (lindane)	608,625*	58-89-9	0.1	.005
107.	toxaphene	608,625*	8001-35-2	0.4	.050
108.	PCB-1016	608,625*	12674-11-2	0.1	.050
109.	PCB-1221	608,625*	11104-28-2	0.1	.100
110.	PCB-1232	608,625*	11141-16-5	0.1	.100
111.	PCB-1242	608,625*	53469-21-9	0.1	.050
112.	PCB-1248	608,625*	12672-29-6	0.1	.100
113.	PCB-1254	608,625*	11097-69-1	0.1	.100
114.	PCB-1260	608,625*	11096-82-5	0.1	.200

*Pesticides and PCB's are verified by Method 625 if detected at levels adequate for analysis by that method.

Revised 12/83

	Parameter (ug/l)	Method No.	CAS #	Detection Limit Medium Level ug/g or ug/ml	Detection Limit Low Level ug/L
115.	acetone	624	67-64-1	1	5
116.	aniline	625	62-53-3	1	5
117.	benzoic acid	625	65-85-0	90	100
118.	benzyl alcohol	625	100-51-6	10	20
119.	2-butanone	624	78-93-3	1	5
120.	carbondisulfide	624	75-15-0	0.5	1
121.	4-chloroaniline	625	106-47-8	50	50
122.	dibenzofuran	625	132-64-9	5	10
123.	2-hexanone	624	519-78-6	1	5
124.	2-methylnaphthalene	625	91-57-6	10	20
125.	4-methyl-2-pentanone	624	108-10-1	1	5
126.	2-methylphenol	625	95-48-7	1	5
127.	4-methylphenol	625	108-39-4	1	5
128.	2-nitroaniline	625	88-74-4	90	100
129.	3-nitroaniline	625	99-09-2	70	100
130.	4-nitroaniline	625	100-01-6	100	100
131.	styrene	624	100-42-5	1	5
132.	2,4,5-trichlorophenol	625	95-95-4	100	100
133.	vinyl acetate	624	108-05-4	1	5
134.	o-xylene	624	95-47-6	1	5

Revised 12/83

APPENDIX B.6

EPA Method 624

Purgeables—Method 624

1. *Scope and Application.*

1.1 This method is designed to determine volatile organic materials that are amenable to the purge and trap method. The parameters listed in Table 1 may be determined by this method.

1.2 This method is applicable to the determination of these compounds in municipal and industrial discharges. It is designed to be used to meet the monitoring requirements of the National Pollutants Discharge Elimination System (NPDES).

1.3 The detection limit of this method is usually dependent upon the level of interferences rather than instrumental limitations. The limits listed in Table 2 represent sensitivities that can be achieved in wastewaters.

1.4 The GC/MS parts of this method are recommended for use only by persons experienced in GC/MS analysis or under the close supervision of such qualified persons.

1.5 The trapping and chromatographic procedures described do not apply to the very volatile pollutant, dichlorodifluoromethane. An alternative three stage trap containing charcoal is to be used if this compound is to be analyzed. See EPA Method 601 and Reference 1. Primary ion for quantitative analysis of this compound is 101. The secondary ions are 85, 87, and 103.

1.6 Although this method can be used for measuring acrolein and acrylonitrile, the purging efficiencies are low and erratic. For a more reliable quantitative analysis of these compounds, use direct aqueous injection (Ref. 4–6) or EPA Method 603, Acrolein and Acrylonitrile, EMSL, Cincinnati, Ohio.

2. *Summary of Method.*

2.1 A sample of wastewater is purged with a stream of inert gas. The gas is bubbled through a 5 ml water sample contained in a specially designed purging chamber. The volatile organics are efficiently transferred from the aqueous phase into the gaseous phase where they are passed through a sorbent bed designed to trap out the organic volatiles. After purging is complete, the trap is backflushed while being rapidly heated in order to thermally desorb the components into the inlet of a gas chromatograph. The components are separated via the gas chromatograph and detected using a mass spectrometer which is used to provide both qualitative and quantitative information. The chromatographic conditions as well as typical mass spectrometer operating parameters are given.

3. *Interferences.*

3.1 Interferences coextracted from the samples will vary considerably from source to source, depending upon the diversity of the industrial complex or municipality being sampled. Impurities in the purge gas and organic compounds out-gassing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Method blanks are run by charging the purging device with organic-free water and analyzing it in a normal manner. The use of non-TFE plastic tubing, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride) through the septum seal into the sample during shipment and storage. A field blank prepared from organic-free water and carried through the sampling and handling protocol can serve as a check on such contamination.

3.3 Cross contamination can occur whenever high level and low level samples are sequentially analyzed. To reduce cross contamination, it is recommended that the purging device and sample syringe be rinsed out twice, between samples, with organic-free water. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of organic-free water to check for cross-contamination. For samples containing large amounts of water soluble materials, suspended solids, high boiling compounds, or high organochlorine levels, it may be necessary to wash out the purging device with a soap solution, rinse with distilled water, and then dry in a 105°C oven between analyses.

4. *Apparatus and Materials.*

4.1 Sampling equipment, for discrete sampling.

4.1.1 Vial, with cap—40 ml capacity screw cap (Pierce #13075 or equivalent). Detergent wash and dry vial at 105°C for one hour before use.

4.1.2 Septum—Teflon-faced silicone (Pierce #12722 or equivalent). Detergent wash and dry at 105°C for one hour before use.

4.2 Purge and trap device—The purge and trap equipment consists of three separate pieces of apparatus: a purging device, a trap, and a desorber. The complete device is available commercially from several vendors or can be constructed in the laboratory according to the specifications of Bellar and Lichtenberg (Ref. 2,3). The sorbent trap consists of ¼ in. O.D. (0.105 in. I.D.) x 25 cm long stainless steel tubing packed with 15 cm of Tenax-GC (60–80 mesh) and 8 cm of Davison Type-15 silica gel (35–60 mesh). See figures 1 through 4. Ten cm³ purge traps may be used providing that the recoveries are comparable to the 25 cm³ trap.

4.3 Gas chromatograph—Analytical system complete with a temperature programmable gas chromatograph suitable for on-column injection and all required accessories including an analytical column.

4.3.1 Column 1—An 8 ft. stainless steel column (⅛ in. OD x 0.90 to 0.105 in. ID) packed with 1% SP-1000 coated on 60/80 mesh Carbopack B preceded by a 6-cm precolumn packed with 1% SP-1000 coated on 60/80 mesh Chromosorb W. A glass column (⅛ in. OD x 2 mm ID) may be substituted. The precolumn is necessary only during conditioning.

4.3.2 Column 2—An 8 ft. stainless steel column (⅛ in. OD x 0.09 to 0.105 in. ID) packed with 0.2% Carbowax 1500 coated on 80/80 mesh Carbopack C preceded by a 1 ft. stainless steel column (⅛ in. OD x 0.09 to 0.105 in. ID) packed with 3% Carbowax 1500 coated on 60/80 mesh Chromosorb W. A glass column (⅛ in. OD x 2 mm ID) may be substituted. The precolumn is necessary only during conditioning.

4.4 Syringes—glass, 5-ml hypodermic with Luer-Lok tip (3 each).

4.5 Micro syringes—10, 25, 100 µl.

4.6 2-way syringe valve with Luer ends (3 each, Teflon or Kel-F).

4.7 Syringe—5 ml gas-tight with shut-off valve.

4.8 8-inch, 20-gauge syringe needle—One per each 5-ml syringe.

4.9 Mass Spectrometer—capable of scanning from 20–350 in not seconds or less at 70 volts (nominal), and producing a recognizable mass spectrum at unit resolution from 50 ng of DFTPP when injected through the GC inlet. The mass spectrometer must be interfaced with a gas chromatograph equipped with an all-glass, on-column injector system designed for packed column analysis. All sections of the transfer lines must be glass or glass-lined and deactivated. Use Sylon-CT, Supelco, (or equivalent) to deactivate. The GC/MS interface may utilize any separator that gives recognizable mass spectra (background corrected) and acceptable calibration points at the limit of detection specified for each compound in Table 2.

4.10 A computer system should be interfaced to the mass spectrometer to allow acquisition of continuous mass scans for the duration of the chromatographic program. The computer system should also be equipped with mass storage devices for saving all data from GC–MS runs. There must be

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computer software available to allow searching any GC/MS run for specific ions and plotting the intensity of the ions with respect to time or scan number. The ability to integrate the area under a specific ion plot peak is essential for quantification.

5. *Reagents.*

5.1 Sodium thiosulfate—(ACS) Granular.

5.2 Trap Materials

5.2.1 Porous polymer packing 60/80 mesh chromatographic grade Tenax GC (2,6-diphenylene oxide).

5.2.3 Silica gel-(35–60 mesh)—

5.2.2 Three percent OV–1 on Chromosorb-W 60/80 mesh. Davison, grade-15 or equivalent.

5.3 Activated carbon—Filtrasorb-200 (Calgon Corp.) or equivalent.

5.4 Organic-free water

5.4.1 Organic-free water is defined as water free of interference when employed in the purge and trap procedure described herein. It is generated by passing tap water or well water through a carbon filter bed containing about 1 lb. of activated carbon.

5.4.2 A water system (Millipore Super-Q or equivalent) may be used to generate organic-free deionized water.

5.4.3 Organic-free water may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the temperature at 90°C, bubble a contaminant-free inert gas through the water for one hour. While still hot, transfer the water to a narrow mouth screw cap bottle equipped with a Teflon seal.

5.5 Stock standards (2 mg/ml)—Prepare stock standard solutions in methanol using assayed liquids or gases as appropriate. Because of the toxicity of some of the organochlorides, primary dilutions of these materials should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of such materials.

5.5.1 Place about 9.8 ml of methanol into a 10 ml ground glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes or until all alcohol wetted surfaces have dried. Tare the flask to the nearest 0.1 mg.

5.5.2 Add the assayed reference material:

5.5.2.1 Liquids—using a 100 µl syringe, immediately add 2 to 3 drops of assayed reference material to the flask. Then reweigh. Be sure that the drops fall directly into the alcohol without contacting the neck of the flask.

5.5.2.2 Gases—To prepare standards of bromomethane, chloroethane, chloromethane, and vinyl chloride, fill a 5-ml valved gas-tight syringe with the reference standard to the 5.0-ml mark. Lower the needle to 5 mm above the methyl alcohol meniscus. Slowly inject the reference standard into the neck of the flask (the heavy gas will rapidly dissolve into the methyl alcohol).

5.5.3 Reweigh the flask, dilute to volume, stopper, then mix by inverting the flask several times. Transfer the standard solution to a 15-ml screw-cap bottle equipped with a Teflon cap liner.

5.5.4 Calculate the concentration in mg per ml (equivalent to µg per µl) from the net gain in weight.

5.5.5 Store stock standards at 4° C. Prepare fresh standards every second day for the four gases and 2-chloroethylvinyl ether. All other standards must be replaced with fresh standards each week.

5.6 Surrogate Standard Dosing Solution—From stock standard solutions prepared as above, add a volume to give 1000 µg each of bromochloromethane, 2-bromo-1-chloropropane, and 1,4-dichlorobutane to 40 ml of organic-free water contained in a 50-ml volumetric flask, mix and dilute to volume. Prepare a fresh surrogate standard dosing solution weekly. Dose the surrogate standard mixture into every 5-ml sample and reference standard analyzed.

6. *Calibration.*

6.1 Using the stock standards, prepare secondary dilution standards of the compounds of interest, either singly or mixed together in methanol. The standards should be at concentrations such that the aqueous standards prepared in 6.2 will bracket the working range of the chromatographic system. If the limit of detection listed in Table 2 is 10 µg/l, for example, prepare secondary methanolic standards at 100 µg/l, and 500 µg/l, so that aqueous standards prepared from these secondary calibration standards, and the primary standards, will define the linearity of the detector in the working range.

6.2 Using both the primary and secondary dilution standards, prepare calibration standards by carefully adding 20.0 µl of the standard in methanol to 100, 500, or 1000 ml of organic-free water. A 25 µl syringe (Hamilton 702N or equivalent) should be used for this operation. These aqueous standards must be prepared fresh daily.

6.3 Assemble the necessary gas chromatographic and mass spectrometer apparatus and establish operating parameters equivalent to those indicated in Table 2. By injecting secondary dilution standards, establish the linear range of the analytical system for each compound and demonstrate that the analytical system meets the limit of detection requirements in Table 2.

6.4 Assemble the necessary purge and trap device. Pack the trap as shown in Figure 2 and condition overnight at a nominal 180° C by backflushing with an inert gas flow of at least 20 ml/min. Daily, prior to use, condition the traps for 10 minutes by backflushing at 180° C. Analyze aqueous calibration standards (6.2) according to the purge and trap procedure in Section 9. Compare the responses to those obtained by injection of standards (6.3), to determine the analytical precision. The analytical precision of the analysis of aqueous standards must be comparable to data presented by Bellar and Lichtenberg (1978, Ref. 1) before reliable sample analysis may begin.

6.5 Internal Standard Method—The internal standard approach is acceptable for the purgeable organics. The utilization of the internal standard method requires the periodic determination of response factors (RF) which are defined in equation 1.

Eq. (1) $RF = (A_s C_{is})/(A_{is} C_s)$

Where:

A_s is the integrated area or peak height of the characteristic ion for the priority pollutant standard.

A_{is} is the integrated area or peak height of the characteristic ion for the internal standard.

C_{is} is the amount of the internal standard in ng.

C_s is the amount of the pollutant standard in ng.

The relative response ratio for each pollutant should be known for at least two concentration values—50 ng injected to approximate 10 µg/l and 500 ng to approximate the 100 µg/l level. Those compounds that do not respond at either of these levels may be run at concentrations appropriate to their response. The response factor (RF) must be determined over all concentration ranges of standard (C_s) which are being determined. (Generally, the amount of internal standard added to each extract is the same so that C_{is} remains constant.) This should be done by preparing a calibration curve where the response factor (RF) is plotted against the standard concentration (C_s). Use a minimum of three concentrations over the range of interest. Once this calibration curve has been determined, it should be verified daily by injecting at least one standard solution containing internal standard. If significant drift has occurred, a new calibration curve must be constructed.

Note—EPA, through its contractors and certain of its Regional Laboratories, is currently evaluating selected compounds for

use as internal standards in the analysis of organics by purge and trap.

6.6 The external standard method can also be used at the discretion of the analyst. Prepare a master calibration curve using a minimum of three standard solutions of each of the compounds that are to be measured. Plot concentrations versus integrated areas or peak heights (selected characteristic ion for GC/MS). One point on each curve should approach the method detection limit. After the master set of instrument calibration curves have been established, they should be verified daily by injecting at least one standard solution. If significant drift has occurred, a new calibration curve must be constructed.

7. Quality Control.

7.1 Before processing any samples, the analyst should daily demonstrate, through the analysis of an organic-free water method blank, that the entire analytical system is interference-free.

7.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the accuracy of the analysis.

7.3 The analyst should maintain constant surveillance of both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix by determining the precision of the method in blank water and spiking each 5-ml sample, standard, and blank with surrogate halocarbons.

7.3.1 Determine the precision of the method by dosing blank water with the compounds selected as surrogate standards—bromochloromethane, 2-bromo-1-chloropropane, and 1,4-dichlorobutane—and running replicate analyses. Calculate the recovery and its standard deviation. These compounds represent early, middle, and late eluters over the range of the pollutant compounds.

7.3.2 The sample matrix can affect the purging efficiencies of individual compounds; therefore, each sample must be dosed with the surrogate standards and analyzed in a manner identical to the internal standards in blank water. If the recovery of the surrogate standard shows a deviation greater than two standard deviations (7.3.1), repeat the dosed sample analyses. If the deviation is again greater than two standard deviations, dose another aliquot of the same sample with the compounds of interest at approximately two times the measured values and analyze. Calculate the recovery for the individual compounds using these data.

8. Sample Collection, Preservation, and Handling.

8.1 Grab samples must be collected in glass containers having a total volume greater than 20 ml. Fill the sample bottles in such a manner that no air bubbles pass through the sample as the bottle is being filled. Seal the bottles so that no air bubbles are entrapped in it. Maintain the hermetic seal on the sample bottle until time of analysis.

8.2 The sample must be iced or refrigerated from the time of collection until extraction. If the sample contains residual chlorine, add sodium thiosulfate preservative (10 mg/40 ml) to the empty sample bottles just prior to shipping to the sample site. Fill with sample just to overflowing, seal the bottle, and shake vigorously for 1 minute.

8.3 All samples must be analyzed within 7 days of collection.

9. Sample Extraction and Gas Chromatography.

9.1 Remove standards and samples from cold storage (approximately an hour prior to an analysis) and bring to room temperature by placing in a warm water bath at 20–25°C.

9.2 Adjust the purge gas (nitrogen or helium) flow rate to 40 ml/min. Attach the trap inlet to the purging device, and set the device to the purge mode. Open the syringe valve located on the purging device sample introduction needle.

9.3 Remove the plunger from a 5 ml syringe and attach a closed syringe valve. Open the sample bottle (or standard) and carefully pour the sample into the syringe barrel until it overflows. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 ml. Since this process of taking an aliquot destroys the validity of the sample for future analysis, the analyst should fill a second syringe at this time to protect against possible loss of data. Add 5.0 µl of the surrogate spiking solution (7.3) through the valve bore, then close the valve.

9.4 Attach the syringe-valve assembly to the syringe valve on the purging device. Open the syringe valve and inject the sample into the purging chamber.

9.5 Close both valves and purge the sample for 12.0 ± .05 minutes.

9.6 After the 12-minute purge time, attach the trap to the chromatograph, and adjust the device to the desorb mode. Introduce the trapped materials to the GC column by rapidly heating the trap to 180°C while backflushing the trap with an inert gas at 20 to 60 ml/min for 4 minutes. If rapid heating cannot be assured, the gas chromatographic column must be used as a secondary trap by cooling it to 30°C (or subambient, if problems persist) instead of the initial program temperature of 45°C.

9.7 While the trap is being desorbed into the gas chromatograph, empty the purging chamber using the sample introduction syringe. Wash the chamber with two 5-ml flushes of organic-free water. After the purging device has been emptied, continue to allow the purge gas to vent through the chamber until the frit is dry, and ready for the next sample.

9.8 After desorbing the sample for four minutes, recondition the trap by returning the purge and trap device to the purge mode. Wait 15 seconds then close the syringe valve on the purging device to begin gas flow through the trap. Maintain the trap temperature at 180°C. After approximately seven minutes, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When cool, the trap is ready for the next sample. (Note: If this bake out step is omitted, the amount of water entering the GC/MS system will progressively increase causing deterioration of and potential shut down of the system.)

9.9 The analysis of blanks is most important in the purge and trap technique since the purging device and the trap can be contaminated by residues from very concentrated samples or by vapors in the laboratory. Prepare blanks by filling a sample bottle with organic-free water that has been prepared by passing distilled water through a pretested activated carbon column. Blanks should be sealed, stored at 4°C, and analyzed with each group of samples.

10. Gas Chromatography—Mass Spectrometry.

10.1 Table 2 summarizes the recommended gas chromatographic column materials and operating conditions for the instrument. Included in this table are estimated retention times and sensitivities that should be achieved by this method. An example of the separation achieved by Column 1 is shown in Figure 3.

10.2 GC–MS Determination—Suggested analytical conditions for determination of the pollutants amenable to purge and trap, using the Tekmar LCS–1 and GC/MS are given below. Operating conditions vary from one system to another; therefore, each analyst must optimize the conditions for each purge and trap and GC/MS system.

10.3 Purge Parameters.

Sample size—5.0 ml.
Purge gas—Helium high purity grade.
Purge time—12 minutes.
Purge flow—40 ml/min.
Trap dimensions—⅛ in. O.D. (0.105 in. I.D.) x 25 cm long.
Trap sorbent—Tenax-GC, 60/80 mesh (15 cm), plus Type 15 silica gel, 35/80 mesh (8 cm).
Desorption flow—20 ml/min.
Desorption time—4 min.
Desorption temperature—180° C.

10.4 Mass Spectrometer Parameters.

Electron energy—70 volts (nominal).
Mass range—20–27, 33–260 amu.
Scan time—6 seconds or less.

10.5 Calibration of the gas chromatography-mass spectrometry (GC–MS system—Evaluate the system performance each day that it is to be used for the analysis of samples or blanks by examining the mass spectrum of DFTPP or BFB.

10.5.1 To use DFTPP, remove the analytical column and substitute a column more appropriate to the boiling point of the reference compound (e.g. 3% SP–2250 on Supelcoport). Inject a solution containing 50 ng DFTPP and check to insure that the performance criteria listed in Table 3 are met.

10.5.2 To use BFB, inject a solution containing 20 ng BFB and check to insure that the performance criteria listed in Table 4 are met.

10.5.3 If the system performance criteria are not met for either test, the analyst must retune the spectrometer and repeat the performance check. The performance criteria must be met before any samples or standards may be analyzed.

10.6 Analyze an internal or external calibration standard to develop response factors for each compound.

11. *Qualitative and Quantitative Determination.*

11.1 To qualitatively identify a compound, obtain an Extracted Ion Current Profile (EICP) for the primary ion and at least two other ions (if available) listed in Table 5. The criteria below must be met for a qualitative identification.

11.1.1 The characteristic ions for the compound must be found to maximize in the same or within one spectrum of each other.

11.1.2 The retention time at the experimental mass spectrum must be within ±30 seconds of the retention time of the authentic compound.

11.1.3 The ratios of the three EICP peak heights must agree within ±20% with the ratios of the relative intensities for these ions in a reference mass spectrum. The reference mass spectrum can be obtained from either a standard analyzed through the GC–MS system or from a reference library.

11.1.4 Structural isomers that have very similar mass spectra can be explicitly identified only if the resolution between the isomers in a standard mix is acceptable. Acceptable resolution is achieved if the valley height between isomers is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

11.2 The primary ion listed in Table 5 is to be used to quantify each compound. If the sample produces an interference for the primary ion, use a secondary ion to quantify.

11.3 For low concentrations, or direct aqueous injection of acrylonitrile and acrolein, the characteristic masses listed for the compounds in Table 5 may be used for selected ion monitoring (SIM). SIM is the use of a mass spectrometer as a substance selective detector by measuring the mass spectrometric response at one or several characteristic masses in real time.

11.4 Internal Standard Method Calculations—By adding a constant known amount of internal standard (C_{is} in μg) to every sample extract, the concentration of the pollutant (C_x) in μg/l in the sample is calculated using equation 2.

$$\text{Eq. 2 } C_x = \frac{(A_x)(C_{is})}{(A_{is})(V_o)}$$

Where:

V_o is the volume of the original sample in liters, and the other terms are defined as in Section 6.5. To quantify, add the internal standard to the 5.0 ml sample no more than a few minutes before purging to minimize the possibility of losses due to evaporation, adsorption, or chemical reaction. Calculate the concentrations by using the previous equations with the appropriate response factor taken from the calibration curve.

11.5 External Standard Method Calculations—The concentration of the unknown can be calculated from the slope and intercept of the multiple point calibration curve. The unknown concentration can be determined using equation 3.

$$\text{Eq. 3 micrograms per liter} = \text{ng/ml} = \frac{(A)}{(V_o)}$$

Where:

A = Mass of compound from calibration curve (ng/5 ml).

V_o = volume of water purged (5 ml).

11.6 An alternate external standard approach for purgeables utilizes a single point calibration. Prepare and analyze a reference standard that closely approximates the response for each component in a sample. Calculate the concentration in the sample using Equation 4.

$$\text{Eq. 4 micrograms per liter} = \frac{(A)(B)}{(C)}$$

Where:

A = area of the unknown
B = concentration of standard (μg/l)
C = area of the standard.

11.7 Report all results to two significant figures. When duplicate and spiked samples are analyzed, all data obtained should be reported. Report results in micrograms per liter without correction for recovery data.

12. *References.*

1. "The Analysis of Halogenated Chemical Indicators of Industrial Contamination in Water by the Purge and Trap Method." U.S. EPA, Environmental Monitoring and Support Laboratory, Cincinnati, OH, 45268, Dec. 1978.

2. "Symposium on Measurement of Organic Pollutants in Water and Wastewater." ASTM Special Publication, 1979 (In Press).

3. "Determining Volatile Organics at Microgram-per-Liter Levels by Gas Chromatography," T. A. Bellar and J. J. Lichtenberg, *Jour. AWWA*, 66, 739–744, Dec. 1974.

4. ASTM Annual Standards—Water, part 31, Method D3508 "Standard Recommended Practice for Measuring Water by Aqueous-Injection Gas Chromatography."

5. ASTM Annual Standards—Water, part 31, Method D3371 "Tentative Method of Test for Nitriles in Aqueous Solution of Gas Liquid Chromatograph."

6. "Direct Analysis of Water Samples for Organic Pollutants with Gas Chromatography-Mass Spectrometry," Harris, L. E., Budde, W. L., and Eichelberger, J. W., *Anal. Chem.*, 46, 1912 (1974).

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2. "Proceedings: Seminar on Analytical Methods for Priority Pollutants," Volume 1—Denver, Colorado, November 1977; Volume 2—Savannah, Georgia, May 1978; Volume 3—Norfolk, Virginia, March 1979, USEPA, Effluent Guidelines Division, Washington, D.C. 20460.

Table 1

Parameter	STORET No.
Acrolein	
Acrylonitrile	
Benzene	
Bromoform	
Bromodichloromethane	
Bromomethane	
Carbon tetrachloride	
Chlorobenzene	
Chloroethane	
2-Chloroethyl vinyl ether	
Chloroform	
Chloromethane	
Dibromochloromethane	
1,2-Dichloroethane	

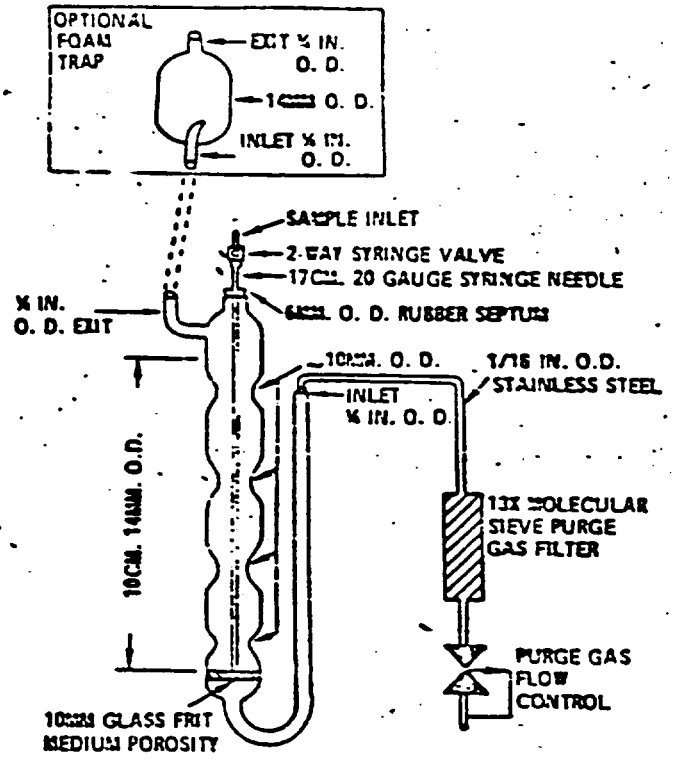

Figure 1. Purging device

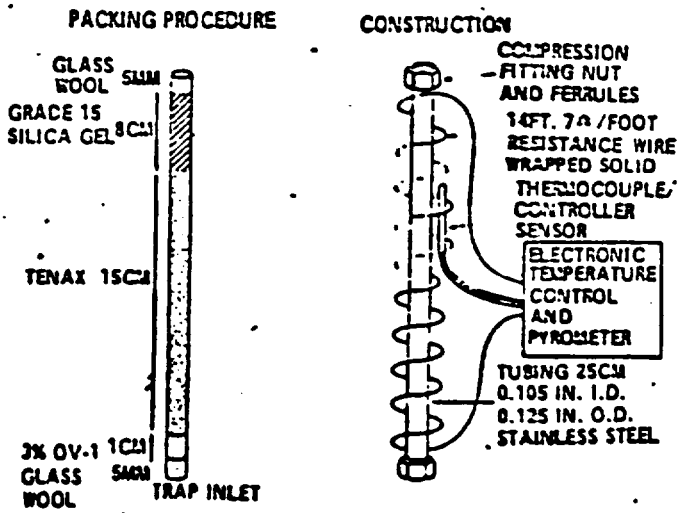

Figure 2. Trap packings and construction to include desorb capability

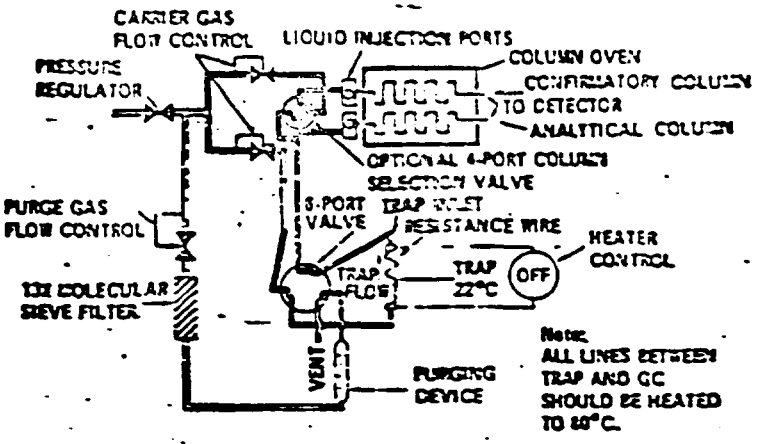

Figure 3. Schematic of purge and trap device - purge mode

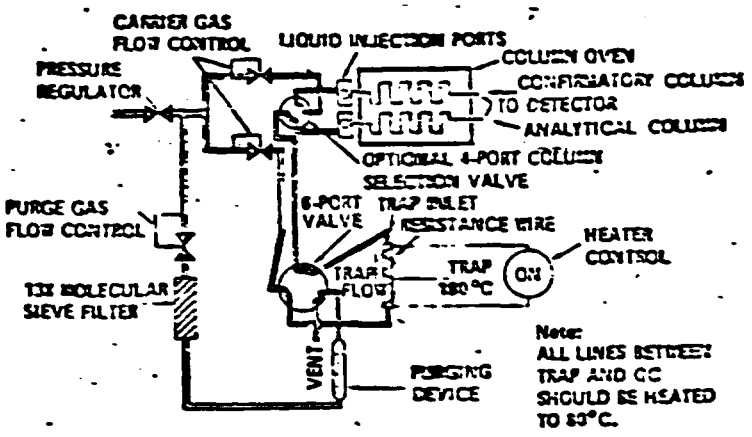

Figure 4. Schematic of purge and trap device - desorb mode

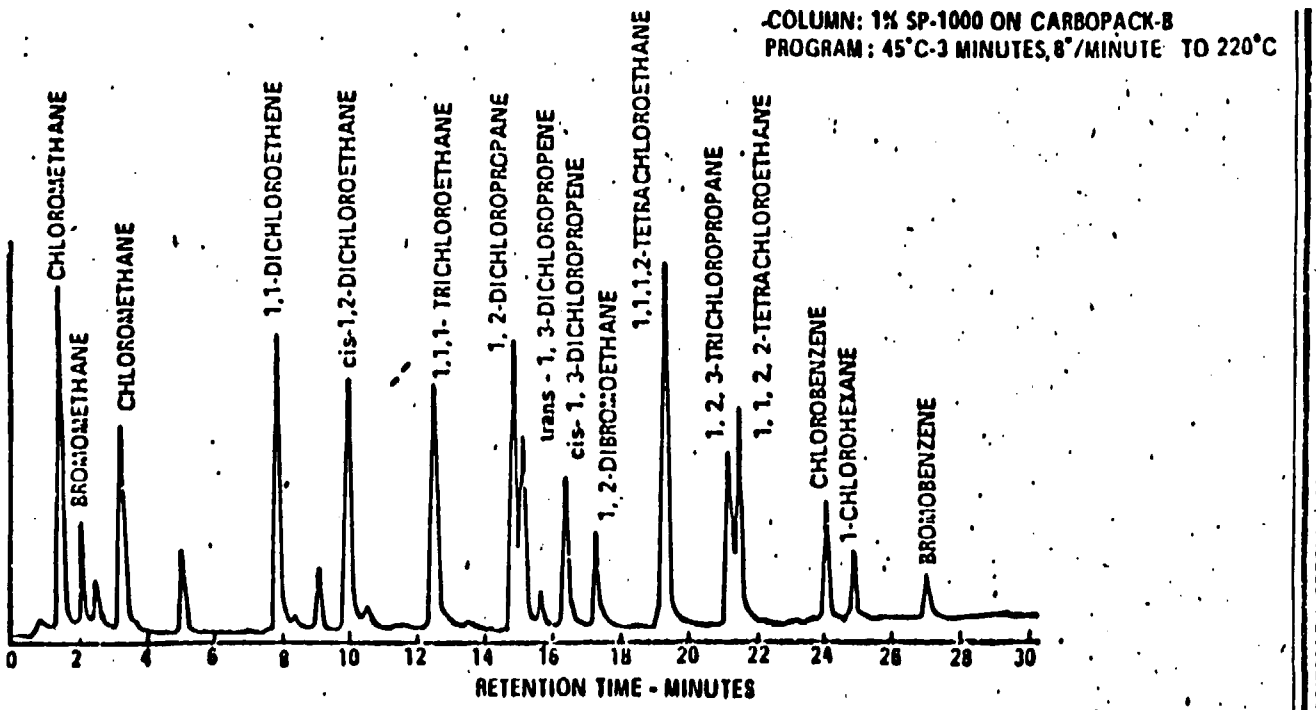

Figure 5. Gas chromatogram of volatile organics by purge and trap

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APPENDIX B.7

Modified EMSL-Ci VOA Procedure

Appendix B.7
Modified EMSL-Ci Procedure

Modified EMSL-Ci Procedure to be Used for Low Levels of VOAs in Soils and Sediments

The procedure that shall be used in this study is a modification of the Purgeable-Method 624, page 69532, Federal Register, Monday, December 3, 1979, Part III. The modifications were proposed by J. M. Blazevich, Region X. The modifications to the Federal Register procedures are:

1. The purging chamber is a modified 40 mL screw top vial (Figure 1).

2. The soil or sediment sample is prepared as follows:

   Transfer 10 gm of the soil or sediment to the purge chamber and add 10 mL of organic-free water containing the internal standard to the sample. Attach the purge chamber to the purge and trap system.

3. Heat the chamber to 55°C and maintain this temperature while purging for 12.0 ± 0.05 minutes.

4. Proceed as specified in the above cited Federal Register procedure.

Purge and trap recoveries on spike sediment samples averaged 80 percent with an average coefficient of variation of 30 percent (Table I).

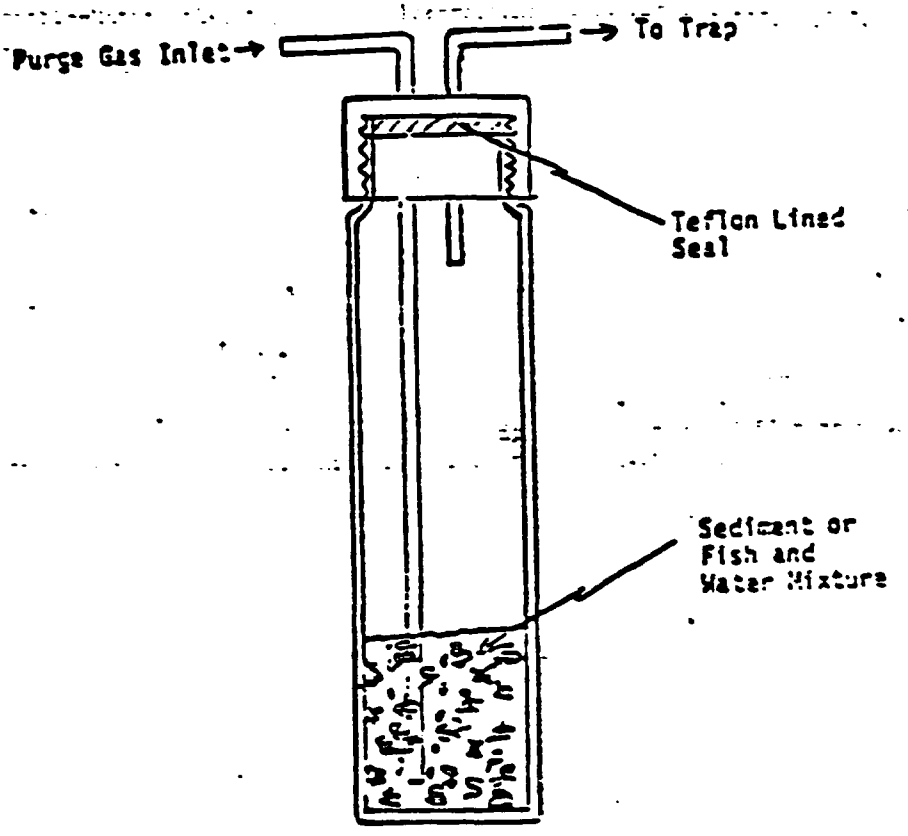

Figure 1.

Soil VOA Purging

11.4 The sample in the purging device is purged with helium to transfer the volatile components to the trap. The trap is then heated to desorb the volatile components which are swept by the helium carrier gas onto the GC column for analysis.

11.4.1 Adjust the gas (helium) flow rate to 40 ± 3 mL/min. Set the purging device to purge and purge the sample for 11.0 ± 0.1 minutes at ambient temperature.

11.4.2 At the conclusion of the purge time, adjust the device to the desorb mode, and begin the GC/MS analysis and data acquisition using the following GC operating conditions:

Column - 6 ft x 2 mm ID glass column packed with 1% SP-1000 on Carbopack B (60-80 mesh)

Temperature - Isothermal at 45°C for 3 minutes, then increased at 8°C per minute to 250°C, and maintained at 250°C for 15 minutes.

Concurrently, introduce the trapped materials to the GC column by rapidly heating the trap to 180°C while backflushing the trap with helium at a flow rate of 30 mL/min for 4 minutes. If this rapid heating requirement cannot be met, the GC column must be used as a secondary trap by cooling it to 30°C or lower during the 4-minute desorb step and starting the GC program after the desorb step.

11.4.3 Return the purge trap device to the purge mode and continue acquiring GC/MS data.

11.4.4 Allow the trap to cool for 8 minutes. Replace the purging chamber with a clean purging chamber fitted with a new septum. The purging chamber is cleaned after each use by sequential washing with acetone, methanol, detergent solution, and distilled water and drying at 105°C.

11.4.5 Purge the trap at ambient temperature for 4 minutes. Recondition the trap by heating it to 180°C. Do not allow the trap temperature to exceed 180°C, since the sorption/desorption is adversely affected by heating the trap to higher temperatures. After heating the trap for approximately seven minutes, turn off the trap heater. When cool, the trap is ready for use for the next sample.

11.5 If the response for any ion exceeds the working range of the system, repeat the analysis using a correspondingly smaller aliquot of the sample extract described in Section 11.2.3.

12. Qualitative Identification

12.1 The criteria listed in Exhibit A under Task III must be met to make a qualitative identification. Qualitative identification shall be accomplished by using the procedures listed in Federal Register Method 624.

13. Quantitative Determination

13.1 When a compound has been identified, the quantification of that compound will be accomplished by using procedures listed in Federal Register Method 624.

14. Dry Weight Determination

14.1 Add a portion of the sample to a tared weighing dish. Weigh and record the weight.

14.2 Place weighing dish plus sample, with the cover tipped to allow for moisture escape, in a drying oven that is set at 105°C. Perform this task in a well ventilated area.

14.3 Dry the sample to constant weight. Cool the sample in a dessicator with the weighing dish cover in place before each weighing. Record each weight. Do not analyze the dried sample.

14.4 Calculate and report data on a dry weight basis. Also report the percent moisture for each sample.

15. References

1. Bellar, T. A., and J. J. Lichtenberg, Journal American Water Works Association, 66, 739 (1974).

2. Bellar, T. A., and J. J. Lichtenberg, "Semi-Automated Headspace Analysis of Drinking Waters and Industrial Waters for Purgeable Volatile Organic Compounds", Measurement of Organic Pollutants in Water and Wastewater, C. E. Van Hall, editor, American Society for Testing and Materials, Philadelphia, PA. Special Technical Publications 686, 1978.

3. "Carcinogens—Working With Carcinogens", Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute of Occupational Safety and Health, Publications No. 77-206, August 1977.

4. "OSHA Safety and Health Standards, General Industry", (29CFR 1910), Occupational Safety and Health Administration, OSHA 2206, (Revised, January 1976).

5. "Safety in Academic Chemistry Laboratories", American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

APPENDIX B.8

EPA Method 625

Base/Neutrals, Acids, and Pesticides—Method 625

1. *Scope and Application.*

1.1 This method covers the determination of a number of organic compounds that are solvent extractable and amenable to gas chromatography. The parameters listed in Tables 1, 2 and 3 may be determined by this method.

1.2 This method is applicable to the determination of these compounds in municipal and industrial discharges. It is designed to be used to meet the monitoring requirements of the National Pollutants Discharge Elimination System (NPDES).

1.3 The detection limit of this method is usually dependent upon the level of interferences rather than instrumental limitations. The limits listed in Tables 4, 5, and 6 represent the minimum quantity that must be injected into the system to get confirmation by the mass spectrometric method described below.

1.4 The GC/MS parts of this method are recommended for use only by analysts experienced with GC/MS or under the close supervision of such qualified persons.

2. *Summary of Method.*

2.1 A 1 to 2 liter sample of wastewater is extracted with methylene chloride using separatory funnel or continuous extraction techniques. If emulsions are a problem, continuous extraction techniques should be used. The extract is dried over sodium sulfate and concentrated to a volume of 1 ml using a Kuderna-Danish (K–D) evaporator. Chromatographic conditions are described which allow for the separation of the compounds in the extract.

2.2 Quantitative analysis is performed by GC/MS using either the internal standard or external standard technique.

3. *Interferences.*

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences coextracted from the samples will vary considerably from source to source, depending upon the diversity of the industrial complex or municipality being sampled.

3.3 The recommended analytical procedure may not have sufficient resolution to differentiate between certain isomeric pairs. These are anthracene and phenanthrene, chrysene and benzo(a)anthracene, and benzo(b)fluoranthene and benzo(k)fluoranthene. The GC retention time and mass spectral data are not sufficiently unique to make an unambiguous distinction between these compounds. Alternative techniques should be used to identify and quantify these specific compounds. See Reference 1.

4. *Apparatus and Materials.*

4.1 Sampling equipment, for discrete or composite sampling.

4.1.1 Grab sample bottle—amber glass, 1-liter to 1-gallon volume. French or Boston Round design is recommended. The container must be washed and solvent rinsed before use to minimize interferences.

4.1.2 Bottle caps—Threaded to fit sample bottles. Caps must be lined with *Teflon*. Aluminum foil may be substituted if sample is not corrosive.

4.1.3 Compositing equipment—Automatic or manual compositing system. Must incorporate glass sample containers for the collection of a minimum of 1000 ml. Sample containers must be kept refrigerated during sampling. No plastic or rubber tubing other than Teflon may be used in the system.

4.2 Separatory funnel—2000 ml, with Teflon stopcock (Ace Glass 7228–T–72 or equivalent).

4.3 Drying column—A 20 mm ID pyrex chromatographic column equipped with coarse glass frit or glass wool plug.

4.4 Kuderna-Danish (K–D) Apparatus

4.4.1 Concentrator tube—10 ml, graduated (Kontes K–570050–1025 or equivalent). Calibration must be checked. Ground glass stopper (size 19/22 joint) is used to prevent evaporation of extracts.

4.4.2 Evaporative flask—500 ml (Kontes K–57001–0500 or equivalent). Attach to concentrator tube with springs. (Kontes K–662750–0012).

4.4.3 Snyder column—three-ball macro (Kontes K503000–0232 or equivalent).

4.4.4 Snyder column—two-ball micro (Kontes K–569002–0219 or equivalent).

4.4.5 Boiling chips—extracted, approximately 10/40 mesh.

4.5 Water bath—Heated, with concentric ring cover, capable of temperature control (±2° C). The bath should be used in a hood.

4.6 Gas chromatograph—Analytical system complete with gas chromatograph capable of on-column injection and all required accessories including column supplies, gases, etc.

4.6.1 Column 1—For Base/Neutral and Pesticides a 6-foot glass column (¼ in OD x 2 mm ID) packed with 3% SP–2250 coated on 100/120 Supelcoport (or equivalent).

4.6.2 Column 2—For Acids, a 6-foot glass column (¼ in OD x 2 mm ID) packed with 1% SP–1240 DA coated on 100/120 mesh Supelcoport (or equivalent).

4.7 Mass Spectrometer—Capable of scanning from 35 to 450 a.m.u. every 7 seconds or less at 70 volts (nominal) and producing a recognizable mass spectrum at unit resolution from 50 ng of DFTPP when the sample is introduced through the GC inlet (Reference 2). The mass spectrometer must be interfaced with a gas chromatograph equipped with an injector system designed for splitless injection and glass capillary columns or an injector system designed for on-column injection with all-glass packed columns. All sections of the transfer lines must be glass or glass-lined and must be deactivated. (Use Sylon-CT, Supelco, Inc., or equivalent to deactivate.)

Note.—Systems utilizing a jet separator for the GC effluent are recommended since membrane separators may lose sensitivity for light molecules and glass frit separators may inhibit the elution of polynuclear aromatics. Any of these separators may be used provided that it gives reproducible mass spectra and acceptable calibration points at the limit of detection specified for each individual compound listed in Tables 4, 5, and 6.

4.8 A computer system must be interfaced to the mass spectrometer to allow acquisition of continuous mass scans for the duration of the chromatographic program. The computer system should also be equipped with mass storage devices for saving all data from GC–MS runs. There must be computer software available to allow searching any GC–MS run for specific ions and plotting the intensity of the ions with respect to time or scan number. The ability to integrate the area under any specific ion plot peak is essential for quantification.

4.9 Continuous liquid-liquid extractors—Teflon or glass connecting joints and stopcocks, no lubrication. (Hershberg-Wolf Extractor—Ace Glass Co., Vineland, N.J. P/N 6841–10 or equivalent).

5. *Reagents.*

5.1 Sodium hydroxide—(ACS) 6N in distilled water.

5.2 Sulfuric acid—(ACS) 6N in distilled water.

5.3 Sodium sulfate—(ACS) granular anhydrous (rinsed with methylene chloride (20 ml/g) and conditioned at 400° C for 4 hrs.).

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5.4 Methylene chloride—Pesticide quality or equivalent.

5.5 Stock standards—Obtain stock standard solutions at a concentration of 1.00 µg/µl. For example, dissolve 0.100 grams of assayed reference material in pesticide quality isooctane or other appropriate solvent and dilute to volume in a 100 ml ground glass stoppered volumetric flask. The stock solution is transferred to 15 ml Teflon lined screw cap vials, stored in a refrigerator, and checked frequently for signs of degradation or evaporation, especially just prior to preparing working standards from them. Protect PNA standards from light.

6. *Calibration.*

6.1 Prepare calibration standards that contain the compounds of interest, either singly or mixed together. The standards should be prepared at concentrations that will bracket the working range of the chromatographic system (two or more orders of magnitude are suggested). If the limit of detection (Tables 4, 5, or 6) can be calculated as 20 ng injected, for example, prepare standards at 1 µg/ml, 10 µg/ml, 100 µg/ml, etc. so that injections of 1–5 µl of the calibration standards will define the linearity of the detector in the working range.

6.2 Assemble the necessary gas chromatographic apparatus and establish operating parameters equivalent to those indicated in Tables 4, 5, and 6. By injecting calibration standards, establish the linear range of the analytical system and demonstrate that the analytical system meets the limits of detection requirements of Tables 4, 5, and 6. If the sample gives peak areas above the working range, dilute and reanalyze.

6.3 Internal Standard Method—The internal standard approach is acceptable for all of the semivolatile organics. The utilization of the internal standard method requires the periodic determination of response factors (RF) which are defined in equation 1.

Eq. 1 $RF = (A_s C_{is})/(A_{is} C_s)$

Where:

A_s is the integrated area or peak height of the characteristic ion for the pollutant standard.

A_{is} is the integrated area or peak height of the characteristic ion for the internal standard.

C_{is} is the amount (µg) of the internal standard.

C_s is the amount (µg) of the pollutant standard.

6.3 The relative response ratio for the pollutants should be known for at least two concentration values—20 ng injected to approximate 10 µg/l and 200 ng injected to approximate the 100 µg/l level. (Assuming 1 ml final volume and a 2 µl injection). Those compounds that do not respond at either of these levels may be run at concentrations appropriate to their response.

The response factor (RF) should be determined over all concentration ranges of standard (C_s) which are being determined. (Generally, the amount of internal standard added to each extract is the same (20 µg) so that C_{is} remains constant.) This should be done by preparing a calibration curve where the response factor (RF) is plotted against the standard concentration (C_s) using a minimum of three concentrations over the range of interest. Once this calibration curve has been determined, it should be verified daily by injecting at least one standard solution containing internal standard. If significant drift has occurred, a new calibration curve must be constructed. To quantify, add the internal standard to the concentrated sample extract no more than a few minutes before injecting into the GC/MS to minimize the possibility of losses due to evaporation, adsorption, or chemical reaction. Calculate the concentration by using the previous equations with the appropriate response factor taken from the calibration curve. Either deuterated or fluorinated compounds can be used as internal standards and surrogate standards. Naphthalene-d_8, acenaphthene-d_{10}, pyridine-d_5, aniline-d_5, nitrobenzene-d_5, 1-fluoronaphthalene, 2-fluoronaphthalene, 2-fluorobiphenyl, 2,2'-difluorobiphenyl, and 1,2,3,4,5-pentafluorobiphenyl have been used or suggested as appropriate internal standards/surrogates for the base-neutral compounds. Phenol-d_6, pentafluorophenol, 2-perfluoromethyl phenol, and 2-fluorophenol have been used or suggested for the acid compounds. Compounds used as internal standards are not to be used as surrogate standards. The internal standard must be different from the surrogate standards.

6.5 The external standard method can also be used at the discretion of the analyst. Prepare a master calibration curve using a minimum of three standard solutions of each of the compounds that are to be measured. Plot concentrations versus integrated areas or peak heights (selected characteristic ion for GC/MS). One point on each curve should approach the limit of detection (Tables 4, 5, and 6). After the master set of instrument calibration curves have been established, they should be verified daily by injecting at least one standard solution. If significant drift has occurred, a new calibration curve must be constructed.

7. *Quality Control.*

7.1 Before processing any samples, demonstrate through the analysis of a method blank, that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination.

7.2 Standard quality assurance practices should be used with this method. Field replicates should be collected and analyzed to determine the precision of the sampling technique. Laboratory replicates should be analyzed to determine the precision of the analysis. Fortified samples should be analyzed to determine the accuracy of the analysis. Field blanks should be analyzed to check for contamination introduced during sampling and transportation.

8. *Sample Collection, Preservation, and Handling.*

8.1 Grab samples must be collected in glass containers. Conventional sampling practices should be followed, except that the bottle must not be prerinsed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be free of tygon and other potential sources of contamination.

8.2 The samples must be iced or refrigerated from the time of collection until extraction. Chemical preservatives should not be used in the field unless more than 24 hours will elapse before delivery to the laboratory. If the samples will not be extracted within 48 hours of collection, they must be preserved as follows:

8.2.1 If the sample contains residual chlorine, add 35 mg of sodium thiosulfate per 1 ppm of free chlorine per liter of sample.

8.2.2 Adjust the pH of the water sample to a pH of 7 to 10 using sodium hydroxide or sulfuric acid. Record the volume of acid or base used.

8.3 All samples must be extracted within 7 days and completely analyzed within 30 days of collection.

9. *Sample Extraction (Base/Neutrals, Acids, and Pesticides).*

9.1 Samples may be extracted by separatory funnel techniques or with a continuous extractor as described in Section 10. Where emulsions prevent acceptable solvent recovery with the separatory funnel technique, the analyst must use the continuous extractor.

9.2 The details of the extraction technique should be adjusted according to the sample volume. The technique described below assumes a sample

volume of 1000 ml. For volumes approximating 2-liters, the volume of extraction solvent should be adjusted to 250, 100, and 100 ml for the serial extraction of the base neutrals, and 200, 100, and 100 ml for the acids.

9.3 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a two-liter separatory funnel. Adjust the pH of the sample with 6N NaOH to 11 or greater. Use multirange pH paper for the measurements. Proceed to Section 10 if continuous extraction is used.

9.4 Add 60 ml methylene chloride to the sample bottle, cap, and shake 30 seconds to rinse the walls. Transfer the solvent into the separatory funnel, and extract the sample by shaking the funnel for two minutes with periodic venting to release excess vapor pressure. Allow the organic layer to separate from the water phase for a minimum of ten minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, or centrifugation. (If the emulsion cannot be broken, that is, recovery is less than 80% of the added solvent corrected for the water solubility of methylene chloride, transfer the sample, solvent, and emulsion into a continuous extractor and proceed as described in Section 10). Collect the methylene chloride extract in a 250-ml Erlenmeyer flask.

9.5 Add a second 60-ml volume of methylene chloride to the sample bottle and complete the extraction procedure a second time, combining the extracts in the Erlenmeyer flask.

9.6 Perform a third extraction in the same manner. Pour the combined extract through a drying column containing 3–4 inches of anhydrous sodium sulfate, and collect it in a 500 ml K–D flask equipped with 10 ml concentrator tube. Rinse the Erlenmeyer with 20 to 40 ml of methylene chloride. Pour this through the drying column. Seal, label as base/neutral fraction, and proceed with the acid extraction. If the extract must be stored overnight before analysis by GC/MS, it may be transferred to a 2 ml serum vial equipped with a Teflon-lined rubber septum and crimp cap.

9.7 Acid (Phenols) Extraction—Adjust the pH of the water, previously extracted for base-neutrals, with 6N H_2SO_4 to 2 or below. Serially extract with 60, 60 and 60 ml portions of distilled-in-glass methylene chloride. Collect and combine the extracts in a 250-ml Erlenmeyer flask then dry by passing through a column of anhydrous sodium sulfate. Rinse the Erlenmeyer with 20 to 40 ml of methylene chloride and pour through the drying column. Seal, label acid fraction and prepare for concentration.

9.8 Concentrate the extracts (Base/Neutrals and Acids) in a 500 ml K–D flask equipped with a 10 ml concentrator tube.

9.9 Add 1 to 2 clean boiling chips to the flask and attach a three-ball macro-Snyder column. Prewet the Snyder column by adding about 1 ml methylene chloride through the top. Place the K–D apparatus on a warm water bath (60 to 65°C) so that the concentrator tube is partially immersed in the water, and the entire lower rounded surface of the flask is bathed with water vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 minutes. At the proper rate of distillation the balls of the column actively chatter but the chambers do not flood. When the liquid has reached an apparent volume 1 ml, remove the K–D apparatus and allow the solvent to drain for at least 10 minutes while cooling. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 ml of methylene chloride. A 5-ml syringe is recommended for this operation.

9.10 Add a clean boiling chip and attach a two-ball micro-Snyder column to the concentrator tube in 9.8. Prewet the column by adding about 0.5 ml methylene chloride through the top. Place the K–D apparatus on a warm water bath (60 to 65°C) so that the concentrator tube is partially immersed in the water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5–10 minutes. At the proper rate of distillation the balls of the column actively chatter but the chambers do not flood. When the liquid reaches an apparent volume of about 0.5 ml, remove the K–D from the water bath and allow the solvent to drain and cool for at least 10 minutes. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with approximately 0.2 ml of methylene chloride. Adjust the final volume to 1.0 ml, seal, and label as acid fraction.

9.11 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1,000-ml graduated cylinder. Record the sample volume to the nearest 5 ml.

10. *Emulsions/Continuous Extraction.*

10.1 Place 100 to 150 ml of methylene chloride in the extractor and 200–500 ml methylene chloride in the distilling flask.

10.2 Add the aqueous sample (pH 11 or greater) to the extractor. Add blank water as necessary to operate the extractor and extract for 24 hours. Remove the distilling flask and pour the contents through a drying column containing 7 to 10 cm of anhydrous sodium sulfate. Collect the methylene chloride in a 500 ml K–D evaporator flask equipped with a 10 ml concentrator tube. Seal, label as the base/neutral fraction, and concentrate as per sections 9.8 to 9.10.

10.3 Adjust the pH of the sample in the continuous extractor to 2 or below using 6N sulfuric acid. Charge a clean distilling flask with 500 ml of methylene chloride. Extract for 24 hours. Remove the distilling flask and pour the contents through a drying column containing 7 to 10 cm of anhydrous sodium sulfate. Collect the methylene chloride layer on a K–D evaporator flask equipped with a 10 ml concentrator tube. Label as the acid fraction. Concentrate as per sections 9.8 to 9.10.

11. *Calibration of the GC–MS System.*

11.1 At the beginning of each day, the mass calibration of the GC–MS system must be checked and adjusted if necessary to meet DFTPP specifications (11.3). Each day base-neutrals are measured, the column performance specification (12.1) with benzidine must be met. Each day the acids are measured, the column performance specification (13.1) with pentachlorophenol must be met. DFTPP can be mixed in solution with either of these compounds to complete two specifications with one injection, if desired.

11.2 To perform the mass calibration test of the GC–MS system, the following instrumental parameters are required:

Electron energy—70 volts (nominal).
Mass range—35 to 450 a.m.u.
Scan time—7 seconds or less.

11.3 GC–MS system calibration—Evaluate the system performance each day that it is to be used for the analysis of samples or blanks by examining the mass spectrum of DFTPP. Inject a solution containing 50 ug DFTPP and check to insure that performance criteria listed in Table 10 are met. If the system performance criteria are not met, the analyst must retune the spectrometer and repeat the performance check. The performance criteria must be met before any samples or standards may be analyzed.

12. *Gas Chromatography-Mass Spectrometry of Base/Neutral Fraction.*

12.1 At the beginning of each day that base/neutral analyses are to be performed, inject 100 nanograms of benzidine either separately or as part of a standard mixture that may also contain 50 ng of DFTPP. The tailing factor for benzidine should be less than 3. Calculation of the tailing factor is given in Reference 2 and described in Figure 6.

12.2 Establish chromatographic conditions equivalent to those in Tables 4 and 5. Included in these tables are estimated retention times and sensitivities that can be achieved by this method. Examples of the separations achieved by these columns are shown in Figures 1 and 3 through 7.

12.3 Program the GC/MS to operate in the Extracted Ion Current Profile (EICP) mode, and collect EICP for the three ions listed in Tables 7 and 8 for each compound being measured. Operating in this mode, calibrate the system response for each compound as described in Section 6, using either the internal or external standard procedure.

12.4 If the internal standard approach is being used, the analyst may not add the standard to sample extracts until immediately before injection into the instrument. Mix thoroughly.

12.5 Inject 2 to 5 µl of the sample extract. The solvent-flush technique is preferred. If external calibration is employed, record the volume injected to the nearest 0.05 µl. If the response for any ion exceeds the linear range of the system, dilute the extract and reanalyze.

12.6 Qualitative and quantitative measurements are made as described in Section 14. When the extracts are not being used for analysis, store them in vials with unpierced septa in the dark at 4° C.

13. *Gas Chromatography/Mass Spectrometry of Acid Fraction.*

13.1 At the beginning of each day that acid fraction analyses are to be performed, inject 50 nanograms of pentachlorophenol either separately or as part of a standard mixture that may also contain DFTPP. The tailing factor for pentachlorophenol should be less than 5. Calculation of the tailing factor is given in Reference 2 and described in Figure 8.

13.2 Establish chromatographic conditions equivalent to those in Table 6. Included in this table are estimated retention times and sensitivities that can be achieved by this method. An example of the separation achieved by the column is shown in Figure 2.

13.3 Program the GC/MS to operate in the Extracted Ion Current Profile mode, and collect EICP for the three ions listed in Table 9 for each phenol being measured. Operating in this mode, calibrate the system response for each compound as described in Section 6 using either the internal or external standard procedure.

13.4 If the internal standard approach is being used, the analyst may not add the standard to sample extracts until immediately before injection into the instrument. Mix thoroughly.

13.5 Inject 2 to 5 µl of the sample extract. The solvent-flush technique is preferred. If external standard calibration is employed, record the volume injected to the nearest 0.05 µl. If the response for any ion exceeds the linear range of the system, dilute the extract and reanalyze.

13.6 Qualitative and quantitative measurements are made as described in Section 14. When the extracts are not being used for analysis, store them in vials with unpierced septa in the dark at 4° C.

14. *Qualitative and Quantitative Determination.*

14.1 To qualitatively identify a compound, obtain an Extracted Ion Current Profile (EICP) for the primary ion and the two other ions listed in Tables 7, 8, or 9. The criteria below must be met for a qualitative identification.

14.1.1 The characteristic ions for the compound must be found to maximize in the same or within one spectrum of each other.

14.1.2 The retention time of the experimental mass spectrum must be within ±30 seconds of the retention time of the authentic compound.

14.1.3 The ratios of the three EICP peak heights must agree within ±20% with the ratios of the relative intensities for these ions in a reference mass spectrum. The reference mass spectrum can be obtained from either a standard analyzed through the GC–MS system or from a reference library.

14.1.4 Structural isomers that have very similar mass spectra can be explicitly identified only if the resolution between the isomers in a standard mix is acceptable. Acceptable resolution is achieved if the valley height between isomers is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

14.2 In samples that contain an inordinate number of interferences the chemical ionization (CI) mass spectrum may make identification easier. In Tables 7 and 8 characteristic CI ions for most of the compounds are given. The use of chemical ionization MS to support EI is encouraged but not required.

14.3 When a compound has been identified, the quantification of that compound will be based on the integrated area from the specific ion plot of the first listed characteristic ion in Tables 7, 8 and 9. If the sample produces an interference for the first listed ion, use a secondary ion to quantify. Quantification will be done by the external or internal standard method.

14.4 Internal Standard—By adding a constant known amount of internal standard (C_{is} in µg) to every sample extract, the concentration of pollutant (C_x) in µg/l in the sample is calculated using equation 2.

$$\text{Eq. 2} \qquad C_x = \frac{(A_x)(C_{is})}{(A_{is})(RF)(V_o)}$$

Where: V_o is the volume of the original sample in liters, and the other terms are defined as in Section 6.3.

14.5 External Standard—The concentration of the unknown can be calculated from the slope and intercept of the calibration curve. The unknown concentration can be determined using equation 3.

$$\text{Eq. 3} \qquad \text{Micrograms/liter} = \text{ng/ml} = \frac{(A)(V_t)}{(V_i)(V_o)}$$

where:
A = mass of compound from calibration curve (ng).
V_i = volume of extract injected (µl).
V_t = volume of total extract (µl).
V_o = volume of water extracted (ml).

14.6 Report all results to two significant figures. Report results in micrograms per liter (Base/Neutrals and Acids) without correction for recovery data. When duplicate and spiked samples are analyzed, all data obtained should be reported.

14.7 In order to minimize unnecessary GC–MS analysis of method blanks and field blanks, the field blank may be screened on a *FID–GC* equipped with the appropriate SP–2250 or SP–1240 DA columns.

15. References

1. Method 610, Polynuclear Aromatic Hydrocarbons, EMSL, Cincinnati, Ohio 45268, 1979.
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Table 1.—*Base-Neutral Extractables*

Compound	STORET No.
Acenaphthene	34205
Acenaphthylene	34200
Anthracene	34220
Benzidine	34030
Benzo(a)anthracene	34526
Benzo(a)pyrene	34247
Benzo(b)fluoranthene	34230
Benzo(ghi)perylene	34521
Benzo(k)fluoranthene	34242
Benzyl chloride	34273
Bis(2-chloroethoxy) methane	34278
Bis(2-chloroethyl) ether	34273
Bis(2-chloroisopropyl) ether	34283
Bis(2-ethylhexyl) phthalate	39100
4-Bromophenyl phenyl ether	34636
Butyl benzyl phthalate	34292
2-Chloronaphthalene	34581
4-Chlorophenyl phenyl ether	34641
Chrysene	34320
Dibenzo(a,h)anthracene	34556
Di-n-butyl phthalate	39110
1,3-Dichlorobenzene	34566
1,4-Dichlorobenzene	34571
1,2-Dichlorobenzene	34536
3,3'-Dichlorobenzidine	34631
Diethyl phthalate	34336
Dimethyl phthalate	34341
2,4-Dinitrotoluene	34611
2,6-Dinitrotoluene	34626
Di-n-octyl phthalate	34596
1,2-Diphenylhydrazine	34346
Fluoranthene	34376
Fluorene	34381
Hexachlorobenzene	39700
Hexachlorobutadiene	34391
Hexachlorocyclopentadiene	34386
Hexachloroethane	34396
Indeno(1,2,3-cd)pyrene	34403
Isophorone	34408
Naphthalene	34696
Nitrobenzene	34447
N-Nitrosodimethylamine	34438
N-Nitrosodi-n-propylamine	34428
N-Nitrosodiphenylamine	34433
Phenanthrene	34461
Pyrene	34469
2,3,7,8-Tetrachlorodibenzo-p-dioxin	34675
1,2,4-Trichlorobenzene	34551

Table 2.—*Acid Extractables*

Compound	STORET No.
4-Chloro-3-methylphenol	34452
2-Chlorophenol	34586
2,4-Dichlorophenol	34601
2,4-Dimethylphenol	34606
2,4-Dinitrophenol	34616
2-Methyl-4,6-dinitrophenol	34657
2-Nitrophenol	34591
4-Nitrophenol	34646
Pentachlorophenol	39032
Phenol	34694
2,4,6-Trichlorophenol	34621

Table 3.—*Pesticide Extractables*

Compound	STORET No.
Aldrin	39330
α-BHC	39337
β-BHC	39338
γ-BHC	39340
δ-BHC	34259
Chlordane	39350
4,4'-DDD	39310
4,4'-DDE	39320
4,4'-DDT	39300
Dieldrin	39380
Endosulfan I	34361
Endosulfan II	34356
Endosulfan Sulfate	34351
Endrin	39390
Endrin Aldehyde	34366
Heptachlor	39410
Heptachlor Epoxide	39420
Toxaphene	39400
PCB-1016	34671
PCB-1221	39488
PCB-1232	39492
PCB-1242	39488
PCB-1248	39500
PCB-1254	39504
PCB-1260	39508

Table 4.—*Gas Chromatography of Base/Neutral Extractables*

Compound	Retention time (min)	Limit of detection µg/l
1,3-Dichlorobenzene	7.6	10
1,4-Dichlorobenzene	7.8	10
Hexachloroethane	8.4	10
Bis(2-chloroethyl) ether	8.4	10
1,2-Dichlorobenzene	8.4	10
Bis(2-chloroisopropyl) ether	8.8	10
N-nitroso-di-n-propyl amine	9.3	10
Isophorone	11.1	10
Bis(2-chloroethoxy) methane	11.4	10
1,2,4-Trichlorobenzene	11.6	10
Naphthalene	11.9	10
Hexachlorobutadiene	12.1	10
Bis(2-chloroethyl) ether	12.2	10
Hexachlorocyclopentadiene	13.9	10
2-Chloronaphthalene	13.9	10
Acenaphthylene	17.4	10
Acenaphthene	17.6	10
Dimethyl phthalate	18.3	10
2,6-Dinitrotoluene	18.7	10
Fluorene	19.2	10
4-Chlorophenyl phenyl ether	19.2	10
2,4-Dinitrotoluene	19.2	10
1,2-Diphenylhydrazine*	19.2	10
Diethyl phthalate	19.2	10
4-Bromophenyl phenyl ether**	20.9	10
Hexachlorobenzene	20.9	10
4,6-Dinitro-2-methylphenol	21.2	50
Phenanthrene	21.2	10
Anthracene	21.2	10
Di-n-butyl phthalate	21.7	10
Fluoranthene	22.8	10
Pyrene	23.3	10
Benzidine	23.6	50
Butyl benzyl phthalate	23.6	10
Benzo(a)anthracene	25.2	10
Chrysene	25.5	10

Table 4.—*Gas Chromatography of Base/Neutral Extractables*—Continued

Compound	Retention time (min)	Limit of detection µg/l
3,3'-Dichlorobenzidine	25.8	10
Bis(2-ethylhexyl) phthalate	25.8	10
Di-n-octyl phthalate	26.1	10
Benzo(b)fluoranthene	26.1	10
Benzo(k)fluoranthene	26.1	10
Benzo(a)pyrene	26.4	10
Indeno(1,2,3-cd)pyrene	26.7	10
Dibenzo(a,h)anthracene	26.7	10
Benzo(ghi)perylene	26.7	10
N-nitrosodiphenylamine		
Benzyl chloride		
2,3,7,8-Tetrachlorodibenzo-p-dioxin		

*The test glass column (1% w. OV-1 on 2 mm ID) packed with 3% SP-2250 coated on 100/120 mesh Supelcoport. Carrier gas helium at 30 ml per min. Temperature program: isothermal for 4 minutes at 50° C, then 8° per min to 270° C. Hold at 270° C for 30 minutes. A capillary or SCOT column may be used.

**This is a minimum level at which the entire analytical system must give mass spectral confirmation. Analyses are based on a 2 µl injection of a one liter sample that has been extracted and concentrated to a volume of 1.0 ml.

***Detected as azobenzene.

****Detected as diphenylamine.

Table 5.—*Gas Chromatography of Pesticide Extractables*

Compound	Retention time (min)	Limit of detection µg/l
α-BHC	11.1	0.05
β-BHC	12.4	0.05
γ-BHC	12.8	0.05
Heptachlor	13.2	0.05
δ-BHC	13.7	0.05
Aldrin	14.0	0.05
Heptachlor epoxide	15.6	0.05
Endosulfan I	16.2	0.05
Dieldrin	17.2	0.05
4,4'-DDE	17.2	0.05
Endrin	17.8	0.05
Endosulfan II	18.2	0.05
4,4'-DDD	18.2	0.05
4,4'-DDT	20.1	0.05
Endosulfan sulfate	20.8	0.05
Chlordane	21.0	0.05
Toxaphene	21.0	0.05
PCB-1242	21.0	0.05
PCB-1254	23.0	0.05

*The test glass column (1% w. OV-1 on 2 mm ID) packed with 3% SP-2250 coated on 100/120 mesh Supelcoport. Carrier gas helium at 30 ml per min. Temperature program: isothermal for 4 minutes at 50° C, then 8° per minute to 270° C, held at 270° C for 30 minutes. A capillary or SCOT column may be used.

**This is a minimum level at which the entire analytical system must give mass spectral confirmation. Analyses are based on a 2 µl injection of a one liter sample that has been extracted and concentrated to a volume of 1.0 ml.

Table 6.—*Gas Chromatography of Acid Extractables*

Compound	Retention time (min)	Limit of detection µg/l
2-Chlorophenol	5.5	10
2-Nitrophenol	6.5	10
Phenol	7.5	10
2,4-Dimethylphenol	8.5	10
2,4-Dichlorophenol	9.5	10
2,4,6-Trichlorophenol	10.5	10
4-Chloro-3-methylphenol	11.5	10
2,4-Dinitrophenol	12.5	50

Table 8.—Pesticides Characteristic Ions

Compound	Characteristic ion masses		
[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

Table 9.—Acid Extractable Characteristic Ions

Compound	Characteristic ions					
	Electron impact			Chemical ionization (methane)		
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

Table 10.—DFTPP Key Ions and Ion Abundance Criteria

Mass	Ion abundance criteria
51	30 to 60 percent of mass 198.
68	Less than 2 percent of mass 69.
70	Less than 2 percent of mass 69.
197	40 to 60 percent of mass 198.
198	Less than 1 percent of mass 199.
199	Base peak, 100 percent relative abundance.
275	5 to 9 percent of mass 198.
365	10 to 30 percent of mass 198.
365	Greater than 1 percent of mass 198.
441	Present but less than mass 443.
442	Greater than 40 percent of mass 198.
443	17 to 23 percent of mass 442.

BILLING CODE [illegible]

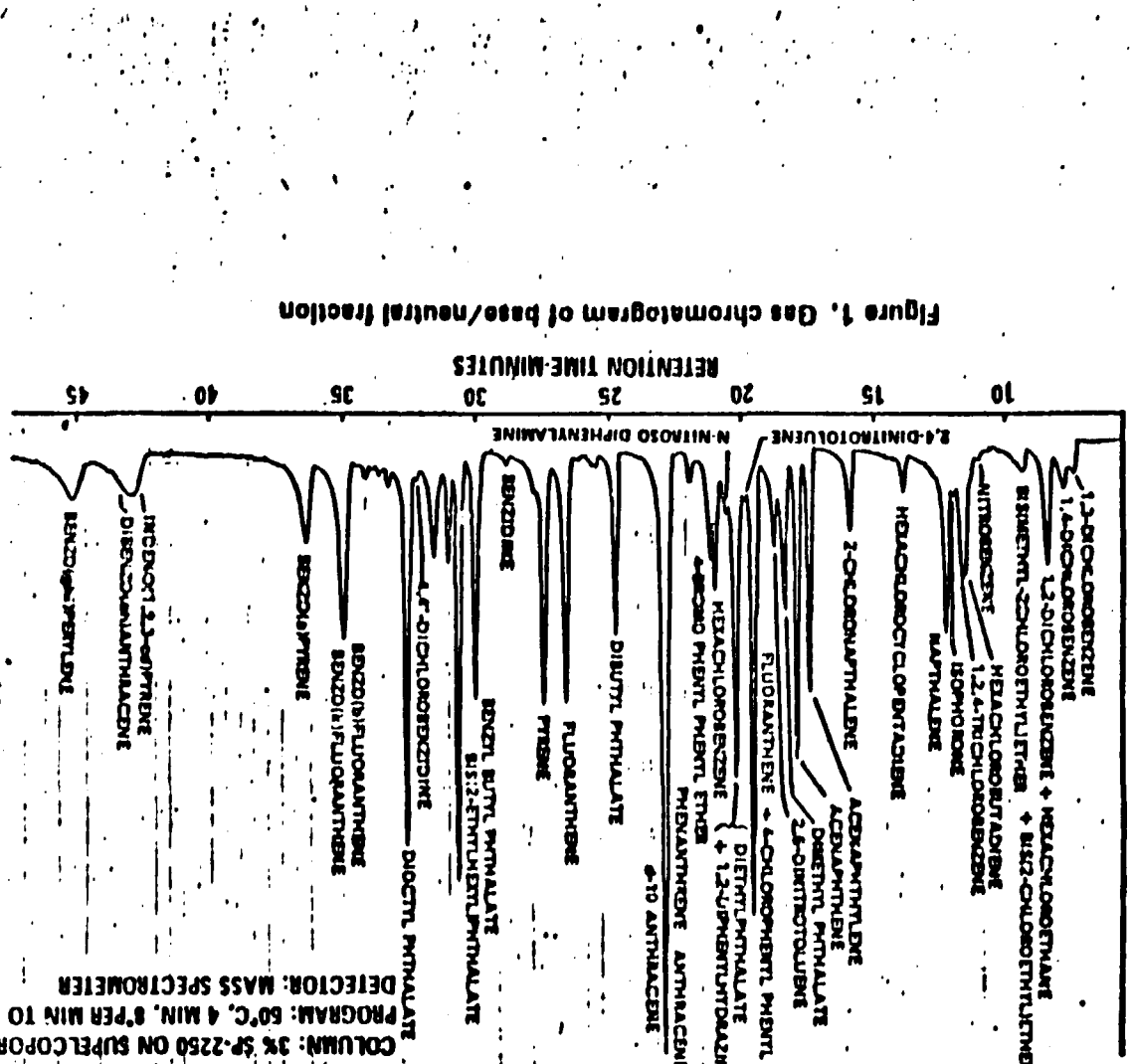
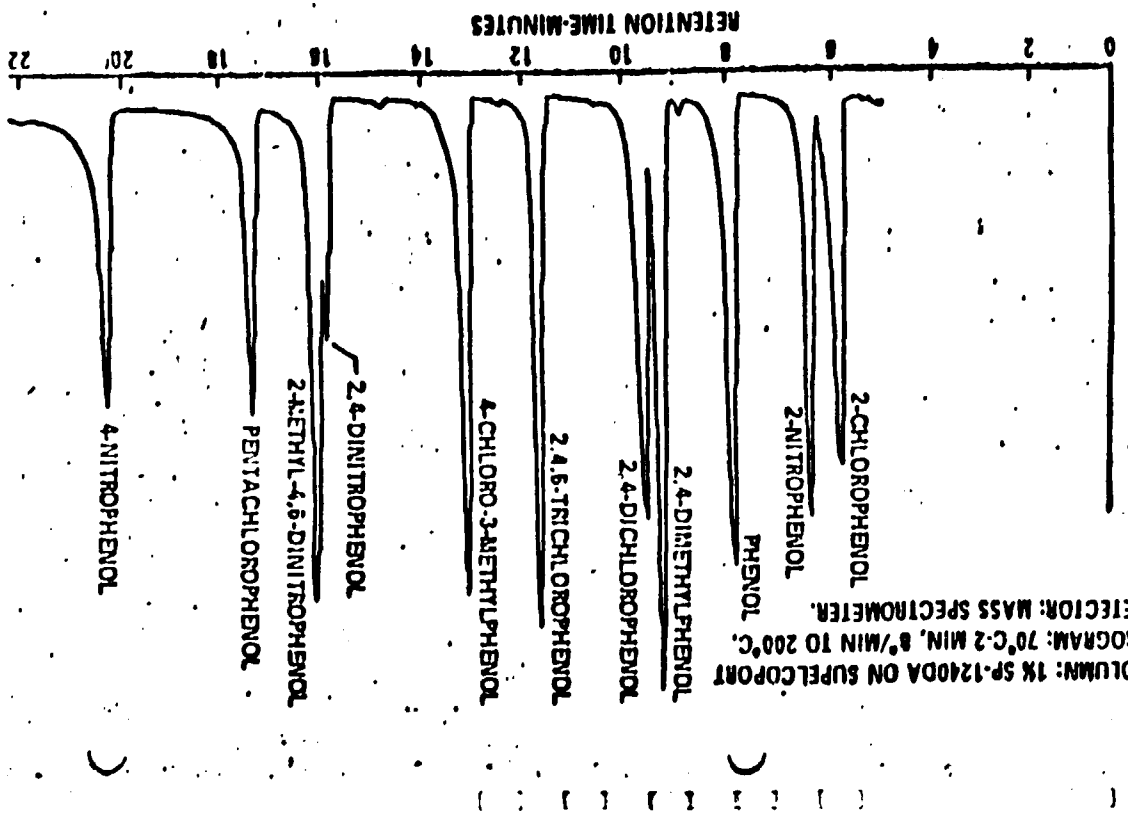


Figure 1. Gas chromatogram of base/neutral fraction

Figure 2. Gas chromatogram of acid fraction



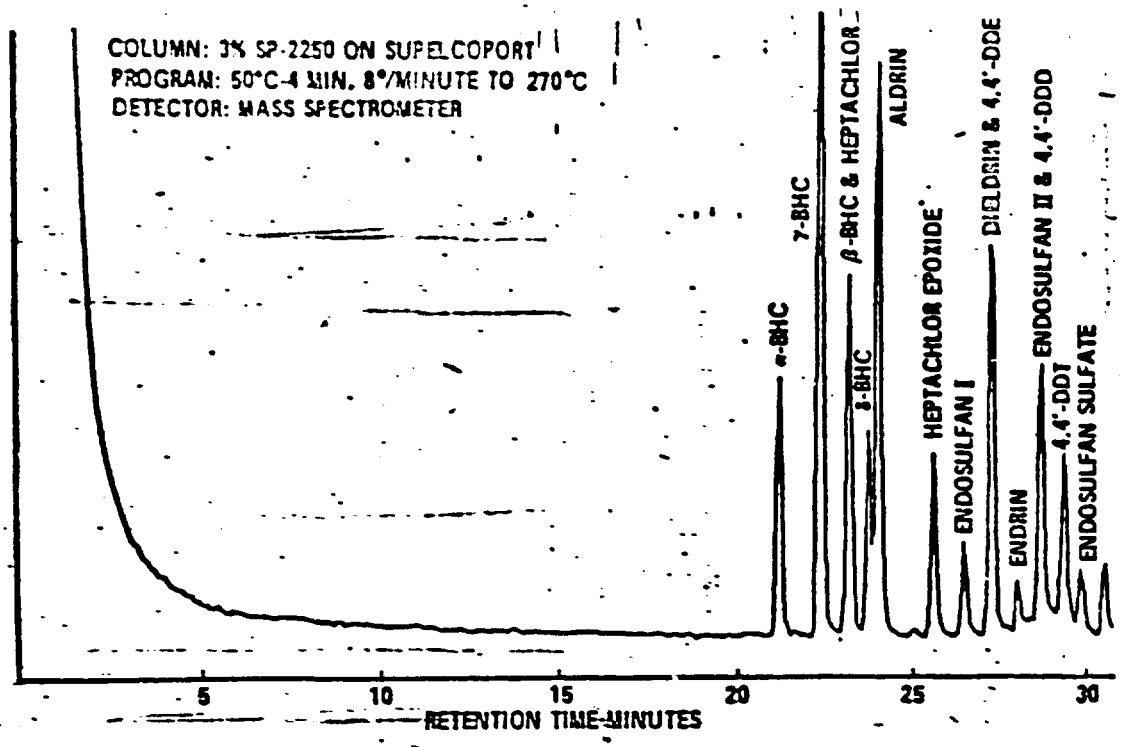


Figure 3. Gas chromatogram of pesticide fraction

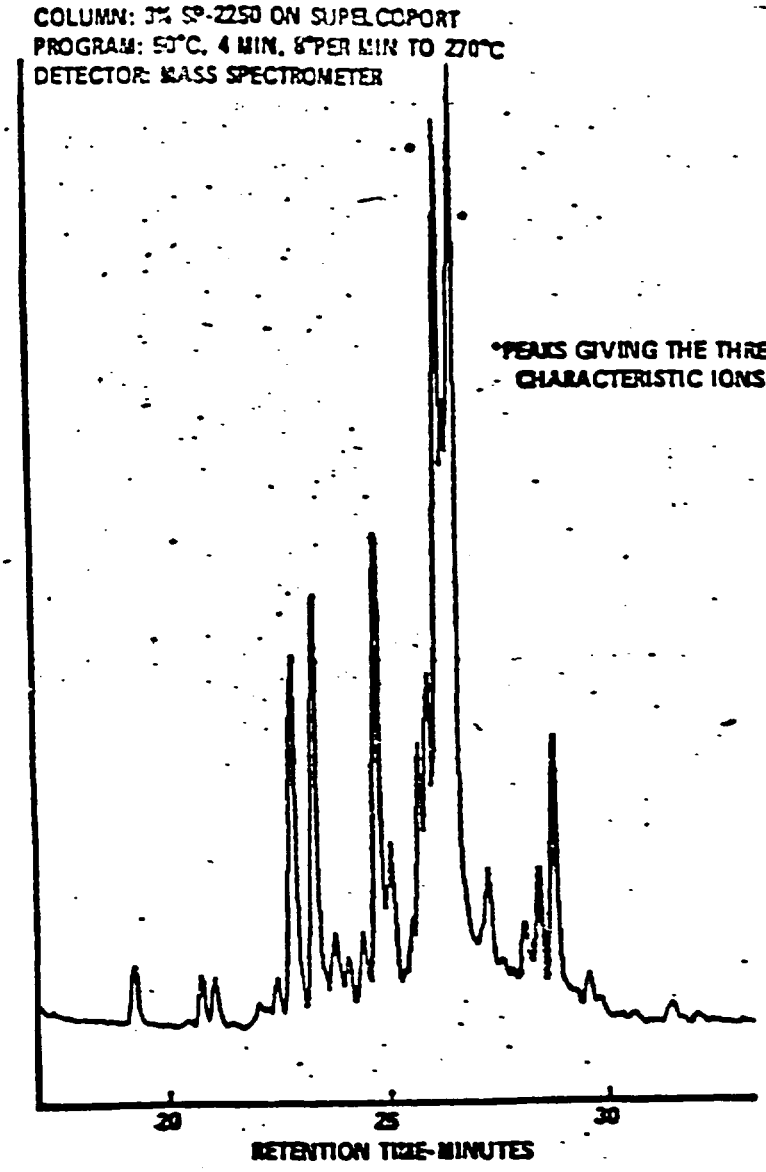


Figure 4. Gas chromatogram of chlordane

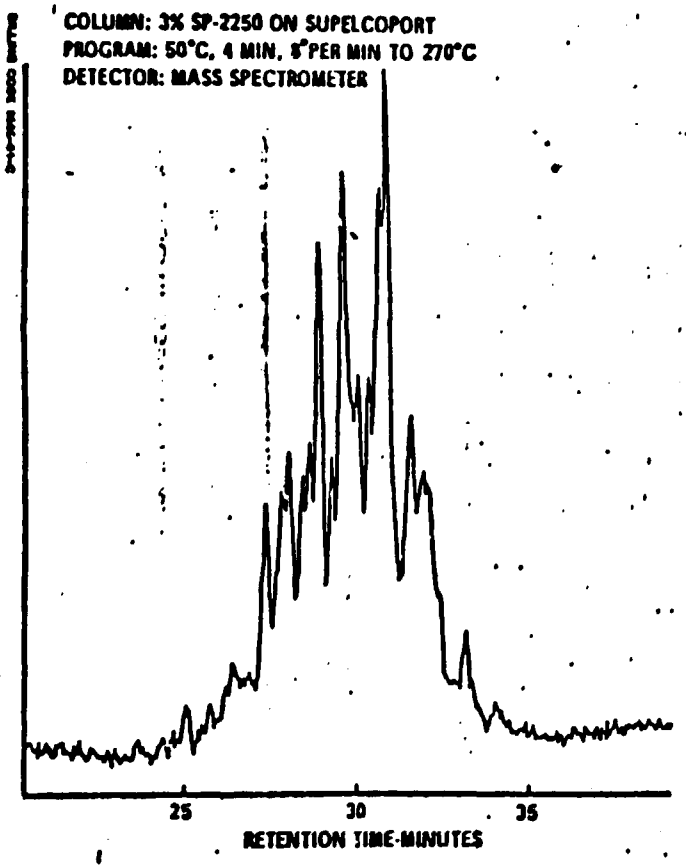


Figure 5. Gas chromatogram of toxaphene

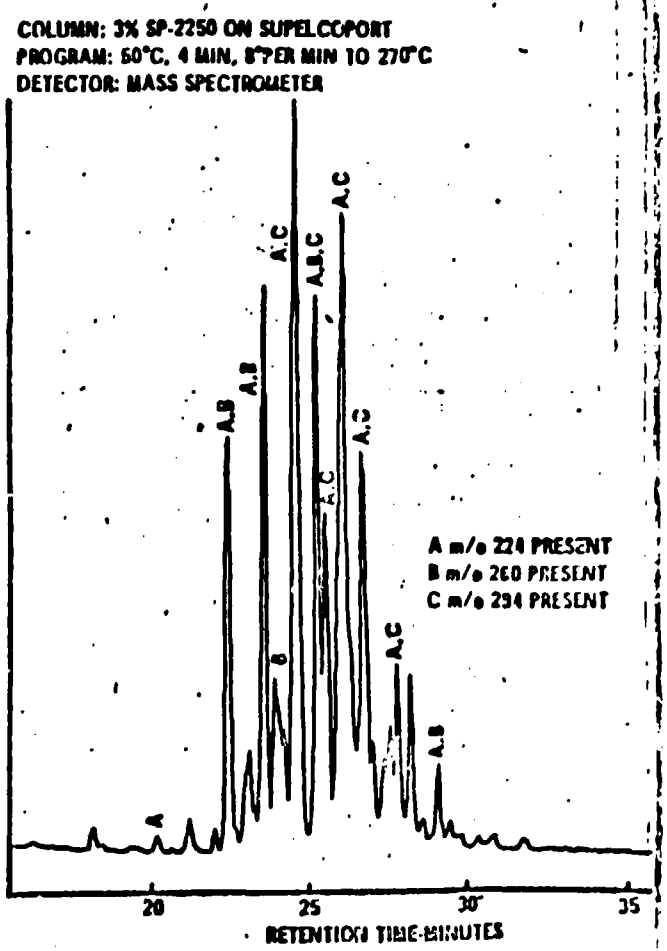


Figure 6. Gas chromatogram of Arochlor 1248

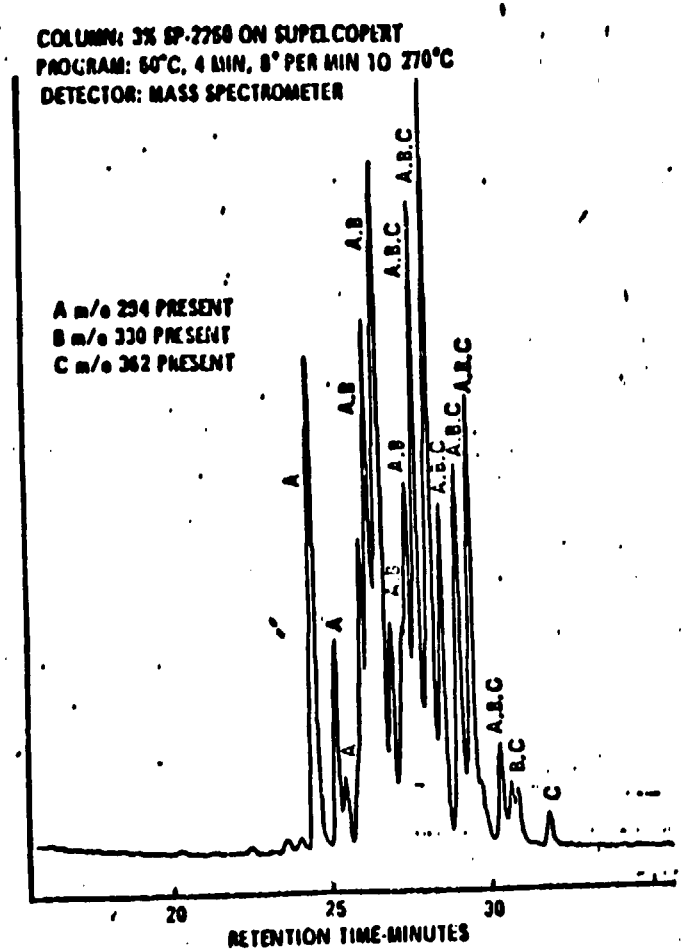


Figure 7. Gas chromatogram of Arochlor 1254

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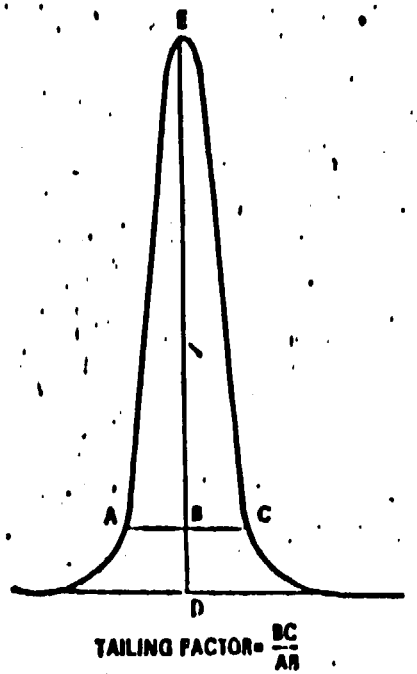


TAILING FACTOR = $\frac{BC}{AB}$

Example calculation: Peak Height = DE = 100 mm
10% Peak Height = BD = 10 mm
Peak Width at 10% Peak Height = AC = 23 mm
AB = 11 mm
BC = 12 mm

Therefore: Tailing Factor = $\frac{12}{11}$ = 1.1

Figure 1, Tailing factor calculation

APPENDIX B.9

EMSL-LV Procedure No. 2

EMSL-LV Procedure No. 2 - November 10, 1981

METHOD FOR THE DETERMINATION OF SEMIVOLATILE ORGANIC COMPOUNDS IN SOLID WASTES

1. Scope and Application

1.1 This method covers the determination of semivolatile organic compounds in a variety of solid waste matrices.

1.2 This method is applicable to nearly all types of samples, regardless of water content, including aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments.

1.3 This method is applicable to the determination of most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and are capable of being eluted without derivatization as sharp peaks from a gas chromatographic fused silica capillary column coated with a slightly polar silicone. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols including nitrophenols.

1.4 The detection limit of the method for determining an individual compound is approximately 1 µg/g (wet weight). For samples which contain more than 1 mg/g of total solvent extractable material, the detection limit is proportionately higher.

1.5 This method is based upon a solvent extraction, gas chromatographic/mass spectrometric (GC/MS) procedure.

1.6 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra. Each

analyst must demonstrate the ability to generate acceptable results with this method.

2. Summary of Method

2.1 A measured weight of sample, 3.0 g wet weight, is adjusted to pH 7.0 and sonified with 150 mL of methylene chloride. Anhydrous sodium sulfate is added to bind the water present. A portion of the methylene chloride supernatant is concentrated and analyzed by GC/MS using a fused silica capillary column. Qualitative identification is performed using the retention time of the compound and the relative abundance of three or more characteristic ions. Quantitative analysis is performed using an internal standard technique with a single characteristic ion.

A GC/FID screen is used to determine if the sample is medium or low level. If the sample is judged to be medium, this screen is also used to determine the concentration or dilution factor for GC/MS analysis. If judged to be low level, the sample is analyzed by the "Modified EMSL-Ci Procedure" on page 64 of this Exhibit.

3. Interferences

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the total ion current profiles. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks.

3.1.1 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. Heating in a muffle furnace at 450°C for 5 to 15 hours is recommended whenever feasible. Alternatively detergent washes, water rinses, acetone rinses, and oven drying may be used. Cleaned glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants.

3.1.2 The use of high purity reagents and solvents helps to minimize interference problems.

3.2 Matrix interferences may be caused by components that are coextracted from the sample but are not normally of interest. The most common such components are petroleum-derived naphthenes, high molecular weight polymeric components, and long-chain components such as waxes and triglycerides. The extent of such matrix interferences will vary considerably from source to source. A

cleanup procedure using gel permeation chromatography has been incorporated into the method for certain cases to remove long-chain and high-molecular-weight material. No cleanup procedure is available for the removal of naphthenes. When such matrix interferences are present, the sample extract is diluted and the detection limit is increased proportionately. Many of the matrix interferences are solvent-extractable nonvolatile components which necessitate the more frequent cleaning of the GC injection port and the more frequent removal of the injection end of the GC capillary column.

4. Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be minimized by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis.

4.2 All operations involving the use of methylene chloride, including the extraction of the waste sample, filtration of the extract, and concentration of the extract, must be performed in a fume hood. Care should be taken to avoid the contact of skin with methylene chloride.

5. Apparatus

5.1 Sampling equipment - Glass screw-cap vials or jars of at least 100 mL capacity. Screw caps must be Teflon lined.

5.2 Glassware

5.2.1 Beaker - 400 mL

5.2.2 Centrifuge tubes - approximately 200-mL capacity, glass with screw cap (Corning #1261 or equivalent). Screw caps must be fitted with Teflon liners.

5.2.3 Concentrator tube, Kuderna-Danish - 25 mL, graduated (Kontes K 570050-2526 or equivalent). Calibration must be checked at the volumes employed in the test. A ground glass stopper is used to prevent evaporation of extracts.

5.2.4 Evaporative flask, Kuderna-Danish 250-mL (Kontes K-570001-0250 or equivalent). Attach to concentrator tube with springs.

5.2.5 Snyder column, Kuderna-Danish - Three-ball macro (Kontes K-503000-0121 or equivalent).

5.2.6 Snyder column, Kuderna-Danish - Two-ball micro (Kontes K-569001-0219 or equivalent).

5.3 Filter assembly

5.3.1 Syringe - 10 mL gas-tight with Teflon Luer Lock (Hamilton 1010TLL or equivalent).

5.3.2 Filter holder - 13-mm Swinny (Millipore XX30-012 or equivalent).

5.3.3 Prefilters - glass fiber (Millipore AP-20-010 or equivalent).

5.3.4 Membrane filter - 0.2 µm Teflon (Millipore FGLP-013 or equivalent).

5.4 Micro syringe - 100 uL (Hamilton #84858 or equivalent).

5.5 Weighing pans, micro - approximately 1-cm diameter aluminum foil. Purchase or fabricate from aluminum foil.

5.6 Boiling chips - approximately 10-40 mesh carborundum (A. H. Thomas #1590-D30 or equivalent). Heat to 450°C for 5-10 hours or extract with methylene chloride.

5.7 Water bath - Heated, capable of temperature control (±2°C). The bath should be used in a hood.

5.8 Balance - Analytical, capable of accurately weighing 0.0001 g.

5.9 Microbalance - Capable of accurately weighing to 0.001 mg (mettler model MZ-30 or equivalent).

5.10 Sonifier - 375 watt, fitted with a 1/2-inch probe and a half-wave extension, capable of pulsed operation at variable power settings. (Heat Systems-Ultrasonics Sonicator Model W-375 with #200 1/2-inch disrupter horn and #406-BH-050-T half-wave extender, or equivalent).

5.11 Centrifuge - Capable of accommodating 200-mL glass centrifuge tubes.

5.12 pH Meter and electrodes - Capable of accurately measuring pH to ±0.1 pH unit.

5.13 Spatula - Having a metal blade 1-2 cm in width.

5.14 Heat lamp - 250 watt reflector-type bulb (GE #250R-40/4 or equivalent) in a heat-resistant fixture whose height above the sample may be conveniently adjusted.

5.15 Gas chromatograph/mass spectrometer system.

5.15.1 Gas chromatograph - An analytical system complete with a temperature programmable gas chromatograph suitable for splitless injection and all required accessories including syringes, analytical columns, and gases.

5.15.2 Column - 30 m x 0.25 mm bonded-phase silicone coated fused silica capillary column (J&W Scientific DB-5 or equivalent).

5.15.3 Mass spectrometer - Capable of scanning from 40 to 450 amu every 1 second or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode and producing a mass spectrum which meets all required criteria when 50 ng of decafluorotriphenylphosphine (DFTPP) is injected through the GC inlet.

5.15.4 Data system - A computer system must be interfaced to the mass spectrometer that allows the continuous acquisition and storage on machine readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specific mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile

(EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits.

5.16 Gel permeation chromatography system.

5.16.1 Chromatographic column - 600 mm x 25 mm I.D. glass column fitted for upward flow operation.

5.16.2 Bio-Beads S-X8 - 80 g per column.

5.16.3 Pump - capable of constant flow of 0.1 to 5 mL/min at up to 100 psi.

5.16.4 Injector - with 5-mL loop.

5.16.5 Ultraviolet detector - 254 nm.

5.16.6 Strip chart recorder.

6. Reagents

6.1 Reagent water - Reagent water is defined as a water in which an interference is not observed at the method detection limit of each compound of interest.

6.2 Potassium phosphate, tribasic (K_3PO_4) - Granular (ACS).

6.3 Phosphate buffer, 4M - 2.0 moles of Na_2HPO_4 and 2.0 moles of NaH_2PO_4 dissolved in reagent water and diluted to 1000 mL. The solution is very temperature sensitive; it must be checked carefully before using and, if necessary, warmed to redissolve any crystals that may have formed.

6.4 Phosphoric acid (H_3PO_4) - 85% aqueous solution (ACS).

6.5 Sodium sulfate, anhydrous (Na_2SO_4) - Powder (ACS).

6.6 Methylene chloride - Distilled-in-glass quality (Burdick and Jackson, or equivalent).

6.7 Internal standards - 1,4-dichlorobenzene-d_4, d_8-naphthalene, d_{10}-phenanthrene, d_{12}-chrysene, and d_{12}-benzo-(a)pyrene, d_{10}-acenaphthene

6.8 Column performance standards - D_5-phenol, D_5-aniline, D_5-nitrobenzene, and D_3-2,4-dinitrophenol.

6.9 Surrogate standards -

Extractable Organic Analysis - Base/Neutrals	Extractable Organic Analysis - Acids
1. nitrobenzene-d_5	1. phenol-d_5
2. 2-fluorobiphenyl	2. 2-fluorophenol
3. terphenyl-d_{14}	3. 2,4,6-tribromophenol
4. optional*	4. optional*

6.10 Decafluorotriphenylphosphine (DFTPP).

6.11 GPC calibration solution - Methylene chloride containing 100 mg of corn oil, 20 mg of di-n-octyl phthalate, 3 mg of coronene, and 2 mg of sulfur per 100 mL.

7. Calibration

7.1 A multiple internal standard calibration procedure as described by Sauter, et al.[1] is used. To use this approach, the analyst must select five or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurements of the internal standard are not affected by method or matrix interferences. Use the base peak ion as the primary ion for quantification of the standards. If interferences are noted, use the next most intense ion as the secondary ion. The internal standards are added to all calibration standards and all sample extracts analyzed by GC/MS. Column performance standards, and a mass spectrometer tuning standard are included in the internal standard solution used.

7.1.1 A set of five or more internal standards is selected that will permit all components of interest in a chromatogram to have retention times of 0.80 to 1.20 relative to at least one of the internal standards. The following internal standards are recommended for general use: 1,4-dichlorobenzene-d_4, naphthalene-d_8, phenanthrene-d_{10}, chrysene-d_{12}, and benzo(a)pyrene-d_{12}, acenaphthene-d_{10}.

7.1.2 Representative acidic, basic, and polar neutral compounds are added with the internal standards to assess the column performance of the GC/MS system. The following column performance standards are recommended for general use: d_5-phenol, d_5-aniline, d_5-nitrobenzene, and d_3-2,4-dinitrophenol. These compounds can also serve as internal standards if appropriate and the internal standards recommended in Section 7.1.1 can serve as column performance standards if appropriate.

*Lab is requested to add an additional acid and an additional B/N compound to generate data for further modification of the list.

7.1.3 Tuning shall be accomplished by injecting 50 ng of decalfluorotriphenyl phosphine (DFTPP) and hardware tuning to the criteria listed in Table 3, Exhibit E, Section VI.

7.1.4 Prepare the internal standard solution by dissolving in 50.0 mL of methylene chloride 10.0 mg of each standard compound specified in Sections 7.1.1, 7.1.2, and 7.1.3. The resulting solution will contain each standard at a concentration of 200 ug/mL. A solution containing 500 ug/mL of each standard can be prepared by using 5 percent benzene in methylene chloride as the solvent.

7.2 Prepare calibration standards at a minimum of three concentration levels. Each calibration standard should contain each compound of interest and each surrogate standard. Each calibration standard should be mixed with an appropriate amount of the internal standard solution. One of the calibration standards should be at a concentration of two to five times the method detection limit, 1 to 10 ug/mL; one should be at a concentration near, but below the concentration that causes saturation of the mass spectrometer; and, the third should be at a concentration in the middle of this working range of the GC/MS system.

7.3 Analyze 1-2 uL of each calibration standard and tabulate the area of the primary characteristic ion against concentration for each compound including the surrogate compounds. Calculate response factors (RF) for each compound using Equation 1.

Eq. 1 $RF = (A_s C_{is})/(A_{is} C_s)$

Where:

A_s = Area of the characteristic ion for the compound to be measured.

A_{is} = Area of the characteristic ion for the internal standard; the internal standard chosen should be such that the relative retention time of the compound is within the range of 0.80 to 1.20 and as close as possible to 1.00.

C_{is} = Concentration of the internal standard (ug/mL).

C_s = Concentration of the compound to be measured (ug/mL).

If the RF value over the working range is constant (< 10% RSD), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is}, vs. RF.

7.4 The RF must be verified on each working day by the measurement of two or more calibration standards, including one at the beginning of the day and one at the end of the day. The response factors obtained for the calibration standards analyzed immediately before and after a set of samples must be within ± 20% of the response factor used for quantification of the sample concentrations.

8. Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control program. See Exhibit E for guidelines to establish a formal QA/QC plan. For specific QA/QC requirements, see Exhibit A, Tasks II, IV and VI. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of spiked samples as a continuing check on performance. The laboratory is required to maintain performance records to define the quality of data that are generated. Ongoing performance checks must be compared with established performance criteria to determine if the results of analyses are within the accuracy and precision limits expected of the method.

9. Sample Preservation and Handling

9.1 The samples must be refrigerated at 4°C until extraction is complete.

9.2 All samples must be extracted within 5 days of receipt.

10. Sample Extraction

10.1 The extraction procedure involves sonification of the sample with methylene chloride, neutralization to pH 7, and the addition of anhydrous sodium sulfate to remove the water. The amount of acid or base required for the neutralization is determined by titration of the sample. The particle size of all samples, except those comprised of nonporous inorganic particles (e.g. soils and sediments), should be reduced to less than 0.1 mm diameter before extraction. A glass mortar and pestle is recommended for grinding the sample.

10.1.1 Thoroughly mix the sample to enable a representative sample to be obtained. Weigh 3.0 g (wet weight) of sample into a 200-mL centrifuge tube. Add 15 mL methylene chloride and 15 mL of water.

10.1.2 Sonify the mixture for two minutes by inserting the sonifier horn 0.5-1.0 cm below the surface and using a power setting of 5 and a 50 percent pulsed duty cycle.

10.1.3 Transfer the contents of the centrifuge tube to a 400-mL beaker using 50 mL of methylene chloride followed by 150 mL of water as rinses.

10.1.4 Adjust the pH of the mixture to 7.0 ± 0.2 by titration with 0.4 M H_3PO_4 or 0.4 M K_3PO_4 using a pH meter to measure the pH. Record the volume of acid or base required.

10.2 The extraction with methylene chloride is performed using a fresh portion of the sample. Weigh 3.0 g (wet weight) of sample into a 200-mL centrifuge tube. Add 15 mL of methylene chloride. Spike the sample with surrogate standards as described in Exhibit E, page 24. Add 1.0 mL of 4 M phosphate buffer pH 7.0, and an amount of 4 M H_3PO_4 or 4 M K_3PO_4 equal to one tenth of the pH 7 acid or base volume requirement determined in Section 10.1.4. For example, if the acid requirement in Section 10.1.4 was 2.0 mL of 0.4 M H_3PO_4, the amount of 4 M H_3PO_4 needed would be 0.2 mL.

10.3 Sonify the mixture for 1 minute by inserting the sonifier horn 0.5-1.0 cm below the surface and using a power setting of 5 and a 50 percent pulsed duty cycle. Cool the mixture in an ice bath or cold water bath, if necessary, to maintain a temperature of 20-30°C. Add 135 mL of methylene chloride, adjust the position of the sonifier horn to 0.5-1.0 cm below the surface and repeat the sonification for 1 minute. Some samples, especially those that contain much water, may not disperse well in this step but will disperse after sodium sulfate is added. Add all at once an amount of anhydrous sodium sulfate powder equal to 15.0 g plus 3.0 g per mL of the 4 M H_3PO_4 or 4 M K_3PO_4 added in Section 10.2. Immediately cap the centrifuge tube and shake it vigorously for 1 minute. Insert the sonifier horn 0.5-1.0 cm below the surface and sonify for 2 minutes as described above. Allow the mixture to stand until a clear supernatant is obtained. Centrifuge if necessary to facilitate the phase separation. Filter the supernatant required for Sections 10.4, 10.5, and 10.7 (at least 2 mL) through a 0.2 m Teflon filter.

10.4 Estimate the total solvent extractable content (TSEC) of the sample by determining the residue weight of an aliquot of the supernatant from Section 10.3. Transfer 0.1 mL of the supernatant to a tared

aluminum weighing dish, place the weighing dish under a heat lamp at a distance of 8 cm from the lamp for one minute to allow the solvent to evaporate, and weigh on a microbalance. If the residue weight of the 0.1-mL aliquot is less than 0.05 mg, concentrate 25 mL of the supernatant to 1.0 mL and obtain a residue weight on 0.1 mL of the concentrate. For the concentration step use a 25-mL evaporator tube fitted with a micro Snyder column; add two boiling chips and heat in a water bath at 60-65°C. Calculate the TSEC as milligrams of residue per gram of sample using Equation 2 if concentration was not required or Equation 3 if concentration was required.

$$\text{Eq. 2.} \quad \frac{\text{mg of Residue}}{\text{g of Sample}} = \frac{\text{Residue Wt., mg, of 0.1 mL of Supernatant}}{0.002}$$

$$\text{Eq. 3.} \quad \frac{\text{mg of Residue}}{\text{g of Sample}} = \frac{\text{Residue Wt., mg, of 0.1 mL of Concd. Supernatant}}{0.05}$$

10.5 If the TSEC of the sample (as determined in Section 10.4) is less than 50 mg/g, concentrate an aliquot of the supernatant that contains a total of only 10 to 20 mg of residual material. For example, if the TSEC is 44 mg/g, use a 20-mL aliquot of the supernatant, which will contain 17.6 mg of residual material, or if the TSEC is 16 mg/g, use a 50-mL aliquot of the supernatant, which will contain 16.0 mg of residual material. If the TSEC is less than 10 mg/g use 100 mL of the supernatant. Perform the concentration by transferring the aliquot of the supernatant to a K-D flask fitted into a 25-mL concentrator tube. Add two boiling chips, attach a three-ball macro Snyder column to the K-D flask, and concentrate the extract using a water bath at 60 to 65°C. Place the K-D apparatus in the water bath so that the concentrator tube is about half immersed in the water and the entire rounded surface of the flask is bathed with water vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 minutes. At the proper rate of distillation the balls of the column actively chatter but the chambers do not flood. When the liquid has reached an apparent volume of 5 to 6 mL, remove the K-D apparatus from the water bath and allow the solvent to drain for at least 5 minutes while cooling. Remove the Snyder column and rinse the flask and the lower joint of the flask into the concentrator tube with methylene chloride to bring the volume to 10.0 mL. Mix the contents of the concentrator tube by inserting a stopper and inverting several times.

10.6 Analyze the concentrate from Section 10.5 or, if the TSEC of the sample is 50 mg/g or more, analyze the supernatant from Section 10.3 using gas chromatography. Use a 30-m x 0.25 mm bonded-phase silicone coated fused silica capillary column under the chromatographic conditions described in Section 13. Standardize the GC/FID for half scale response for 50 ng injected of the internal standard to be used in the GC screen. Estimate the concentration factor or dilution factor required to give the optimum concentration for the subsequent GC/MS analysis. In general the optimum concentration will be one in which the average peak height of the five largest peaks or the height of an unresolved envelope of peaks is the same as that of an internal standard (e.g., phenanthrene-d_{10}) at a concentration of 50-100 ug/mL.

If there is no concentration factor which will yield a major component with GC peak height exceeding 25% of the internal standard peak height then the sample is low level. In that case proceed to the EMSL-Ci Procedure for Semivolatiles on page 64 of this Exhibit, otherwise, proceed with this method.

10.7 If the optimum concentration determined in Section 10.6 is 20 mg of residual material per mL or less proceed to Section 10.8. If the optimum concentration is greater than 20 mg of residual material per mL and if the TSEC is greater than 50 mg/g, apply the GPC cleanup procedure described in Section 11. For the GPC cleanup concentrate 90 mL of the supernatant from Section 10.3 or a portion of the supernatant that contains a total of 600 mg of residual material (whichever is the smaller volume). Use the concentration procedure described in Section 10.5 and concentrate to a final volume of 15.0 mL. Stop the concentration prior to reaching 15.0 mL if any oily or semisolid material separates out and dilute as necessary (up to a maximum final volume equal to the volume of supernatant used) to redissolve the material. (Disregard the presence of small amounts of inorganic salts that may settle out).

10.8 Concentrate further or dilute as necessary an aliquot of the concentrate from Section 10.5 or an aliquot of the supernatant from Section 10.3, or if GPC cleanup was necessary, an aliquot of the concentrate from Section 11.3 to obtain 1.0 mL of a solution having the optimum concentration, as described in Section 10.6, for the GC/MS analysis. If the aliquot needs to be diluted, dilute it to a volume of 1.0 mL with methylene chloride. If the aliquot needs to be concentrated, concentrate it to 1.0 mL as described in Section 10.4. Do not let the volume in the concentrator tube go below 0.6 mL at any time. Stop the concentration prior to reaching 1.0 mL if any oily or semisolid material separates out and dilute as necessary (up to a maximum final volume of 10 mL) to redissolve the material. (Disregard the presence of small amounts of inorganic salts that may settle out). Add a volume of the internal standard solution that contains 50 ug each of the internal standards, column performance

standards, to 1.0 mL of the final concentrate and save for GC/MS analysis as described in Section 13. Calculate the concentration in the original sample that is represented by the internal standard using Equation 4 if an aliquot of the concentrate from Section 10.5 was used in Section 10.8, Equation 5 if an aliquot of the supernatant from Section 10.3 was used in Section 10.8, or Equation 6 if an aliquot of the GPC concentrate from Section 11.3 was used in Section 10.8.

$$\text{Eq. 4} \quad \frac{\text{ug of Int. Std.}}{\text{g of Sample}} = \frac{50}{S} \times \frac{150}{V_{s(10.5)}} \times \frac{10}{V_{c(10.8)}} \times \frac{\text{Final Vol., mL}}{1}$$

$$\text{Eq. 5} \quad \frac{\text{ug of Int. Std.}}{\text{g of Sample}} \times \frac{50}{S} \times \frac{150}{V_{s(10.8)}} \times \frac{\text{Final Vol., mL}}{1}$$

$$\text{Eq. 6} \quad \frac{\text{ug of Int. Std.}}{\text{g of Sample}} = \frac{50}{S} \times \frac{150}{V_{s(10.7)}} \times \frac{V_F}{V_{GPC(10.7)}} \times \frac{\text{Final Vol., mL}}{1}$$

where:

V_s = Volume of supernatant from Section 10.3 used in Sections 10.5, 10.8, or 10.7.

$V_{c(10.8)}$ = Volume of concentrate from Section 10.5 used in Section 10.8.

$V_{F(10.7)}$ = Final volume of concentrate in Section 10.7.

V_{GPC} = Volume of GPC concentrate from Section 11.3 used in Section 10.8.

Use this calculated value for the quantification of individual compounds as described in Section 13.2.

11. Cleanup Using Gel Permeation Chromatography

11.1 Prepare a 600 mm x 25 mm I.D. gel permeation chromatography (GPC) column using a slurry containing 80 g of Bio-Beads S-X8 that have been swelled in methylene chloride for at least 4 hours. Prior to initial use, rinse the column with methylene chloride at 1 mL/min for 16 hours to remove any traces of contaminants. Calibrate the

system by injecting 5 mL of the GPC calibration solution, eluting with methylene chloride at 5 mL/min for 50 minutes and observing the resultant UV detector trace. The column may be used indefinitely as long as no darkening or pressure increases occur and a column efficiency of at least 500 theoretical plates is achieved. The pressure should not be permitted to exceed 50 psi. Recalibrate the system daily.

11.2 Inject a 5-mL aliquot of the concentrate from Section 10.7 onto the GPC column and elute with methylene chloride at 5 mL/min for 50 minutes. Discard the first fraction that elutes up to a rentention time represented by the minimum between the corn oil peak and the di-n-octyl phthalate peak in the calibration run. Collect the next fraction eluting up to a rentention time represented by the minimum between the coronene peak and the sulfur peak in the calibration run. Apply the above GPC separation to a second 5-mL aliquot of the concentrate from Section 10.7 and combine the fractions collected.

11.3 Concentrate the combined GPC fractions to 10.0 mL as described in Section 10.5. Estimate the TSEC of the concentrate as described in Section 10.4. Estimate the concentration factor or dilution factor required to give the optimum concentration for the subsequent GC/MS analysis as described in Section 10.6.

12. Daily GC/MS Performance Tests

12.1 At the beginning of each day that analyses are to be performed, the GC/MS system must be checked to see that the tuning sensitivity and overall performance of the system are acceptable. The quality control protocols required for the fused silica capillary column GC/MS analyses are described in Exhibit E, Section VIII. Where inconsistencies occur between EMSL-LV Procedure No. 2 and Exhibit E, Exhibit E shall have precedence.

12.2 The following instrumental parameters are required for all performance tests and for all sample analyses:

Electron Energy - 70 volts (nominal)
Mass Range - 40 to 450 amu
Scan Time - 1 second per scan.

12.3 The mass spectrometer must be tuned to achieve all of the key ion criteria for the mass spectrum of DFTPP given in Table 3 of Exhibit E, Section VI, when a solution containing 50 ng of DFTPP is injected into the GC/MS system.

13. GC/MS Analysis

13.1 Analyze the 1-mL concentrate from Section 10.8 by GC/MS using a 30 m x 0.25 mm bonded-phase silicone-coated fused silica capillary column. The recommended GC operating conditions to be used are as follows:

Initial Column Temperature Hold - 30°C for 4 minutes

Column Temperature Program - 30-300°C at 8 degrees/min

Final Column Temperature Hold - 300°C for 10 minutes

Injector Temperature - 300°C

Transfer Line Temperature - 300°C

Injector - Grob-type, splitless

Sample Volume - 1 µL

Carrier Gas - Helium at 30 cm/sec

14. Qualitative Identification

14.1 The criteria list in Exhibit A under Task III must be met to make a qualitative identification. Qualitative identification shall be accomplished by using the procedures listed in Federal Register Method 625.

15. Quantitative Determination

15.1 When a compound has been identified, the quantification of that compound shall be accomplished using the procedures listed in Federal Register Method 625.

16. Dry Weight Determination

16.1 Add a portion of the sample to a tared weighing dish. Weigh and record the weight.

16.2 Place weighing dish plus sample, with the cover tipped to allow for moisture escape, in a drying oven that is set at 105°C. Perform this task in a well ventilated area.

16.3 Dry the sample to constant weight. Cool the sample in a dessicator with the weighing dish cover in place before each weighing. Record each weight. Do not analyze the dried sample.

17. References

1. Sauter, A. D., Betowski, L. D., Smith, T. R., Strickler, V. A., Reimer, R. C., Colby, B. N., and Wilkinson, J. E., "Fused Silica Capillary Column GC/MS for the Analysis of Priority Pollutants", J. High Resolut. Chromatogr. Chromatogr. Commun., 4, 366 (1981).

TABLE 1. RECOVERY OF COMPOUNDS SPIKED INTO DRY SRM-1645(d)

Compound	Percent Recovery		
	Spike Extract(a)	Dry Neutral Extract(b)	Wet Acid-Base Extract(c)
1. 2,4-Dimethylpyridine	58	59	54
2. 2-Fluoroaniline	70	65	49
3. 2,4,6-Trimethylpyridine	49	42	43
4. 4-Methylaniline	63	37	20
5. 4-Chlorophenol	92	80	77
6. Quinoline	79	76	60
7. 4-Chlorobenzoic acid	103	36	62
8. 4-Brombenzoic acid	86	18	56
9. 4-Nitrophenol	56	51	0
10. 2-Methyl-4,6-dinitrophenol	33	32	28
11. 2,6-Dichloro-4-nitroaniline	61	57	49
12. 2,4-Dinitroaniline	63	59	46
13. Diethylstilbestrol	42	33	23

(a)Spike compounds were added to an extract of an unspiked sample; the values given are the averages obtained from two analyses.

(b)Spiked sample was extracted using the method specified for the inter-laboratory study; the values given are the averages obtained from two analyses of each of two extracts.

(c)Spiked sample was extracted using an acid-base extraction method; the values given are the averages obtained from two analyses of each of two acid extracts and each of two base extracts.

(d)NBS standard reference river sediment.

APPENDIX B.10

Modified EMSL-LV Procedure No. 2

Appendix B.10
Modified EMSL-LV Procedure No. 2

EMSL-LV Procedure No. 2
BNAPT Extraction
As done by IT, Cerritos

1. Weigh 2.0g or 50.0g of sample, for Medium or Low extractions respectively, into a 250ml erlenmeyer flask.
2. Add all surrogate and spiking solutions, except TCDD spiking solutions.
3. Add ~2ml phosphate buffer solution.
4. Add 10-15g anhydrous Sodium Sulfate, dependent on the moisture content of the sample.
5. Add 100ml Methylene Chloride.
6. Sonicate samples for 3 minutes, power setting 5, 50% pulsed duty cycle.
7. Decant or pipet off Methylene Chloride layer.
8. Dry extract through Sodium Sulfate and collect in a K-D/Receiver apparatus. Be sure to use a graduated Receiver if volume adjustment will be done in the Receiver.
9. Repeat 5. through 8. twice more (total 3 extractions) combining extracts in the same K-D/Receiver apparatus.
10. Concentrate extract by heating on a steambath until the apparent volume in the receiver is ~1ml.
11. Remove the K-D/Receiver apparatus from the steambath, place upright in a holder, and allow to cool. It is important that the extract does not go to dryness.
12. Remove the K-D from the Receiver, adjust the volume to 10.0ml with Methylene Chloride, mix and transfer to a vial for storage.

BNA Extraction Completed

13. Remove two 1.0ml aliquots from the vial, place them each in a K-D/Receiver apparatus, label one as the Pesticide fraction and one as the TCDD fraction.
14. Add 50ml Hexane to each K-D/Receiver apparatus and concentrate as before in 10. and 11.
15. Adjust the volume of the Pesticide fraction to about 10ml with Hexane.
16. Clean-up the extract by eluting through a 300mm x 10mm glass column containing activated Florisil PR (pre-eluted with 50ml of 50% Ether/50% Hexane) with 200ml 50% Ether/50% Hexane.
17. Collect the eluate in a K-D/Receiver apparatus; concentrate as in 10.; exchange into Hexane as in 14.
18. Quantitatively transfer to a 10ml volumetric flask and adjust the volume to 10.0ml with Hexane, mix and transfer to a vial for storage.

Pesticide Extraction/Preparation Completed

19. Remove the K-D from the Receiver of the TCDD fraction.
20. Add TCDD Surrogate spiking solution, in Tetradecane.
21. With a stream of Nitrogen concentrate to less than 1ml.
22. Adjust the volume to 1.0ml with tetradecane, mix and transfer to a vial for storage.

TCDD Extraction/Preparation Completed

Store all extracts refrigerated at 4°C until analysis.

APPENDIX B.11

EPA Method 608

Organochlorine Pesticides and PCB's—Method 608

1. *Scope and Application.*

1.1 This method covers the determination of certain organochlorine pesticides and polychlorinated biphenyls (PCBs). The following parameters may be determined by this method:

Parameter	Storet No.
Aldrin	[illegible]
α-BHC	[illegible]
β-BHC	[illegible]
δ-BHC	[illegible]
γ-BHC	[illegible]
Chlordane	[illegible]
4,4'-DDD	[illegible]
4,4'-DDE	[illegible]
4,4'-DDT	[illegible]
Dieldrin	[illegible]
Endosulfan I	[illegible]
Endosulfan II	[illegible]
Endosulfan Sulfate	[illegible]
Endrin	[illegible]
Endrin Aldehyde	[illegible]
Heptachlor	[illegible]
Heptachlor Epoxide	[illegible]
Toxaphene	[illegible]
PCB-1016	[illegible]
PCB-1221	[illegible]
PCB-1232	[illegible]
PCB-1242	[illegible]
PCB-1248	[illegible]
PCB-1254	[illegible]
PCB-1260	[illegible]

1.2 This method is applicable to the determination of these compounds in municipal and industrial discharges. It is designed to be used to meet the monitoring requirements of the National Pollutant Discharge Elimination System (NPDES). As such, it presupposes a high expectation of finding the specific compounds of interest. If the user is attempting to screen samples for any or all of the compounds above, he must develop independent protocols for the verification of identity.

1.3 The sensitivity of this method is usually dependent upon the level of interferences rather than instrumental limitations. The limits of detection listed in Table I represent sensitivities that can be achieved in wastewaters in the absence of interferences.

1.4 This method is recommended for use only by experienced residue analysts or under the close supervision of such qualified persons.

2. *Summary of Method.*

2.1 A 1-liter sample of wastewater is extracted with methylene chloride using separatory funnel techniques. The extract is dried and concentrated to a volume of 10 ml or less. Chromatographic conditions are described which allow for the accurate measurement of the compounds in the extract.

2.2 If interferences are encountered, the method provides selected general purpose cleanup procedures to aid the analyst in their elimination.

3. *Interferences.*

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences coextracted from the samples will vary considerably from source to source, depending upon the diversity of the industrial complex or municipality being sampled. While general cleanup techniques are provided as part of this method, unique samples may require additional cleanup approaches to achieve the sensitivities stated in Table 1.

3.3 Glassware must be scrupulously clean. Clean all glassware as soon as possible after use by rinsing with the last solvent used. This should be followed by detergent washing in hot water. Rinse with tap water, distilled water, acetone and finally pesticide quality hexane. Heavily contaminated glassware may require treatment in a muffle furnace at 400°C for 15 to 30 minutes. Some high boiling materials, such as PCBs, may not be eliminated by this treatment. Volumetric ware should not be heated in a muffle furnace. Glassware should be sealed/stored in a clean environment immediately after drying or cooling to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

3.4 Interferences by phthalate esters can pose a major problem in pesticide analysis. These materials elute in the 15% and 50% fractions of the Florisil cleanup. They usually can be minimized by avoiding contact with any plastic materials. The contamination from pathalate esters can be completely eliminated with the use of a microcoulometric or electrolytic conductivity detector.

4. *Apparatus and Materials.*

4.1 Sampling equipment, for discrete or composite sampling.

4.1.1 Grab sample bottle—amber glass, 1-liter or 1-quart volume. French or Boston Round design is recommended. The container must be washed and solvent rinsed before use to minimize interferences.

4.1.2 Bottle caps—Threaded to screw on to the sample bottles. Caps must be lined with Teflon. Foil may be substituted if sample is not corrosive.

4.1.3 Compositing equipment—Automatic or manual compositing system. Must incorporate glass sample containers for the collection of a minimum of 250 ml. Sample containers must be kept refrigerated during sampling. No tygon or rubber tubing may be used in the system.

4.2 Separatory funnel—2000 ml, with Teflon stopcock.

4.3 Drying column—20 mm ID pyrex chromatographic column with coarse frit.

4.4 Kuderna-Danish (K-D) Apparatus

4.4.1 Concentrator tube—10 ml, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at 1.0 and 10.0 ml level. Ground glass stopper (size 19/22 joint) is used to prevent evaporation of extracts.

4.4.2 Evaporative flask—500 ml (Kontes K-57001-0500 or equivalent). Attach to concentrator tube with springs. (Kontes K-662750-0012).

4.4.3 Snyder column—three-ball macro (Kontes K503000-0121 or equivalent).

4.4.4 Boiling chips—extracted, approximately 10/40 mesh.

4.5 Water bath—Heated, with concentric ring cover, capable of temperature control (±2°C). The bath should be used in a hood.

4.6 Gas chromatograph—Analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including electron capture or halogen-specific detector, column supplies, recorder, gases, syringes. A data system for measuring peak areas is recommended.

4.7 Chromatographic column—Pyrex, 400 mm × 25 mm OD, with coarse fritted plate and Teflon stopcock (Kontes K-42054-213 or equivalent).

5. *Reagents.*

5.1 Preservatives:

5.1.1 Sodium hydroxide—(ACS) 10 N in distilled water.

5.1.2 Sulfuric acid (1+1)—(ACS) Mix equal volumes of conc. H_2SO_4 with distilled water.

5.2 Methylene chloride—Pesticide quality or equivalent.

5.3 Sodium Sulfate—(ACS) Granular, anhydrous (purified by heating at 400°C for 4 hrs. in a shallow tray).

5.4 Stock standards—Prepare stock standard solutions at a concentration of 1.00 μg/μl by dissolving 0.100 grams of assayed reference material in pesticide quality isooctane or other appropriate solvent and diluting to volume in a 100 ml ground glass stoppered volumetric flask. The stock solution is transferred to ground glass stoppered reagent bottles, stored in a refrigerator, and checked frequently for signs of degradation or evaporation, especially just prior to preparing working standards from them.

Appendix B.11
EPA Method 608

8.5 Boiling chips—Hengar granules (Hengar Co.; Fisher Co.) or equivalent.

8.6 Mercury—triple distilled.

8.7 Aluminum oxide—basic or neutral, active.

8.8 Hexane—pesticide residue analysis grade.

8.9 Isooctane (2,2,4-trimethyl pentane)—pesticide residue analysis grade.

8.10 Acetone—pesticide residue analysis grade.

8.11 Diethyl ether—Nanograde, redistilled in glass if necessary.

8.11.1 Must be free of peroxides as indicated by EM Quant test strips (Test strips are available from EM Laboratories, Inc., 500 Executive Blvd., Elmsford, N.Y., 10523).

8.1.2 Procedures recommended for removal of peroxides are provided with the test strips. After cleanup 20 ml ethyl alcohol preservative must be added to each liter of ether.

8.12 Florisil—PR grade (60/100 mesh); purchase activated at 1250°F and store in glass containers with glass stoppers or foil-lined screw caps. Before use activate each batch at least 16 hours at 130°C in a foil covered glass container.

6. *Calibration.*

6.1 Prepare calibration standards that contain the compounds of interest, either singly or mixed together. The standards should be prepared at concentrations covering two or more orders of magnitude that will completely bracket the working range of the chromatographic system. If the sensitivity of the detection system can be calculated from Table 1 as 100 μg/l in the final extract, for example, prepare standards at 10 μg/l, 50 μg/l, 100 μg/l, 500 μg/l, etc., so that injections of 1–5 μl of each calibration standard will define the linearity of the detector in the working range.

6.2 Assemble the necessary gas chromatographic apparatus and establish operating parameters equivalent to those indicated in Table 1. By injecting calibration standards, establish the sensitivity limit of the detector and the linear range of the analytical system for each compound.

6.3 The cleanup procedure in Section 10 utilizes Florisil chromatography. Florisil from different batches or sources may vary in absorption capacity. To standardize the amount of Florisil which is used, the use of lauric acid value (Mills, 1966) is suggested. The referenced procedure determines the adsorption from hexane solution of lauric acid (mg) per gram Florisil. The amount of Florisil to be used for each column is calculated by dividing this factor into 110 and multiplying by 20 grams.

6.4 Before using any cleanup procedure, the analyst must process a series of calibration standards through the procedure to validate elution patterns and the absence of interferences from the reagents.

7. *Quality Control.*

7.1 Before processing any samples, the analyst should demonstrate through the analysis of a distilled water method blank, that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination.

7.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the accuracy of the analysis. Where doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as mass spectroscopy should be used.

8. *Sample Collection, Preservation, and Handling.*

8.1 Grab samples must be collected in glass containers. Conventional sampling practices should be followed, except that the bottle must not be prewashed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be free of tygon and other potential sources of contamination.

8.2 The samples must be iced or refrigerated from the time of collection until extraction. Chemical preservatives should not be used in the field unless more than 24 hours will elapse before delivery to the laboratory. If the samples will not be extracted within 48 hours of collection, the sample should be adjusted to a pH range of 6.0–8.0 with sodium hydroxide or sulfuric acid.

8.3 All samples must be extracted within 7 days and completely analyzed within 30 days of collection.

9. *Sample Extraction.*

9.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a two-liter separatory funnel. Check the pH of the sample with wide-range pH paper and adjust to within the range of 5–9 with sodium hydroxide or sulfuric acid.

9.2 Add 60 ml methylene chloride to the sample bottle, seal, and shake 30 seconds to rinse the inner walls. Transfer the solvent into the separatory funnel, and extract the sample by shaking the funnel for two minutes with periodic venting to release vapor pressure. Allow the organic layer to separate from the water phase for a minimum of ten minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, or centrifugation. Collect the methylene chloride extract in a 250-ml Erlenmeyer flask.

9.3 Add a second 60-ml volume of methylene chloride to the sample bottle and complete the extraction procedure a second time, combining the extracts in the Erlenmeyer flask.

9.4 Perform a third extraction in the same manner. Pour the combined extract through a drying column containing 3–4 inches of anhydrous sodium sulfate, and collect it in a 500-ml Kuderna-Danish (K–D) flask equipped with a 10 ml concentrator tube. Rinse the Erlenmeyer flask and column with 20–30 ml methylene chloride to complete the quantitative transfer.

9.5 Add 1–2 clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 ml methylene chloride to the top. Place the K–D apparatus on a hot water bath (60–65°C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed in vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15–20 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 1 ml, remove the K–D apparatus and allow it to drain for at least 10 minutes while cooling.

9.6 Increase the temperature of the hot water bath to about 80°C. Momentarily remove the Snyder column, add 50 ml of hexane and a new boiling chip and reattach the Snyder column. Pour about 1 ml of hexane into the top of the Snyder column and concentrate the solvent extract as before. The elapsed time of concentration should be 5 to 10 minutes. When the apparent volume of liquid reaches 1 ml, remove the K–D apparatus and allow it to drain at least 10 minutes while cooling. Remove the Snyder column and rinse the flask and

its lower joint into the concentrator tube with 1–2 ml of hexane, and adjust the volume to 10 ml. A 3-ml syringe is recommended for this operation. Stopper the concentrator tube and store refrigerated if further processing will not be performed immediately. If the sample extract requires no further cleanup, proceed with gas chromatographic analysis. If the sample requires cleanup, proceed to Section 10.

9.7 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000 ml graduated cylinder. Record the sample volume to the nearest 5 ml.

10. *Cleanup and Separation.*

10.1 Cleanup procedures are used to extend the sensitivity of a method by minimizing or eliminating interferences that mask or otherwise configure the gas chromatographic response to the pesticides and PCB's. The Florisil column allows for a select fractionation of the compounds and will eliminate polar materials. Elemental sulfur interferes with the electron capture gas chromatography of certain pesticides but can be removed by the techniques described below.

10.2 Florisil Column Cleanup

10.2.1 Add a weight of Florisil, (nominally 21g.) predetermined by calibration (8.3, 8.4), to a chromatographic column. Settle the Florisil by tapping the column. Add sodium sulfate to the top of the Florisil to form a layer 1–2 cm deep. Add 60 ml of hexane to wet and rinse the sodium sulfate and Florisil. Just prior to exposure of the sodium sulfate to air, stop the elution of the hexane by closing the stopcock on the chromatography column. Discard the eluate.

10.2.2 Adjust the sample extract volume to 10 ml and transfer it from the K–D concentrator tube to the Florisil column. Rinse the tube twice with 1–2 ml hexane, adding each rinse to the column.

10.2.3 Place a 500 ml K–D flask and clean concentrator tube under the chromatography column. Drain the column into the flask until the sodium sulfate layer is nearly exposed. Elute the column with 200 ml of 6% ethyl ether in hexane (Fraction 1) using a drip rate of about 5 ml/min. Remove the K–D flask and set aside for later concentration. Elute the column again, using 200 ml of 15% ethyl ether in hexane (Fraction 2), into a second K–D flask. Perform the third elution using 200 ml of 50% ethyl in hexane (Fraction 3). The elution patterns for the pesticides and PCB's are shown in Table II.

10.2.4 Concentrate the eluates by standard K–D techniques (9.5), substituting hexane for the glassware rinses and using the water bath at about 85° C. Adjust final volume to 10 ml with hexane. Analyze by gas chromatography.

10.3 Elemental sulfur will usually elute entirely in Fraction 1. To remove sulfur interference from this fraction or the original extract, pipet 1.00 ml of the concentrated extract into a clean concentrator tube or Teflon-sealed vial. Add 1–3 drops of mercury and seal. Agitate the contents of the vial for 15–30 seconds. Place the vial in an upright position on a reciprocal laboratory shaker and shake for 2 hours. Analyze by gas chromatography.

11. *Gas Chromatography.*

11.1 Table I summarizes some recommended gas chromatographic column materials and operating conditions for the instrument. Included in this table are estimated retention times and sensitivities that should be achieved by this method. Examples of the separations achieved by these columns are shown in Figures 1 through 10. Calibrate the system daily with a minimum of three injections of calibration standards.

11.2 Inject 2–5 µl of the sample extract using the solvent-flush technique. Smaller (1.0 µl) volumes can be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 µl, and the resulting peak size, in area units.

11.3 If the peak area exceeds the linear range of the system, dilute the extract and reanalyze.

11.4 If the peak area measurement is prevented by the presence of interferences, further cleanup is required.

12. *Calculations.*

12.1 Determine the concentration of individual compounds according to the formula:

$$\text{Concentration, } \mu g/l = \frac{A(B)(V_t)}{(V_s)(V_i)}$$

Where:

A = Calibration factor for chromatographic system, in nanograms material per area unit.

B = Peak size in injection of sample extract, in area units

V_i = Volume of extract injected (µl)

V_t = Volume of total extract (µl)

V_s = Volume of water extracted (ml)

12.2 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed, all data obtained should be reported.

13. *Accuracy and Precision.*

13.1 The U.S. EPA Environmental Monitoring and Support Laboratory in Cincinnati is in the process of conducting an interlaboratory method study to determine the accuracy and precision of this test procedure.

Bibliography

1. "Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters. Category 10–Pesticides and PCB's." Report for EPA Contract 68–03–2608.

2. Mills, P. A., "Variation of Florisil Activity: Simple Method for Measuring Absorbent Capacity and Its Use in Standardizing Florisil Columns." Journal of the Association of Official Analytical Chemists, *51*, 29 (1968).

Table I.—*Gas Chromatography of Pesticides and PCB's*

Parameter	Retention time, min. Col. 1[1]	Col. 2[2]	Sensitivity, ng. Col. 1[3]	Col. 2[3]
Aldrin	2.0	4.0	0.5	0.5
α-BHC	2.5	4.5	0.5	0.5
β-BHC	2.8	5.0	0.5	0.5
γ-BHC	2.6	4.8	0.5	0.5
δ-BHC	2.2	4.2	0.5	0.5
Chlordane	5.0	8.0	0.5	0.5
4,4'-DDD	5.8	9.0	0.5	0.5
4,4'-DDE	4.0	7.0	0.5	0.5
4,4'-DDT	5.0	8.0	0.5	0.5
Dieldrin	4.0	7.0	0.5	0.5
Endosulfan I	4.5	7.5	0.5	0.5
Endosulfan II	5.5	8.5	0.5	0.5
Endosulfan sulfate	6.5	9.5	0.5	0.5
Endrin	5.0	8.0	0.5	0.5
Endrin aldehyde	6.0	9.0	0.5	0.5
Heptachlor	2.5	4.5	0.5	0.5
Heptachlor epoxide	3.5	6.0	0.5	0.5
Isodrin	3.0	5.5	0.5	0.5
Kepone	6.0	9.0	0.5	0.5
Methoxychlor	6.0	9.0	0.5	0.5
Toxaphene	5.0	8.0	0.5	0.5
PCB-1016	3.0	5.5	0.5	0.5
PCB-1221	3.0	5.5	0.5	0.5
PCB-1232	3.0	5.5	0.5	0.5
PCB-1242	3.0	5.5	0.5	0.5
PCB-1248	3.0	5.5	0.5	0.5
PCB-1254	3.0	5.5	0.5	0.5
PCB-1260	3.0	5.5	0.5	0.5

[1] Tenax GC/SE-30 (4 ft. + 6 ft.) glass column with 5% SP-2250/1.95% SP-2401 packed in a 1/8 in. glass tube with 5% methanol/95% Argon carrier gas at 60 ml/min flow rate. Column temperature = 200°C.

[2] Tenax GC/SE-30 (4 ft. + 6 ft.) glass column with 5% OV-1 + 4 ft. 1/8 in. glass tube with 5% methanol/95% Argon carrier gas at 60 ml/min flow rate. Column temperature = 200°C.

[3] Detection limit is estimated from the minimum detectable GC response using signal to noise ratio of 2:1. Sensitivity will vary with the volume of the final solution of the sample extract, and assuming a GC response of 5 millimeters.

[4] Multiple peak response. See Figures 3–10.

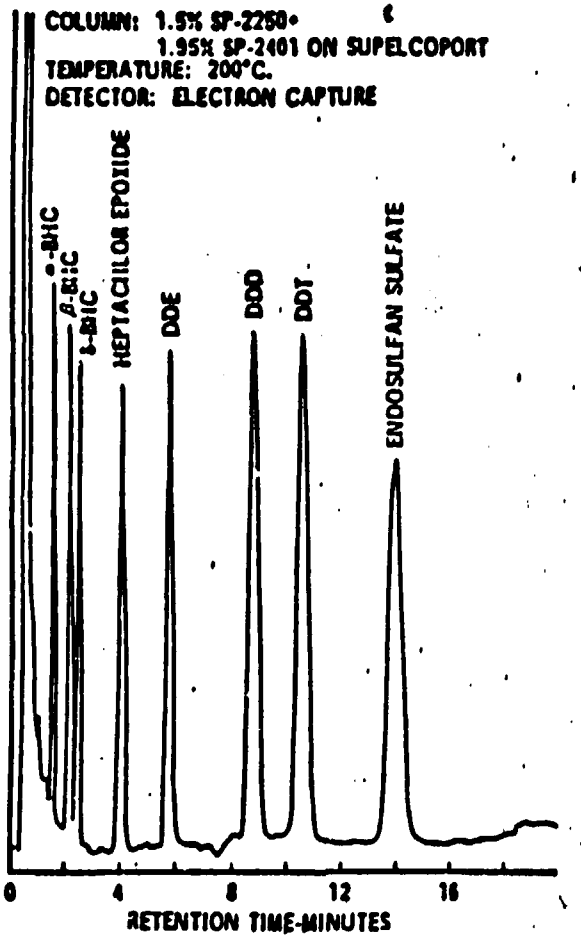


Figure 1. Gas chromatogram of pesticides

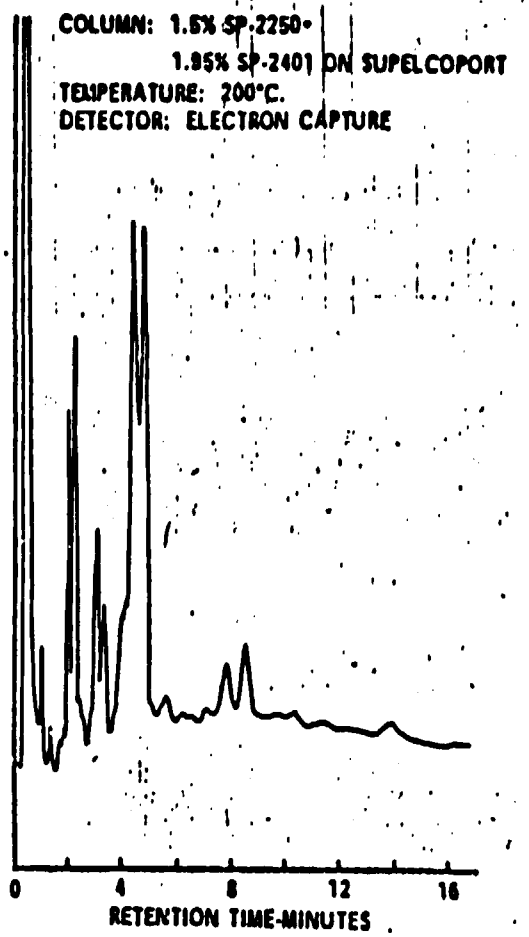


Figure 2. Gas chromatogram of chlordane

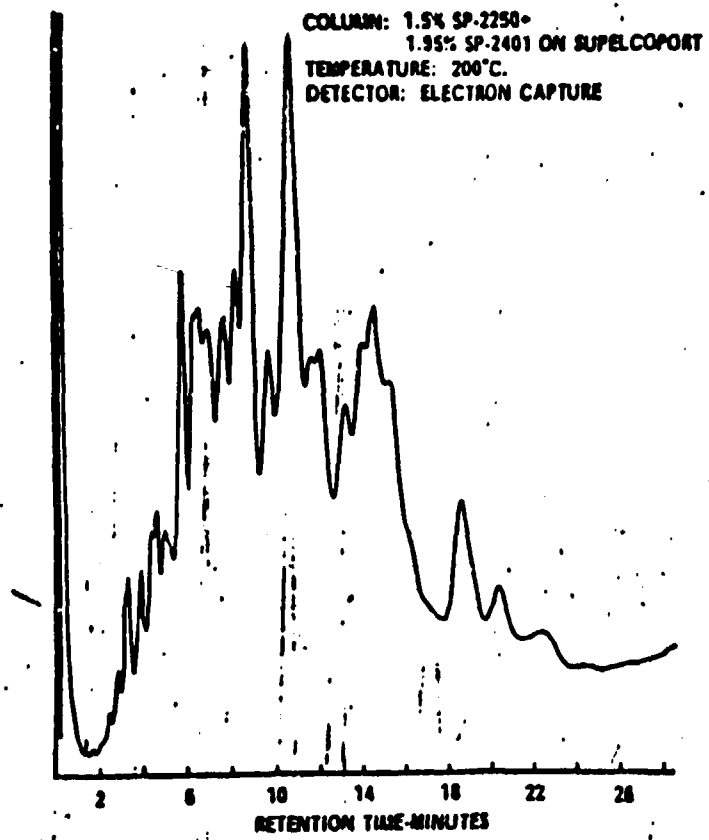


Figure 3. Gas chromatogram of toxaphene

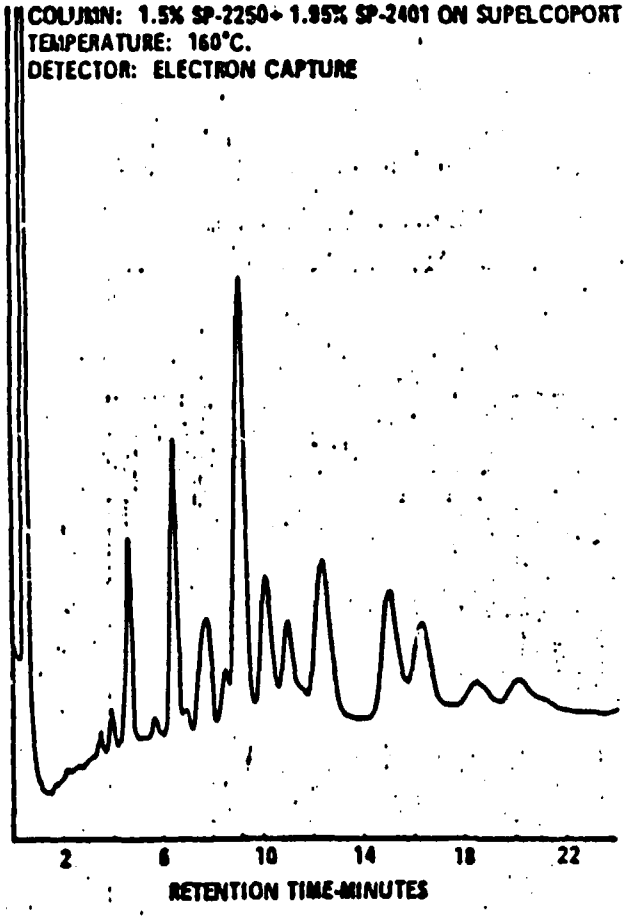


Figure 4. Gas chromatogram of PCB-1016

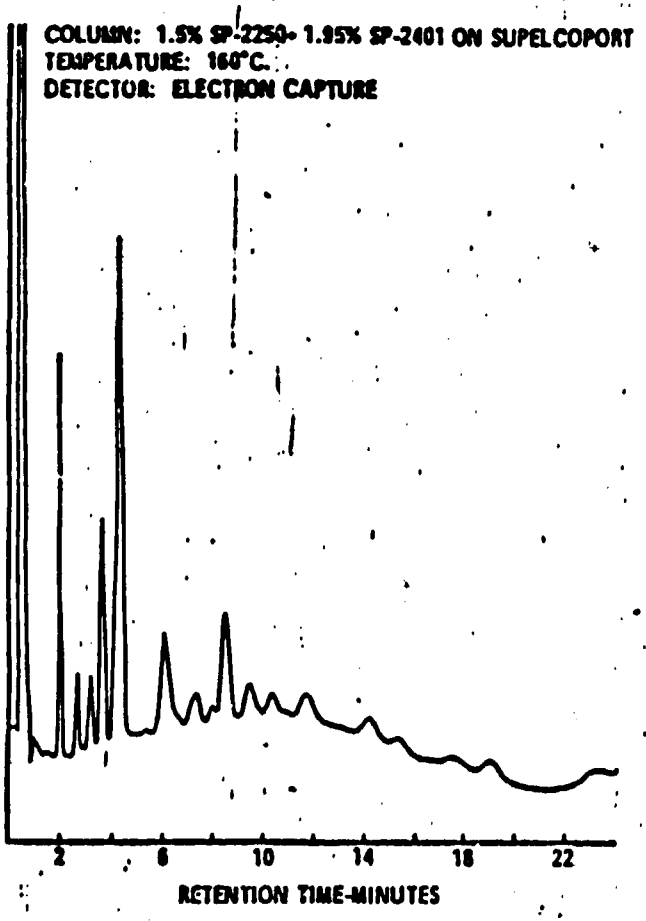


Figure 5. Gas chromatogram of PCB-1221

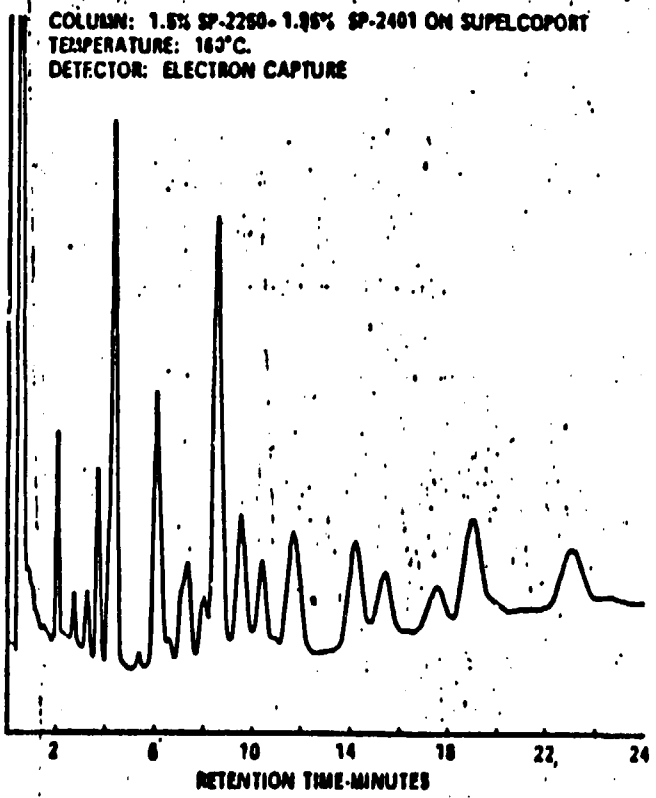


Figure 6. Gas chromatogram of PCB-1232

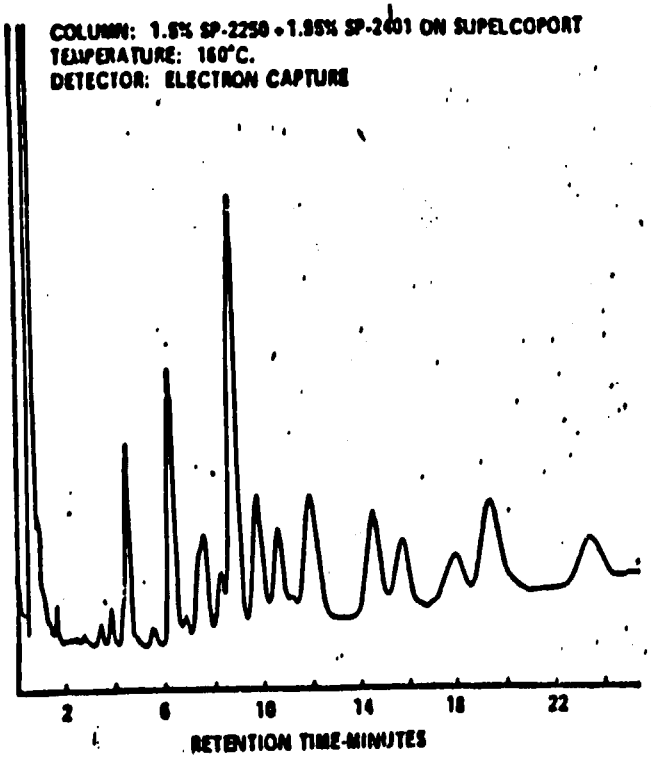


Figure 7. Gas chromatogram of PCB-1242

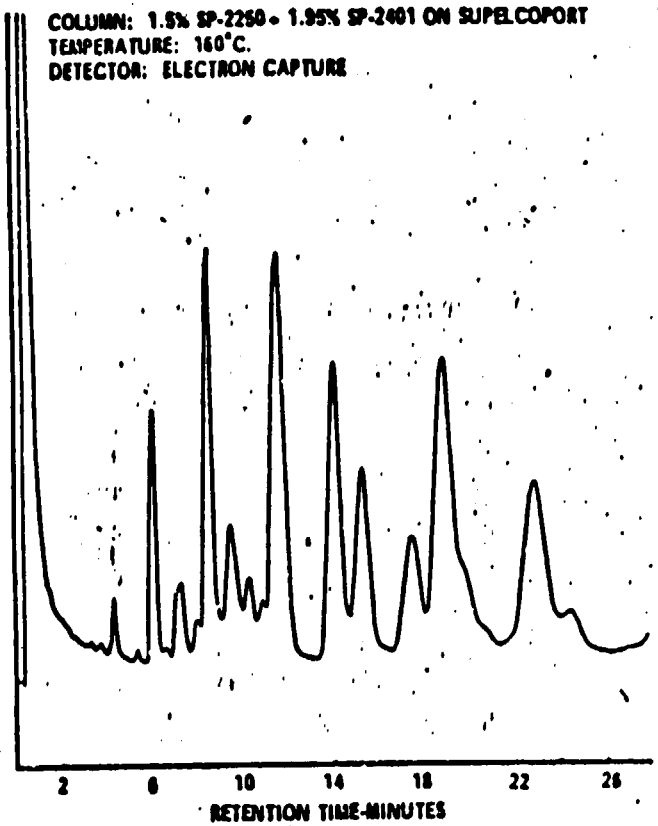


Figure 8. Gas chromatogram of PCB-1248

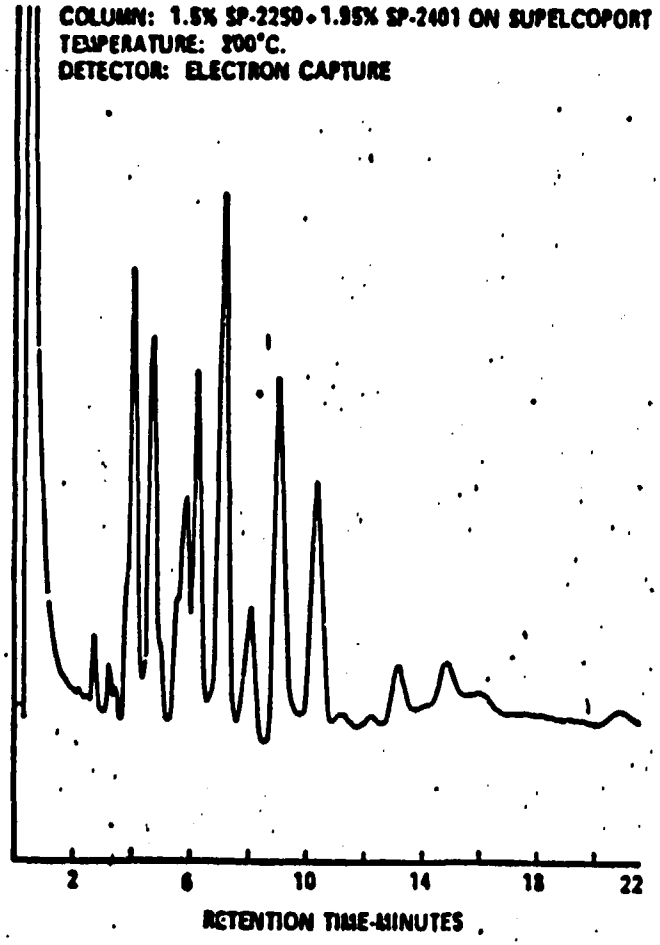


Figure 9. Gas chromatogram of PCB-1254

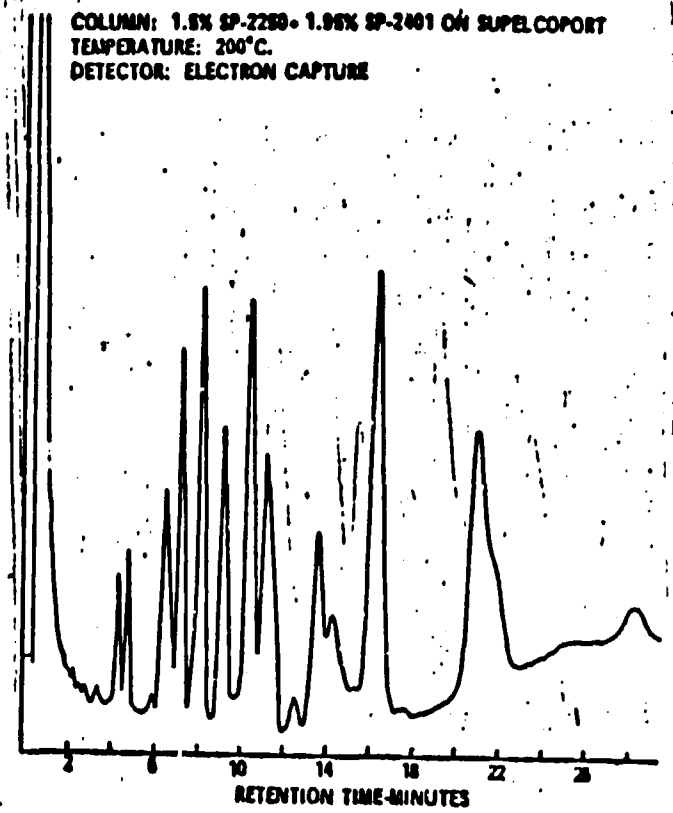


Figure 10. Gas chromatogram of PCB-1260

APPENDIX 8.12

H_2SO_4/Hg Clean-up

Appendix 6.12
H_2SO_4/Hg Clean-up

Appendix

Sulfuric Acid and Mercury Clean-up Procedure

1. Samples are prepared by weighing approximately 100 milligrams into a 10.0ml volumetric flask and bringing to volume by adding pesticide quality hexane. Approximately 5mls of the hexane solution was transferred to a 10ml screw cap vial equipped with a Teflon-lined cap.

2. Add approximately 5.0ml concentrated sulfuric acid. Shake well for approximately 10 minutes and allow layers to separate (approximately 15 minutes).

3. Transfer the top layer to another 10ml screw cap vial containing approximately 0.5 grams mercury. Shake well for 2-3 minutes and allow to sit for approximately 15 minutes.

4. Transfer to a clean 10ml screw cap vial leaving the mercury and precipitate behind.

5. Repeat steps 2-4 two more times or more as needed.

6. The purified samples were then analyzed directly by injection onto the gas chromatograph.

APPENDIX B.13

EPA Method 8150

METHOD 8150

CHLORINATED HERBICIDES

1.0 Scope and Application

1.1 Method 8150 is a gas chromatographic (GC) method for determining certain chlorinated acid herbicides in groundwater and waste samples. Specifically, Method 8150 may be used to determine the following compounds:

2,4-D
2,4-DB
2,4,5-T
2,4,5-TP
Dalapon
Dicamba
Dichloroprop
Dinoseb
MCPA
MCPP

Since these compounds are produced and used in various forms (i.e., acid, salt, ester, etc.), the method includes a hydrolysis step to convert the herbicide to the acid form prior to analysis.

1.2 When Method 8150 is used to analyze unfamiliar samples, compound identifications should be supported by at least one additional qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm measurements made with the primary column. Section 8.3 provides gas chromatograph/mass spectrometer (GC/MS) criteria appropriate for the qualitative confirmation of compound identifications.

1.3 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatography and in the interpretation of gas chromatograms. Only experienced analysts should be allowed to work with diazomethane due to the potential hazards associated with its use (explosive, carcinogenic).

2.0 Summary of Method

Method 8150 provides extraction, esterification and gas chromatographic conditions for the analysis of chlorinated acid herbicides in water and waste samples. Spiked samples are used to verify the applicability of the chosen extraction technique to each new sample type. The esters are hydrolyzed with potassium hydroxide and extraneous organic material is removed by a solvent wash. After acidification, the acids are extracted with solvent and converted to their methyl esters using diazomethane as the derivatizing agent. After excess reagent is removed, the esters are determined by gas chromatography

employing an electron capture detector, microcoulometric detector, or electrolytic conductivity detector (2). The results are reported as the acid equivalents.

2.2 The sensitivity of Method 8150 usually depends on the level of interferences rather than on instrumental limitations. Table 1 lists the limits of detection that can be obtained in wastewaters in the absence of interferences. Detection limits for a typical waste sample would be significantly higher.

TABLE 1. CHROMATOGRAPHIC CONDITIONS AND DETECTION LIMITS FOR METHOD 8150 IN WASTEWATER

Parameter	Retention time (min)[a]				Estimated detection limit (µg/l)
	Col. 1a	Col. 1b	Column 2	Column 3	
Dicamba	1.2	--	1.0	--	1.0
2,4-D	2.0	--	1.6	--	1.0
2,4,5-TP	2.7	--	2.0	--	0.1
2,4,5-T	3.4	--	2.4	--	0.1
2,4-DB	4.1	--	--	--	1.0
Dalapon	--	--	--	5.0	1.0
MCPP	--	3.4	--	--	200
MCPA	--	4.1	--	--	200
Dichloroprop	--	4.8	--	--	1.0
Dinoseb	--	11.2	--	--	0.1

[a]Column conditions are as follows:

Column 1a conditions: 95% Argon/5% Methane carrier gas as a flow rate of 70 ml/min. Column temperature isothermal at 185° C.

Column 1b temperature: 140° C for 6 min and then programmed to 200° C at 10°/min.

Column 2 conditions: 95% Argon/5% Methane carrier gas at a flow rate of 70 ml/min. Column temperature isothermal at 185° C.

Column 3 conditions: UHP Nitrogen carrier gas at a flow rate of 25 ml/min. Column temperature programmed from 100° C to 150° C at 10°/min.

3.0 Interferences

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing hardware that lead to discrete artifacts or elevated baselines in gas chromatograms. All these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Section 8.1.

3.1.1 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. This should be followed by detergent washing with hot water and rinses with tap and distilled water. The glassware should then be drained dry and heated in a muffle furnace at 400° C for 15 to 30 min. Some thermally stable materials such as PCB's may not be eliminated by this treatment. Solvent rinses with acetone and pesticide quality hexane may be substituted for the muffle furnace heating. Volumetric ware should not be heated in a muffle furnace. After drying and cooling, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

3.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

3.2 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from waste to waste, depending upon the nature and diversity of the waste being sampled.

3.3 Organic acids, especially chlorinated acids, cause the most direct interference with the determination. Phenols, including chlorophenols, may also interfere with this procedure.

3.4 Alkaline hydrolysis and subsequent extraction of the basic solution removes many chlorinated hydrocarbons and phthalate esters that might otherwise interfere with the electron capture analysis.

3.5 The herbicides, being strong organic acids, react readily with alkaline substances and may be lost during analysis. Therefore, glassware and glass wool must be acid-rinsed and sodium sulfate must be acidified with sulfuric acid prior to use to avoid this possibility.

3.6 Before processing any samples, the analyst should demonstrate daily through the analysis of an organic-free water or solvent blank that the entire analytical system is interference-free. Standard quality assurance practices should be used with this method. Field replicates should be

collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the accuracy of the analyses. Where doubt exists over the identification of a peak on the gas chromatogram, confirmatory techniques such as mass spectroscopy should be used. Detection limits for groundwater and EP extracts are given in Table 1. Detection limits for these compounds in wastes should be set at 1 µg/g.

4.0 Apparatus and Materials

4.1 Glassware (all specifications are suggested. Catalog numbers are included for illustration only).

4.1.1 Separatory funnel: 2000-ml, with Teflon stopcock.

4.1.2 Drying column: Chromatographic column 400 mm long x 19 mm I.D. with coarse frit.

4.1.3 Chromatographic column: 300 mm long x 10 mm I.D. with coarse fritted disc at bottom and Teflon stopcock.

4.1.4 Concentrator tube, Kuderna-Danish: 10-ml, graduated. Calibration must be checked at the volumes employed in the test. Ground-glass stopper is used to prevent evaporation of extracts.

4.1.5 Evaporative flask, Kuderna-Danish: 500-ml. Attach to concentrator tube with springs.

4.1.6 Snyder column, Kuderna-Danish: three-ball macro.

4.1.7 Snyder column, Kuderna-Danish: two-ball micro.

4.1.8 Vials: Amber glass, 10- to 15-ml capacity with Teflon-lined screw-cap.

4.1.9 Erlenmeyer flask: Pyrex, 250-ml with 24/40 ground-glass joint.

4.2 Boiling chips: approximately 10/40 mesh. Heat to 400° C for 30 min or Soxhlet extract with methylene chloride.

4.3 Diazald Kit: recommended for the generation of diazomethane (available from Aldrich Chemical Co., Cat. No. 210,025-2).

4.4 Water bath: Heated, with concentric ring cover, capable of temperature control (±2° C). The bath should be used in a hood.

4.5 Glass wool: Acid washed.

4.6 Balance: Analytical, capable of accurately weighing to the nearest 0.0001 g.

4.7 Pipet: Pasteur, glass, disposable (140-mm x 5-mm I.D.).

4.8 Gas chromatograph: Analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including syringes, analytical columns, gases, detector and stripchart recorder. A data system is recommended for measuring peak areas.

4.8.1 Column 1: 180 cm long x 4 mm I.D. glass, packed with 1.5% SP-2250/1.95% SP-2401 on Supelcoport (100/120 mesh) or equivalent.

4.8.2 Column 2: 180 cm long x 4 mm I.D. glass, packed with 5% OV-210 on Gas Chrom Q (100/120 mesh) or equivalent.

4.8.3 Column 3: 180 cm long x 2 mm I.D. glass, packed with 0.1% SP-1000 on 80/100 mesh Carbopak C or equivalent.

4.8.4 Detector: Electron capture. This detector has proven effective in the analysis of wastewaters for the parameters listed in Section 1.1. Guidelines for the use of alternate detectors are provided in Section 7.4.

4.9 Wrist Shaker: Burrel Model 75 or equivalent.

5.0 Reagents

5.1 Reagent water: Reagent water is defined as a water in which an interferent is not observed at the method detection limit of each parameter of interest.

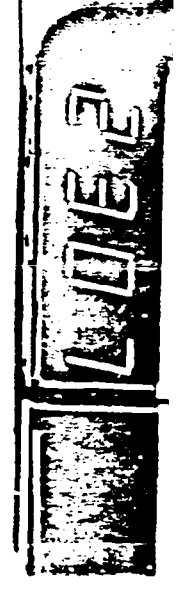
5.2 Sodium hydroxide solution (10 N): Dissolve 40 g NaOH in reagent water and dilute to 100 ml.

5.3 Sulfuric acid solution (1:1): Slowly add 50 ml H_2SO_4 (sp. gr. 1.84) to 50 ml of reagent water.

5.4 Sulfuric acid solution (1:3): Slowly add 1 part H_2SO_4 (sp. gr. 1.84) to 3 parts reagent water.

5.5 Hydrochloric acid: (ACS) Mix 1 part of concentrated acid with 9 parts distilled water (v/v).

5.6 Potassium hydroxide solution: 37% aqueous solution (w/v). Prepare with reagent grade potassium hydroxide pellets and distilled water.



5.7 Acetone, hexane, toluene, methanol: Pesticide quality or equivalent.

5.8 Diethyl ether: Nanograde, redistilled in glass if necessary. Must be free of peroxides as indicated by EM Quant test strips (available from Scientific Products Co., Cat. No. P1126-8, and other suppliers). Procedures recommended for removal of peroxides are provided with the test strips. After cleanup, 20 ml ethyl alcohol preservative must be added to each liter of ether.

5.9 Sodium sulfate: (ACS) Granular, acidified as follows: Slurry 100 g sodium sulfate with enough diethyl ether to just cover the solid, then add 0.1 ml of concentrated sulfuric acid. Remove the ether under a vacuum. Mix 1 g of the resulting solid with 5 ml of reagent water and measure the pH of the mixture. It must be below pH 4. Store at 130° C. Several levels of purification may be required in order to reduce background phthalate levels to an acceptable level: (1) Heat 4 hr at 400° C in a shallow tray, (2) Heat 16 hr at 450-400° C in a shallow tray, (3) Soxhlet extract with methylene chloride for 48 hr.

5.10 Carbitol (diethylene glycol monoethyl ether).

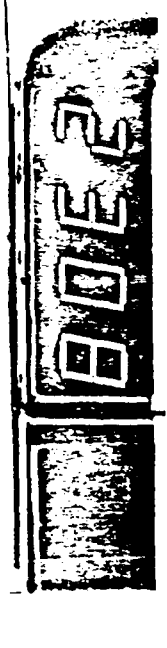
5.11 N-methyl (-N-nitroso-p-toluenesulfonamide (Diazald): High purity available from Aldrich Chemical Co.

5.12 5% acidified Na_2SO_4: Use 50 g of acidified anhydrous Na_2SO_4 to every 1000 ml distilled H_2O.

5.13 Stock standard solutions (1.00 µg/µl): Stock standard solutions can be prepared from pure standard materials or purchased as certified solutions.

5.13.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure acids. Dissolve the material in pesticide-quality diethyl ether and dilute to volume in a 10-ml volumetric flask. Larger volumes can be used at the convenience of the analyst. If compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.13.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4° C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.



5.13.3 Stock standard solutions must be replaced after 1 week, or sooner if comparison with check standards indicates a problem.

5.14 Diazomethane solution: Follow generator kit instructions. Store in freezer in glass bottle stoppered with cork. Check for deterioration.

6.0 Sample Collection, Preservation, and Handling

6.1 Grab samples must be collected in glass containers. Conventional sampling practices should be followed; however, the bottle must not be prerinsed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be as free as possible of Tygon and other potential sources of contamination.

6.2 The samples must be iced or refrigerated at 4° C from the time of collection until extraction.

6.3 All samples must be extracted within 7 days and completely analyzed within 30 days of extraction.

7.0 Procedures

7.1 Sample preparation

7.1.1 Solid extraction

7.1.1.1 Thoroughly mix moist solids and weigh an amount of wet sample equivalent to 50 g of dry weight into 500-ml wide-mouth Erlenmeyer flasks.

7.1.1.2 Acidify solids with reagent grade concentrated hydrochloric acid using 2-3 ml to pH 2. Allow to stand for 15 min with occasional stirring until the pH remains below 2. Add more acid if necessary.

7.1.1.3 Add 20 ml of acetone to each flask containing the acidified sample and clamp the stopper in place. Mix the contents of the flasks for 20 min using the wrist-action shaker. Add 80 ml of redistilled ethyl ether to the same flasks and shake again for 20 min.

7.1.1.4 Decant the extracts into 2-liter separatory funnels containing 250 ml of 5% acidified sodium sulfate. If an emulsion forms, slowly add 5 g of acidified sodium sulfate (anhydrous) until the solvent-water mixture separates. A quantity of acidified

sodium sulfate equal to the weight of the sample may be added if necessary.

7.1.1.5 To ensure adequate recovery, measure the volume of extract into a graduated cylinder at each decanting step before adding the extract to the separatory funnel. If the recovered volume is not better than 75%, an additional extraction must be conducted.

7.1.1.6 Check the pH to ensure that it remains below 2. If the pH is not below 2, add more hydrochloric acid until stabilized. Add 20 ml of acetone to each Erlenmeyer flask containing the sediment and shake on the wrist-action shaker for 10 min. Again, add 80 ml of ethyl ether, shake for 10 min and decant extract into their respective separatory funnels. Repeat this step once more, collecting the acetone-ether extracts in the funnels containing the 5% acidified sodium sulfate solution.

7.1.1.7 Gently mix the content of each separatory funnel for about 1 min and allow the layers to separate. Collect the aqueous phase in a clean beaker and the extract (top layer) in a 500-ml ground-glass Erlenmeyer flask. Reextract the water layer with 25 ml of ethyl ether. Allow the layers to separate and discard the aqueous layer. Combine the ether extracts in the respective Erlenmeyer flasks.

7.1.1.8 Add 30 ml of distilled water to the extract in the Erlenmeyer flasks and refrigerate. Note: This is a good stopping point or, if time permits, continue to step 7.1.1.12.

7.1.1.9 Add 5 ml of 37% (w/w) aqueous potassium hydroxide and boiling chips to the extract in the flask and fit them with a one-ball Snyder column. Evaporate the ethyl ether on the steam bath and continue to heat for 90 min.

7.1.1.10 Remove the flasks from the steam bath, allow them to cool, and transfer the water solutions to 125-ml separatory funnels. Extract the basic solutions once with 40 ml and then twice with 20 ml of redistilled ethyl ether. Allow sufficient time for the layers to separate, and discard the ether layer each time. Note: This is a solvent cleanup step. The phenoxy acid herbicides remain soluble in the aqueous phase as potassium salts.

7.1.1.11 Add 5 ml cold 25% (v/v) sulfuric acid to the contents of each funnel to adjust the pH to 2. Be sure to check the pH at this point. Extract the herbicides once with 40 ml and two more times with 20 ml of ethyl ether.

7.1.1.12 Collect the ether extracts in 125-ml Erlenmeyer flasks containing 1.0 g of acidified anhydrous Na_2SO_4. Stopper and allow the extracts to remain in contact with the acidified Na_2SO_4. Store the samples overnight in the refrigerator. Note: This is a good stopping point.

7.1.1.13 Concentrate extract and perform esterification, starting with step 7.2.2.7.

7.1.2 *Liquid extraction*

7.1.2.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a 2-liter separatory funnel. Check the pH with wide-range pH paper and adjust to pH less than 2 with sulfuric acid (1:1).

7.1.2.2 Add 150 ml diethyl ether to the sample bottle, seal, and shake 30 sec to rinse the walls. Transfer the solvent into the separatory funnel. Extract the sample by shaking the funnel for 2 min with periodic venting to release excess vapor pressure. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between the layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, or centrifugation. Drain the water phase into a 1-liter Erlenmeyer flask. Then collect the extract in a 250-ml ground-glass Erlenmeyer flask containing 2 ml of 37% aqueous potassium hydroxide. Approximately 80 ml of the diethyl ether will remain dissolved in the aqueous phase.

7.1.2.3 Extract the sample two more times using 50 ml of diethyl ether each time. Combine the extracts in the Erlenmeyer flask. (Rinse the 1-liter flask with each additional aliquot of extracting solvent.)

7.1.2.4 Add 1 or 2 clean boiling chips to the 250-ml flask, add 15 ml distilled water, and attach a three-ball Snyder column. Prewet the Snyder column by adding 1 ml diethyl ether to the top. Place the apparatus on a hot water bath (60° to 65° C), such that the bottom of the flask is bathed in the water vapor. Although the diethyl ether will evaporate in about 15 min, continue heating for a total of 60 min, beginning from the time the flask is placed in the water bath. Remove the apparatus and let stand at room temperature for at least 10 min.

7.1.2.5 Transfer the solution to a 60-ml separatory funnel using 5 to 10 ml of distilled water. Wash the basic solution twice by shaking for 1 min with 20-ml portions of diethyl ether. Discard the organic phase. The herbicides remain in the aqueous phase.

7.1.2.6 Acidify the contents of the separatory funnel to pH 2 by adding 2 ml of cold (4° C) sulfuric acid (1:3). Test with pH indicator paper. Add 20 ml diethyl ether and shake vigorously for 2 min. Drain the aqueous layer into the 250-ml Erlenmeyer, then pour the organic layer into a 125-ml Erlenmeyer containing about 0.5 g of acidified anhydrous sodium sulfate. Repeat the extraction twice more with 10-ml aliquots of diethyl ether, combining all solvent in the 125-ml flask. Allow the extract to remain in contact with the sodium sulfate for approximately 2 hr.

7.1.2.7 Transfer the ether extract, through a funnel plugged with acid-washed glass wool, into a 500-ml Kuderna-Danish flask equipped with a 10-ml concentrator tube. Use liberal washings of ether. Use a glass rod to crush any caked sodium sulfate during the transfer.

7.1.2.8 Add 1 to 2 clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 ml diethyl ether to the top. Place the K-D apparatus on a hot water bath (60° to 65° C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed in vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 min. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 1 ml, remove the K-D apparatus and allow it to drain for at least 10 min while cooling.

7.1.2.9 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 ml of diethyl ether. Final volume should be 4.0 ml. The sample is now ready for derivatization with diazomethane to form methyl esters.

7.1.3 Esterification

7.1.3.1 The diazomethane derivatization (1) procedure described below will react efficiently with all of the chlorinated herbicides described in this method and should be used only by experienced analysts, due to the potential hazards associated with its use. Diazomethane is a carcinogen and can explode under certain conditions. The following precautions should be taken:

- Use a safety screen.
- Use mechanical pipetting aides.
- Do not heat above 90° C - EXPLOSION may result.
- Avoid grinding surfaces, ground-glass joints, sleeve bearings, glass stirrers - EXPLOSION may result.
- Store away from alkali metals - EXPLOSION may result.
- Solutions of diazomethane decompose rapidly in the presence of solid materials such as copper powder, calcium chloride, and boiling chips.

7.1.3.2 Instructions for preparing diazomethane are provided with the generator kit.

7.1.3.3 Add 2 ml of diazomethane solution and let sample stand for 10 min with occasional swirling.

7.1.3.4 Rinse inside wall of ampule with several hundred µl of ethyl ether. Take sample to approximately 2 ml to remove excess diazomethane by allowing solvent to evaporate spontaneously (room temperature).

7.1.3.5 Dissolve residue in 5 ml of hexane. Analyze by gas chromatography.

7.2 Gas chromatography conditions

7.2.1 The recommended gas chromatographic column materials and operating conditions for the instrument are:

Parameter	Column
Dicamba	1a,2
2,4-D	1a,2
2,4,5-TP	1a,2
2,4,5-T	1a,2
2,4-DB	1a
Dalapon	3
MCPP	1b
MCPA	1b
Dichloroprop	1b
Dinoseb	1b

Column 1a conditions: 95% Argon/5% Methane carrier gas at a flow rate of 70 ml/min. Column temperature isothermal at 185° C.

Column 1b temperature: 140° C for 6 min and then programmed to 200° C at 10°/min.

Column 2 conditions: 95% Argon/5% Methane carrier gas at a flow rate of 70 ml/min. Column temperature, isothermal at 185° C.

Column 3 conditions: UHP Nitrogen carrier gas at a flow rate of 25 ml/min. Column temperature programmed from 100° to 150° C at 10°/min.

7.2.2 The use of capillary (open-tubular) columns is acceptable if appropriate response and separation can be demonstrated.

7.3 Calibration

7.3.1 Establish gas chromatographic operating parameters equivalent to those indicated above in Table 1. The gas chromatographic system can be calibrated using the external standard technique (Section 7.3.2) or the internal standard technique (Section 7.3.3).

7.3.2 External standard calibration procedure

7.3.2.1 For each parameter of interest, prepare working standards at a minimum of three concentration levels by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with diethyl ether. One of the external standards should be at a concentration near, but above, the method detection limit. The other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.3.2.2 Prepare calibration standards from the free acids by esterification of the working standards as described under Liquid Extraction, Section 7.1.2. Using injections of 2 to 5 µl of each esterified working standard, tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each parameter. Alternatively, the ratio of the response to the mass injected, defined as the calibration factor (CF), can be calculated for each parameter at each standard concentration. If the relative standard deviation of the calibration factor is less than 10% over the working range, linearity through the origin can be assumed and the average calibration factor can be used in place of a calibration curve.

7.3.2.3 The working calibration curve or calibration factor must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ±10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve or calibration factor may be prepared for that parameter.

7.3.3 Internal standard calibration procedure. To use this approach, the analyst must select one or more internal standards similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Due to these limitations, no internal standard applicable to all samples can be suggested.

7.3.3.1 Prepare working standards at a minimum of three concentration levels for each parameter of interest in the acid form by adding volumes of one or more stock standards to a volumetric flask, and dilute to volume with diethyl ether. One of the standards should be at a concentration near, but above, the method detection limit. The other concentrations should correspond to the expected range of concentrations found in real samples, or should define the working range of the detector.

7.3.3.2 Prepare calibration standards from the free acids by esterification of the working standards as described under Liquid Extraction, Section 7.1.2.

7.3.3.3 Prior to injection, add a known constant amount of one or more internal standards to each calibration standard.

7.3.3.4 Using injections of 2 to 5 µl of each calibration standard, tabulate the peak height or area responses against the concentration for each compound and internal standard. Calculate response factors (RF) for each compound as follows:

$$RF = (A_s C_{is})/(A_{is} C_s)$$

where:

A_s = Response for the parameter to be measured.

A_{is} = Response for the internal standard.

C_{is} = Concentration of the internal standard in µg/l.

C_s = Concentration of the parameter to be measured in µg/l.

If the RF value over the working range is constant, less than 10% relative standard deviation, the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is} against RF.

7.3.3.5 The working calibration curve or RF must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ±10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared for that compound.

7.3.4 Before using any cleanup procedure, the analyst must process a series of standards through the procedure to validate elution patterns and the absence of interferences from the reagents.

7.4 Analysis

7.4.1 Inject 2 to 5 µl of the sample extract using the solvent-flush technique. Smaller (1.0-µl) volumes can be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 µl, and the resulting peak size, in area units.

7.4.2 If the peak area exceeds the linear range of the system, dilute the extract and reanalyze.

7.4.3 If peak detection is prevented by the presence of interferences, further cleanup is required. Before using any cleanup procedure, the analyst must process a series of calibration standards through the procedure to validate elution patterns and the absence of interferences from the reagents.

7.4.4 Examples of chromatograms for chlorophenoxy herbicides are shown in Figures 1 to 3.

8.0 Quality Control

8.1 Before processing any samples, the analyst should demonstrate through the analysis of a distilled water method blank that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination.

8.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of

Column: 1.5% SP-2250/1.95% SP-2401 on Supelcoport (100/120 Mesh)
Temperature: Isothermal at 185°C
Detector: Electron Capture

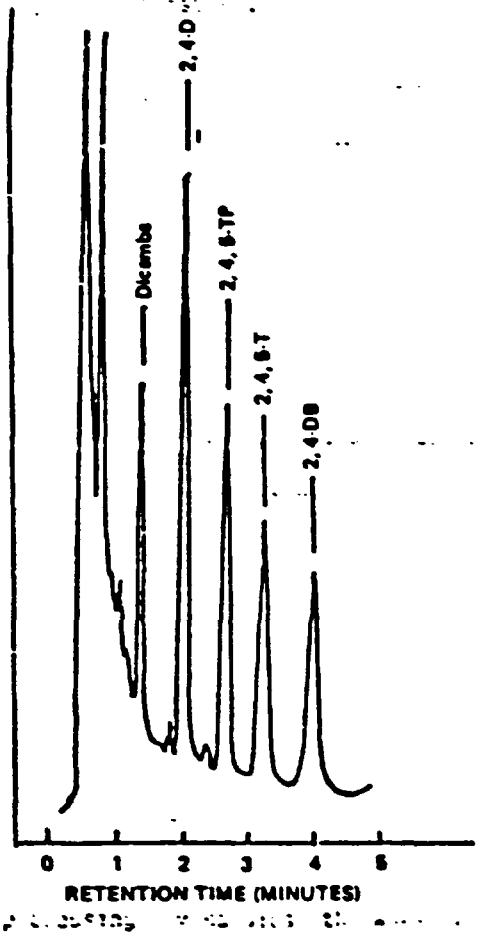


Figure 1. Gas chomatogram of chlorinated herbicides.

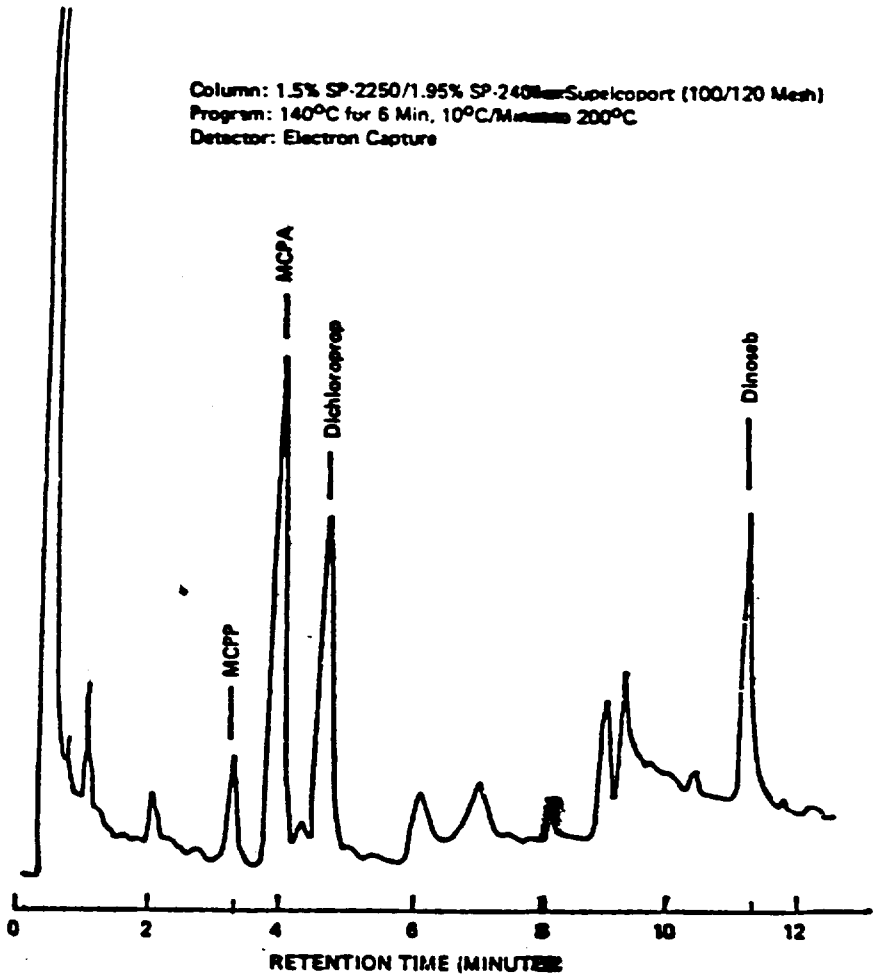


Figure 2. Gas chromatogram of chlorinated herbicides.

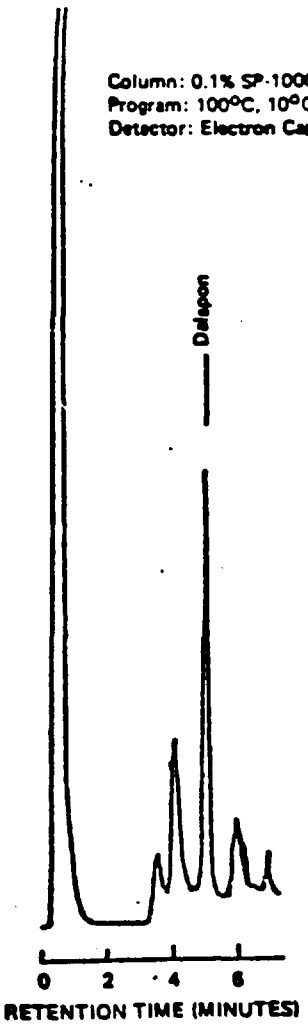


Figure 3. Gas chromatogram of dalapon, column 2

the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified waste samples should be analyzed to validate the accuracy of the analysis. Detection limits to be used for groundwater samples are indicated in Table 1. Where doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as mass spectrometry should be used (Section 8.3).

8.3 GC/MS confirmation

8.3.1 GC/MS techniques should be judiciously employed to support qualitative identifications made with this method. The mass spectrometer should be capable of scanning the mass range from 35 amu to a mass 50 amu above the molecular weight of the compound. The instrument must be capable of scanning the mass range at a rate to produce at least 5 scans per peak but not to exceed 3 sec per scan utilizing 70 V (nominal) electron energy in the electron impact ionization mode. A GC-to-MS interface constructed of all-glass or glass-lined materials is recommended. A computer system that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program should be interfaced to the mass spectrometer.

8.3.2 Gas chromatographic columns and conditions should be selected for optimum separation and performance. The conditions selected must be compatible with standard GC/MS operating practices, such as those described for Method 8250.

8.3.3 At the beginning of each day that confirmatory analyses are to be performed, the GC/MS system must be checked to see that all DFTPP (decafluorotriphenyl phosphine) performance criteria are achieved, as described in Method 8250.

8.3.4 To confirm an identification of a compound, the background-corrected mass spectrum of the compound must be obtained from the sample extract and compared with a mass spectrum from a stock or calibration standard analyzed under the same chromatographic conditions. At least 25 ng of material should be injected into the GC/MS. The following criteria must be met for qualitative confirmation:

1. The molecular ion and all other ions present above 10% relative abundance in the mass spectrum of the standard must be present in the mass spectrum of the sample with agreement to $\pm$10%. For example, if the relative abundance of an ion is 30% in the mass spectrum of the standard, the allowable limits for the relative abundance of that ion in the mass spectrum for the sample would be 20-40%.

2. The retention time of the compound in the sample must be within 6 sec of the retention time for the same compound in the standard solution.

3. Compounds that have very similar mass spectra can be explicitly identified by GC/MS only on the basis of retention time data.

8.3.5 Where available, chemical ionization mass spectra may be employed to aid the qualitative identification process.

8.3.6 Should these MS procedures fail to provide satisfactory results, additional steps may be taken before reanalysis. These steps may include the use of alternate packed or capillary GC columns or additional cleanup.

9.0 References

1. U.S. EPA. 1971. National Pollutant Discharge Elimination System, Appendix A, Fed. Reg., 38, No. 75, Pt. II, Method for Chlorinated Phenoxy Acid Herbicides in Industrial Effluents, Cincinnati, Ohio.

2. Goerlitz, D.G., and W.L. Lamar. 1967. Determination of phenoxy acid herbicides in water by electron capture and microcoulometric gas chromatography. U.S. Geol. Survey Water Supply Paper, 1817-C.

3. Burke, J.A., 1965. Gas chromatography for pesticide residue analysis; some practical aspects. Journal of the Association of Official Analytical Chemists 48:1037.

4. U.S. EPA. 1972. Extraction and cleanup procedure for the determination of phenoxy acid herbicides in sediment. EPA Toxicant and Analysis Center, Bay St. Louis, Mississippi.

APPENDIX 8.14

Method 615 Chlorinated Herbicides

Appendix B.14
EPA Method 615

CHLORINATED HERBICIDES

METHOD 615

1. Scope and Application

1.1 This method covers the determination of various chlorinated acid pesticides in water and wastewater. The following compounds may be determined by this method.

PARAMETER	STORET NO.
2,4-D	39736
2,4-DB	-
2,4,5-T	39740
2,4,5-TP	39760
Dicamba	-

1.2 Since these compounds are produced and used in various forms (i.e., acid, salt, ester, etc.) the method includes a hydrolysis step to convert the herbicide to the acid form prior to analysis.

1.3 This method is applicable to the determination of these compounds in municipal and industrial discharges. It is designed to be used to meet the monitoring requirements of the National Pollutant Discharge Elimination System (NPDES). As such, it presupposes a high expectation of finding the specific compounds of interest. When screening samples for any or all of the compounds above, independent protocols for verifing the identity of the compounds must be applied.

1.4 The limit of detection for this method is usually dependent upon the level of interferences rather than instrumental limitations. The limits of detection listed in Table 1 represent the limits that can be achieved in wastewaters in the absence of interferences.

1.5 This method is recommended for use only by experienced residue analysts or under the close supervision of such qualified persons.

2. Summary of Method

2.1 A 1-liter sample of wastewater is acidified and the acids and their esters are extracted with diethyl ether using separatory funnel techniques. The esters are hydrolyzed with potassium hydroxide and extraneous organic material is removed by a solvent wash. After acidification, the acids are extracted and converted to their methyl esters using boron trifluoride in methanol. After excess reagent is removed, the esters are determined by electron capture, microcoulometric or electrolytic conductivity gas chromatography (1). The results are reported in micrograms per liter as the acid equivalents.

2.2 Where Dicamba must be measured, methylation of the acids is performed using diazomethane.

3. Interferences

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences coextracted from the samples will vary considerably from source to source, depending upon the diversity of the industrial complex or municipality being sampled. While a general cleanup technique is incorporated into this method, unique samples may require additional cleanup approaches to achieve the limits of detection listed in Table 1.

3.3 Glassware must be scrupulously clean and acid-rinsed. Clean as soon as possible after use by rinsing with the last solvent used. This should be followed by detergent washing in hot water. Rinse with tap water, dilute hydrochloric acid, distilled water, acetone and finally pesticide quality hexane. Heavily contaminated glassware may require treatment in a muffle furnace at 400°C for 15 to 30 minutes. Volumetric ware should not be heated in a muffle furnace. Glassware should be stored immediately after drying or cooling to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

3.4 Organic acids, especially chlorinated acids, cause the most direct interference with the determination. Phenols, including chlorophenols, may also interfere with this procedure.

3.5 Alkaline hydrolysis and subsequent extraction of the basic solution removes many chlorinated hydrocarbons and phthalate esters that might otherwise interfere with the electron capture analysis.

3.6 The herbicides, being strong organic acids, react readily with alkaline substances and may be lost during analysis. Therefore, glassware and glass wool must be acid-rinsed and sodium sulfate must be acidified with sulfuric acid prior to use to avoid this possibility.

4. Apparatus and Materials

4.1 Sampling equipment, for discrete or composite sampling.

4.1.1 Discrete samples - Amber glass bottles, (1-liter or 1-quart volume) fitted with metal caps lined with Teflon. Foil may be substituted for Teflon if the sample is not corrosive. French or Boston Round bottle design is recommended. The container must be washed and solvent rinsed before use to minimize interferences.

4.1.2 Compositing equipment - Automatic or manual compositing system. Must incorporate glass sample containers for the collection of a minimum increment of 250 ml. Sample containers must be kept refrigerated during sampling. No Tygon or rubber tubing or fittings may be used in the system.

4.2 Separatory funnels - 2000-ml, 60-ml, with Teflon stopcock.

4.3 Drying column - A 20-mm ID pyrex chromatographic column with coarse frit.

4.4 Kuderna-Danish (K-D) Apparatus

4.4.1 Concentrator tube - 10-ml, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at 1.0 and 10.0 ml level. A ground glass stopper (size 19/22 joint) is used to prevent evaporation of extracts.

4.4.2 Evaporative flask - 500-ml (Kontes K-57001-0500 or equivalent). Attach to concentrator tube with springs (Kontes K-662750-0012).

4.4.3 Snyder column - three-ball macro (Kontes K503000-0121 or equivalent).

4.4.4 Snyder column - two ball micro (Kontes K569001-0219 or equivalent).

4.4.5 Boiling chips - solvent extracted, approximately 10/40 mesh.

4.5 Water bath - Heated, with concentric ring cover, capable of temperature control (± 2°C). The bath should be used in a hood.

4.6 Gas chromatograph - Analytical system complete with gas chromatograph suitable for on-column injection and all required accessories, including: electron capture, electrolytic conductivity or microcoulometric detector, column supplies, recorder, gases, and syringes. A data system for measuring peak areas is recommended.

4.6.1 Columns and Analytical Conditions.

Column 1: Gas Chrom Q (100/200 mesh) coated with 1.5% OV-17 + 1.95% QF-1 (OV-210) packed in a pyrex glass column 180 cm long x 4 mm ID with argon (95%)/methane (5%) carrier gas at a flow rate of 70 ml/min. Column temperature, isothermal at 185°C.

Column 2: Gas-Chrom Q (100/200 mesh) coated with 5% OV-210 packed in a pyrex glass column 180 cm long x 4 mm ID with argon (95%)/methane (5%) carrier gas at a flow rate 70 ml/min. Column temperature, isothermal at 185°C.

4.7 Pipets - Pasteur, glass, disposable (140 mm x 5 mm ID).

4.8 Glass wool, acid washed (Supelco 2-0383 or equivalent).

4.9 Erlenmeyer flask - Pyrex, 250 ml with 24/40 ground glass joint.

5. Reagents

5.1 Sodium hydroxide - (ACS) 10 N in distilled water.

5.2 Sodium Sulfate - (ACS) granular, acidified as follows: Slurry 100 g sodium sulfate with enough diethyl ether to just cover the solid then add 0.1 ml of conc. sulfuric acid. Remove the ether under a vacuum. Mix 1 g of the resulting solid with 5 ml of reagent water and measure the pH of the mixture. It must be below pH 4. Store at 130°C.

5.3 Sulfuric acid - (ACS) Concentrated, (Sp. Gr. 1.84). Two concentrations are required.

5.3.1 Mix equal volumes with distilled water (1+1).

5.3.2 Mix 1 part of acid to 3 parts of distilled water (1+3).

5.4 Hydrochloric Acid - (ACS) Mix 1 part of concentrated acid with 9 parts distilled water, (v:v).

5.5 Potassium Hydroxide Solution - 37% aqueous solution (W:V). Prepare with reagent grade potassium hydroxide pellets and distilled water.

5.6 Acetone, pesticide residue analysis grade.

5.7 Diethyl ether, preserved with 2% methanol (v:v).

5.7.1 Must be free of peroxides as indicated by EM Quant test strips (EM Laboratories, Inc., 500 Executive Blvd., Elmsford, N.Y. 10523).

5.7.2 If test indicates, remove peroxides by eluting through basic or neutral grade aluminum oxide. Retest for peroxides before using.

5.7.3 Distill deperoxidized ether in glass. Preserve with 2% (V:V) methanol.

5.8 Hexane, pesticide residue analysis grade.

5.9 Toluene - pesticide analysis grade.

5.10 Boron Trifluoride, 14% in Methanol (W:W).

5.11 Aluminum oxide, basic or neutral (active) for removal of peroxides from diethyl ether.

5.12 Florisil - PR grade (60/100 mesh); purchase activated at 1250°F and store in glass containers with glass stoppers or foil-lined screw caps. Store at 130°C or activate each batch for at least 16 hours at 130°C in a foil covered glass container before use.

5.13 Stock standards - Prepare stock standard solutions at a concentration of 1.00 ug/ul by dissolving 0.0100 grams of assayed reference acids in a minimum quantity of diethyl ether or other appropriate solvent and diluting to volume with hexane in a 10.0 ml ground glass stoppered volumetric flask. Transfer the stock solution to a small vial with Teflon lined screw cap and store in a refrigerator. Check frequently for signs of degradation or evaporation, especially just prior to preparing working standards.

6. Calibration

6.1 Prepare working standards of the acid form of the compounds of interest, either singly or mixed together. The standards should be prepared at concentrations covering two or more orders of magnitude that will bracket the working range of the chromatographic system. If the sensitivity of the detection system can be calculated from Table 1 as 100 ug/l in the final extract, for example, prepare standards at 10 ug/l, 50 ug/l, 100 ug/l, 500 ug/l, etc. so that injections of 1 to 5 ul of each the esterified calibration standards (after the 5-fold dilution in preparation) will define the linearity of the detector in the working range.

6.2 Prepare calibration standards from the free acids by esterification of the working standard. For the boron trifluoride procedure, pipet 1.0 ml of working standard into a glass stoppered concentrator tube. Add 0.5 ml of toluene and evaporate to 0.4 ml using a two-ball Snyder microcolumn and a steam bath. Proceed as in 10.2 to 10.3.

6.3 Assemble the necessary gas chromatographic apparatus and establish operating parameters equivalent to those indicated in 4.6.1. By injecting calibration standards establish the sensitivity limit of the detector and the linear range of the analytical system for each compound. A typical gas chromatogram of selected phenoxy acid methyl esters is shown in Figure 2.

6.4 Before applying any cleanup procedure to the samples, the analyst must process a series of calibration standards through the system to validate elution patterns and demonstrate the absence of interferences in the reagents.

7. Quality Control

7.1 Before processing any samples, the analyst must demonstrate through the analysis of a distilled water method blank, that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination.

7.2 Standard quality assurance practices should be used with this method. Field replicates should be collected and analyzed to validate the precision of the sampling technique. Field blanks should be collected and analyzed to monitor contamination during sampling and transit. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the accuracy of the analysis. Where doubt exists over the identification of a peak in the chromatogram, confirmatory techniques such as mass spectrometry should be used.

8. Sample Collection, Preservation, and Handling

8.1 Grab samples must be collected in glass containers. Standard sampling practices (2,3) should be followed, except that the bottle must not be prewashed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be free of Tygon plastic and other potential sources of contamination.

8.2 The samples must be iced or refrigerated from the time of collection until extraction. Chemical preservatives should not be used in the field unless more than 24 hours will elapse before delivery to the laboratory. If the samples will not be received in the laboratory within 24 hours of collection, the sample must be acidified to pH 2 with sulfuric acid (1+1). Samples not acidified in the field must be acidified immediately upon arrival in the laboratory. Prior to adding acid or base, mark the water meniscus on the side of the sample bottle for later measurement of the volume.

8.3 All samples must be extracted within 7 days and completely analyzed within 30 days of collection.

9. Sample Extraction and Hydrolysis

9.1 Pour the entire sample into a two-liter separatory funnel. Check the pH with wide-range pH paper and adjust to pH less than 2 with sulfuric acid. (1+1)

9.2 Add 150 ml diethyl ether to the sample bottle seal and shake 30 seconds to rinse the walls. Transfer the solvent into the separatory funnel. Extract the sample by shaking the funnel for two minutes with periodic venting to release excess vapor pressure. Allow the organic layer to separate from the water phase for a minimum of ten minutes. If the emulsion interface between the layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, or

centrifugation. Drain the water phase into a 1-liter Erlenmeyer flask. Then collect the extract in a 250-ml ground-glass Erlenmeyer flask containing 2 ml of 37 percent aqueous potassium hydroxide. Approximately 80 ml of the diethyl ether will remain dissolved in the aqueous phase.

9.3 Extract the sample two more times using 50 ml of diethyl ether each time. Combine the extracts in the Erlenmeyer flask. (Rinse the 1-liter flask with each additional aliquot of extracting solvent.)

9.4 Add 1 or 2 clean boiling chips to the 250-ml flask, add 15 ml distilled water, and attach a three-ball Snyder column. Prewet the Snyder column by adding 1 ml diethyl ether to the top. Place the apparatus on a hot water bath (60 to 65°C), such that the bottom of the flask is bathed in the water vapor. Although the diethyl ether will evaporate in about 15 minutes, continue heating for a total of 60 minutes, beginning from the time the flask is placed in the water bath. Remove the apparatus and let stand at room temperature for at least 10 minutes.

9.5 Transfer the solution to a 60-ml separatory funnel using 5 to 10 ml of distilled water. Wash the basic solution twice by shaking for one minute with 20-ml portions of diethyl ether. Discard the organic phase. The herbicides remain in the aqueous phase.

9.6 Acidify the contents of the separatory funnel to pH 2 by adding 2 ml of cold (4°C) sulfuric acid (1+3). Test with pH indicator

paper. Add 20 ml diethyl ether and shake vigorously for two minutes. Drain the aqueous layer into the 250-ml Erlenmeyer, then pour the organic layer into a 125-ml Erlenmeyer flask containing about 0.5 g of acidified anhydrous sodium sulfate. Repeat the extraction twice more with 10-ml aliquots of diethyl ether, combining all solvent in the 125-ml flask. Allow the extract to remain in contact with the sodium sulfate for approximately two hours.

9.7 Transfer the ether extract, through a funnel plugged with acid washed glass wool, into a 500-ml Kuderna-Danish flask equipped with a 10-ml concentrator tube. Use liberal washings of ether. Use a glass rod to crush any caked sodium sulfate during the transfer. Evaporate the extract to 6 to 10 ml on the hot water bath (60 to 65°C).

9.8 Add 1 to 2 clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 ml diethyl ether to the top. Place the K-D apparatus on a hot water bath (60 to 65°C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed in vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 1 ml, remove the K-D apparatus and allow it to drain for at least 10 minutes while cooling.

9.9 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 ml of diethyl ether. A 5-ml syringe is recommended for this operation. Add 0.5 ml toluene and a fresh boiling chip. Attach a micro-Snyder column to the concentrator tube and prewet the column by adding about 0.5 ml of diethyl ether to the top. Place the micro K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete concentration in 5 to 10 minutes. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood. When the distillation has ceased for at least 5 minutes, remove the micro K-D from the bath and allow it to cool. The volume of toluene solution should be 0.4 to 0.5 ml. Proceed with esterification after the solution has cooled.

10. Esterification of Acids

10.1 The boron trifluoride derivatization procedure is applicable to the herbicides listed in Section 1.1 except Dicamba. If Dicamba must be measured, refer to Appendix I.

10.2 To the toluene solution from 6.2 or 9.9, add 0.5 ml of borontrifluoride methanol reagent. Use a two-ball Snyder microcolumn as an air-cooled condenser and hold the contents of the tube for 30 minutes on a 50°C hot water bath.

10.3 Cool and add about 4.5 ml of a neutral 5 percent aqueous sodium sulfate solution. Seal the flask with a ground glass stopper and shake vigorously for about one minute. Allow to stand for three minutes for phase separation. Using a pipet, withdraw the bottom water phase and discard.

10.4 Pipet the solvent layer from the concentrator tube to the top of a small column prepared by plugging a disposable Pasteur pipet with glass wool and packing with 2.0 cm of sodium sulfate over 1.5 cm of Florisil adsorbent. Collect the eluate in another graduated concentrator tube. Complete the transfer by repeatedly rinsing the original tube with small quantities to toluene and passing the rinses through the column until a final volume of 5.0 ml of eluate is obtained. Analyze by gas chromatography.

11. Gas Chromatography

11.1 Section 4.6.1 gives the recommended gas chromatographic column materials and operating conditions for the instrument. Table 1 lists the retention times and detection limits that should be achieved by this method. An example gas chromatogram is shown in Figure 1. Calibrate the GC system daily with injections from a minimum of three calibration standards.

11.2 Inject 2 to 5 ul of the sample extract using the solvent-flush technique (6). Smaller (1.0 ul) volumes may be injected when automatic devices are employed. Record the volume injected to the nearest 0.05 ul. Measure and record the resulting peak height or peak area.

11.3 If the peak area or the peak height exceeds the linear range of the system, dilute the extract and reanalyze.

12. Calculations

12.1 Determine the concentration of individual compounds according to the formula:

$$\text{Concentration, ug/l} = \frac{(A)\ (V_t)\ (1000)}{(V_i)\ \ (V_s)}$$

where A = mass of component from calibration curve in ng.

V_i = Volume of extract injected (ul)

V_t = Volume of total extract (ml)

V_s = Volume of water extracted (ml)

12.2 Report results in micrograms per liter as the acid equivalent without correction for recovery data. When duplicate and spiked samples are analyzed, all data obtained should be reported.

13. Accuracy and Precision

13.1 This method has been validated by a single laboratory for 2,4-D and 2,4-DB using the boron trifluoride esterification procedure. The following results were obtained from the analysis of seven replicates of two relevant wastewaters. The results are listd below:

Parameter	Concentration[a] (µg/l)	Relative Standard Deviation %
2,4-D	—	16
	—	6.4
	—	17
2,4-DB	—	21

[a] Data on file at EMSL-CI.

13.2 Seven replicates of one of the wastewters were spiked and analyzed to provide an indication of the method accuracy. The results are listed below:

Parameter	Background Concentration[a] (µg/l)	Spike Level (µg/l)	Recovery (%)	Relative Standard Deviation (%)
2,4-D	--	96	100	31
2,4-DB	--	47	96	23

[a] Data on file at EMSL-CI

Table 1

Gas Chromatography of Phenoxy Acid Methyl Esters

Parent Herbicide	Retention Time[a] (min.) Column 1	Column 2	Detection Limit[c] (ug/l)
Dicamba	1.2	0.99	1.0
2,4-D	2.0	1.6	1.0
2,4,5-TP	2.7	2.0	0.1
2,4,5-T	3.4	2.4	0.1
2,4-DB	4.1[b]	—	1.0

[a] Absolute retention time of 2,4-D methyl ester was 2.00 minutes on column 1 and 1.62 minutes on column 2.

[b] Retention time determined at 190°C all others at 185°C.

[c] Detection limit is calculated from the minimum detectable GC response being equal to five times the GC background noise, assuming a 10 ml final volume of the extract from a 1-liter sample, and assuming a GC injection volume of 5 microliters.

REFERENCES

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4. Metcalf, L.D., and A. A. Schmitz, "The Rapid Preparation of Fatty Acid Esters for Gas Chromatographic Analysis," Anal. Chem., 33, 363 (1961).

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6. Pesticide Analytical Manual, Vol. I, Food and Drug Administration, Washington, D.C., Rev. 1969, Sec. 221.12c.

7. Burke, J. A., "Gas Chromatograhy for Pesticide Residue Analysis; Some Practical Aspects," JAOAC, 48, 1037 (1965).

RECOMMENDED READING

1. Yip, G., "Determination of 2,4-D and Other Chlorinated Phenoxy Alkyl Acids," JAOAC, 45, 367 (1962).

2. Yip, G., "Improved Method for Determination of Chlorophenoxy Acid Residues in Total Diet Samples," JAOAC, 54, 966 (1971).

3. Howard, S.F., and G. Yip, "Diazomethane Methylation of a Mixture of Chlorophenoxy Acids and Nitrophenols," JAOAC, 54, 970 (1971).

APPENDIX I

Derivatization with Diazomethane

A. Scope - Boron trifluoride/methanol is not effective for esterification of Dicamba. The diazomethane procedure described below will react efficiently with all of the chlorinated herbicides described in this method but may be used only when Dicamba must be measured, due to potential hazards associated with its use.

B. Precautions - Diazomethane is a toxic carcinogen and can explode under certain conditions. The following precautions should be followed:

1. Use only a well ventilated hood - do not breath vapors.
2. Use a safety screen.
3. Use mechanical pipetting aides.
4. Do not heat above 90°C - EXPLOSION may result.
5. Avoid grinding surfaces, ground glass joints, sleeve bearings, glass stirrers - EXPLOSION may result.
6. Store away from alkali metals - EXPLOSION may result.
7. Solutions of diazomethane decompose rapidly in the presence of solid materials such as copper powder, calcium chloride, and boiling chips.

C. Reagents and Supplies - In addition to those listed in sections 4 and 5 of the primary method the following materials are required:

1. A diazomethane generator assembled from two 20 x 150 mm test tubes, two Neoprene rubber stoppers and a source of nitrogen. The generator assembly is shown in Figure I-1.

2. Carbitol (diethylene glycol monoethyl ether).
3. N-methyl (-N-nitroso-p-toluenesulfonamide (Diazald) - High purity available from Aldrich Chemical Co.
4. Silica Acid - chromatographic grade (nominal 100 mesh). Store at 130°C.

D. Procedure

1. Unless otherwise indicated, the procedures described in the body of Method 615 apply to the diazomethane approach also.
2. Prepare calibration standards directly from 1-ml quantities of the working standard (6.1).
3. Do not add toluene in section 9.9. Instead, concentrate the ethyl ether solution down to about 0.5 ml, add 0.1 ml of methanol, and adjust the volume to 1.0 ml with diethyl ether.
4. Assemble the diazomethane generator (See Figure I-1) in a hood using two 20 x 150 mm test tubes. Use neoprene rubber stoppers with holes drilled in them to accomodate glass delivery tubes. The exit tube must be drawn to a point to bubble diazomethane through the sample.
5. Add 5 ml of diethyl ether to the first test tube. Add 1 ml of diethyl ether, 1 ml of carbitol, 1.5 ml of 37% (W/V) aqueous KOH, and 0.1 to 0.2 g Diazald to the second test tube. Immediately place the exit tube into the concentrator tube containing the sample extract. Apply nitrogen flow (10 ml/min) to bubble diazomethane through the extract for 10 minutes or until the yellow color of diazomethane persists.

6. Remove the concentrator tube and stopper it with a Neoprene or Teflon plug. Store at room temperature in a hood for 20 minutes.

7. Destroy any unreacted diazomethane by adding 0.1 to 0.2 g silicic acid to the concentrator tube. Allow to stand until the evolution of nitrogen gas has stopped. Adjust the sample volume to 5.0 ml with hexane and analyze by gas chromatography.

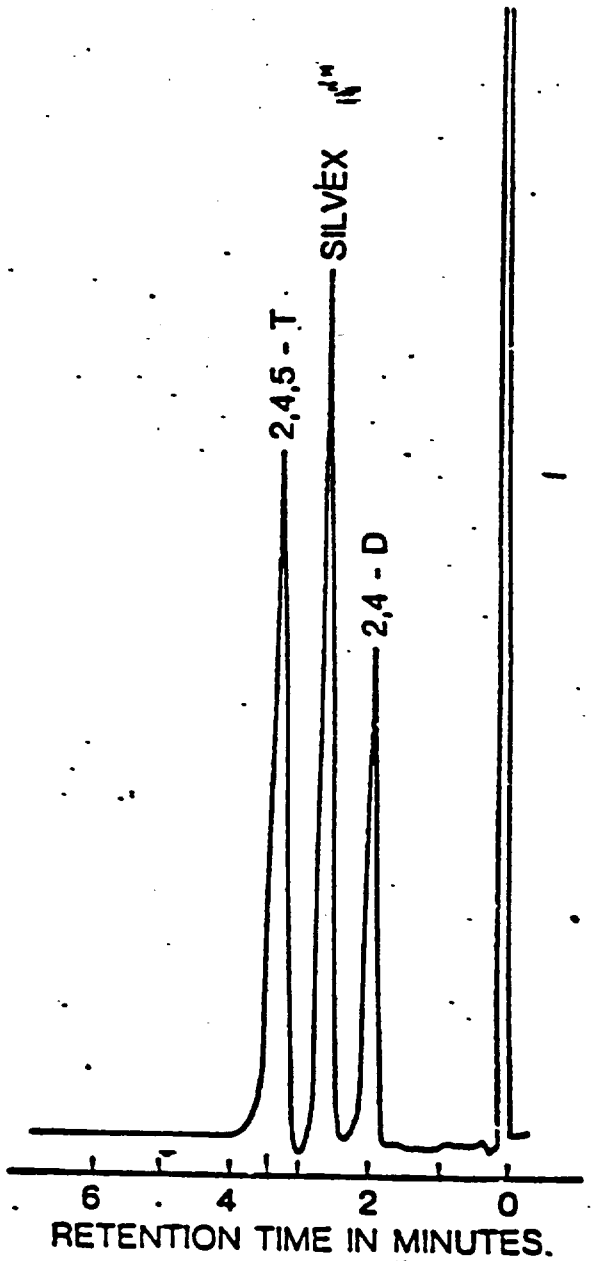


Fig.1. Column: 1.5% OV - 17 + 1.95% QF -1, Carrier Gas: Argon (5%)/Methane: 70 ml/min., Column Temp. 185 C, Detector: Electron Capture.

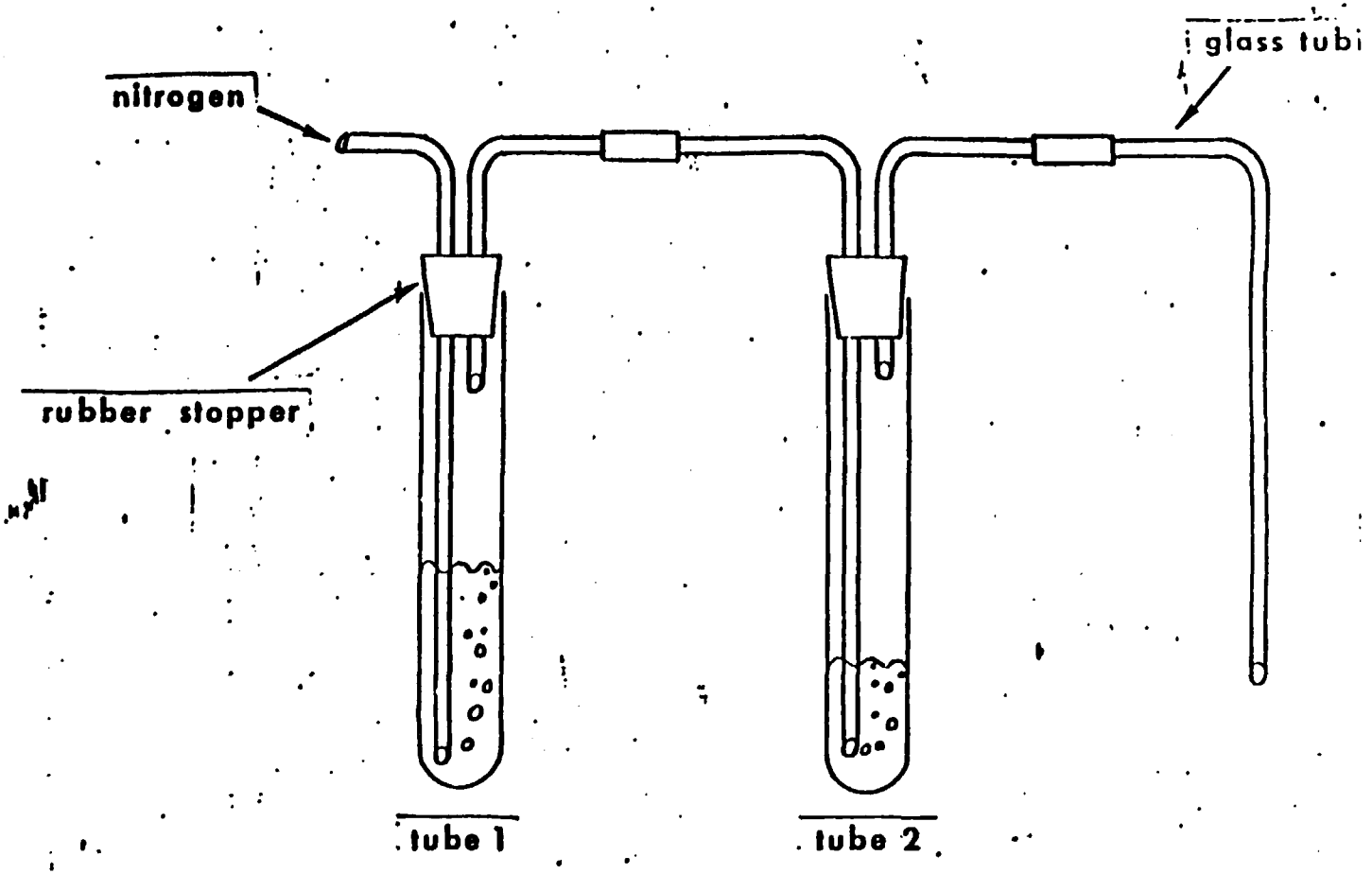


Figure I-1. Diagram of diazomethane generator.

APPENDIX B.15

Amended QC Plan

4.6.8 Quality Control Checks

The overall effectiveness of a quality control (QC) program is dependent upon operation of the laboratory in accordance with a program which systematically assures the precision and accuracy of analyses by detecting errors and preventing their recurrence or measuring the degree of error inherent in the methods applied.

Toward this end, the IT Corporation routine laboratory quality control program includes the following:

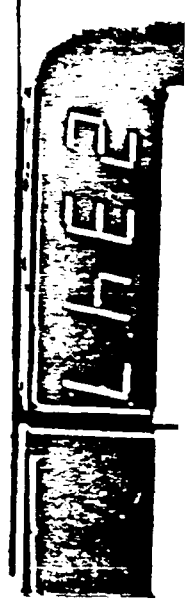
- Daily calibration of instruments is performed as described in Section 4.6.5 of this project plan
- Instrumental control charts are maintained for each pertinent method
- Glassware is checked for cleanliness before each analysis
- Each lot of solvent, reagent and chromatographic adsorbents is evaluated to assure its suitability for the intended analysis

In addition, project specific QC checks are developed. Internal quality control is initiated at the laboratory level, and is intended to review sample data within a set. External quality control is initiated at the overall program level, by the QA Program Manager, and is designed to review the interrelationships between sets of samples over the scope of the project.

The specific QC checks and their established frequencies for this project are summarized in Table _____. The check frequencies are influenced by the applicable analytical method requirements.

4.6.8.1 External Quality Control

For every set of 20 samples (or portion thereof) collected of a similar matrix, a Field Travel Blank will be included for analysis. Travel Blanks at this frequency will be associated with wipe, chip, and scrape samples, and will be analyzed with each sample set for 2, 3, 7, 8 -TCDD. For each set of soil/sediment/sludge and water matrix samples, travel blanks will be collected at the same 5% frequency, and routinely analyzed for volatile organics. At the discretion of the QA Program Manager, travel blanks will be associated with



soil/sediment/sludge and water samples at a frequency of 1%, and randomly assigned for dioxin, semi-volatile organics, priority pollutant metals, cyanide, and phenols analysis.

Travel blanks consist of appropriate sample containers filled with laboratory demonstrated analyte-free water, which are handled, transported, and analyzed in the same manner as their associated samples. Wipe travel blanks consist of an unused gauze wipe, soaked in solvent.

Five percent of all samples will be split at the time of collection and provided to the OSC to be analyzed independently by the NJDEP. The OSC, or other NJDEP representative will determine what specific samples are to be split.

The QA Program Manager will randomly select one percent of the total number of samples collected for interlaboratory analysis within ITC. These splits, together with NJDEP split analyses, will verify laboratory and method performance.

4.6.8.2 Internal Quality Control

At each laboratory, spiked sample (or blank spike) analyses and blind split (duplicate) sample analyses will each be performed at a frequency of 5%, or one per set of 20 samples or portion thereof.

Method blanks will be initiated at the same frequency, as well as whenever new reagents or solvent lots are used for sample preparation.

All samples, spikes, duplicates, and method blanks are carried through the same analytical process, including review, reporting and storage.

For organic analyses (dioxin, volatiles and semi-volatiles), internal standards and surrogate methods are added to each sample to monitor instrument performance and recovery. For all parameter analyses, reference standards are run at a minimum of one per shift.

The laboratory QA Coordinators, senior chemists experienced in environmental analysis, will be responsible for reviewing, implementing and overseeing this QA program in their respective laboratories.

In addition, the laboratory QA Coordinators will:

- Statistically review the data and submit weekly reports to the QA Program Manager
- Ensure that all instrumentation is properly maintained and calibrated.
- Submit performance standards for select compounds to be analyzed as blinds.
- Prepare samples and standard solutions for submission as unknowns to each analyst during the project for evaluation of the methodology, analyst's ability, work environment, and instrumental reproducibility.
- Document the results of blind spikes and performance standards in a central logbook which will be reviewed periodically with the QA Program Manager.

The laboratory QA Coordinators, the QA Program Manager, the analytical task leaders, and the Analytical Program Manager will communicate on a regular basis to assure that all QA/QC practices are being carried out and to review potential problem areas.

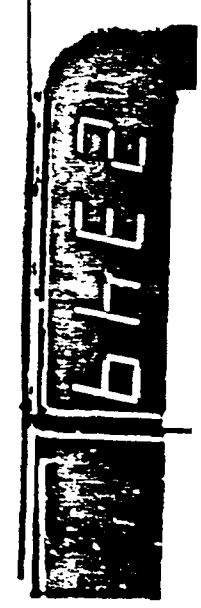
4.6.8.3 Summary - Overall QC Check Frequencies

At the indicated frequencies for initiation of the QC check samples described, one set of 20 samples (or portion thereof) collected of a similar matrix will generate the following QC samples, for a single analysis parameter:

1	Field Travel Blank
1	Split with NJDEP
1	Method Blanks
1	Blind Split (Duplicate)
1	Blank or Sample Spike
5	Total QC Samples

Of these, 4 will be analyzed by ITC with each sample set; this excludes the NJDEP split. Thus, the overall ITC QC level for a set of samples analyzed for a single parameter is 20%.

Many samples will be analyzed for all six analysis parameters. From this perspective, a set of 20 samples (or portion thereof) collected of a similar matrix will generate the following QC check samples:



2	Field Travel Blanks	(estimated)
6	NJDEP Splits	
6	Method Blanks	
6	Blind Splits (duplicates)	
6	Blank or Sample Spikes	
26	Total QC Samples	

Of these, 20 will be analyzed by ITC for the appropriate parameters, providing a 100% QC analysis frequency.

ITC is confident that the indicated QC checks will provide sufficient data to monitor and evaluate the performance of all aspects of the analytical program. When necessary, the QA Program Manager will initiate additional QC checks to control specific problems areas that may develop.

D184-SW

Table _____. Quality Control Sample and Check Frequencies

	(% of Sample)							
	Field Travel Blanks	Splits with NJDEP	ITC Interlaboratory Analyses	Method Blanks	Blind Splits	Sample/Blank Spikes	Internal Surrogate Standards	Reference (Calibration Standards
DIOXIN								
Wipes/Chips/Scrapes	5	--	--	5	--	5	100	1/shift
Soil/Sediment Sludge	1	5	1	5	5	5	100	1/shift
Water	1	5	1	5	5	5	100	1/shift
VOLATILES								
Soil/Sediment/Sludge	5	5	1	5	5	5	100	1/shift
Water	5	5	1	5	5	5	100	1/shift
SEMI-VOLATILES								
Soil/Sediment Sludge	1	5	1	5	5	5	100	1/shift
Water	1	5	1	5	5	5	100	1/shift
PP Metals								
Soil/Sediment/Sludge	1	5	1	5	5	5	--	1/shift
Water	1	5	1	5	5	5	--	1/shift
CYANIDE								
Soil/Sediment/Sludge	1	5	1	5	5	5	--	1/shift
Water	1	5	1	5	5	5	--	1/shift
TOTAL PHENOLS								
Soil/Sediment/Sludge	1	5	1	5	5	5	--	1/shift
Water	1	5	1	5	5	5	--	1/shift

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APPENDIX B.16

2,3,7,8-Tetrachloro-p-dioxin and 2,3,7,8-Tetrachloro-p-furan
Analysis Procedures by Multiple Ion Detection (Mid) High
Resolution Gas Chromatography/Low Resolution Mass Spectrometry (HRGC/LRMS)

2,3,7,8-TETRACHLORO-P-DIOXIN and 2,3,7,8-TETRACHLORO-p-FURAN ANALYSIS PROCEDURES BY MULTIPLE ION DETECTION (MID) HIGH RESOLUTION GAS CHROMATOGRAPHY/LOW RESOLUTION MASS SPECTROMETRY (HRGC/LRMS)

1.0 INTRODUCTION

1.1 This is a qualitative and quantitative (high resolution) GC/(low resolution) MS analysis specific for the 2,3,7,8 isomer of tetrachlorodibenzo-p-dioxin using selected ion monitoring. A sample is spiked with isotopically labeled $^{13}C_{12}$-2,3,7,8-TCDD, ^{13}C-2,3,7,8-TCDF and ^{13}C-OCDD as internal standards, and ^{37}Cl-TCDD as a surrogate. Quantitation is based on the response of native TCDD relative to the internal standard. Performance is based on accuracy of the surrogate versus both ^{13}C-TCDD and ^{13}C-TCDF.

Due to the commercial unavailability of all of the furan and dioxin isomers, some basic assumptions must be made as to the isomer specificity of the GC column with respect to 2,3,7,8-TCDF. Following the EPA protocol stated in the "Determination of 2,3,7,8-TCDD in Soil and Sediment," September 1983, the laboratory must show isomer specificity with respect to 2,3,7,8-TCDD. Using a 60 M SP2330, isomer specificity is possible for 2,3,7,8-TCDD. Rappe[1] has shown that the same 60 M SP2330 column is also isomer specific for 2,3,7,8-TCDF. If the column can separate 2,3,7,8-TCDF from 2,3,4,8 and 1,2,6,9-TCDF. The column performance mixture run before and after each eight-hour shift will contain the two above stated furans in addition to the seven dioxin isomers. The dioxin analysis will follow the SOP for dioxin in Section 4.

2.0 SAFETY

2.1 Samples are sent to IT Corporation from suspected or known hazardous waste sites. Samples are to be handled from receipt to storage by qualified personnel only. Analysts must have a working knowledge of safety protocols and be adept at safety procedures. GC/MS instruments must be equipped with vapor contamination traps on the capillary split and sweep vents and on the rough pump effluent lines prior to use (see Safety SOP).

3.0 SET-UP AND INSTALLATION

3.1 Install a 60 meter, 0.25 mm ID, fused silica SP2330, 0.20 micron film thickness capillary column. Set the head pressure to approximately 20 to 25 psi and the split and sweep flows to 30 ml/min and 8 ml/min respectively.

3.2 Create a reasonable unit resolution tune, for PFTBA. Adjust the zero according to the instrument manufacturers suggested settings. Set the preamp sensitivity to 10^{-8} amps/volts. The electron multiplier must be set to achieve 800,000 area units for 2 ng of $^{13}C_{12}$-TCDD as injected for M/E 334. Calibrate the instrument.

3.3 Establish the following MID descriptors:

3.3.1 NAME "TC" for running column performance mixture

3.3.2 NAME "TD" for running standards and samples

3.4 Set the GC conditions as follows:

Injection Port Temp	260°C
Separator Temp	260°C
Initial Temp	70°C
Initial Time	4 min
Ramp Rate 1	20°C/min
Temp 2	200°C
Hold Time 2	0 min
Ramp Rate 2	4°C/min
Temp 3	260°C
Hold Time 3	5 min*
Split/Sweep	85 sec
Filament/Mult turn on time	10 min

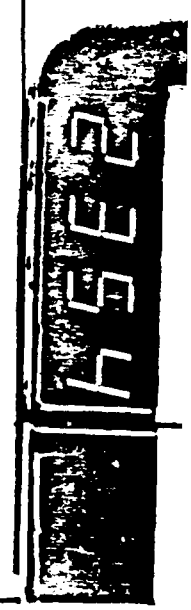
* Hold for at least 2 min beyond the retention time of the last isomer of TCDD in the performance mixture.

3.5 Analyze the 7 isomer EPA test mixture plus the three furan isomers. If no isomers are co-eluting with 2,3,7,8-TCDD or 2,3,7,8-TCDF, conditions stated above are acceptable to proceed. If co-elution does occur with 2,3,7,8-isomers, the column must be changed or conditions modified in order to stop co-elution.

4.0 ANALYSIS

4.1 General Description

4.1.1 A three-point calibration consisting of a 200 pg/µl (1 ppb equivalent), a 1000 pg/µl (5 ppb equivalent) and a 5000 pg/µl (25 ppb equivalent) standard must be run and a linear response curve generated before samples are analyzed. The 200 pg/µl standard is analyzed at the beginning of each eight hour shift to verify system performance and conformity to the multipoint calibration (see QA section on standard paperwork). Samples are received in 50 µl volumes and require no further preparation by the GC/MS laboratory.



4.1.2 COMPOSITION OF CONCENTRATION CALIBRATION SOLUTIONS

Solution No.	Concentration of 2,3,7,8-TCDD TCDF			
	Isotopically Labeled			Unlabeled 2,3,7,8
	$^{13}C_{12}$-TCDD	$^{37}Cl_4$-TCDD	^{13}C-TCDF	TCDD and TCDF
1	1 ng/µL	0.06 ng/µL	0.2 ng/µl	0.2 ng/µL
2	1 ng/µL	0.12 ng/µL	0.2 ng/µl	1 ng/µL
3	1 ng/µL	0.2 ng/µL	0.2 ng/µl	5 ng/µL

4.2 Procedures for GC/MS Analysis Initial Calibration

4.2.1 The GC conditions for all standards, samples, and the column performance mixture are as stated in Section 3.4.

4.2.2 Tune and calibrate the instrument as in step 3.2 or verify that the instrument has been tuned and calibrated within the past week and has performed satisfactorily when last used. If the method has not been performed successfully within the last seven days, check the tune and recalibrate.

4.2.3 Acquire the seven isomer EPA test mix. If no isomers are co-eluting with 2,3,7,8-TCDD and 2,3,7,8-TCDF, proceed with 4.2.4. If co-elution does occur, the conditions must be modified or the column must be changed. The MID descriptor TC must be used for this analysis (section 3.3).

4.2.3.1 Determine and document acceptable system performance with the following criteria:

A. Five data points for each GC peak are acquired.

B. GC column performance -- The valley between the 2,3,7,8-isomers and the peaks representing all other TCDD or TCDF isomers must be resolved with a valley $\leq$25%. Valley % = x/y X 100 when y is peak height of 2,3,7,8-TCDD and x is baseline to valley height (Fig. 1).

C. Ratio of integrated ion current for m/z 320 to m/z 322 for 2,3,7,8-TCDD must be $\geq$ 0.67 and $\leq$ 0.87.

D. MS resolution -- Ratio of integrated ion current for m/z 323 relative to m/z 322 for unlabeled 2,3,7,8-TCDD should be $\geq$ 0.07 and $\leq$ 0.20.

E. Ratio of integrated ion current for m/z 332 to m/z 334 for $^{13}C_{12}$-2,3,7,8-TCDD must be $\geq$ 0.67 and $\leq$ 0.87.

F. Response factor for $^{37}Cl_4$-2,3,7,8-TCDD relative to $^{13}C_{12}$-2,3,7,8-TCDD must be within ± 10% of the mean value established by triplicate analyses of the concentration calibration solutions (section 4.1.2).

4.2.3.2 Remedial action must be taken if all of the criteria are not met.

4.2.4 Using the same GC conditions that produced acceptable results with the performance solution, analyze 2 µl of each of the three concentration calibration solutions in section 4.1.2. MID descriptor TD (3.3.2) is used for all calibration standards and samples.

4.2.5 Calculate the response factor for $^{37}Cl_4$-2,3,7,8-TCDD and for unlabeled 2,3,7,8-TCDD relative to $^{13}C_{12}$-2,3,7,8-TCDD, $^{37}Cl_4$-2,3,7,8-TCDD, and unlabeled 2,3,7,8-TCDF relative to $^{13}C_{12}$-2,3,7,8-TCDF:

$$RF = \frac{A_x \bullet Q_{is}}{A_{is} \bullet Q_x}$$

where A_x = integrated ion abundance (corrected for native contribution) of m/z 328 for $^{37}Cl_4$-2,3,7,8-TCDD or the sum of integrated ion abundances of m/z 320 (304) and m/z 322 (306) for unlabeled 2,3,7,8-TCDD (TCDF),

A_{is} = the sum of integrated abundances of m/z 332 (316) and m/z 334 (318) for $^{13}C_{12}$-2,3,7,8-TCDD ($^{13}C_{12}$-2,3,7,8-TCDF),

Q_{is} = quantity of $^{13}C_{12}$-2,3,7,8-TCDD, ($^{13}C_{12}$-2,3,7,8-TCDF)

Q_x = quantity of unlabeled 2,3,7,8-TCDD (TCDF) or $^{37}Cl_4$-2,3,7,8-TCDD injected.

RF is a unitless number; units used to express quantities must be equivalent.

4.2.6 For both $^{37}Cl_4$-2,3,7,8-TCDD and unlabeled 2,3,7,8-TCDD (TCDF), calculate the RF of each of the three concentration calibration solutions. Variation of the RF calculated for each compound at each concentration level must not exceed 10% RSD. If the three RFs for each compound do not differ by more than ± 10%, the RF can be considered to be independent of analyte quantity for the calibration concentration range, and the mean of the three RFs shall be used for concentration calculations.

4.2.7 Fill out all necessary paperwork for the standard calibration QA/QC.

NOTE: Dioxin analysis still follows the procedure for 2,3,7,8-TCDD including the use of a 15 point calibration.

4.2.8 Plot the response factor vs concentration for the three point calibration curve for QA/QC reporting.

4.3 Calibration before the start of each eight hour shift

4.3.1 Inject 2 µl of the performance check solution as in 4.2.3 - 4.2.3.1F.

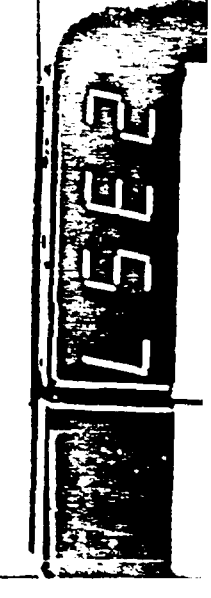
4.3.2 Inject 2 µl of the concentration calibration solution No. 1 (200 pg/µl) determine and document acceptable performance for

4.3.2.1 MS sensitivity - signal-to-noise (S/N) ratio of $\geq$ 2.5 for m/z 257 and $\geq$ 10 for m/z 322 for unlabeled 2,3,7,8-TCDD. The ratio of integrated ion current for m/z 257 to m/z 322 must be $\geq$ 0.20 and $\leq$ 0.45.

4.3.2.2 Measured response factor for unlabeled 2,3,7,8-TCDD (TCDF) relative to $^{13}C_{12}$-2,3,7,8-TCDD (TCDF) is within $\pm$ 10% of the mean values established (Section 4.2) by the analyses of the concentration calibration solutions.

4.3.2.3 If both these criteria are met, fill out the bottom portion of form 248A (QA/QC section). If the RF ratios are within 10% of the calibration average, samples may then be analyzed. DO NOT UPDATE the shift standard to the response list. Use R;S;T only. If the 10% criteria are not met, reanalyze the shift standard. If still out of bounds, a new multipoint must be run. Multipoints may continue to be used for as long as the shift standards conform to this criteria. Xerox a copy of Form 248A for inclusion with the shift standard packages and an extra copy to be placed in the instrument log book so that subsequent shift standard entries may be made on the same form.

4.3.2.4 Acquire sample analyses. Samples may be analyzed following a successful shift standard analysis. Performance standards must be rerun within every eight hours. The injection procedure must be carefully adhered to to avoid cross contamination. If the background of a sample analysis remains high towards the end of an acquisition, the column should be baked out for an extra period of time to avoid possible chromatographic carryover into the next sample injection. Septa should be changed after approximately 40 injections. Capillary injection port liners should be cleaned or exchanged with every other septum change. Good sense and experience prevail.



4.3.3 After eight hours from the injection of the column performance check solution (4.3.1), the tune is over and the performance check solution must be analyzed again. If all criteria (4.2.3.1 a-f) are met, the samples analyzed during that eight hour period are acceptable. If the criteria are not met, the samples must be reanalyzed.

4.4 For all injections, a hot needle injection technique is used.

4.4.1 Injection Technique (Hot Needle) - The syringe must be thoroughly cleaned between injections to avoid cross-contamination. Remove the plunger between injections and wipe it thoroughly with a Kimwipe. Rinse the syringe with ten to fifteen full syringe volumes of hexane solvent wash. Replace the solvent wash with pesticide quality hexane daily. If a Hamilton syringe cleaner is available that is equipped with a vacuum source, use this also. Do not use the Hamilton syringe cleaner if there is no vacuum pump attached. Insert the needle into the septum port, wait approximately ten seconds for the needle to heat, then pump the plunger back and forth a few times. Rinse with the solvent wash hexane again. Work the plunger up and down in the syringe barrel to reduce excess hexane wash. There should be approximately 0.5 µl of solvent left in the syringe barrel following this final rinse.

Draw back the plunger so that there are about 2 µl of air in the barrel. Draw 2.1 ml of sample into the needle. Usually to get a total of 2 µl of sample, it is necessary to pull the plunger back approximately 1.2 µl. The sample should be drawn up into the barrel and the amount confirmed to be 2 µl. If it is not, the sample should be expelled and process repeated.

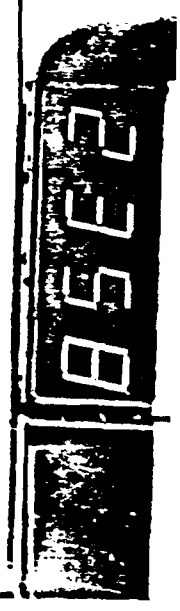
After getting 2.0 µl of sample into the barrel, insert the needle into the injector port and wait 6 seconds. Rapidly make the injection.

After making the injection, remove the needle as quickly as possible. As soon as the injection is made, start the GC.

4.5 Identification criteria for native 2,3,7,8-TCDD

4.5.1 Retention time (at maximum peak height) of the sample component must be within 3 seconds of the retention time of the $^{13}C_{12}$-2,3,7,8-TCDD. Retention times are required for all chromatograms, but scan numbers are optional. These parameters should be printed next to the appropriate peak.

4.5.2 The integrated ion currents detected for m/z 257, 320, and 322 must maximize simultaneously. If there are peaks that will affect the maximization or quantitation of peaks of interest, attempts should be made to narrow the scan window to eliminate the interfering peaks. This should be reported on a separate chromatogram.



4.5.3 The integrated ion current for each analyte and surrogate compound ion (m/z 257, 320, 322 and 328) must be at least 2.5 times background noise and must not have saturated the detector; internal standard ions (m/z 332 and 334) must be at least 10 times background and must not have saturated the detector.

4.5.4 Relative abundance of m/z 257 to m/z 322 should be $\geq$ 20% and $\leq$ 45%.

4.5.5 Abundance of integrated ion counts detected for m/z 320 must be $\geq$ 67% and $\leq$ 87% of integrated ion counts detected for m/z 322.

4.6 Identification Criteria for Native 2,3,7,8-TCDF

4.6.1 Retention time of the sample component must be within 3 seconds of the retention time of the $^{13}C_{12}$-2,3,7,8-TCDF.

4.6.2 Integrated ion currents detected for m/z 304, 306, and 241 must maximize simultaneously.

4.6.3 The integrated ion current for each analyte compound ion (m/z 241, 304, and 306) must be at least 2.5 times background noise and must not have saturated the detector; internal standard ions (m/z, 316 and 318) must be at least 10 times background noise and must not saturate the detector.

4.6.4 Relative abundance of m/z 241 to m/z 306 must be >20% and >45%.

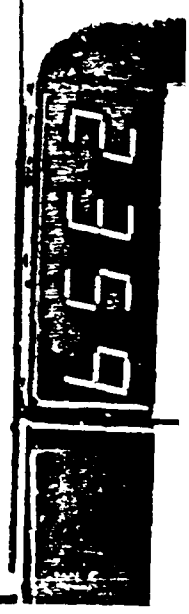
4.6.5 Abundance of integrated ion counts detected for m/z 304 must be >67% and <87% of the integrated ion counts detected for m/z 306.

5.0 DELIVERABLES

5.1 Each sample "package" must include the following:

a) RIC (1000 - end of run)
b) Complete quantitation report. (Input area and scan No. manually if missed)
c) (EICP of m/e 332; m/e 334; m/e 316, and m/e 318)
d) (EICP of 320; 322; 332; and 257)
e) (EICP of 304; 306; and 241)
f) Quan (320; 322; 257; 5 scans) The center of the 5 scan window is the retention time of $^{13}C_{12}$-2,3,7,8-TCDD
g) A standard package including all of (a) through (e) plus an attached copy of the TCDD calibration summary (Form 248A)

5.1.1 See QA/QC section for batch report deliverables



APPENDIX B.17

Analysis Procedures for OCDD

ANALYSIS PROCEDURES FOR OCDD

1.0 INTRODUCTION

1.1 Based on the request for OCDD, a modification of the procedures for the "Determination of 2,3,7,8-TCDD in Soil and Sediment," September 1983, must be employed. Samples are initially spiked with ^{13}C-TCDD; ^{13}C-TCDF; ^{13}C-OCDD; and ^{37}Cl-TCDD. Native OCDD results are calculated using a relative response factor versus ^{13}C-OCDD.

Performance of the system is based on surrogate standard (^{13}Cl-2,3,7,8-TCDD) results for every sample. This performance is calculated against ^{13}C-OCDD.

2.0 SAFETY

2.1 Samples are sent to IT Corporation from suspected or known hazardous waste sites. Samples are to be handled from receipt to storage by qualified personnel only. Analysts must have a working knowledge of safety protocols and be adept at safety procedures. GC/MS instruments must be equipped with vapor contamination traps on the capillary split and sweep vents and on the rough pump effluent lines prior to use.

3.0 SET-UP AND INSTALLATION

3.1 Install a 30 meter, 0.25 mm i.d., fused silica SE-54, 0.20 micron film thickness capillary column. Set the head pressure to approximately 20-25 psi and the split and sweep flows to 30 ml/min and 8 ml/min respectively.

3.2 Create a reasonable unit resolution tune for PFTBA. Adjust the zero according to the instrument manufacturers suggested settings. Set the preamp sensitivity to 10^{-8} amps/volts. The electron multiplier must be set to achieve 800,000 area units for 2 ng of $^{13}C_{12}$-TCDD as injected for M/E 334. Calibrate the instrument.

3.3 Establish MID descriptors which include the ions for ^{13}C-TCDD (332, 334); ^{13}C-TCDF (316, 318); ^{37}Cl-TCDD (328); ^{13}C-OCDD (470, 472); and OCDD (458, 460)

3.4 Set the GC conditions as follows:

Injection Port Temp	300°C
Separator Temp	300°C
Initial Temp	70°C
Initial Time	4 min
Ramp Rate 1	20°C/min
Temp 2	200°C
Hold Time 2	0 min
Ramp Rate 2	10°C/min
Temp 3	300°C
Hold Time 3	5 min*

Split/Sweep	85 sec
Filament/Mult turn on time	10 min

* Hold for at least 2 min beyond the retention time of isomer PCDD in the standard.

4.0 ANALYSIS

4.1 General Description

4.1.1 A three point calibration consisting of a 200 pg/µl (1 ppb equivalent), a 1000 pg/µl (5 ppb equivalent), and a 5000 pg/µl (25 ppb equivalent), standard must be run and a linear response curve generated before samples are analyzed. The 200 pg/µl standard is analyzed at the beginning of each eight hour shift to verify system performance and conformity to the multipoint calibration. Samples are received in 50 µl volumes and require no further preparation by the GC/MS laboratory.

4.1.2 COMPOSITION OF CONCENTRATION CALIBRATION SOLUTIONS

Concentration of PCDD/PCDF Standards

Solution Number	$^{13}C_{12}$	$^{37}Cl_4$	^{13}C-TCDF	^{13}C-OCDD	OCDD
1	1 ng/µL	0.06 ng/µL	0.2 ng/µl	1 ng	0.2 ng/ml
2	1 ng/µL	0.12 ng/µL	0.2 ng/µl	1 ng	1 ng/ml
3	1 ng/µL	0.2 ng/µL	0.2 ng/µl	1 ng	5 ng/ml

4.2 Procedures for GC/MS Analysis Initial Calibration

4.2.1 The GC conditions for all standards, samples, and the column performance mixture are as stated in Section 3.4.

4.2.2 Tune and calibrate the instrument as in step 3.2 or verify that the instrument has been tuned and calibrated within the past week and has performed satisfactorily when last used. If the method has not been performed successfully within the last seven days, check the tune and recalibrate.

4.2.3 Using the same GC conditions stated in Section 3.4, analyze 2 µl of each of the three concentration calibration solutions in section 4.1.2.

4.2.4 Calculate the response factor for $^{37}Cl_4$-2,3,7,8-TCDD and for unlabeled OCDD versus ^{13}C-OCDD.

$$RF = \frac{A_x \bullet Q_{is}}{A_{is} \bullet Q_x}$$

where A_x = integrated ion abundance (corrected for native contribution) of m/z 328 for $^{37}Cl_4$-2,3,7,8-TCDD or the sum of integrated ion abundances of characteristic ions for the unlabeled OCDD,

A_{1s} = the sum of integrated abundances of m/z 470 and m/z 472 for $^{13}C_{12}$-OCDD,

Q_{1s} = quantity of $^{13}C_{12}$-OCDD,

Q_x = quantity of the unlabeled OCDD or $^{37}Cl_4$-2,3,7,8-TCDD injected.

RF is a unitless number; units used to express quantities must be equivalent.

4.2.5 For both $^{37}Cl_4$-2,3,7,8-TCDD and unlabeled OCDD, calculate the RF of each of the three concentration calibration solutions. Variation of the RF calculated for each compound at each concentration level must not exceed 10% RSD. If the three RFs for each compound do not differ by more than ± 10%, the RF can be considered to be independent of analyte quantity for the calibration concentration range, and the mean of the three mean RFs shall be used for concentration calculations.

4.2.6 Fill out all necessary paperwork for the standard calibration QA/QC.

4.2.7 Plot the response factor vs concentration for the three point calibration curve for QA/QC reporting.

4.3 Calibration before the start of each eight hour shift

4.3.1 Inject 2 µl of the concentration calibration solution #1 (200. pg/µl) determine and document acceptable performance for

4.3.1.1 MS sensitivity - signal-to-noise (S/N) ratio of ≥ 10 for m/z 458 and 460 for unlabeled OCDD.

4.3.1.2 Measured response factor for unlabeled OCDD relative to $^{13}C_{12}$-OCDD is within ± 10% of the mean values established (Section 4.2) by analyses of the concentration calibration solutions.

4.3.1.3 If both these criteria are met, fill out the bottom portion of form 243A (QA/QC section). If the RF ratios are within 10% of the calibration average samples may then be analyzed. DO NOT UPDATE the shift standard to the response list. Use R;S;T only. If the 10% criteria are not met, reanalyze the shift standard. If still out of bounds, a new multipoint must be run. Multipoints may continue to be used for as long as the shift standards

conform to this criteria. Xerox a copy of Form 248A for inclusion with the shift standard packages and an extra copy to be placed in the instrument log book so that subsequent shift standard entries may be made on the same form.

4.3.1.4 Acquire sample analyses. Samples may be analyzed following a successful shift standard analysis. Performance standards must be rerun within every eight hours. The injection procedure must be carefully adhered to to avoid cross contamination. If the background of a sample analysis remains high towards the end of an acquisition, the column should be baked out for an extra period of time to avoid possible chromatographic carryover into the next sample injection.

4.3.1.5 Septa should be changed after approximately 40 injections. Capillary injection port liners should be cleaned or exchanged with every other septum change. Good sense and experience prevail.

4.3.2 After eight hours from the injection of the shift standard, the tune is over.

4.4 For all injections, a hot needle injection technique is used.

4.4.1 Injection Technique (Hot Needle) - The syringe must be thoroughly cleaned between injections to avoid cross contamination. Remove the plunger between injections and wipe it thoroughly with a kimwipe. Rinse the syringe with ten to fifteen full syringe volumes of hexane solvent wash. Replace the solvent wash with pesticide quality hexane daily. If a hamilton syringe cleaner is available that is equipped with a vacuum source, use this also. Do not use the hamilton syringe cleaner if there is no vacuum pump attached. Insert the needle into the septum port, wait approximately ten seconds for the needle to heat, then pump the plunger back and forth a few times. Rinse with the solvent wash hexane again. Work the plunger up and down in the syringe barrel to reduce excess hexane wash. There should be approximately 0.5 µl of solvent left in the syringe barrel following this final rinse.

Draw back the plunger so that there are about 2 µl of air in the barrel. Draw 2.1 ml of sample into the needle. Usually to get a total of 2 µl of sample, it is necessary to pull the plunger back approximately 1.2 µl. The sample should be drawn up into the barrel and the amount confirmed to be 2 µl. If it is not, the sample should be expelled and process repeated.

After getting 2.0 µl of sample into the barrel, insert the needle into the injector port and wait 6 seconds. Rapidly make the injection.

After making the injection, remove the needle as quickly as possible. As soon as the injection is made, start the GC.

4.5 Identification Criteria for OCDD

4.5.1 Integrated ion currents detected for m/z 458 and 460 must maximize simultaneously.

4.5.2 The integrated ion current for all ions of interest must be at least 2.5 times signal to noise of background.

4.5.3 The integrated ion ratios 458:460 must be within ±20% of the same ratio of the standard.

4.5.4 Retention time of OCDD must be within ±3 scans of ^{13}C-OCDD.

APPENDIX C

APPENDIX C

FIELD SAMPLING PROTOCOL EXPANSION

APPENDIX C

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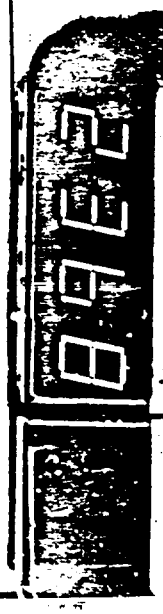

C.1 STANDARD OPERATING PROCEDURE, WIPE SAMPLING TECHNIQUE

The routine wipe sampling procedure is as follows and utilizes a sorbent cotton gauze pad which has been dampened with hexane before collecting the sample. The damp (wet) wipe sample pad will be hand held and the area to be wiped will be either measured using a 2,500 cm^2 template or measured and marked to determine actual area by another acceptable means comparable to field conditions. The wet wipe sampling procedure will collect both the material on the surface of a matrix and the material that is easily extracted from the matrix. The wet wipe procedure may result in material other than the analyte of interest being collected, such as wax, on surface floors, which could interfere with the sample analysis. Therefore, during collection of wet wipe samples, sampling personnel will carefully document all conditions that exist on each surface sampled.

As part of all sampling procedures, field blanks will be collected to determine if specific analytical interferences may be present in either the sorbent pads or the hexane used as the solvent on the sorbent pads. The field blank will also determine whether procedures used to collect a wet wipe sample introduce any interferences to the samples, and will be included at a frequency of five percent (one per 20 samples collected).

The standard operating procedures established for collecting wet wipe samples are as follows:

1. Materials and Apparatus

   - 3" x 3" sterile cotton gauze pads, individually wrapped
   - Disposable, nonlinear, polyethyiene food serving gloves
   - Sample bottles, 240 ml, amber glass with teflon liners

- Hexane (pesticide grade)
- Glass graduated cylinder
- Sample labels
- Field log notebook/chain-of-custody records
- Master floor plan map
- Indelible ink pen
- Metric ruler.

2. Before sampling a specific matrix type, collect a field blank using the following procedure:
   - Put on a new pair of disposable gloves
   - Remove gauze pad from package
   - Hold pad in hand
   - Soak pad with 8 ml of hexane
   - Carefully fold pad and place into the sample collection bottle
   - Prepare sample label for collection bottle
   - Record sample information.
3. Select area for collecting a series of wet wipe samples for a matrix type. Ensure surface area is sufficient to collect all required samples. If the surface is not large enough, either select another area or carefully measure the area before sampling so the analytical results can be presented as a concentration per m^2 or ft^2.
4. Hold the template in position for sampling and mark the location on the master floor plan map, mark the outer perimeter of template or surface, or mark perimeter of sample area (when template not used).
5. To collect a wipe sample, use the following procedure:

- Put on a clean pair of disposable gloves
- Remove a gauze pad from its individually wrapped package
- Hold pad in hand
- Soak pad with 8 ml of hexane using the graduated cylinder to measure volume. Fill cylinder from laboratory squeeze bottle.

6. Sampling an area is conducted by applying pressure to the pad and drawing it towards the body in straight, even strokes, moving from left to right (horizontal for walls) in the area designated. Attempt to have a slight overlap of each stroke. Upon completion of wiping left to right, repeat the wipe effort by evenly drawing the pad over the area in a (vertical for walls) line starting at the top of the designated area and moving down to the bottom (this second wiping is at a 90-degree angle to the first wipe and should provide a thorough wiping of the entire area).

7. Upon completion of the wet wipe sampling in both directions, carefully fold the gauze pad over at least twice, being careful not to touch the contaminated side of the wipe pad, and place in labeled sample collection bottle. Bottles should be temporarily stored in plastic bags until all samples have been collected.

8. The sampling person in charge of field data should ensure the following information is accurately recorded:
   - Sample number, both on bottle and data sheet
   - Sample location (include floor number)
   - Sample description (i.e., wet wipe of vinyl-covered wallboard)
   - Sample date and time
   - Area sampled in square centimeters
   - Observations/problems, if pertinent
   - Names of sampling personnel.

9. The final step in sampling a specific area is to clearly mark the sample location on the master floor plan map. If appropriate, the sampling area will also be left outlined with duct, masking tape, or spray paint, with the sample number written on this "frame." This marking of the specific areas sampled may be used for future reference.

10. Change gloves after taking each sample. Take one field blank sample for each matrix type.

11. Upon completion of the day's or batch sampling activities, samples should be removed from the site as directed by the on-site safety officer or his deputy.

12. Upon removal of samples from the site, a chain-of-custody form shall be established for the samples. The chain-of-custody will act as a transmittal form from sampling personnel to laboratory personnel, and will be signed at this time to document that samples are properly relinquished and received by appropriate staff members.

C.2 STANDARD OPERATING PROCEDURE, DRUM OPENING

- A visual inspection will be made of all drums on site. Drums with no obvious corrosion, which are not bulged (due to pressure), will be opened and sampled "where-is," if they are in a safe, secure location.

- Drums not in a safe, secure location will be moved to an outside area between the process building and the warehouse.

- Drums which are corroded, or are bulged, must be segregated. The segregation will be by means of a hand truck to a forklift with drum hooks. In drums which need to be lowered, a drum saddle will be put around the drum, and it will be lowered by means of a chainfall with snatchblocking. A drum which is extremely corroded must first be placed in an overpack drum prior to segregation.

- Pressurized or corroded drums which have been segregated will be placed behind a barrier, or "bomb shield," and opened by means of a remote, automatic drum opener. The technician opening the drums will stand behind a separate barrier.

- Bungs will be opened slowly without excessive pressure. Once the bung is loosened, if a pressure leak is detected (by sound), step back and wait for the drum to vent. Once the drum has vented, remove the bung and proceed with sampling.

- If the bung on a nonbulging, noncorrosive drum cannot be removed, move the drum to the segregated area and open by means of the automatic drum opener.

- Prior to and during drum opening activities, monitoring will be done by means of HNU/PID and combustible gas indicator. Operations will be suspended and the on-site health and safety coordinator contacted if a Lower Explosive Limit (LEL) of 10 percent is reached, or if there is a concentration of contaminants greater than 500 parts per million.

- Respirators will be worn during drum opening. Corroded or pressurized drums will be handled in self-contained breathing apparatus.

APPENDIX
D

APPENDIX D
MISCELLANEOUS FIGURES AND TABLES

APPENDIX D

MISCELLANEOUS FIGURES AND TABLES
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FIGURES:

TABLES:

TABLE D-1

Process and Plant Changes

Date	Change
Early 1951	Initiated production of 2,4,5-TCP and 1,2,4,5 tetrachlorobenzene in a 500 gallon reactor. Used a dilution process with filtration to remove water insoluble organics from reaction mix.
January 1952	Initiated the use of purchased 1,2,4,5 tetrachlorobenzene because time was not available to make our own.
May 1952	Decision to increase capacity from 40,000 lb/mo to 120,000 lb/mo by installation of an additional 1,000 gallon reactor.
Feb/March 1953	Probable time for start-up of the new 1,000 gallon reactor.
September 1954	Steam stripping substituted for dilution process for the removal of organics on a routine basis.
December 1954	Do not remove salt (sodium chloride) from the NaTCP reaction mass but carry it through to the 2,4,5-T process and then separate all the salts at one time.
January 1955 to November 1956	No major process changes were made during this time frame.
December 1956	Initiated recycle of recovered organics.
January 1956 to February 1960	No major process changes during this period.
February 20, 1960	Explosion in NaTCP autoclave. Process building destroyed. Production of all materials ceased.
June 1960	Approval to reconstruct the plant. Reconstruction included complete replacement of the old process building.
February 1961	Rebuilt plant start-up. NaTCP now involved two 1,000 gallon reactors. Salt to be removed from NaTCP after steam stripper.
August 1967	2,4,5-T acid facility (old 2,4-D unit) was completed to produce a capacity of 3 MM lbs/yr of 2,4,5-T.

September 1967	2,4,5-TCP purification facility completed for removal of p-dioxin (2,3,7,8-TCDD).
November 1967	New 2,4-D acid facility completed with a capacity of 12 MM lb/yr.
August 1969	All production terminated.