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VELSICOL CHEMICAL CORPORATION



POST - CONSTRUCTION QUARTERLY MONITORING REPORT December 12 - 14, 1984

Plant Site, St. Louis, Michigan

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1.0 INTRODUCTION

1.1 GENERAL

In accordance with the terms of the technical appendix to the Consent Judgment entered into by Velsicol Chemical Corporation (Velsicol), the United States Environmental Protection Agency, (USEPA) and the Michigan Department of Natural Resources (MDNR), Velsicol is required to perform specified monitoring activities at quarterly intervals following closure of its St. Louis, Michigan plant site. The monitoring program is designed to address the following:

- 1. Performance of gas vents
- 2. Performance of the site perimeter containment wall
- 3. Determination of site groundwater elevations

This report details the initial site monitoring which occured during the period December 12 to December 14, 1984.

1.2 PARTICIPATION BY REGULATORY AGENCIES

Mr. M. Strimbu (USEPA) was present on site and participated in the entire monitoring program. Mr. B.

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Hall (MDNR) was present during the collection of the containment wall sample. Ms. A. Couture and Mr. R. Teoh (MDNR) were present on site on December 12, 1984 to discuss the proposed gas vent sampling protocol.

1.3 MONITORING AND SAMPLING PERSONNEL

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The monitoring and sampling program was carried out by Mr. D. Robinson and Ms. C. Cull (Conestoga-Rovers and Associates) assisted by Mr. Gene DeGeer, the Velsicol site custodian.

2.0 GAS VENT MONITORING

2.1 GENERAL

The gas vent monitoring began on December 14, 1984 and was completed the same day.

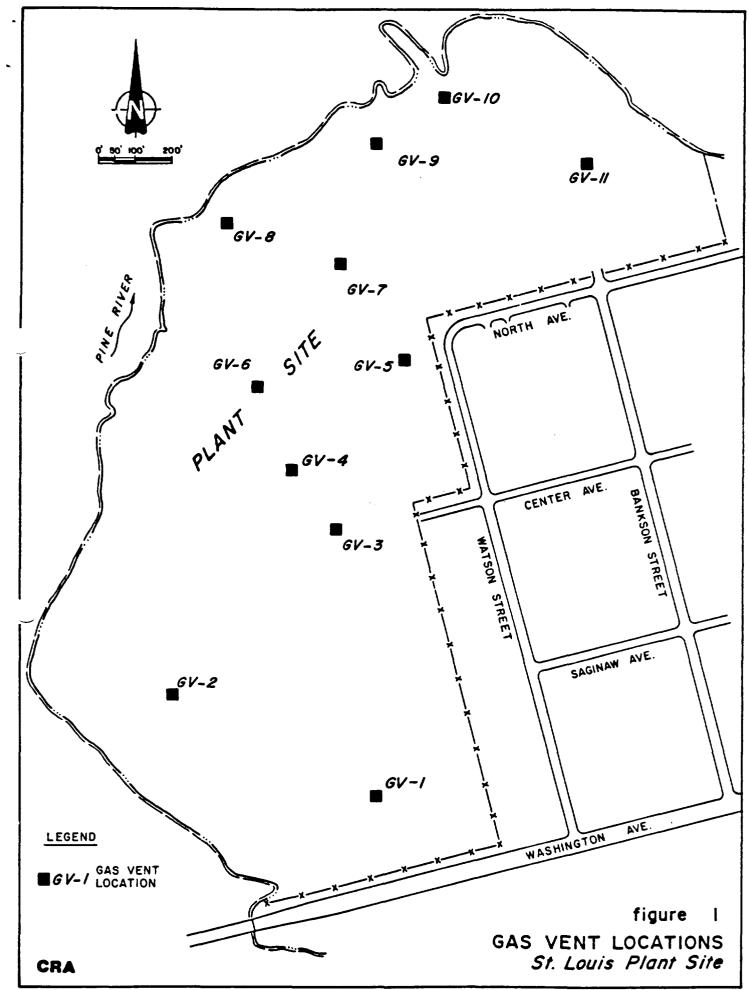
2.1.1 Equipment

Two Gilian model HFS 113 hi flow samplers were used to collect gas vent samples. The samplers were field calibrated using a rotometer prior to sampling. Samples from each gas vent were collected in two 6-mm diameter x 70-mm long Tenax tubes and two charcoal tubes of similar dimensions. The samples were collected simultaneously using dual parallel/series tube holder sets.

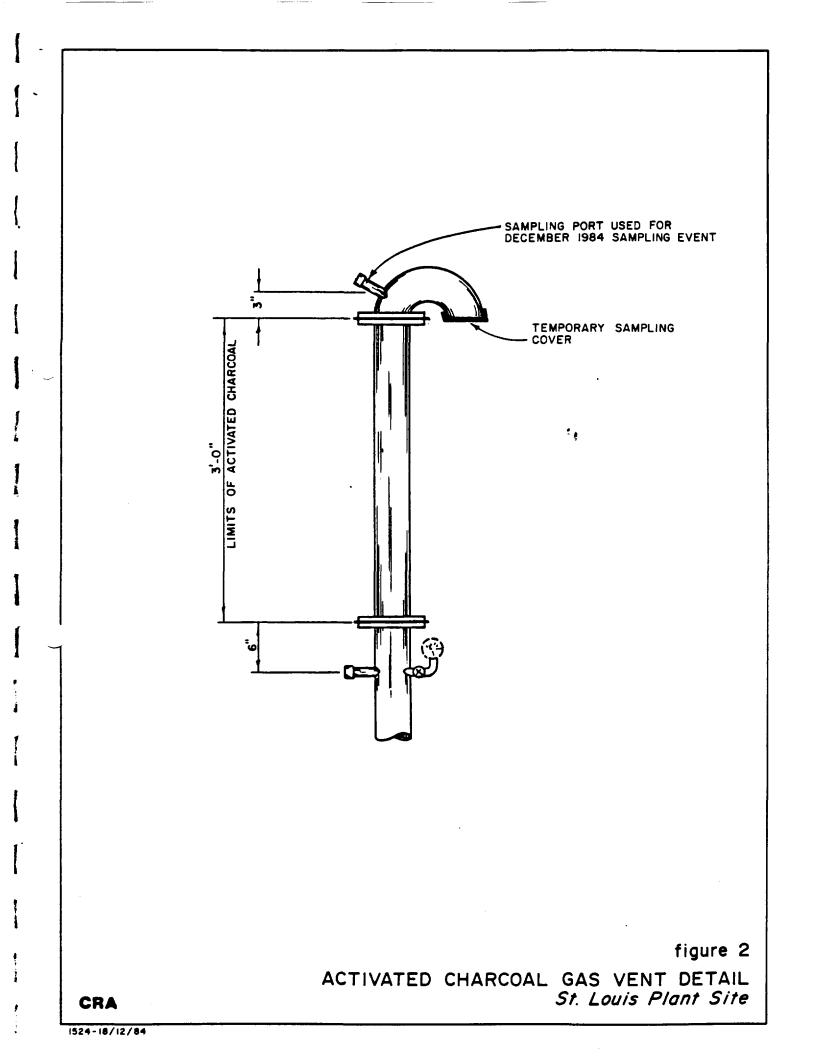
2.2 SAMPLE COLLECTION

Samples were obtained at each of the 11 gas vents. The location of the gas vents within the closed plant site is detailed on Figure 1. One blank set and one duplicate set of samples were also collected.

Sampling was conducted at the downstream sampling post on each gas vent as detailed on Figure 2. The



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tube holder was attached directly to the gas vent sampling port using a copper manifold assembly which was environmentally cleaned prior to use. Tygon tubing was used to connect the tube holder to the sampler and was connected between the base of the tube holder and suction port of the sampler. The sampler which was pre-calibrated to 250cc/min/tube set, was operated for a period of 20 minutes for each sampling event, resulting in a collected sample volume of five liters per tube set.

Prior to sample collection, the gas vent upper chamber was purged by pumping at 500 cc/minute for a period of ten minutes. This precluded the possiblity of sampling retained atmospheric air from the gas vent upper chamber. During the purging and sampling operations, the open end of the gas vent was capped using a 4-inch diameter plastic cover to prevent atmospheric air being drawn into the sample.

At the conclusion of each gas vent sampling, the set of four sample tubes were capped, labelled and stored in a cooler maintained at 0°C.

2.2.1 Sample Storage and Shipment

The samples were stored overnight in a freezer located within the project offices. On the morning

of December 15, 1984, the samples were transferred to a cooler containing frozen cold packs and styrofoam packing materials. The cooler was shipped under chain of custody protocol, to Velsicol's Memphis, Tennessee laboratory by overnight courier for analysis. A copy of the chain of custody is provided in Appendix A.

2.2.2 Sample Analysis

The sample tubes will be stored in a freezer until prepared for analysis and will be desorbed within thirty days of the sampling event. Analysis of the charcoal tubes will be conducted in accordance with NIOSH protocols for the following parameters:

	NIOSH
COMPOUND	METHOD NO.
Carbon Tetrachloride	1003
Trichloroethylene	S-336
Vinyl Chloride	1007

Should any of the above compounds be detected on any charcoal tube, the corresponding Tenax tubes will be analyzed by GC/MS using EPA Method 624.

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Data will be reported in written form to USEPA and MDNR within seven days after receipt by CRA of final laboratory data which is anticipated to be available during the last week of January 1985. A summary data report will be submitted to both Agencies following completion of the entire gas vent sampling program, in the fall of 1987.

2.2.3 Sampling Protocol

All sampling was performed in accordance with the methodology detailed within the St. Louis plant site Post-Closure Maintenance and Monitoring Plan, as approved by USEPA and MDNR. A copy of the sampling protocol is contained in Appendix B.

3.0 SITE PERIMETER CONTAINMENT WALL MONITORING

3.1 GENERAL

The monitoring program consisting of the collection of an undisturbed sample of the containment wall with subsequent permeability testing was initiated on December 15, 1983. Subsequent sampling events occurred on March 15, 1984, June 15, 1984, September 14, 1984. The current sampling event occured December 13 and December 14, 1984. All testing completed to date has confirmed the permeability of the site perimeter containment wall to be less than 1.0 x 10^{-7} cm/sec.

3.2 EQUIPMENT

A CME 175 trailer mounted drill rig equipped with rotary head and 6-inch diameter hollow stem augers was utilized to advance the borehole into the containment wall. A 3-inch diameter Shelby tube, hydraulically pushed and retrieved, was used to collect the samples.

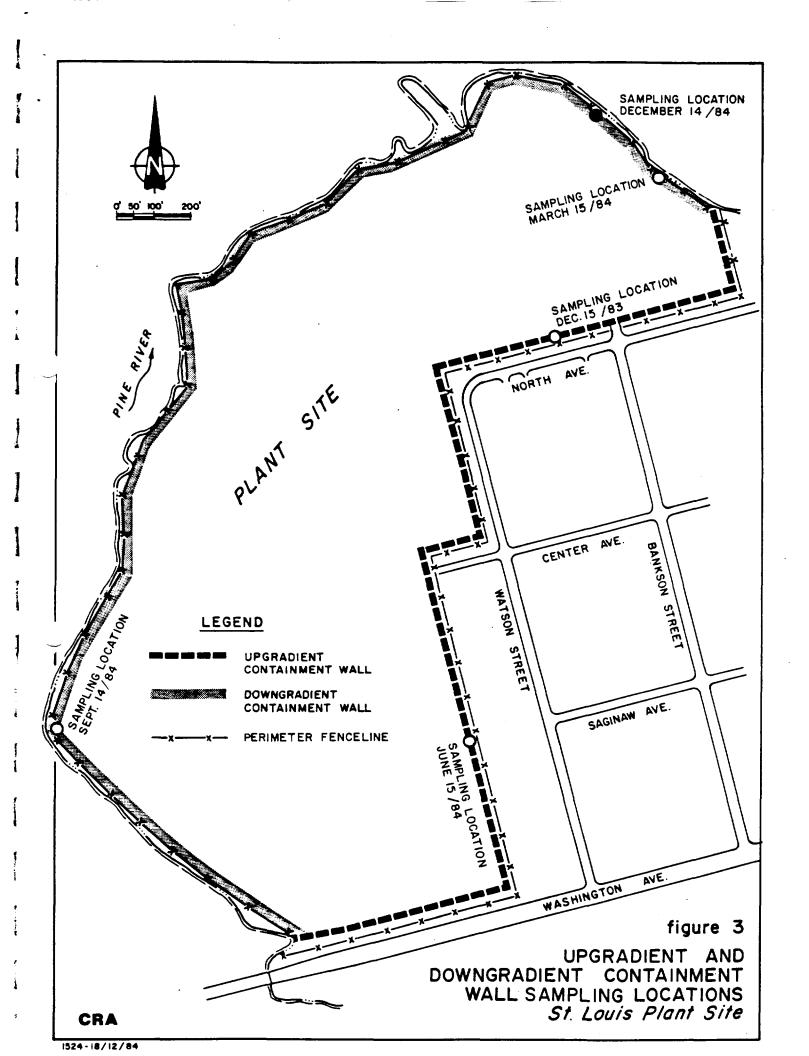
3.3. SAMPLE COLLECTION

The containment wall was located by field survey on December 14, 1984. The sampling borehole was

begun at Station DGW 69+90 by augering through the clay cap into the underlying material.

The presence of soil/bentonite backfill material was confirmed by examination of cuttings on the auger flights. A Shelby tube was introduced into the borehole and a sample was retrieved at a depth of eight feet. Examination of the contents visible at the base of the tube indicated that the sample contained native material. The sample was discarded and disposed within the borehole which was then backfilled with bentonite and abandoned. It was concluded that the borehole had been located on the inside edge of the containment wall. The program was postponed until the next day due to inclement weather and impending darkness.

On the morning of December 15, 1984 the sampling program was resumed and the drill rig was moved two feet to the north. A borehole was advanced to a depth of six feet. A Shelby tube was introduced into the borehole and a sample was withdrawn. Examination of material in the base of the tube confirmed that the sample was obtained from the containment wall. A further sample was withdrawn for testing by MDNR. The locations of this and prior sampling events are detailed on Figure 3.



3.3.1 Sample Preparation and Shipping

The Shelby tubes were capped and taped at both ends to prevent sample loss and drying. One sample was hand delivered to the Michigan Testing Engineer's laboratory in Detroit, Michigan for permeability testing. The sample collected for MDNR was handed over to Mr. Ben Hall.

3.3.2 Sample Testing

The undisturbed sample is to be tested for permeability using a falling head permeameter set up in accordance with ASTM D 2434. Results of the testing will be provided in written form to USEPA and MDNR within seven days after receipt of final laboratory data by CRA. A summary data report will be prepared and presented to both Agencies following completion of the containment wall monitoring program in the fall of 1986.

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4.0 GROUNDWATER TABLE MONITORING

4.1 GENERAL

The initial monitoring of plant site groundwater elevation was performed on December 12, 1984. The water elevation of the St. Louis reservoir was also determined at this time.

4.2 WATER LEVEL DETERMINATION

The elevation of the groundwater was determined by measuring the distance from the top of each site monitoring well to the watertable. This distance was measured by lowering a chalked surveyors tape into the monitoring well. Readings of the tape, which was graduated in increments of one one-hundredth of a foot, were taken at the water level and at the top of the well casing. The former reading was deducted from the latter and the resultant dimension was subtracted from the previously established top of well casing elevation. Well head and watertable elevations are presented on Table 1.

The elevation of the St. Louis reservoir was determined by level and rod survey.

TABLE 1

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WATER LEVEL MEASUREMENTS

DECEMBER 12, 1984

	WELL HEAD	MEASURED DISTANCE TO	WATERTABLE
MONITORING WELL	ELEVATION (AMSL)	WATER TABLE (ft.)	ELEVATION (AMSL)
1	735.88	14.14	721.74
2	742.07	19.42	722.65
3	749.92	27.44	722.48
4	735.99	13.73	722.26
5	739.35	17.45	721.90
6	734.43	13.11	721.32
7	734.02	12.33	721.69
8	734.30	13.35	720.95
9	734.52	13.30	721.22
10	733.43	12.46	720.97
11	734.38	13.33	721.05
12	730.74	9.71	721.03
13	734.43	13.50	720.93
14	735.95	14.92	721.03

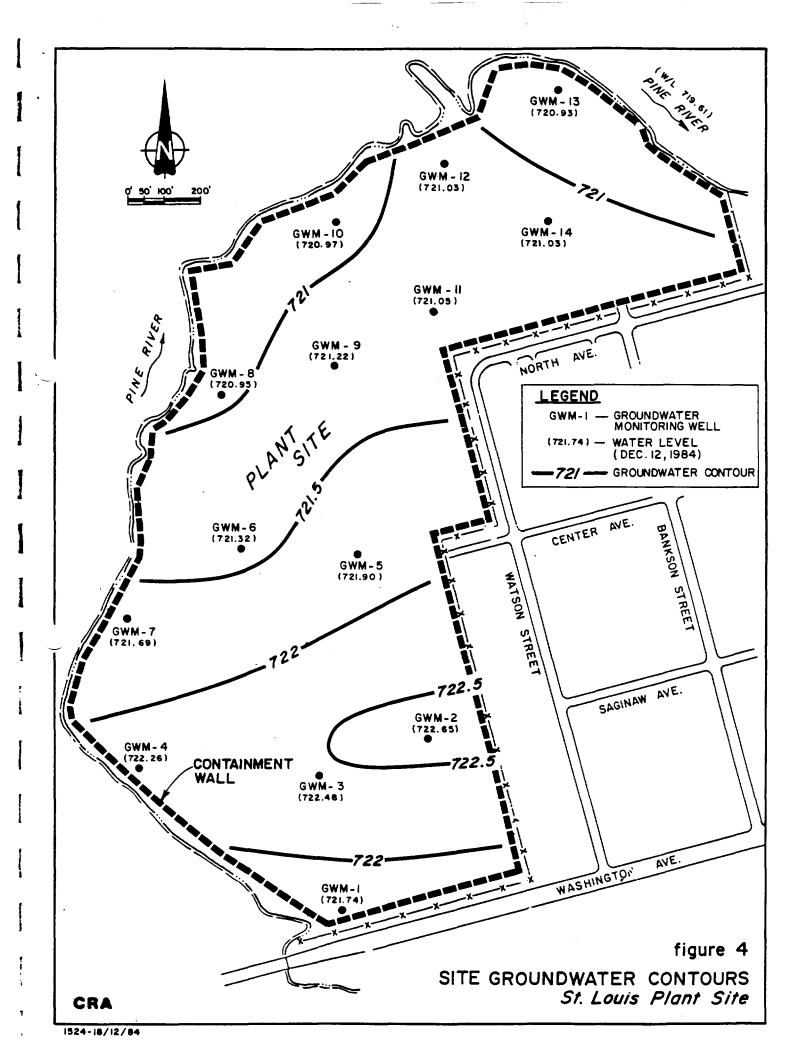
Water level elevation, St. Louis Reservoir 719.61

4.3 GROUNDWATER CONTOUR MAP

The groundwater elevation data were used to construct a site groundwater elevation contour map which is presented in Figure 4.

4.4 SITE MEAN GROUNDWATER ELEVATION

The mean elevation of site groundwater is calculated to be 721.52. The maximum allowable site groundwater elevation stipulated by the Consent Judgement is 724.13.



All monitoring activities stipulated by the Consent Judgment were carried out between December 12 and December 14, 1984.

Data from the chemical analysis of the gas vent samples and the permeability testing of the contaminant wall sample will be provided to MDNR and USEPA within seven days of receipt by CRA of laboratory final data.

The present mean site groundwater table elevation is calculated to be 721.52. The elevation in the Pine River/St. Louis reservoir was determined to be 719.61.

The next sampling and monitoring event will occur on or about March 15, 1985.

All of which is respectfully submitted, CONESTOGA-ROVERS & ASSOCIATES LIMITED

D. Robinson

R.G. Shepherd, P. Eng.

APPENDIX A

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CHAIN OF CUSTODY

APPENDIX B

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GAS SAMPLING PROTOCOLS

APPENDIX B

GAS VENT SAMPLING PROTOCOL

In accordance with the Consent Judgment, Velsicol has submitted a post-closure maintenance and monitoring plan for its environmentally secured plant site in St. Louis, Michigan. The post-closure maintenance and monitoring plan requires quarterly monitoring of 11 gas vents that have been installed to release and appropriately treat internal gases. This program will be conducted over a period of three years.

The gas vents, as detailed in Exhibit F of the Consent Judgment, are designed with two sampling ports; one below the base of the installed activated charcoal filter, and one above the filter. Samples will be collected from the downstream port. Results will indicate whether or not containment breakthrough has occured through the carbon filter.

Samples will be analyzed for three separate compounds: carbon tetrachloride, trichloroethylene and vinyl chloride.

Samples will be collected with a Gilian HFS-113 AU DK variable flow pump. This particular unit allows the operator to run a series of tubes concurrently in parallel arrangement. Four tubes will be collected from each gas vent: two standard NIOSH 100/50 mg activated charcoal tube, and two 30/15 mg tenax tubes, each tube measuring 6 mm x 70 mm. One blank set and one duplicate set of tubes will be collected during each quarterly sampling event.

As vinyl chloride represents the least adsorptive of the three compounds, the sampling program is designed to accomodate this compound. Therefore, sample volume shall not exceed 5 liters.

Prior to sampling, the vent will be sealed off with a plastic cap, and purged for 10 minutes at a rate of 500 cc/min. This is to eliminate the possibility of sampling atmospheric air contained within the upper portion of the gas vent.

Two samples from each gas vent shall be collected simultaneously at a rate of 250 cc/min. for 20 minutes. The pump shall be lab calibrated with sample tubes in-line to determine the exact flow rate. Additionally, flow will be checked after field sampling to verify that a constant flow was maintained throughout the sampling period.

Following sample collection, each tube will be sealed with a plastic cap at each end, labelled, placed in a cold storage environment and shipped under chain-of-custody via a commercial courier service to Velsicol's analytical laboratory in Memphis.

Analysis of the charcoal tube will be conducted in accordance with NIOSH protocol as detailed below:

Compound	Revised Method No.
Carbon Tetrachloride	1003
Trichloroethylene	S-336
Vinyl Chloride	1007

Analysis will proceed by first eluting the carbon sample tubes with carbon disulfide and then analyzing by GC with a flame ionization detector. All samples will be initially analyzed in this fashion. If any of the above compounds are detected on the charcoal tube, the corresponding tenax tube will be analyzed by thermal desorption and GC/MS under EPA Method 624.

Turnaround time for the completed analysis at the laboratory is anticipated to be 30 days from date of sample collection. Samples will be desorbed within the 10 day limit specified for vinyl chloride. Analytical data will be reported to CRA as mg/tube. Final results for the carbon tube will be calculated by CRA, using the following formula.

1. Corrections for the blank to be made for each sample
 mg = mg sample - mg blank

This calculation is performed separately for each tube.

- 2. Add the amounts present in the front tube and backup tube to determine the total weight in the sample.
- 3. Calculate the corrected mg/sample by dividing the total weight by the desorption efficiency (D.E.) which is provided by the lab.

corrected mg/sample = total weight DE

- 4. Calculate the concentration of the analyte in air $mg/m^3 = \frac{Corrected mg \times 1000 \text{ liters/m}^3}{\text{Air volume Sampled (liters)}}$
- 5. Concentration will be reported as ppm, corrected to standard conditions of 25°C and 760 mm Hg

 $ppm = mg/m \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{(T+273)}{298}$

where P	= pressure (mm Hg) of air sampled
Т	= temperature (°C) of air sampled
24.4	5 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW	= Molecular Weight
760	= standard pressure (mm Hg)
298	= standard temperature (°K)

- NOTE: Temperature and pressure uncorrected to sea level will be collected for the duration of the sampling event and averaged for use in the above calculations. Information will be provided from the National Weather Service in Lansing, Michigan.
 - 6. If the concentration of the back tube exceeds 10% of the concentration of the front tube, the results will be reported as a sample breakthrough and possible sample loss.
 - 7. A similar procedure will be followed for the tenax tube, should analysis be required.

Data will be reported to USEPA and MDNR officials within seven days after receipt of final laboratory data for each quarterly sampling. Additionally, a summary data report will be provided at the conclusion of the three year sampling period, or sooner, should breakthrough of any compound occur prior to the three year program.

In addition to the set of field blanks to be collected per quarterly sampling event, an additional set of 15 charcoal tubes and 15 tenax tubes will be forwarded unopened to the lab during the initial sampling event.

These "blank" tubes will be used as internal calibration standards on which each of the three compounds will be spiked at five different concentrations. The data from this analysis will be used to calculate the desorption efficiency for a specific lot of activated charcoal. Therefore, the lot number of carbon tubes and tenax tubes shall be recorded during each quarterly sampling. Should the lot number change, a new set of 15 charcoal tubes and 15 tenax tubes shall be forwarded to the laboratory for determination of the new desorption efficiency.

The allowable limits for these compounds have been established by the MDNR and are site specific for the St. Louis site. These limits are documented in section 4.3 of the post-closure maintenance and monitoring plan.

Copies of all three analytical protocols, the chain of custody and the data collection sheet are provided in the following sections.

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FORMULA: Table 1

HYDROCARBONS, HALOGENATED

M.W.: Table 1

METHOD: 1003 ISSUED: 2/14/84

COMPOUNDS: benzyl chloride (synonyms bromoform in Table 1) carbon tetrachloride o-dichlorobenzene chlorobenzene

chlorobromomethane chloroform p-dichlorobenzene

1,1-dichloroethane hexachloroethane 1,2-dichloroethylene methylchloroform ethylene dichloride propylene dichloride

SAMPLING	MEASUREMENT
SAMPLER: SOLID SORBENT TUBE	! !TECHNIQUE: GAS CHROMATOGRAPHY, FID
	•
(coconut shell charcoal, 100 mg/50 mg	
	ANALYTE: compounds above
FLOW RATE: 0.01 to 0.2 L/min	
	IDESORPTION: 1 mL CS2, stand 30 min
VOL-MIN: Table 2	!
-MAX: Table 2	INJECTION VOLUME: 5 μL
÷	!
SHIPMENT: routine	!TEMPERATURES: Table 2
	1
SAMPLE STABILITY: at least 1 week @ 25 °C	CARRIER GAS: N2 or He, 30 mL/min
• • •	1
BLANKS: 2 to 10 field blanks per set	:COLUMN: Table 2; alternates are SP-2100,
	SP-2100 with 0.1% Carbowax 1500
_	 is -2100 with 0.1% carbowax 1500 or DB-1 fused silica capillary column
400 IDAOV	
ACCURACY	
	CALIBRATICH: solutions of analyte in CSo with
se solo o de teore control de teorem (13	and an end of in the second of a
BIAS: not significant [1]	!RANGE: Table 2
	¥;
OVERALL PRECISION (sr): see EVALUATION OF	ESTIMATED LOD: 0.01 mg per sample [2]
METHOD [1]	
	PRECISION (sr): see EVALUATION OF METHOD [1]
	· · · · · · · · · · · · · · · · · · ·

APPLICABILITY: This method uses a simple desorption and can be used for simultaneous analysis of two or more substances suspected to be present by changing the gas chromatographic conditions (i.e., temperature programmed). High numidity during sampling will prevent organic vapors from being trapped efficiently on the sorbent and greatly decreases breakthrough volume.

INTERFERENCES: None identified. The chromatographic column or separation conditions may be changed to circumvent interference problems.

OTHER METHODS: This method combines and replaces Methods P&CAM 127 [3]; S95, S101, S110, S113, \$114, \$115, \$122, \$123 and \$133 [4]; and \$135, \$281, \$314, \$328 and \$351 [5].

- a. Remove and discard back sorbent section of a media blank sampler.
- b. Inject a known amount of analyte or calibration stock solution directly onto front sorbent section with a microliter syringe.
- c. Cap the tube. Allow to stand overnight.
- d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).e. Prepare a graph of DE vs. mg analyte recovered.
- 10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

METHOD: 1003

 Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1003-1. Inject sample aliquot manually using solvent flush technique or with autosampler.

NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.

12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of analyte found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.

NOTE: If $W_{\rm D} > W_{\rm f}/10$, report breakthrough and possible sample loss.

14. Calculate concentration, C, of analyte in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, mg/m^3.$$

INCLOSEICH OF DEFROD:

Laboratory testing was performed with spiked samples and generated atmosphere [1]. All analytes are stable at least one week. All methods were validated using SKC Lot 105 coconut shell charcoal. Results were:

METHOD: 1003

- [9] Criteria for a Recommended Standard...Occupational Exposure to 1,1,1-Trichloroethane, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 76-184 (1976).
- [10] Criteria for a Recommended Standard...Occupational Exposure to Carbon Tetrachloride, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 76-133 (1976).

METHOD REVISED BY: G. D. Foley; Y. T. Gagnon; and K. J. Williams, NIOSH/DPSE; methods originally validated under NIOSH Contract CDC-99-74-45.

Compounds	Formula	M.W.; mg/m³ 1 ppm_	Synonyms	OSHA N1OSH [6-10] ACGIH	BP (°C)	VP (9 20 °C	Density (g/mL @ 20 °C)
p-Dichlorobenzene	1,4-C ₆ H ₄ C1 ₂	147.00; 6.01	1dichlorobenzene; (* #106-467	75 ppm 75 ppm, STEL 110 ppm	174	50 Pa	1.241
1,1-Dichloroethane	сн _з снс1 ₂ ; с ₂ н ₄ с1 ₂	98.96; 4.05	ethylidene chloride; Car #75-34-3	100 ppm 100 ppm 200 ppm, STEL 250 ppm	57	24.3 kPa	1. 174
1,2-Dichloroethylene	C1CH=CHC1; C_H_C1 2_4_2	96.95; 3.96	acet ylene dichloride; 1,2- dichloroethene; C #540–59–0	200 ppm 200 ppm 200 ppm, STEL 250 ppm	60 (cis) 47 (trans)	24-35 kPa	1.28
Ethylene dichloride*	c1cH ₂ CH ₂ C1; C ₂ H ₄ C1 ₂	98.96; 4.05	1, '- dichloroethane; Cr > #107-06-2	50 ppm, C 100 ppm 5 ppm; 15 ppm/15 mi 10 ppm, STEL 15 ppm	83 n	8.3 kPa	1.255
Hexachloroethane*	cc1 ₃ cc1 ₃ ; c ₂ c1 ₆	236.74; 9.68	p.:.chloroethane; ()#67-72-1	1 ppm (skin) 1 ppm (skin) 10 ppm	187 (sublimes)	30 Pa	2.09
Methylchloroform	сн ₃ сс1 ₃ ; с ₂ н ₃ с1 ₃ ;	133.42; 5.45	3, i, 1-trichloroethane; (3 #71-55-6	350 ppm 350 ppm/15 min CAS #71-55-6 STEL 450 ppm	74 350 ppm,	13.3 kPa	1.335
Propylene dichloride	сн _з снс1сн ₂ с1 с ₃ н ₆ с1 ₂	; 112.99; 4.62	1,27-dich1oropropane Cove #78-87-5	75 ppm 75 ppm 75 ppm, 51EL 110 ppm	95	5.3 kPa	1. 156 (25 °C

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1003-7

HYDROCARBONS, HALOGENATED

HETHOD: 1003

*Suspect carcinogen.

		Sampling	ing				Measurement	ement	
	Air Sample						t (°C)		
	Volume (L)				W ork ing		Column		Range
Compound	Hin	Max	Break the ough	ou gh Air	Range (mg/m³)	Co)umn*	Injector Detector	Internal Standard	(mg per samole)
1, 1-Dichloroethane	1 (j 100 ppm	· 0	18.3 L	em/gm 6	40 to 1215 (10 L)	<			0.4 to 12
1,2-Dichloroethylene	0.5 8 200 ppm	e	ية 2.4 1,	em/fim 6 0;	80 to 2370 (3 l)	۲	60 170 210	ţ	0.2 to 7
Ethylene dichloride	1 (3 50 ppm	01		€m/tin	40 to 1215 (3 L)	۲	70 225 260	octane	0.1 to 4
Hexachloroethane	mqq 1 (a) 1	0	4 3 L	6 m/[h	1 to 30 (10 L)	٥	011 011 012	n-tridecane	0.01 to 0.3
Nethylchloroform	0.5 & 350 ppm	e.	9.5 t v	em/gm 8 0)	190 to 5700 (3 L)	<	70 225 250	octane	0.6 to 17
Propylene dichlorive	1 (j 75 ppm	2	18 T	€m/bu	35 to 1050 (10 L)	۲	80 170 210	n-undecane	0.3 to 10
the second seco	3 an stainbes steel, 10 3 an other is same as	101 SP-	101 SP-1040 -	toO mesh Supelcoport;	pelcoport;				
		- 00 - 80/	101. 0V-101 (01. 02 on 80/100 (02. 02	20 mesh Su alconort.	+20 mesh Supelcoport; or alconort:	·			

2/15/84

METHOD: 1003

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1003-9

HYDROCARBONS, HALOGENATED

Trichloroethylene

Analyte:	Trichloroethylene	Method No.: S336
Matrix:	Air	Range: 519-2176 mg/cu m
OSHA Standard:	200 ppm (1075 mg/cu m)-Ceiling 100 ppm (535 mg/cu m)-T.W.A.	Precision (\overline{CV}_{T}) : 0.082
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 6/6/75

1. Principle of the Method

- 1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.
- 1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.
- 1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.
- 1.4 The area of the resulting peak is determined and compared with areas obtained from injection of standards.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 519-2176 mg/cu m at an atmospheric temperature and pressure of 24.5°C and 759.4 mm Hg, using a 3-liter sample. Under the conditions of sample size (3 liters) the probable useful range of this method is 108-3225 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 9.7 mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.
- 2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 42 mg of analyte when a test atmosphere containing 2266 mg/cu m of analyte in air was sampled at 0.187 liters per minute for 99 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent.

(The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

- 3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.
- 3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.
- 3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.
- 3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation $(\overline{CV_T})$ for the total analytical and sampling method in the range of 519-2176 mg/cu m was 0.082. This value corresponds to an 88.2 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.
- 4.2 On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 6.4 % lower than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result.

These data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

- 5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.
- 5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

- 6.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3).
- 6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.
- 6.3 Gas chromatograph equipped with a flame ionization detector.
- 6.4 Column (10-ft x 1/8-in stainless steel) packed with 10% OV-101 stationary phase on 100/120 mesh Supelcoport.
- 6.5 An electronic integrator or some other suitable method for measuring peak areas.
- 6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.
- 6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.
- 6.8 Pipets: 1.0 ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

- 7.1 Chromatographic quality carbon disulfide.
- 7.2 Trichloroethylene, reagent grade
- 7.3 Octane, or other suitable internal standard
- 7.4 Purified nitrogen
- 7.5 Prepurified hydrogen.
- 7.6 Filtered compressed air.

8. Procedure

- 8.1 Cleaning of equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.
- 8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.
- 8.3 Collection and Shipping of Samples
 - 8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).
 - 8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.
 - 8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.
 - 8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.
 - 8.3.5 At the ceiling and peak concentrations, a sample size of 3 liters is recommended. Sample for 15 minutes at a flow of 0.2 liters per minute. At the T.W.A. concentration, a sample size of 10 liters is recommended. Sample at a flow of 0.2 liters per minute or less. The flow rates should be known with an accuracy of at least +5%.
 - 8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

- 8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.
- 8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.
- 8.3.9 Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.
- 8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

- 8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.
- 8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.
- 8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

30 ml/min (60 psig) Nitrogen carrier gas flow
 35 ml/min (25 psig) Hydrogen gas flow to detector
 400 ml/min (60 psig) Air flow to detector
 225°C injector temperature
 250°C manifold temperature (detector)
 70°C column temperature

- 8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.
- 8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.
- 8.5 Determination of Desorption Efficiency
 - 8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.
 - 8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. When using an automatic sample injector, the sample injector vials, capped with Teflon-faced septa, may be used in place of the glass tubes.

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Six tubes at each of three concentration levels (0.5X,1X and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 3-liter sample at the selected level. The tubes are allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 1.0 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

D.E. = <u>Average Weight (mg) recovered</u> Weight (mg) added

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg per 1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2% the standard. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

- 10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.
- 10.2 Corrections for the blank must be made for each sample.

mg = mg sample - mg blank

where:

mg sample = mg found in front section of sample tube
mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

- 10.3 Add the amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.
- 10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

Corrected mg/sample = Total weight D.E.

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

mg/cu m = Corrected mg (Section 10.4) x 1000 (liters/cu m) Air Volume Sampled (liters)

10.6 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$ppm = mg/cu m x \frac{24.45}{MW} x \frac{760}{P} x \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

- 11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," <u>Amer. Ind. Hyg. Assoc. J.</u>, <u>31</u>: 225 (1970).
- 11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.
- 11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

FORMULA: CH2=CHC1; C2H3C1

VINYL CHLORIDE

M.W.: 62.50

METHOD: 1007 ISSUED: 2/15/84

OSHA: 1 ppm; C 5 ppm __ NIOSH: minimum measurable ACGIH: 5 ppm (human carcinogen) [1] (1 ppm = 2.56 mg/m³ @ NTP) PROPERTIES: BP -14 *C; vapor density 2.2 (air = 1)

SYNONYMS: chloroethylene; chloroethene; CAS #75-01-4.

SAMPLING	MEASUREMENT
SAMPLER: SOLID SORBENT TUBE (2 tandem tubes, each with 150 mg	! !TECHNIQUE: GAS CHROMATOGRAPHY, FID !
activated coconut charcoal)	ANALYTE: vinyl chloride
FLOW RATE: 0.05 L/min	: !DESORPTION: 1 mL carbon disulfide; 30 min !
VOL-MIN: 0.7 L -MAX: 5 L	INJECTION ALIQUOT: 5 µL
SHIPMENT: separate primary and backup tubes and cap each	<pre>!COLUMN: stainless steel, 6.1 m x 3.2 mm, 10% ! SE-30 on 80/100 mesh Chromosorb W ! (AW-DMCS) </pre>
SAMPLE STABILITY: 10 days @ 25 °C	CARRIER GAS: He, 40 mL/min
BLANKS: 2 to 10 field blanks per set	: !TEMPERATURE-INJECTOR: 230 °C ! -DETECTOR: 230 °C ! -COLUMN: 60 °C
ACCURACY	1
RANGE STUDIED: 1 to 64 mg/m ³ [2]	<pre>!CALIBRATION: solutions of vinyl chloride in CS2 ! !RANGE: 0.002 to 0.2 mg per sample [2]</pre>
BIAS: -6% of calculated concentration [2]	! ! !ESTIMATED LOD: 0.00004 mg per sample [2]
OVERALL PRECISION (sr): 0.06 [2]	! !PRECISION (s _r): not determined

APPLICABILITY: The working range is 0.4 to 40 mg/m³ (0.16 to 16 ppm) for a 5-L air sample. The method is applicable to 15-min samples at concentrations of 1 ppm or higher.

INTERFERENCES: Other than the possibility of loss of sample upon storage of two weeks or more at room temperature, none have been noted.

OTHER METHODS: This is a revision of P&CAM 178 [3].

VINYL CHLORIDE

REAGENTS:

- Carbon disulfide,* chromatographic quality.
- Vinyl chloride,*, 99.9%, in lecture bottle fitted with valve and septum.
- Calibration stock solution, 0.26 mg/mL.
 - a. Insert the tip of a gas syringe containing 1 mL vinyl chloride gas under the surface of 5 mL CS₂ in a 10-mL volumetric flask.
 - b. Open the value of the syringe and withdraw the plunger to pull CS₂ into the barrel. (As vinyl chloride dissolves, a vacuum will be created, pulling CS₂ into the syringe.)
 - c. Push the solution from the syringe into the flask. Rinse the syringe twice with 1-mL portions of CS₂ and add the washings to the flask.
 - d. Dilute to the mark with CS₂.

4. Helium, purified.

- 5. Hydrogen, purified.
- 6. Air, filtered.

*See Special Precautions.

EQUIPMENT:

- 1. Sampler: two tandem glass tubes, 7 cm long, 6 mm 00, 4 mm ID, flame-sealed ends, each containing 150 mg of 20/40 mesh activated (600 °C) coconut shell charcoal. A silylated glass wool plug precedes the charcoal beds and a 3-mm urethane foam plug follows the charcoal beds. Plastic caps are included for sealing after use. Pressure drop across each tube at 1 L/min airflow must be less than 3.4 kPa.
 - NOTE: A pair of two-section (100 mg/50 mg) tubes may be used.
- Personal sampling pump, 0.05 L/min, with flexible connecting tubing.
- 3. Gas chromatograph, flame ionization detector, integrator and column (page 1007-1).
- 4. File.
- 5. Bent wire for removing plugs from sampling tube.
- 6. Vials, 2-mL, glass with PTFE-lined septa and crimp-on seals.
- Volumetric flasks, 10-mL, with polyethylene stoppers.
- Pipettes, delivery, 1.0-mL, graduated in 0.1-mL increments, 2- and 5-mL, with pipet bulb.
- 9. Air sampling bags, Tedlar, 10-L.
- 10. Gas syringe, with gas-tight valve, 0.1- and 1-mL.
- 11. Syringe, 10-µL, with 0.1-µL graduations.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = -30 °C); work with it only in a hood.

Vinyl chloride is a human carcinogen [1].

SAMPLING:

- 1. Calibrate each personal sampling pump with a representative sampler in line.
- 2. Break the ends of the tubes immediately before sampling. Attach two tubes, with ends touching, with a short piece of tubing. Label one tube as the back tube and insert the
- back tube into the flexible tubing attached to the personal sampling pump.
- 3. Sample at 0.05 L/min for 15 to 100 min. Do not sample more than 5 L of air.
- 4. Separate the primary and backup tubes and cap each tube for shipment.

SAMPLE PREPARATION:

- 5. Add 1.0 mL CS_2 to an empty vial. Loosely cap the vial.
- 6. Score each sampler tube with a file in front of the glass wool plug. Break the tube at the score line.

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METHOD: 1007

- 7. Transfer the charcoal from the front and back tubes to separate vials. Discard the glass wool and foam plugs. Seal the vials with septum caps immediately.
- 8. Allow to stand for 30 min, with occasional agitation. Analyze the sample within the next 30-min period.

CALIBRATION AND QUALITY CONTROL:

- 9. Calibrate with at least five working standards covering the range 0.0002 to 0.2 mg per sample.
 - a. Add known amounts of calibration stock solution to CS_2 in 10-mL volumetric flasks and dilute to the marks, using serial dilution as appropriate.

NOTE: Working standards can be stored at -20 °C for at least three days.

- b. Analyze together with samples and blanks (steps 12 and 13).
- c. Prepare calibration graphs of peak area vs. quantity (mg) of vinyl chloride per tube and peak area vs. quantity (ng) per injection.
- Determine desorption efficiency (DE) at least once for each lot of charcoal used in the calibration range (step 9). Prepare three tubes at each of five levels plus three media blanks.
 - a. Prepare three atmospheres of vinyl chloride in air by injecting 0.01, 0.08, and 0.2 mL vinyl chloride gas into 10 L air in Tedlar bags. The resulting concentrations are approximately 2.6, 21 and 52 mg/m³.
 - b. Following steps 1 through 4, sample these atmospheres according to the following scheme:

Concentration in Bag (mg/m³)	Volume Sampled (L)	Quantity of Vinyl Chloride (mg)
2.6	0.8	0.002
	2.2	0.006
21	0.8	0.017
	2.2	0.046
52	2.5	0.13

Obtain three samples at each level.

- c. Desorb (steps 6 through 8) and analyze together with working standards (steps 12 and 13). No vinyl chloride should be found on the back tubes.
- d. Analyze the atmospheres in the bags (steps 12 and 13) using 1-mL gas samples. Read from the calibration graph the quantity (ng) per injection, which for a 1-mL injection of gas is numerically equal to the concentration in mg/m³.
- e. Calculate DE from the mass (mg) of vinyl chloride on the front tube (W_f) , the average blank (B), the concentration of vinyl chloride in the synthetic atmospheres $(C_s, mg/m^3)$, and the volume of air sampled (V, L):

$$DE = \frac{(W_{f} - B) \cdot 10^{3}}{(C_{s}) (V)}$$

- f. Prepare a graph of DE vs. mass found (W_{f} B).
- 11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

VINYL CHLORIDE

12. Set the gas chromatogrph according to manufacturer's instructions and to conditions given on page 1007-1. Inject sample aliquot manually using solvent flush technique or with autosampler. The retention time of vinyl chloride is about 1.7 min.

NOTE: If peak area is above the linear range of the working standards, dilute with CS₂, reanalyze and apply the appropriate dilution factor in calculations.

13. Measure peak area.

CALCULATIONS:

- 14. Determine the mass, mg (corrected for DE) of vinyl chloride found in the sample front $(W_{\rm f})$ and back $(W_{\rm D})$ tubes, and in the average media blank (B).
 - NOTE: If $W_{\rm b} > W_{\rm f}/10$, report breakthrough and possible sample loss.

15. Calculate concentration, C, of vinyl chloride in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - 2B) \cdot 10^3}{V} mg/m^3$$

EVALUATION OF METHOD:

The method was evaluated using single 150-mg sampling tubes with 100-mg front beds and 50-mg back beds [2]. At four concentrations between 1 and 64 mg/m³, the pooled relative standard deviation was 0.06 and the measurements averaged 94% of the concentrations calculated from the volumes of vinyl chloride and air used for the atmospheres sampled; samples at the 3- μ g level showed no loss of vinyl chloride when stored for 12 days at room temperature or 19 days at -20 °C. There may be significant loss of vinyl chloride from samples stored for 14 days at room temperature [4]. The 1% breakthrough capacity for a 150-mg bed of coconut charcoal challenged at 100 mL/min with vinyl chloride in air at 16 mg/m³ and a relative humidity of 70% was 4.6 L [5].

REFERENCES :

[1] <u>TLVs - Threshold Limit Values for Chemical Substances and Physical Agents in the Work Environment with Intended Changes for 1983-84</u>, ACGIH, Cincinnati, OH (1983).

- [2] Hill, R. H., Jr., C. S. McCammon, A. T. Saalwaechter, A. W. Teass, and W. J. Woodfin. Anal. Chem., 48, 1395-1398 (1976).
- [3] NIOSH Manual of Analytical Methods, 2nd. ed., V. 1, P&CAM 178, U.S. Department of Health and Human Services, Publ. (NIOSH) 77-157-A (1977).
- [4] Cuddeback, J. E., W. R. Burg, and S. R. Birch, Environ. Sci. Technol., 9, 1168-1171 (1975).
- [5] Matsumura, Y. Ind. Health, 18, 61-67 (1980).

METHOD REVISED BY: A. W. Teass, Ph.D., NIOSH/DPSE.

METHOD: 1007

PROJECT No. 1524

GAS VENT SAMPLING VELSICOL CHEMICAL CORPORATION

CHEMICALS OF INTEREST: - CARBON TETRACHLORIDE -TRICHLOROETHYLENE -VINYL CHLORIDE

DATE OF COLLECTION:

SAMPLER:

TEMPERATURE:

HUMIDITY:

PRESSURE:

CHARCOAL LOT No. :

TENAX LOT No .:

GAUGE READING:

GAS VENT NUMBER	SAMPLE RATE (cc /min.)	VOLUME (1)	TIME
1			
2			
3	· · · · · · · · · · · · · · · · · · ·		
4			
5			
6			
7			
8			
9			
10			
11			
DUPLICATE			

DATE OF SAMPLE SHIPMENT:

COMMENTS:

1524 - 10/12/84

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VELSICOL CHEMICAL CORPORATION



SUMMARY OF POST-CONSTRUCTION CONTAINMENT WALL MONITORING December, 1983 to September, 1986

St. Louis, Michigan

PRINTED ON

FEB 1 2 1987



VELSICOL CHEMICAL CORPORATION

SUMMARY OF POST-CONSTRUCTION CONTAINMENT WALL MONITORING December, 1983 to September, 1986

St. Louis, Michigan

February 1987 Ref. No. 1524

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3.0 CONCLUSIONS

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LIST OF APPENDICES

APPENDIX A SECTION 8.d OF THE ST. LOUIS CONSENT JUDGEMENT

APPENDIX B ANALYTICAL RESULTS FOR POST-CONSTRUCTION CONTAINMENT WALL TESTING ŝ

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Construction of a soil/bentonite containment wall along the perimeter of the former Velsicol Chemical Corporation (Velsicol) plant site in St. Louis, Michigan was completed in August 1983. The containment wall was constructed in accordance with the provisions of the Consent Judgement negotiated between Velsicol, the United States Environmental Protection Agency (USEPA), the Michigan Department of Natural Resources (MDNR) and the United States Department of Justice. A copy of Section 8.d of the Consent Judgement, which details the post-construction testing requirements for the containment wall, is contained in Appendix A.

A stringent quality assurance/quality control (QA/QC) program was implemented during the construction of the containment wall. The QA/QC testing has been previously documented and submitted to the USEPA and MDNR in the report entitled "Quality Assurance/Quality Control Testing -Containment Wall Construction" (Conestoga-Rovers & Associates, March, 1984).

In accordance with the Consent Judgement, a post-construction testing program on the containment wall has been undertaken. This report summarizes data collected during the post-construction testing program.

2.0 POST CONSTRUCTION CONTAINMENT WALL MONITORING

2.1 GENERAL

The post-construction containment wall monitoring program, consisting of the collection of an undisturbed sample of the containment wall with subsequent permeability testing, was initiated three months after the completion of the wall on December 15, 1983. Subsequent sampling events occurred on March 15, 1984, June 15, 1984, September 14, 1984, December 14, 1984, March 16, 1985, June 19, 1985, September 16, 1985, December 14, 1985, March 13, 1986, June 9, 1986 and September 22, 1986. All testing completed to date has confirmed the permeability of the site perimeter containment wall to be less than 1.0 x 10^{-7} cm/sec.

2.2 SAMPLING EQUIPMENT

For sampling completed through March 1985, a CME 175 trailer-mounted drill rig equipped with rotary head and 6-inch diameter hollow stem augers was utilized to advance the borehole into the containment wall. A 3-inch diameter Shelby tube, hydraulically pushed and retrieved, was used to collect the samples.

For all remaining sampling events, a Mobil Truck mounted drill rig equipped with rotary head and 4-inch O.D. diameter augers was utilized to advance the borehole into the containment wall. A 3-inch diameter Shelby tube, hydraulically pushed and retrieved, was used to collect the samples.

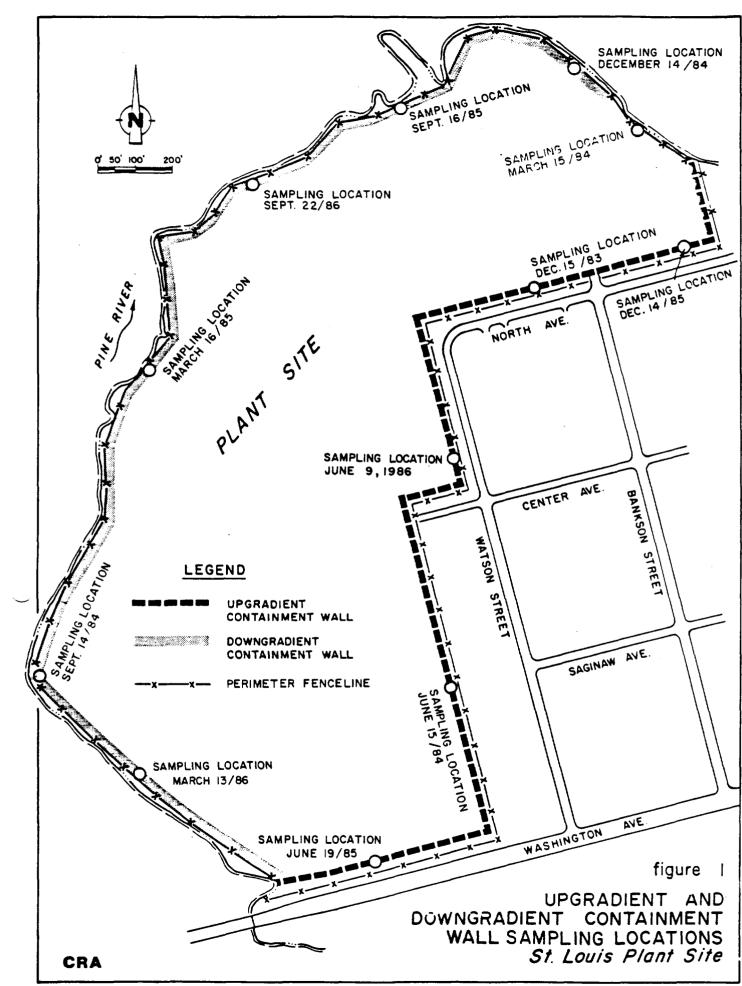
Figure 1 details the sampling locations for each sampling event.

2.3 PERMEABILITY TESTING PROTOCOL

In accordance with Section 8.d of the Consent Judgement, all collected samples were tested in accordance with ASTM D 2434.

2.4 ANALYTICAL RESULTS

A summary of all post-construction containment wall testing data is presented in Table 1. Individual analyses are included in Appendix B.



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	ST. LOUIS, MICHIGAN		
STATION	DEPTH	DATE	PERMEABILITY (cm/sec)
UGW 7+70	4'-6'	12/15/83	2.2×10^{-8}
DWG 71+25	5'-7'	03/15/84	1.1 x 10 ⁻⁷
UGW 19+50	6'-8'	06/15/84	5.3 x 10-8
DWG 42+50	12'-14'	09/14/84	3.8×10^{-8}
DWG 69+90	12.5'-14.5'	12/14/84	2.7×10^{-8}
DWG 47+50	8'-10'	03/16/85	3 x 10 ⁻⁸
UGW 31+00	7'-9'	06/19/85	9.9 x 10 ⁻⁸
DWG 63+25	8'-10'	09/16/85	3.9 x 10-8
UGW 2+60	5'-7'	12/14/85	6.5 x 10-8
DWG 38+10	6'-8'	03/13/86	5.8 x 10-8
UGW 15+00	5'-7'	06/09/86	7 x 10 ⁻⁸
DGW 58+25	4'-6'	09/22/86	3.3×10^{-8}

SUMMARY OF QUARTERLY PERMEABILITY TESTING ST. LOUIS, MICHIGAN

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3.0 CONCLUSIONS

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Velsicol, for a period of three years, has collected and tested samples of the soil/bentonite containment wall constructed at its former St. Louis, Michigan plant site, in accordance with the Consent Judgement between Velsicol, USEPA and MDNR.

Testing indicates that the containment wall has essentially achieved and maintained a permeability of 1.0 $\times 10^{-7}$ cm/sec or less, and that the performance standard stipulated in the Consent Judgement for the containment wall has been achieved.

All of which is respectfully submitted CONESTOGA-ROVERS& ASSOCIATES

Catherine A Cull

C. Cull, B.Sc.

R.G. Shepherd, P. Eng.

APPENDIX A

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SECTION 8.d OF THE

ST. LOUIS CONSENT JUDGEMENT

5) Slurry samples which shall be pumped from the bottom of the trench, and backfill samples from mix being added to the trench, shall be tested for unit weight, in accordance with API-RP-13B, at least once each hour of the working shift.

8. d. Post Construction Testing

Following installation, falling head laboratory testing, set up in accordance with ASTM D 2434, on a single collected sample of the installed containment wall shall be done every three (3) months for thirty-six (36) months to evaluate maintenance of a permeability of 1 x 10⁻⁷ cm/sec., or less. Analysis of the data shall be carried out as specified in subparagraph 8.a.4, above.

APPENDIX B

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ANALYTICAL RESULTS FOR POST CONSTRUCTION CONTAINMENT WALL TESTING

Professional Service I tries

PERMEABILITY RESULTS OF CONTAINMENT WALL AND CLAY CAP SAMPLES

TABLE NO. 2

CONTAINMENT WALL SAMPLES

Sample	Time	Sample	Sample	Permeability
Number	In-Place	Location	Depth	(cm/s)
UGW-R1	3-months	Station 7+70	4.0'	2.2 x 10 ⁻⁸
DGW-R2	6-months	Station 71+25	5.0'	1.1 x 10 ⁻⁷
UGW-R4	9-months	Station 19+50	6.0'	5.3 x 10-8
DGW-R5	12-months	Station 42+50	12.0'	3.8 x 10-8

CLAY CAP SAMPLES

Sample Number	Sample Location	Sample Depth	Permeability (cm/s)
CC-7	Station 3+50B & 350 Feet Right	Grade	6.2 × 10 ⁻⁸
CC-8	Station 11+00B & 400 Feet Right	Grade	7.2 x 10 ⁻⁸
CC-9	Station 12+00A & 250 Feet Left	Grade	3.5 x 10-8
CC-10	Station 5+00 & 700 Feet Left	Grade	6.2 x 10 ⁻⁸

RESULTS OF PERMEABILITY TEST

(Triaxial Cell With Back Pressure Saturation)

Project St. Louis, Michigan

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Sample Number Shelby Tube DDW-69-90 11 1/2' -	14 1/2'			
Sample Description Sandy, clay, brown				
Permeability	2.7×10^{-8}	cm./sec.		
Dry Density	104.9	p.c.f.		
Percent Compaction %				
Height of Sample (L) 4.2 in.				
Area of Sample (A) 6.69 in.2				
Head Differentialp.s.i.				
Top Pressure	45	p.s.i.		
Bottom Pressure 50				
Cell Pressure	55	p.s.1.		
Specific Gravity	•• . 			

NOTE: Specific gravity is determined by back calculation assuming zero air voids after completion of test.



Professional Service Industries, Inc.

Michigan Testing Engineers Division

TESTED FOR: Conestoga Rovers & Associates, LTD PROJECT: St. Louis, Michigan 651 Colby Drive Waterloo, Ontario Canada N2V-1C2

DATE: March 29, 1985

OUR REPORT NO .: 406-55004

REMARKS:

PERMEABILITY TEST RESULTS

Procedure: Sample was placed in triaxial chamber and subjected to a confining pressure. Sample was saturated using back pressure. A differential pressure was applied across the sample and the flow was monitored until flow into the sample equaled flow out of the sample. Permeability was calculated using Darcy's Law.

Sample No.: Shelby Tube Sample		Date Sampled: MARCH 16, 1985		
Sample Location:	DGW 4	7 🕂 50	8' - 10'	
Height of Sample:	4.0	in.	Dia. of Sample:	2.8 in.
Initial Weight of	Sample:	920.7g	Initial Moisture Co	ontent:
Confining Pressure	:	60 psi	Saturation Pressure:	50 psi
Bottom Pressure:		50 psi	Top Pressure:	45 psi

Elapsed Time (min.)	Flow In (cc)	Flow Out (cc)	Remarks
1250	2.95	2.95	
141	. 30	. 30	

Permeability: 3×10^{-8} cm/sec.

TESTED FOR: Conestoga Rovers & Associates, LTD PROJECT: St. Louis, Michigan 651 Colby Drive Waterloo, Ontario Canada N2V-1C2

July 12, 1985

OUR REPORT NO .: 406-55004

T

R JARKS:

DATE:

PERMEABILITY TEST RESULTS

Procedure: Sample was placed in triaxial chamber and subjected to a confining pressure. Sample was saturated using back pressure. A differential pressure was applied across the sample and the flow was monitored until flow into the sample equaled flow out of the sample. Permeability was calculated using Darcy's Law.

Sample No.: Shelby Tube Sample	Date Sampled: by CRA JUNF 9 995
Sample Location: <u>Dow 47 - 50 - 81</u>	10-10- UGW 31+00 7'-91
Height of Sample: 5.0 inches	Dia. of Sample: 2.85 inches
Initial Weight of Sample: 1173 grams	Initial Moisture Content: 19.7%
Confining Pressure: <u>62 psi</u>	Saturation Pressure: 50 psi
Bottom Pressure: <u>60 psi</u>	Top Pressure: 50 psi

Elapsed Time (min.)	Flow In (cc)	Flow Out (cc)	Remarks
120	1.35	1.35	
1016	13.75	13.75	

Permeability: <u>9.9 x 10⁻⁸ cm/sec</u>

)

TESTED FOR: Conestoga Rovers & Associates, LTD PROJECT: St. Louis, Michigan 651 Colby Drive Waterloo, Ontario Canada N2V-1C2

DATE: 9-24-85

OUR REPORT NO .: 406-55004

REMARKS:

PERMEABILITY TEST RESULTS

Procedure: Sample was placed in triaxial chamber and subjected to a confining pressure. Sample was saturated using back pressure. A differential pressure was applied across the sample and the flow was monitored until flow into the sample equaled flow out of the sample. Permeability was calculated using Darcy's Law.

Sample No.:8	'_to_10'		Date Sampled:	By CRA	916/85
Sample Location:	DGW 63	+ 25			· · · ·
Height of Sample:	4.925"		Dia. of	Sample:	2.91"
Initial Weight of	Sample: _	1124 grams	Initial Mo	isture Conte	ent: <u>6.0</u>
Confining Pressure	:	72 psi	_ Saturation P	ressure:	<u>60 psi</u>
Bottom Pressure: _		70 psi	_ Top Pressur_		60 psi

Elapsed Time (min.)	Flow In (cc)	Flow Out (cc)	Remarks
374	2.10	2.10	
			Dry density = 123.3 pcf
			Final Moisture Content = 12.7%

Permeability: <u>3.9 x10⁻⁸ cm/sec</u>

TESTED FOR: Conestoga Rovers & Associates, LTD PROJECT: St. Louis, Michigan 651 Colby Drive Waterloo, Ontario Canada, N2V-1C2

DATE: January 6, 1986 OUR REPORT NO.: 406-55004

REMARKS:

1

PERMEABILITY TEST RESULTS

Procedure: Sample was placed in triaxial chamber and subjected to a confining pressure. Sample was saturated using back pressure. A differential pressure was applied across the sample and the flow was monitored until flow into the sample equaled flow out of the sample. Permeability was calculated using Darcy's Law.

Sample No.:	51-7			Date	Sampled:	by CR	A 12/14/85
Sample Location:	Baseli	ne "B"	Station	0+50	Ugu) 2+6	,0
Height of Sample:	4.652"				Dia. of	Sample:	2.877"
Initial Weight of S	ample:	1161	grams	1	nitial Mos	sture Co	ntent: 10.8%
Confining Pressure:		72 ps	i	Sat	uration Pr	essure:	60 psi
Bottom Pressure:		70 ps	i	Тор	Pressure	_	60 psi

Elapsed Time (min.)	Flow In (cc)	Flow Out (cc)	Remarks
210	2.05	2.05	
			Final dry density = 131.9 pcf
			Final moisture content = 10.8%

Permeability: 6.5 X 10⁻⁸ cm/sec.

TESTED FOR:

Conestoga-Rovers & Ass. Ltd. 651 Colby Drive Waterloo, Ontario Canada, N2V IC2 PROJECT:

St. Louis, Michigan

406-55004

DATE: March 26, 1986

OUR REPORT NO .:

REMARKS:

PERMEABILITY TEST RESULTS

Procedure: Sample was placed in triaxial chamber and subjected to a confining pressure. Sample was saturated using back pressure. A differential pressure was applied across the sample and the flow was monitored until flow into the sample equaled flow out of the sample. Permeability was calculated using Darcy's Law.

Sample No.:6	- 8' Depth.	Date Sampled:by CF	RA MARCH 13 1986
Sample Location:	Station 38 + 10		
Height of Sample:	5.19"	Dia. of Sample:	2.94"
Initial Weight of S	aple: 1292 grams	Initial Moisture Con	tent: <u>17.5</u> %
Confining Pressure:		Saturation Pressure:	<u>61.5 psi</u>
Bottom Pressure:	70.0 psi	Top Pressure:	61.5 psi

Elapsed Time (min.)	Flow In (cc)	Flow Out (cc)	Remarks
1257	8,65	8.65	Final dry density = 118.4 pcf
			Final moisture content = 13.6%

Permeability: <u>5.8 x 10⁻⁸ cm/sec</u>



Professional Service Industries, Inc. Michigan Testing Engineers Division

Conestoga Rovers & Associates, LTD PROJECT: St. Louis, Michigan TESTED FOR: 651 Colby Drive Waterloo, Ontario N2V-1C2 Canada

> 406-55004 OUR REPORT NO :

REMARKS:

D'

PERMEABILITY TEST RESULTS

Sample was placed in triaxial chamber and subjected to a confining pressure. Sample was saturated using back pressure. A Procedure: differential pressure was applied across the sample and the flow was monitored until flow into the sample equaled flow out of the sample. Permeability was calculated using Darcy's Law.

Sample No.: #1524 5'-	7'	Date Sampled: JUNE 9	1986
Sample Location:			
Height of Sample:	23"	Dia. of Sample:2	.954"
Initial Weight of Sample:	<u>1453.4 grams</u>	Initial Moisture Conter	nt:
Confining Pressure:	73 psi	Saturation Pressure:	60 psi
Bottom Pressure:	70 psi	Top Pressur.:	60 psi

Elapsed Time (min.)	Flow In (cc)	Flow Out (cc)	Remarks
55	.55	.55	
			Dry Density = 125.7 PCF

Permeability: 7.0 X 10⁻⁸ cm/sec

TESTED FOR: Conestoga Rovers & Associates, LTD PROJECT St. Louis, Michigan 651 Colby Drive Waterloo, Ontario Canada N2V-1C2

OUR REPORT NO 406-55004

LIARKS:

DATE:

PERMEABILITY TEST RESULTS

Procedure: Sample was placed in triaxial chamber and subjected to a confining pressure. Sample was saturated using beek pressure. A differential pressure was applied across the semple and the flow was monitored until flow into the sample equaled flow out of the sample. Permeability was calculated using Darcy's Lew.

Sample No.:6	5'	Date Sampled:	September 22/86 By CRA DGW 58+25
Sample Location:			,
Height of Sample:	4.785 inches	Dia. of	Sample: 2.96 inches
Initial Weight of	Sample: <u>1200 grams</u>	Initial Mo	isture Content: 20.3%
Confining Pressure	: <u>73 psi</u>	Saturation P	ressure: <u>60 psi</u>
Bottom Pressure: _	70 psi	Top Pressur_	: <u>60 psi</u>

Elapsed Time (min.)	Flow In (cc)	Flow Out (cc)	Rem arks
100	0.50	0.50	
			Dry Density = 115.5 PCF
			Final Moisture Content + 15.0%

Permeability: 3.3 x 10⁻⁸ cm pec

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" VELSICOL CHEMICAL CORPORATION

POST - CONSTRUCTION QUARTERLY MONITORING REPORT March 13-16, 1985

Plant Site, St. Louis, Michigan

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5.0 SUMMARY

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	DECEMBER 12, 1984	

1.0 INTRODUCTION

1.1 GENERAL

In accordance with the terms of the technical appendix to the Consent Judgment entered into by Velsicol Chemical Corporation (Velsicol), the United States Environmental Protection Agency, (USEPA) and the Michigan Department of Natural Resources (MDNR), Velsicol is required to perform specified monitoring activities at quarterly intervals following closure of its St. Louis, Michigan plant site. The monitoring program is designed to address the following:

- 1. Performance of gas vents
- 2. Performance of the site perimeter containment wall
- 3. Determination of site groundwater elevations

This report details the site monitoring which occured during the period March 13 to March 16, 1985.

1.2 PARTICIPATION BY REGULATORY AGENCIES

Mr. R. Teoh (MDNR) was present on-site on March 14, 1985 and observed the carbon changeout of gas vents 7 and 8.

1.3 MONITORING AND SAMPLING PERSONNEL

The monitoring and sampling program was carried out by Mr. D. Robinson and Ms. C. Cull (Conestoga-Rovers and Associates) assisted by Mr. Gene DeGeer, the Velsicol site custodian.

2.0 GAS VENT MONITORING

2.1 GENERAL

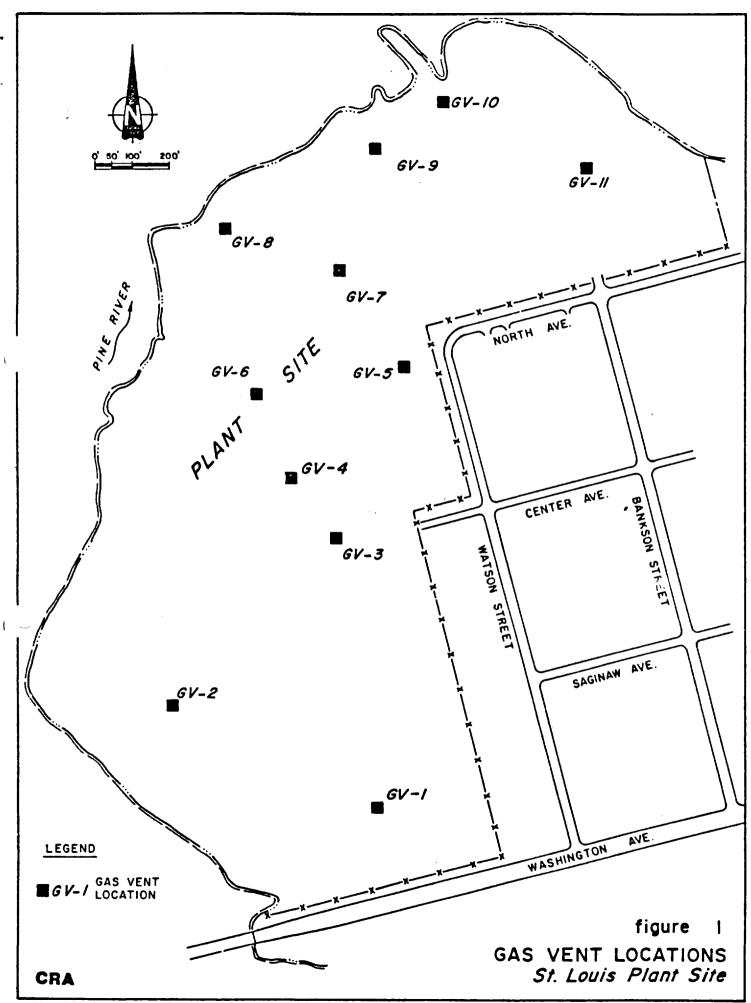
The gas vent monitoring began on March 15, 1985 and was completed the same day.

2.1.1 Equipment

Two Gilian model HFS 113 hi flow samplers were used to collect gas vent samples. The samplers were field calibrated using a rotometer prior to sampling. The calibration data is presented within Appendix B. Samples from each gas vent were collected in two 6-mm diameter x 70-mm long Tenax tubes and two charcoal tubes of similar dimensions. The samples were collected simultaneously using dual parallel/series tube holder sets.

2.2 SAMPLE COLLECTION

Samples were obtained at each of the ll gas vents. The location of the gas vents within the closed plant site is detailed on Figure 1. One blank set and one duplicate set of samples were also collected.



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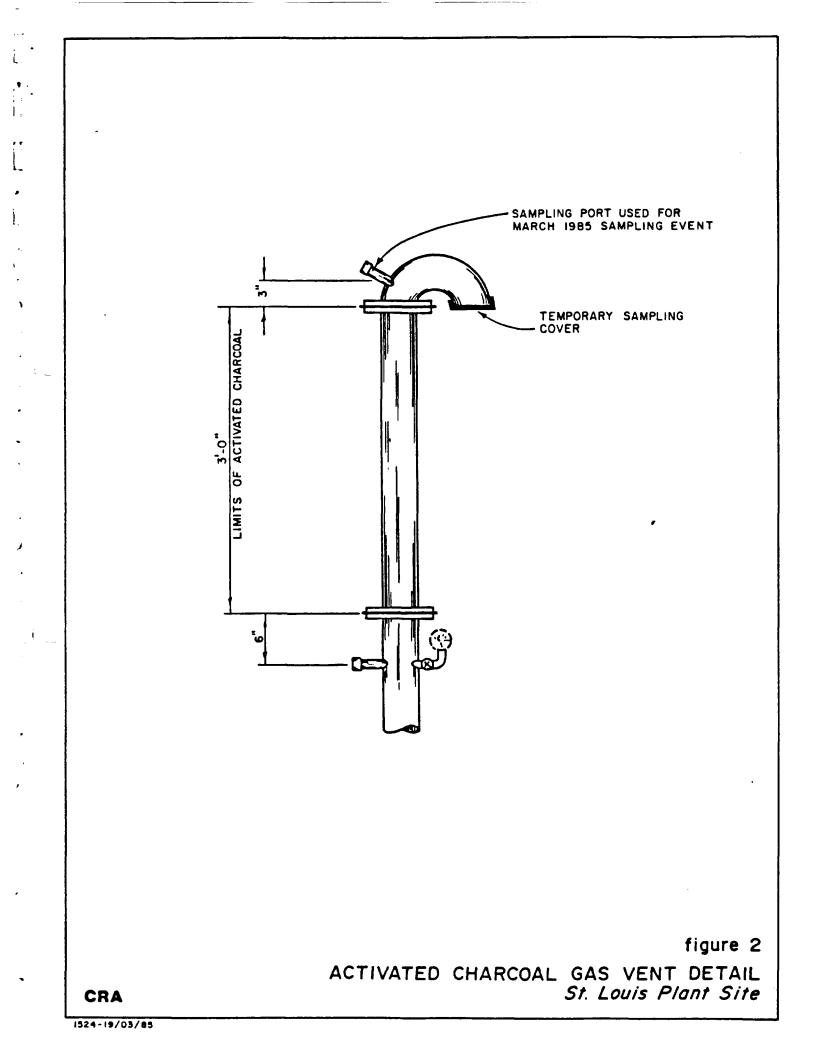
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Sampling was conducted at the downstream sampling port on each gas vent as detailed on Figure 2. The tube holder was attached directly to the gas vent sampling port using a copper manifold assembly which was environmentally cleaned prior to use. Tygon tubing was used to connect the tube holder to the sampler and was connected between the base of the tube holder and suction port of the sampler. The sampler which was pre-calibrated to 250cc/min/tube set, was operated for a period of 20 minutes for each sampling event, resulting in a collected sample volume of five liters per tube set.

Prior to sample collection, the gas vent upper chamber was purged by pumping at 500 cc/minute for a period of ten minutes. This precluded the possiblity of sampling retained atmospheric air from the gas vent upper chamber. During the purging and sampling operations, the open end of the gas vent was capped using a 4-inch diameter plastic cover to prevent atmospheric air being drawn into the sample.

At the conclusion of each gas vent sampling, the set of four sample tubes were capped, labelled and stored in a cooler maintained at 0°C.

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2.2.1 Sample Storage and Shipment

On the afternoon of March 15, 1985, the samples were transferred to a cooler containing frozen cold packs and styrofoam packing materials. The cooler was shipped under chain of custody protocol, to Velsicol's Memphis, Tennessee laboratory by overnight courier for analysis. A copy of the chain of custody is provided in Appendix A.

2.2.2 Sample Analysis

All of the samples were desorbed and analyzed during the period March 18 to March 21, 1985. Analysis was conducted in accordance with NIOSH protocols as follows:

Compound	NIOSH Method
Carbon Tetrachloride	1003
Trichloroethylene	S-336
Vinyl Chloride	1007

Results were reported verbally as non detectable for all parameters for all samples.

A hard copy of the laboratory report will be forwarded to USEPA and MDNR as it becomes available.

2.2.3 Sampling Protocol

All sampling was performed in accordance with the methodology detailed within the St. Louis plant site Post-Closure Maintenance and Monitoring Plan, as approved by USEPA and MDNR. A copy of the sampling protocol is contained in Appendix B.

2.3 CARBON CHANGEOUT

2.3.1 General

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The terms of the Consent Judgment requires that should the presence of carbon tetrachloride, vinyl chloride or trichloroethylene be detected in any gas vent sampling in exceedence of stipulated concentrations, the carbon will be changed and the program be revised.

In order to comply with the terms of the Consent Judgment, the activated carbon filters were changed on March 14, 1985. At the recommendation of the supplier, the product was changed to a grade of activated carbon which will more readily adsorb the three parameters. The revised product is referred to as Calgon PTL 4 x 10 activated carbon.

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2.3.2 Method

Initially, the top section of the gas vent was removed and examined for damage or corrosion; none was observed.

The 3-foot long section containing the activated carbon was removed and the spent carbon was poured directly into a three ply polyethylene bag. The bag was closed by tying a knot in the neck of the bag.

The three foot section was examined for damage or corrosion; none was observed. The stainless steel screens were examined and replaced.

The 3-foot section was replaced on the gas vent and filled with the revised activated carbon product. The top section was replaced. All bolts were given a final tightening. The bags containing the spent carbon were deposited in a D.O.T. approved 55-gallon drum for subsequent disposal. The disposal method has not yet been identified.

2.3.3 Health and Safety

During the carbon changeout, personnel were required to wear disposable tyvek coveralls and disposable

vinyl gloves. Those were deposited into an on-site D.O.T. approved 55-gallon drum for subsequent disposal following completion of carbon changeout.

3.0 SITE PERIMETER CONTAINMENT WALL MONITORING

3.1 GENERAL

The monitoring program consisting of the collection of an undisturbed sample of the containment wall with subsequent permeability testing was initiated on December 15, 1983. Subsequent sampling events occurred on March 15, 1984, June 15, 1984, September 14, 1984 and December 14, 1985. The current sampling event occured March 15 and March 16, 1985. All testing completed to date has confirmed the permeability of the site perimeter containment wall to be less than 1.0 x 10-7 cm/sec.

3.2 EQUIPMENT

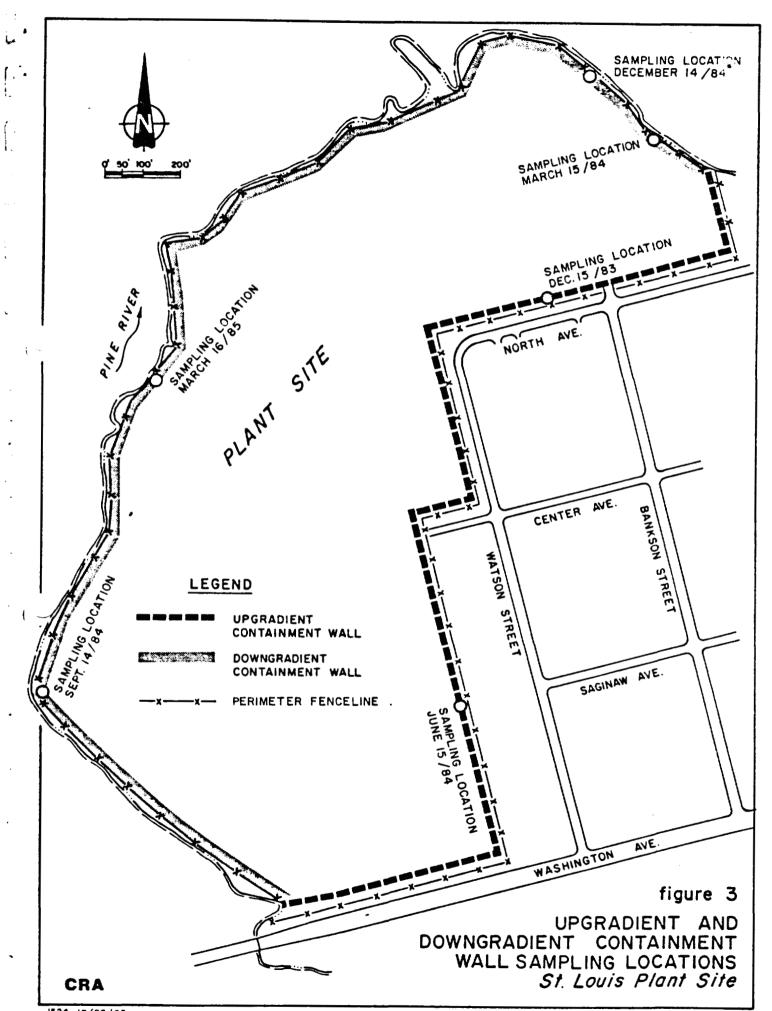
A CME 175 trailer mounted drill rig equipped with rotary head and 6-inch diameter hollow stem augers was utilized to advance the borehole into the containment wall on March 15 and a truck-mounted CME 175 drill rig was used on March 16, 1985. A 3-inch diameter Shelby tube, hydraulically pushed and retrieved, was used to collect the samples.

3.3 SAMPLE COLLECTION

The containment wall was located by field survey on March 14, 1985. The sampling borehole was begun at Station DGW 47+50 by augering through the clay cap into the underlying material.

The presence of soil/bentonite backfill material was confirmed by examination of cuttings on the auger flights. A Shelby tube was introduced into the borehole and a sample was retrieved at a depth of eight feet. Examination of the contents as the sample was extruded in the laboratory indicated that the sample contained native material. The sample was discarded. It was concluded that the borehole had been located on the inside edge of the containment wall.

On the morning of March 16, 1985 the sampling program was resumed and the drill rig was moved three feet to the west. A borehole was advanced to a depth of eight feet. A Shelby tube was introduced into the borehole and a sample was withdrawn. Examination of material in the base of the tube confirmed that the sample was obtained from the containment wall. The locations of this and prior sampling events are detailed on Figure 3. The boreholes were backfilled with bentonite and abandoned.



3.3.1 Sample Preparation and Shipping

The Shelby tube was capped and taped at both ends to prevent sample loss and drying. The sample was hand delivered to the Michigan Testing Engineer's laboratory in Detroit, Michigan for permeability testing.

3.3.2 Sample Testing

The undisturbed sample is to be tested for permeability using a falling head permeameter set up in accordance with ASTM D 2434. Results of the testing will be provided in written form to USEPA and MDNR within seven days after receipt of final laboratory data by CRA. A summary data report will be prepared and presented to both Agencies following completion of the containment wall monitoring program in the fall of 1986.

4.0 GROUNDWATER TABLE MONITORING

4.1 GENERAL

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The monitoring of plant site groundwater elevation was performed on March 13, 1985. The water elevation of the St. Louis reservoir was determined on March 15, 1985.

4.2 WATER LEVEL DETERMINATION

The elevation of the groundwater was determined by measuring the distance from the top of each site monitoring well to the watertable. This distance was measured by lowering a chalked, weighted surveyors tape into the monitoring well. Readings of the tape, which was graduated in increments of one one-hundredth of a foot, were taken at the water level and at the top of the well casing. The former reading was deducted from the latter and the resultant dimension was subtracted from the previously established top of well casing elevation. Well head and watertable elevations are presented on Table 1.

The elevation of the St. Louis reservoir was determined by level and rod survey.

CONESTOGA-ROVERS & ASSOCIATES LIMITED

TABLE 1

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WATER LEVEL MEASUREMENTS

MARCH 13, 1985

MONITORING WELL	WELL HEAD ELEVATION (AMSL)	MEASURED DISTANCE TO WATER TABLE (ft.)	WATERTABLE ELEVATION (AMSL)
1	735.88	13.82	722.06
2	742.07	19.04	723.03
3	749.92	27.38	722.54
4	735.99	13.56	722.43
5	739.35	17.58	721.77
6	734.43	13.00	721.43
7	734.02	12.29	721.73
8	734.30	13.14	721.16
9	734.52	13.33	721.19
10	733.43	12.33	721.10
11	734.38	13.21	721.17
12	730.74	9.53	721.21
13	734.43	13.27	721.16
14	735.95	14.67	721.28

Water level elevation, St. Louis Reservoir (March 15, 1985) 720.41

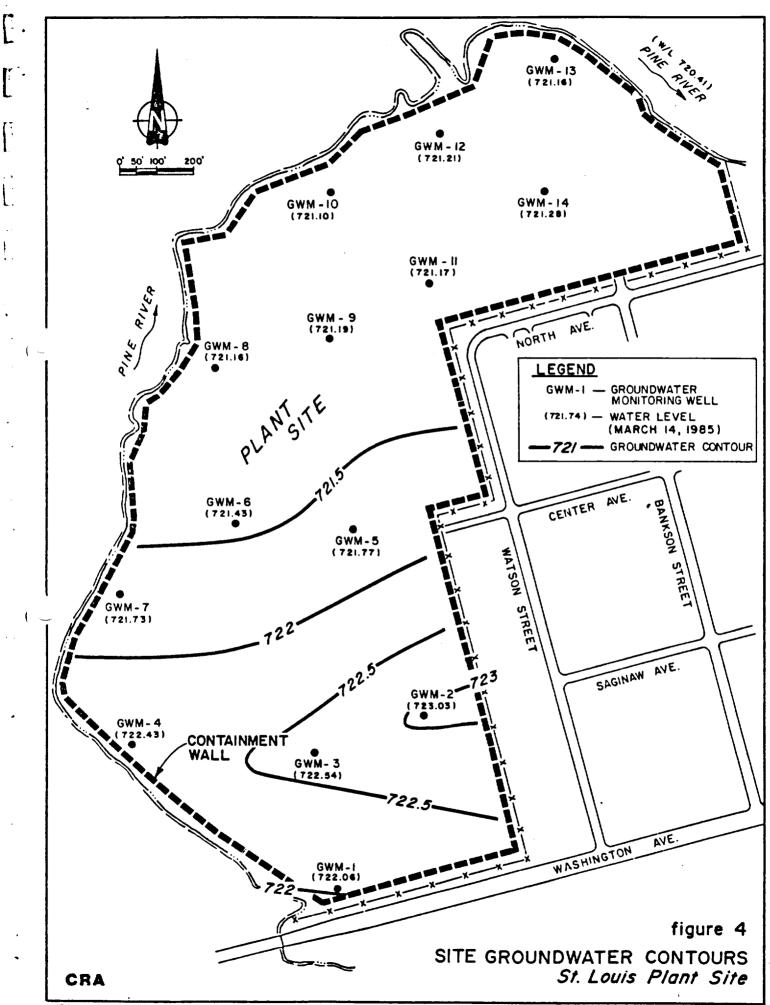
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4.3 GROUNDWATER CONTOUR MAP

The groundwater elevation data were used to construct a site groundwater elevation contour map which is presented in Figure 4.

4.4 SITE MEAN GROUNDWATER ELEVATION

The mean elevation of site groundwater is calculated to be 721.66. The maximum allowable site groundwater elevation stipulated by the Consent Judgement is 724.13.



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All monitoring activities stipulated by the Consent Judgment were carried out between March 13, and March 16, 1985.

The gas vent activated carbon filters were changed on March 14, 1986.

Data from the chemical analysis of the gas vent samples and the permeability testing of the contaminant wall sample will be provided to MDNR and USEPA within seven days of receipt by CRA of laboratory final data.

The present mean site groundwater table elevation is calculated to be 721.66. The elevation in the Pine River/St. Louis reservoir was determined to be 720.41.

The next sampling and monitoring event will occur on or about June 15, 1985. Interim gas vent sampling will be performed on or about April 29, 1985.

All of Which is Respectfully Submitted, CONESTOGA-ROVERS & ASSOCIATES LIMITED

D. Robinson

R.G. Shepherd, P. Eng.

CONESTOGA-ROVERS & ASSOCIATES LIMITED

APPENDIX A

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CHAIN OF CUSTODY

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CHAI								OL CHEMICAL CORPORATION 5 V. WASHINGTON STREET DUIS, MICHIGAN 48880			
SAMPLER	R'S SIGNAT										
SAMPLE Nº	SEQ Nº	DATE	(SIC TIME	SN) FRONT REAR	TENAX CHARCOAL		SAMPLE TYPE		Nº OF CONTAINERS	REMARKS	
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1	١			1	C				١		
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7.	2			F	7				1		
2	2			1-	C.				1		
2	2			F	C,				1		
72.	2			12	T		<u>, , , , , , , , , , , , , , , , , , , </u>		l		
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						TO	TAL NO. OF CONTAINERS		12		
RELING	UISHED_ BY	()	DATE/T		EIVED BY.		RELINQUISHED BY	DATE / TIM	E REC	CEIVED BY:	
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RELINQU	ISHED B	f :	DATE/T	IME RE	CEIVED BY:		RELINQUISHED BY:	DATE/TIM	E RE	CEIVED BY:	
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RELINGU	JISHED B	Y:	DATE/T	IME RE	CEIVED BY :		RELINQUISHED BY:	DATE / TIM	IE RE	CEIVED BY:	
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CHAIN OF CUSTODY PROJECT N2. RECORD 1524

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PROJECT NAME - GAS VENT MONITORING PLANT SITE ST. LOUIS, MICHIGAN



VELSICOL CHEMICAL CORPORATION 701 W. WASHINGTON STREET ST. LOUIS, MICHIGAN 48880

SHEET - OF

SAMPLER	S SIGNAT	URE	<u> </u>	IN)			NR OF	
SAMPLE Nº	SEQ Nº	DATE		FRONT	TENAX CHARCOAL	SAMPLË TYPE	CONTAINERS	REMARKS
4	4	315	10.27	Ŧ	· \	and Winter grad and a state		
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4	4			R	7		· ·	
5	15		11.05	ŦĿ				
5	ŝ			R				
57	C)			F	4		1	
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APPENDIX B

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GAS SAMPLING PROTOCOLS

APPENDIX B

GAS VENT SAMPLING PROTOCOL

In accordance with the Consent Judgment, Velsicol has submitted a post-closure maintenance and monitoring plan for its environmentally secured plant site in St. Louis, Michigan. The post-closure maintenance and monitoring plan requires quarterly monitoring of 11 gas vents that have been installed to release and appropriately treat internal gases. This program will be conducted over a period of three years.

The gas vents, as detailed in Exhibit F of the Consent Judgment, are designed with two sampling ports; one below the base of the installed activated charcoal filter, and one above the filter. Samples will be collected from the downstream port. Results will indicate whether or not containment breakthrough has occured through the carbon filter.

Samples will be analyzed for three separate compounds: carbon tetrachloride, trichloroethylene and vinyl chloride.

Samples will be collected with a Gilian HFS-113 AU DK variable flow pump. This particular unit allows the operator to run a series of tubes concurrently in parallel arrangement. Four tubes will be collected from each gas vent: two standard NIOSH 100/50 mg activated charcoal tube, and two 30/15 mg tenax tubes, each tube measuring 6 mm x 70 mm. One blank set and one duplicate set of tubes will be collected during each quarterly sampling event.

As vinyl chloride represents the least adsorptive of the three compounds, the sampling program is designed to accomodate this compound. Therefore, sample volume shall not exceed 5 liters.

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Prior to sampling, the vent will be sealed off with a plastic cap, and purged for 10 minutes at a rate of 500 cc/min. This is to eliminate the possibility of sampling atmospheric air contained within the upper portion of the gas vent.

Two samples from each gas vent shall be collected simultaneously at a rate of 250 cc/min. for 20 minutes. The pump shall be lab calibrated with sample tubes in-line to determine the exact flow rate. Additionally, flow will be checked after field sampling to verify that a constant flow was maintained throughout the sampling period.

Following sample collection, each tube will be sealed with a plastic cap at each end, labelled, placed in a cold storage environment and shipped under chain-of-custody via a commercial courier service to Velsicol's analytical laboratory in Memphis.

Analysis of the charcoal tube will be conducted in accordance with NIOSH protocol as detailed below:

Compound	Revised Method No.
Carbon Tetrachloride	1003
Trichloroethylene	S-336
Vinyl Chloride	1007

Analysis will proceed by first eluting the carbon sample tubes with carbon disulfide and then analyzing by GC with a flame ionization detector. All samples will be initially analyzed in this fashion. If any of the above compounds are detected on the charcoal tube, the corresponding tenax tube will be analyzed by thermal desorption and GC/MS under EPA Method 624.

Turnaround time for the completed analysis at the laboratory is anticipated to be 30 days from date of sample collection. Samples will be desorbed within the 10 day limit specified for vinyl chloride. Analytical data will be reported to CRA as mg/tube. Final results for the carbon tube will be calculated by CRA, using the following formula.

1. Corrections for the blank to be made for each sample
 mg = mg sample - mg blank

This calculation is performed separately for each tube.

- 2. Add the amounts present in the front tube and backup tube to determine the total weight in the sample.
- Calculate the corrected mg/sample by dividing the total weight by the desorption efficiency (D.E.) which is provided by the lab.

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- 4. Calculate the concentration of the analyte in air $mg/m^3 = Corrected mg \times 1000 liters/m^3$ Air volume Sampled (liters)
- 5. Concentration will be reported as ppm, corrected to standard conditions of 25°C and 760 mm Hg

 $ppm = mg/m = x \frac{24.45}{MW} \times \frac{760}{P} \times \frac{(T+273)}{298}$

where P	= pressure (mm Hg) of air sampled
т	<pre>= temperature (°C) of air sampled</pre>
24.45	= molar volume (liter/mole) at 25°C and 760 mm Hg
MW	= Molecular Weight
760	= standard pressure (mm Hg)
298	= standard temperature (°K)

- 2 -

- NOTE: Temperature and pressure uncorrected to sea level will be collected for the duration of the sampling event and averaged for use in the above calculations. Information will be provided from the National Weather Service in Lansing, Michigan.
 - 6. If the concentration of the back tube exceeds 10% of the concentration of the front tube, the results will be reported as a sample breakthrough and possible sample loss.
 - 7. A similar procedure will be followed for the tenax tube, should analysis be required.

Data will be reported to USEPA and MDNR officials within seven days after receipt of final laboratory data for each quarterly sampling. Additionally, a summary data report will be provided at the conclusion of the three year sampling period, or sooner, should breakthrough of any compound occur prior to the three year program.

In addition to the set of field blanks to be collected per quarterly sampling event, an additional set of 15 charcoal tubes and 15 tenax tubes will be forwarded unopened to the lab during the initial sampling event.

These "blank" tubes will be used as internal calibration standards on which each of the three compounds will be spiked at five different concentrations. The data from this analysis will be used to calculate the desorption efficiency for a specific lot of activated charcoal. Therefore, the lot number of carbon tubes and tenax tubes shall be recorded during each quarterly sampling. Should the lot number change, a new set of 15 charcoal tubes and 15 tenax tubes shall be forwarded to the laboratory for determination of the new desorption efficiency.

The allowable limits for these compounds have been established by the MDNR and are site specific for the St. Louis site. These limits are documented in section 4.3 of the post-closure maintenance and monitoring plan.

Copies of all three analytical protocols, the chain of custody and the data collection sheet are provided in the following sections.

- 3 -

HYDROCARBONS, HALOGENATED

FORMULA: Table 1

M.W.: Table 1

METHOD: 1003 ISSUED: 2/14/84

COMPOUNDS:benzyl chloridechlorobromomethanel,l-dichloroethanehexachloroethane(synonymsbromoformchloroforml,2-dichloroethylenemethylchloroformin Table])carbon tetrachlorideo-dichlorobenzeneethylene dichloridepropylene dichloridechlorobenzenep-dichlorobenzeneethylenedichloridepropylene

SAMPLING	MEASUREMENT
SAMPLER: SOLID SORBENT TUBE	! !TECHNIQUE: GAS CHROMATOGRAPHY, FID
(coconut shell charcoal, 100 mg/50 mg	
FLOW RATE: 0.01 to 0.2 L/min	ANALYTE: compounds above
	: !DESORPTION: 1 mL CS ₂ , stand 30 min
VOL-MIN: Table 2	
-MAX: Table 2	INJECTION VOLUME: 5 µL
	!
SHIPMENT: routine	!TEMPERATURES: Table 2
SAMPLE STABILITY: at least l week @ 25 °C	: !CARRIER GAS: N ₂ or He, 30 mL/min
BLANKS: 2 to 10 field blanks per set	! !COLUMN: Table 2; alternates are SP-2100, ! SP-2100 with 0.1% Carbowax 1500 ! or DB-1 fused silica capillary column
ACCURACY	1
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and state to the state of a state of the first of the state of the sta	n an early the state of the sta
BIAS: not significant [1]	: !RANGE: Table 2
	1 1
OVERALL PRECISION (s _r): see EVALUATION OF METHOD [1]	<pre>!ESTIMATED LOD: 0.01 mg per sample [2] !</pre>
	PRECISION (s_r) : see EVALUATION OF METHOD [1]
	•

APPLICABILITY: This method uses a simple desorption and can be used for simultaneous analysis of two or more substances suspected to be present by changing the gas chromatographic conditions (i.e., temperature programmed). High humidity during sampling will prevent organic vapors from being trapped efficiently on the sorbent and greatly decreases breakthrough volume.

INTERFERENCES: None identified. The chromatographic column or separation conditions may be changed to circumvent interference problems.

OTHER METHODS: This method combines and replaces Methods P&CAM 127 [3]; S95, S101, S110, S113, S114, S115, S122, S123 and S133 [4]; and S135, S281, S314, S328 and S351 [5].

:

a. Remove and discard back sorbent section of a media blank sampler.

1.

- b. Inject a known amount of analyte or calibration stock solution directly onto front sorbent section with a microliter syringe.
- c. Cap the tube. Allow to stand overnight.
- d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
- e. Prepare a graph of DE vs. mg analyte recovered.
- 10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

- Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1003-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
 - NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.
- 12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

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13. Determine the mass, mg (corrected for DE) of analyte found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.

NOTE: If $W_{\rm b} > W_{\rm f}/10$, report breakthrough and possible sample loss.

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14. Calculate concentration, C, of analyte in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, mg/m^3.$$

THE LATION OF METHODS

Laboratory testing was performed with spiked samples and generated atmosphere [1]. All analytes are stable at least one week. All methods were validated using SKC Lot 105 coconut shell charcoal. Results were:

METHOD: 1003

[9] Criteria for a Recommended Standard...Occupational Exposure to 1,1,1-Trichloroethane, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 76-184 (1976).

[10] Criteria for a Recommended Standard...Occupational Exposure to Carbon Tetrachloride, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 76-133 (1976).

METHOD REVISED BY: G. D. Foley; Y. T. Gagnon; and K. J. Williams, NIOSH/DPSE; methods originally validated under NIOSH Contract CDC-99-74-45.

		.W.; mg/m ³		OSHA NIOSH [6-10]		VP (9 20 °C	Density (g/mL
Compounds	Formula	= 1 ppm	Synonyms	ACGIH	<u>BP (°C)</u>		<mark>@ 20 ℃)</mark>
g-Dichlorobenzene	1,4-C ₆ H ₄ C1 ₂	147.00; 6.01	1 - 1-dichlorøbenzene; (#106-46-7	75 ppm 75 ppm, STEL 110 ppm	174	50 Pa	1.241
1,1-Dichloroethane	ai ₃ chc1 ₂ ; c ₂ H ₄ C1 ₂	98.96; 4.05	ethylidene chloride; Cas #15-34-3	100 ppm 100 ppm 200 ppm, STEL 250 ppm	57	24.3 kPa	1. 174
1,2-Dichloroethylene	c1cH=CHC1; c_H_C1 2_4_2	96.95; 3.96	acet ylene_dichloride; 1,7- dichloroethene; Care #540-59-0	200 ppm 200 ppm 200 ppm, STEL 250 ppm	60 (cis) 47 (trans)	24-35 kPa	1.28
Ethylene dichloride*	c1cH2cH2c1; c2H4c12	98.96; 4.05	1, : dich1oroethane; C:-> #107-06-2	50 ppm, C 100 ppm 5 ppm; 15 ppm/15 min 10 ppm, STEL 15 ppm	83 :	8.3 kPa	1.255
Hexachloroethane*	cc1 ₃ cc1 ₃ ; c ₂ c1 ₆	236.74; 9.68	µch1oroethane; (#67–72–1	1 ppm (skin) 1 ppm (skin) 10 ppm	187 (sublimes)	30 Pa	2.09
Methylchloroform	c ² H ³ Cl ³ ;	133.42; 5.45	1, 1, 1-trichioroethane; (5 #71-55-6	350 ppm 350 ppm/15 min CAS #11-55-6 STEL 450 ppm	74 350 ppm,	13.3 kPa	1.335
Propylene dichloride	сн ₃ снс1сн ₂ с1; с ₃ н ₆ с1 ₂	112.99; 4.62	1,∷-dich1oropropane ©⊕ #78-87-5	75 ppm 75 ppm 75 ppm, STEL 110 ppm	95	5.3 kPa	1.156 (25 °C)

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2/15/84

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1003-7

*Suspect carcinogen.

HYDROCARBONS, HALOGENATED

HETHOD: 1003

Sampling				Measurement					
	Air Sample Volume (L)				Working		<u>t (°C)</u> Column		Range
Compound	<u> </u>	<u>Max</u>	Breakthe <u>in</u> Dr	-	Range (mg/m³)	<u>Column</u> *	Injector <u>Detector</u>	Internal <u>Standard</u>	(mg per sample)
1,1-Dichloroethane	1 (2 100 ppm	10	18.3 L ·	38 mg∕m³	40 to 1215 (10 L)	A	50 100 175		0.4 to 12
1,2-Dichloroethylene	0.5 (8 200 ppm	3	5.4 L e	:0 9 my/m^a	80 to 2370 (3 L)	A	60 170 210		0.2 to 7
Ethylene dichloride	1 @ 50 ppm	10	29 L 3 F	∙ ⊪y/ m⁹	40 to 1215 (3 L)	` A	10 225 250	octane	0.1 to 4
Hexach1oroethane	1@1ppm	10	43 1 <i>3 2</i>	⊪]/m³	1 tu 30 (10 L)	D	110 110 210	n-tridecane	0.01 to 0.
Methylchloroform	0.5 @ 350 ppm	6	9.5 t v	i8 8 mg/m³	190 to 5700 (3 L)	۸	10 225 250	octane	0.6 to 17
Propylene dichloride	1 @ 75 ppm	10	18 L 3	ng/m ³	35 to 1050 (10 L)	A	80 170 210	n-undecane	0.3 to 10

2/15/84

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*A = 3'm x 3 am stainless steel, 10% SP-1000 to 100 mesh Supelcoport;

 $B = \delta m \times 3$ way otherwise same as A;

 $C=3~m~x/3~{\rm mar}$ statules) steel, 10% OV-101 ${\rm mar}$ = 120 mesh Supelcoport; or

 METHOD: 1003

Trichloroethylene

Analyte:	Trichloroethylene	Method No.: S336			
Matrix:	Air	Range: 519-2176 mg/cu m			
OSHA Standard:	200 ppm (1075 mg/cu m)-Ceiling 100 ppm (535 mg/cu m)-T.W.A.	Precision (\overline{CV}_{T}) : 0.082			
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 6/6/75			

1. Principle of the Method

- 1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.
- 1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.
- 1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.
- 1.4 The area of the resulting peak is determined and compared with areas obtained from injection of standards.

2. Range and Sensitivity

1 -

- 2.1 This method was validated over the range of 519-2176 mg/cu m at an atmospheric temperature and pressure of 24.5°C and 759.4 mm Hg, using a 3-liter sample. Under the conditions of sample size (3 liters) the probable useful range of this method is 108-3225 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 9.7 mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.
- 2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 42 mg of analyte when a test atmosphere containing 2266 mg/cu m of analyte in air was sampled at 0.187 liters per minute for 99 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent.

(The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

- 3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.
- 3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.
- 3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.
- 3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation $(\overline{CV_T})$ for the total analytical and sampling method in the range of 519-2176 mg/cu m was 0.082. This value corresponds to an 88.2 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.
- 4.2 On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 6.4 % lower than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result.

These data are based on validation experiments using the internal standard method.

- 5. Advantages and Disadvantages of the Method
 - 5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

- 5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.
- 5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

1 -

- 6.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3).
- 6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm 0.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.
- 6.3 Gas chromatograph equipped with a flame ionization detector.
- 6.4 Column (10-ft x 1/8-in stainless steel) packed with 10% OV-101 stationary phase on 100/120 mesh Supelcoport.
- 6.5 An electronic integrator or some other suitable method for measuring peak areas.
- 6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.
- 6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.
- 6.8 Pipets: 1.0 ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

- 7.1 Chromatographic quality carbon disulfide.
- 7.2 Trichloroethylene, reagent grade
- 7.3 Octane, or other suitable internal standard
- 7.4 Purified nitrogen
- 7.5 Prepurified hydrogen.
- 7.6 Filtered compressed air.
- 8. Procedure
 - 8.1 Cleaning of equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.
 - 8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.
 - 8.3 Collection and Shipping of Samples
 - 8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).
 - 8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.
 - 8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.
 - 8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.
 - 8.3.5 At the ceiling and peak concentrations, a sample size of 3 liters is recommended. Sample for 15 minutes at a flow of 0.2 liters per minute. At the T.W.A. concentration, a sample size of 10 liters is recommended. Sample at a flow of 0.2 liters per minute or less. The flow rates should be known with an accuracy of at least +5%.
 - 8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

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- 8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.
- 8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.
- 8.3.9 Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.
- 8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.
- 8.4 Analysis of Samples
 - ÷.,
 - 8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.
 - 8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.
 - 8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

30 ml/min (60 psig) Nitrogen carrier gas flow
 35 ml/min (25 psig) Hydrogen gas flow to detector
 400 ml/min (60 psig) Air flow to detector
 225°C injector temperature
 250°C manifold temperature (detector)
 70°C column temperature

- 8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.
- 8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.
- 8.5 Determination of Desorption Efficiency

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- 8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.
- 8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. When using an automatic sample injector, the sample injector vials, capped with Teflon-faced septa, may be used in place of the glass tubes.

Six tubes at each of three concentration levels (0.5X,1X and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 3-liter sample at the selected level. The tubes are allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 1.0 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

D.E. = <u>Average Weight (mg) recovered</u> Weight (mg) added

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg per 1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2% the standard. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

- 10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.
- 10.2 Corrections for the blank must be made for each sample.

mg = mg sample - mg blank

where:

mg sample = mg found in front section of sample tube
mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

- 10.3 Add the amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.
- 10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

Corrected mg/sample = <u>Total weight</u> D.E.

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

mg/cu m = Corrected mg (Section 10.4) x 1000 (liters/cu m) Air Volume Sampled (liters)

10.6 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$ppm = mg/cu = x \frac{24.45}{MW} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled T = temperature (°C) of air sampled 24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg MW = molecular weight 760 = standard pressure (mm Hg) 298 = standard temperature (°K)

11. References

- 11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," <u>Amer. Ind. Hyg. Assoc. J.</u>, <u>31</u>: 225 (1970).
- 11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.
- 11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

VINYL CHLORIDE

FORMULA: CH2=CHC1; C2H3C1

METHOD: 1007 ISSUED: 2/15/84

M.W.: 62.50

OSHA: 1 ppm; C 5 ppm NIOSH: minimum measurable ACGIH: 5 ppm (human carcinogen) [1] (1 ppm = 2.56 mg/m³ @ NTP) PROPERTIES: BP -14 *C; vapor density 2.2 (air = 1)

SYNONYMS: chloroethylene; chloroethene; CAS #75-01-4.

SAMPLING	MEASUREMENT
SAMPLER: SOLID SORBENT TUBE	! !TECHNIQUE: GAS CHROMATOGRAPHY, FID
(2 tandem tubes, each with 150 mg activated coconut charcoal)	! !ANALYTE: vinyl chloride
FLOW RATE: 0.05 L/min	: !DESORPTION: 1 mL carbon disulfide; 30 min 1
VOL-MIN: 0.7 L -Max: 5 L	INJECTION ALIQUOT: 5 μL
SHIPMENT: separate primary and backup tubes and cap each	COLUMN: stainless steel, 6.1 m x 3.2 mm, 10% SE-30 on 80/100 mesh Chromosorb W (AM-DMCS)
SAMPLE STABILITY: 10 days @ 25 °C	: !CARRIER GAS: He, 40 mL/min
BLANKS: 2 to 10 field blanks per set	: !TEMPERATURE-INJECTOR: 230 °C ! -DETECTOR: 230 °C ! -COLUMN: 60 °C
ACCURACY	!
RANGE STUDIED: 1 to 64 mg/m ³ [2]	<pre>!CALIBRATION: solutions of vinyl chloride in CS₂ ! !RANGE: 0.002 to 0.2 mg per sample [2]</pre>
BIAS: -6% of calculated concentration [2]	! ! !ESTIMATED LOD: 0.00004 mg per sample [2]
OVERALL PRECISION (sr): 0.06 [2]	.! !PRECISION (s _r): not determined

APPLICABILITY: The working range is 0.4 to 40 mg/m³ (0.16 to 16 ppm) for a 5-L air sample. The method is applicable to 15-min samples at concentrations of 1 ppm or higher.

INTERFERENCES: Other than the possibility of loss of sample upon storage of two weeks or more at room temperature, none have been noted.

OTHER METHODS: This is a revision of P&CAM 178 [3].

VINYL CHLORIDE

REAGENTS:	EQUIPMENT:
 Carbon disulfide,* chromatographic quality. 	 Sampler: two tandem glass tubes, 7 cm long, 6 mm OD, 4 mm ID, flame-sealed ends, each
 Vinyl chloride,*, 99.9%, in lecture bottle fitted with valve and septum. 	containing 150 mg of 20/40 mesh activated (600 °C) coconut shell charcoal. A silylated glass wool plug precedes the charcoal beds and a 3-mm urethane
 3. Calibration stock solution, 0.26 mg/mL. a. Insert the tip of a gas syringe containing 1 mL vinyl chloride gas under the surface of 5 mL CS₂ in a 10-mL volumetric 	<pre>foam plug follows the charcoal beds. Plastic caps are included for sealing after use. Pressure drop across each tube at 1 L/min airflow must be less than 3.4 kPa. NOTE: A pair of two-section (100 mg/50 mg) tubes may be used.</pre>
flask. b. Open the valve of the syringe	Personal sampling pump, 0.05 L/min, with flexible connecting tubing.
and withdraw the plunger to pull CS ₂ into the barrel. (As vinyl chloride dissolves, a	 Gas chromatograph, flame ionization detector, integrator and column (page 1007-1). 4. File.
vacuum will be created, pulling CS ₂ into the syringe.)	5. Bent wire for removing plugs from sampling tube. 6. Vials, 2-mL, glass with PTFE-lined septa and
c. Push the solution from the syringe into the flask. Rinse the syringe twice with l-mL	<pre>crimp-on seals. 7. Volumetric flasks, 10-mL, with polyethylene stoppers.</pre>
portions of CS ₂ and add the washings to the flask.	 B. Pipettes, delivery, 1.0-mL, graduated in 0.1-mL increments, 2- and 5-mL, with pipet bulb.
d Dilute to the mark with rs.	9 Air campling bags Tedlar 10-1

- d. Dilute to the mark with CS₂.
- 4. Helium, purified.
- 5. Hydrogen, purified.
- 6. Air, filtered.

*See Special Precautions.

- 9. Air sampling bags, Tedlar, 10-L.
- 10. Gas syringe, with gas-tight valve, 0.1- and 1-mL.
- 11. Syringe, 10-µL, with 0.1-µL graduations.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = -30 °C); work with it only in a hood.

Vinyl chloride is a human carcinogen [1].

SAMPLING:

- 1. Calibrate each personal sampling pump with a representative sampler in line.
- 2. Break the ends of the tubes immediately before sampling. Attach two tubes, with ends touching, with a short piece of tubing. Label one tube as the back tube and insert the back tube into the flexible tubing attached to the personal sampling pump.
- 3. Sample at 0.05 L/min for 15 to 100 min. Do not sample more than 5 L of air.

4. Separate the primary and backup tubes and cap each tube for shipment.

SAMPLE PREPARATION:

- 5. Add 1.0 mL CS₂ to an empty vial. Loosely cap the vial.
- 6. Score each sampler tube with a file in front of the glass wool plug. Break the tube at the score line.

METHOD: 1007

- 7. Transfer the charcoal from the front and back tubes to separate vials. Discard the glass wool and foam plugs. Seal the vials with septum caps immediately.
- B. Allow to stand for 30 min, with occasional agitation. Analyze the sample within the next 30-min period.

CALIBRATION AND QUALITY CONTROL:

- Calibrate with at least five working standards covering the range 0.0002 to 0.2 mg per sample.
 - a. Add known amounts of calibration stock solution to CS₂ in 10-mL volumetric flasks and dilute to the marks, using serial dilution as appropriate.
 - NOTE: Working standards can be stored at -20 °C for at least three days.
 - b. Analyze together with samples and blanks (steps 12 and 13).
 - c. Prepare calibration graphs of peak area vs. quantity (mg) of vinyl chloride per tube and peak area vs. quantity (ng) per injection.
- Determine desorption efficiency (DE) at least once for each lot of charcoal used in the calibration range (step 9). Prepare three tubes at each of five levels plus three media blanks.
 - a. Prepare three atmospheres of vinyl chloride in air by injecting 0.01, 0.08, and 0.2 mL vinyl chloride gas into 10 L air in Tedlar bags. The resulting concentrations are approximately 2.6, 21 and 52 mg/m³.
 - b. Following steps 1 through 4, sample these atmospheres according to the following scheme:

Concentration in Bag (mg/m ²)	Volume Sampled (L)	Quantity of Vinyl Chloride (mg)
2.6	0.8	0.002
	2.2	0.006
21	0.8	0.017
	2.2	0.046
52	2.5	0.13

Obtain three samples at each level.

- c. Desorb (steps 6 through 8) and analyze together with working standards (steps 12 and 13). No vinyl chloride should be found on the back tubes.
- d. Analyze the atmospheres in the bags (steps 12 and 13) using 1-mL gas samples. Read from the calibration graph the quantity (ng) per injection, which for a 1-mL injection of gas is numerically equal to the concentration in mg/m³.
- e. Calculate DE from the mass (mg) of vinyl chloride on the front tube (W_f) , the average blank (B), the concentration of vinyl chloride in the synthetic atmospheres $(C_s, mg/m^3)$, and the volume of air sampled (V, L):

$$DE = \frac{(W_{f} - B) \cdot 10^{3}}{(C_{S})(V)}$$

f. Prepare a graph of DE vs. mass found (Wr - B).

11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

VINYL CHLORIDE

12. Set the gas chromatogrph according to manufacturer's instructions and to conditions given on page 1007-1. Inject sample aliquot manually using solvent flush technique or with autosampler. The retention time of vinyl chloride is about 1.7 min.

NOTE: If peak area is above the linear range of the working standards, dilute with CS₂, reanalyze and apply the appropriate dilution factor in calculations.

13. Measure peak area.

CALCULATIONS:

14. Determine the mass, mg (corrected for DE) of vinyl chloride found in the sample front (W_f) and back (W_b) tubes, and in the average media blank (B).

NOTE: If $W_p > W_c/10$, report breakthrough and possible sample loss.

15. Calculate concentration, C, of vinyl chloride in the air volume sampled, V (L):

$$C = \frac{(H_f + H_b - 2B) \cdot 10^3}{V}$$
, mg/m³

EVALUATION OF METHOD:

The method was evaluated using single 150-mg sampling tubes with 100-mg front beds and 50-mg back beds [2]. At four concentrations between 1 and 64 mg/m³, the pooled relative standard deviation was 0.06 and the measurements averaged 94% of the concentrations calculated from the volumes of vinyl chloride and air used for the atmospheres sampled; samples at the 3-µg level showed no loss of vinyl chloride when stored for 12 days at room temperature or 19 days at -20 °C. There may be significant loss of vinyl chloride from samples stored for 14 days at room temperature [4]. The 1% breakthrough capacity for a 150-mg bed of coconut charcoal challenged at 100 mL/min with vinyl chloride in air at 16 mg/m³ and a relative humidity of 70% was 4.6 L [5].

REFERENCES:

[1] <u>TLVs</u> - <u>Threshold Limit Values for Chemical Substances and Physical Agents in the Work</u> Environment with <u>Intended Changes for 1983-84</u>, ACGIH, Cincinnati, OH (1983).

- [2] Hill, R. H., Jr., C. S. McCanmon, A. T. Saalwaechter, A. W. Teass, and W. J. Woodfin. <u>Anal. Chem.</u>, <u>48</u>, 1395-1398 (1976).
- [3] NIOSH Manual of Analytical Methods, 2nd. ed., V. 1, P&CAM 178, U.S. Department of Health and Human Services, Publ. (NIOSH) 77-157-A (1977).
- [4] Cuddeback, J. E., W. R. Burg, and S. R. Birch, Environ. Sci. Technol., 9, 1168-1171 (1975).
- [5] Matsumura, Y. <u>Ind</u>. <u>Health</u>, <u>18</u>, 61-67 (1980).

METHOD REVISED BY: A. W. Teass, Ph.D., NIOSH/DPSE.

HETHOD: 1007

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VELSICOL CHEMICAL CORPORATION ST. LOUIS, MICHIGAN PROJECT Nº 1524

GAS VENT SAMPLING PUMPS CALIBRATION LOG

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DATE	; <u>I</u>	1-15 1	155		CALIB	RATED	BY	- -		· · · · · · · · · · · · · · · · · · ·						
				BEFORE S			1135			ER SAMP		15/85		AVI		15/85
PUMP NUMBER	PUMP TYPE	TEMP. (°F)	HUMIDITY (%)	BAROM. PRESSURE (Inches Hg)	INITIAL FLOW (cc/min.)	CALL FLOW (cc/min.)	24-HR. TIME	TEMP. (°F)	HUMIDITY (%)	BAROM. PRESSURE (Inches Hg)	FLOW (cc/min.)	24-HR. TIME	TEMP. (°F)	HUMIDITY (%)	BAROM. PRESSURE (Inches Hg)	FLOW (cc/min.)
	MUMI a	42	55	27.76.	255		' i	32	55	30 33		12:30	37.5	57	30.145	250
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- La	en mi a	42	55	27.56	2.25	25.1	Э	33	59	30.32	2 50	12:35	37.5	57	30.145	250
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COMMENTS

VELSICOL CHEMICAL CORPORATION ST. LOUIS, MICHIGAN PROJECT Nº 1524

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GAS VENT SAMPLING

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DATE OF COLLECTION 3 15 85	SAMPLER ROBINGON	BAROMETRIC 30. 145
TEMPERATURE TE 37.5	RELATIVE 57%	GAUGE 1 2 3 4 5 6 7 8 9 10 11
CHARCOAL 120	TENAX LOT Nº ZTI	READING OF S S S

GAS VENT	PUMP	SAMPLE		SAMPLING TIME		SAMPLING RATE	SAMPLE
NUMBER	NUMBER	NUMBER	START	FINISH	ELAPSED	(cc/min.)	VOLUME (1)
t	1	7	11.44	12.01	70	2,50	50
2	1	5	1105	11.25	20	750	5 a
3	}	4	10.27	10.47	20	750	5.0
4		3	9.50	10.10	20	250	50
5							
6	ľ	2	913	933	20	250	50
7	· · · · · · · · · · · · · · · · · · ·						
8							
9							<u></u>
10	<u>,, ,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,</u>						
11	1	1	8 36	8.54	20	25000	5.0
DUPLICATE							
BLANK		6	11-15				
DATE OF SAMPLE SH	IPMENT SI		METH	HOD OF F	A.26+6.11	871626	3/11/81-
	AKBINI C		3/14/25	المستحداد الفقا الأداماني ويهيها			

VELSICOL CHEMICAL CORPORATION ST. LOUIS, MICHIGAN PROJECT Nº 1524

GAS VENT SAMPLING

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DATE OF COLLECTION	3-(5-35)	SAMPLER COLL	BAROME		Ċ	30	<u>.</u>	45	5					
TEMPERATURE	37.5	RELATIVE 57%	GAUGE	1	2	3	4	5	6	7	8	9	10	11
CHARCOAL Lot Nº	120	TENAX LOT Nº 211	READING					Ü		0	Ö	Ĵ)	0	

GAS VENT	PUMP	SAMPLE		SAMPLING TIME	SAMPLING TIME		SAMPLE
NUMBER	NUMBER	NUMBER	START	FINISH	ELAPSED	(cc/min.)	VOLUME (1)
1							
2							
3							
4							
5	Z	9	10:50	11:10	20	250	5.0
6							
7	2_	10	10:09	10129	Za	250	5.0
8	2	8*	11.32	11.'52	20	Z50	5.0
9	2.	1 :	01/21	07,49	20	250	5.0
10	2.	12.	08:53	2417/J	20	250	5.0
11							
DUPLICATE	2 18)	13 *	11:55	12:15	20	250	5.0
BLANK							
DATE OF	IPMENT 2		METH	NOD OF TE	A. 18 C.11 E	571626	3/15/8-

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VELSICOL CHEMICAL CORPORATION

POST - CONSTRUCTION QUARTERLY MONITORING REPORT June 19 - 21, 1985

Plant Site, St. Louis Michigan

June 1985 Ref. No. 1524

CONESTOGA-ROVERS & ASSOCIATES LIMITED

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	JUNE 19, 1985	

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FIGURE 1 GAS VENT LOCATIONS

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1.0 INTRODUCTION

1.1 GENERAL

In accordance with the terms of the technical appendix to the Consent Judgment entered into by Velsicol Chemical Corporation (Velsicol), the United States Environmental Protection Agency, (USEPA) and the Michigan Department of Natural Resources (MDNR), Velsicol is required to perform specified monitoring activities at quarterly intervals following closure of its St. Louis, Michigan plant site. The monitoring program is designed to address the following:

- 1. Performance of gas vents
- 2. Performance of the site perimeter containment wall
- 3. Determination of site groundwater elevations

This report details the site monitoring which occured during the period June 19 to June 21, 1985.

1.2 PARTICIPATION BY REGULATORY AGENCIES

The regulatory agencies did not participate in or attend this monitoring event.

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1.3 MONITORING AND SAMPLING PERSONNEL

The monitoring and sampling program was carried out by Mr. D. Robinson (Conestoga-Rovers and Associates) assisted by Mr. Gene DeGeer, the Velsicol site custodian.

2.0 GAS VENT MONITORING

2.1 GENERAL

The gas vent monitoring began on June 20, 1985 and was completed June 21, 1985.

2.1.1 Equipment

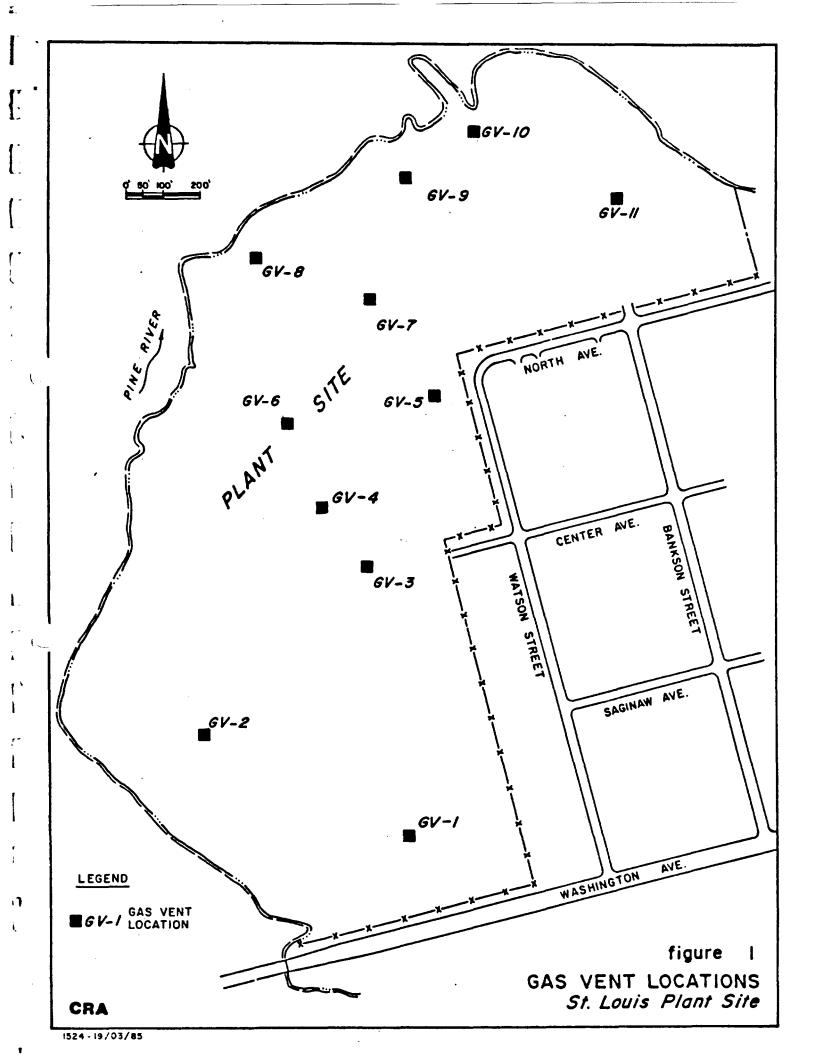
Two Gilian model HFS 113 hi flow samplers were used to collect gas vent samples. The samplers were field calibrated using a rotometer prior to sampling. The calibration data is presented within Appendix B. Samples from each gas vent were collected in two 6-mm diameter x 70-mm long Tenax tubes and two charcoal tubes of similar dimensions. The samples were collected simultaneously using dual parallel/series tube holder sets.

2.2 SAMPLE COLLECTION

Samples were obtained at each of the 11 gas vents. The location of the gas vents within the closed plant site is detailed on Figure 1. One blank set and one duplicate set of samples were also collected.

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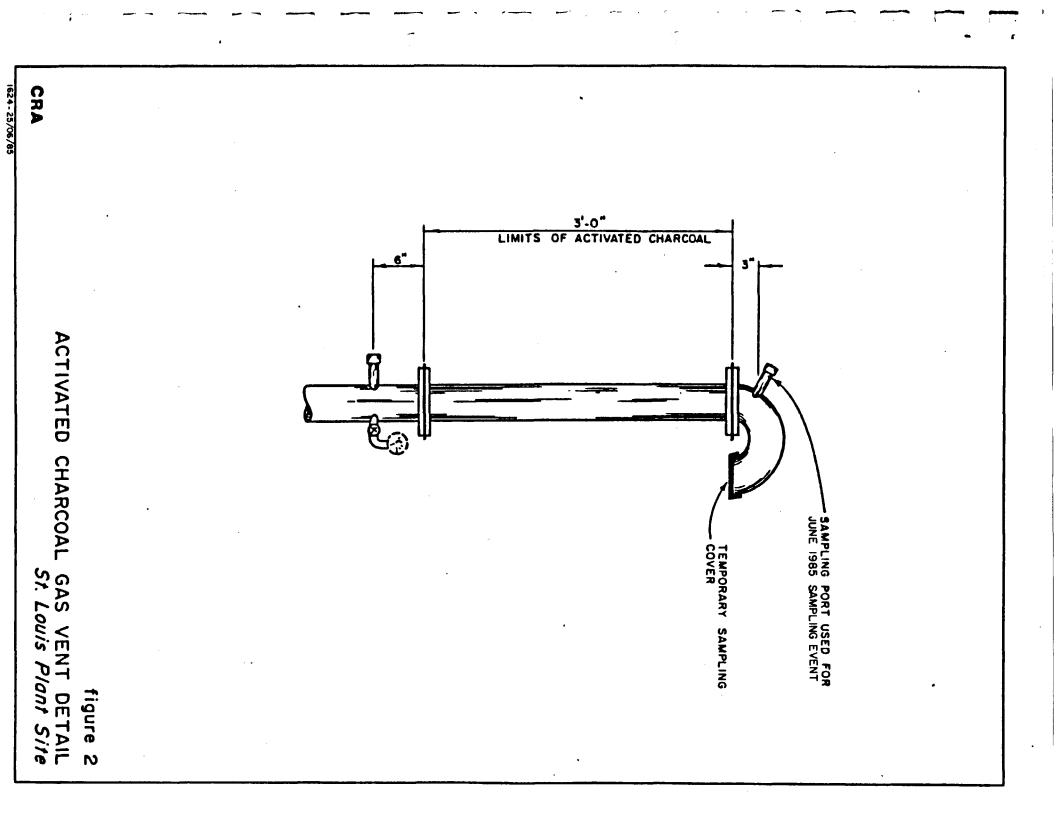
Sampling was conducted at the downstream sampling port on each gas vent as detailed on Figure 2. The tube holder was attached directly to the gas vent sampling port using a copper manifold assembly which was environmentally cleaned prior to use. Tygon tubing was used to connect the tube holder to the sampler and was connected between the base of the tube holder and suction port of the sampler. The sampler which was pre-calibrated to 250cc/min/tube set, was operated for a period of 20 minutes for each sampling event, resulting in a collected sample volume of five liters per tube set.

Prior to sample collection, the gas vent upper chamber was purged by pumping at 500 cc/minute for a period of ten minutes. This precluded the possiblity of sampling retained atmospheric air from the gas vent upper chamber. During the purging and sampling operations, the open end of the gas vent was capped using a 4-inch diameter plastic cover to prevent atmospheric air being drawn into the sample.

At the conclusion of each gas vent sampling, the set of four sample tubes were capped, labelled and stored in a cooler maintained at 0°C.

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2.2.1 Sample Storage and Shipment

On the afternoon of June 21, 1985 the samples were transferred to a cooler containing frozen cold packs and styrofoam packing materials. The cooler was shipped under chain of custody protocol, to Velsicol's Memphis, Tennessee laboratory by overnight courier for analysis. A copy of the chain of custody is provided in Appendix A.

2.2.2 Sample Analysis

Analysis will be conducted in accordance with NIOSH protocols as follows:

Compound	NIOSH Method
Carbon Tetrachloride	1003
Trichloroethylene	S-336
Vinyl Chloride	1007

Results will be reported verbally as they become available.

A hard copy of the laboratory report will be forwarded to USEPA and MDNR within seven days after receipt of final laboratory data by CRA.

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2.2.3 Sampling Protocol

All sampling was performed in accordance with the methodology detailed within the St. Louis plant site Post-Closure Maintenance and Monitoring Plan, as approved by USEPA and MDNR. A copy of the sampling protocol is contained in Appendix B.

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3.0 SITE PERIMETER CONTAINMENT WALL MONITORING

3.1 GENERAL

The monitoring program consisting of the collection of an undisturbed sample of the containment wall with subsequent permeability testing was initiated on December 15, 1983. Subsequent sampling events occurred on March 15, 1984, June 15, 1984, September 14, 1984, December 14, 1985 and March 16, 1985. The current sampling event occured June 19, 1985. All testing completed to date has confirmed the permeability of the site perimeter containment wall to be less than 1.0 x 10-7 cm/sec.

3.2 EQUIPMENT

A Mobil Truck mounted drill rig equipped with rotary head and 6-inch diameter augers was utilized to advance the borehole into the containment wall. A 3-inch diameter Shelby tube, hydraulically pushed and retrieved, was used to collect the samples.

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3.3 SAMPLE COLLECTION

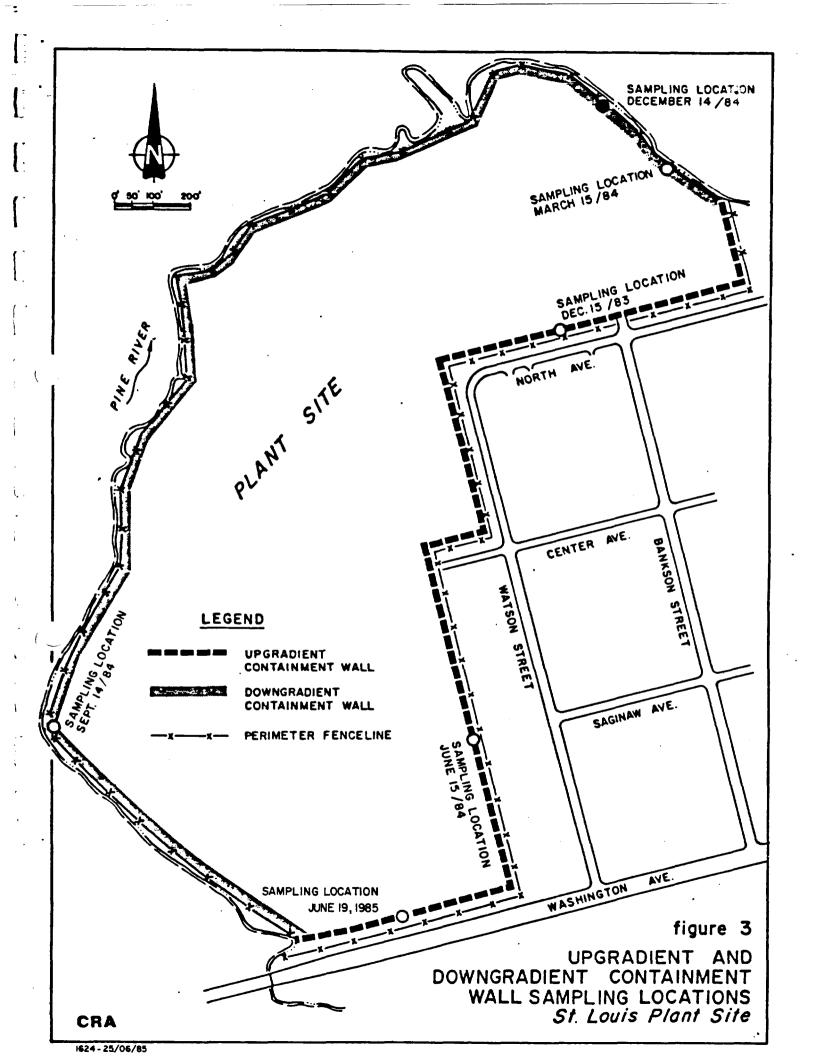
The containment wall was located by field survey on June 19, 1985. The sampling borehole was begun at Station DGW 31+00 by augering through the clay cap into the underlying material.

The presence of soil/bentonite backfill material was confirmed by examination of cuttings on the auger flights. A borehole was advanced to a depth of seven feet. A Shelby tube was introduced into the borehole and a sample was withdrawn. Examination of material in the base of the tube confirmed that the sample was obtained from the containment wall. The locations of this and prior sampling events are detailed on Figure 3. The boreholes were backfilled with bentonite and abandoned.

3.3.1 Sample Preparation and Shipping

The Shelby tube was capped and taped at both ends to prevent sample loss and drying. The sample was hand delivered to the Michigan Testing Engineer's laboratory in Detroit, Michigan for permeability testing.

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3.3.2 Sample Testing

The undisturbed sample is to be tested for permeability using a falling head permeameter set up in accordance with ASTM D 2434. Results of the testing will be provided in written form to USEPA and MDNR within seven days after receipt of final laboratory data by CRA. A summary data report will be prepared and presented to both Agencies following completion of the containment wall monitoring program in the fall of 1986.

4.0 GROUNDWATER TABLE MONITORING

4.1 GENERAL

The monitoring of plant site groundwater elevation was performed and the elevation of the St. Louis reservoir was determined on June 19, 1985.

4.2 WATER LEVEL DETERMINATION

The elevation of the groundwater was determined by measuring the distance from the top of each site monitoring well to the watertable. This distance was measured by lowering a chalked, weighted surveyors tape into the monitoring well. Readings of the tape, which was graduated in increments of one one-hundredth of a foot, were taken at the water level and at the top of the well casing. The former reading was deducted from the latter and the resultant dimension was subtracted from the previously established top of well casing elevation. Well head and watertable elevations are presented on Table 1.

The elevation of the St. Louis reservoir was determined by level and rod survey.

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TABLE 1

WATER LEVEL MEASUREMENTS

JUNE 19, 1985

MONITORING WELL	WELL HEAD ELEVATION (AMSL)	MEASURED DISTANCE TO WATER TABLE (ft.)	WATERTABLE ELEVATION (AMSL)
1	735.91	14.07	721.84
2	742.06	19.33	722.73
3	749.91	27.58	722.33
4	736.00	13.63	722.37
5	739.35	17.73	721.62
6	734.48	12.95	721.53
7	733.98	12.20	721.78
8	734.30	13.04	721.26
9	734.60	13.21	721.39
10	733.48	12.16	721.32
11	734.47	13.05	721.42
12	730.78	9.39	721.39
13	734.49	13.06	721.43
14	736.00	14.44	721.56

Water	level	elevation,	St.	Louis	Reservoir	
(June	19, 1	985)				720.03

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4.3 GROUNDWATER CONTOUR MAP

The groundwater elevation data were used to construct a site groundwater elevation contour map which is presented in Figure 4.

4.4 SITE MEAN GROUNDWATER ELEVATION

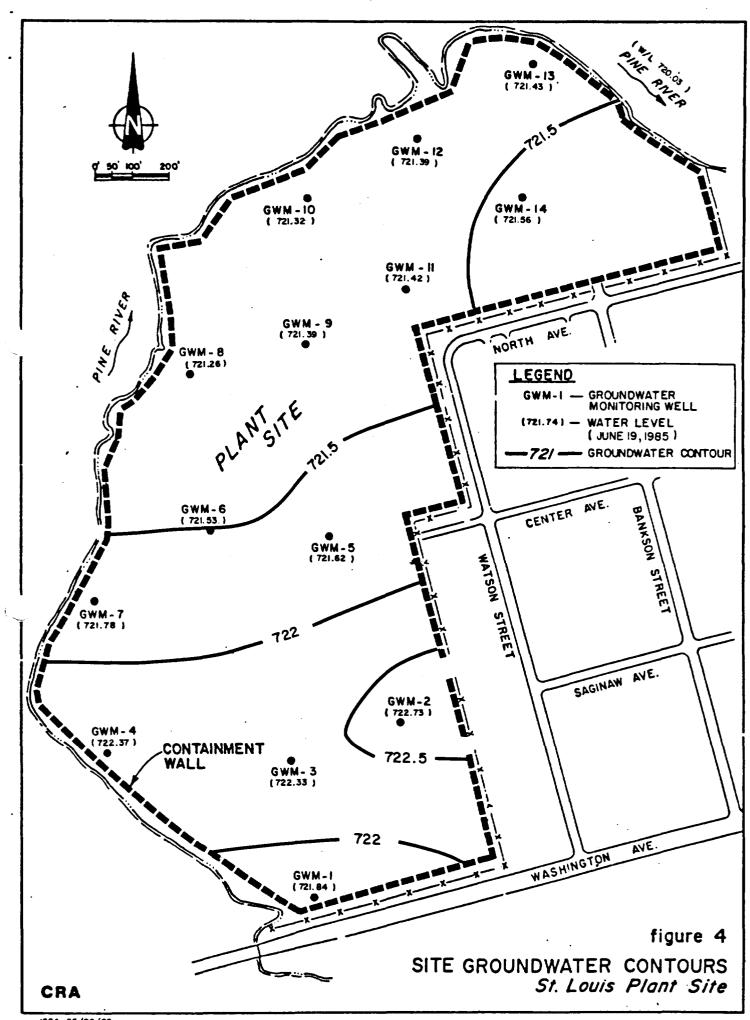
The mean elevation of site groundwater is calculated to be 721.71. The maximum allowable site groundwater elevation stipulated by the Consent Judgment is 724.13.

4.5 WELL HEAD ELEVATION SURVEY

In accordance with the Post Closure Maintenance and Monitoring Plan, the well head elevations were re-surveyed to ensure accuracy of the elevations. Minor differences from previous surveys were recorded and the groundwater elevations were adjusted accordingly.

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5.0 SUMMARY

All monitoring activities stipulated by the Consent Judgment were carried out between June 19 and 21, 1985.

Data from the chemical analysis of the gas vent samples and the permeability testing of the contaminant wall sample will be provided to MDNR and USEPA within seven days of receipt by CRA of laboratory final data.

The present mean site groundwater table elevation is calculated to be 721.71. The elevation in the Pine River/St. Louis reservoir was determined to be 720.03.

The next sampling and monitoring event will occur on or about September 15, 1985.

All of Which is Respectfully Submitted, CONESTOGA-ROVERS & ASSOCIATES LIMITED

D. Robinson

R.G. Shepherd, P. Eng.

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APPENDIX A

CHAIN OF CUSTODY

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4-1988 C.	967 92 - 1989	4) () () () ()	Carlos College Sa	1.400 A.M.M.		TOTAL Nº. OF CONTAINERS		

CHAIN OF CUSTODY RECORD

PROJECT Nº. 1524

PLANT SITE ST. LOUIS, MICHIGAN VELSICOL CHEMICAL CORPORATION 701 W. WASHINGTON STREET ST. LOUIS, MICHIGAN 48880

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APPENDIX B

GAS SAMPLING PROTOCOLS

APPENDIX B

GAS VENT SAMPLING PROTOCOL

In accordance with the Consent Judgment, Velsicol has submitted a post-closure maintenance and monitoring plan for its environmentally secured plant site in St. Louis, Michigan. The post-closure maintenance and monitoring plan requires quarterly monitoring of 11 gas vents that have been installed to release and appropriately treat internal gases. This program will be conducted over a period of three years.

The gas vents, as detailed in Exhibit F of the Consent Judgment, are designed with two sampling ports; one below the base of the installed activated charcoal filter, and one above the filter. Samples will be collected from the downstream port. Results will indicate whether or not containment breakthrough has occured through the carbon filter.

Samples will be analyzed for three separate compounds: carbon tetrachloride, trichloroethylene and vinyl chloride.

Samples will be collected with a Gilian HFS-113 AU DK variable flow pump. This particular unit allows the operator to run a series of tubes concurrently in parallel arrangement. Four tubes will be collected from each gas vent: two standard NIOSH 100/50 mg activated charcoal tube, and two 30/15 mg tenax tubes, each tube measuring 6 mm x 70 mm. One blank set and one duplicate set of tubes will be collected during each quarterly sampling event.

As vinyl chloride represents the least adsorptive of the three compounds, the sampling program is designed to accomodate this compound. Therefore, sample volume shall not exceed 5 liters.

Prior to sampling, the vent will be sealed off with a plastic cap, and purged for 10 minutes at a rate of 500 cc/min. This is to eliminate the possibility of sampling atmospheric air contained within the upper portion of the gas vent.

Two samples from each gas vent shall be collected simultaneously at a rate of 250 cc/min. for 20 minutes. The pump shall be lab calibrated with sample tubes in-line to determine the exact flow rate. Additionally, flow will be checked after field sampling to verify that a constant flow was maintained throughout the sampling period.

Following sample collection, each tube will be sealed with a plastic cap at each end, labelled, placed in a cold storage environment and shipped under chain-of-custody via a commercial courier service to Velsicol's analytical laboratory in Memphis.

Analysis of the charcoal tube will be conducted in accordance with NIOSH protocol as detailed below:

No.

Compound	Revised Method
Carbon Tetrachloride	1003
Trichloroethylene	5-336
Vinyl Chloride	1007

Analysis will proceed by first eluting the carbon sample tubes with carbon disulfide and then analyzing by GC with a flame ionization detector. All samples will be initially analyzed in this fashion. If any of the above compounds are detected on the charcoal tube, the corresponding tenax tube will be analyzed by thermal desorption and GC/MS under EPA Method 624.

Turnaround time for the completed analysis at the laboratory is anticipated to be 30 days from date of sample collection. Samples will be desorbed within the 10 day limit specified for vinyl chloride. Analytical data will be reported to CRA as mg/tube. Final results for the carbon tube will be calculated by CRA, using the following formula.

1. Corrections for the blank to be made for each sample
 mg = mg sample - mg blank

This calculation is performed separately for each tube.

- 2. Add the amounts present in the front tube and backup tube to determine the total weight in the sample.
- 3. Calculate the corrected mg/sample by dividing the total weight by the desorption efficiency (D.E.) which is provided by the lab.

corrected mg/sample = total weight DE

- 4. Calculate the concentration of the analyte in air $mg/m^3 = \frac{Corrected mg x 1000 liters/m^3}{Air volume Sampled (liters)}$
- 5. Concentration will be reported as ppm, corrected to standard conditions of 25°C and 760 mm Hg

 $ppm = mg/m \quad x \quad \frac{24.45}{MW} \quad \frac{x}{P} \quad \frac{(T+273)}{298}$

3

where	P T	<pre>= pressure (mm Hg) of air sampled = temperature (°C) of air sampled</pre>
	24.45	= molar volume (liter/mole) at 25°C and 760 mm Hg
	MW	= Molecular Weight
	760	= standard pressure (mm Hg)
	298	= standard temperature (*K)

- 2 -

- NOTE: Temperature and pressure uncorrected to sea level will be collected for the duration of the sampling event and averaged for use in the above calculations. Information will be provided from the National Weather Service in Lansing, Michigan.
 - 6. If the concentration of the back tube exceeds 10% of the concentration of the front tube, the results will be reported as a sample breakthrough and possible sample loss.
 - 7. A similar procedure will be followed for the tenax tube, should analysis be required.

Data will be reported to USEPA and MDNR officials within seven days after receipt of final laboratory data for each quarterly sampling. Additionally, a summary data report will be provided at the conclusion of the three year sampling period, or sooner, should breakthrough of any compound occur prior to the three year program.

In addition to the set of field blanks to be collected per quarterly sampling event, an additional set of 15 charcoal tubes and 15 tenax tubes will be forwarded unopened to the lab during the initial sampling event.

These "blank" tubes will be used as internal calibration standards on which each of the three compounds will be spiked at five different concentrations. The data from this analysis will be used to calculate the desorption efficiency for a specific lot of activated charcoal. Therefore, the lot number of carbon tubes and tenax tubes shall be recorded during each quarterly sampling. Should the lot number change, a new set of 15 charcoal tubes and 15 tenax tubes shall be forwarded to the laboratory for determination of the new desorption efficiency.

The allowable limits for these compounds have been established by the MDNR and are site specific for the St. Louis site. These limits are documented in section 4.3 of the post-closure maintenance and monitoring plan.

Copies of all three analytical protocols, the chain of custody and the data collection sheet are provided in the following sections.

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HYDROCARBONS, HALOGENATED

FORMULA: Table 1

M.W.: Table 1

METHOD: 1003 ISSUED: 2/14/84

COMPOUNDS: benzyl chloride (synonyms bramoform in Table]) carbon tetrachloride chlorobenzene

C 1401 7110

chloroform o-dichlorobenzene p-dichlorobenzene

chlorobromomethane 1,1-dichloroethane hexachloroethane 1,2-dichloroethylene methylchloroform ethylene dichloride propylene dichloride

SAMPLING	MEASUREHENT
	!
SAMPLER: SOLID SORBENT TUBE	!TECHNIQUE: GAS CHROMATOGRAPHY, FID
(coconut shell charcoal, 100 mg/50 m	g)!
	ANALYTE: compounds above
FLOW RATE: 0.01 to 0.2 L/min	!
	DESORPTION: 1 mL CS2, stand 30 min
VOL-MIN: Table 2	1 · ·
-MAX: Table 2	INJECTION VOLUME: 5 µL
SHIPMENT: routine	! !TEMPERATURES: Table 2
	!
SAMPLE STABILITY: at least 1 week @ 25 °C	CARRIER GAS: N ₂ or He, 30 mL/min
BLANKS: 2 to 10 field blanks per set	: !COLUMN: Table 2; alternates are SP-2100,
	SP-2100 with 0.1% Carbowax 1500
<u> </u>	: or DB-1 fused silica capillary column
ACCURACY	1
	CALIBRATICH: solutions of analyte in CS- with
136 STUDIO: HE FUILLINE DE CENTER [1]	an a
BIAS: not significant [1]	IRANGE: Table 2
OVERALL PRECISION (s _p): see EVALUATION OF METHOD [1]	ESTIMATED LOD: 0.01 mg per sample [2]
	PRECISION (Sp): See EVALUATION OF METHOD [1]

APPLICABILITY: This method uses a simple desorption and can be used for simultaneous analysis of two or more substances suspected to be present by changing the gas chromatographic conditions (i.e., temperature programmed). High humidity during sampling will prevent organic vapors from being trapped efficiently on the sorbent and greatly decreases breakthrough volume.

INTERFERENCES: None identified. The chromatographic column or separation conditions may be changed to circumvent interference problems.

OTHER METHODS: This method combines and replaces Methods P&CAM 127 [3]; S95, S101, S110, S113, \$114, \$115, \$122, \$123 and \$133 [4]; and \$135, \$281, \$314, \$328 and \$351 [5].

1003-1

a. Remove and discard back sorbent section of a media blank sampler.

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- b. Inject a known amount of analyte or calibration stock solution directly onto front sorbent section with a microliter syringe.
- c. Cap the tube. Allow to stand overnight.
- d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
- e. Prepare a graph of DE vs. mg analyte recovered.
- 10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1003-1. Inject sample aliquot manually using solvent flush technique or with autosampler.

NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.

12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of analyte found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.

NOTE: If $W_p > W_{f}/10$, report breakthrough and possible sample loss.

:

14. Calculate concentration, C, of analyte in the air volume sampled, V (L):

$$C = \frac{(W_{f} + W_{b} - B_{f} - B_{b}) \cdot 10^{3}}{V}, mg/m^{3}.$$

EVALUATION OF METHOD:

Laboratory testing was performed with spiked samples and generated atmosphere [1]. All analytes are stable at least one week. All methods were validated using SKC Lot 105 coconut shell charcoal. Results were:

1003

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METHOD: 1003

- [9] Criteria for a Recommended Standard...Occupational Exposure to 1,1,1-Trichloroethane, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 76-184 (1976).
- [10] Criteria for a Recommended Standard...Occupational Exposure to Carbon Tetrachloride, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 76-133 (1976).

METHOD REVISED BY: G. D. Foley; Y. T. Gagnon; and K. J. Williams, NIOSH/DPSE; methods originally validated under NIOSH Contract CDC-99-74-45.

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1003-5

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Compounds	Formula	M.W.; mg/m ³ <u>=) ppm</u>	Synonyms	OSHA NIOSH [6-10] ACGIH	<u>BP (°C)</u>	VP () 20 °C	Density (g/mL @ 20 °C)
p-Dichlorobenzene	1,4-C ₆ H ₄ C1 147.00; 6.01		! dichlorobenzene; (° #106-46-7	75 ppm 75 ppm, STEL 110 ppm	174	50 Pa	1.241
l,1-Dichloroethane	al ₃ aic1 ₂ ; C ₂ H ₄ C1 ₂	98.96; 4.05	ciliy lidene chioride; (%) #15-34-3	100 ppm 100 ppm 200 ppm, STEL 250 ppm	57	24.3 kPa	1. 174
1,2-Dichloroethylene	C1CH=CHC1; C_H_C1 2_4_2	96.95; 3.96	acetylene dichloride; 1,2-dichloroethene; C.J. #540-59-0	200 ppm 200 ppm 200 ppm, 200 ppm, STEL 250 ppm	60 (cis) 47 (trans)	24-35 kPa	1.28
Ethylene dichloride*	c1cH ₂ CH ₂ C1; C ₂ H ₄ C1 ₂	98.96; 4.05	1,∷-dich1oroethane; C→ #107-06-2	50 ppm, C 100 ppm 5 ppm; 15 ppm/15 min	83	8.3 kPa	1.255
	•	• • •	•	10 ppm, STEL 15 ppm	2		·
Hexach loroethane*	cc1 ₃ cc1 ₃ ; c ₂ c1 ₆	236.74; 9.68	p. (chloroethane; () #61-72-1	l ppm (skin) l ppm (skin) 10 ppm	187 (sublines)	30 Pa	2.09
Nethylchloroform	ai ₃ cci ³ ; c ⁵ H ³ ci ³	133.42; 5.45	1, 1, 1-trichloroethane; (5 #71-55-6	350 ppm 350 ppm/15 min CAS #71–55–6 STEL 450 ppm	74 350 ppm,	13.3 kPa	1.335
Propylene dichloride	ai ₃ chc1ai ₂ c1; c ₃ H ₆ c1 ₂	112.99; 4.62	1,∵-dich1oropropane Crav #78-87-5	75 ppm 75 ppm 75 ppm, STEL 110 ppm	95	5.3 kPa	1.156 (25 °C)

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*Suspect carcinogen.

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HYDROCARBONS, HALOGENATED

1		Sampl	ing			Neasur	ement	
Compound	Air Sample <u>Volume (L)</u> <u>Min</u>		Breaktheough	Working Range (mg/m ³)	<u>Column*</u>	<u>t (°C)</u> Column Injector <u>Detector</u>	Interna) Standard	Range (mg per sample)
1,1-Dichloroethane	1 @ 100 ppm	10	18.3 L → ì3 mg/m ³	40 to 1215 (10 L)	A	50 100 175		0.4 to 12
1,2-Dichloroethylene	0.5 @ 200 ppm	3	5.4 L € 009 mg/m ⁹	80 to 2370 (3 L)	۸	60 170 210		0.2 to 1
Ethylene dichloride	1 @ 50 ppm	10	29 L 3 /	40 to 1215 (3 L)	٨	10 225 250	octane	0.1 to 4
Hexachloroethane	101ppm	10	43 L (/ //m ³	1 to 30 (10 L)	D	110 110 210	n-tridecane	0.01 to 0,3
Hethylchloroform	0.5 @ 350 ppm	6	9.5 L v - /08 mg/m ³	190 to 5700 (3 L)	٨	10 225 250	octane	0.6 to 17
Propylene dichloride	1 @ 75 ppm	10	18 L 🗧 ing/m³	35 to 1050 (10 L)	۸	80 170 210	n-undecane	0.3 to 10

2/15/84

*A = 3'm x 3 an stainless steel, 10% SP-1000 and a

100 mesh Supelcoport;

 $B = \delta m \times 3$ in, other is same as A;

C = 3 m x 3 mm stainless steel, 10% OV-101 mmD = 3 m x 6 mm glass, 17 SP-2250 on 80/109 mm

120 mesh Supelcoport; or

al elcoport.

HYDROCARBONS, HALOGENATED

1003

Trichloroethylene

Analyte:	Trichloroethylene	Method No.: S336
Matrix:	Air	Range: 519-2176 mg/cu m
OSHA Standard:	200 ppm (1075 mg/cu m)-Ceiling 100 ppm (535 mg/cu m)-T.W.A.	Precision (\overline{CV}_{T}) : 0.082
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 6/6/75

1. Principle of the Method

- 1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.
- 1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.
- 1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.
- 1.4 The area of the resulting peak is determined and compared with areas obtained from injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 519-2176 mg/cu m at an atmospheric temperature and pressure of 24.5°C and 759.4 mm Hg, using a 3-liter sample. Under the conditions of sample size (3 liters) the probable useful range of this method is 108-3225 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 9.7 mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 42 mg of analyte when a test atmosphere containing 2266 mg/cu m of analyte in air was sampled at 0.187 liters per minute for 99 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent.

(The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

- 3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.
- 3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.
- 3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.
- 3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation $(\overline{CV_T})$ for the total analytical and sampling method in the range of 519-2176 mg/cu m was 0.082. This value corresponds to an 88.2 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.
- 4.2 On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 6.4 % lower than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result.

These data are based on validation experiments using the internal standard method.

- 5. Advantages and Disadvantages of the Method
 - 5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

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The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

- 5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.
- 5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

- 6.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3).
- 6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane form. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane form is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.
- 6.3 Gas chromstograph equipped with a flame ionization detector.
- 6.4 Column (10-ft x 1/8-in stainless steel) packed with 10% OV-101 stationary phase on 100/120 mesh Supelcoport.
- 6.5 An electronic integrator or some other suitable method for measuring peak areas.
- 6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.
- 6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 1.0 ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

- 7.1 Chromatographic quality carbon disulfide.
- 7.2 Trichloroethylene, reagent grade
- 7.3 Octame, or other suitable internal standard
- 7.4 Purified nitrogen
- 7.5 Prepurified hydrogen.
- 7.6 Filtered compressed air.

8. Procedure

- 8.1 Cleaning of equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.
- 8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.
- 8.3 Collection and Shipping of Samples
 - 8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).
 - 8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.
 - 8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.
 - 8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.
 - 8.3.5 At the ceiling and peak concentrations, a sample size of 3 liters is recommended. Sample for 15 minutes at a flow of 0.2 liters per minute. At the T.W.A. concentration, a sample size of 10 liters is recommended. Sample at a flow of 0.2 liters per minute or less. The flow rates should be known with an accuracy of at least +5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

- 8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.
- 8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.
- 8.3.9 Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.
- 8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.
- 8.4 Analysis of Samples
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 - 8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container. The separating section of fosm is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.
 - 8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.
 - 8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

30 ml/min (60 psig) Nitrogen carrier gas flow
 35 ml/min (25 psig) Hydrogen gas flow to detector
 400 ml/min (60 psig) Air flow to detector
 225°C injector temperature
 5. 250°C manifold temperature. (detector) and the second se

- 8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.
- 8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.
- 8.5 Determination of Desorption Efficiency

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- 8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.
- 8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known smount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. When using an automatic sample injector, the sample injector vials, capped with Teflon-faced septa, may be used in place of the glass tubes.

Six tubes at each of three concentration levels (0.5X,1X and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 3-liter sample at the selected level. The tubes are allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 1.0 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

D.E. = <u>Average Weight (mg) recovered</u> Weight (mg) added

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg per 1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2% the standard. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. <u>Calculations</u>

- 10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.
- 10.2 Corrections for the blank must be made for each sample.

mg = mg sample - mg blank

where:

mg sample = mg found in front section of sample tube
mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

- 10.3 Add the amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.
- 10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

Corrected mg/sample = Total weight D.E.

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

10.6 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$ppm = mg/cu m x \frac{24.45}{MW} x \frac{760}{P} x \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled T = temperature (°C) of air sampled 24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg MW = molecular weight 760 = standard pressure (mm Hg) 298 = standard temperature (°K)

11. References

- 11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," <u>Amer. Ind. Hyg. Assoc. J.</u>, <u>31</u>: 225 (1970).
- 11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.
- 11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

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VINYL CHLORIDE

FORMULA: CH2=CHC1; C2H3C1

METHOD: 1007 ISSUED: 2/15/84

M.W.: 62.50

OSHA: 1 ppm; C 5 ppm NIOSH: minimum measurable ACGIH: 5 ppm (human carcinogen) [1] (1 ppm = 2.56 mg/m² @ NTP) PROPERTIES: BP -14 °C; vapor density 2.2 (air = 1)

SYNONYMS: chloroethylene; chloroethene; CAS #75-01-4.

SAMPLING	MEASUREMENT
SAMPLER: SOLID SORBENT TUBE	
	TECHNIQUE: GAS CHROMATOGRAPHY, FID
(2 tandem tubes, each with 150 mg activated coconut charcoal)	: !ANALYTE: vinyl chloride
	1
FLOW RATE: 0.05 L/min	:DESORPTION: 1 mL carbon disulfide; 30 min
VOL-MIN: 0.7 L	INJECTION ALIQUOT: 5 µL
-MAX: 5 L	••••••••••••••••••••••••••••••••••••••
	COLUMN: stainless steel, 6.1 m x 3.2 mm, 10%
SHIPMENT: separate primary and backup tubes	! SE-30 on 80/100 mesh Chromosorb W
and cap each	! (AH-OMCS)
	:
SAMPLE STABILITY: 10 days @ 25 °C	CARRIER GAS: He, 40 mL/min
BLANKS: 2 to 10 field blanks per set	: !TENPERATURE-INJECTOR: 230 °C
	! -DETECTOR: 230 °C
	-COLUMN: 60 °C
ACCURACY	• • • • • • • • • • • • • • • • • • •
	CALIBRATION: solutions of vinyl chloride in CS2
RANGE STUDIED: 1 to 64 mg/m ³ [2]	!
	RANGE: 0.002 to 0.2 mg per sample [2]
BIAS: -6% of calculated concentration [2]	!
	ESTINATED LOD: 0.00004 mg per sample [2]
OVERALL PRECISION (ST): 0.06 [2]	
	PRECISION (sp): not determined

APPLICABILITY: The working range is 0.4 to 40 mg/m³ (0.16 to 16 ppm) for a 5-L air sample. The method is applicable to 15-min samples at concentrations of 1 ppm or higher.

INTERFERENCES: Other than the possibility of loss of sample upon storage of two weeks or more at room temperature, none have been noted.

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OTHER METHODS: This is a revision of P&CAM 178 [3].

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VINYL CHLORIDE

REAGENTS:

- Carbon disulfide,* chromatographic guality.
- Vinyl chloride,*, 99.9%, in lecture bottle fitted with valve and septum.
- Calibration stock solution, 0.26 mg/mL.
 - a. Insert the tip of a gas syringe containing 1 mL vinyl chloride gas under the surface of 5 mL CS₂ in a 10-mL volumetric flask.
 - b. Open the value of the syringe and withdraw the plunger to pull CS₂ into the barrel. (As vinyl chloride dissolves, a vacuum will be created, pulling CS₂ into the syringe.)
 - c. Push the solution from the syringe into the flask. Rinse the syringe twice with 1-mL portions of CS₂ and add the washings to the flask.
 - d. Dilute to the mark with CS2.
- 4. Helium, purified.
- 5. Hydrogen, purified.
- 6. Air, filtered.

*See Special Precautions.

- EQUIPHENT:
- 1. Sampler: two tandem glass tubes, 7 cm long, 6 mm 00, 4 mm ID, flame-sealed ends, each containing 150 mg of 20/40 mesh activated (600 °C) coconut shell charcoal. A silylated glass wool plug precedes the charcoal beds and a 3-mm urethane foam plug follows the charcoal beds. Plastic caps are included for sealing after use. Pressure drop across each tube at 1 L/min airflow must be less than 3.4 kPa.
 - NOTE: A pair of two-section (100 mg/50 mg) tubes may be used.
- 2. Personal sampling pump, 0.05 L/min, with flexible connecting tubing.
- 3. Gas chromatograph, flame ionization detector, integrator and column (page 1007-1).
- 4. File.
- 5. Bent wire for removing plugs from sampling tube.
- Vials, 2-ML, glass with PTFE-lined septa and crimp-on seals.
- Volumetric flasks, 10-mL, with polyethylene stoppers.
- Pipettes, delivery, 1.0-mL, graduated in 0.1-mL increments, 2- and 5-mL, with pipet bulb.
- 9. Air sampling bags, Tedlar, 10-L.
- 10. Gas syringe, with gas-tight valve, 0.1- and 1-mL.
- 11. Syringe, 10-µL, with 0.1-µL graduations.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = -30 °C); work with it only in a hood.

Vinyl chloride is a human carcinogen []].

SAMPLING:

- 1. Calibrate each personal sampling pump with a representative sampler in line.
- Break the ends of the tubes immediately before sampling. Attach two tubes, with ends touching, with a short piece of tubing. Label one tube as the back tube and insert the back tube into the flexible tubing attached to the personal sampling pump.
- 3. Sample at 0.05 L/min for 15 to 100 min. Do not sample more than 5 L of air.
- 4. Separate the primary and backup tubes and cap each tube for shipment.

SAMPLE PREPARATION:

- 5. Add 1.0 mL CS₂ to an empty vial. Loosely cap the vial.
- .6. Score each sampler tube with a file in front of the glass wool plug. Break the tube at the score line.

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HETHOD: 1007

- 7. Transfer the charcoal from the front and back tubes to separate vials. Discard the glass wool and foam plugs. Seal the vials with septum caps immediately.
- 8. Allow to stand for 30 min, with occasional agitation. Analyze the sample within the next 30-min period.

CALIBRATION AND QUALITY CONTROL:

- 9. Calibrate with at least five working standards covering the range 0.0002 to 0.2 mg per sample.
 - a. Add known amounts of calibration stock solution to CS_2 in 10-mL volumetric flasks and dilute to the marks, using serial dilution as appropriate.
 - NOTE: Working standards can be stored at -20 °C for at least three days.
 - b. Analyze together with samples and blanks (steps 12 and 13).
 - c. Prepare calibration graphs of peak area vs. quantity (mg) of vinyl chloride per tube and peak area vs. quantity (ng) per injection.
- Determine desorption efficiency (DE) at least once for each lot of charcoal used in the calibration range (step 9). Prepare three tubes at each of five levels plus three media blanks.
 - a. Prepare three atmospheres of vinyl chloride in air by injecting 0.01, 0.08, and 0.2 mL vinyl chloride gas into 10 L air in Tedlar bags. The resulting concentrations are approximately 2.6, 21 and 52 mg/m³.
 - b. Following steps 1 through 4, sample these atmospheres according to the following scheme:

Concentration in Bag (mg/m ²)	Volume Sampled (L)	Quantity of Vinyl Chloride (mg)
2.6	0.8	0.002
	2.2	0.006
21	0.8	0.017
	2.2	0.046
52	2.5	0.13

Obtain three samples at each level.

- c. Desorb (steps 6 through 8) and analyze together with working standards (steps 12 and 13). No vinyl chloride should be found on the back tubes.
- d. Analyze the atmospheres in the bags (steps 12 and 13) using 1-mL gas samples. Read from the calibration graph the quantity (ng) per injection, which for a 1-mL injection of gas is numerically equal to the concentration in mg/m^3 .
- e. Calculate DE from the mass (mg) of vinyl chloride on the front tube (W_f) , the average blank (B), the concentration of vinyl chloride in the synthetic atmospheres $(C_s, mg/m^3)$, and the volume of air sampled (V, L):

$$DE = \frac{(H_{f} - B) \cdot 10^{3}}{(C_{e}) (V)}$$

f. Prepare a graph of DE vs. mass found $(W_f - B)$.

11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

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VINYL CHLORIDE

HEASUREMENT:

12. Set the gas chromatogrph according to manufacturer's instructions and to conditions given on page 1007-1. Inject sample aliquot manually using solvent flush technique or with , autosampler. The retention time of vinyl chloride is about 1.7 min.

NOTE: If peak area is above the linear range of the working standards, dilute with CS₂, reanalyze and apply the appropriate dilution factor in calculations.

13. Measure peak area.

CALCULATIONS:

14. Determine the mass, mg (corrected for DE) of vinyl chloride found in the sample front $(M_{\rm F})$ and back $(M_{\rm D})$ tubes, and in the average media blank (B).

MOTE: If $W_{\rm b} > W_{\rm f}/10$, report breakthrough and possible sample loss.

15. Calculate concentration, C, of vinyl chloride in the air volume sampled, V (L):

$C = \frac{(W_{f} + W_{D} - 2B) \cdot 10^{3}}{V} mg/m^{3}$

EVALUÁTION OF METHOD:

The method was evaluated using single 150-mg sampling tubes with 100-mg front beds and 50-mg back beds [2]. At four concentrations between 1 and 64 mg/m³, the pooled relative standard deviation was 0.06 and the measurements averaged 94% of the concentrations calculated from the volumes of vinyl chloride and air used for the atmospheres sampled; samples at the 3-µg level showed no loss of vinyl chloride when stored for 12 days at room temperature or 19 days at -20 °C. There may be significant loss of vinyl chloride from samples stored for 14 days at room temperature [4]. The 1% breakthrough capacity for a 150-mg bed of coconut charcoal challenged at 100 mL/min with vinyl chloride in air at 16 mg/m³ and a relative humidity of 70% was 4.6 L [5].

REFERENCES :

[1] <u>TLVs - Threshold Limit Values for Chemical Substances and Physical Agents in the Work</u> <u>Environment with Intended Changes for 1983-84</u>, ACGIH, Cincinnati, OH (1983).

[2] Hill, R. H., Jr., C. S. McCannon, A. T. Saalwaechter, A. W. Teass, and W. J. Woodfin. <u>Anal. Chem.</u>, <u>48</u>, 1395-1398 (1976).

[3] NIOSH Manual of Analytical Methods, 2nd. ed., V. 1, PSCAM 178, U.S. Department of Health and Human Services, Publ. (NIOSH) 77-157-A (1977).

[4] Cuddeback, J. E., W. R. Burg, and S. R. Birch, <u>Environ</u>. <u>Sci</u>. <u>Technol</u>., <u>9</u>, 1168-1171 (1975).

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[5] Matsumura, Y. <u>Ind</u>. <u>Health</u>, <u>18</u>, 61-67 (1980).

METHOD REVISED BY: A. W. Teass, Ph.D., NIOSH/DPSE.

2/15/84

VELSICOL CHEMICAL CORPORATION ST. LOUIS, MICHIGAN PROJECT Nº 1524

GAS VENT SAMPLING

COLLECTION June ZI 85	SAMPLER ROBINSON	BAROMETRIC 29.955					
TEMPERATURE TO S	RELATIVE HUMIDITY 60%	GAUGE 1 2 3 4 5 6 7 8 9 10 11					
CHARCOAL 126	TENAX LOT Nº こつし	READING PP\$					

GAS VENT	PUMP	SAMPLE		SAMPLING TIME	SAMPLING RATE	SAMPLE		
NUMBER	NUMBER	NUMBER	START	FINISH	ELAPSED	(cc/min.)	VOLUME (1)	
ł				· ·				
2				•			· · · ·	
3							. 	
4								
5			,					
6								
7	9370 9 11.14		11.14	1134	20	250	5.0	
8	9370	10	8.29	849	70	250	50	
9	9370	11	949	10.09	20	250	5.0	
10	9370	12	12.03	12.23	20	250	5.0	
11	9370	13	1326	1346	26	250	50	
DUPLICATE							• *	
BLANK								
DATE OF SAMPLE SH	IIPMENT 3.	-======================================	୫.େ METH Shipm	ENT FED. E.P	eess AwB	611 891 593		

COMMENTS

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VELSICOL CHEMICAL CORPORATION ST. LOUIS, MICHIGAN

GAS VENT SAMPLING

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PROJECT Nº 1524

DATE OF COLLECTION JUNE 20/85	SAMPLER D. Robasson	BAROMETRIC 29 935				
TEMPERATURE 63.5	RELATIVE 58.5	GAUGE 2 3 4 5 6 7 8 9 10 11				
CHARCOAL 120	TENAX LOT Nº 271	READING ØØØØØ				

GAS VENT	PUMP	SAMPLE				SAMPLING RATE			
NUMBER			START	FINISH	ELAPSED	(cc/min.)	VOLUME ()		
1	9369	١	10.20	10.40	20	250	5.0		
2	7369	3	1246	13.06	20	250	5.0		
3	9369	4	13 25	13 45	20	250	5.0		
4	9369	5	14.03	14.23	20	250	50		
· 5	9369	7	14.42	15.02	20	250	5.0		
6	9369	8	16.00	16.20	20	250	5.0		
7									
8									
9									
10									
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VELSICOL CHEMICAL CORPORATION ST. LOUIS, MICHIGAN PROJECT Nº 1524

GAS VENT SAMPLING PUMPS CALIBRATION LOG

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VELSICOL CHEMICAL CORPORATION ST. LOUIS, MICHIGAN PROJECT Nº 1524

GAS VENT SAMPLING PUMPS CALIBRATION LOG

DATE JUNE 20 1985					CALIBRATED BY D ZOBINSON											
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PUMP NUMBER	PUMP TYPE	TEMP. (°F)	HUMIDITY	BAROM. PRESSURE (Inches Hg)	INITIAL FLOW (cc/min.)	CAL. FLOW (cc/min.)	24-HR. TIME	TEMP. (°F)	HUMIDITY (%)	BAROM. PRESSURE (Inches Hg)	FLOW (cc/min.)	24-HR. TIME	TEMP. (°F)	HUMIDITY (%)	BAROM. PRESSURE (Inches Hg)	FLOW (cc/min.)
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COMMENTS



VELSICOL CHEMICAL CORPORATION

POST - CONSTRUCTION QUARTERLY MONITORING REPORT SEPTEMBER 16-17, 1985

Plant Site, St. Louis Michigan

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1.0 INTRODUCTION

1.1 GENERAL

In accordance with the terms of the technical appendix to the Consent Judgment entered into by Velsicol Chemical Corporation (Velsicol), the United States Environmental Protection Agency, (USEPA) and the Michigan Department of Natural Resources (MDNR), Velsicol is required to perform specified monitoring activities at quarterly intervals following closure of its St. Louis, Michigan plant site. The monitoring program is designed to address the following:

- 1. Performance of gas vents
- 2. Performance of the site perimeter containment wall
- 3. Determination of site groundwater elevations

This report details the site monitoring which occured during the period September 16 to September 17, 1985.

1.2 PARTICIPATION BY REGULATORY AGENCIES

The regulatory agencies did not participate in or attend this monitoring event.

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1.3 MONITORING AND SAMPLING PERSONNEL

The monitoring and sampling program was carried out by Ms. C. Cull (Conestoga-Rovers and Associates) assisted by Mr. Gene DeGeer, the Velsicol site custodian.

2.0 GAS VENT MONITORING

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2.1 GENERAL

The gas vent monitoring began on September 16, 1985 and was completed September 17, 1985.

2.1.1 Equipment

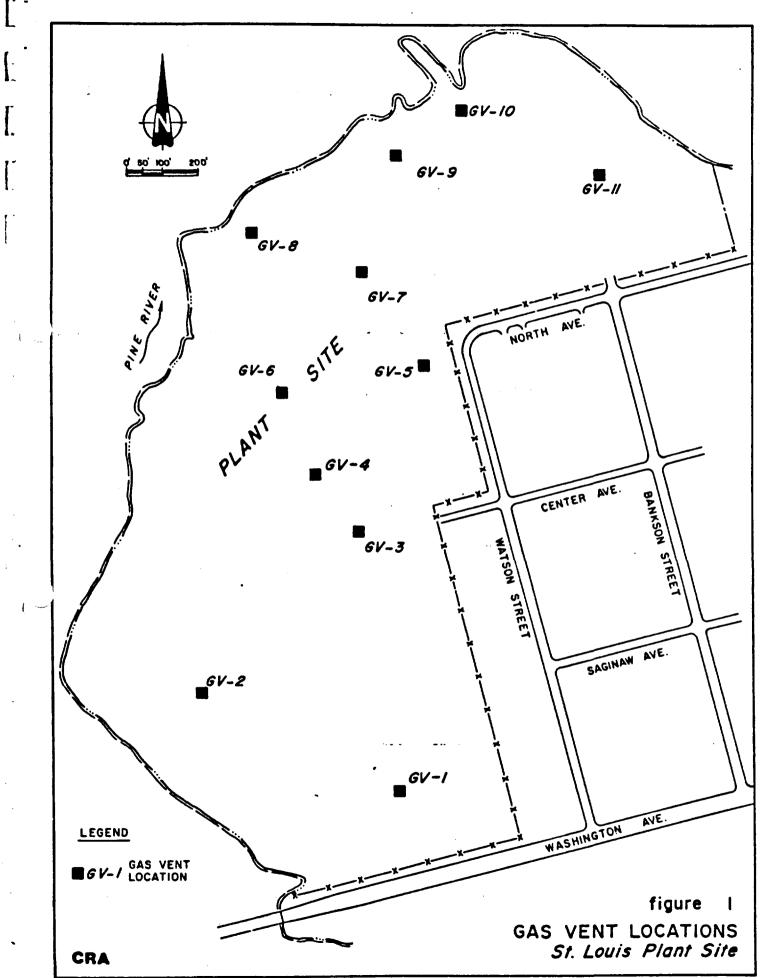
Two Gilian model HFS 113 hi flow samplers were used to collect gas vent samples. The samplers were field calibrated using a rotometer prior to sampling. The calibration data is presented within Appendix B. Samples from each gas vent were collected in two 6-mm diameter x 70-mm long Tenax tubes and two charcoal tubes of similar dimensions. The samples were collected simultaneously using dual parallel/series tube holder sets.

2.2 SAMPLE COLLECTION

Samples were obtained at each of the 11 gas vents. The location of the gas vents within the closed plant site is detailed on Figure 1. One blank set and one duplicate set of samples were also collected.

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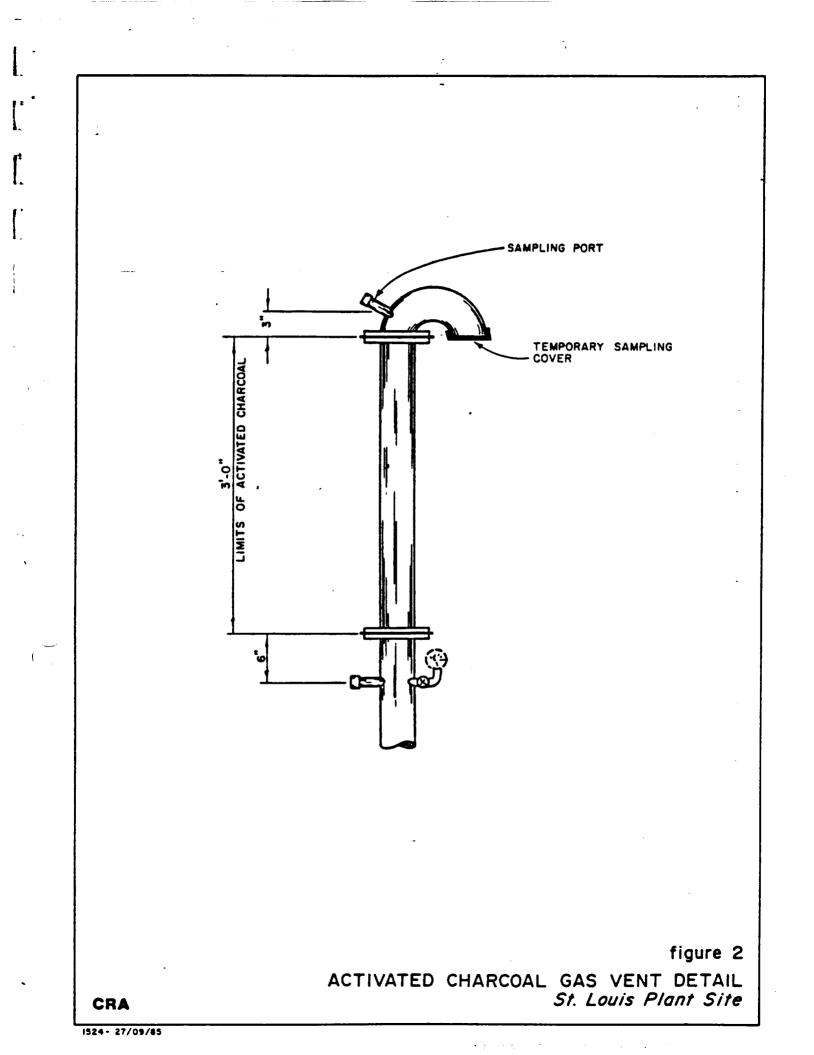


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Sampling was conducted at the downstream sampling port on each gas vent as detailed on Figure 2. The tube holder was attached directly to the gas vent sampling port using a copper manifold assembly which was environmentally cleaned prior to use. Tygon tubing was used to connect the tube holder to the sampler and was connected between the base of the tube holder and suction port of the sampler. The sampler which was pre-calibrated to 250cc/min/tube set, was operated for a period of 20 minutes for each sampling event, resulting in a collected sample volume of five liters per tube set.

Prior to sample collection, the gas vent upper chamber was purged by pumping at 500 cc/minute for a period of ten minutes. This precluded the possiblity of sampling retained atmospheric air from the gas vent upper chamber. During the purging and sampling operations, the open end of the gas vent was capped using a 4-inch diameter plastic cover to prevent atmospheric air being drawn into the sample.

At the conclusion of each gas vent sampling, the set of four sample tubes were capped, labelled and stored in a cooler maintained at 0°C.



2.2.1 <u>Sample Storage and Shipment</u>

On the afternoon of September 17, 1985 the samples were transferred to a cooler containing frozen cold packs and styrofoam packing materials. The cooler was shipped under chain of custody protocol, to Velsicol's Memphis, Tennessee laboratory by overnight courier for analysis. A copy of the chain of custody is provided in Appendix A.

2.2.2 Sample Analysis

Analysis will be conducted in accordance with NIOSH protocols as follows:

Compound	NIOSH Method
Carbon Tetrachloride	1003
Trichloroethylene	5-336
Vinyl Chloride	1007

Results will be reported verbally as they become available.

A hard copy of the laboratory report will be forwarded to USEPA and MDNR within seven days after receipt of final laboratory data by CRA.

2.2.3 <u>Sampling Protocol</u>

All sampling was performed in accordance with the methodology detailed within the St. Louis plant site Post-Closure Maintenance and Monitoring Plan, as approved by USEPA and MDNR. A copy of the sampling protocol is contained in Appendix B.

3.0 SITE PERIMETER CONTAINMENT WALL MONITORING

3.1 GENERAL

The monitoring program consisting of the collection of an undisturbed sample of the containment wall with subsequent permeability testing was initiated on December 15, 1983. Subsequent sampling events occurred on March 15, 1984, June 15, 1984, September 14, 1984, December 14, 1985, March 16, 1985 and June 19, 1985. The current sampling event occured September 16, 1985. All testing completed to date has confirmed the permeability of the site perimeter containment wall to be less than 1.0 x 10^{-7} cm/sec.

3.2 EQUIPMENT

A Mobil Truck mounted drill rig equipped with rotary head and 4-inch diameter augers was utilized to advance the borehole into the containment wall. A 3-inch diameter Shelby tube, hydraulically pushed and retrieved, was used to collect the samples.

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3.3 SAMPLE COLLECTION

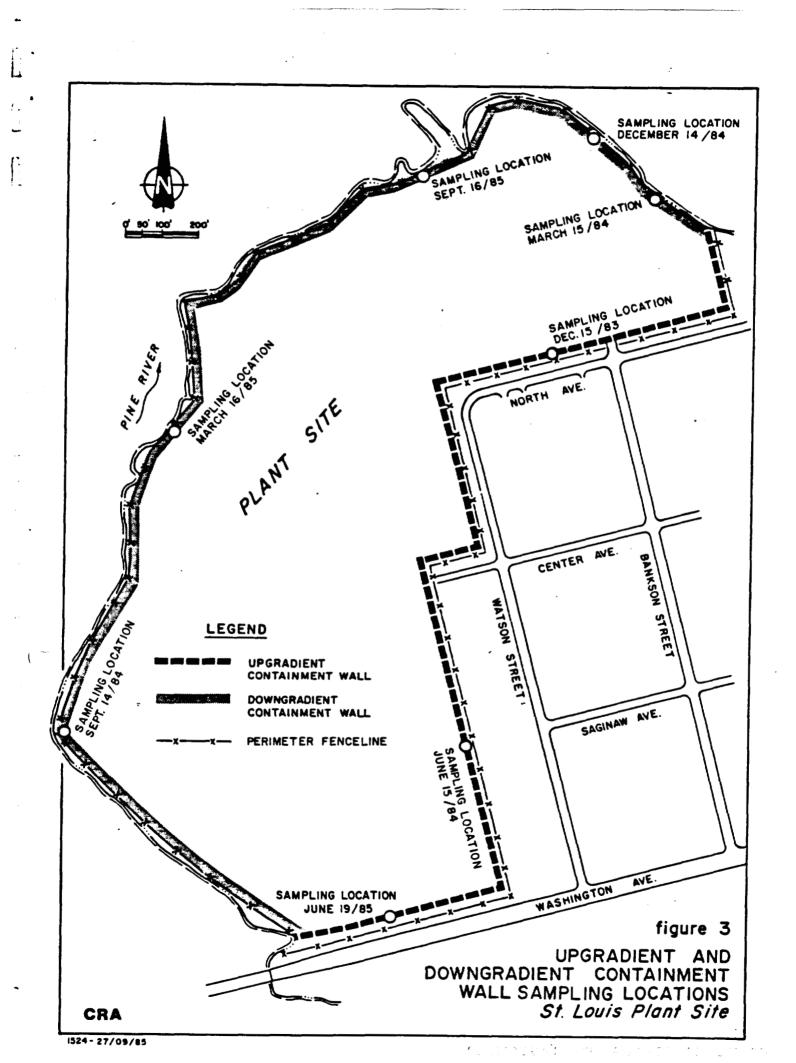
The containment wall was located by field survey on September 16, 1985. The sampling borehole was begun at Station DGW 63+25 by augering through the clay cap into the underlying material.

The presence of soil/bentonite backfill material was confirmed by examination of cuttings on the auger flights. A borehole was advanced to a depth of seven feet below grade. A Shelby tube was introduced into the borehole and a sample was withdrawn. Examination of material in the base of the tube confirmed that the sample was obtained from the containment wall. The locations of this and prior sampling events are detailed on Figure 3. The boreholes were backfilled with bentonite and abandoned.

3.3.1 Sample Preparation and Shipping

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The Shelby tube was capped and taped at both ends to prevent sample loss and drying. The sample was hand delivered to the Michigan Testing Engineer's laboratory in Detroit, Michigan for permeability testing.



3.3.2 <u>Sample Testing</u>

The undisturbed sample is to be tested for permeability using a falling head permeameter set up in accordance with ASTM D 2434. Results of the testing will be provided in written form to USEPA and MDNR within seven days after receipt of final laboratory data by CRA. A summary data report will be prepared and presented to both Agencies following completion of the containment wall monitoring program in the fall of 1986.

4.0 GROUNDWATER TABLE MONITORING

4.1 GENERAL

The monitoring of plant site groundwater elevation was performed and the elevation of the St. Louis reservoir was determined on September 17, 1985.

4.2 WATER LEVEL DETERMINATION

The elevation of the groundwater was determined by measuring the distance from the top of each site monitoring well to the watertable. This distance was measured by lowering a chalked, weighted surveyors tape into the monitoring well. Readings of the tape, which was graduated in increments of one one-hundredth of a foot, were taken at the water level and at the top of the well casing. The former reading was deducted from the latter and the resultant dimension was subtracted from the previously established top of well casing elevation. Well head and watertable elevations are presented on Table 1.

The elevation of the St. Louis reservoir was determined by level and rod survey.

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TABLE 1

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WATER LEVEL MEASUREMENTS

SEPTEMBER 17, 1985

MONITORING WELL	WELL HEAD ELEVATION (AMSL)	MEASURED DISTANCE TO WATER TABLE (ft.)	WATERTABLE ELEVATION (AMSL)
1	735.91	14.42	721.49
2	742.06	19.33	722.73
3	749.91	27.63	722.28
4	736.00	13.79	722.21
5	739.35	17.92	721.43
6	734.48	13.19	721.29
7	733.98	12.65	721.33
8	734.30	13.25	721.05
9	734.60	13.42	721.18
10	733.48	12.40	721.08
11	734.47	13.33	721.14
12	730.78	9.68	721.10
13	734.49	13.27	721.22
14	736.00	14.73	721.27

Water level elevation, St. Louis Reservoir (September 17, 1985)

719.39

4.3 GROUNDWATER CONTOUR MAP

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The groundwater elevation data were used to construct a site groundwater elevation contour map which is presented in Figure 4.

4.4 SITE MEAN GROUNDWATER ELEVATION

The mean elevation of site groundwater is calculated to be 721.49. The maximum allowable site groundwater elevation stipulated by the Consent Judgment is 724.13.

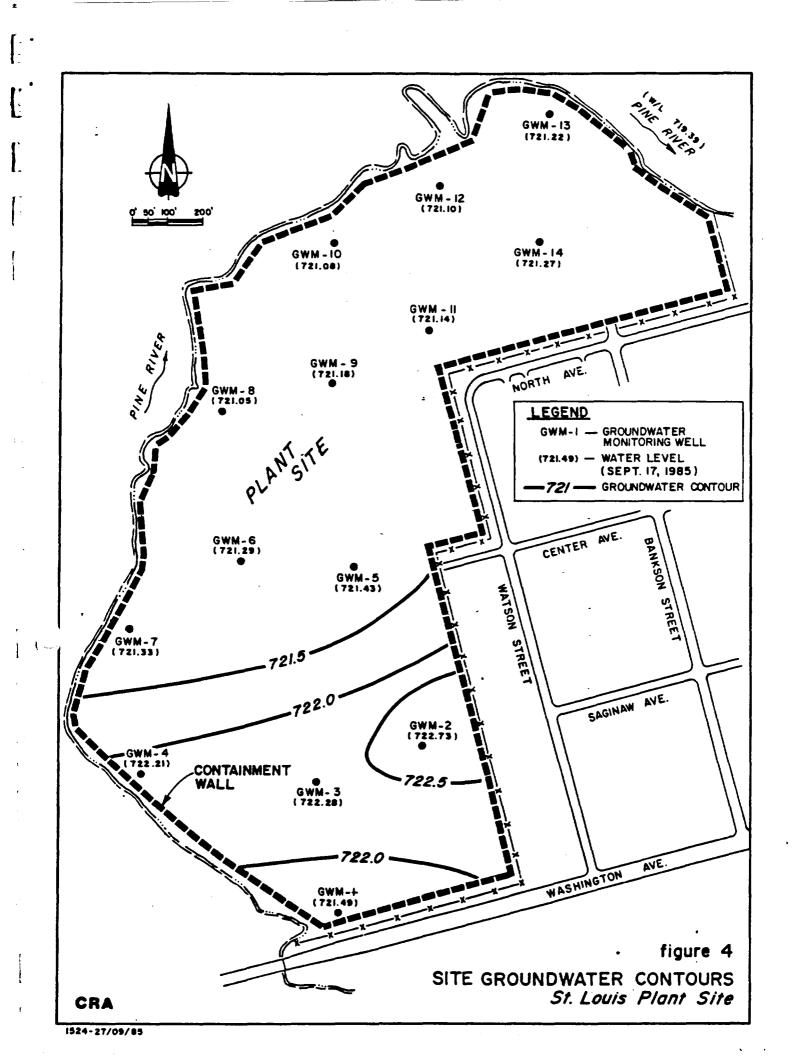
4.5 WELL HEAD ELEVATION SURVEY

In accordance with the Post Closure Maintenance and Monitoring Plan, the well head elevations were re-surveyed in March to ensure accuracy of the elevations. Minor differences from previous surveys were recorded and the groundwater elevations were adjusted accordingly. This phase of the program will be conducted yearly.

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5.0 SUMMARY

All monitoring activities stipulated by the Consent Judgment were carried out between September 16 and 17, 1985.

Data from the chemical analysis of the gas vent samples and the permeability testing of the contaminant wall sample will be provided to MDNR and USEPA within seven days of receipt by CRA of laboratory final data.

The present mean site groundwater table elevation is calculated to be 721.49. The elevation in the Pine River/St. Louis reservoir was determined to be 719.39.

The next sampling and monitoring event will occur on or about December 15, 1985.

All of Which is Respectfully Submitted, CONESTOGA-ROVERS & ASSOCIATES LIMITED

Cathens A Call

C. Cull, B.Sc.

R.G. Shepherd, P. Eng.

APPENDIX A

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APPENDIX B

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GAS SAMPLING PROTOCOLS

APPENDIX B

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GAS VENT SAMPLING PROTOCOL

In accordance with the Consent Judgment, Velsicol has submitted a post-closure maintenance and monitoring plan for its environmentally secured plant site in St. Louis, Michigan. The post-closure maintenance and monitoring plan requires quarterly monitoring of 11 gas vents that have been installed to release and appropriately treat internal gases. This program will be conducted over a period of three years.

The gas vents, as detailed in Exhibit F of the Consent Judgment, are designed with two sampling ports; one below the base of the installed activated charcoal filter, and one above the filter. Samples will be collected from the downstream port. Results will indicate whether or not containment breakthrough has occured through the carbon filter.

Samples will be analyzed for three separate compounds: carbon tetrachloride, trichloroethylene and vinyl chloride.

Samples will be collected with a Gilian HFS-113 AU DK variable flow pump. This particular unit allows the operator to run a series of tubes concurrently in parallel arrangement. Four tubes will be collected from each gas vent: two standard NIOSH 100/50 mg activated charcoal tube, and two 30/15 mg tenax tubes, each tube measuring 6 mm x 70 mm. One blank set and one duplicate set of tubes will be collected during each quarterly sampling event.

As vinyl chloride represents the least adsorptive of the three compounds, the sampling program is designed to accomodate this compound. Therefore, sample volume shall not exceed 5 liters.

Prior to sampling, the vent will be sealed off with a plastic cap, and purged for 10 minutes at a rate of 500 cc/min. This is to eliminate the possibility of sampling atmospheric air contained within the upper portion of the gas vent.

Two samples from each gas vent shall be collected simultaneously at a rate of 250 cc/min. for 20 minutes. The pump shall be lab calibrated with sample tubes in-line to determine the exact flow rate. Additionally, flow will be checked after field sampling to verify that a constant flow was maintained throughout the sampling period.

Following sample collection, each tube will be sealed with a plastic cap at each end, labelled, placed in a cold storage environment and shipped under chain-of-custody via a commercial courier service to Velsicol's analytical laboratory in Memphis.

Analysis of the charcoal tube will be conducted in accordance with NIOSH protocol as detailed below:

Compound	Revised Method No.
Carbon Tetrachloride	1003
Trichloroethylene	S-336
Vinyl Chloride	1007

Analysis will proceed by first eluting the carbon sample tubes with carbon disulfide and then analyzing by GC with a flame ionization detector. All samples will be initially analyzed in this fashion. If any of the above compounds are detected on the charcoal tube, the corresponding tenax tube will be analyzed by thermal desorption and GC/MS under EPA Method 624.

Turnaround time for the completed analysis at the laboratory is anticipated to be 30 days from date of sample collection. Samples will be desorbed within the 10 day limit specified for vinyl chloride. Analytical data will be reported to CRA as mg/tube. Final results for the carbon tube will be calculated by CRA, using the following formula.

1. Corrections for the blank to be made for each sample
 mg = mg sample - mg blank

This calculation is performed separately for each tube.

- 2. Add the amounts present in the front tube and backup tube to determine the total weight in the sample.
 - 3. Calculate the corrected mg/sample by dividing the total weight by the desorption efficiency (D.E.) which is provided by the lab.

 $ppm = mg/m \times 24.45 \times 760 \times (T+273)$

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- 4. Calculate the concentration of the analyte in air $mg/m^3 = \frac{Corrected mg \times 1000 \text{ liters/m}^3}{\text{Air volume Sampled (liters)}}$
- 5. Concentration will be reported as ppm, corrected to standard conditions of 25°C and 760 mm Hg

MW P 298
where P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = Molecular Weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

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- 2 -

- NOTE: Temperature and pressure uncorrected to sea level will be collected for the duration of the sampling event and averaged for use in the above calculations. Information will be provided from the National Weather Service in Lansing, Michigan.
 - 6. If the concentration of the back tube exceeds 10% of the concentration of the front tube, the results will be reported as a sample breakthrough and possible sample loss.
 - 7. A similar procedure will be followed for the tenax tube, should analysis be required.

Data will be reported to USEPA and MDNR officials within seven days after receipt of final laboratory data for each quarterly sampling. Additionally, a summary data report will be provided at the conclusion of the three year sampling period, or sooner, should breakthrough of any compound occur prior to the three year program.

In addition to the set of field blanks to be collected per quarterly sampling event, an additional set of 15 charcoal tubes and 15 tenax tubes will be forwarded unopened to the lab during the initial sampling event.

These "blank" tubes will be used as internal calibration standards on which each of the three compounds will be spiked at five different concentrations. The data from this analysis will be used to calculate the desorption efficiency for a specific lot of activated charcoal. Therefore, the lot number of carbon tubes and tenax tubes shall be recorded during each quarterly sampling. Should the lot number change, a new set of 15 charcoal tubes and 15 tenax tubes shall be forwarded to the laboratory for determination of the new desorption efficiency.

The allowable limits for these compounds have been established by the MDNR and are site specific for the St. Louis site. These limits are documented in section 4.3 of the post-closure maintenance and monitoring plan.

Copies of all three analytical protocols, the chain of custody and the data collection sheet are provided in the following sections.

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FORMULA: Table 1

HYDROCARBONS, HALOGENATED

M.W.: Table 1

1003 METHOD: ISSUED: 2/14/84

hexachloroethane

propylene dichloride

COMPOUNDS: benzyl chloride (synonyms bronoform in Table]) carbon tetrachloride chlorobenzene

chlorobromomethane 1,1-dichloroethane chloroform 1,2-dichloroethylene methylchloroform o-dichlorobenzene ethylene dichloride p-dichlorobenzene

SAMPLING	MEASUREMENT		
SAMPLER: SOLID SORBENT TUBE	! !TECHNIQUE: GAS CHROMATOGRAPHY, FID		
(coconut shell charcoal, 100 mg/50 mg			
FLOW RATE: 0.01 to 0.2 L/min	ANALYTE: compounds above		
	!DESORPTION: 1 mL CS ₂ , stand 30 min		
OL-MIN: Table 2	1		
-MAX: Table 2	INJECTION VOLUME: 5 µL		
SHIPMENT: routine	! !TEMPERATURES: Table 2		
AMPLE STABILITY: at least 1 week @ 25 °C	! !CARRIER GAS: N ₂ or He, 30 mL/min		
BLANKS: 2 to 10 field blanks per set	<pre>! ! COLUMN: Table 2; alternates are SP-2100, ! SP-2100 with 0.1% Carbowax 1500 ! or OB-1 fused silica capillary column</pre>		
ACCURACY	!		
nak storn de Heinen drummende der mit (1)	ICALIBRATICA: solutions of analyte in CSn with		
BIAS: not significant [1]	RANGE: Table 2		
OVERALL PRECISION (sp): See EVALUATION OF METHOD [1]	ESTIMATED LOD: 0.01 mg per sample [2]		
	PRECISION (Sp): See EVALUATION OF METHOD [1]		

APPLICABILITY: This method uses a simple desorption and can be used for simultaneous analysis of two or more substances suspected to be present by changing the gas chromatographic conditions (i.e., temperature programmed). High humidity during sampling will prevent organic vapors from being trapped efficiently on the sorbent and greatly decreases breakthrough volume.

INTERFERENCES: None identified. The chromatographic column or separation conditions may be changed to circumvent interference problems. · · · ·

OTHER METHODS: This method combines and replaces Methods P&CAM 127 [3]; 595, 5101, 5110, 5113, S114, S115, S122, S123 and S133 [4]; and S135, S281, S314, S328 and S351 [5].

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a. Remove and discard back sorbent section of a media blank sampler.

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- b. Inject a known amount of analyte or calibration stock solution directly onto front sorbent section with a microliter syringe.
- c. Cap the tube. Allow to stand overnight.
- d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).e. Prepare a graph of DE vs. mg analyte recovered.
- 10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

 Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1003-1. Inject sample aliquot manually using solvent flush technique or with autosampler.

NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.

12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of analyte found in the sample front (W_f) and back (W_D) sorbent sections, and in the average media blank front (B_f) and back (B_D) sorbent sections.

NOTE: If $W_{\rm b} > W_{\rm f}/10$, report breakthrough and possible sample loss.

14. Calculate concentration, C, of analyte in the air volume sampled, V (L):

$$C = \frac{(H_F + H_D - B_F - B_D) + 10^3}{V}$$
, mg/m³.

ENDLUSTION OF SETHOD:

Laboratory testing was performed with spiked samples and generated atmosphere [1]. All analytes are stable at least one week. All methods were validated using SKC Lot 105 coconut shell charcoal. Results were:

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METHOD: 1003

HYDROCARBONS HALOGENATED

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[9] Criteria for a Recommended Standard...Occupational Exposure to 1,1,1-Trichloroethane, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 76-184 (1976).

[10] Criteria for a Recommended Standard...Occupational Exposure to Carbon Tetrachloride, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 76-133 (1976).

METHOD REVISED BY: G. D. Foley; Y. T. Gagnon; and K. J. Williams, NIOSH/DPSE; methods originally validated under NIOSH Contract CDC-99-74-45.

2/15/84

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Compounds	formula	H.W.; mg/m ³ <u>= 1 ppm</u>	Synonyms	OSHA N1OSH [6-10] ACGIH	<u>BP (*C)</u> _	VP (* 20 °C	Density (g/mL (<u>@ 20 °C)</u>
<u>e</u> -Dichlorobenzene	1,4-c ₆ H ₄ C1 ₂	147.00; 6.01	I :-dichlorobenzene; (°∥106–46–7	75 ppm 75 ppm, STEL 110 ppm	174	50 Pa	1.241
,1-Dichloroethane	ai ₃ aici ₂ ; c ₂ ii4ci2	98.96; 4.05	eth ylidene chloride; Crap #15-34-3	100 ppm 100 ppm 200 ppm, S1EL 250 ppm	51	24.3 kPa	1.174
),2-Dichloroethylene	c101=04c1; c_H_c1 2_4_2	96.95; 3.96	acetylene dichloride; 1,2-dichloroethene; C #540-59-0	200 ppm 200 ppm 200 ppm, 5TEL 250 ppm	60 (cis) 47 (trans)	24-35 kPa	1.28
Ethylene dichloride*	c1a1 ₂ a1 ₂ c1; c ₂ 11 ₄ c1 ₂	98.96; 4.05	1, '-dichloroethane; C== #107-06-2	50 ppm, C 100 ppm 5 ppm; 15 ppm/15 mlr 10 ppm, STEL 15 ppm	83	8.3 kPa	1.255
lexach loroethane*	cc1 ₃ cc1 ₃ ; c ₂ c1 ₆	236.74; 9.60	ja i chioroethane; U. // #67-72-1	1 ppm (skin) 1 ppm (skin) 10 ppm	187 (sublines)	30 Pa	2.09
Hethylchloroform	ai ₃ cci ₃ ; c ₂ ii ₃ ci ₃	133.42; 5.45	1,1,1-trichloroethane; (350 ppm 350 ppm/15 min CAS #11-55-6 STEL 450 ppm	74 350 ppm,	13.3 kPa	1.335
Propylene dichloride	ai ₃ aiciai ₂ ci; c ₃ i6ci ₂	; 112.99; 4.62	1,2-dichioropropane Cov. #78-87-5	75 ppm 75 ppm 75 ppm, 75 ppm, 51EL 110 ppm	95	5.3 kPa	1. 156 (25 °C)

2/15/84

		Sampl	ina	Measurement					
A	Air Sample <u>Volume (L)</u>	<u></u>	Breaktiv ough	Norking Range	0-1	<u>t (°C)</u> Column Injector	Internal	Range (mg per	
Compound	Min	Max	<u>in ir Air</u>	(mg/m²)	<u>Column*</u>	Detector	Standard	sample)	
1,1-Dichloroethane	1 († 100 ppm	10	18.3 L → Դ3 mg/m ⁹	40 to 1215 (10 L)	A	50 100 175		0.4 to 12	
1,2-Dichloroethylene	0.5 @ 200 ppm	3	5.4 L € 309 mg/m ^a	80 to 2370 (3 L)	٨	60 170 210	••••	0.2 to 7	
Ethylene dichloride	1 @ 50 ppm	10	• 29 t. 3 t. ⊨ my/m³	40 to 1215 (3 L)	٨	70 225 250	octane	0.1 to 4	
Hexach1oroethane	101ppm	10	43 L 1 2	1 to 30 (10 L)	D	110 170 210	n-tridecane	0.01 to 0.3	
Methylchloroform	0.5 @ 350 ppm	6	9.5 L (- i\\8 mg/m ^a	190 to 5100 (3 L)	٨	10 225 250	oclane	0.6 to 17	
Propylene dichloride	1 (9 75 ppm	10	18 L 3 mg/m ^a	35 to 1050 (10 L)	۸	90 170 210 ,	n-undecane	0.3 to 10	

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*A = 3'm x 3 wh stainless steel, 10% SP-1060 e_{0} = 100 mesh Supercoport; B = 5 m x 3 wh stainless steel, 10% OV-101 on b_{0} +20 mesh Supercoport; C = 3 m x 3 wh stainless steel, 10% OV-101 on b_{0} +20 mesh Supercoport;

D = 3 m x 6 an glats, ... SP-2250 on 00/100 m 1

!?0 mesh Supelcoport; or palcoport. HYDROCARBONS, HALOGENATED

ETHO: 1003

Trichloroethylene

Analyte:	Trichloroethylene	Method No.: \$336
Matrix:	Air .	Range: 519-2176 mg/cu m
OSHA Standard:	200 ppm (1075 mg/cu m)-Ceiling 100 ppm (535 mg/cu m)-T.W.A.	Precision (\overline{CV}_{T}) : 0.082
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 6/6/75

1. Principle of the Method

- 1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.
- 1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.
- 1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.
- 1.4 The area of the resulting peak is determined and compared with areas obtained from injection of standards.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 519-2176 mg/cu m at an atmospheric temperature and pressure of 24.5°C and 759.4 mm Hg, using a 3-liter sample. Under the conditions of sample size (3 liters) the probable useful range of this method is 108-3225 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 9.7 mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.
- 2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 42 mg of analyte when a test atmosphere containing 2266 mg/cu m of analyte in air was sampled at 0.187 liters per minute for 99 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent.

(The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

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3. Interference

- 3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.
- 3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.
- 3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.
- 3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation (\overline{CV}_T) for the total analytical and sampling method in the range of 519-2176 mg/cu m was 0.082. This value corresponds to an 88.2 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.
- 4.2 On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 6.4 % lower than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result.

These data are based on validation experiments using the internal standard method.

- 5. Advantages and Disadvantages of the Method
 - 5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

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The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

- 5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.
- 5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

- 6.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommanded flow rate. (Reference 11.3).
- 6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane form. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane form is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.
- 6.3 Gas chromatograph equipped with a flame ionization detector.
- 6.4 Column (10-ft x 1/8-in stainless steel) packed with 10% OV-101 stationary phase on 100/120 mesh Supelcoport.
- 6.5 An electronic integrator or some other suitable method for measuring peak areas.
- 6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.
- 6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 1.0 ml type graduated in 0.1-ml increments.

5336-3

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

- 7.1 Chromatographic quality carbon disulfide.
- 7.2 Trichloroethylene, reagent grade
- 7.3 Octame, or other suitable internal standard
- 7.4 Purified mitrogen
- 7.5 Prepurified hydrogen.
- 7.6 Filtered compressed air.

8. Procedure

- 8.1 Cleaning of equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.
- 8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.
- 8.3 Collection and Shipping of Samples -
 - 8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-balf the internal diameter of the tube (2 mm).
 - 8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.
 - 8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.
 - 8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.
 - 8.3.5 At the ceiling and peak concentrations, a sample size of 3 liters is recommended. Sample for 15 minutes at a flow of 0.2 liters per minute. At the T.W.A. concentration, a sample size of 10 liters is recommended. Sample at a flow of 0.2 liters per minute or less. The flow rates should be known with an accuracy of at least ±5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation. \$336-4

- 8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no . circumstances should rubber caps be used.
- 8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.
- 8.3.9 Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.
- 8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

- 8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.
- 8.4.2 Description of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Description should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.
- 8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

30 ml/min (60 psig) Nitrogen carrier gas flow
 35 ml/min (25 psig) Hydrogen gas flow to detector
 400 ml/min (60 psig) Air flow to detector
 225°C injector temperature
 250°C manifold temperature (detector) and the provide the provide temperature
 70°C column temperature

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8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 37 difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

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- 8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.
- 8.5.2 Procedure for determining desorption afficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. When using an automatic sample injector, the sample injector vials, capped with Teflon-faced septa, may be used in place of the glass tubes.

\$336-6

Six tubes at each of three concentration levels (0.5X,1X and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 3-liter sample at the selected level. The tubes are allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 1.0 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

D.E. = <u>Average Weight (mg) recovered</u> Weight (mg) added

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

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It is convenient to express concentration of standards in terms of mg per 1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2% the standard. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

- 10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.
- 10.2 Corrections for the blank must be made for each sample.

mg = mg sample - mg blank

where:

mg sample = mg found in front section of sample tube
mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

- 10.3 Add the amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.
- 10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

Corrected mg/sample = Total weight D.E.

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

mg/cu m = Corrected mg (Section 10.4) x 1000 (liters/cu m) Air Volume Sampled (liters)

10.6 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$ppm = mg/cu = x \frac{24.45}{MW} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled T = temperature (°C) of air sampled 24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg HW = molecular weight 760 = standard pressure (mm Hg) 298 = standard temperature (°K)

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11. References

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- 11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," <u>Amer. Ind. Hyg. Assoc. J.</u>, <u>31</u>: 225 (1970).
- 11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.
- 11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

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S336-9

FORMULA: CH2=CHC1; C2H3C1

VINYL CHLORIDE

M.W.: 62.50

METHOD: 1007 ISSUED: 2/15/94

OSHA: 1 ppm; C 5 ppm NIOSH: minimum measurable ACGIH: 5 ppm (human carcinogen) [1] (1 ppm = 2.56 mg/m³ @ NTP) PROPERTIES: BP -14 *C; vapor density 2.2 (air = 1)

SYNONYMS: chloroethylene; chloroethene; CAS #75-01-4.

SAMPLING	MEASUREMENT
SAMPLER: SOLID SORBENT TUBE	! !TECHNIQUE: GAS CHROMATOGRAPHY, FID
(2 tandem tubes, each with 150 mg activated coconut charcoal)	! !ANALYTE: vinyl chloride !
FLOW RATE: 0.05 L/min	DESORPTION: 1 mL carbon disulfide; 30 min
VOL-MIN: 0.7 L -MAX: 5 L	INJECTION ALIQUOT: 5 µL
SHIPMENT: separate primary and backup tubes and cap each	COLLMM: stainless steel, 6.1 m x 3.2 mm, 105 ! SE-30 on 80/100 mesh Chromosorb W ! (AM-OMCS)
SAMPLE STABILITY: 10 days @ 25 °C	CARRIER GAS: He, 40 mL/min
BLANKS: 2 to 10 field blanks per set	! !TEMPERATURE-INJECTOR: 230 °C ! -DETECTOR: 230 °C ! -COLLANN: 60 °C
ACCURACY	• • • • • • • • • • • • • • • • • • •
RANGE STUDIED: 1 to 64 mg/m ³ [2]	CALIBRATION: solutions of vinyl chloride in CS ₂ !
BIAS: -5% of calculated concentration [2]	<pre>!RANGE: 0.002 to 0.2 mg per sample [2] ! !ESTIMATED LOD: 0.00004 mg per sample [2]</pre>
OVERALL PRECISION (s _T): 0.06 [2]	. ! !PRECISION (sp): not determined

APPLICABILITY: The working range is 0.4 to 40 mg/m² (0.16 to 16 ppm) for a 5-L air sample. The method is applicable to 15-min samples at concentrations of 1 ppm or higher.

INTERFERENCES: Other than the possibility of loss of sample upon storage of two weeks or more at room temperature, none have been noted.

OTHER METHODS: This is a revision of PSCAM 178 [3].

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1007-1

VINYL CHLORIDE

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REAGENTS:	EQUIPMENT:
 Carbon disulfide,* chromatographic quality. 	 Sampler: two tandem glass tubes, 7 cm long, 6 mm OD, 4 mm ID, flame-sealed ends, each
 Vinyl chloride,*, 99.9%, in lecture bottle fitted with valve and septum. 	containing 150 mg of 20/40 mesh activated (600 °C) coconut shell charcoal. A silylated glass wool plug precedes the charcoal beds and a 3-mm urethane
 Calibration stock solution, 0.26 mg/mL. a. Insert the tip of a gas syringe containing 1 mL vinyl chloride 	foam plug follows the charcoal beds. Plastic caps are included for sealing after use. Pressure drop across each tube at 1 L/min airflow must be less than 3.4 kPa.
gas under the surface of 5 mL CS ₂ in a 10-mL volumetric	NOTE: A pair of two-section (100 mg/50 mg) tubes may be used.
flask.	2. Personal sampling pump, 0.05 L/min, with flexible
b. Open the value of the syringe	connecting tubing.
and withdraw the plunger to pull CS2 into the barrel. (As	 Gas chromatograph, flame ionization detector, integrator and column (page 1007-1).
vinyl chloride dissolves, a	4. File.

- 5. Bent wire for removing plugs from sampling tube.
- 6. Vials, 2-mL, glass with PTFE-lined septa and crimo-on seals.
- 7. Volumetric flasks, 10-mL, with polyethylene stoppers.
- 8. Pipettes, delivery, 1.0-mL, graduated in 0.1-mL increments, 2- and 5-ML, with pipet bulb.
- 9. Air sampling bags, Tedlar, 10-L.
- 10. Gas syringe, with gas-tight valve, 0.1- and 1-mL.
- 11. Syringe, 10-µL, with 0.1-µL graduations.

5. Hydrogen, purified. 6. Air, filtered.

4. Helium, purified.

*See Special Precautions.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = -30 °C); work with it only in a hood.

Vinyl chloride is a human carcinogen [1].

vacuum will be created, pulling

syringe into the flask. Rinse

the syringe twice with 1-mL portions of CS₂ and add the

CS₂ into the syringe.)

washings to the flask.

d. Dilute to the mark with CS2.

c. Push the solution from the

SAMPLING:

- 1. Calibrate each personal sampling pump with a representative sampler in line.
- 2. Break the ends of the tubes immediately before sampling. Attach two tubes, with ends touching, with a short piece of tubing. Label one tube as the back tube and insert the back tube into the flexible tubing attached to the personal sampling pump.
- 3. Sample at 0.05 L/min for 15 to 100 min. Do not sample more than 5 L of air.
- 4. Separate the primary and backup tubes and cap each tube for shipment.

SAMPLE PREPARATION:

- 5. Add 1.0 mL CS₂ to an empty vial. Loosely cap the vial.
- 6. Score each sampler tube with a file in front of the glass wool plug. Break the tube at the score line.

HETHOD: 1007

- Transfer the charcoal from the front and back tubes to separate vials. Discard the glass wool and foam plugs. Seal the vials with septum caps immediately.
- 8. Allow to stand for 30 min, with occasional agitation. Analyze the sample within the next 30-min period.

CALIBRATION AND QUALITY CONTROL:

- 9. Calibrate with at least five working standards covering the range 0.0002 to 0.2 mg per sample.
 - a. Add known amounts of calibration stock solution to CS2 in 10-mL volumetric flasks and dilute to the marks, using serial dilution as appropriate.

NOTE: Working standards can be stored at -20 °C for at least three days.

- b. Analyze together with samples and blanks (steps 12 and 13).
- c. Prepare calibration graphs of peak area vs. quantity (mg) of vinyl chloride per tube and peak area vs. quantity (ng) per injection.
- Determine desorption efficiency (DE) at least once for each lot of charcoal used in the calibration range (step 9). Prepare three tubes at each of five levels plus three media blanks.
 - a. Prepare three atmospheres of vinyl chloride in air by injecting 0.01, 0.08, and 0.2 mL vinyl chloride gas into 10 L air in Tedlar bags. The resulting concentrations are approximately 2.6, 21 and 52 mg/m³.
 - b. Following steps 1 through 4, sample these atmospheres according to the following scheme:

Concentration	Volume	Quantity of			
in Bag (mg/m³)	Sampled (L)	Vinyl Chloride (mg)			
2.6	0.8	0.002			
	2.2	0.006			
21	0.8	0.017			
	2.2	0.046			
52	2.5	0.13			

Obtain three samples at each level.

- c. Desorb (steps 6 through 8) and analyze together with working standards (steps 12 and 13). No vinyl chloride should be found on the back tubes.
- d. Analyze the atmospheres in the bags (steps 12 and 13) using 1-mL gas samples. Read from the calibration graph the quantity (ng) per injection, which for a 1-mL injection of gas is numerically equal to the concentration in mg/m^3 .
- e. Calculate DE from the mass (mg) of vinyl chloride on the front tube (W_f), the average blank (B), the concentration of vinyl chloride in the synthetic atmospheres (C_S , mg/m³), and the volume of air sampled (V, L):

$$DE = \frac{(W_{\rm f} - 8) \cdot 10^3}{(C_{\rm c}) (V)}$$

f. Prepare a graph of DE vs. mass found (Wr - B).

11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

VINYL CHLORIDE

MEASUREMENT:

12. Set the gas chromatogrph according to manufacturer's instructions and to conditions given on page 1007-1. Inject sample aliquot manually using solvent flush technique or with autosampler. The retention time of vinyl chloride is about 1.7 min.

NOTE: If peak area is above the linear range of the working standards, dilute with CS₂, reanalyze and apply the appropriate dilution factor in calculations.

13. Heasure peak area.

CALCULATIONS:

- 14. Determine the mass, mg (corrected for DE) of vinyl chloride found in the sample front $(W_{\rm P})$ and back $(W_{\rm D})$ tubes, and in the average media blank (B).
- NOTE: If $W_{\rm b} > W_{\rm f}/10$, report breakthrough and possible sample loss.
- 15. Calculate concentration, C, of vinyl chloride in the air volume sampled, V (L):

$$C = \frac{(W_{f} + W_{b} - 2B) \cdot 10^{3}}{V} mg/m^{3}$$

EVALUATION OF METHOD:

The method was evaluated using single 150-mg sampling tubes with 100-mg front beds and 50-mg back beds [2]. At four concentrations between 1 and 64 mg/m³, the pooled relative standard deviation was 0.06 and the measurements averaged 94% of the concentrations calculated from the volumes of vinyl chloride and air used for the atmospheres sampled; samples at the 3-ug level showed no loss of vinyl chloride when stored for 12 days at room temperature or 19 days at -20 °C. There may be significant loss of vinyl chloride from samples stored for 14 days at room temperature [4]. The 1% breakthrough capacity for a 150-mg bed of coconut charcoal challenged at 100 mL/min with vinyl chloride in air at 16 mg/m³ and a relative humidity of 70% was 4.6 L [5].

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- [4] Cuddeback, J. E., W. R. Burg, and S. R. Birch, <u>Environ</u>. <u>Sci</u>. <u>Technol</u>., <u>9</u>, 1168-1171 (1975).

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[5] Matsumura, Y. Ind. Health, 18, 61-67 (1980).

HETHOD REVISED BY: A. W. Teass, Ph.D., NIOSH/DPSE.

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VELSICOL CHEMICAL CORPORATION ST. LOUIS, MICHIGAN PROJECT Nº 1524

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DATE OF COLLECTION 16	SEPTEMBER 1985	SAMPLER	CAC	ULL	BAROME1 PRESSUR		C					30	. 1	7	
TEMPERATURE		RELATIVE		50%	GAUGE	1	2	34	5	6	7	8	9	10	11
CHARCOAL LOT Nº	120	TENAX LOT Nº	220		READING	0	0	00	0	0	0	Ō	ø	0	Ø

GAS VENT PUMP SAMPLE				SAMPLING TIME	SAMPLING RATE	SAMPLE	
NUMBER	NUMBER	NUMBER	START	FINISH	V ELAPSED	(cc/min.)	VOLUME (1)
1	1	4 0	16 14:25	14:45	20 min	250	5
2	2	3	14:40	15:00	20	250	5
3	1	7	14:58	15:18	20	250	5
4	2	٩	15:15	15:35	20	250	5
5	1	5	15:32	15: 52	20	250	5
6	2	10	15:46	16:06	20	250	5
7	2	8	16:22	16:42	20	250	5
8	l	2	16:04	16:24	20	250	5
9	2	6	4/17 8.35	8:55	20	250	.5
10	1	11	8:50	9:10	20	250	5
11	2	12	9:09	9:29	20	250	5
DUPLICATE	1	1	9:14	9:34	20	250	5
BLANK		13					.5
DATE OF SAMPLE SHIPMENT 9/17/85 METHOD OF Federal Express							
COMMENTS							

GAS VENT SAMPLING

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VELSICOL CHEMICAL CORPORATION ST. LOUIS, MICHIGAN PROJECT Nº 1524

GAS VENT SAMPLING PUMPS CALIBRATION LOG

DATE 16 SEPTEMBER 1985 CALIBRA					RATED	BY C	2 A	CULL								
				BEFORE				AFTER SAMPLING					ÂV	ERAGE		
PUMP NUMBER	PUMP TYPE	TEMP. (°F)	HUMIDITY (%)	BAROM. PRESSURE (Inches Hg)	INITIAL FLOW (cc/min.)	CAL. FLOW (cc/min.)	24-HR. TIME	TEMP. (°F)	HUMIDITY	BAROM. PRESSURE (Inches Hg)	FLOW (cc/min.)	24-HR. TIME	TEMP. (°F)	HUMIDITY (%)	BAROM. PRESSURE (Inches Hg)	FLOW (cc/min.)
	GILIAN(A)	69	42	30.24	250		12:50	59	3-+67	30.11	250	10:5	68°	50	30.17	
	(6)				240	250	12:53				250	10:17				250
2	GILIAN (A)				250	250	12:56				250	10:20				250
	(6)				260	250	12:55				250	10:23				250
														 		
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VELSICOL CHEMICAL CORPORATION

POST - CONSTRUCTION QUARTERLY MONITORING REPORT

DECEMBER 14-15 , 1985

Plant Site, St. Louis Michigan

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	DECEMBER 15, 1985	

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1.0 INTRODUCTION

1.1 GENERAL

In accordance with the terms of the technical appendix to the Consent Judgment entered into by Velsicol Chemical Corporation (Velsicol), the United States Environmental Protection Agency, (USEPA) and the Michigan Department of Natural Resources (MDNR), Velsicol is required to perform specified monitoring activities at quarterly intervals following closure of its St. Louis, Michigan plant site. The monitoring program is designed to address the following:

- 1. Performance of gas vents
- 2. Performance of the site perimeter containment wall
- 3. Determination of site groundwater elevations

This report details the site monitoring which occured during the period December 14 to December 15, 1985.

1.2 PARTICIPATION BY REGULATORY AGENCIES

The regulatory agencies did not participate in or attend this monitoring event.

1.3 MONITORING AND SAMPLING PERSONNEL

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The monitoring and sampling program was carried out by Mr D. Robinson (Conestoga-Rovers and Associates) assisted by Mr. Gene DeGeer, the Velsicol site custodian.

2.0 GAS VENT MONITORING

2.1 GENERAL

The gas vent monitoring began on December 14, 1985 and was completed December 15, 1985.

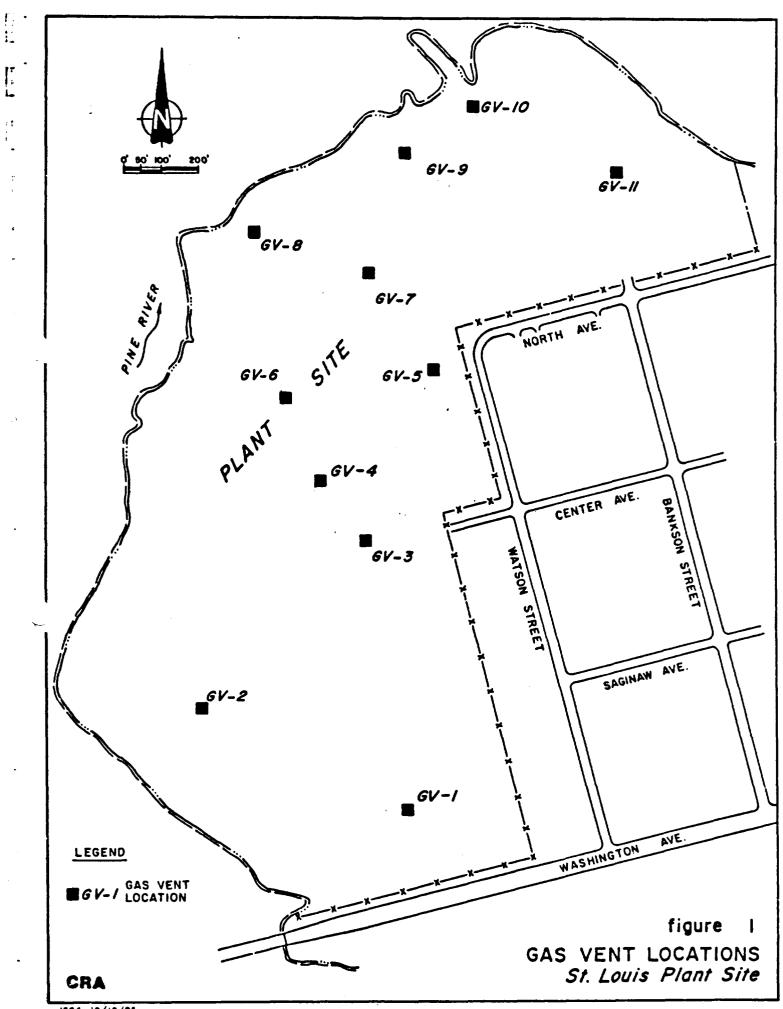
2.1.1 Equipment

Two Gilian model HFS 113 hi flow samplers were used to collect gas vent samples. The samplers were field calibrated using a rotometer prior to sampling. The calibration data is presented within Appendix B. Samples from each gas vent were collected in two 6-mm diameter x 70-mm long Tenax tubes and two charcoal tubes of similar dimensions. The samples were collected simultaneously using dual parallel/series tube holder sets.

2.2 SAMPLE COLLECTION

Samples were obtained at each of the 11 gas vents. The location of the gas vents within the closed plant site is detailed on Figure 1. One blank set and one duplicate set of samples were also collected.

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Sampling was conducted at the downstream sampling port on each gas vent as detailed on Figure 2. The tube holder was attached directly to the gas vent sampling port using a copper manifold assembly which was environmentally cleaned prior to use. Tygon tubing was used to connect the tube holder to the sampler and was connected between the base of the tube holder and suction port of the sampler. The sampler which was pre-calibrated to 250cc/min/tube set, was operated for a period of 20 minutes for each sampling event, resulting in a collected sample volume of five liters per tube set.

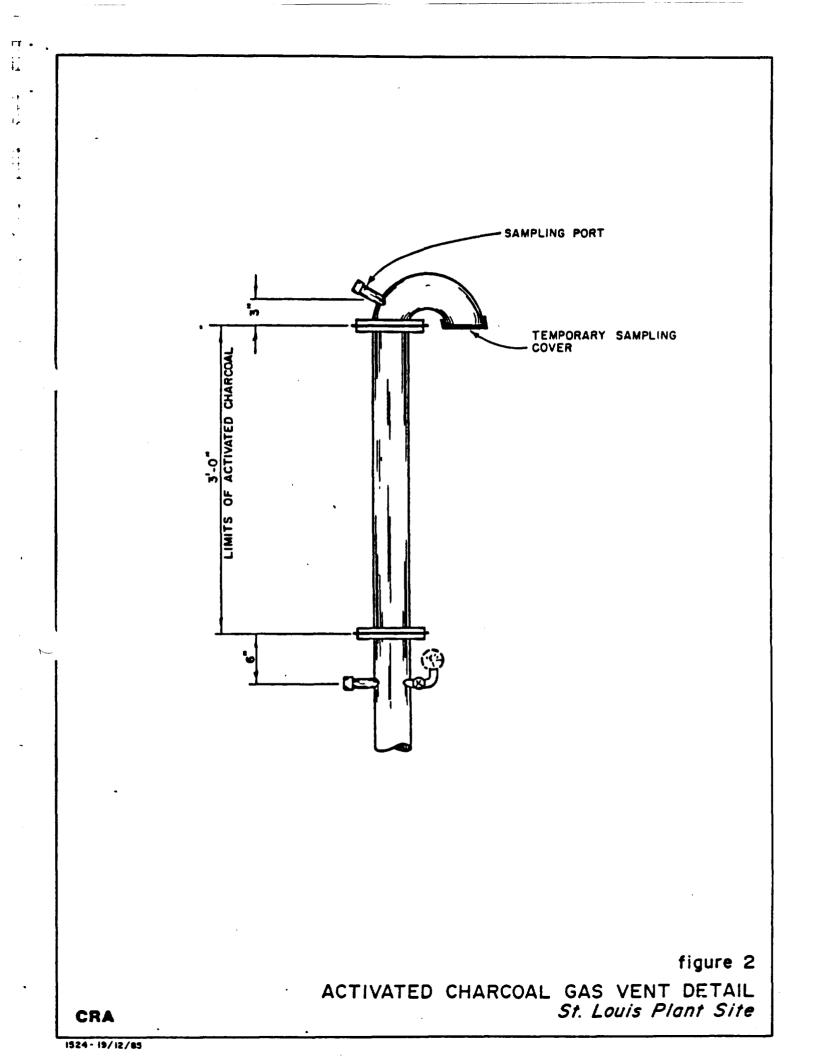
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Prior to sample collection, the gas vent upper chamber was purged by pumping at 500 cc/minute for a period of ten minutes. This precluded the possiblity of sampling retained atmospheric air from the gas vent upper chamber. During the purging and sampling operations, the open end of the gas vent was capped using a 4-inch diameter plastic cover to prevent atmospheric air being drawn into the sample.

At the conclusion of each gas vent sampling, the set of four sample tubes were capped, labelled and stored in a cooler maintained at 0°C.



2.2.1 Sample Storage and Shipment

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On the Morning of December 16, 1985 the samples were transferred to a cooler containing frozen cold packs and styrofoam packing materials. The cooler was shipped under chain of custody protocol, to Velsicol's Memphis, Tennessee laboratory by overnight courier for analysis. A copy of the chain of custody is provided in Appendix A.

2.2.2 Sample Analysis

Analyses were conducted in accordance with NIOSH protocols as follows:

Compound	NIOSH Method
Carbon Tetrachloride	1003
Trichloroethylene	S-336
Vinyl Chloride	1007

Results have been reported verbally by the laboratory as non-detectable for all parameters at all sampling points. A hard copy of the laboratory report will be forwarded to USEPA and MDNR within seven days after receipt of final laboratory data by CRA.

2.2.3 Sampling Protocol

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All sampling was performed in accordance with the methodology detailed within the St. Louis plant site Post-Closure Maintenance and Monitoring Plan, as approved by USEPA and MDNR. A copy of the sampling protocol is contained in Appendix B.

3.0 SITE PERIMETER CONTAINMENT WALL MONITORING

3.1 GENERAL

The monitoring program consisting of the collection of an undisturbed sample of the containment wall with subsequent permeability testing was initiated on December 15, 1983. Subsequent sampling events occurred on March 15, 1984, June 15, 1984, September 14, 1984, December 14, 1985, March 16, 1985, June 19, 1985 and September 16, 1985. The current sampling event occured December 14, 1985. All testing completed to date has confirmed the permeability of the site perimeter containment wall to be less than 1.0 x 10^{-7} cm/sec.

3.2 EQUIPMENT

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A Mobil Truck mounted drill rig equipped with rotary head and 4-inch diameter augers was utilized to advance the borehole into the containment wall. A 3-inch diameter Shelby tube, hydraulically pushed and retrieved, was used to collect the samples.

3.3 SAMPLE COLLECTION

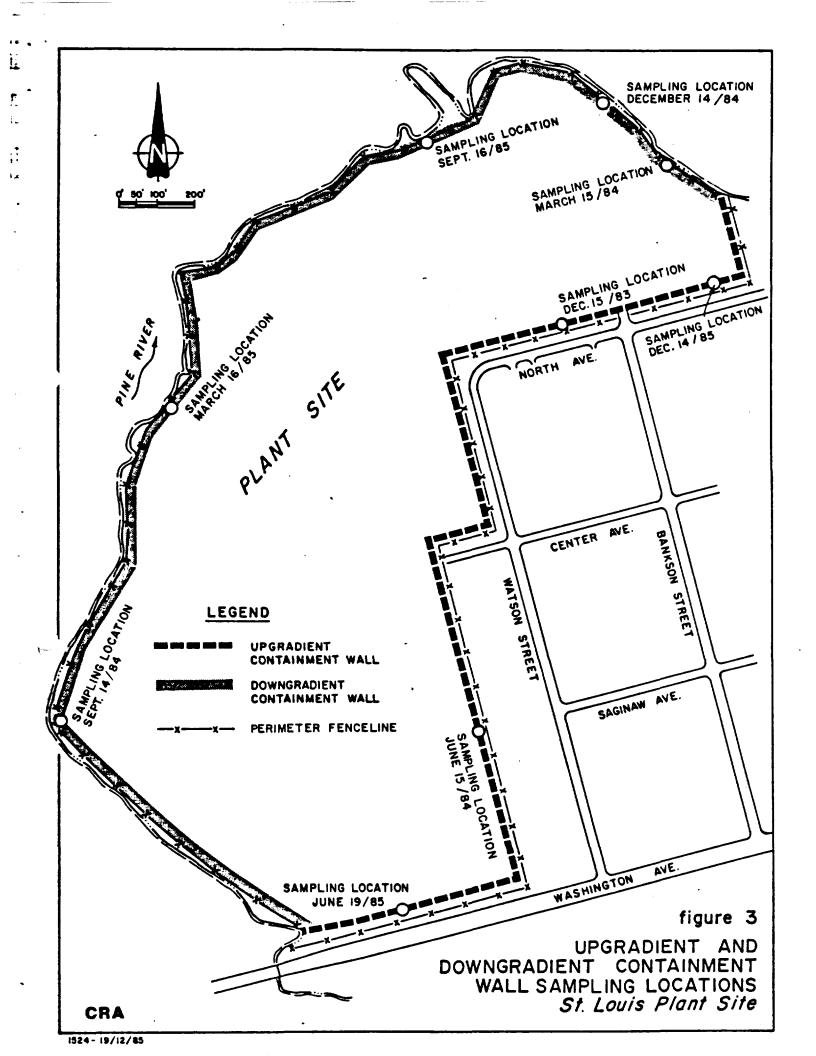
The containment wall was located by field survey on December 14, 1985. The sampling borehole was begun at Station 0+50, Baseline B by augering through the clay cap into the underlying material.

The presence of soil/bentonite backfill material was confirmed by examination of cuttings on the auger flights. A borehole was advanced to a depth of seven feet below grade. A Shelby tube was introduced into the borehole and a sample was withdrawn. Examination of material in the base of the tube confirmed that the sample was obtained from the containment wall. The locations of this and prior sampling events are detailed on Figure 3. The boreholes were backfilled with bentonite and abandoned.

3.3.1 Sample Preparation and Shipping

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The Shelby tube was capped and taped at both ends to prevent sample loss and drying. The sample was hand delivered to the Michigan Testing Engineer's laboratory in Detroit, Michigan for permeability testing.



3.3.2 Sample Testing

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The undisturbed sample is to be tested for permeability using a falling head permeameter set up in accordance with ASTM D 2434. Results of the testing will be provided in written form to USEPA and MDNR within seven days after receipt of final laboratory data by CRA. A summary data report will be prepared and presented to both Agencies following completion of the containment wall monitoring program in the fall of 1986.

4.0 GROUNDWATER TABLE MONITORING

4.1 GENERAL

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The monitoring of plant site groundwater elevation was performed and the elevation of the St. Louis reservoir was determined on December 15, 1985.

4.2 WATER LEVEL DETERMINATION

The elevation of the groundwater was determined by measuring the distance from the top of each site monitoring well to the watertable. This distance was measured by lowering a chalked, weighted surveyors tape into the monitoring well. Readings of the tape, which was graduated in increments of one one-hundredth of a foot, were taken at the water level and at the top of the well casing. The former reading was deducted from the latter and the resultant dimension was subtracted from the previously established top of well casing elevation. Well head and watertable elevations are presented on Table 1.

The elevation of the St. Louis reservoir was determined by level and rod survey.

TABLE 1

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WATER LEVEL MEASUREMENTS ______DECEMBER 15, 1985

MONITORING	WELL HEAD ELEVATION (AMSL)	MEASURED DISTANCE TO WATER TABLE (ft.)	WATERTABLE ELEVATION (AMSL)
1	735.91	14.42	721.49
2	742.06	19.25	722.81
3	749.91	27.42	722.49
4	736.00	13.79	722.21
5	739.35	17.79	721.56
6	734.48	13.25	721.23
7	733.98	12.76	721.22
8	734.30	13.17	721.13
9	734.60	13.33	721.27
10	733.48	12.27	721.21
11	734.47	13.21	721.26
12	730.78	9.56	721.22
13	734.49	13.23	721.26
14	736.00	14.69	721.31

Water level elevation, St. Louis Reservoir719.60

4.3 GROUNDWATER CONTOUR MAP

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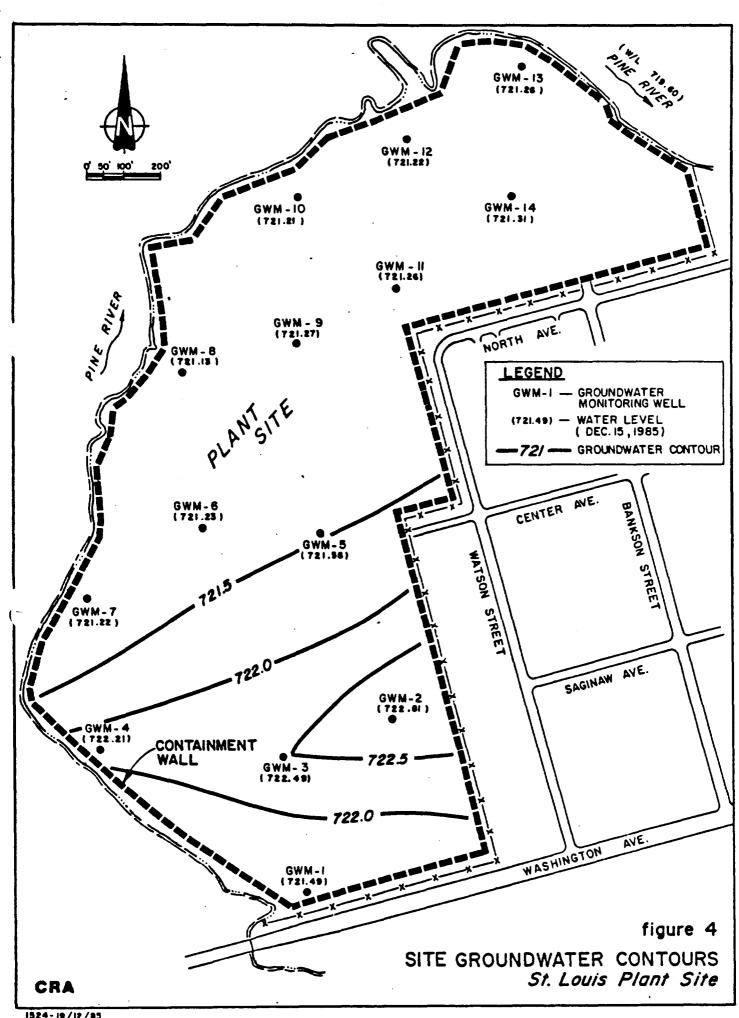
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The groundwater elevation data were used to construct a site groundwater elevation contour map which is presented in Figure 4.

4.4 SITE MEAN GROUNDWATER ELEVATION

The mean elevation of site groundwater is calculated to be 721.55. The maximum allowable site groundwater elevation stipulated by the Consent Judgment is 724.13.



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All monitoring activities stipulated by the Consent Judgment were carried out between December 14 and 15, 1985.

Data from the chemical analysis of the gas vent samples and the permeability testing of the contaminant wall sample will be provided to MDNR and USEPA within seven days of receipt by CRA of laboratory final data.

The present mean site groundwater table elevation as of December 15, 1985 was calculated to be 721.55. The elevation in the Pine River/St. Louis reservoir at that time was determined to be 719.60.

The next sampling and monitoring event will occur on or about March 15, 1986.

All of Which is Respectfully Submitted, CONESTOGA-ROVERS & ASSOCIATES LIMITED

R.G. Shepherd, P. Eng.

D. Robinson

APPENDIX A

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CHAIN OF CUSTODY

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SAMPLER	'S SIGNAT	URE		GN)					nt or	
SAMPLE	SEQ Nº	DATE	TIME	FRONT	TENAX CHARCOAL	. SA	MPLE TYPE		CONTAINERS	REMARKS
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2	2	12/14	3.46	3-2	in an	6 66	:		<u>ل</u>	
3	З	12/14	4.06	2/2	2/2	11 n	•		4	
4	4	12/14	4-31	2/2	2/2	64. ⁻ 44	••		4.	
5	5	12/15	1.00	2/2	2/2				A	
6	6	12/15	1.04	2/2	2/2	h h	۰ <i>. ب</i> ۰		4	
7	8	12 15	1.37	2/2	2/2		••		4.	
8	-7	12/15	1.45	2/2	2/2	K	•		4.	
9	5	2.15	12 15	2/2	2/2	<u> </u>	· · · ·		11	
10	10	12/15	2.22	2/2	2/2	n, h	•.		41_	
"	11	12/15	2.26	2/2	7/2	•• · ••	•	·····	4	
12	12	12.15	2.42	2/2	7/2	\$ \$	· ·		4_	
	a la a se					TOTAL NO.	OF CONTAINERS -		-	See
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RELING	IISHED-BI		DATE/1	1 1	EIVED BY:	RELING	UISHED BY:	DATE / TI	MEREC	CEIVED BY:
	(SIGN)		12/15	<u> </u>]	(SIGN)	[<u>]</u>	(SIGN)		(3-	(SIGN)
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5	(SIGN)				(SIGN)		(SIGN)		-0-	(SIGN)
METHOD	OF SHIPM	IENTI		SHI	PPED BY:	RECEIV	ED FOR LABORAT	ORY		DATE / TIME
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ANB 650. 405-221

3. 			TOTAL NO OF CONTAINERS	4	
RELINQUISHED BY:	DATE/TIME	RECEIVED BY:	RELINQUISHED BY	DATE / TIME	RECEIVED BY:
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RELINQUISHED BY:	DATE / TIME	RECEIVED BY:	RELINQUISHED BY	DATE/TIME	RECEIVED BY:
[3] (SIGN)	l	(\$IGN)	(SIGN)	·	(SIGN)
RELINQUISHED BY:	DATE/TIME	RECEIVED BY :	RELINQUISHED BY	DATE / TIME	RECEIVED BY:
(SIGN)		6	(\$IGN)		(\$IGN)
METHOD OF SHIPMENT		SHIPPED BY:	RECEIVED FOR LABORATORY	1	DATE / TIME
FEDEXP.		G. DEGGAR	(SIGN)		

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SAMPLER	SAMPLER'S SIGNATURE						· · · · · · · · · · · · · · · · · · ·	HR 07	
SAMPLE Nº	SEQ Nº	DATE	TIME	FRONT			SAMPLE TYPE	CONTAINERS	REMARKS
13	13	12/15	3.00	2/2	2/2	Gins .	VER	14.	
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MARIA E	alda Test	17.542				TOTAL	NS. OF CONTAINERS	5%-	Maria Property Carestand

CHAIN OF CUSTODY RECORD PROJECT Nº. PROJECT NAME : GAS VENT MONITORING 1524

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PLANT SITE ST. LOUIS, MICHIGAN

VELSICOL CHEMICAL CORPORATION TOI W. WASHINGTON STREET . ST. LOUIS, MICHIGAN 48880

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APPENDIX B

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GAS SAMPLING PROTOCOLS

APPENDIX B

GAS VENT SAMPLING PROTOCOL

In accordance with the Consent Judgment, Velsicol has submitted a post-closure maintenance and monitoring plan for its environmentally secured plant site in St. Louis, Michigan. The post-closure maintenance and monitoring plan requires quarterly monitoring of 11 gas vents that have been installed to release and appropriately treat internal gases. This program will be conducted over a period of three years.

The gas vents, as detailed in Exhibit F of the Consent Judgment, are designed with two sampling ports; one below the base of the installed activated charcoal filter, and one above the filter. Samples will be collected from the downstream port. Results will indicate whether or not containment breakthrough has occured through the carbon filter.

Samples will be analyzed for three separate compounds: carbon tetrachloride, trichloroethylene and vinyl chloride.

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Samples will be collected with a Gilian HFS-113 AU DK variable flow pump. This particular unit allows the operator to run a series of tubes concurrently in parallel arrangement. Four tubes will be collected from each gas vent: two standard NIOSH 100/50 mg activated charcoal tube, and two 30/15 mg tenax tubes, each tube measuring 6 mm x 70 mm. One blank set and one duplicate set of tubes will be collected during each quarterly sampling event.

As vinyl chloride represents the least adsorptive of the three compounds, the sampling program is designed to accomodate this compound. Therefore, sample volume shall not exceed 5 liters.

Prior to sampling, the vent will be sealed off with a plastic cap, and purged for 10 minutes at a rate of 500 cc/min. This is to eliminate the possibility of sampling atmospheric air contained within the upper portion of the gas vent.

Two samples from each gas vent shall be collected simultaneously at a rate of 250 cc/min. for 20 minutes. The pump shall be lab calibrated with sample tubes in-line to determine the exact flow rate. Additionally, flow will be checked after field sampling to verify that a constant flow was maintained throughout the sampling period.

Following sample collection, each tube will be sealed with a plastic cap at each end, labelled, placed in a cold storage environment and shipped under chain-of-custody via a commercial courier service to Velsicol's analytical laboratory in Memphis.

Analysis of the charcoal tube will be conducted in accordance with NIOSH protocol as detailed below:

Compound	Revised Method No.				
Carbon Tetrachloride	1003				
Trichloroethylene	S-336				
Vinyl Chloride	1007				

Analysis will proceed by first eluting the carbon sample tubes with carbon disulfide and then analyzing by GC with a flame ionization detector. All samples will be initially analyzed in this fashion. If any of the above compounds are detected on the charcoal tube, the corresponding tenax tube will be analyzed by thermal desorption and GC/MS under EPA Method 624.

Turnaround time for the completed analysis at the laboratory is anticipated to be 30 days from date of sample collection. Samples will be desorbed within the 10 day limit specified for vinyl chloride. Analytical data will be reported to CRA as mg/tube. Final results for the carbon tube will be calculated by CRA, using the following formula.

1. Corrections for the blank to be made for each sample
 mg = mg sample - mg blank

This calculation is performed separately for each tube.

- 2. Add the amounts present in the front tube and backup tube to determine the total weight in the sample.
- 3. Calculate the corrected mg/sample by dividing the total weight by the desorption efficiency (D.E.) which is provided by the lab.

corrected mg/sample = total weight DE

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- 4. Calculate the concentration of the analyte in air $mg/m^3 = Corrected mg \times 1000 liters/m^3$ Air volume Sampled (liters)
- 5. Concentration will be reported as ppm, corrected to standard conditions of 25°C and 760 mm Hg

 $ppm = mg/m \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{(T+273)}{298}$

where	Р	= pressure (mm Hg) of air sampled
	т	<pre>= temperature (*C) of air sampled</pre>
	24.45	= molar volume (liter/mole) at 25°C and 760 mm Hg
	MW	= Molecular Weight
	760	= standard pressure (mm Hg)
	298	= standard temperature (°K)

- NOTE: Temperature and pressure uncorrected to sea level will be collected for the duration of the sampling event and averaged for use in the above calculations. Information will be provided from the National Weather Service in Lansing, Michigan.
 - 6. If the concentration of the back tube exceeds 10% of the concentration of the front tube, the results will be reported as a sample breakthrough and possible sample loss.
 - 7. A similar procedure will be followed for the tenax tube, should analysis be required.

Data will be reported to USEPA and MDNR officials within seven days after receipt of final laboratory data for each quarterly sampling. Additionally, a summary data report will be provided at the conclusion of the three year sampling period, or sooner, should breakthrough of any compound occur prior to the three year program.

In addition to the set of field blanks to be collected per quarterly sampling event, an additional set of 15 charcoal tubes and 15 tenax tubes will be forwarded unopened to the lab during the initial sampling event.

These "blank" tubes will be used as internal calibration standards on which each of the three compounds will be spiked at five different concentrations. The data from this analysis will be used to calculate the desorption efficiency for a specific lot of activated charcoal. Therefore, the lot number of carbon tubes and tenax tubes shall be recorded during each quarterly sampling. Should the lot number change, a new set of 15 charcoal tubes and 15 tenax tubes shall be forwarded to the laboratory for determination of the new desorption efficiency.

The allowable limits for these compounds have been established by the MDNR and are site specific for the St. Louis site. These limits are documented in section 4.3 of the post-closure maintenance and monitoring plan.

Copies of all three analytical protocols, the chain of custody and the data collection sheet are provided in the following sections.

- 3 -

FORMULA: Table 1

HYDROCARBONS, HALOGENATED

METHOD: 1003

M.W.: Table 1

ISSUED: 2/14/84

COMPOUNDS: benzyl chloride chlorobromomethane 1,1-dichloroethane hexachloroethane 1,2-dichloroethylene methylchloroform (synonyms bromoform chloroform ethylene dichloride propylene dichloride chlorobenzene p-dichlorobenzene SAMPLING MEASUREMENT !TECHNIQUE: GAS CHROMATOGRAPHY, FID SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)! IANALYTE: compounds above FLOW RATE: 0.01 to 0.2 L/min 1DESORPTION: 1 mL CS2, stand 30 min VOL-MIN: Table 2 -MAX: Table 2 INJECTION VOLUME: 5 µL SHIPMENT: routine !TEMPERATURES: Table 2 SAMPLE STABILITY: at least 1 week @ 25 °C !CARRIER GAS: N2 or He, 30 mL/min BLANKS: 2 to 10 field blanks per set !COLUMN: Table 2; alternates are SP-2100, SP-2100 with 0.1% Carbowax 1500 or DB-1 fused silica capillary column ACCURACY ICALIBRATION: solutions of analyte in CS- with 32 31 TTTTTTTTT .. : BIAS: not significant [1] !RANGE: Table 2 ¥ -OVERALL PRECISION (s_{p}) : see EVALUATION OF !ESTIMATED LOD: 0.01 mg per sample [2] METHOD [1] PRECISION (s,): see EVALUATION OF METHOD [1]

APPLICABILITY: This method uses a simple desorption and can be used for simultaneous analysis of two or more substances suspected to be present by changing the gas chromatographic conditions (i.e., temperature programmed). High humidity during sampling will prevent organic vapors from being trapped efficiently on the sorbent and greatly decreases breakthrough volume.

INTERFERENCES: None identified. The chromatographic column or separation conditions may be changed to circumvent interference problems.

OTHER METHODS: This method combines and replaces Methods P&CAM 127 [3]; S95, S101, S110, S113, S114, S115, S122, S123 and S133 [4]; and S135, S281, S314, S328 and S351 [5].

a. Remove and discard back sorbent section of a media blank sampler.

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- b. Inject a known amount of analyte or calibration stock solution directly onto front sorbent section with a microliter syringe.
- c. Cap the tube. Allow to stand overnight.
- d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
 e. Prepare a graph of DE vs. mg analyte recovered.
- 10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

 Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1003-1. Inject sample aliquot manually using solvent flush technique or with autosampler.

NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.

12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of analyte found in the sample front (W_f) and back (W_D) sorbent sections, and in the average media blank front (B_f) and back (B_D) sorbent sections.

NOTE: If $W_p > W_f/10$, report breakthrough and possible sample loss.

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14. Calculate concentration, C, of analyte in the air volume sampled, V (L):

$$C = \frac{(W_{f} + W_{b} - B_{f} - B_{b}) + 10^{3}}{V}, mg/m^{3}.$$

ZUTION OF SEPACE

Laboratory testing was performed with spiked samples and generated atmosphere [1]. All analytes are stable at least one week. All methods were validated using SKC Lot 105 coconut shell charcoal. Results were:

METHOD: 1003

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[9] Criteria for a Recommended Standard...Occupational Exposure to 1,1,1-Trichloroethane, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 76-184 (1976).

[10] Criteria for a Recommended Standard...Occupational Exposure to Carbon Tetrachloride, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 76-133 (1976).

METHOD REVISED BY: G. D. Foley; Y. T. Gagnon; and K. J. Williams, NIOSH/DPSE; methods originally validated under NIOSH Contract CDC-99-74-45.

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HETHOD: 1003

Compounds	M. <u>Formula</u>	.W.; mg/m³ <u>= 1 ppm</u>	Synonyms	OSIA NIOSH [6-10] ACGIH	BP(°C)	VP (9 20 °C	Density (g/mL @ 20 °C)
g-Dichlorobenzene	1,4-C ₆ H ₄ C1 6 4	147.00; 6.01	↓ +-dichlorobenzene; { #106-46-7	75 ppm 75 ppm, STEL 110 ppm	174	50 Pa	1.241
1,1-Dichloroethane	CII3CICI2; C2H4CI2	98.96; 4.05	ethyllidene chloride; Crac #15-34-3	100 ppm 100 ppm 200 ppm, STEL 250 ppm	57	24.3 kPa	1.174
1,2-Dichloroethylene	C1CH=CHC1; C_H_C1 2_4_2	96.95; 3.96	acet ylene dichloride; 1,: dichloroethene; C #540-59-0	200 ppm 200 ppm 200 ppm, STEL 250 ppm	60 (cis) 41 (trans)	24-35 kPa	1.28
Ethylene dichloride*	c1a1 ₂ a1 ₂ c1; c ₂ 11 ₄ c1 ₂	98.96; 4.05	1, '-dichloroethane; Cr > #107-06-2	50 ppm, C 100 ppm 5 ppm; 15 ppm/15 min 10 ppm, STEL 15 ppm	83	8.3 kPa	1.255
Hexach loroethane*	cc1 ₃ cc1 ₃ ; c ₂ c1 ₆	236.74; 9.68	i… + ch1oroethane; (#67-72-1	l ppm (skin) l ppm (skin) 10 ppm	187 (sublines)	30 Pa	2.09
Hethylchloroform	аі _з ссі _з ; с ₂ іізсіз	133.42; 5.45	1, 1, 1-trichloroethane; 1 5 #71-55-6	350 ppm 350 ppm/15 min CAS #71-55-6 STEL 450 ppm	74 350 ppm,	13.3 kPa	1.335
Propylene dichloride	ai ₃ cic1ai ₂ c1; c ₃ ii ₆ c1 ₂	112.99; 4.62	1, -dich1oropropane C #18-81-5	75 ppm 75 ppm 75 ppm, 51EL 110 ppm	95	5.3 kPa	1.156 (25 °C)

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1003-7

HYDROCARBONS, HALOGENATED

*Suspect carcinogen.

		Samp Ing	Euj				Measurement	ement	
	1						t (°C)		
	Volume (L)				Working		Column		Range
Compound	Nin	Max	Breakthrough	v o <mark>ugh</mark> Air	Range (mg/m³)	Column*	Injector Detector	Interna I Standard	(mg per sample)
1, 1-Dichloroethane	n (J 100 ppm	· 9	18.3 L	"m/gm fit	40 to 1215 (10 t)	<	50 100 112	1	0.4 to 12
1,2-Dichloroethylcne	0.5 8 200 ppm	m	یت ۲۰۰۰ ۲۰۰۰ ۴۰۰	"w/fiw 6 ();	00 to 2370 (3 L)	<	60 170 210	:	0.2 to 7
Ethylene dichloride	1 (3 50 ppm	2	29 1 3 1	Cm/y an si fi	40 to 1215 (3 L)	<	70 225 250	octane	0.1 to 4
Hexach loroethane	ngg lý	9	1 1 1 8	ew/(ii	1 to 30 (10 t)	c	210 210 210	n - tri decane	0.01 to 0.3
Nethyl chloroform	0.5 ê 350 ppm	ف	9.5 1 1	am/gm B ();	190 to 5700 (3 L)	<	70 225 250	octane	0.6 to 17
Propylene dichloride	1 (1 75 ppm	9	99 101	e W/fw	35 to 1050 (10 L)	<	80 170 210	n-undecane	0.3 to 10
ters un 3 m x 3 m stat b = 6 m x 3 m stat		SP-	105 SP-10:00	1:00 mesh Supelcoport;	pelcoport;				
C = 3 m x 3 lui stai B = 3 m x 6 liin gla:	m x 3 and stated on steel, 100 m x 6 and glacs, of SP-2250 on	-20 - -20 -	101. 0V~101 Har 2	120 mesh Su lcoport.	<pre>/20 mesh Supelcuport; or .alcoport.</pre>				

METHOD: 1003

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HYDROCARBONS, HALOGENATED

2/15/84

1003-9

Trichloroethylene

Analyte:	Trichloroethylene	Method No.: S336
Matrix:	Air	Range: 519-2176 mg/cu m
OSHA Standard:	200 ppm (1075 mg/cu m)-Ceiling 100 ppm (535 mg/cu m)-T.W.A.	Precision (\overline{CV}_{T}) : 0.082
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 6/6/75

1. Principle of the Method

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- 1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.
- 1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.
- 1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.
- 1.4 The area of the resulting peak is determined and compared with areas obtained from injection of standards.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 519-2176 mg/cu m at an atmospheric temperature and pressure of 24.5°C and 759.4 mm Hg, using a 3-liter sample. Under the conditions of sample size (3 liters) the probable useful range of this method is 108-3225 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 9.7 mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.
- 2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 42 mg of analyte when a test atmosphere containing 2266 mg/cu m of analyte in air was sampled at 0.187 liters per minute for 99 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent.

(The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

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3. Interference

- 3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.
- 3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.
- 3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.
- 3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation (\overline{CV}_T) for the total analytical and sampling method in the range of 519-2176 mg/cu m was 0.082. This value corresponds to an 88.2 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.
- 4.2 On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 6.4 % lower than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result.

These data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

- 5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.
- 5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

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- 6.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3).
- 6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.
- 6.3 Gas chromatograph equipped with a flame ionization detector.
- 6.4 Column (10-ft x 1/8-in stainless steel) packed with 10% OV-101 stationary phase on 100/120 mesh Supelcoport.
- 6.5 An electronic integrator or some other suitable method for measuring peak areas.
- 6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.
- 6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.
- 6.8 Pipets: 1.0 ml type graduated in 0.1-ml increments.

- 6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.
- 7. Reagents
 - 7.1 Chromatographic quality carbon disulfide.
 - 7.2 Trichloroethylene, reagent grade
 - 7.3 Octame, or other suitable internal standard
 - 7.4 Purified nitrogen
 - 7.5 Prepurified hydrogen.
 - 7.6 Filtered compressed air.
- 8. Procedure
 - 8.1 Cleaning of equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.
 - 8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.
 - 8.3 Collection and Shipping of Samples
 - 8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).
 - 8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.
 - 8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.
 - 8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.
 - 8.3.5 At the ceiling and peak concentrations, a sample size of 3 liters is recommended. Sample for 15 minutes at a flow of 0.2 liters per minute. At the T.W.A. concentration, a sample size of 10 liters is recommended. Sample at a flow of 0.2 liters per minute or less. The flow rates should be known with an accuracy of at least <u>+57</u>.
 - 8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

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S336-4

- 8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.
- 8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.
- 8.3.9 Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.
- 8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

- 8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.
- 8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.
- 8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:
 - 30 ml/min (60 psig) Nitrogen carrier gas flow
 35 ml/min (25 psig) Hydrogen gas flow to detector
 400 ml/min (60 psig) Air flow to detector
 225°C injector temperature
 250°C manifold temperature (detector)
 70°C column temperature

- 8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.
- 8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.
- 8.5 Determination of Desorption Efficiency
 - 8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.
 - 8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. When using an automatic sample injector, the sample injector vials, capped with Teflon-faced septa, may be used in place of the glass tubes.

Six tubes at each of three concentration levels (0.5X,1X and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 3-liter sample at the selected level. The tubes are allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 1.0 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

D.E. - <u>Average Weight (mg) recovered</u> Weight (mg) added

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

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It is convenient to express concentration of standards in terms of mg per 1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2% the standard. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

mg = mg sample - mg blank

where:

mg sample = mg found in front section of sample tube
mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

- 10.3 Add the amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.
- 10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

Corrected mg/sample = Total weight D.E.

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

mg/cu m = Corrected mg (Section 10.4) x 1000 (liters/cu m) Air Volume Sampled (liters)

10.6 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$ppm = mg/cu = x \frac{24.45}{MW} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
MW = molecular weight
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

- 11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," <u>Amer. Ind. Hyg. Assoc. J.</u>, <u>31</u>: 225 (1970).
- 11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.
- 11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

FORMULA: CH2=CHC1; C2H3C1

VINYL CHLORIDE

M.W.: 62.50

HETHOD: 1007 ISSUED: 2/15/84

OSHA: 1 ppm; C 5 ppm _____ NIOSH: minimum measurable ACGIH: 5 ppm (human carcinogen) [1] (1 ppm = 2.56 mg/m³ @ NTP)

PROPERTIES: BP -14 *C; vapor density 2.2 (air = 1)

SYNONYMS: chloroethylene; chloroethene; CAS #75-01-4.

SAMPLING	MEASUREMENT
SAMPLER: SOLID SORBENT TUBE (2 tandem tubes, each with 150 mg	! !TECHNIQUE: GAS CHROMATOGRAPHY, FID !
activated coconut charcoal)	!ANALYTE: vinyl chloride
FLOW RATE: 0.05 L/min	: !DESORPTION: 1 mL carbon disulfide; 30 min !
VOL-MIN: 0.7 L -MAX: 5 L	INJECTION ALIQUOT: 5 µL
SHIPMENT: separate primary and backup tubes and cap each	!COLUMN: stainless steel, 6.1 m x 3.2 mm, 10% ! SE-30 on 80/100 mesh Chromosorb W ! (AM-DMCS)
SAMPLE STABILITY: 10 days @ 25 °C	: CARRIER GAS: He, 40 mL/min
BLANKS: 2 to 10 field blanks per set	: !TEMPERATURE-INJECTOR: 230 °C ! -DETECTOR: 230 °C ! -COLUMN: 60 °C
ACCURACY	!
RANGE STUDIED: 1 to 64 mg/m ³ [2]	<pre>!CALIBRATION: solutions of vinyl chloride in CS₂ ! !RANGE: 0.002 to 0.2 mg per sample [2]</pre>
BIAS: -6% of calculated concentration [2]	! ! !ESTINATED LOD: 0.00004 mg per sample [2]
OVERALL PRECISION (s _r): 0.06 [2]	PRECISION (sp): not determined

APPLICABILITY: The working range is 0.4 to 40 mg/m³ (0.16 to 16 ppm) for a 5-L air sample. The method is applicable to 15-min samples at concentrations of 1 ppm or higher.

INTERFERENCES: Other than the possibility of loss of sample upon storage of two weeks or more at room temperature, none have been noted.

OTHER METHODS: This is a revision of P&CAM 178 [3].

VINYL CHLORIDE

- Carbon disulfide,* chromatographic quality.
- Vinyl chloride,*, 99.9%, in lecture bottle fitted with valve and septum.
- Calibration stock solution, 0.26 mg/mL.
 - a. Insert the tip of a gas syringe containing 1 mL vinyl chloride gas under the surface of 5 mL CS₂ in a 10-mL volumetric flask.
 - b. Open the value of the syringe and withdraw the plunger to pull CS₂ into the barrel. (As vinyl chloride dissolves, a vacuum will be created, pulling CS₂ into the syringe.)
 - c. Push the solution from the syringe into the flask. Rinse the syringe twice with 1-ML portions of CS₂ and add the washings to the flask.
 - d. Dilute to the mark with CS2.
- 4. Helium, purified.
- 5. Hydrogen, purified.
- 6. Air, filtered.

*See Special Precautions.

EQUIPMENT:

1. Sampler: two tandem glass tubes, 7 cm long, 6 mm OD, 4 mm ID, flame-sealed ends, each containing 150 mg of 20/40 mesh activated (600 °C) coconut shell charcoal. A silylated glass wool plug precedes the charcoal beds and a 3-mm urethane foam plug follows the charcoal beds. Plastic caps are included for sealing after use. Pressure drop across each tube at 1 L/min airflow must be less than 3.4 kPa.

NOTE: A pair of two-section (100 mg/50 mg) tubes may be used.

- 2. Personal sampling pump, 0.05 L/min, with flexible connecting tubing.
- 3. Gas chromatograph, flame ionization detector, integrator and column (page 1007-1).
- 4. File.
- 5. Bent wire for removing plugs from sampling tube.
- 6. Vials, 2-mL, glass with PTFE-lined septa and crimp-on seals.
- Volumetric flasks, 10-mL, with polyethylene stoppers.
- Pipettes, delivery, 1.0-mL, graduated in 0.1-mL increments, 2- and 5-mL, with pipet bulb.
- 9. Air sampling bags, Tedlar, 10-L.
- 10. Gas syringe, with gas-tight valve, 0.1- and 1-mL.
- 11. Syringe, 10-µL, with 0.1-µL graduations.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = -30 °C); work with it only in a hood.

Vinyl chloride is a human carcinogen [1].

SAMPLING:

- 1. Calibrate each personal sampling pump with a representative sampler in line.
- Break the ends of the tubes immediately before sampling. Attach two tubes, with ends touching, with a short piece of tubing. Label one tube as the back tube and insert the back tube into the flexible tubing attached to the personal sampling pump.
- 3. Sample at 0.05 L/min for 15 to 100 min. Do not sample more than 5 L of air.
- 4. Separate the primary and backup tubes and cap each tube for shipment.

SAMPLE PREPARATION:

- 5. Add 1.0 mL CS_2 to an empty vial. Loosely cap the vial.
- 6. Score each sampler tube with a file in front of the glass wool plug. Break the tube at the score line.

METHOD: 1007

HETHOD: 1007

- 7. Transfer the charcoal from the front and back tubes to separate vials. Discard the glass wool and foam plugs. Seal the vials with septum caps immediately.
- 8. Allow to stand for 30 min, with occasional agitation. Analyze the sample within the next 30-min period.

CALIBRATION AND QUALITY CONTROL:

- 9. Calibrate with at least five working standards covering the range 0.0002 to 0.2 mg per sample.
 - a. Add known amounts of calibration stock solution to CS_2 in 10-mL volumetric flasks and dilute to the marks, using serial dilution as appropriate.
 - NOTE: Working standards can be stored at -20 °C for at least three days.
 - b. Analyze together with samples and blanks (steps 12 and 13).
 - c. Prepare calibration graphs of peak area vs. quantity (mg) of vinyl chloride per tube and peak area vs. quantity (ng) per injection.
- Determine desorption efficiency (DE) at least once for each lot of charcoal used in the calibration range (step 9). Prepare three tubes at each of five levels plus three media blanks.
 - a. Prepare three atmospheres of vinyl chloride in air by injecting 0.01, 0.08, and 0.2 mL vinyl chloride gas into 10 L air in Tedlar bags. The resulting concentrations are approximately 2.6, 21 and 52 mg/m³.
 - b. Following steps 1 through 4, sample these atmospheres according to the following scheme:

Concentration in Bag (mg/m ³)	Volume Sampled (L)	Quantity of Vinyl Chloride (mg)				
2.6	0.8	0.002				
	2.2	0.006				
21	0.8	0.017				
	2.2	0.046				
52	2.5	0.13				

Obtain three samples at each level.

- c. Desorb (steps 6 through 8) and analyze together with working standards (steps 12 and 13). No vinyl chloride should be found on the back tubes.
- d. Analyze the atmospheres in the bags (steps 12 and 13) using 1-mL gas samples. Read from the calibration graph the quantity (ng) per injection, which for a 1-mL injection of gas is numerically equal to the concentration in mg/m³.
- e. Calculate DE from the mass (mg) of vinyl chloride on the front tube (W_f) , the average blank (B), the concentration of vinyl chloride in the synthetic atmospheres (C_S , mg/m³), and the volume of air sampled (V, L):

$$DE = \frac{(W_{f} - B) \cdot 10^{3}}{(C_{c})(V)}$$

- f. Prepare a graph of DE vs. mass found (Wr B).
- 11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

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VINYL CHLORIDE

HEASUREMENT:

12. Set the gas chromatogrph according to manufacturer's instructions and to conditions given on page 1007-1. Inject sample aliquot manually using solvent flush technique or with autosampler. The retention time of vinyl chloride is about 1.7 min.

NOTE: If peak area is above the linear range of the working standards, dilute with CS₂, reanalyze and apply the appropriate dilution factor in calculations.

13. Measure peak area.

CALCULATIONS:

- 14. Determine the mass, mg (corrected for DE) of vinyl chloride found in the sample front $(W_{\rm F})$ and back $(W_{\rm D})$ tubes, and in the average media blank (B).
 - NOTE: If $M_{\rm b} > M_{\rm c}/10$, report breakthrough and possible sample loss.

15. Calculate concentration, C, of vinyl chloride in the air volume sampled, V (L):

$$C = \frac{(h_f + h_b - 2B) + 10^3}{V}, mg/m^3$$

EVALUATION OF METHOD:

The method was evaluated using single 150-mg sampling tubes with 100-mg front beds and 50-mg back beds [2]. At four concentrations between 1 and 64 mg/m³, the pooled relative standard deviation was 0.06 and the measurements averaged 94% of the concentrations calculated from the volumes of vinyl chloride and air used for the atmospheres sampled; samples at the 3-ug level showed no loss of vinyl chloride when stored for 12 days at room temperature or 19 days at -20 °C. There may be significant loss of vinyl chloride from samples stored for 14 days at room temperature [4]. The 1% breakthrough capacity for a 150-mg bed of coconut charcoal challenged at 100 mL/min with vinyl chloride in air at 16 mg/m³ and a relative humidity of 70% was 4.6 L [5].

REFERENCES :

- [1] <u>TLVs Threshold Limit Values for Chemical Substances and Physical Agents in the Work Environment with Intended Changes for 1983-84</u>, ACGIH, Cincinnati, OH (1983).
- [2] Hill, R. H., Jr., C. S. McCannon, A. T. Saalwaechter, A. W. Teass, and W. J. Woodfin. <u>Anal. Chem.</u>, <u>48</u>, 1395-1398 (1976).
- [3] NIOSH Manual of Analytical Methods, 2nd. ed., V. 1, P&CAM 178, U.S. Department of Health and Human Services, Publ. (NIOSH) 77-157-A (1977).
- [4] Cuddeback, J. E., W. R. Burg, and S. R. Birch, Environ. Sci. Technol., 9, 1168-1171 (1975).
- [5] Matsumura, Y. Ind. Health, 18, 61-67 (1980).

METHOD REVISED BY: A. W. Teass, Ph.D., NIOSH/DPSE.

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VELSICOL CHEMICAL CORPORATION ST. LOUIS, MICHIGAN PROJECT Nº 1524

GAS VENT SAMPLING PUMPS CALIBRATION LOG

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DATE	DEC 1h-	15,	1985	· · · · · · · · · · · · · · · · · · ·	CALIB	RATED	BY 📐	Ros	31250	ى						
					SAMPLING	12 4	85		AFT	ER SAMP	LING	15 85		AV	ERAGE	
PUMP NUMBER	PUMP Type	TEMP. (°F)	HUMIDITY	BAROM. PRESSURE (Inches Hg)	INITIAL FLOW (cc/min.)	CAL. FLOW (cc/min.)	24-HR. TIME	TEMP. (°F)	HUMIDITY (%)	BAROM. PRESSURE (Inches Hg)	FLOW (cc/min.)	24-HR. TIME	TEMP. (°F)	HUMIDITY (%)	BAROM. PRESSURE (Inches Hg)	FLOW (cc/min.)
9369	Frizz a)	20	30	29.90	250	250	1500	18	33	30.15	250	1530	19	31.5	30.03	250
	b)	20	30	29.90	250	250	1500	18	33	30.15		1530		31.5	30.03	250
9370	GELIAS O)	20	30	Z9.90	250	250	1500	18	33	30.15	250	1530	19	31.5	30.03	250
	b)	20	30	23.90	250	250	1500	18	33	30.15		1530	19	31.5	3003	2.50
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COMMENTS

VELSICOL CHEMICAL CORPORATION ST. LOUIS, MICHIGAN PROJECT Nº 1524

DATE OF COLLECTION 12	114 - 12/15	SAMPLER	ROBINSON		BAROME 1 PRESSURI		С	29).9	0					7
TEMPERATURE	20°	RELATIVE	30 %	•	GAUGE	1	2	3	4 !	5 6	7	8	9	10	11
CHARCOAL LOT Nº	120	TENAX LOT Nº	271	•	READING	Ø	-	.0	a	2		Ø.	Þ	8	ð

GAS VENT	PUMP	SAMPLE		SAMPLING TIME		SAMPLING RATE	SAMPLE	
NUMBER	NUMBER	NUMBER	START	FINISH	ELAPSED	(cc/min.)	VOLUME (1)	
1	9370	ļ	3.29	3.49	20	250	5 0	
2	^c)369	2	3.46	406	20	750	650	
3	9370	Ś	4.06	4 26	20	250	50	
4	\$369	4	4.31	4.51	20	250	5.0	
5	9370	5	1.00	1.20	Zo	250	50	
6	9369	4	1.04	1 24	70	250	5.0	
7	9369	8	1.45	2.05	20	250	5.0	
8	9370	7	1.37	1.57	20	250	5.0	
9	9369	9	2.15	2.35	20	250	5.0	
10	9370	10	2.22	2.42	20	250	5.0	
	9369	18	3.00	3.20	20	250	5.0	
DUPLICATE	# 199	12	2.42	3.02				
BLANK		11	2.26					
DATE OF SAMPLE SHIPMENT 12/16/81 METHOD OF FED EX AWB 650-405-221								

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POST - CONSTRUCTION **QUARTERLY MONITORING REPORT**

July 1988

Plant Site, St. Louis Michigan

PRINTED ON · AUG 0 9 1988

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VELSICOL CHEMICAL CORPORATION

POST - CONSTRUCTION QUARTERLY MONITORING REPORT

July 1988

Plant Site, St. Louis Michigan

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1.0 INTRODUCTION

1.1 GENERAL

In accordance with the terms of the technical appendix to the Consent Judgment entered into by Velsicol Chemical Corporation (Velsicol), the United States Environmental Protection Agency, (USEPA) and the Michigan Department of Natural Resources (MDNK), Velsicol is required to perform specified monitoring activities at quarterly intervals following closure of its St. Louis, Michigan plant site. The monitoring program as stipulated by the Consent Judgement addressed the following:

- 1. Performance of gas vents
- 2. Performance of the site perimeter containment wall
- 3. Determination of site groundwater elevations

As of December 1987, Velsicol had completed all activities pursuant to the Consent Judgement in regard to monitoring activities for the gas vents and the perimeter containment wall. Final reports for each completed monitoring activity have been submitted to both Michigan and USEPA kegion IV.

This report details the site monitoring which occurred July 8, 1988.

1.2 MONITORING AND SAMPLING PERSONNEL

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The monitoring program was carried out by D. kobinson of Conestoga-kovers & Associates (CRA) assisted by Mr. Gene DeGeer, Site Custodian under Contract to Velsicol.

2.0 GROUNDWATER TABLE MONITOKING

2.1 GENERAL

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Plant site groundwater elevations were measured and the elevation of the St. Louis reservoir was determined on July 8, 1988.

2.2 WATER LEVEL DETERMINATION

The elevation of the groundwater was determined by measuring the distance from the top of each site monitoring well to the watertable. This distance was measured by lowering a chalked, weighted surveyors tape into the monitoring well. keadings of the tape, which was graduated in increments of one one-hundredth of a toot, were taken at the water level and at the top of the well casing. The former reading was deducted from the latter and the resultant dimension was subtracted from the previously established top of well casing elevation. Well head and watertable elevations are presented on Table 1.

The elevation of the St. Louis reservoir was determined by level and rod survey.

TABLE 1

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WATER LEVEL MEASUREMENTS JULY 8, 1988

MONITORING WELL	WELL HEAD ELEVATION (AMSL)	MEASURED DISTANCE TO WATER TABLE (feet)	WATERTABLE ELEVATION (AMSL)
1	736.00	14.55	721.45
2	742.10	19.74	722.36
3	749.91	27.69	722.22
4	736.06	13.87	722.19
5	739.37	18.48	720.89
6	734.52	12.88	721.64
7	734.08	12.31	721.77
8	734.31	12.77	721.54
9	734.60	12.97	721.63
10	733.50	11.87	721.63
11	734.46	12.78	721.68
12	730.79	9.16	721.63
13	734.52	12.81	721.70
14	736.00	14.27	721.73

Water level elevation, St. Louis Reservoir July 8, 1988 718.23 2.3 GROUNDWATER CONTOUR MAP

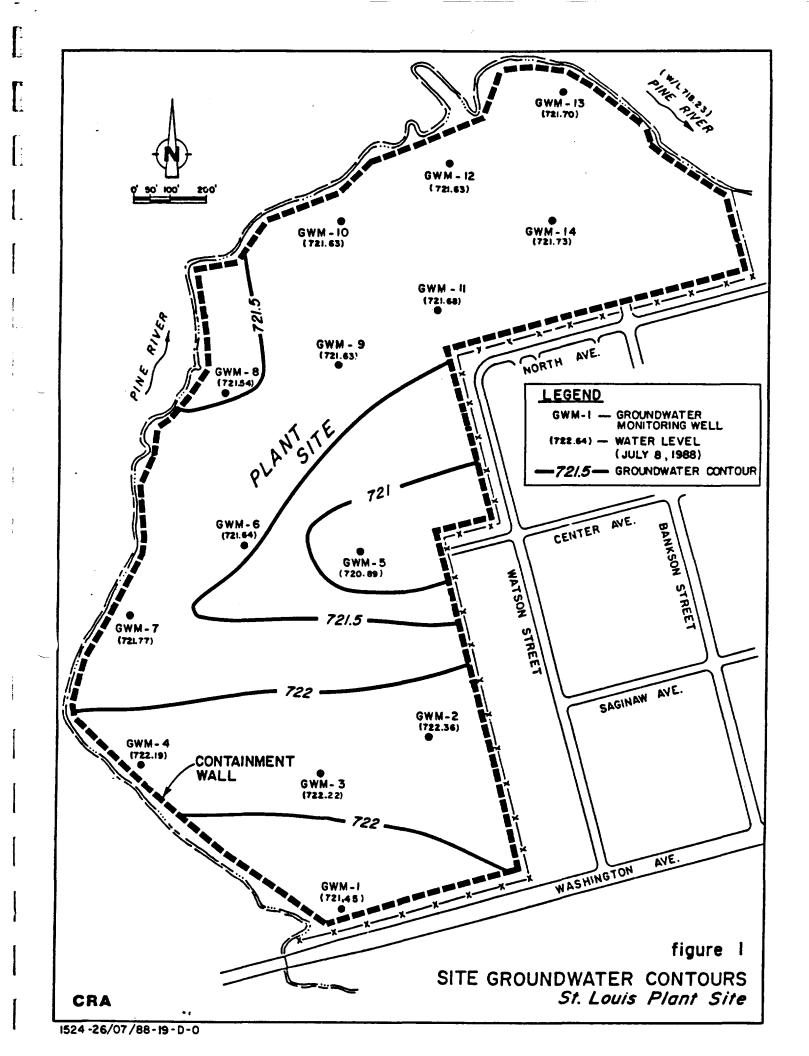
> The groundwater elevation data were used to construct a site groundwater elevation contour map which is presented in Figure 1.

2.4 SITE MEAN GROUNDWATER ELEVATION

The mean elevation of site groundwater is calculated to be 721.72. The maximum allowable mean site groundwater elevation stipulated by the Consent Judgment is 724.13.

2.5 WELL HEAD ELEVATION SURVEY

In accordance with the Post Closure Maintenance and Monitoring Plan, the well head elevations are re-surveyed on a yearly basis to ensure accuracy of the elevations. All well head elevations were surveyed during the July, 1988 monitoring event.



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OCT 5 1989

Plant Site, St. Louis Michigan

POST - CONSTRUCTION **QUARTERLY MONITORING REPORT**

SEPTEMBER, 1989

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VELSICOL CHEMICAL CORPORATION

POST - CONSTRUCTION QUARTERLY MONITORING REPORT SEPTEMBER, 1989

Plant Site, St. Louis Michigan

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SEPTEMBER 27, 1989

1.0 INTRODUCTION

1.1 <u>GENERAL</u>

In accordance with the terms of the technical appendix to the Consent Judgement entered into by Velsicol Chemical Corporation (Velsicol), the United States Environmental Protection Agency, (USEPA) and the Michigan Department of Natural Resources (MDNR), Velsicol is required to perform specified monitoring activities at quarterly intervals following closure of its St. Louis, Michigan plant site. The monitoring program as stipulated by the Consent Judgement addressed the following:

- 1. Performance of gas vents
- 2. Performance of the site perimeter containment wall
- 3. Determination of site groundwater elevations

As of December 1987, Velsicol had completed all activities pursuant to the Consent Judgement in regard to monitoring activities for the gas vents and the perimeter containment wall. Final reports for each completed monitoring activity have been submitted to both Michigan and USEPA Region IV.

This report details the site monitoring which occurred September 27, 1989.

1.2 MONITORING AND SAMPLING PERSONNEL

The monitoring program was carried out by W. Pochron of Conestoga-Rovers & Associates (CRA) assisted by Mr. Gene DeGeer, Site Custodian under Contract to Velsicol.

TABLE 1

WATER LEVEL MEASUREMENTS SEPTEMBER 27, 1989

		Measured	
	Well Head	Distance to	Water Table
Monitoring	Elevation	Water Table	Elevation
Well	(AMSL)	(feet)	(AMSL)
1	736.10	14.00	722.10
2	742.19	19.53	722.66
3	749.98	27.46	722.52
4	736.17	13.70	722.47
5	739.55	17.28	722.27
6	734.65	11.50	723.15
7	734.18	11.88	722.30
8	734.43	12.30	722.13
9	734.66	12.55	722.11
10	733.55	11.56	721.99
11	734.53	12.40	722.13
12	730.85	8.83	722.02
13	734.54	· 12.44	722.10
14	736.05	13.90	722.15

Water level elevation, St. Louis Reservoir September 27, 1989

718.52

2.0 GROUNDWATER TABLE MONITORING

2.1 <u>GENERAL</u>

Plant site groundwater elevations were measured and the elevation of the St. Louis reservoir was determined on September 27, 1989.

2.2 WATER LEVEL DETERMINATION

The elevation of the groundwater was determined by measuring the distance from the top of each site monitoring well to the water table. This distance was measured by lowering a chalked, weighted surveyors tape into the monitoring well. Readings of the tape, which was graduated in increments of one one-hundredth of a foot, were taken at the water level and at the top of the well casing. The former reading was deducted from the latter and the resultant dimension was subtracted from the previously established top of well casing elevation. Well head and water table elevations are presented on Table 1.

The elevation of the St. Louis reservoir was determined by level and rod survey.

2.3 <u>GROUNDWATER CONTOUR MAP</u>

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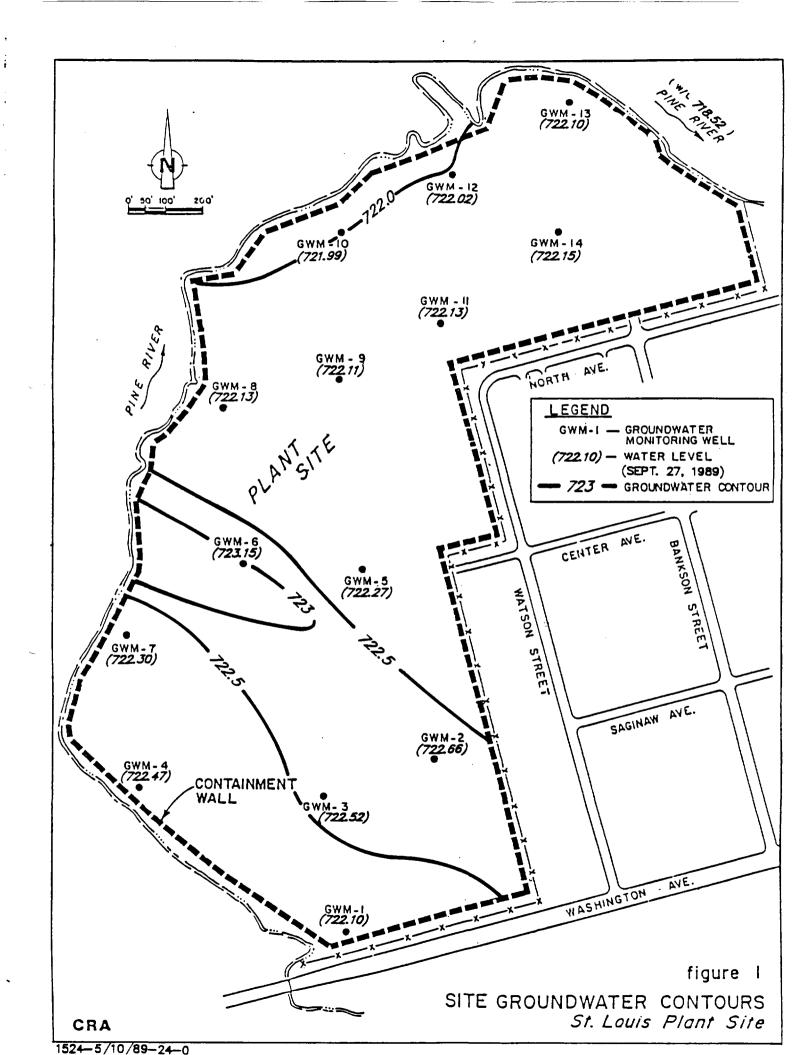
The groundwater elevation data were used to construct a site groundwater elevation contour map which is presented in Figure 1.

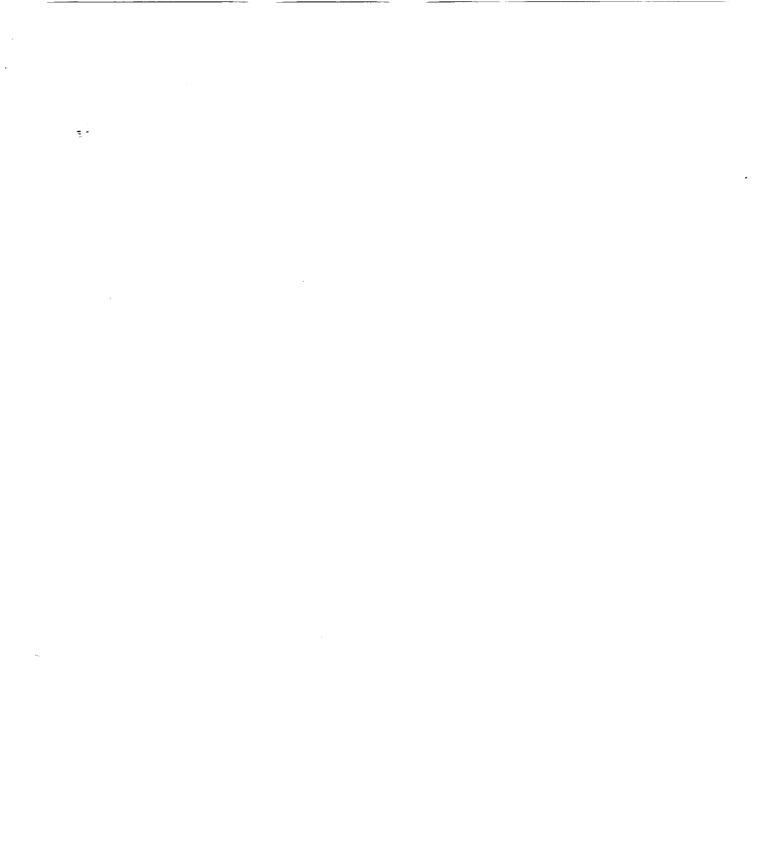
2.4 SITE MEAN GROUNDWATER ELEVATION

The mean elevation of site groundwater is calculated to be 722.29. The maximum allowable mean site groundwater elevation stipulated by the Consent Judgement is 724.13.

2.5 WELL HEAD ELEVATION SURVEY

In accordance with the Post Closure Maintenance and Monitoring Plan, the well head elevations are re-surveyed on a yearly basis to ensure accuracy of the elevations. All well head elevations were surveyed during the March, 1989 monitoring event.





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VELSICOL CHEMICAL CORPORATION

POST - CONSTRUCTION QUARTERLY MONITORING REPORT

MARCH 11-14, 1986

Plant Site, St. Louis Michigan

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6.0 SUMMARY

1.0 INTRODUCTION

1.1 GENERAL

In accordance with the terms of the technical appendix to the Consent Judgment entered into by Velsicol Chemical Corporation (Velsicol), the United States Environmental Protection Agency, (USEPA) and the Michigan Department of Natural Resources (MDNR), Velsicol is required to perform specified monitoring activities at quarterly intervals following closure of its St. Louis, Michigan plant site. The monitoring program is designed to address the following:

- 1. Performance of gas vents
- 2. Performance of the site perimeter containment wall
- 3. Determination of site groundwater elevations

This report details the site monitoring which occured during the period March 11 to March 14, 1986.

1.2 PARTICIPATION BY REGULATORY AGENCIES

Mr. Peter Miller of the USEPA was on-site March 12 to March 14, 1986 to observe all monitoring activities.

1.3 MONITORING AND SAMPLING PERSONNEL

The monitoring and sampling program was carried out by Ms. C. Cull of Conestoga-Rovers & Associates (CRA) assisted by Mr. Gene DeGeer, the Velsicol site custodian. Don Robinson of CRA supervised the mechanical integrity testing of the Disposal Well #2 annulus.

2.0 GAS VENT MONITORING

2.1 GENERAL

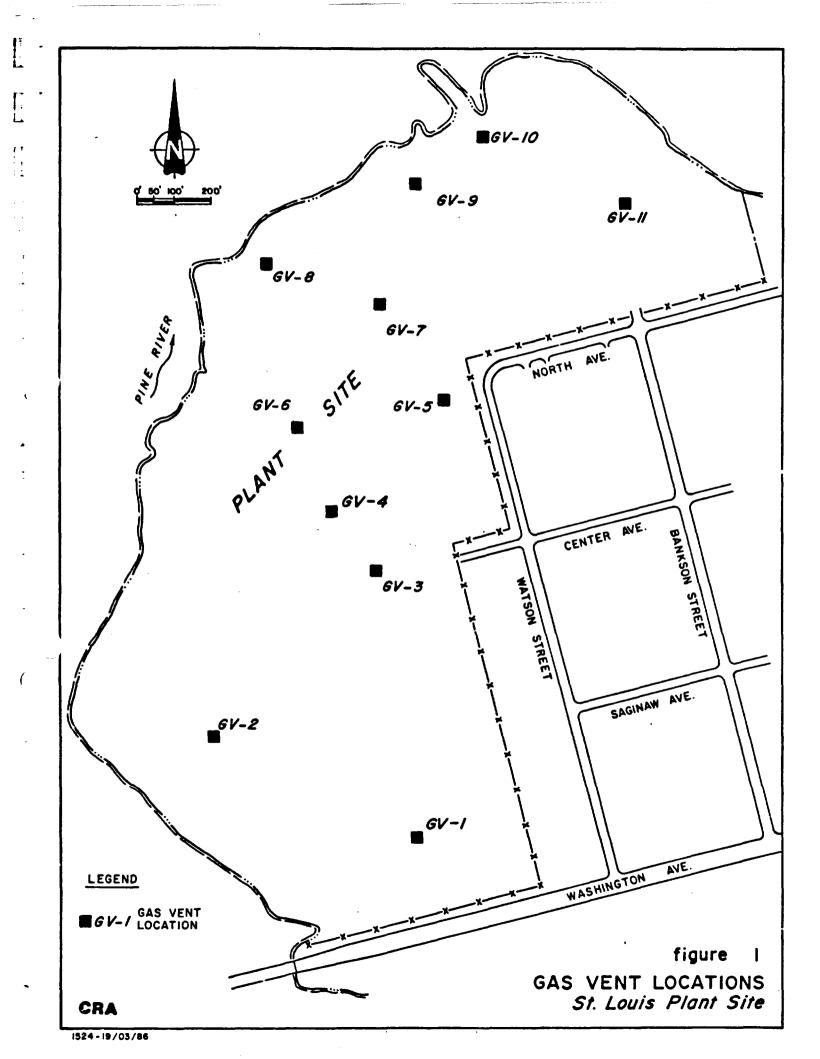
The gas vent monitoring began on March 12, 1986 and was completed that same day.

2.1.1 Equipment

Two Gilian model HFS 113 hi flow samplers were used to collect gas vent samples. The samplers were field calibrated using a rotometer prior to sampling. The calibration data is presented within Appendix A. Samples from each gas vent were collected in two 6-mm diameter x 70-mm long Tenax tubes and two charcoal tubes of similar dimensions. The samples were collected simultaneously using dual parallel/series tube holder sets.

2.2 SAMPLE COLLECTION

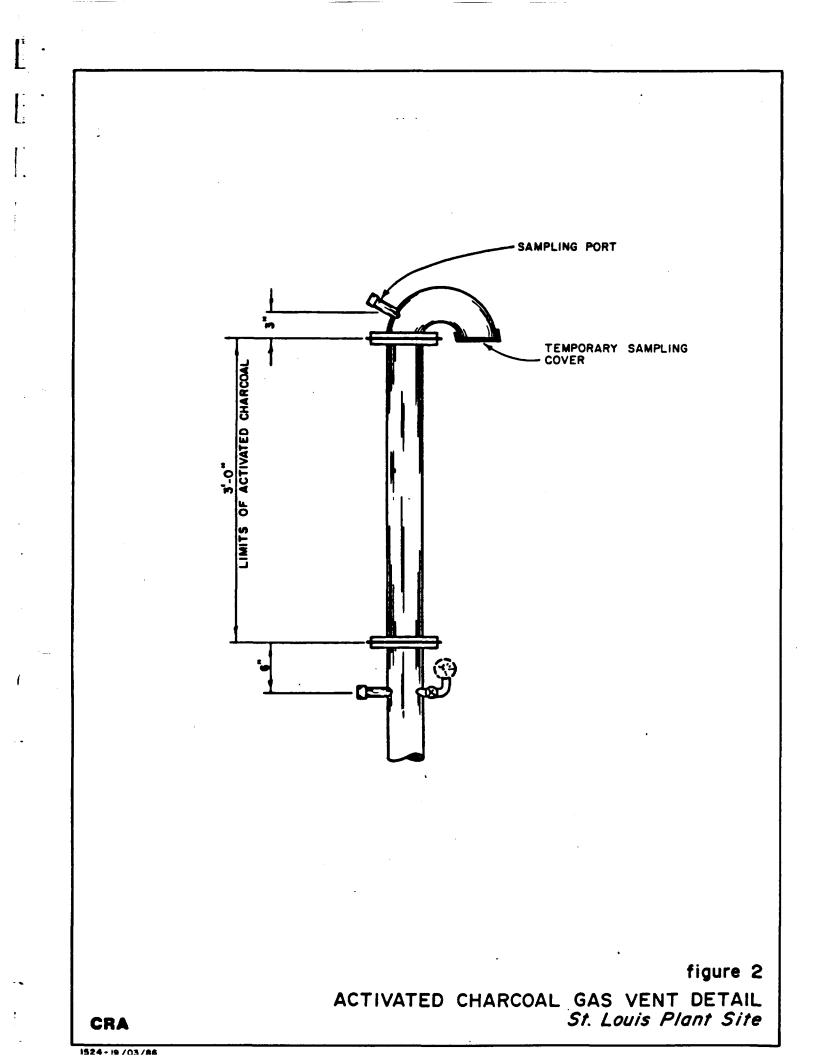
Samples were obtained at each of the 11 gas vents. The location of the gas vents within the closed plant site is detailed on Figure 1. One blank set and one duplicate set of samples were also collected.



Sampling was conducted at the downstream sampling port on each gas vent as detailed on Figure 2. The tube holder was attached directly to the gas vent sampling port using a copper manifold assembly. Tygon tubing was used to connect the tube holder to the sampler and was connected between the base of the tube holder and suction port of the sampler. The sampler which was pre-calibrated to 250cc/min/tube set, was operated for a period of 20 minutes for each sampling event, resulting in a collected sample volume of five liters per tube set.

Prior to sample collection, the gas vent upper chamber was purged by pumping at 500 cc/minute for a period of ten minutes. This precluded the possiblity of sampling retained atmospheric air from the gas vent upper chamber. During the purging and sampling operations, the open end of the gas vent was capped using a 4-inch diameter plastic cover to prevent atmospheric air being drawn into the sample.

At the conclusion of each gas vent sampling, the set of four sample tubes were capped, labelled and stored in a cooler maintained at 0°C.



2.2.1 Sample Storage and Shipment

On the afternoon of March 12, 1986 the samples were transferred to a cooler containing frozen cold packs and styrofoam packing materials. The cooler was shipped under chain of custody protocol, to Velsicol's Memphis, Tennessee laboratory by overnight courier for analysis. A copy of the chain of custody is provided in Appendix B.

2.2.2 Sample Analysis

Analysis will be conducted in accordance with NIOSH protocols as follows:

Compound	NIOSH Method
Carbon Tetrachloride	1003
Trichloroethylene	S-336
Vinyl Chloride	1007

Results will be reported verbally as they become available.

A hard copy of the laboratory report will be forwarded to USEPA and MDNR within seven days after receipt of final laboratory data by CRA.

2.2.3 <u>Sampling Protocol</u>

All sampling was performed in accordance with the methodology detailed within the St. Louis plant site Post-Closure Maintenance and Monitoring Plan, as approved by USEPA and MDNR. A copy of the sampling protocol is contained in Appendix A.

3.0 SITE PERIMETER CONTAINMENT WALL MONITORING

3.1 GENERAL

The monitoring program consisting of the collection of an undisturbed sample of the containment wall with subsequent permeability testing was initiated on December 15, 1983. Subsequent sampling events occurred on March 15, 1984, June 15, 1984, September 14, 1984, December 14, 1985, March 16, 1985 and June 19, 1985, September 16, 1985 and December 14, 1985. The current sampling event occured March 13, 1986. All testing completed to date has confirmed the permeability of the site perimeter containment wall to be less than 1.0 x 10^{-7} cm/sec.

3.2 EQUIPMENT

A Mobil Truck mounted drill rig equipped with rotary head and 4-inch O.D. diameter augers was utilized to advance the borehole into the containment wall. A 3-inch diameter Shelby tube, hydraulically pushed and retrieved, was used to collect the samples.

3.3 SAMPLE COLLECTION

The containment wall was located by field survey on March 13, 1986. The sampling borehole was begun at Station DGW 37+00 by augering through the clay cap into the underlying material.

Five attempts were made to locate the slurry wall at Station 37+00, beginning at the fence and moving at 2-foot intervals away from the fence. The presence of the soil/bentonite wall could not be confirmed at this location and, therefore, the rig was moved to Station 37+60. Two attempts were made at this location, beginning at the fence, and moving out two feet. The presence of the containment wall could not be confirmed. Again, the rig was moved, this time to Station 38+10. The first attempt at this location was successful. It is believed that the soil/containment wall is beneath the fence along the areas in which initial drilling took place.

The presence of soil/bentonite backfill material was confirmed by examination of cuttings on the auger flights. A borehole was advanced to a depth of nine feet below grade. Two Shelby tubes were introduced into the borehole and samples were collected at 4'-6' and 6'-8' from the top of the containment wall. Examination of material in the base of the tube confirmed that the sample was obtained

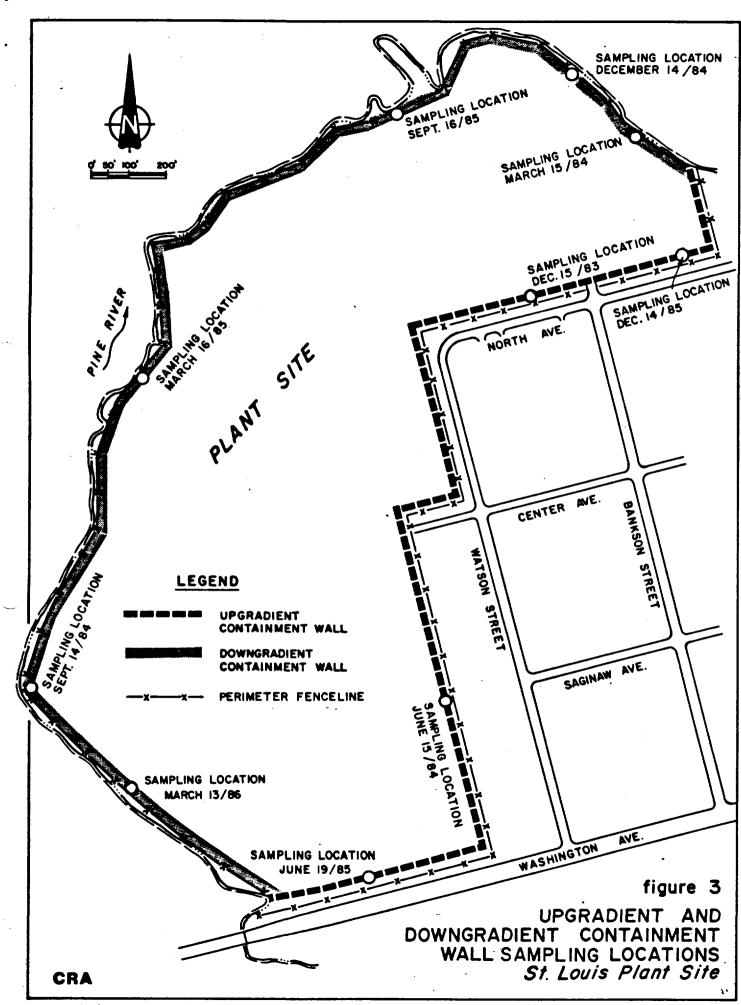
from the containment wall. The location of this and prior sampling events are detailed on Figure 3. The boreholes were backfilled with bentonite and abandoned.

3.3.1 Sample Preparation and Shipping

The Shelby tubes were waxed, capped and taped at both ends to prevent sample loss and drying. The samples were hand delivered to the Michigan Testing Engineer's laboratory in Detroit, Michigan for permeability testing.

3.3.2 Sample Testing

The undisturbed sample is to be tested for permeability using a falling head permeameter set up in accordance with ASTM D 2434. Results of the testing will be provided in written form to USEPA and MDNR within seven days after receipt of final laboratory data by CRA. A summary data report will be prepared and presented to both Agencies following completion of the containment wall monitoring program in the fall of 1986.



4.0 GROUNDWATER TABLE MONITORING

4.1 GENERAL

The monitoring of plant site groundwater elevation was performed and the elevation of the St. Louis reservoir was determined on March 13, 1986.

4.2 WATER LEVEL DETERMINATION

The elevation of the groundwater was determined by measuring the distance from the top of each site monitoring well to the watertable. This distance was measured by lowering a chalked, weighted surveyors tape into the monitoring well. Readings of the tape, which was graduated in increments of one one-hundredth of a foot, were taken at the water level and at the top of the well casing. The former reading was deducted from the latter and the resultant dimension was subtracted from the previously established top of well casing elevation. Well head and watertable elevations are presented on Table 1.

The elevation of the St. Louis reservoir was determined by level and rod survey.

TABLE	1
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WATER LEVEL MEASUREMENTS

MARCH 13, 1986

	WELL HEAD	MEASURED DISTANCE TO	WATERTABLE
MONITORING WELL	ELEVATION (AMSL)	WATER TABLE (ft.)	ELEVATION (AMSL)
1	735.93	14.50	721.43
2	742.08	19.29	722.79
3	749.93	27.85	722.08
4	736.03	13.92	722.11
5	739.38	18.17	721.21
6	734.51	13.42	721.09
7	734.03	12.75	721.28
8	734.36	13.35	721.01
9	734.61	13.42	721.19
10	733.48	13.31	720.17
11	734.45	13.31	721.14
12	730.81	9.68	721.13
13	734.49	13.40	721.09
14	736.02	14.81	721.21

Water level elevation, St. Louis Reservoir March 13, 1986

720.07

4.3 GROUNDWATER CONTOUR MAP

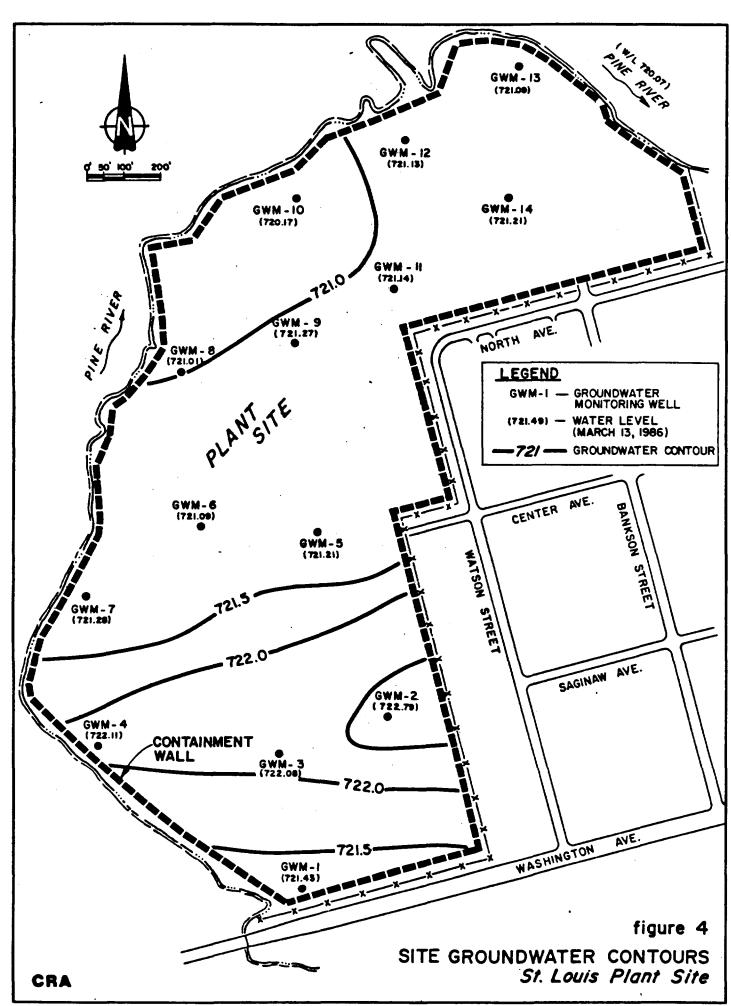
The groundwater elevation data were used to construct a site groundwater elevation contour map which is presented in Figure 4.

4.4 SITE MEAN GROUNDWATER ELEVATION

The mean elevation of site groundwater is calculated to be 721.35. The maximum allowable site groundwater elevation stipulated by the Consent Judgment is 724.13.

4.5 WELL HEAD ELEVATION SURVEY

In accordance with the Post Closure Maintenance and Monitoring Plan, the well head elevations were re-surveyed on March 11, 1986 to ensure accuracy of the elevations. Minor differences from previous surveys were recorded and the groundwater elevations were adjusted accordingly. This phase of the program will be conducted yearly.



5.0 DISPOSAL WELL TESTING

A mechanical integrity test was conducted in the Disposal Well #2 annulus on March 14, 1986. The following were in attendance, Mr. D. Robinson and Ms. C. Cull (CRA), Mr. G. DeGeer (Velsicol), and Mr. H. Novakowski and Mr. P. Miller (USEPA). The test was performed by Long and Wetzel Co. of Mt. Pleasant, Michigan.

The test consisted of pressurizing the annulus to 300 psi and holding it constant for a period of 30 minutes. The well lost 4 lbs. of pressure during this test, and was re-pressurized to approximately 115 psi after the completion of the test. Data generated from this test is presented in Appendix C. All monitoring activities stipulated by the Consent Judgment were carried out between March 11 and March 14, 1986.

Data from the chemical analysis of the gas vent samples and the permeability testing of the contaminant wall sample will be provided to MDNR and USEPA within seven days of receipt by CRA of laboratory final data.

The present mean site groundwater table elevation is calculated to be 721.35. The elevation in the Pine River/St. Louis reservoir was determined to be 720.07.

The next sampling and monitoring event will occur on or about June 15, 1986.

All of Which is Respectfully Submitted, CONESTOGA-ROVERS & ASSOCIATES LIMITED

CA Cull

C. A. Cull, B.Sc.

R.G. Shepherd, P. Eng.

APPENDIX A CALIBRATION DATA AND

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GAS SAMPLING PROTOCOLS

APPENDIX B

GAS VENT SAMPLING PROTOCOL

In accordance with the Consent Judgment, Velsicol has submitted a post-closure maintenance and monitoring plan for its environmentally secured plant site in St. Louis, Michigan. The post-closure maintenance and monitoring plan requires quarterly monitoring of 11 gas vents that have been installed to release and appropriately treat internal gases. This program will be conducted over a period of three years.

The gas vents, as detailed in Exhibit F of the Consent Judgment, are designed with two sampling ports; one below the base of the installed activated charcoal filter, and one above the filter. Samples will be collected from the downstream port. Results will indicate whether or not containment breakthrough has occured through the carbon filter.

Samples will be analyzed for three separate compounds: carbon tetrachloride, trichloroethylene and vinyl chloride.

Samples will be collected with a Gilian HFS-113 AU DK variable flow pump. This particular unit allows the operator to run a series of tubes concurrently in parallel arrangement. Four tubes will be collected from each gas vent: two standard NIOSH 100/50 mg activated charcoal tube, and two 30/15 mg tenax tubes, each tube measuring 6 mm x 70 mm. One blank set and one duplicate set of tubes will be collected during each quarterly sampling event.

As vinyl chloride represents the least adsorptive of the three compounds, the sampling program is designed to accomodate this compound. Therefore, sample volume shall not exceed 5 liters.

1

Prior to sampling, the vent will be sealed off with a plastic cap, and purged for 10 minutes at a rate of 500 cc/min. This is to eliminate the possibility of sampling atmospheric air contained within the upper portion of the gas vent.

Two samples from each gas vent shall be collected simultaneously at a rate of 250 cc/min. for 20 minutes. The pump shall be lab calibrated with sample tubes in-line to determine the exact flow rate. Additionally, flow will be checked after field sampling to verify that a constant flow was maintained throughout the sampling period.

Following sample collection, each tube will be sealed with a plastic cap at each end, labelled, placed in a cold storage environment and shipped under chain-of-custody via a commercial courier service to Velsicol's analytical laboratory in Memphis.

Analysis of the charcoal tube will be conducted in accordance with NIOSH protocol as detailed below:

Compound	Revised Method No.
Carbon Tetrachloride	1003
Trichloroethylene	S-336
Vinyl Chloride	1007

Analysis will proceed by first eluting the carbon sample tubes with carbon disulfide and then analyzing by GC with a flame ionization detector. All samples will be initially analyzed in this fashion. If any of the above compounds are detected on the charcoal tube, the corresponding tenax tube will be analyzed by thermal desorption and GC/MS under EPA Method 624.

Turnaround time for the completed analysis at the laboratory is anticipated to be 30 days from date of sample collection. Samples will be desorbed within the 10 day limit specified for vinyl chloride. Analytical data will be reported to CRA as mg/tube. Final results for the carbon tube will be calculated by CRA, using the following formula.

1. Corrections for the blank to be made for each sample
 mg = mg sample - mg blank

This calculation is performed separately for each tube.

- 2. Add the amounts present in the front tube and backup tube to determine the total weight in the sample.
- 3. Calculate the corrected mg/sample by dividing the total weight by the desorption efficiency (D.E.) which is provided by the lab.

corrected mg/sample = total weight

- 4. Calculate the concentration of the analyte in air $mg/m^3 = Corrected mg \times 1000 liters/m^3$ Air volume Sampled (liters)
- 5. Concentration will be reported as ppm, corrected to standard conditions of 25°C and 760 mm Hg
 3

 $ppm = mg/m \quad x \; \frac{24.45}{MW} \; x \; \frac{760}{P} \; x \; \frac{(T+273)}{298}$

where P T	= pressure (mm Hg) of air sampled = temperature (°C) of air sampled
•	= molar volume (liter/mole) at 25°C and 760 mm Hg
MW	= Molecular Weight
760	= standard pressure (mm Hg)
298	= standard temperature (°K)

- 2 -

- NOTE: Temperature and pressure uncorrected to sea level will be collected for the duration of the sampling event and averaged for use in the above calculations. Information will be provided from the National Weather Service in Lansing, Michigan.
 - 6. If the concentration of the back tube exceeds 10% of the concentration of the front tube, the results will be reported as a sample breakthrough and possible sample loss.
 - 7. A similar procedure will be followed for the tenax tube, should analysis be required.

Data will be reported to USEPA and MDNR officials within seven days after receipt of final laboratory data for each quarterly sampling. Additionally, a summary data report will be provided at the conclusion of the three year sampling period, or sooner, should breakthrough of any compound occur prior to the three year program.

In addition to the set of field blanks to be collected per quarterly sampling event, an additional set of 15 charcoal tubes and 15 tenax tubes will be forwarded unopened to the lab during the initial sampling event.

These "blank" tubes will be used as internal calibration standards on which each of the three compounds will be spiked at five different concentrations. The data from this analysis will be used to calculate the desorption efficiency for a specific lot of activated charcoal. Therefore, the lot number of carbon tubes and tenax tubes shall be recorded during each quarterly sampling. Should the lot number change, a new set of 15 charcoal tubes and 15 tenax tubes shall be forwarded to the laboratory for determination of the new desorption efficiency.

The allowable limits for these compounds have been established by the MDNR and are site specific for the St. Louis site. These limits are documented in section 4.3 of the post-closure maintenance and monitoring plan.

Copies of all three analytical protocols, the chain of custody and the data collection sheet are provided in the following sections.

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- 3 -

HYDROCARBONS, HALOGENATED

FORMULA: Table 1

METHOD: 1003

M.W.: Table 1

ISSUED: 2/14/84

COMPOUNDS: benzyl chloride (synonyms branoform in Table]) carbon tetrachloride ch lorobenzene

chlorobromomethane chloroform o-dichlorobenzene p-dichlorobenzene

1,1-dichloroethane hexachloroethane 1,2-dichloroethylene methylchloroform ethylene dichloride propylene dichloride

SAMPLING	MEASUREMENT
SAMPLER: SOLID SORBENT TUBE	! !TECHNIQUE: GAS CHROMATOGRAPHY, FID
(coconut shell charcoal, 100 mg/50 mg): !ANALYTE: compounds above
FLOW RATE: 0.01 to 0.2 L/min	1 1 DESORPTION: 1 mL CS ₂ , stand 30 min
VOL-MIN: Table 2	! -
-MAX: Table 2	!INJECTION VOLUME: 5 µL !
SHIPMENT: routine	TEMPERATURES: Table 2
SAMPLE STABILITY: at least 1 week @ 25 °C	CARRIER GAS: N2 or He, 30 mL/min
BLANKS: 2 to 10 field blanks per set	: COLUMN: Table 2; alternates are SP-2100, SP-2100 with 0.1% Carbowax 1500 or DB-1 fused silica capillary column
ACCURACY	!
	ICALIBRATICA: solutions of analyte in CS- with
BIAS: not significant [1]	RANGE: Table 2
OVERALL PRECISION (sp): see EVALUATION OF	: :ESTIMATED LOD: 0.01 mg per sample [2]
METHOD [1]	: PRECISION (Sp): See EVALUATION OF METHOD [1]

APPLICABILITY: This method uses a simple desorption and can be used for simultaneous analysis of two or more substances suspected to be present by changing the gas chromatographic conditions (i.e., temperature programmed). High humidity during sampling will prevent organic vapors from being trapped efficiently on the sorbent and greatly decreases breakthrough volume.

INTERFERENCES: None identified. The chromatographic column or separation conditions may be changed to circumvent interference problems.

OTHER METHODS: This method combines and replaces Methods P&CAM 127 [3]; S95, S101, S110, S113, \$114, \$115, \$122, \$123 and \$133 [4]; and \$135, \$281, \$314, \$328 and \$351 [5].

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2/15/84

METHOD: 1003

a. Remove and discard back sorbent section of a media blank sampler.

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- b. Inject a known amount of analyte or calibration stock solution directly onto front sorbent section with a microliter syringe.
- c. Cap the tube. Allow to stand overnight.
- d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
- e. Prepare a graph of DE vs. mg analyte recovered.
- 10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

 Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1003-1. Inject sample aliquot manually using solvent flush technique or with autosampler.

NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.

12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of analyte found in the sample front (W_f) and back (W_D) sorbent sections, and in the average media blank front (B_f) and back (B_D) sorbent sections.

NOTE: If $W_{\rm b} > W_{\rm f}/10$, report breakthrough and possible sample loss.

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14. Calculate concentration, C, of analyte in the air volume sampled, V (L):

$$C = \frac{(H_{f} + H_{b} - B_{f} - B_{b}) + 10^{3}}{V}$$
, mg/m³.

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Laboratory testing was performed with spiked samples and generated atmosphere [1]. All analytes are stable at least one week. All methods were validated using SKC Lot 105 coconut shell charcoal. Results were:

1003-3

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[9] Criteria for a Recommended Standard...Occupational Exposure to 1,1,1-Trichloroethane, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 76-184 (1976).

[10] Criteria for a Recommended Standard...Occupational Exposure to Carbon Tetrachloride, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 76-133 (1976).

METHOD REVISED BY: G. D. Foley; Y. T. Gagnon; and K. J. Williams, NIOSH/DPSE; methods originally validated under NIOSH Contract CDC-99-74-45.

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ار به ۲۰۰۰ می از به هداوین به آمادید. **میر**د و دوازی این قدیمی و فرز موادید در در بود و ر

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Campounds	Formula	M.W.; mg/m ³ <u>= 1 ppm</u>	<u>Synonyms</u>	OSHA N105H [6-10] <u>ACG1H</u>	<u>8P (°C)</u>	VP () 20 °C	Density (g/mL @ 20 °C)
<u>p</u> -Dìch ìorobenzene	1,4-C ₆ H ₄ C1 ₂	147.00; 6.01)dichlorobenzene; (*#106-467	75 ppm 75 ppm, STEL 110 ppm	.174	50 Pa	1.241
I, 1-Dichloroethane	ai ₃ aici ₂ ; c ₂ H4Ci ₂	98.96; 4.05	c Hylldene chldride; Cra, #15-34-3	100 ppm 100 ppm 200 ppm, STEL 250 ppm	57	24.3 kPa	1.174
1,2-Dìchloroethylene	c)ai=aic); c_ii_c) 2 4 2	96.95; 3.96	acetylene dichloride; 1,2-dichloroethene; Corr #540-59-0	200 ppm 200 ppm 200 ppm, STEL 250 ppm	60 (cis) 47 (trans)	24-35 kPa	1.28
Ethylene dichloride*	c1a1 ₂ a1 ₂ c1; c ₂ 11 ₄ c1 ₂	98.96; 4.05	1, '-dichloroethane; C== #107-06-2	50 ppm, C 100 ppm 5 ppm; 15 ppm/15 min 10 ppm, STEL 15 ppm	83	8.3 kPa	1.255
Hexach loroethane*	cc1 ₃ cc1 ₃ ; c ₂ c1 ₆	236.14; 9.68	µ++ ch1oroethane; (), , #67-72-1	l ppm (skin) l ppm (skin) 10 ppm	187 (sublimes)	30 Pa	2.09
Hethylchloroform	c ⁵ 11 ³ c1 ³	133.42; 5.45	1,1,1-trichioroethane; (;#11-55-6	350 ppm 350 ppm/15 min CAS #71-55-6 S1EL 450 ppm	74 350 ppm,	13.3 kPa	1.335
Propylene dichloride	ai ₃ aiciai ₂ ci; c ₃ ii ₆ ci ₂	112.99; 4.62	1,∷-dich1oropropane (°√~ #78-87-5	75 ррт 75 ррт 75 ррт, 75 ррт, 51EL 110 ррт	95	5.3 kPa	1.156 (25 °C)

2/15/84

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	Air Sample Volume (L)				thet inc			t (°C)		
Compound	Afa	Nav	Break through In its with	r augh Tàr	Range	ڈ		Injector	Internal	(mg per
l, l-Dichloroethane	1 (J 100 ppm	· 9	18.3 L	em/gm (ii	40 to 1215 (10 t)		K	50 100	Standard	0.4 to 12
1,2-Dichloroethylcne 0.5 8 200 ppm	0.5 @ 200 ppm	~	5.4 L fr *	e ^{w/fiw} 60):	. 80 to 2370 (3 L)	0[<	175 176 210 210	:	0.2 to 7
Ethylene dichloride	1 @ 50 ppm	2	29 L 31	3 1 . : : mJ/m 2	40 to 1215 (3 t)	SI	<	70 225	oclane	0.1 to 4
Hexach loroethane	l é l ppm	2		a m/Ci	1 tu 30 (10 t.)		۵	250 110 210 210	n-tridecane	0.01 to 0.3
Rethylchloroform	0.5 Å 350 ppm	•	9.5 t .	9.5 to ville mg/m ^a	190 to 5700 (3 L)	8	<	70 225 250	octane	0.6 to 17
Propylene dichloride	mtd 5/ 6) 1	0	84, 1 01	e **/fier	35 to 1050 (10 t)	8	<	80 170 210	n-undecane	0.3 to 10
*A = 3 m × 3 km stainless steel, 10% B = 6 m × 3 km stainless same as A C = 3 m × 3 km stainless steel, 10% D = 3 m × 6 km stainless for 2500 see	3 am stainles steel, 105 SP-1040 per 3 au, sthored e same as A; 3 au stainles steel, 105 0V-101 au	-ds -0	SP-10'10 1.	100 mesh Supelcoport; 120 mesh Supelcoport; or	pelcoport; pelcoport;	5				

METHOD: 1003

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HYDROCARBONS, HALOGENATED

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1003-9

Trichloroethylene

Analyte:	Trichloroethylene	Mathod No.: \$336
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Matrix:	Air	Range: 519-2176 mg/cu m
OSHA Standard:	200 ppm (1075 mg/cu m)-Ceiling 100 ppm (535 mg/cu m)-T.W.A.	Precision (\overline{CV}_{T}) : 0.082
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 6/6/75

1. Principle of the Mathod

- 1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.
- 1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.
- 1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.
- 1.4 The area of the resulting peak is determined and compared with areas obtained from injection of standards.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 519-2176 mg/cu m at an atmospheric temperature and pressure of 24.5°C and 759.4 mm Hg, using a 3-liter sample. Under the conditions of sample size (3 liters) the probable useful range of this method is 108-3225 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 9.7 mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.
- 2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 42 mg of analyte when a test atmosphere containing 2266 mg/cu m of analyte in air was sampled at 0.187 liters per minute for 99 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent.

(The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

- 3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.
- 3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.
- 3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.
- 3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation $(\overline{CV_T})$ for the total analytical and sampling method in the range of 519-2176 mg/cu m was 0.082. This value corresponds to an 88.2 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.
- 4.2 On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 6.4 % lower than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result.

These data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

- 5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.
- 5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be impracise, because the pump is usually calibrated for one tube only.

6. Apparatus

- 6.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3).
- 6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm 0.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.
- 6.3 Gas chromatograph equipped with a flame ionization detector.
- 6.4 Column (10-ft x 1/8-in stainless steel) packed with 10% OV-101 stationary phase on 100/120 mesh Supelcoport.
- 6.5 An electronic integrator or some other suitable method for measuring peak areas.
- 6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.
- 6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.
- 6.8 Pipets: 1.0 ml type graduated in 0.1-ml increments.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

- 7.1 Chromatographic quality carbon disulfide.
- 7.2 Trichloroethylene, reagent grade
- 7.3 Octame, or other suitable internal standard
- 7.4 Purified mitrogen
- 7.5 . Prepurified hydrogen.
- 7.6 Filtered compressed air.

8. Procedure

- 8.1 Cleaning of equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.
- 8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.
- 8.3 Collection and Shipping of Samples -
 - 8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).
 - 8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.
 - 8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.
 - 8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.
 - 8.3.5 At the ceiling and peak concentrations, a sample size of 3 liters is recommended. Sample for 15 minutes at a flow of 0.2 liters per minute. At the T.W.A. concentration, a sample size of 10 liters is recommended. Sample at a flow of 0.2 liters per minute or less. The flow rates should be known with an accuracy of at least ±52.
 - 8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

S336-4

- 8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no . circumstances should rubber caps be used.
- 8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.
- 8.3.9 Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.
- 8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

- 4
- 8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.
- 8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.
- 8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

30 ml/min (60 psig) Nitrogen carrier gas flow
 35 ml/min (25 psig) Hydrogen gas flow to detector
 400 ml/min (60 psig) Air flow to detector
 225°C injector temperature
 250°C manifold temperature (detector) and the second
- 8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.
- 8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.
- 8.5 Determination of Desorption Efficiency

- 8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.
- 8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. When using an automatic sample injector, the sample injector vials, capped with Teflon-faced septa, may be used in place of the glass tubes.

Six tubes at each of three concentration levels (0.5%,1% and 2% of the standard) are prepared by adding an amount of analyte equivalent to that present in a 3-liter sample at the selected level. The tubes are allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 1.0 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

D.E. = <u>Average Weight (mg) recovered</u> Weight (mg) added

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg per 1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2% the standard. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

VINYL CHLORIDE

MEASUREMENT:

- 12. Set the gas chromatogrph according to manufacturer's instructions and to conditions given on page 1007-1. Inject sample aliquot manually using solvent flush technique or with autosampler. The retention time of vinyl chloride is about 1.7 min.
 - NOTE: If peak area is above the linear range of the working standards, dilute with CS₂, reanalyze and apply the appropriate dilution factor in calculations.

13. Measure peak area.

CALCULATIONS:

14. Determine the mass, mg (corrected for DE) of vinyl chloride found in the sample front $(M_{\rm F})$ and back $(M_{\rm D})$ tubes, and in the average media blank (B).

NOTE: If $W_{\rm b} > W_{\rm f}/10$, report breakthrough and possible sample loss.

15. Calculate concentration, C, of vinyl chloride in the air volume sampled, V (L):

$$C = \frac{(H_{f} + H_{b} - 2B) \cdot 10^{3}}{V}, mg/m^{3}$$

EVALUATION OF METHOD:

The method was evaluated using single 150-mg sampling tubes with 100-mg front beds and 50-mg back beds [2]. At four concentrations between 1 and 64 mg/m³, the pooled relative standard deviation was 0.06 and the measurements averaged 94% of the concentrations calculated from the volumes of vinyl chloride and air used for the atmospheres sampled; samples at the 3-µg level showed no loss of vinyl chloride when stored for 12 days at room temperature or 19 days at -20 °C. There may be significant loss of vinyl chloride from samples stored for 14 days at room temperature [4]. The 1% breakthrough capacity for a 150-mg bed of coconut charcoal challenged at 100 mL/min with vinyl chloride in air at 16 mg/m³ and a relative humidity of 70% was 4.6 L [5].

REFERENCES:

 <u>TLVs</u> - <u>Threshold Limit Values for Chemical Substances and Physical Agents in the Work</u> <u>Environment with Intended Changes for 1983-84</u>, ACGIH, Cincinnati, OH (1983).

- [2] Hill, R. H., Jr., C. S. McCammon, A. T. Saalwaechter, A. W. Teass, and W. J. Woodfin. <u>Anal. Chem.</u>, <u>48</u>, 1395-1398 (1976).
- [3] NIOSH Manual of Analytical Methods, 2nd. ed., V. 1, PSCAM 178, U.S. Department of Health and Human Services, Publ. (NIOSH) 77-157-A (1977).
- [4] Cuddeback, J. E., W. R. Burg, and S. R. Birch, Environ. Sci. Technol., 9, 1168-1171 (1975).

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[5] Matsumura, Y. Ind. Health, 18, 61-67 (1980).

METHOD REVISED BY: A. W. Teass, Ph.D., NIOSH/DPSE.

VELSICOL CHEMICAL CORPORATION ST. LOUIS, MICHIGAN PROJECT Nº 1524

GAS VENT SAMPLING PUMPS CALIBRATION LOG

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DATE	1. 1.				CALIB	RATED	BY ;		·								
				BEFORE		MPLING AFTER SAMPLING							AVERAGE				
PUMP NUMBER	PUMP Type	TEMP. (°F)	HUMIDITY (%)	BAROM. PRESSURE (Inches Hg)	INITIAL FLOW (cc/min.)	CAL. FLOW (cc/min.)	24-HR. TIME	TEMP. (°F)	HUMIDITY	BAROM. PRESSURE (Inches Hg)	FLOW (cc/min.)	24-HR. TIME	TEMP. (°F)	HUMIDITY (%)	BAROM. PRESSURE (Inches Hg)	FLOW (cc/min.)	
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COMMENTS

VELSICOL CHEMICAL CORPORATION ST. LOUIS, MICHIGAN

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GAS VENT SAMPLING

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PROJECT Nº 1524

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1 1 1

DATE OF COLLECTION 3-12-86	SAMPLER CAC/EDG	BAROMETRIC PRESSURE 30.05
TEMPERATURE 33°F	RELATIVE HUMIDITY SOCOS 91 70	GAUGE 1 2 3 4 5 6 7 8 9 10 11
CHARCOAL 120	TENAX LOT Nº 271	READING 0 0 0 0 0 0 0 0 0 0 0

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GAS VENT PUMP SAMPLE			SAMPLING TIM	SAMPLING RATE	SAMPLE			
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2	2	2	8:48	9:08	20 mm	/	5 I	
3		7	9:12	9.32	ZO min		51	
4	٢	9	9:25	f 4 5	20 mm		5 J	
5	1.	1	122 9:47	F0:01	20 mm		5 J	
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7	2	13	11:49	12:09	ZG MM		51	
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9	1	6	Hing- 11:55	12:15	Dana.		54	
10	2	4	1212 1228	12.51	23 min		5.75l	
	1	10	1300	13 20	20 min		51	
DUPLICATE	1 (#9)	8	1728 12:21	12,41	20 min		5 I	
BLANK		3	12:00				5l	
DATE OF SAMPLE SHI	PMENT 3-	12-86		IOD OF MENT FEDERAL	(Sarda)			
OMMENTS								

10. Calculations

- 10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.
- 10.2 Corrections for the blank must be made for each sample.

mg = mg sample - mg blank

where:

mg sample = mg found in front section of sample tube mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

- 10.3 Add the amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.
- 10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

Corrected mg/sample = Total weight D.E.

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

mg/cu m = Corrected mg (Section 10.4) x 1000 (liters/cu m) Air Volume Sampled (liters)

10.6 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$ppm = mg/cu = x \frac{24.45}{MW} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled T = temperature (°C) of air sampled 24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg MM = molecular weight 760 = standard pressure (mm Hg) 298 = standard temperature (°K)

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11. References

- 11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).
- 11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.
- 11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.



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VINYL CHLORIDE

FORMULA: CH2=CHC1; C2H3C1

METHOD: 1007 ISSUED: 2/15/84

N.W.: 62.50

OSHA: 1 ppm; C 5 ppm ~ NIOSH: minimum measurable ACGIH: 5 ppm (human carcinogen) [1] (1 ppm = 2.56 mg/m² @ NTP) PROPERTIES: BP =14 *C; vapor density 2.2 (air = 1)

SYNCHYMS: chloroethylene; chloroethene; CAS #75-01-4.

SAMPLING	MEASUREMENT
SAMPLER: SOLID SORBENT TUBE	! !TECHNIQUE: GAS CHROMATOGRAPHY, FID
(2 tandem tubes, each with 150 mg	
activated coconut charcoal)	ANALYTE: vinyl chloride
FLOW RATE: 0.05 L/min	: !DESORPTION: 1 mL carbon disulfide; 30 min !
VOL-MIN: 0.7 L	INJECTION ALIQUOT: 5 UL
-NAX: 5 L	
	COLUMN: stainless steel, 6.1 m x 3.2 mm, 10%
SHIPMENT: separate primary and backup tubes and cap each	! SE-30 on 80/100 mesh Chromosorb W ! (AW-OMCS)
SAMPLE STABILITY: 10 days @ 25 °C	: !CARRIER GAS: He, 40 mL/min
BLANKS: 2 to 10 field blanks per set	: !TEMPERATURE-INJECTOR: 230 °C
	!OETECTOR: 230 °C
	: -COLUMN: 60 °C
ACCURACY	!
· · · · · · · · · · · · · · · · · · ·	:CALIBRATION: solutions of vinyl chloride in CS2
RANGE STUDIED: 1 to 64 mg/m ³ [2]	1
	!RANGE: 0.002 to 0.2 mg per sample [2]
BIAS: -6% of calculated concentration [2]	! • •
	ESTIMATED LOD: 0.00004 mg per sample [2]
OVERALL PRECISION (ST): 0.06 [2]	.! !PRECISION (sp): not determined

APPLICABILITY: The working range is 0.4 to 40 mg/m³ (0.16 to 16 ppm) for a S-L air sample. The method is applicable to 15-min samples at concentrations of 1 ppm or higher.

INTERFERENCES: Other than the possibility of loss of sample upon storage of two weeks or more at room temperature, none have been noted.

OTHER METHODS: This is a revision of PSCAN 178 [3].

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VINYL CHLORIDE

1 :

- Carbon disulfide,* chromatographic quality.
- Vinyl chloride,*, 99.9%, in lecture bottle fitted with valve and septum.
- Calibration stock solution, 0.26 mg/mL.
 - a. Insert the tip of a gas syringe containing 1 mL vinyl chloride gas under the surface of 5 mL CS₂ in a 10-mL volumetric flask.
 - b. Open the value of the syringe and withdraw the plunger to pull CS₂ into the barrel. (As vinyl chloride dissolves, a vacuum will be created, pulling CS₂ into the syringe.)
 - c. Push the solution from the syringe into the flask. Rinse the syringe twice with 1-ML portions of CS₂ and add the washings to the flask.
 - d. Dilute to the mark with CS_2 .
- 4. Helium, purified.
- 5. Hydrogen, purified.
- 6. Air, filtered.

*See Special Precautions.

- EQUIPMENT:
- 1. Sampler: two tandem glass tubes, 7 cm long, 6 mm OD, 4 mm ID, flame-sealed ends, each
 - containing 150 mg of 20/40 mesh activated (600 °C) coconut shell charcoal. A silylated glass wool plug precedes the charcoal beds and a 3-mm urethane foam plug follows the charcoal beds. Plastic caps are included for smaling after use. Pressure drop across each tube at 1 L/min airflow must be less than 3.4 kPa.
 - NOTE: A pair of two-section (100 mg/50 mg) tubes may be used.
- Personal sampling pump, 0.05 L/min, with flexible connecting tubing.
- Gas chromatograph, flame ionization detector, integrator and column (page 1007-1).
 File.
- 5. Bent wire for removing plugs from sampling tube.
- Vials, 2-mL, glass with PTFE-lined septa and crimp-on seals.
- Volumetric flasks, 10-mL, with polyethylene stoppers.
- Pipettes, delivery, 1.0-mL, graduated in 0.1-mL incruments, 2- and 5-mL, with pipet bulb.
- 9. Air sampling bags, Tedlar, 10-L.
- 10. Gas syringe, with gas-tight valve, 0.1- and 1-mL.
- 11. Syringe, 10-µL, with 0.1-µL graduations.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = -30 °C); work with it only in a hood.

Vinyl chloride is a human carcinogen [1].

SAMPLING:

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- 1. Calibrate each personal sampling pump with a representative sampler in line.
- 2. Break the ends of the tubes immediately before sampling. Attach two tubes, with ends touching, with a short piece of tubing. Label one tube as the back tube and insert the back tube into the flexible tubing attached to the personal sampling pump.
- 3. Sample at 0.05 L/min for 15 to 100 min. Do not sample more than 5 L of air.
- 4. Separate the primary and backup tubes and cap each tube for shipment.

SAMPLE PREPARATION:

- 5. Add 1.0 mL CS₂ to an empty vial. Loosely cap the vial.
- Score each sampler tube with a file in front of the glass wool plug. Break the tube at the score line.

METHOD: 1007

HETHOD: 1007

- 7. Transfer the charcoal from the front and back tubes to separate vials. Discard the glass wool and foam plugs. Seal the vials with septum caps immediately.
- 8. Allow to stand for 30 min, with occasional agitation. Analyze the sample within the next 30-min period.

CALIBRATION AND QUALITY CONTROL:

- 9. Calibrate with at least five working standards covering the range 0.0002 to 0.2 mg per sample.
 - a. Add known amounts of calibration stock solution to CS_2 in 10-mL volumetric flasks and dilute to the marks, using serial dilution as appropriate.

NOTE: Working standards can be stored at -20 °C for at least three days.

- b. Analyze together with samples and blanks (steps 12 and 13).
- c. Prepare calibration graphs of peak area vs. quantity (mg) of vinyl chloride per tube and peak area vs. quantity (ng) per injection.
- 10. Determine desorption efficiency (DE) at least once for each lot of charcoal used in the calibration range (step 9). Prepare three tubes at each of five levels plus three media blanks.
 - a. Prepare three atmospheres of vinyl chloride in air by injecting 0.01, 0.08, and 0.2 mL vinyl chloride gas into 10 L air in Tedlar bags. The resulting concentrations are approximately 2.6, 21 and 52 mg/m³.
 - b. Following steps 1 through 4, sample these atmospheres according to the following scheme:

Concentration in Bag (mg/m ²) ⁻	Volume Sampled (L)	Quantity of Vinyl Chloride (mg)
2.6	0.8	0.002
-	2.2	0.006
21	0.8	0.017
	2.2	0.046
52	2.5	0.13

Obtain three samples at each level.

- c. Desorb (steps 6 through 8) and analyze together with working standards (steps 12 and 13). No vinyl chloride should be found on the back tubes.
- d. Analyze the atmospheres in the bags (steps 12 and 13) using 1-mL gas samples. Read from the calibration graph the quantity (ng) per injection, which for a 1-mL injection of gas is numerically equal to the concentration in mg/m².
- e. Calculate DE from the mass (mg) of vinyl chloride on the front tube (W_{f}), the average blank (B), the concentration of vinyl chloride in the synthetic atmospheres (C_{s} , mg/m^{3}), and the volume of air sampled (V, L):

$$DE = \frac{(W_{f} - B) \cdot 10^{3}}{(C_{e})(V)}$$

f. Prepare a graph of DE vs. mass found (Wg - B).

11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

APPENDIX B

CHAIN OF CUSTODY

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APPENDIX C

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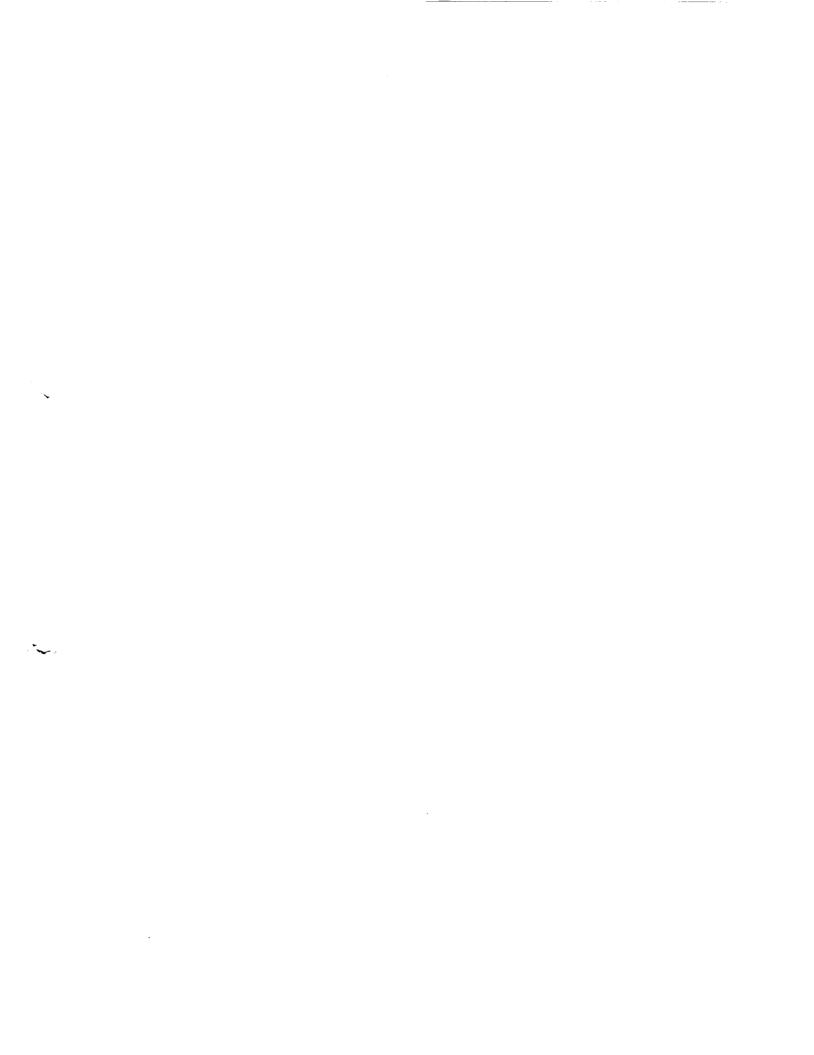
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MECHANICAL INTEGRITY TESTING

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FIGURE 1	GAS VENT LOCATIONS	3a
FIGURE 2	ACTIVATED CARBON GAS VENT DETAIL	4a
FIGURE 3	UPGRADIENT AND DOWNGRADIENT CONTAINMENT WALL SAMPLING LOCATIONS.	10a
FIGURE 4	SITE GROUNDWATER CONTOURS	13a
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TABLE 1	WATER LEVEL MEASUREMENTS	12a
	DECEMBER 12, 1984	

1.0 INTRODUCTION

1.1 GENERAL

In accordance with the terms of the technical appendix to the Consent Judgment entered into by Velsicol Chemical Corporation (Velsicol), the United States Environmental Protection Agency, (USEPA) and the Michigan Department of Natural Resources (MDNR), Velsicol is required to perform specified monitoring activities at quarterly intervals following closure of its St. Louis, Michigan plant site. The monitoring program is designed to address the following:

- 1. Performance of gas vents
- 2. Performance of the site perimeter containment wall
- 3. Determination of site groundwater elevations

This report details the site monitoring which occured during the period March 13 to March 16, 1985.

1.2 PARTICIPATION BY REGULATORY AGENCIES

Mr. R. Teoh (MDNR) was present on-site on March 14, 1985 and observed the carbon changeout of gas vents 7 and 8.

1.3 MONITORING AND SAMPLING PERSONNEL

The monitoring and sampling program was carried out by Mr. D. Robinson and Ms. C. Cull (Conestoga-Rovers and Associates) assisted by Mr. Gene DeGeer, the Velsicol site custodian.

2.0 GAS VENT MONITORING

2.1 GENERAL

The gas vent monitoring began on March 15, 1985 and was completed the same day.

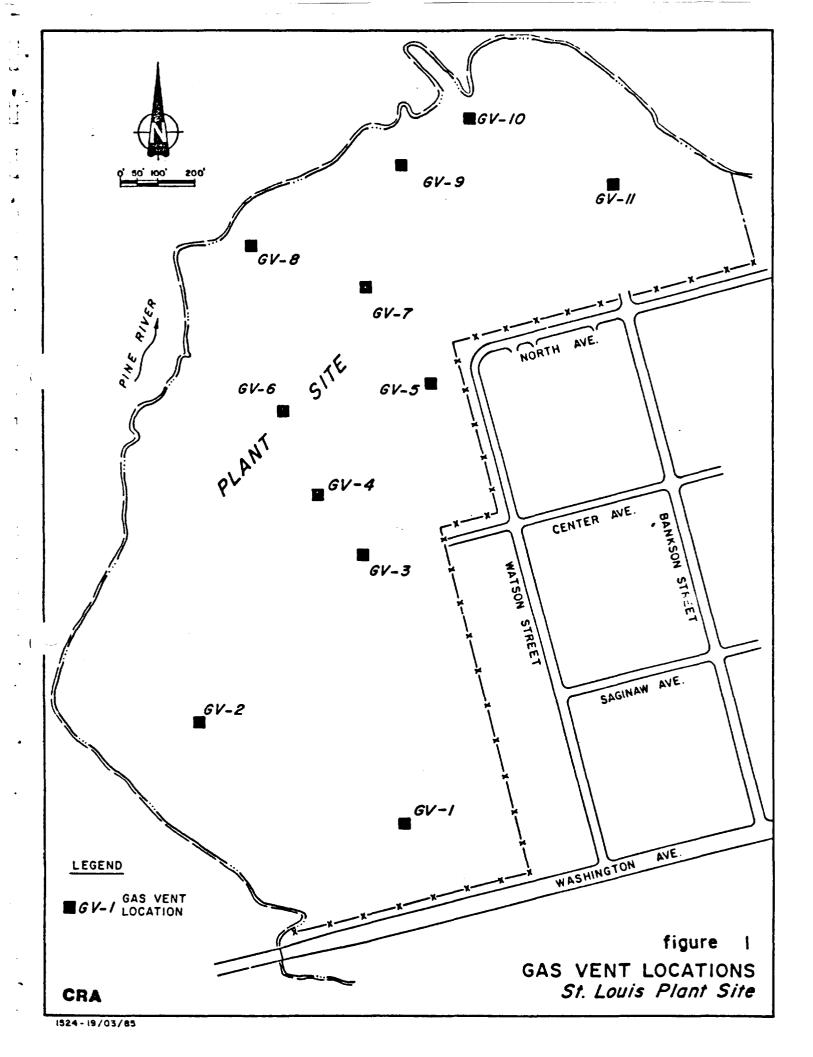
2.1.1 Equipment

Two Gilian model HFS 113 hi flow samplers were used to collect gas vent samples. The samplers were field calibrated using a rotometer prior to sampling. The calibration data is presented within Appendix B. Samples from each gas vent were collected in two 6-mm diameter x 70-mm long Tenax tubes and two charcoal tubes of similar dimensions. The samples were collected simultaneously using dual parallel/series tube holder sets.

2.2 SAMPLE COLLECTION

Samples were obtained at each of the 11 gas vents. The location of the gas vents within the closed plant site is detailed on Figure 1. One blank set and one duplicate set of samples were also collected.

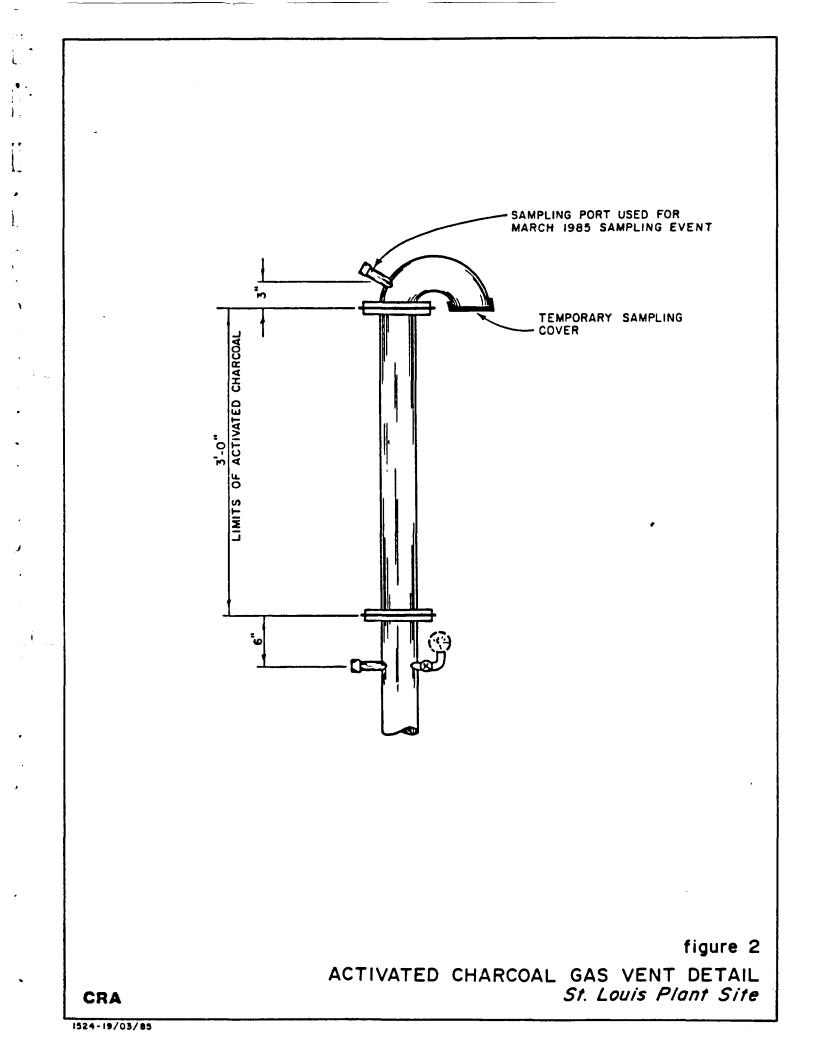
CONESTOGA-ROVERS & ASSOCIATES LIMITED



Sampling was conducted at the downstream sampling port on each gas vent as detailed on Figure 2. The tube holder was attached directly to the gas vent sampling port using a copper manifold assembly which was environmentally cleaned prior to use. Tygon tubing was used to connect the tube holder to the sampler and was connected between the base of the tube holder and suction port of the sampler. The sampler which was pre-calibrated to 250cc/min/tube set, was operated for a period of 20 minutes for each sampling event, resulting in a collected sample volume of five liters per tube set.

Prior to sample collection, the gas vent upper chamber was purged by pumping at 500 cc/minute for a period of ten minutes. This precluded the possiblity of sampling retained atmospheric air from the gas vent upper chamber. During the purging and sampling operations, the open end of the gas vent was capped using a 4-inch diameter plastic cover to prevent atmospheric air being drawn into the sample.

At the conclusion of each gas vent sampling, the set of four sample tubes were capped, labelled and stored in a cooler maintained at 0°C.



2.2.1 Sample Storage and Shipment

On the afternoon of March 15, 1985, the samples were transferred to a cooler containing frozen cold packs and styrofoam packing materials. The cooler was shipped under chain of custody protocol, to Velsicol's Memphis, Tennessee laboratory by overnight courier for analysis. A copy of the chain of custody is provided in Appendix A.

2.2.2 Sample Analysis

All of the samples were desorbed and analyzed during the period March 18 to March 21, 1985. Analysis was conducted in accordance with NIOSH protocols as follows:

Compound	NIOSH Method
Carbon Tetrachloride	1003
Trichloroethylene	S-336
Vinyl Chloride	1007

Results were reported verbally as non detectable for all parameters for all samples.

A hard copy of the laboratory report will be forwarded to USEPA and MDNR as it becomes available.

2.2.3 Sampling Protocol

All sampling was performed in accordance with the methodology detailed within the St. Louis plant site Post-Closure Maintenance and Monitoring Plan, as approved by USEPA and MDNR. A copy of the sampling protocol is contained in Appendix B.

2.3 CARBON CHANGEOUT

2.3.1 General

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The terms of the Consent Judgment requires that should the presence of carbon tetrachloride, vinyl chloride or trichloroethylene be detected in any gas vent sampling in exceedence of stipulated concentrations, the carbon will be changed and the program be revised.

In order to comply with the terms of the Consent Judgment, the activated carbon filters were changed on March 14, 1985. At the recommendation of the supplier, the product was changed to a grade of activated carbon which will more readily adsorb the three parameters. The revised product is referred to as Calgon PTL 4 x 10 activated carbon.

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2.3.2 Method

Initially, the top section of the gas vent was removed and examined for damage or corrosion; none was observed.

The 3-foot long section containing the activated carbon was removed and the spent carbon was poured directly into a three ply polyethylene bag. The bag was closed by tying a knot in the neck of the bag.

The three foot section was examined for damage or corrosion; none was observed. The stainless steel screens were examined and replaced.

The 3-foot section was replaced on the gas vent and filled with the revised activated carbon product. The top section was replaced. All bolts were given a final tightening. The bags containing the spent carbon were deposited in a D.O.T. approved 55-gallon drum for subsequent disposal. The disposal method has not yet been identified.

2.3.3 Health and Safety

During the carbon changeout, personnel were required to wear disposable tyvek coveralls and disposable

vinyl gloves. Those were deposited into an on-site D.O.T. approved 55-gallon drum for subsequent disposal following completion of carbon changeout.

3.0 SITE PERIMETER CONTAINMENT WALL MONITORING

3.1 GENERAL

The monitoring program consisting of the collection of an undisturbed sample of the containment wall with subsequent permeability testing was initiated on December 15, 1983. Subsequent sampling events occurred on March 15, 1984, June 15, 1984, September 14, 1984 and December 14, 1985. The current sampling event occured March 15 and March 16, 1985. All testing completed to date has confirmed the permeability of the site perimeter containment wall to be less than 1.0 x 10-7 cm/sec.

3.2 EQUIPMENT

A CME 175 trailer mounted drill rig equipped with rotary head and 6-inch diameter hollow stem augers was utilized to advance the borehole into the containment wall on March 15 and a truck-mounted CME 175 drill rig was used on March 16, 1985. A 3-inch diameter Shelby tube, hydraulically pushed and retrieved, was used to collect the samples.

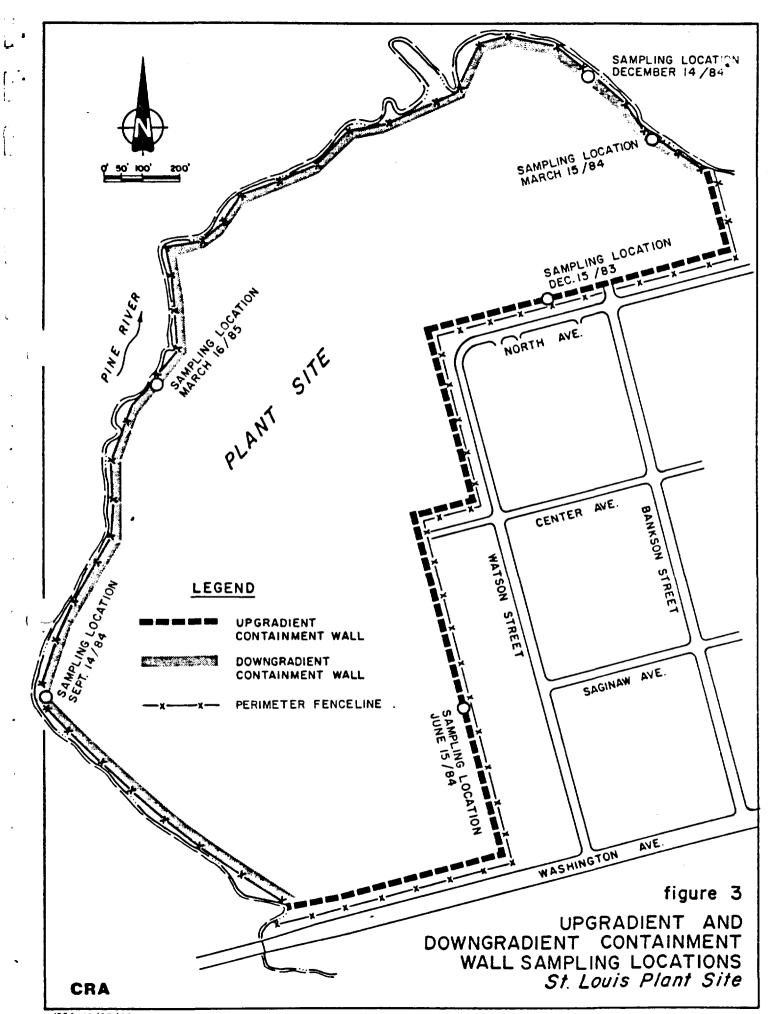
3.3 SAMPLE COLLECTION

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The containment wall was located by field survey on March 14, 1985. The sampling borehole was begun at Station DGW 47+50 by augering through the clay cap into the underlying material.

The presence of soil/bentonite backfill material was confirmed by examination of cuttings on the auger flights. A Shelby tube was introduced into the borehole and a sample was retrieved at a depth of eight feet. Examination of the contents as the sample was extruded in the laboratory indicated that the sample contained native material. The sample was discarded. It was concluded that the borehole had been located on the inside edge of the containment wall.

On the morning of March 16, 1985 the sampling program was resumed and the drill rig was moved three feet to the west. A borehole was advanced to a depth of eight feet. A Shelby tube was introduced into the borehole and a sample was withdrawn. Examination of material in the base of the tube confirmed that the sample was obtained from the containment wall. The locations of this and prior sampling events are detailed on Figure 3. The boreholes were backfilled with bentonite and abandoned.



3.3.1 Sample Preparation and Shipping

The Shelby tube was capped and taped at both ends to prevent sample loss and drying. The sample was hand delivered to the Michigan Testing Engineer's laboratory in Detroit, Michigan for permeability testing.

3.3.2 Sample Testing

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The undisturbed sample is to be tested for permeability using a falling head permeameter set up in accordance with ASTM D 2434. Results of the testing will be provided in written form to USEPA and MDNR within seven days after receipt of final laboratory data by CRA. A summary data report will be prepared and presented to both Agencies following completion of the containment wall monitoring program in the fall of 1986.

4.0 GROUNDWATER TABLE MONITORING

4.1 GENERAL

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The monitoring of plant site groundwater elevation was performed on March 13, 1985. The water elevation of the St. Louis reservoir was determined on March 15, 1985.

4.2 WATER LEVEL DETERMINATION

The elevation of the groundwater was determined by measuring the distance from the top of each site monitoring well to the watertable. This distance was measured by lowering a chalked, weighted surveyors tape into the monitoring well. Readings of the tape, which was graduated in increments of one one-hundredth of a foot, were taken at the water level and at the top of the well casing. The former reading was deducted from the latter and the resultant dimension was subtracted from the previously established top of well casing elevation. Well head and watertable elevations are presented on Table 1.

The elevation of the St. Louis reservoir was determined by level and rod survey.

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TABLE 1

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WATER LEVEL MEASUREMENTS

MARCH 13, 1985

MONITORING WELL	WELL HEAD ELEVATION (AMSL)	MEASURED DISTANCE TO WATER TABLE (ft.)	WATERTABLE ELEVATION (AMSL)
1	735.88	13.82	722.06
2	742.07	19.04	723.03
3	749.92	27.38	722.54
4	735.99	13.56	722.43
5	739.35	17.58	721.77
6	734.43	13.00	721.43
7	734.02	12.29	721.73
8	734.30	13.14	721.16
9	734.52	13.33	721.19
10	733.43	12.33	721.10
11	734.38	13.21	721.17
12	730.74	9.53	721.21
13	734.43	13.27	721.16
14	735.95	14.67	721.28

Water level elevation, St. Louis Reservoir (March 15, 1985)

720.41

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4.3 GROUNDWATER CONTOUR MAP

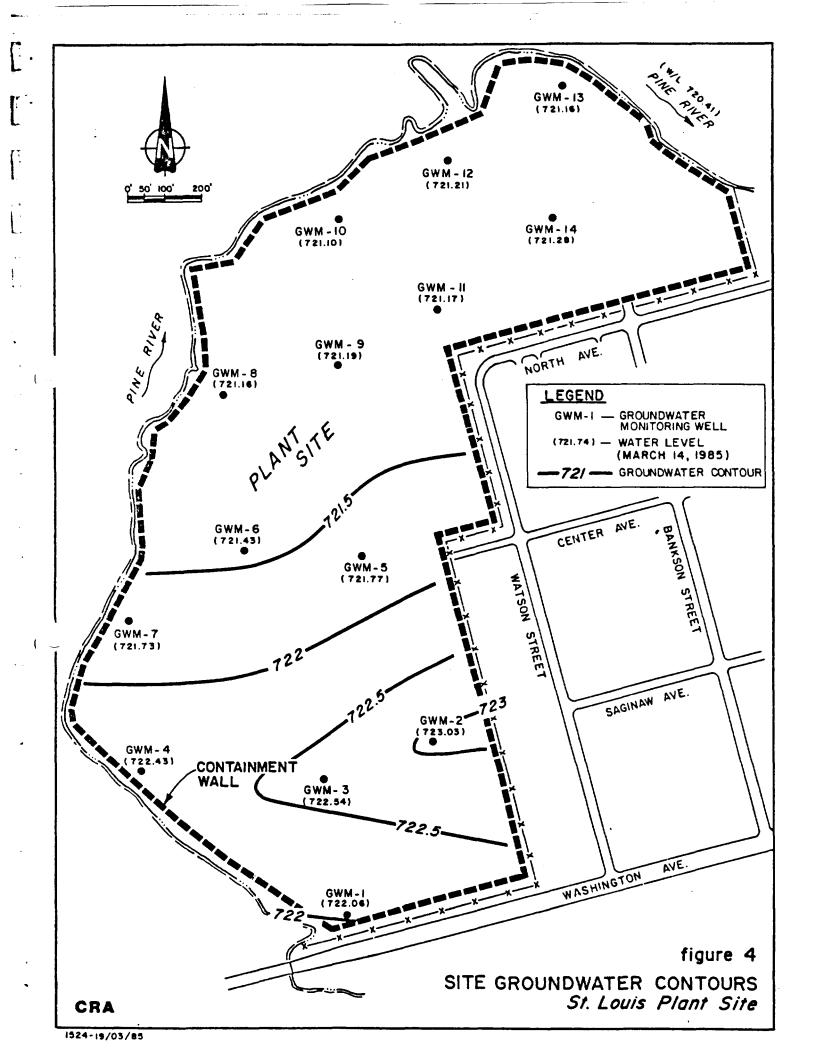
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The groundwater elevation data were used to construct a site groundwater elevation contour map which is presented in Figure 4.

4.4 SITE MEAN GROUNDWATER ELEVATION

The mean elevation of site groundwater is calculated to be 721.66. The maximum allowable site groundwater elevation stipulated by the Consent Judgement is 724.13.



All monitoring activities stipulated by the Consent Judgment were carried out between March 13, and March 16, 1985.

The gas vent activated carbon filters were changed on March 14, 1986.

Data from the chemical analysis of the gas vent samples and the permeability testing of the contaminant wall sample will be provided to MDNR and USEPA within seven days of receipt by CRA of laboratory final data.

The present mean site groundwater table elevation is calculated to be 721.66. The elevation in the Pine River/St. Louis reservoir was determined to be 720.41.

The next sampling and monitoring event will occur on or about June 15, 1985. Interim gas vent sampling will be performed on or about April 29, 1985.

All of Which is Respectfully Submitted, CONESTOGA-ROVERS & ASSOCIATES LIMITED

D. Robinson

R.G. Shepherd, P. Eng.

CONESTOGA-ROVERS & ASSOCIATES LIMITED

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APPENDIX A

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VELSICOL CHEMICAL CORPORATION 701 W. WASHINGTON STREET ST. LOUIS, MICHIGAN 48880

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APPENDIX B

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GAS SAMPLING PROTOCOLS

APPENDIX B

GAS VENT SAMPLING PROTOCOL

In accordance with the Consent Judgment, Velsicol has submitted a post-closure maintenance and monitoring plan for its environmentally secured plant site in St. Louis, Michigan. The post-closure maintenance and monitoring plan requires quarterly monitoring of 11 gas vents that have been installed to release and appropriately treat internal gases. This program will be conducted over a period of three years.

The gas vents, as detailed in Exhibit F of the Consent Judgment, are designed with two sampling ports; one below the base of the installed activated charcoal filter, and one above the filter. Samples will be collected from the downstream port. Results will indicate whether or not containment breakthrough has occured through the carbon filter.

Samples will be analyzed for three separate compounds: carbon tetrachloride, trichloroethylene and vinyl chloride.

Samples will be collected with a Gilian HFS-113 AU DK variable flow pump. This particular unit allows the operator to run a series of tubes concurrently in parallel arrangement. Four tubes will be collected from each gas vent: two standard NIOSH 100/50 mg activated charcoal tube, and two 30/15 mg tenax tubes, each tube measuring 6 mm x 70 mm. One blank set and one duplicate set of tubes will be collected during each quarterly sampling event.

As vinyl chloride represents the least adsorptive of the three compounds, the sampling program is designed to accomodate this compound. Therefore, sample volume shall not exceed 5 liters.

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Prior to sampling, the vent will be sealed off with a plastic cap, and purged for 10 minutes at a rate of 500 cc/min. This is to eliminate the possibility of sampling atmospheric air contained within the upper portion of the gas vent.

Two samples from each gas vent shall be collected simultaneously at a rate of 250 cc/min. for 20 minutes. The pump shall be lab calibrated with sample tubes in-line to determine the exact flow rate. Additionally, flow will be checked after field sampling to verify that a constant flow was maintained throughout the sampling period.

Following sample collection, each tube will be sealed with a plastic cap at each end, labelled, placed in a cold storage environment and shipped under chain-of-custody via a commercial courier service to Velsicol's analytical laboratory in Memphis.

Analysis of the charcoal tube will be conducted in accordance with NIOSH protocol as detailed below:

Compound	Revised Method No.
Carbon Tetrachloride	1003
Trichloroethylene	S-336
Vinyl Chloride	1007

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Analysis will proceed by first eluting the carbon sample tubes with carbon disulfide and then analyzing by GC with a flame ionization detector. All samples will be initially analyzed in this fashion. If any of the above compounds are detected on the charcoal tube, the corresponding tenax tube will be analyzed by thermal desorption and GC/MS under EPA Method 624.

Turnaround time for the completed analysis at the laboratory is anticipated to be 30 days from date of sample collection. Samples will be desorbed within the 10 day limit specified for vinyl chloride. Analytical data will be reported to CRA as mg/tube. Final results for the carbon tube will be calculated by CRA, using the following formula.

1. Corrections for the blank to be made for each sample
 mg = mg sample - mg blank

This calculation is performed separately for each tube.

- 2. Add the amounts present in the front tube and backup tube to determine the total weight in the sample.
- 3. Calculate the corrected mg/sample by dividing the total weight by the desorption efficiency (D.E.) which is provided by the lab.

- 4. Calculate the concentration of the analyte in air $mg/m^3 = \frac{Corrected mg \times 1000 \text{ liters/m}^3}{\text{Air volume Sampled (liters)}}$
- 5. Concentration will be reported as ppm, corrected to standard conditions of 25°C and 760 mm Hg

 $ppm = mg/m = x \frac{24.45}{MW} \times \frac{760}{P} \times \frac{(T+273)}{298}$

where P	= pressure (mm Hg) of air sampled
Ţ	<pre>= temperature (°C) of air sampled</pre>
24.45	= molar volume (liter/mole) at 25°C and 760 mm Hg
MW	= Molecular Weight
760	= standard pressure (mm Hg)
298	= standard temperature (°K)

- 2 -

- NOTE: Temperature and pressure uncorrected to sea level will be collected for the duration of the sampling event and averaged for use in the above calculations. Information will be provided from the National Weather Service in Lansing, Michigan.
 - 6. If the concentration of the back tube exceeds 10% of the concentration of the front tube, the results will be reported as a sample breakthrough and possible sample loss.
 - 7. A similar procedure will be followed for the tenax tube, should analysis be required.

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Data will be reported to USEPA and MDNR officials within seven days after receipt of final laboratory data for each quarterly sampling. Additionally, a summary data report will be provided at the conclusion of the three year sampling period, or sooner, should breakthrough of any compound occur prior to the three year program.

In addition to the set of field blanks to be collected per quarterly sampling event, an additional set of 15 charcoal tubes and 15 tenax tubes will be forwarded unopened to the lab during the initial sampling event.

These "blank" tubes will be used as internal calibration standards on which each of the three compounds will be spiked at five different concentrations. The data from this analysis will be used to calculate the desorption efficiency for a specific lot of activated charcoal. Therefore, the lot number of carbon tubes and tenax tubes shall be recorded during each quarterly sampling. Should the lot number change, a new set of 15 charcoal tubes and 15 tenax tubes shall be forwarded to the laboratory for determination of the new desorption efficiency.

The allowable limits for these compounds have been established by the MDNR and are site specific for the St. Louis site. These limits are documented in section 4.3 of the post-closure maintenance and monitoring plan.

Copies of all three analytical protocols, the chain of custody and the data collection sheet are provided in the following sections.

- 3 -

HYDROCARBONS, HALOGENATED

FORMULA: Table 1

METHOD: 1003 ISSUED: 2/14/84

M.W.: Table 1

COMPOUNDS:benzylchloridechlorobromomethanel,1-dichloroethanehexachloroethane(synonymsbromoformchloroforml,2-dichloroethylenemethylchloroformin Table 1)carbon tetrachlorideo-dichlorobenzeneethylenedichloridepropylenedichloridechlorobenzenep-dichlorobenzeneethylenedichloridepropylenedichloride

SAMPLING	MEASUREMENT
SAMPLER: SOLID SORBENT TUBE	! !TECHNIQUE: GAS CHROMATOGRAPHY, FID
(coconut shell charcoal, 100 mg/50 mg)!
	ANALYTE: compounds above
FLOW RATE: 0.01 to 0.2 L/min	!
	<pre>!DESORPTION: 1 mL CS2, stand 30 min</pre>
VOL-MIN: Table 2	!
-MAX: Table 2	INJECTION VOLUME: 5 µL
SHIPMENT: routine	! !TEMPERATURES: Table 2
	!
SAMPLE STABILITY: at least l week @ 25 °C	CARRIER GAS: N2 or He, 30 mL/min
BLANKS: 2 to 10 field blanks per set	: !COLUMN: Table 2; alternates are SP-2100,
	! SP-2100 with 0.1% Carbowax 1500
<u> </u>	! or DB-1 fused silica capillary column
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BIAS: not significant [1]	RANGE: Table 2
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OVERALL PRECISION (s _r): see EVALUATION OF METHOD [1]	!ESTIMATED LOD: 0.01 mg per sample [2]
	: !PRECISION (sr): see EVALUATION OF METHOD [1]

APPLICABILITY: This method uses a simple desorption and can be used for simultaneous analysis of two or more substances suspected to be present by changing the gas chromatographic conditions (i.e., temperature programmed). High humidity during sampling will prevent organic vapors from being trapped efficiently on the sorbent and greatly decreases breakthrough volume.

INTERFERENCES: None identified. The chromatographic column or separation conditions may be changed to circumvent interference problems.

OTHER METHODS: This method combines and replaces Methods P&CAM 127 [3]; S95, S101, S110, S113, S114, S115, S122, S123 and S133 [4]; and S135, S281, S314, S328 and S351 [5].

a. Remove and discard back sorbent section of a media blank sampler.

3+

- b. Inject a known amount of analyte or calibration stock solution directly onto front sorbent section with a microliter syringe.
- c. Cap the tube. Allow to stand overnight.
- d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
- e. Prepare a graph of DE vs. mg analyte recovered.
- 10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

- 11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1003-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
 - NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.
- 12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of analyte found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.

NOTE: If $W_D > W_f/10$, report breakthrough and possible sample loss.

11 - F

14. Calculate concentration, C, of analyte in the air volume sampled, V(L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, mg/m^3.$$

ENTITY OF SETAD:

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Laboratory testing was performed with spiked samples and generated atmosphere []]. All analytes are stable at least one week. All methods were validated using SKC Lot 105 coconut shell charcoal. Results were:

METHOD: 1003

- [9] Criteria for a Recommended Standard...Occupational Exposure to 1,1,1-Trichloroethane, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 76-184 (1976).
- [10] Criteria for a Recommended Standard...Occupational Exposure to Carbon Tetrachloride, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 76-133 (1976).

METHOD REVISED BY: G. D. Foley; Y. T. Gagnon; and K. J. Williams, NIOSH/DPSE; methods originally validated under NIOSH Contract CDC-99-74-45.

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Compounds	N.W.; mg/m ³ <u>Formula = 1 ppm</u> 1,4-C ₆ H ₆ C1 147.00; 6.01		Synonyms	OSHA NIOSH [6-10] ACGIH	BP (°C)	VP (9 20 °C	Density (g/mL <u>@ 20 °C)</u> 1.241	
p-Dichlorobenzene			! i-dichlorobenzene; (#106-46-7	75 ppm 75 ppm, STEL 110 ppm	174	50 Pa		
1,1-Dichloroethane	сн _з снст ₂ ; с ₂ н ₄ ст ₂ ;	98.96; 4.05	callylidene_chloride; CTAP #75-34-3	100 ppm 100 ppm 200 ppm, STEL 250 ppm	57	24.3 kPa	1. 174	
1,2-Dichloroethylene	C1CH=CHC1; C_H_C1 2_4_2	96.95; 3.96	a st ylene dichloride; 1,2-d ichloroethene; C #540-59-0	200 ppm 200 ppm 200 ppm, STEL 250 ppm	60 (cis) 47 (trans)	24-35 kPa	1.28	
Ethylene dichloride*	с1сн ₂ сн ₂ с1; с ₂ н ₄ с1 ₂	98.96; 4.05	1,∴-dichloroethane; Cr \ #107-06-2	50 ppm, C 100 ppm 5 ppm; 15 ppm/15 min 10 ppm, STEL 15 ppm	83	8.3 kPa	1.255	
Hexach loroethane*	cc1 ₃ cc1 ₃ ; c ₂ c1 ₆	236.74; 9.68	parchloroethane; (a #67-72-1	l ppm (skin) l ppm (skin) 10 ppm	187 (sublines)	30 Pa	2.09	
Methylchloroform	сн ₃ сс1 ₃ ; с ₂ н ₃ с1 ₃	133.42; 5.45	1,1,1-trichloroethane; (350 ppm 350 ppm/15 min CAS #71-55-6 STEL 450 ppm	74 350 ppm,	13.3 kPa	1.335	
Propylene dichloride	сн ₃ снс1сн ₂ с1 с ₃ н ₆ с1 ₂	; 112.99; 4.62	1,∷-dich1oropropane C+> #78-87-5	75 pp m 75 ppm 75 ppm, 75 ppm, STEL 110 ppm	95	5.3 kPa	1.156 (25 °C)	

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1003-7

*Suspect carcinogen.

ATED

		Sampl	ing	Measurement						
	Air Sample <u>Volume (L)</u>				Working		<u>t (°C)</u> Column		Range	
Compound	Min	Max	Breakth <u>in</u> Dr	-	Range (mg/m³)	<u>Column</u> *	Injector <u>Detector</u>	Internal <u>Standard</u>	(mg per sample)	
1,1-Dichloroethane	1 (J 100 ppm	10	19.3 L ·	}8 mg/m³	40 to 1215 (10 L)	A	50 100 1 <i>1</i> 5		0.4 to 12	
1,2-Dichloroethylene	0.5 (9 200 ppm	3	5.4 L e	:09 my/m ³	80 to 2370 (3 L)	A	60 170 210		0.2 to 7	
Ethylene dichloride	1 (8 50 ppm	10	29 L ∄ ∔	∷ wy/m³	40 to 1215 (3 L)	۰.	10 225 250	octane	0.1 to 4	
Hexachloroethane	101ppm	10	43 t	«)/m³	1 to 30 (10 L)	D	110 170 210	n-tridecane	0.01 to 0.	
4ethy1ch1oroform	0.5 (0 350 ppm	6	9.5 t v	i 88 mg/m⁹	190 to 5700 (3 L)	A	10 225 250	oclane	0.6 to 17	
Propylene dichloride	1 @ 75 ppm	10	18 L (3)	ing/m ³	35 to 1050 (10 L)	A	80 170 210	n-undecane	0.3 to 10	

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HETHOD: 1003

100 mesh Supelcoport;

 $B = \delta m \times 3$ sat, otherwise same as A;

*A = 3'm x 3 um stainless steel, 10% SP-1000 cm

C = 3 m x 3 m stainless steel, 10% OV-101 on B120 mesh Supelcoport; or $D = 3 \text{ m x 6} \text{ an glass, } M \text{ SP-2250 on 80/100 m}^{-3}$

elcoport.

Trichloroethylene

Analyte:	Trichloroethylene	Method No.: S336
Matrix:	Air	Range: 519-2176 mg/cu m
OSHA Standard:	200 ppm (1075 mg/cu m)-Ceiling 100 ppm (535 mg/cu m)-T.W.A.	Precision (\overline{CV}_{T}) : 0.082
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 6/6/75

1. Principle of the Method

- 1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.
- 1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.
- 1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.
- 1.4 The area of the resulting peak is determined and compared with areas obtained from injection of standards.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 519-2176 mg/cu m at an atmospheric temperature and pressure of 24.5°C and 759.4 mm Hg, using a 3-liter sample. Under the conditions of sample size (3 liters) the probable useful range of this method is 108-3225 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 9.7 mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.
- 2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 42 mg of analyte when a test atmosphere containing 2266 mg/cu m of analyte in air was sampled at 0.187 liters per minute for 99 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent.

(The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

- 3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.
- 3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.
- 3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.
- 3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation (\overline{CV}_{T}) for the total analytical and sampling method in the range of 519-2176 mg/cu m was 0.082. This value corresponds to an 88.2 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.
- 4.2 On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 6.4 % lower than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result.

These data are based on validation experiments using the internal standard method.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

- 5.2 One disadvantage of the method is that the smount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.
- 5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

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- 6.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3).
- 6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.
- 6.3 Gas chromatograph equipped with a flame ionization detector.
- 6.4 Column (10-ft x 1/8-in stainless steel) packed with 10% OV-101 stationary phase on 100/120 mesh Supelcoport.
- 6.5 An electronic integrator or some other suitable method for measuring peak areas.
- 6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.
- 6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.
- 6.8 Pipets: 1.0 ml type graduated in 0.1-ml increments.

- 6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.
- 7. Reagents
 - 7.1 Chromatographic quality carbon disulfide.
 - 7.2 Trichloroethylene, reagent grade
 - 7.3 Octane, or other suitable internal standard
 - 7.4 Purified nitrogen
 - 7.5 Prepurified hydrogen.
 - 7.6 Filtered compressed air.
- 8. Procedure
 - 8.1 Cleaning of equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.
 - 8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.
 - 8.3 Collection and Shipping of Samples
 - 8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).
 - 8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.
 - 8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.
 - 8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.
 - 8.3.5 At the ceiling and peak concentrations, a sample size of 3 liters is recommended. Sample for 15 minutes at a flow of 0.2 liters per minute. At the T.W.A. concentration, a sample size of 10 liters is recommended. Sample at a flow of 0.2 liters per minute or less. The flow rates should be known with an accuracy of at least +5%.
 - 8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

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S336-4

- 8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.
- 8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.
- 8.3.9 Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.
- 8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.
- 8.4 Analysis of Samples
 - ÷.
 - 8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.
 - 8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.
 - 8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

30 ml/min (60 psig) Nitrogen carrier gas flow
 35 ml/min (25 psig) Hydrogen gas flow to detector
 400 ml/min (60 psig) Air flow to detector
 225°C injector temperature
 250°C manifold temperature (detector)
 70°C column temperature

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eli-

tion of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.

- 8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.
- 8.5 Determination of Desorption Efficiency
 - 8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.
 - 8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. When using an automatic sample injector, the sample injector vials, capped with Teflon-faced septa, may be used in place of the glass tubes.

Six tubes at each of three concentration levels (0.5X,1X and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 3-liter sample at the selected level. The tubes are allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 1.0 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

D.E. - <u>Average Weight (mg) recovered</u> Weight (mg) added

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg per 1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2% the standard. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

- 10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.
- 10.2 Corrections for the blank must be made for each sample.

mg = mg sample - mg blank

where:

mg sample = mg found in front section of sample tube
mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

- 10.3 Add the amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.
- 10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

Corrected mg/sample = $\frac{\text{Total weight}}{\text{D.E.}}$

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

mg/cu m = Corrected mg (Section 10.4) x 1000 (liters/cu m) Air Volume Sampled (liters)

10.6 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$ppm = mg/cu = x \frac{24.45}{MW} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled T = temperature (°C) of air sampled 24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg MW = molecular weight 760 = standard pressure (mm Hg) 298 = standard temperature (°K)

11. References

- 11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," <u>Amer. Ind. Hyg. Assoc. J., 31</u>: 225 (1970).
- 11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.
- 11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

VINYL CHLORIDE

FORMULA: CH2=CHC1; C2H3C1

METHOD: 1007 ISSUED: 2/15/84

M.W.: 62.50

OSHA: 1 ppm; C 5 ppm NIOSH: minimum measurable ACGIH: 5 ppm (human carcinogen) [1] (1 ppm = 2.56 mg/m³ @ NTP) PROPERTIES: BP =14 *C; vapor density 2.2 (air = 1)

SYNONYMS: chloroethylene; chloroethene; CAS #75-01-4.

SAMPLING	MEASUREMENT
SAMPLER: SOLID SORBENT TUBE (2 tandem tubes, each with 150 mg	I ITECHNIQUE: GAS CHROMATOGRAPHY, FID I
activated coconut charcoal)	ANALYTE: vinyl chloride
FLOW RATE: 0.05 L/min	: !DESORPTION: 1 mL carbon disulfide; 30 min
VOL-MIN: 0.7 L -MAX: 5 L	INJECTION ALIQUOT: 5 µL
SHIPMENT: separate primary and backup tubes and cap each	COLUMN: stainless steel, 6.1 m x 3.2 mm, 10% SE-30 on 80/100 mesh Chromosorb W (AW-DMCS)
SAMPLE STABILITY: 10 days @ 25 °C	!CARRIER GAS: He, 40 mL/min
BLANKS: 2 to 10 field blanks per set	: !TEMPERATURE-INJECTOR: 230 °C ! -DETECTOR: 230 °C ! -COLUMN: 60 °C
ACCURACY	!
RANGE STUDIED: 1 to 64 mg/m ³ [2]	ICALIBRATION: solutions of vinyl chloride in CS ₂ !
BIAS: -6% of calculated concentration [2]	<pre>!RANGE: 0.002 to 0.2 mg per sample [2] ! !ESTIMATED LOD: 0.00004 mg per sample [2]</pre>
OVERALL PRECISION (sr): 0.06 [2]	<pre>!! !PRECISION (s_p): not determined</pre>

APPLICABILITY: The working range is 0.4 to 40 mg/m³ (0.16 to 16 ppm) for a 5-L air sample. The method is applicable to 15-min samples at concentrations of 1 ppm or higher.

INTERFERENCES: Other than the possibility of loss of sample upon storage of two weeks or more at room temperature, none have been noted.

OTHER METHODS: This is a revision of P&CAM 178 [3].

VINYL CHLORIDE

REAGENTS:	EQUIPMENT:
 Carbon disulfide,* chromatographic quality. 	 Sampler: two tandem glass tubes, 7 cm long, 6 mm OD, 4 mm ID, flame-sealed ends, each
 Vinyl chloride,*, 99.9%, in lecture bottle fitted with valve and septum. 	containing 150 mg of 20/40 mesh activated (600 °C) coconut shell charcoal. A silylated glass wool plug precedes the charcoal beds and a 3-mm urethane
 Calibration stock solution, 0.26 mg/mL. a. Insert the tip of a gas syringe containing 1 mL vinyl chloride gas under the surface of 5 mL CS₂ in a 10-mL volumetric flock 	than 3.4 kPa. NOTE: A pair of two-section (100 mg/50 mg) tubes may be used.
flask. b. Open the valve of the syringe	Personal sampling pump, 0.05 L/min, with flexible connecting tubing.
and withdraw the plunger to pull CS_2 into the barrel. (As	 Gas chromatograph, flame ionization detector, integrator and column (page 1007-1).

- 4. File.
- 5. Bent wire for removing plugs from sampling tube.
- 6. Vials, 2-mL, glass with PTFE-lined septa and crimp-on seals.
- 7. Volumetric flasks, 10-mL, with polyethylene stoppers.
- 8. Pipettes, delivery, 1.0-mL, graduated in 0.1-mL increments, 2- and 5-mL, with pipet bulb.
- 9. Air sampling bags, Tedlar, 10-L.
- 10. Gas syringe, with gas-tight valve, 0.1- and 1-mL.
- 11. Syringe, 10-µL, with 0.1-µL graduations.

- 4. Helium, purified. 5. Hydrogen, purified.
- 6. Air, filtered.

*See Special Precautions.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = -30 °C); work with it only in a hood.

Vinyl chloride is a human carcinogen [1].

vinyl chloride dissolves, a

CS₂ into the syringe.) c. Push the solution from the

washings to the flask.

vacuum will be created, pulling

syringe into the flask. Rinse

the syringe twice with 1-mL

portions of CS2 and add the

d. Dilute to the mark with CS₂.

SAMPLING:

- 1. Calibrate each personal sampling pump with a representative sampler in line.
- 2. Break the ends of the tubes immediately before sampling. Attach two tubes, with ends touching, with a short piece of tubing. Label one tube as the back tube and insert the back tube into the flexible tubing attached to the personal sampling pump.
- 3. Sample at 0.05 L/min for 15 to 100 min. Do not sample more than 5 L of air.
- 4. Separate the primary and backup tubes and cap each tube for shipment.

SAMPLE PREPARATION:

- 5. Add 1.0 mL CS₂ to an empty vial. Loosely cap the vial.
- 6. Score each sampler tube with a file in front of the glass wool plug. Break the tube at the score line.

METHOD: 1007

- 7. Transfer the charcoal from the front and back tubes to separate vials. Discard the glass wool and foam plugs. Seal the vials with septum caps immediately.
- 8. Allow to stand for 30 min, with occasional agitation. Analyze the sample within the next 30-min period.

CALIBRATION AND QUALITY CONTROL:

- 9. Calibrate with at least five working standards covering the range 0.0002 to 0.2 mg per sample.
 - a. Add known amounts of calibration stock solution to CS₂ in 10-mL volumetric flasks and dilute to the marks, using serial dilution as appropriate.
 - NOTE: Working standards can be stored at -20 °C for at least three days.
 - b. Analyze together with samples and blanks (steps 12 and 13).
 - c. Prepare calibration graphs of peak area vs. quantity (mg) of vinyl chloride per tube and peak area vs. quantity (ng) per injection.
- Determine desorption efficiency (DE) at least once for each lot of charcoal used in the calibration range (step 9). Prepare three tubes at each of five levels plus three media blanks.
 - a. Prepare three atmospheres of vinyl chloride in air by injecting 0.01, 0.08, and 0.2 mL vinyl chloride gas into 10 L air in Tedlar bags. The resulting concentrations are approximately 2.6, 21 and 52 mg/m³.
 - b. Following steps 1 through 4, sample these atmospheres according to the following scheme:

Concentration in Bag (mg/m ³)	Volume Sampled (L)	Quantity of Vinyl Chloride (mg)						
2.6	0.8	0.002						
	2.2	0.006						
21	0.8	0.017						
	2.2	0.046						
52	2.5	0.13						

Obtain three samples at each level.

- c. Desorb (steps 6 through 8) and analyze together with working standards (steps 12 and 13). No vinyl chloride should be found on the back tubes.
- d. Analyze the atmospheres in the bags (steps 12 and 13) using 1-mL gas samples. Read from the calibration graph the quantity (ng) per injection, which for a 1-mL injection of gas is numerically equal to the concentration in mg/m³.
- e. Calculate DE from the mass (mg) of vinyl chloride on the front tube (W_{f}) , the average blank (B), the concentration of vinyl chloride in the synthetic atmospheres (C_{s} , mg/m³), and the volume of air sampled (V, L):

$$DE = \frac{(W_{f} - B) \cdot 10^{3}}{(C_{s})(V)}$$

f. Prepare a graph of DE vs. mass found (W_{f} - B).

11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

VINYL CHLORIDE

12. Set the gas chromatogrph according to manufacturer's instructions and to conditions given on page 1007-1. Inject sample aliquot manually using solvent flush technique or with autosampler. The retention time of vinyl chloride is about 1.7 min.

NOTE: If peak area is above the linear range of the working standards, dilute with CS₂, reanalyze and apply the appropriate dilution factor in calculations.

13. Measure peak area.

CALCULATIONS:

14. Determine the mass, mg (corrected for DE) of vinyl chloride found in the sample front $(W_{\rm f})$ and back $(W_{\rm b})$ tubes, and in the average media blank (B).

NOTE: If $W_p > W_p/10$, report breakthrough and possible sample loss.

15. Calculate concentration, C, of vinyl chloride in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - 2B) \cdot 10^3}{V}$$
, mg/m³

EVALUATION OF METHOD:

The method was evaluated using single 150-mg sampling tubes with 100-mg front beds and 50-mg back beds [2]. At four concentrations between 1 and 64 mg/m³, the pooled relative standard deviation was 0.06 and the measurements averaged 94% of the concentrations calculated from the volumes of vinyl chloride and air used for the atmospheres sampled; samples at the 3-µg level showed no loss of vinyl chloride when stored for 12 days at room temperature or 19 days at -20 °C. There may be significant loss of vinyl chloride from samples stored for 14 days at room temperature [4]. The 1% breakthrough capacity for a 150-mg bed of coconut charcoal challenged at 100 mL/min with vinyl chloride in air at 16 mg/m³ and a relative humidity of 70% was 4.6 L [5].

REFERENCES :

 <u>TLVs</u> - <u>Threshold Limit Values for Chemical Substances and Physical Agents in the Work</u> <u>Environment with Intended Changes for 1983-84</u>, ACGIH, Cincinnati, OH (1983).

- [2] Hill, R. H., Jr., C. S. McCammon, A. T. Saalwaechter, A. W. Teass, and W. J. Woodfin. <u>Anal. Chem.</u>, <u>48</u>, 1395-1398 (1976).
- [3] NIOSH Manual of Analytical Methods, 2nd. ed., V. 1, P&CAM 178, U.S. Department of Health and Human Services, Publ. (NIOSH) 77-157-A (1977).
- [4] Cuddeback, J. E., W. R. Burg, and S. R. Birch, Environ. Sci. Technol., 9, 1168-1171 (1975).
- [5] Matsumura, Y. <u>Ind</u>. <u>Health</u>, <u>18</u>, 61-67 (1980).

METHOD REVISED BY: A. W. Teass, Ph.D., NIOSH/DPSE.

HETHOD: 1007

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VELSICOL CHEMICAL CORPORATION ST. LOUIS, MICHIGAN PROJECT Nº 1524

GAS VENT SAMPLING PUMPS CALIBRATION LOG

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DATE	14	1-15 1	155		CALIB	RATED	BY	i								
· · · · ·				BEFORE			1135		AFT	ER SAMP	LING 3	15/85		AVI		15/85
PUMP NUMBER	PUMP TYPE	TEMP. (°F)	HUMIDITY (%)	BAROM. PRESSURE (Inches Hg)	INITIAL FLOW (cc/min.)	CALL FLOW (cc/min.)) 24-HR. TIME	TEMP. (°F)	HUMIDITY (%)	BAROM. PRESSURE (inches Hg)	FLOW (cc/min.)	24-HR. TIME	TEMP. (°F)	HUMIDITY (%)	BAROM. PRESSURE (Inches Hg)	FLOW (cc/min.)
1	(MILINA) a)	42	55	27.96	255		4 1 -	33	50	2003		12:30	37.5	57	30.145	250
	line b	42	55	27.7G	250	2.50	11	33	59	30.33	255	,	37.5	57	30.145	Z52.5
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COMMENTS

VELSICOL CHEMICAL CORPORATION ST. LOUIS, MICHIGAN PROJECT Nº 1524

GAS VENT SAMPLING

1

- N - - 1

1 1

DATE OF COLLECTION 3 15 85	SAMPLER ROBING	BAROMETRIC 30. 145
TEMPERATURE 7 37.5	RELATIVE 57%	GAUGE 2 3 4 5 6 7 8 9 10 11
CHARCOAL 120	TENAX LOT Nº 271	READING OF STORES OF OF

GAS VENT	PUMP	SAMPLE		SAMPLING TIME		SAMPLING RATE	SAMPLE
NUMBER	NUMBER	NUMBER	START	FINISH	ELAPSED	(cc/min.)	VOLUME (1)
1	1	7	11.44	12.01	70	2,70	50
2	1	5	1105	11.25	20	750	50
3		4	10.27	10.47	20	750	5.0
4	l	3	9.50	10.10	20	250	50
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6	ľ	2	913	9 33	20	250	50
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DUPLICATE	<u></u>						
BLANK		6	11-15				
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	AKBAL C		3/14/25				

VELSICOL CHEMICAL CORPORATION ST. LOUIS, MICHIGAN PROJECT Nº 1524

GAS VENT SAMPLING

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CHARCOAL LOT Nº	120	TENAX LOT Nº 211	READING					Û		0	0	Ē)	0	

GAS VENT	PUMP			SAMPLING RATE	SAMPLE		
NUMBER	NUMBER	NUMBER	START	FINISH	ELAPSED	(cc/min.)	VOLUME (1)
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3							
4							
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6							
7	2	10	10:09	10:29	Zo	250	5.0
8	2	8*	11.32	11.52	20	750	5.0
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11							
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BLANK							
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VELSICOL CHEMICAL CORPORATION

POST - CONSTRUCTION QUARTERLY MONITORING REPORT June 19 - 21, 1985

Plant Site, St. Louis Michigan

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1.0 INTRODUCTION

1.1 GENERAL

In accordance with the terms of the technical appendix to the Consent Judgment entered into by Velsicol Chemical Corporation (Velsicol), the United States Environmental Protection Agency, (USEPA) and the Michigan Department of Natural Resources (MDNR), Velsicol is required to perform specified monitoring activities at quarterly intervals following closure of its St. Louis, Michigan plant site. The monitoring program is designed to address the following:

- 1. Performance of gas vents
- 2. Performance of the site perimeter containment wall
- 3. Determination of site groundwater elevations

This report details the site monitoring which occured during the period June 19 to June 21, 1985.

1.2 PARTICIPATION BY REGULATORY AGENCIES

The regulatory agencies did not participate in or attend this monitoring event.

1.3 MONITORING AND SAMPLING PERSONNEL

The monitoring and sampling program was carried out by Mr. D. Robinson (Conestoga-Rovers and Associates) assisted by Mr. Gene DeGeer, the Velsicol site custodian.

2.0 GAS VENT MONITORING

2.1 GENERAL

The gas vent monitoring began on June 20, 1985 and was completed June 21, 1985.

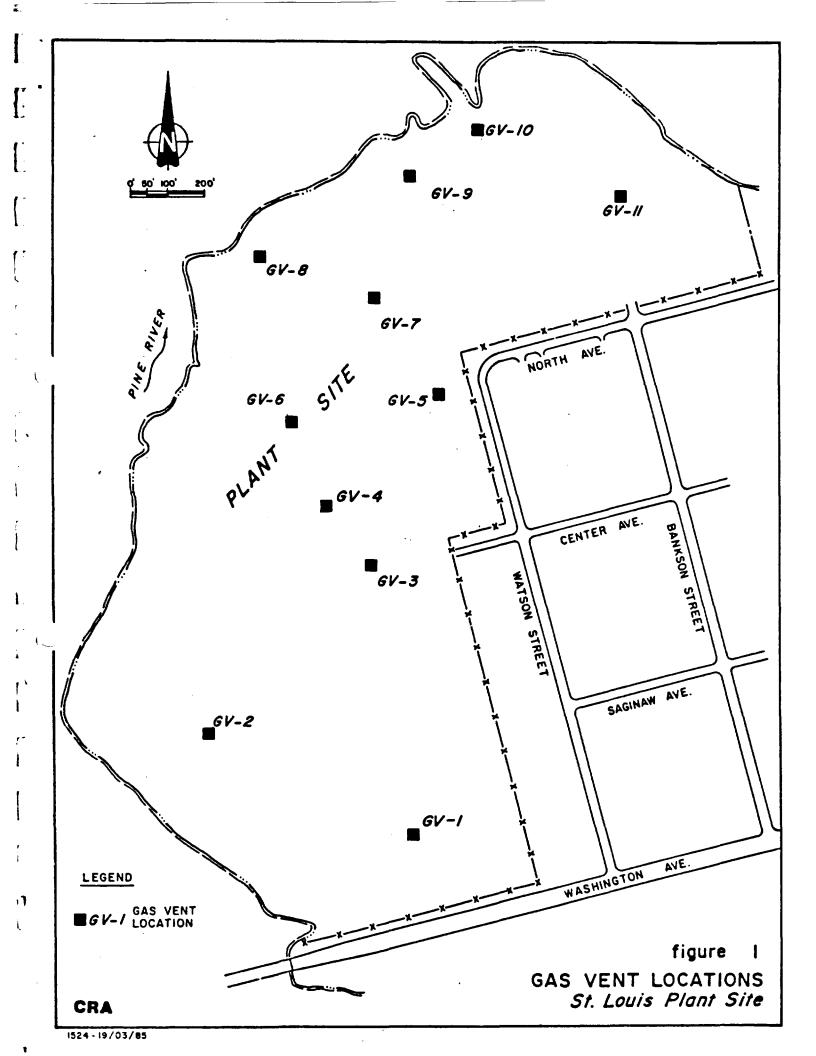
2.1.1 Equipment

Two Gilian model HFS 113 hi flow samplers were used to collect gas vent samples. The samplers were field calibrated using a rotometer prior to sampling. The calibration data is presented within Appendix B. Samples from each gas vent were collected in two 6-mm diameter x 70-mm long Tenax tubes and two charcoal tubes of similar dimensions. The samples were collected simultaneously using dual parallel/series tube holder sets.

2.2 SAMPLE COLLECTION

Samples were obtained at each of the 11 gas vents. The location of the gas vents within the closed plant site is detailed on Figure 1. One blank set and one duplicate set of samples were also collected.

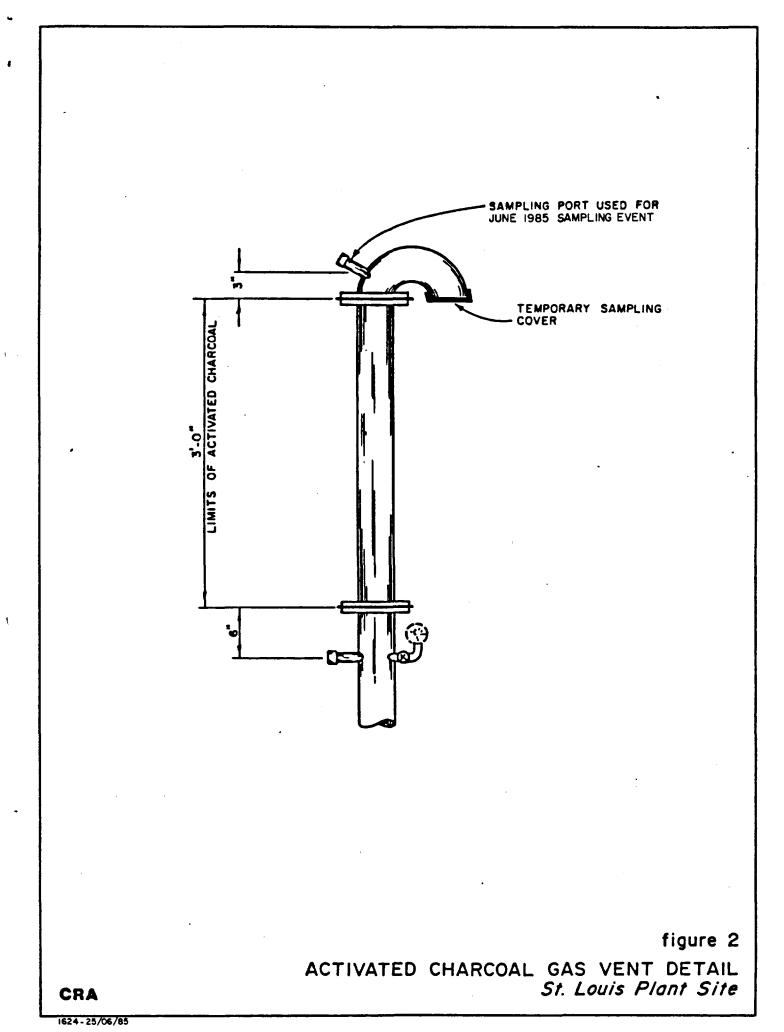
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Sampling was conducted at the downstream sampling port on each gas vent as detailed on Figure 2. The tube holder was attached directly to the gas vent sampling port using a copper manifold assembly which was environmentally cleaned prior to use. Tygon tubing was used to connect the tube holder to the sampler and was connected between the base of the tube holder and suction port of the sampler. The sampler which was pre-calibrated to 250cc/min/tube set, was operated for a period of 20 minutes for each sampling event, resulting in a collected sample volume of five liters per tube set.

Prior to sample collection, the gas vent upper chamber was purged by pumping at 500 cc/minute for a period of ten minutes. This precluded the possiblity of sampling retained atmospheric air from the gas vent upper chamber. During the purging and sampling operations, the open end of the gas vent was capped using a 4-inch diameter plastic cover to prevent atmospheric air being drawn into the sample.

At the conclusion of each gas vent sampling, the set of four sample tubes were capped, labelled and stored in a cooler maintained at 0°C.



2.2.1 Sample Storage and Shipment

On the afternoon of June 21, 1985 the samples were transferred to a cooler containing frozen cold packs and styrofoam packing materials. The cooler was shipped under chain of custody protocol, to Velsicol's Memphis, Tennessee laboratory by overnight courier for analysis. A copy of the chain of custody is provided in Appendix A.

2.2.2 Sample Analysis

Analysis will be conducted in accordance with NIOSH protocols as follows:

Compound	NIOSH Method
Carbon Tetrachloride	1003
Trichloroethylene	S-336
Vinyl Chloride	1007

Results will be reported verbally as they become available.

A hard copy of the laboratory report will be forwarded to USEPA and MDNR within seven days after receipt of final laboratory data by CRA.

2.2.3 Sampling Protocol

All sampling was performed in accordance with the methodology detailed within the St. Louis plant site Post-Closure Maintenance and Monitoring Plan, as approved by USEPA and MDNR. A copy of the sampling protocol is contained in Appendix B.

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3.0 SITE PERIMETER CONTAINMENT WALL MONITORING

3.1 GENERAL

The monitoring program consisting of the collection of an undisturbed sample of the containment wall with subsequent permeability testing was initiated on December 15, 1983. Subsequent sampling events occurred on March 15, 1984, June 15, 1984, September 14, 1984, December 14, 1985 and March 16, 1985. The current sampling event occured June 19, 1985. All testing completed to date has confirmed the permeability of the site perimeter containment wall to be less than 1.0 x 10-7 cm/sec.

3.2 EQUIPMENT

A Mobil Truck mounted drill rig equipped with rotary head and 6-inch diameter augers was utilized to advance the borehole into the containment wall. A 3-inch diameter Shelby tube, hydraulically pushed and retrieved, was used to collect the samples.

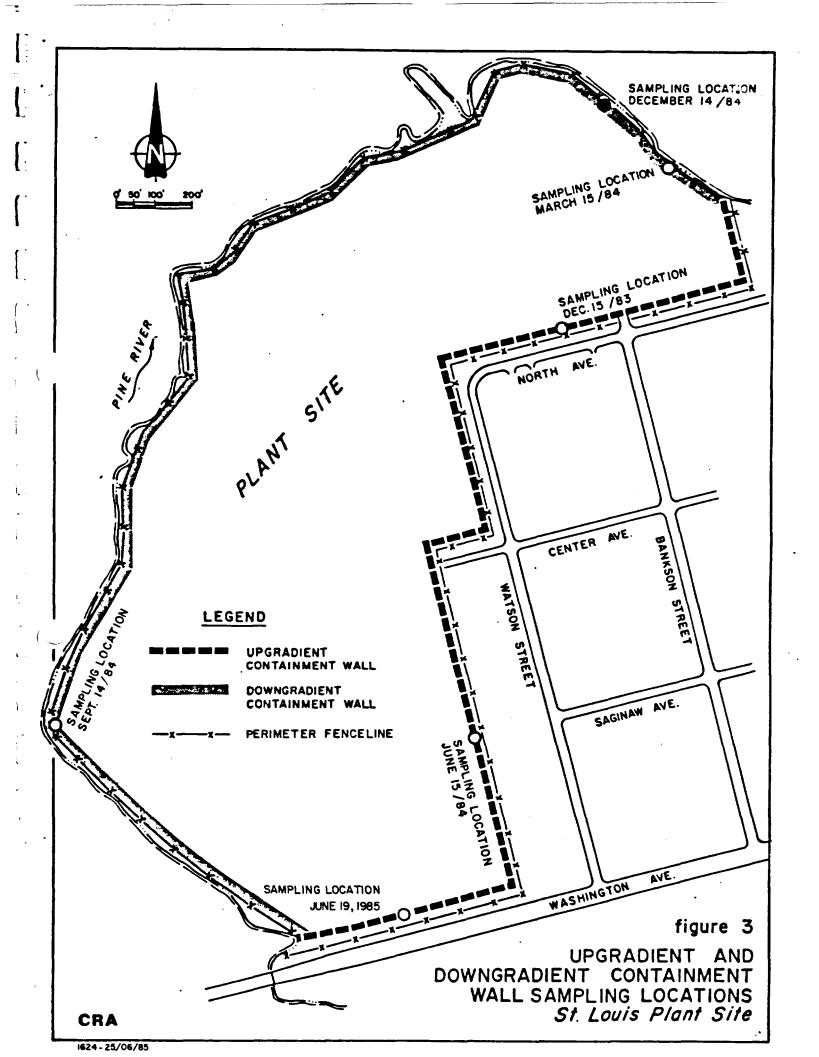
3.3 SAMPLE COLLECTION

The containment wall was located by field survey on June 19, 1985. The sampling borehole was begun at Station DGW 31+00 by augering through the clay cap into the underlying material.

The presence of soil/bentonite backfill material was confirmed by examination of cuttings on the auger flights. A borehole was advanced to a depth of seven feet. A Shelby tube was introduced into the borehole and a sample was withdrawn. Examination of material in the base of the tube confirmed that the sample was obtained from the containment wall. The locations of this and prior sampling events are detailed on Figure 3. The boreholes were backfilled with bentonite and abandoned.

3.3.1 Sample Preparation and Shipping

The Shelby tube was capped and taped at both ends to prevent sample loss and drying. The sample was hand delivered to the Michigan Testing Engineer's laboratory in Detroit, Michigan for permeability testing.



3.3.2 Sample Testing

The undisturbed sample is to be tested for permeability using a falling head permeameter set up in accordance with ASTM D 2434. Results of the testing will be provided in written form to USEPA and MDNR within seven days after receipt of final laboratory data by CRA. A summary data report will be prepared and presented to both Agencies following completion of the containment wall monitoring program in the fall of 1986.

4.0 GROUNDWATER TABLE MONITORING

4.1 GENERAL

The monitoring of plant site groundwater elevation was performed and the elevation of the St. Louis reservoir was determined on June 19, 1985.

4.2 WATER LEVEL DETERMINATION

The elevation of the groundwater was determined by measuring the distance from the top of each site monitoring well to the watertable. This distance was measured by lowering a chalked, weighted surveyors tape into the monitoring well. Readings of the tape, which was graduated in increments of one one-hundredth of a foot, were taken at the water level and at the top of the well casing. The former reading was deducted from the latter and the resultant dimension was subtracted from the previously established top of well casing elevation. Well head and watertable elevations are presented on Table 1.

The elevation of the St. Louis reservoir was determined by level and rod survey.

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TABLE 1

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WATER LEVEL MEASUREMENTS

JUNE 19, 1985

MONITORING WELL	WELL HEAD ELEVATION (AMSL)	MEASURED DISTANCE TO WATER TABLE (ft.)	WATERTABLE ELEVATION (AMSL)
1	735.91	14.07	721.84
2	742.06	19.33	722.73
3	749.91	27.58	722.33
4	736.00	13.63	722.37
5	739.35	17.73	721.62
6	734.48	12.95	721.53
7	733.98	12.20	721.78
8	734.30	13.04	721.26
9	734.60	13.21	721.39
10	733.48	12.16	721.32
11	734.47	13.05	721.42
12	730.78	9.39	721.39
13	734.49	13.06	721.43
14	736.00	14.44	721.56

Water	level	elevation,	St.	Louis	Reservoir	
(June	19, 1	985)				720.03

4.3 GROUNDWATER CONTOUR MAP

The groundwater elevation data were used to construct a site groundwater elevation contour map which is presented in Figure 4.

4.4 SITE MEAN GROUNDWATER ELEVATION

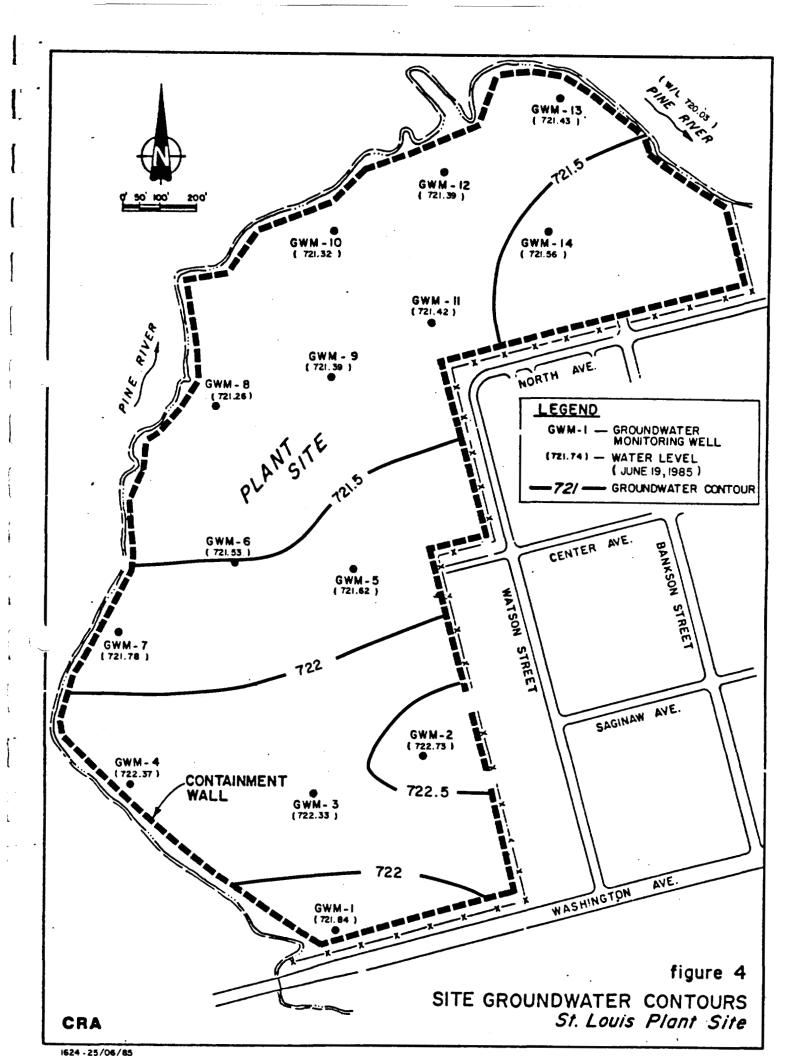
The mean elevation of site groundwater is calculated to be 721.71. The maximum allowable site groundwater elevation stipulated by the Consent Judgment is 724.13.

4.5 WELL HEAD ELEVATION SURVEY

In accordance with the Post Closure Maintenance and Monitoring Plan, the well head elevations were re-surveyed to ensure accuracy of the elevations. Minor differences from previous surveys were recorded and the groundwater elevations were adjusted accordingly.

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5.0 SUMMARY

All monitoring activities stipulated by the Consent Judgment were carried out between June 19 and 21, 1985.

Data from the chemical analysis of the gas vent samples and the permeability testing of the contaminant wall sample will be provided to MDNR and USEPA within seven days of receipt by CRA of laboratory final data.

The present mean site groundwater table elevation is calculated to be 721.71. The elevation in the Pine River/St. Louis reservoir was determined to be 720.03.

The next sampling and monitoring event will occur on or about September 15, 1985.

All of Which is Respectfully Submitted, CONESTOGA-ROVERS & ASSOCIATES LIMITED

D. Robinson

R.G. Shepherd, P. Eng.

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APPENDIX A

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CHAIN OF CUSTODY

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CHAIN OF CUSTODY RECORD

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PROJECT Nº.

1524

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PROJECT

PLANT SITE ST. LOUIS, MICHIGAN

VELSICOL CHEMICAL CORPORATION 701 W. WASHINGTON STREET ST. LOUIS, MICHIGAN 48880

APPENDIX B

GAS SAMPLING PROTOCOLS

APPENDIX B

GAS VENT SAMPLING PROTOCOL

In accordance with the Consent Judgment, Velsicol has submitted a post-closure maintenance and monitoring plan for its environmentally secured plant site in St. Louis, Michigan. The post-closure maintenance and monitoring plan requires quarterly monitoring of 11 gas vents that have been installed to release and appropriately treat internal gases. This program will be conducted over a period of three years.

The gas vents, as detailed in Exhibit F of the Consent Judgment, are designed with two sampling ports; one below the base of the installed activated charcoal filter, and one above the filter. Samples will be collected from the downstream port. Results will indicate whether or not containment breakthrough has occured through the carbon filter.

Samples will be analyzed for three separate compounds: carbon tetrachloride, trichloroethylene and vinyl chloride.

Samples will be collected with a Gilian HFS-113 AU DK variable flow pump. This particular unit allows the operator to run a series of tubes concurrently in parallel arrangement. Four tubes will be collected from each gas vent: two standard NIOSH 100/50 mg activated charcoal tube, and two 30/15 mg tenax tubes, each tube measuring 6 mm x 70 mm. One blank set and one duplicate set of tubes will be collected during each quarterly sampling event.

As vinyl chloride represents the least adsorptive of the three compounds, the sampling program is designed to accomodate this compound. Therefore, sample volume shall not exceed 5 liters.

Prior to sampling, the vent will be sealed off with a plastic cap, and purged for 10 minutes at a rate of 500 cc/min. This is to eliminate the possibility of sampling atmospheric air contained within the upper portion of the gas vent.

Two samples from each gas vent shall be collected simultaneously at a rate of 250 cc/min. for 20 minutes. The pump shall be lab calibrated with sample tubes in-line to determine the exact flow rate. Additionally, flow will be checked after field sampling to verify that a constant flow was maintained throughout the sampling period.

Following sample collection, each tube will be sealed with a plastic cap at each end, labelled, placed in a cold storage environment and shipped under chain-of-custody via a commercial courier service to Velsicol's analytical laboratory in Memphis.

Analysis of the charcoal tube will be conducted in accordance with NIOSH protocol as detailed below:

Compound	Revised Method No.
Carbon Tetrachloride	1003
Trichloroethylene	S-336
Vinyl Chloride	1007

Analysis will proceed by first eluting the carbon sample tubes with carbon disulfide and then analyzing by GC with a flame ionization detector. All samples will be initially analyzed in this fashion. If any of the above compounds are detected on the charcoal tube, the corresponding tenax tube will be analyzed by thermal desorption and GC/MS under EPA Method 624.

Turnaround time for the completed analysis at the laboratory is anticipated to be 30 days from date of sample collection. Samples will be desorbed within the 10 day limit specified for vinyl chloride. Analytical data will be reported to CRA as mg/tube. Final results for the carbon tube will be calculated by CRA, using the following formula.

1. Corrections for the blank to be made for each sample mg = mg sample - mg blank

This calculation is performed separately for each tube.

- 2. Add the amounts present in the front tube and backup tube to determine the total weight in the sample.
- 3. Calculate the corrected mg/sample by dividing the total weight by the desorption efficiency (D.E.) which is provided by the lab.

corrected mg/sample = total weight DE

- 4. Calculate the concentration of the analyte in air mg/m³ = Corrected mg x 1000 liters/m³ Air volume Sampled (liters)
- 5. Concentration will be reported as ppm, corrected to standard conditions of 25°C and 760 mm Hg

 $ppm = mg/m \quad x \; \frac{24.45}{MW} \; x \; \frac{760}{P} \; x \; \frac{(T+273)}{298}$

3

where	T	<pre>= pressure (mm Hg) of air sampled = temperature (°C) of air sampled = molar volume (liter/mole) at 25°C and 760 mm Hg</pre>
	MW	= Molecular Weight
	760	= standard pressure (mm Hg)
	298	= standard temperature (°K)

- 2 -

- NOTE: Temperature and pressure uncorrected to sea level will be collected for the duration of the sampling event and averaged for use in the above calculations. Information will be provided from the National Weather Service in Lansing, Michigan.
 - 6. If the concentration of the back tube exceeds 10% of the concentration of the front tube, the results will be reported as a sample breakthrough and possible sample loss.
 - 7. A similar procedure will be followed for the tenax tube, should analysis be required.

Data will be reported to USEPA and MDNR officials within seven days after receipt of final laboratory data for each quarterly sampling. Additionally, a summary data report will be provided at the conclusion of the three year sampling period, or sooner, should breakthrough of any compound occur prior to the three year program.

In addition to the set of field blanks to be collected per quarterly sampling event, an additional set of 15 charcoal tubes and 15 tenax tubes will be forwarded unopened to the lab during the initial sampling event.

These "blank" tubes will be used as internal calibration standards on which each of the three compounds will be spiked at five different concentrations. The data from this analysis will be used to calculate the desorption efficiency for a specific lot of activated charcoal. Therefore, the lot number of carbon tubes and tenax tubes shall be recorded during each quarterly sampling. Should the lot number change, a new set of 15 charcoal tubes and 15 tenax tubes shall be forwarded to the laboratory for determination of the new desorption efficiency.

The allowable limits for these compounds have been established by the MDNR and are site specific for the St. Louis site. These limits are documented in section 4.3 of the post-closure maintenance and monitoring plan.

Copies of all three analytical protocols, the chain of custody and the data collection sheet are provided in the following sections.

ంటుగు మరిశుత్తున్న సంఘటను విషణనిలో తెత్తున్న ప్రతిశాలు నేత్రిగా గ్రామం ప్రతిష్టించిన సంఘటనల్లో తర్మార్ సరాజంలన కొత్తున

HYDROCARBONS, HALOGENATED

FORMULA: Table 1

METHOD: 1003 ISSUED: 2/14/84

M.W.: Table 1

(synonyms

COMPOUNDS: benzyl chloride

bromoform

chlorobenzene

chloroform in Table 1) carbon tetrachloride o-dichlorobenzene p-dichlorobenzene

chlorobromomethane 1,1-dichloroethane hexachloroethane 1,2-dichloroethylene methylchloroform ethylene dichloride propylene dichloride

SAMPLING	MEASUREMENT
SAMPLER: SOLID SORBENT TUBE	! !TECHNIQUE: GAS CHROMATOGRAPHY, FID
(coconut shell charcoal, 100 mg/50 m	•
•	!ANALYTE: compounds above
FLOW RATE: 0.01 to 0.2 L/min	!
	DESORPTION: 1 mL CS ₂ , stand 30 min
VOL-MIN: Table 2	1 · · ·
-MAX: Table 2	INJECTION VOLUME: 5 µL
SHIPMENT: routine	: !TEMPERATURES: Table 2
SAMPLE STABILITY: at least 1 week @ 25 °C	: !CARRIER GAS: N ₂ or He, 30 mL/min
BLANKS: 2 to 10 field blanks per set	: COLUMN: Table 2; alternates are SP-2100, SP-2100 with 0.1% Carbowax 1500 or DB-1 fused silica capillary column
ACCURACY	
	CALIBRATICH: solutions of analyte in CS- with
ntesticion este contra actanta (1)	a se se se se se se se se se se se se se
BIAS: not significant [1]	: !RANGE: Table 2
OVERALL PRECISION (s _r): see EVALUATION OF HETHOD [1]	: !ESTIMATED LOD: 0.01 mg per sample [2] !
	PRECISION (s_{p}): see EVALUATION OF METHOD [1]

APPLICABILITY: This method uses a simple desorption and can be used for simultaneous analysis of two or more substances suspected to be present by changing the gas chromatographic conditions (i.e., temperature programmed). High humidity during sampling will prevent organic vapors from being trapped efficiently on the sorbent and greatly decreases breakthrough volume.

INTERFERENCES: None identified. The chromatographic column or separation conditions may be changed to circumvent interference problems.

OTHER METHODS: This method combines and replaces Methods P&CAM 127 [3]; S95, S101, S110, S113, S114, S115, S122, S123 and S133 [4]; and S135, S281, S314, S328 and S351 [5].

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a. Remove and discard back sorbent section of a media blank sampler.

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- b. Inject a known amount of analyte or calibration stock solution directly onto front sorbent section with a microliter syringe.
- c. Cap the tube. Allow to stand overnight.
- d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
- e. Prepare a graph of DE vs. mg analyte recovered.
- 10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

 Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1003-1. Inject sample aliquot manually using solvent flush technique or with autosampler.

NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.

12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of analyte found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.

NOTE: If $W_{\rm D} > W_{\rm f}/10$, report breakthrough and possible sample loss.

14. Calculate concentration, C, of analyte in the air volume sampled, V (L):

$$C = \frac{(W_{f} + W_{b} - B_{f} - B_{b}) \cdot 10^{3}}{V}, mg/m^{3}.$$

ENALUSTICS OF METHOD:

Laboratory testing was performed with spiked samples and generated atmosphere [1]. All analytes are stable at least one week. All methods were validated using SKC Lot 105 coconut shell charcoal. Results were:

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METHOD: 1003

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- [9] Criteria for a Recommended Standard...Occupational Exposure to 1,1,1-Trichloroethane, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 76-184 (1976).
- [10] Criteria for a Recommended Standard...Occupational Exposure to Carbon Tetrachloride, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 76-133 (1976).

METHOD REVISED BY: G. D. Foley; Y. T. Gagnon; and K. J. Williams, NIOSH/DPSE; methods originally validated under NIOSH Contract CDC-99-74-45.

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1003-5

Compounds	Formula	M.W.; mg/m ³ <u>= 1 ppm</u>	Synonyms	OSHA NIOSH [6-10] ACG1H	BP (°C)	VP (8 20 °C	Density (g/mL @ 20 °C)
e-Dichlorobenzene	· • • • • • • • • • • • • • • • • • • •		1dichiorobenzene; (* #106-46-7	75 ppm 75 ppm, STEL 110 ppm	174	50 Pa	1.241
l,1-Dichloroethane	ai ₃ aici ₂ ; c ₂ H4Ci ₂	98.96; 4.05	cHi ylidene chioride; Croc #75-34-3	100 ppm 100 ppm 200 ppm, S1EL 250 ppm	57	24.3 kPa	1.174
l,2-Dichloroethylene	C1CH=CHC1; C_H_C1 2_4_2	96.95; 3.96	acetylene dichloride; 1,:-dichloroethene; Con #540-59-0	200 ppm 200 ppm 200 ppm, STEL 250 ppm	60 (cis) 47 (trans)	24-35 kPa	1.28
Ethylene dichloride*	c1c1 ₂ c1 ₂ c1; c ₂ H4c1 ₂	98.96; 4.05	1,∷-dich1oroethane; C→ #107-06-2	50 ppm, C 100 ppm 5 ppm; 15 ppm/15 mls	83	8.3 kPa	1.255
	•	•		10 ppm, STEL 15 ppm	\$		·
lexach loroethane*	cc1 ₃ cc1 ₃ ; c ₂ c1 ₆	236.14; 9.68	perchloroethane; Call #67-72-1	l ppm (skin) l ppm (skin) l0 ppm	187 (sublines)	30 Pa	2.09
Methylchloroform	C ^{2H3} CJ ³ ;	133.42; 5.45	1, 1, 1-trichloroethane; C 5 #71-55-6	350 ppm 350 ppm/15 min CAS #71–55–6 STEL 450 ppm	74 350 ppm,	13.3 kPa	1.335
Propylene dichloride	C3H6C12	; 112.99; 4.62	1,2-dichloropropane C:2: #78-87-5	75 ppm 75 ppm 75 ppm, 75 ppm, 5TEL 110 ppm	95	5.3 kPa	1.156 (25 °C)

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1003

	Sampling			Measurement				
Campound	Air Sample <u>Volume (L)</u> Min		Breaktiv ough in Dr. Air	Working Range (mg/m ³)	Column*	<u>t (°C)</u> Column Injector Detector	Interna) Standard	Range (mg per sample)
			· · · · · · · · · · · · · · · · · · ·					
1,1-Dichloroethane	1 @ 100 ppm	10	18.3 L → 38 mg/m ⁹	40 to 1215 (10 L)	٨	50 100 1 <i>1</i> 5		0.4 to 12
						.,,		•
1,2-Dichloroethylene	0.5 @ 200 ppm	3	5.4 L t 309 my/m ⁹	80 to 2370 (3 L)	۸	60 170	· • •	0.2 to 7
	·		44)* 5.7			210		
Ethylene dichloride	1 @ 50 ppm	10	29 L 3 to ⊨ mg/m [®]	40 to 1215 (3 L)	۸	70 225	octane	0.1 to 4
Hexach loroethane	1 (ð 1 ppm	10	43 L	1 to 30 (10 L)	D	250 110 170 210	n-tridecane	0.01 to 0,
· · · ·					_			
Hethylchloroform	0.5 # 350 ppm	6	9.5 L v /88 mg/m ⁹	190 to 5700 (3 L)	٨	10 225 250	oclane	0.6 to 17
Propylene dichloride	1 @ 75 ppm	10	18 L 🔋 🔐 🗤 🕯	35 to 1050	۸	80 170	n-undecane	0.3 to 10

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*A = 3'm x 3 mm stainless steel, 10% SP-1000 tere

100 mesh Supelcoport;

 $B = \delta m \times 3$ in, other is an as A;

C = 3 m x 3 we stainly a steel, 10% OV-101 on D = 3 m x 6 we glass, D = 3 m x 6 we glass, D = 2250 on 80/100 eV

120 mesh Supelcoport; or

elcoport.

HYDROCARBONS, HALOGENATED

THE HOO

Trichloroethylene

Analyte:	Trichloroethylene	Method No.: S336			
Matrix:	Air	Range: 519-2176 mg/cu m			
OSHA Standard:	200 ppm (1075 mg/cu m)-Ceiling 100 ppm (535 mg/cu m)-T.W.A.	Precision (\overline{CV}_{T}) : 0.082			
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 6/6/75			

1. Principle of the Method

- 1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.
- 1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.
- 1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.
- 1.4 The area of the resulting peak is determined and compared with areas obtained from injection of standards.

2. Range and Sensitivity

2.1 This method was validated over the range of 519-2176 mg/cu m at an atmospheric temperature and pressure of 24.5°C and 759.4 mm Hg, using a 3-liter sample. Under the conditions of sample size (3 liters) the probable useful range of this method is 108-3225 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 9.7 mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 42 mg of analyte when a test atmosphere containing 2266 mg/cu m of analyte in air was sampled at 0.187 liters per minute for 99 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent.

S336-1

(The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

- 3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.
- 3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.
- 3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.
- 3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation $(\overline{CV_T})$ for the total analytical and sampling method in the range of 519-2176 mg/cu m was 0.082. This value corresponds to an 88.2 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.
- 4.2 On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 6.4 % lower than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result.

These data are based on validation experiments using the internal standard method.

- 5. Advantages and Disadvantages of the Method
 - 5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

S336-2

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

- 5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.
- 5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

- 6.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3).
- 6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.
- 6.3 Gas chromatograph equipped with a flame ionization detector.
- 6.4 Column (10-ft x 1/8-in stainless steel) packed with 10% OV-101 stationary phase on 100/120 mesh Supelcoport.
- 6.5 An electronic integrator or some other suitable method for measuring peak areas.
- 6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.
- 6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.

6.8 Pipets: 1.0 ml type graduated in 0.1-ml increments.

S336-3

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6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

- 7.1 Chromatographic quality carbon disulfide.
- 7.2 Trichloroethylene, reagent grade
- 7.3 Octane, or other suitable internal standard
- 7.4 Purified nitrogen
- 7.5 Prepurified hydrogen.
- 7.6 Filtered compressed air.

8. Procedure

- 8.1 Cleaning of equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.
- 8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.
- 8.3 Collection and Shipping of Samples -
 - 8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).
 - 8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.
 - 8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.
 - 8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.
 - 8.3.5 At the ceiling and peak concentrations, a sample size of 3 liters is recommended. Sample for 15 minutes at a flow of 0.2 liters per minute. At the T.W.A. concentration, a sample size of 10 liters is recommended. Sample at a flow of 0.2 liters per minute or less. The flow rates should be known with an accuracy of at least ±5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

\$336-4

- 8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.
- 8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.
- 8.3.9 Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.
- 8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.
- 8.4 Analysis of Samples
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 - 8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.
 - 8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.
 - 8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

30 ml/min (60 psig) Nitrogen carrier gas flow
 35 ml/min (25 psig) Hydrogen gas flow to detector
 400 ml/min (60 psig) Air flow to detector
 225°C injector temperature
 5. 250°C manifold temperature.(detector)
 6. 70°C column temperature

S336-5

- 8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.
- 8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.
- 8.5 Determination of Desorption Efficiency

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- 8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.
- 8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. When using an automatic sample injector, the sample injector vials, capped with Teflon-faced septa, may be used in place of the glass tubes.

S336-6

Six tubes at each of three concentration levels (0.5X,1X and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 3-liter sample at the selected level. The tubes are allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 1.0 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

D.E. = <u>Average Weight (mg) recovered</u> Weight (mg) added

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg per 1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2% the standard. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

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10. Calculations

- 10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.
- 10.2 Corrections for the blank must be made for each sample.

mg = mg sample - mg blank

where:

mg sample = mg found in front section of sample tube
mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

- 10.3 Add the amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.
- 10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

Corrected mg/sample = Total weight D.E.

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

10.6 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$ppm = mg/cu = x \frac{24.45}{MW} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled T = temperature (°C) of air sampled 24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg MW = molecular weight 760 = standard pressure (mm Hg) 298 = standard temperature (°K)

 $(1)(\delta_{2}, \gamma_{2}, \gamma_{2}, \delta_{2}, \gamma_{2}, \kappa_{2}, \kappa_{$

11. References

- 11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," <u>Amer. Ind. Hyg. Assoc. J.</u>, <u>31</u>: 225 (1970).
- 11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.
- 11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

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S336-9

VINYL CHLORIDE

FORMULA: CH2=CHC1; C2H2C1

M.W.: 62.50

HETHOD: 1007 ISSUED: 2/15/84

OSHA: 1 ppm; C 5 ppm NIOSH: minimum measurable ACGIH: 5 ppm (human carcinogen) [1] (1 ppm = 2.56 mg/m³ @ NTP) PROPERTIES: BP -14 *C; vapor density 2.2 (air = 1)

SYNONYMS: chloroethylene; chloroethene; CAS #75-01-4.

SAMPLING	MEASUREMENT
SAMPLER: SOLID SORBENT TUBE (2 tandem tubes, each with 150 mg	! !TECHNIQUE: GAS CHRONATOGRAPHY, FID !
activated coconut charcoal)	ANALYTE: vinyl chloride
FLOW RATE: 0.05 L/min	: !DESORPTION: 1 mL carbon disulfide; 30 min !
VOL-MIN: 0.7 L -MAX: 5 L	INJECTION ALIQUOT: 5 µL
SHIPMENT: separate primary and backup tubes and cap each	!COLUMN: stainless steel, 6.1 m x 3.2 mm, 105 ! SE-30 on 80/100 mesh Chromosorb W ! (AM-DMCS)
SAMPLE STABILITY: 10 days @ 25 °C	CARRIER GAS: He, 40 mL/min
BLANKS: 2 to 10 field blanks per set	: !TEMPERATURE-INJECTOR: 230 °C ! -DETECTOR: 230 °C ! -COLLINN: 60 °C
ACCURACY	• • • • • • • • • • • • • • • • • • •
RANGE STUDIED: 1 to 64 mg/m ³ [2]	<pre>!CALIBRATION: solutions of vinyl chloride in CS₂ ! !RANGE: 0.002 to 0.2 mg per sample [2]</pre>
BIAS: -6% of calculated concentration [2]	! ! !ESTIMATED LOD: 0.00004 mg per sample [2]
OVERALL PRECISION (s _T): 0.06 [2]	! !PRECISION (s _r): not determined
	• • • • • • • • • • • • • • • • • • •

APPLICABILITY: The working range is 0.4 to 40 mg/m³ (0.16 to 16 ppm) for a S-L air sample. The method is applicable to 15-min samples at concentrations of 1 ppm or higher.

INTERFERENCES: Other than the possibility of loss of sample upon storage of two weeks or more at room temperature, none have been noted.

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OTHER METHODS: This is a revision of P&CAM 178 [3].

2/15/84

VINYL CHLORIDE

- REAGENTS:
- Carbon disulfide,* chromatographic quality.
- Vinyl chloride,*, 99.9%, in lecture bottle fitted with valve and septum.
- Calibration stock solution, 0.26 mg/mL.
 - a. Insert the tip of a gas syringe containing 1 mL vinyl chloride gas under the surface of 5 mL CS₂ in a 10-mL volumetric flask.
 - b. Open the value of the syringe and withdraw the plunger to pull CS₂ into the barrel. (As vinyl chloride dissolves, a vacuum will be created, pulling CS₂ into the syringe.)
 - c. Push the solution from the syringe into the flask. Rinse the syringe twice with 1-mL portions of CS₂ and add the washings to the flask.
 - d. Dilute to the mark with CS_2 .
- 4. Helium, purified.
- 5. Hydrogen, purified.
- 6. Air, filtered.

*See Special Precautions.

- EQUIPMENT:
- Sampler: two tandam glass tubes, 7 cm long, 6 mm 00, 4 mm ID, flame-sealed ends, each containing 150 mg of 20/40 mesh activated (600 °C) coconut shell charcoal. A silylated glass wool plug precedes the charcoal beds and a 3-mm urethane foam plug follows the charcoal beds. Plastic caps are included for sealing after use. Pressure drop across each tube at 1 L/min airflow must be less than 3.4 kPa.
 - NOTE: A pair of two-section (100 mg/50 mg) tubes may be used.
- 2. Personal sampling pump, 0.05 L/min, with flexible connecting tubing.
- 3. Gas chromatograph, flame ionization detector, integrator and column (page 1007-1).
- 4. File.
- 5. Bent wire for removing plugs from sampling tube.
- Vials, 2-mL, glass with PTFE-lined septa and crimp-on seals.
- Volumetric flasks, 10-mL, with polyethylene stoppers.
- Pipettes, delivery, 1.0-mL, graduated in 0.1-mL increments, 2- and 5-mL, with pipet bulb.
- 9. Air sampling bags, Tedlar, 10-L.
- 10. Gas syringe, with gas-tight valve, 0.1- and 1-mL.
- 11. Syringe, 10-µL, with 0.1-µL graduations.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point = -30 °C); work with it only in a hood.

Vinyl chloride is a human carcinogen [1].

SAMPLING:

- 1. Calibrate each personal sampling pump with a representative sampler in line.
- Break the ends of the tubes immediately before sampling. Attach two tubes, with ends touching, with a short piece of tubing. Label one tube as the back tube and insert the back tube into the flexible tubing attached to the personal sampling pump.
- 3. Sample at 0.05 L/min for 15 to 100 min. Do not sample more than 5 L of air.

4. Separate the primary and backup tubes and cap each tube for shipment.

SAMPLE PREPARATION:

- 5. Add 1.0 mL CS_2 to an empty vial. Loosely cap the vial.
- .6. Score each sampler tube with a file in front of the glass wool plug. Break the tube at the score line.

2/15/84

1007-2

HETHOD: 1007

- 7. Transfer the charcoal from the front and back tubes to separate vials. Discard the glass wool and foam plugs. Seal the vials with septum caps immediately.
- 8. Allow to stand for 30 min, with occasional agitation. Analyze the sample within the next 30-min period.

CALIBRATION AND QUALITY CONTROL:

- Calibrate with at least five working standards covering the range 0.0002 to 0.2 mg per sample.
 - a. Add known amounts of calibration stock solution to CS_2 in 10-mL volumetric flasks and dilute to the marks, using serial dilution as appropriate.
 - NOTE: Working standards can be stored at -20 °C for at least three days.
 - b. Analyze together with samples and blanks (steps 12 and 13).
 - c. Prepare calibration graphs of peak area vs. quantity (mg) of vinyl chloride per tube and peak area vs. quantity (mg) per injection.
- Determine desorption efficiency (DE) at least once for each lot of charcoal used in the calibration range (step 9). Prepare three tubes at each of five levels plus three media blanks.
 - a. Prepare three atmospheres of vinyl chloride in air by injecting 0.01, 0.08, and 0.2 mL vinyl chloride gas into 10 L air in Tedlar bags. The resulting concentrations are approximately 2.6, 21 and 52 mg/m³.
 - b. Following steps 1 through 4, sample these atmospheres according to the following scheme:

Concentration in Bag (mg/m ³)	Volume Sampled (L)	Quantity of Vinyl Chloride (mg)
2.6	0.8	0.002
	2.2	0.006
21	0.8	0.017
	2.2	0.046
52	2.5	0.13

Obtain three samples at each level.

- c. Desorb (steps 6 through 8) and analyze together with working standards (steps 12 and 13). No vinyl chloride should be found on the back tubes.
- d. Analyze the atmospheres in the bags (steps 12 and 13) using 1-mL gas samples. Read from the calibration graph the quantity (ng) per injection, which for a 1-mL injection of gas is numerically equal to the concentration in mg/m³.
- e. Calculate DE from the mass (mg) of vinyl chloride on the front tube ($W_{\rm f}$), the average blank (8), the concentration of vinyl chloride in the synthetic atmospheres ($C_{\rm S}$, mg/m³), and the volume of air sampled (V, L):

$$DE = \frac{(H_{f} - B) \cdot 10^{3}}{(C_{c}) (V)}$$

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f. Prepare a graph of DE vs. mass found ($W_{f} = B$).

11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

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VINYL CHLORIDE

HEASUREMENT:

- 12. Set the gas chromatogrph according to manufacturer's instructions and to conditions given on page 1007-1. Inject sample aliquot manually using solvent flush technique or with autosampler. The retention time of vinyl chloride is about 1.7 min.
 - NOTE: If peak area is above the linear range of the working standards, dilute with C5₂, reanalyze and apply the appropriate dilution factor in calculations.
- 13. Measure peak area.

CALCULATIONS:

14. Determine the mass, mg (corrected for DE) of vinyl chloride found in the sample front $(W_{\rm F})$ and back $(W_{\rm D})$ tubes, and in the average media blank (B).

NOTE: If $W_{\rm b} > W_{\rm f}/10$, report breakthrough and possible sample loss.

15. Calculate concentration, C, of vinyl chloride in the air volume sampled, V (L):

$C = \frac{(W_{f} + W_{b} - 2B) \cdot 10^{3}}{V}$, mg/m³

EVALUÁTION OF METHOD:

The method was evaluated using single 150-mg sampling tubes with 100-mg front beds and 50-mg back beds [2]. At four concentrations between 1 and 64 mg/m³, the pooled relative standard deviation was 0.06 and the measurements averaged 94% of the concentrations calculated from the volumes of vinyl chloride and air used for the atmospheres sampled; samples at the 3-µg level showed no loss of vinyl chloride when stored for 12 days at room temperature or 19 days at -20 °C. There may be significant loss of vinyl chloride from samples stored for 14 days at room temperature [4]. The 1% breakthrough capacity for a 150-mg bed of coconut charcoal challenged at 100 mL/min with vinyl chloride in air at 16 mg/m³ and a relative humidity of 70% was 4.6 L [5].

REFERENCES :

 <u>TLVs - Threshold Limit Values for Chemical Substances and Physical Agents in the Work</u> <u>Environment with Intended Changes for 1983-84</u>, ACGIH, Cincinnati, OH (1983).

[2] Hill, R. H., Jr., C. S. McCammon, A. T. Saalwaechter, A. W. Teass, and W. J. Woodfin. <u>Anal. Chem.</u>, <u>48</u>, 1395-1398 (1976).

[3] NIOSH Manual of Analytical Methods, 2nd. ed., V. 1, P&CAM 178, U.S. Department of Health and Human Services, Publ. (NIOSH) 77-157-A (1977).

[4] Cuddeback, J. E., W. R. Burg, and S. R. Birch, Environ. Sci. Technol., 9, 1168-1171 (1975).

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[5] Matsumura, Y. <u>Ind. Health, 18,</u> 61-67 (1980).

HETHOD REVISED BY: A. W. Teass, Ph.D., NIOSH/DPSE.

2/15/84

VELSICOL CHEMICAL CORPORATION ST. LOUIS, MICHIGAN PROJECT Nº 1524

GAS VENT SAMPLING

COLLECTION June ZI 85	SAMPLER ROBINSON	BAROMETRIC 29.955
TEMPERATURE TO S	RELATIVE 60%	GAUGE 1 2 3 4 5 6 7 8 9 10 11
CHARCOAL VZG	TENAX LOT Nº こつし	READING PP / D

GAS VENT	PUMP	SAMPLE		SAMPLING TIME	SAMPLING RATE	SAMPLE		
NUMBER	NUMBER	NUMBER	START	FINISH	ELAPSED	(cc/min.)	VOLUME (1)	
1					·			
2	<u></u> .			•			· · · · · · · · · · · · · · · · · · ·	
3								
4								
5		•						
6								
7	9370	9	11.14	1134	20	250	5.0	
8	9370	10	8.29	849	20	250	50	
9	9370	11	949	10.09	20	250	5.0	
10	9370	12	12.03	12.23	20	250	5.0	
11	9370	13	1326	1346	26	250	:5-3	
DUPLICATE							••	
BLANK								
DATE OF Sample Sh	IPMENT 30	-21 19	85 METH SHIPI	HOD OF FELLENP	eess AwB	611 891 593		

VELSICOL CHEMICAL CORPORATION ST. LOUIS, MICHIGAN

GAS VENT SAMPLING

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PROJECT Nº 1524

COLLECTION JUNE 20/85	SAMPLER D. RoBALSON	BAROMETRIC 29 935
TEMPERATURE 63.5	RELATIVE 58.5	GAUGE 1 2 3 4 5 6 7 8 9 10 11
CHARCOAL 120	TENAX LOT Nº 271	READING

GAS VENT	PUMP	SAMPLE		SAMPLING TIME		SAMPLING RATE	SAMPLE	
NUMBER	NUMBER NUMBER		START	FINISH	ELAPSED	(cc/min.)	VOLUME (1)	
1	9369	١	16. ZO	10.40	20	250	5.0	
2	7369	3	1246	13.06	20	250	5.0	
3	9369	4	13 25	13 45	20	250	5.0	
4	9369	5	14.03	14.23	20	250	5.0	
· 5	9369	7	14.42	15.02	20	250	5.0	
6	9369	8	16.00	16.20	.20	250	5.0	
7								
8								
9			<u></u>					
10								
11								
DUPLICATE	3369	Z(GVI)	10.43	11.03	20	250	5.0	
BLANK	9369	36	*=== 3 13 Sc.	1356	20	250	50	
DATE OF SAMPLE SH	IPMENT Jac	a. 21 1985	METHO		upres Awr	3611 291 59	3	

COMMENTS

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VELSICOL CHEMICAL CORPORATION ST. LOUIS, MICHIGAN PROJECT Nº 1524

GAS VENT SAMPLING PUMPS CALIBRATION LOG

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DATE JUNE ZI 1985 CA					CALIB	CALIBRATED BY DROBINS										
		1		BEFORE S		MPLING AFTER SAMPLING					AVERAGE					
PUMP NUMBER	PUMP TYPE	TEMP. (°F)	HUMIDITY (%)	BAROM. PRESSURE (Inches Hg)	INITIAL FLOW (cc/min.)	CAL. FLOW (cc/min.)	24-HR. TIME	TEMP. (°F)	HUMIDITY (%)	BAROM. PRESSURE (Inches Hg)	FLOW (cc/min.)	24-HR. TIME	TEMP. (°F)	HUMIDITY (%)	BAROM. PRESSURE (Inches Hg)	FLOW (cc/min.
9370		61	67	Z9_98		250	0800	03	53	79 93	250	14.00	70.5	60	29 955	250
<u>93.9</u>		61	67	29.98	250	250	0814	દ૦	53	29.93	250	14.10	70.5	60	29.955	250
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COMMENTS

VELSICOL CHEMICAL CORPORATION ST. LOUIS, MICHIGAN PROJECT Nº 1524

GAS VENT SAMPLING PUMPS CALIBRATION LOG

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DATE JUNE 20 1985				CALIB	CALIBRATED BY D ZOBINSO											
[]		1		BEFORE		•			AFT	ER SAMP	LING	AVERAGE				
PUMP NUMBER	PUMP TYPE	TEMP. (°F)	HUMIDITY	BAROM. PRESSURE (Inches Hg)	INITIAL FLOW (cc/min.)	CAL. FLOW (cc/min.)	24-HR. TIME	TEMP. (°F)	HUMIDITY	BAROM. PRESSURE (Inches Hg)	FLOW (cc/min.)	24-HR. TIME	TEMP. (°F)	HUMIDITY (%)	BAROM. PRESSURE (Inches Hg)	FLOW (cc/min.)
9370		55	83	29.93	240	250	0834	72	34	29 54	250	1710	13.5	58.5	29.935	250
<u> </u>		55	83	8993	250	250	0850	<u>יר</u>	34	29.94	250	17 25	635	585	25 535	250
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VELSICOL CHEMICAL CORPORATION

POST - CONSTRUCTION QUARTERLY MONITORING REPORT SEPTEMBER 16-17, 1985

Plant Site, St. Louis Michigan

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APPENDIX A CHAIN OF CUSTODY APPENDIX B GAS SAMPLING PROTOCOLS

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1.0 INTRODUCTION

1.1 GENERAL

In accordance with the terms of the technical appendix to the Consent Judgment entered into by Velsicol Chemical Corporation (Velsicol), the United States Environmental Protection Agency, (USEPA) and the Michigan Department of Natural Resources (MDNR), Velsicol is required to perform specified monitoring activities at quarterly intervals following closure of its St. Louis, Michigan plant site. The monitoring program is designed to address the following:

- 1. Performance of gas vents
- 2. Performance of the site perimeter containment wall
- 3. Determination of site groundwater elevations

This report details the site monitoring which occured during the period September 16 to September 17, 1985.

1.2 PARTICIPATION BY REGULATORY AGENCIES

The regulatory agencies did not participate in or attend this monitoring event.

1.3 MONITORING AND SAMPLING PERSONNEL

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The monitoring and sampling program was carried out by Ms. C. Cull (Conestoga-Rovers and Associates) assisted by Mr. Gene DeGeer, the Velsicol site custodian.

2.0 GAS VENT MONITORING

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2.1 GENERAL

The gas vent monitoring began on September 16, 1985 and was completed September 17, 1985.

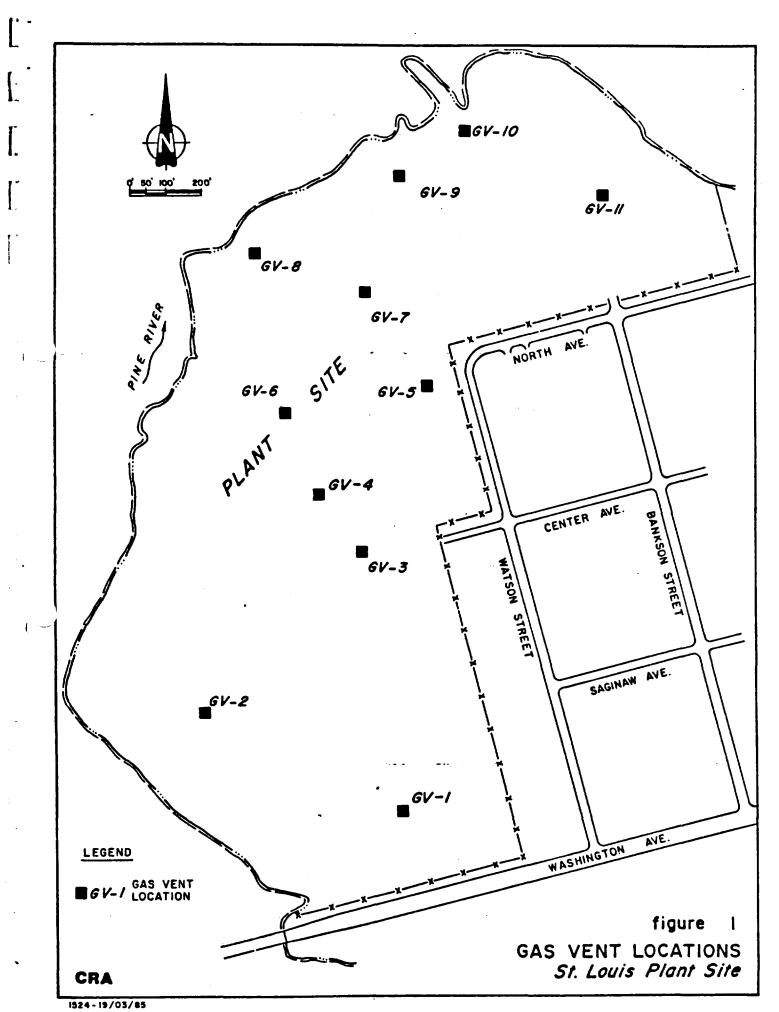
2.1.1 Equipment

Two Gilian model HFS 113 hi flow samplers were used to collect gas vent samples. The samplers were field calibrated using a rotometer prior to sampling. The calibration data is presented within Appendix B. Samples from each gas vent were collected in two 6-mm diameter x 70-mm long Tenax tubes and two charcoal tubes of similar dimensions. The samples were collected simultaneously using dual parallel/series tube holder sets.

2.2 SAMPLE COLLECTION

Samples were obtained at each of the 11 gas vents. The location of the gas vents within the closed plant site is detailed on Figure 1. One blank set and one duplicate set of samples were also collected.

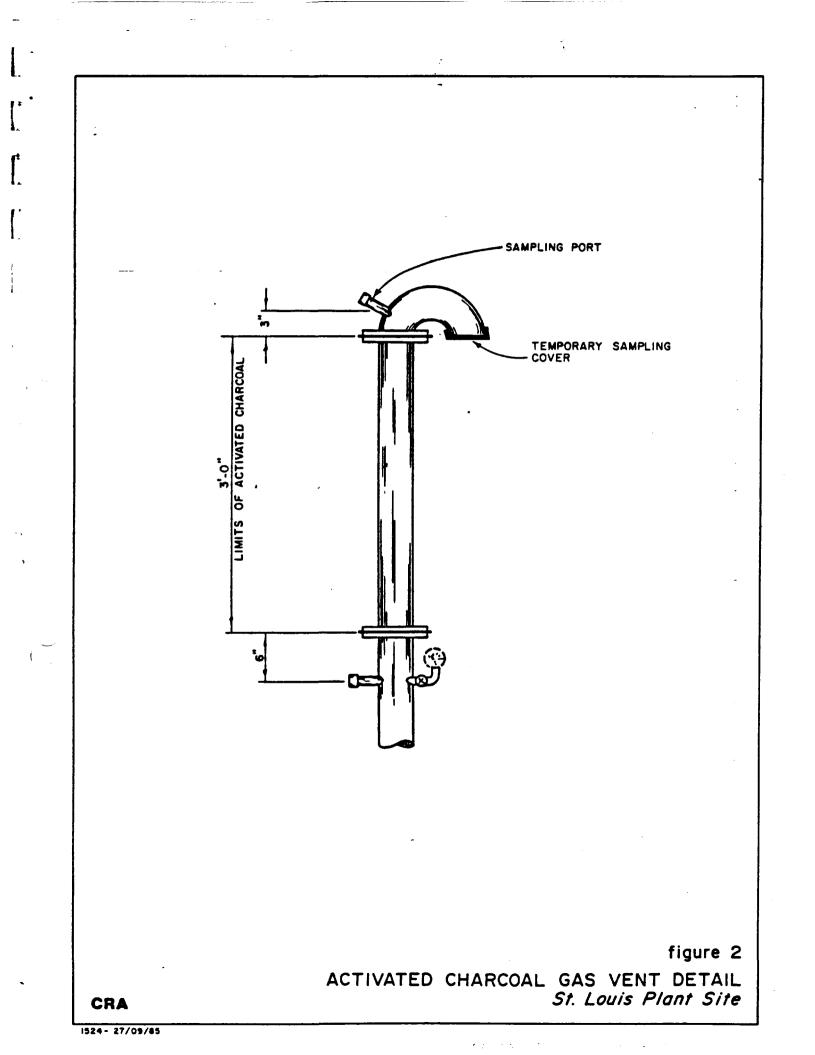
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Sampling was conducted at the downstream sampling port on each gas vent as detailed on Figure 2. The tube holder was attached directly to the gas vent sampling port using a copper manifold assembly which was environmentally cleaned prior to use. Tygon tubing was used to connect the tube holder to the sampler and was connected between the base of the tube holder and suction port of the sampler. The sampler which was pre-calibrated to 250cc/min/tube set, was operated for a period of 20 minutes for each sampling event, resulting in a collected sample volume of five liters per tube set.

Prior to sample collection, the gas vent upper chamber was purged by pumping at 500 cc/minute for a period of ten minutes. This precluded the possiblity of sampling retained atmospheric air from the gas vent upper chamber. During the purging and sampling operations, the open end of the gas vent was capped using a 4-inch diameter plastic cover to prevent atmospheric air being drawn into the sample.

At the conclusion of each gas vent sampling, the set of four sample tubes were capped, labelled and stored in a cooler maintained at $0^{\circ}C$.



2.2.1 Sample Storage and Shipment

On the afternoon of September 17, 1985 the samples were transferred to a cooler containing frozen cold packs and styrofoam packing materials. The cooler was shipped under chain of custody protocol, to Velsicol's Memphis, Tennessee laboratory by overnight courier for analysis. A copy of the chain of custody is provided in Appendix A.

2.2.2 Sample Analysis

Analysis will be conducted in accordance with NIOSH protocols as follows:

Compound	NIOSH Method
Carbon Tetrachloride	1003
Trichloroethylene	S-336
Vinyl Chloride	1007

Results will be reported verbally as they become available.

A hard copy of the laboratory report will be forwarded to USEPA and MDNR within seven days after receipt of final laboratory data by CRA.

2.2.3 Sampling Protocol

All sampling was performed in accordance with the methodology detailed within the St. Louis plant site Post-Closure Maintenance and Monitoring Plan, as approved by USEPA and MDNR. A copy of the sampling protocol is contained in Appendix B.

6

3.0 SITE PERIMETER CONTAINMENT WALL MONITORING

3.1 GENERAL

The monitoring program consisting of the collection of an undisturbed sample of the containment wall with subsequent permeability testing was initiated on December 15, 1983. Subsequent sampling events occurred on March 15, 1984, June 15, 1984, September 14, 1984, December 14, 1985, March 16, 1985 and June 19, 1985. The current sampling event occured September 16, 1985. All testing completed to date has confirmed the permeability of the site perimeter containment wall to be less than 1.0 x 10^{-7} cm/sec.

3.2 EQUIPMENT

A Mobil Truck mounted drill rig equipped with rotary head and 4-inch diameter augers was utilized to advance the borehole into the containment wall. A 3-inch diameter Shelby tube, hydraulically pushed and retrieved, was used to collect the samples.

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3.3 SAMPLE COLLECTION

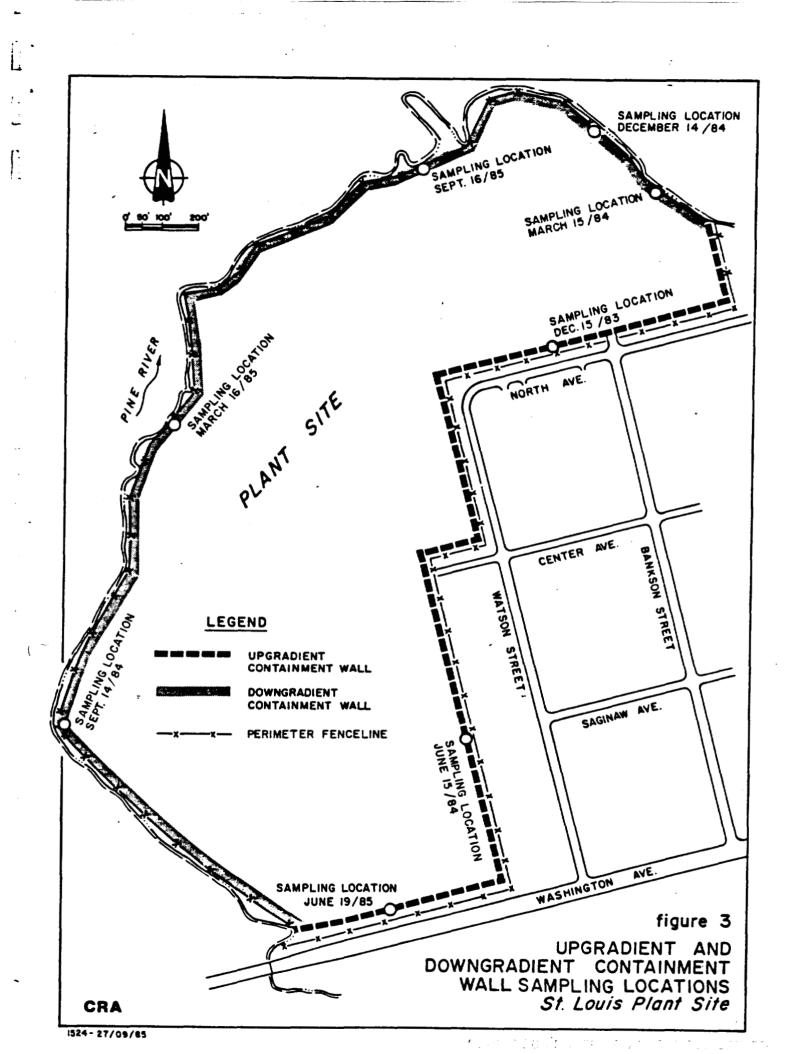
The containment wall was located by field survey on September 16, 1985. The sampling borehole was begun at Station DGW 63+25 by augering through the clay cap into the underlying material.

The presence of soil/bentonite backfill material was confirmed by examination of cuttings on the auger flights. A borehole was advanced to a depth of seven feet below grade. A Shelby tube was introduced into the borehole and a sample was withdrawn. Examination of material in the base of the tube confirmed that the sample was obtained from the containment wall. The locations of this and prior sampling events are detailed on Figure 3. The boreholes were backfilled with bentonite and abandoned.

3.3.1 Sample Preparation and Shipping

1.

The Shelby tube was capped and taped at both ends to prevent sample loss and drying. The sample was hand delivered to the Michigan Testing Engineer's laboratory in Detroit, Michigan for permeability testing.



3.3.2 Sample Testing

1.

The undisturbed sample is to be tested for permeability using a falling head permeameter set up in accordance with ASTM D 2434. Results of the testing will be provided in written form to USEPA and MDNR within seven days after receipt of final laboratory data by CRA. A summary data report will be prepared and presented to both Agencies following completion of the containment wall monitoring program in the fall of 1986.

4.0 GROUNDWATER TABLE MONITORING

4.1 GENERAL

The monitoring of plant site groundwater elevation was performed and the elevation of the St. Louis reservoir was determined on September 17, 1985.

4.2 WATER LEVEL DETERMINATION

The elevation of the groundwater was determined by measuring the distance from the top of each site monitoring well to the watertable. This distance was measured by lowering a chalked, weighted surveyors tape into the monitoring well. Readings of the tape, which was graduated in increments of one one-hundredth of a foot, were taken at the water level and at the top of the well casing. The former reading was deducted from the latter and the resultant dimension was subtracted from the previously established top of well casing elevation. Well head and watertable elevations are presented on Table 1.

The elevation of the St. Louis reservoir was determined by level and rod survey.

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TABLE 1

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WATER LEVEL MEASUREMENTS

SEPTEMBER 17, 1985

MONITORING WELL	WELL HEAD ELEVATION (AMSL)	MEASURED DISTANCE TO WATER TABLE (ft.)	WATERTABLE ELEVATION (AMSL)
1	735.91	14.42	721.49
2	742.06	19.33	722.73
3	749.91	27.63	722.28
4	736.00	13.79	722.21
5	739.35	17.92	721.43
6	734.48	13.19	721.29
7	733.98	12.65	721.33
8	734.30	13.25	721.05
9	734.60	13.42	721.18
10	733.48	12.40	721.08
11	734.47	13.33	721.14
12	730.78	9.68	721.10
13	734.49	13.27	721.22
14	736.00	14.73	721.27

Water level elevation, St. Louis Reservoir (September 17, 1985)

719.39

4.3 GROUNDWATER CONTOUR MAP

1.

The groundwater elevation data were used to construct a site groundwater elevation contour map which is presented in Figure 4.

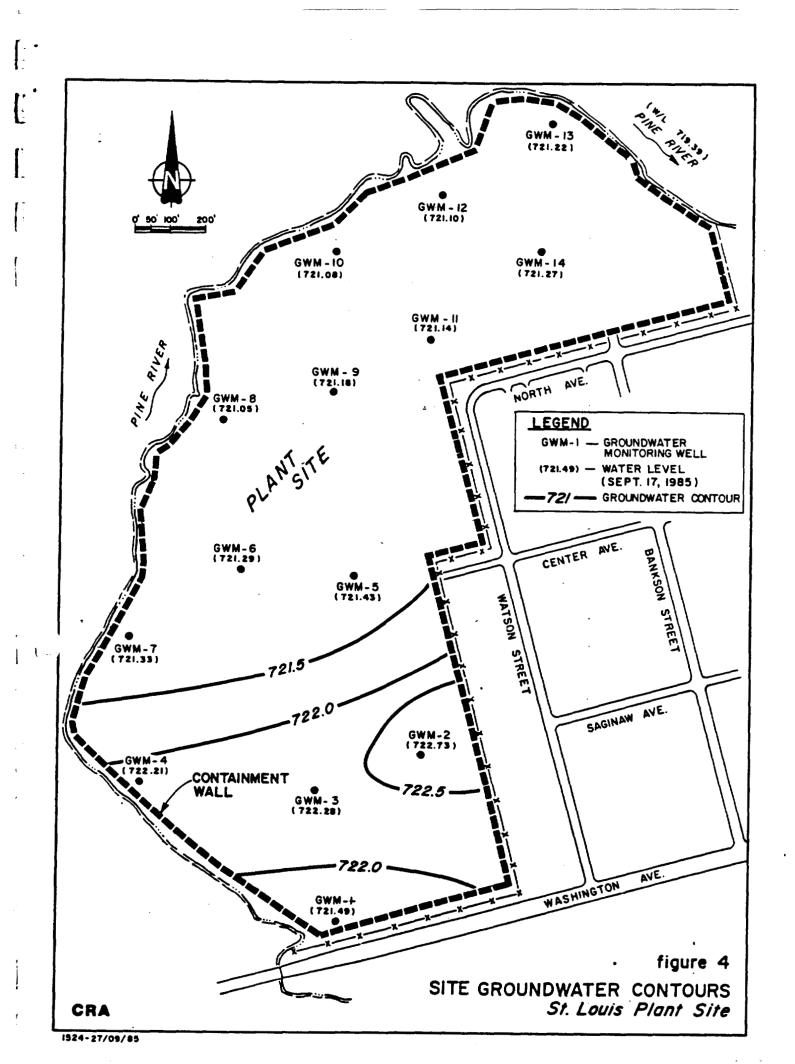
4.4 SITE MEAN GROUNDWATER ELEVATION

The mean elevation of site groundwater is calculated to be 721.49. The maximum allowable site groundwater elevation stipulated by the Consent Judgment is 724.13.

4.5 WELL HEAD ELEVATION SURVEY

In accordance with the Post Closure Maintenance and Monitoring Plan, the well head elevations were re-surveyed in March to ensure accuracy of the elevations. Minor differences from previous surveys were recorded and the groundwater elevations were adjusted accordingly. This phase of the program will be conducted yearly.

11



5.0 SUMMARY

All monitoring activities stipulated by the Consent Judgment were carried out between September 16 and 17, 1985.

Data from the chemical analysis of the gas vent samples and the permeability testing of the contaminant wall sample will be provided to MDNR and USEPA within seven days of receipt by CRA of laboratory final data.

The present mean site groundwater table elevation is calculated to be 721.49. The elevation in the Pine River/St. Louis reservoir was determined to be 719.39.

The next sampling and monitoring event will occur on or about December 15, 1985.

All of Which is Respectfully Submitted, CONESTOGA-ROVERS & ASSOCIATES LIMITED

Catherine A Call

C. Cull, B.Sc.

R.G. Shepherd, P. Eng.

APPENDIX A

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APPENDIX B

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GAS SAMPLING PROTOCOLS

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APPENDIX B

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GAS VENT SAMPLING PROTOCOL

In accordance with the Consent Judgment, Velsicol has submitted a post-closure maintenance and monitoring plan for its environmentally secured plant site in St. Louis, Michigan. The post-closure maintenance and monitoring plan requires quarterly monitoring of 11 gas vents that have been installed to release and appropriately treat internal gases. This program will be conducted over a period of three years.

The gas vents, as detailed in Exhibit F of the Consent Judgment, are designed with two sampling ports; one below the base of the installed activated charcoal filter, and one above the filter. Samples will be collected from the downstream port. Results will indicate whether or not containment breakthrough has occured through the carbon filter.

Samples will be analyzed for three separate compounds: carbon tetrachloride, trichloroethylene and vinyl chloride.

Samples will be collected with a Gilian HFS-113 AU DK variable flow pump. This particular unit allows the operator to run a series of tubes concurrently in parallel arrangement. Four tubes will be collected from each gas vent: two standard NIOSH 100/50 mg activated charcoal tube, and two 30/15 mg tenax tubes, each tube measuring 6 mm x 70 mm. One blank set and one duplicate set of tubes will be collected during each quarterly sampling event.

As vinyl chloride represents the least adsorptive of the three compounds, the sampling program is designed to accomodate this compound. Therefore, sample volume shall not exceed 5 liters.

Prior to sampling, the vent will be sealed off with a plastic cap, and purged for 10 minutes at a rate of 500 cc/min. This is to eliminate the possibility of sampling atmospheric air contained within the upper portion of the gas vent.

Two samples from each gas vent shall be collected simultaneously at a rate of 250 cc/min. for 20 minutes. The pump shall be lab calibrated with sample tubes in-line to determine the exact flow rate. Additionally, flow will be checked after field sampling to verify that a constant flow was maintained throughout the sampling period.

Following sample collection, each tube will be sealed with a plastic cap at each end, labelled, placed in a cold storage environment and shipped under chain-of-custody via a commercial courier service to Velsicol's analytical laboratory in Memphis.

Analysis of the charcoal tube will be conducted in accordance with NIOSH protocol as detailed below:

Compound	Revised Method
Carbon Tetrachloride	1003
Trichloroethylene Vinyl Chloride	S-336 1007

Analysis will proceed by first eluting the carbon sample tubes with carbon disulfide and then analyzing by GC with a flame ionization detector. All samples will be initially analyzed in this fashion. If any of the above compounds are detected on the charcoal tube, the corresponding tenax tube will be analyzed by thermal desorption and GC/MS under EPA Method 624.

Turnaround time for the completed analysis at the laboratory is anticipated to be 30 days from date of sample collection. Samples will be desorbed within the 10 day limit specified for vinyl chloride. Analytical data will be reported to CRA as mg/tube. Final results for the carbon tube will be calculated by CRA, using the following formula.

1. Corrections for the blank to be made for each sample
 mg = mg sample - mg blank

This calculation is performed separately for each tube.

- 2. Add the amounts present in the front tube and backup tube to determine the total weight in the sample.
- 3. Calculate the corrected mg/sample by dividing the total weight by the desorption efficiency (D.E.) which is provided by the lab.

corrected mg/sample = total weight ________DE

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- 4. Calculate the concentration of the analyte in air $mg/m^3 = Corrected mg \times 1000 liters/m^3$ Air volume Sampled (liters)
- 5. Concentration will be reported as ppm, corrected to standard conditions of 25°C and 760 mm Hg

 $ppm = mg/m \times \frac{24.45}{MW} \times \frac{760}{P} \times \frac{(T+273)}{298}$

3

where P	= pressure (mm Hg) of air sampled
- T	= temperature (°C) of air sampled
24.45	= molar volume (liter/mole) at 25°C and 760 mm Hg
MW	= Molecular Weight
760	= standard pressure (mm Hg)
298	= standard temperature (°K)

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- NOTE: Temperature and pressure uncorrected to sea level will be collected for the duration of the sampling event and averaged for use in the above calculations. Information will be provided from the National Weather Service in Lansing, Michigan.
 - 6. If the concentration of the back tube exceeds 10% of the concentration of the front tube, the results will be reported as a sample breakthrough and possible sample loss.
 - 7. A similar procedure will be followed for the tenax tube, should analysis be required.

Data will be reported to USEPA and MDNR officials within seven days after receipt of final laboratory data for each quarterly sampling. Additionally, a summary data report will be provided at the conclusion of the three year sampling period, or sooner, should breakthrough of any compound occur prior to the three year program.

In addition to the set of field blanks to be collected per quarterly sampling event, an additional set of 15 charcoal tubes and 15 tenax tubes will be forwarded unopened to the lab during the initial sampling event.

These "blank" tubes will be used as internal calibration standards on which each of the three compounds will be spiked at (five different concentrations. The data from this analysis will be used to calculate the desorption efficiency for a specific lot of activated charcoal. Therefore, the lot number of carbon tubes and tenax tubes shall be recorded during each quarterly sampling. Should the lot number change, a new set of 15 charcoal tubes and 15 tenax tubes shall be forwarded to the laboratory for determination of the new desorption efficiency.

The allowable limits for these compounds have been established by the MDNR and are site specific for the St. Louis site. These limits are documented in section 4.3 of the post-closure maintenance and monitoring plan.

Copies of all three analytical protocols, the chain of custody and the data collection sheet are provided in the following sections.

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FORMULA: Table 1

HYDROCARBONS, HALOGENATED

M.W.: Table 1

METHOD: 1003 ISSUED: 2/14/84

COMPOUNDS: benzyl chloride (synonyms bromoform in Table]) carbon tetrachloride chlorobenzene chlorobromomethane 1,1-dichloroethane chloroform 1,2-dichloroethylene o-dichlorobenzene ethylene dichloride p-dichlorobenzene

1,1-dichloroethane hexachloroethane 1,2-dichloroethylene methylchloroform ethylene dichloride propylene dichloride

SAMPLING	MEASUREMENT
SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)	I ITECHNIQUE: GAS CHROMATOGRAPHY, FID
	IANALYTE: compounds above
FLOW RATE: 0.01 to 0.2 L/min	!
VOL-MIN: Table 2	DESORPTION: 1 mL CS2, stand 30 min
-MAX: Table 2	INJECTION VOLUME: 5 µL
SHIPMENT: routine	: !TEMPERATURES: Table 2
SAMPLE STABILITY: at least 1 week # 25 °C	CARRIER GAS: N ₂ or He, 30 mL/min
BLANKS: 2 to 10 field blanks per set	: COLUMN: Table 2; alternates are SP-2100, SP-2100 with 0.1% Carbowax 1500 or DB-1 fused silica capillary column
ACCURACY	1
nae stori di recito contra de den milite	ICALIBRATICH: solutions of analyte in CS- with
BIAS: not significant [1]	RANGE: Table 2
OVERALL PRECISION (s _r): see EVALUATION OF METHOD [1]	: ESTIMATED LOD: 0.01 mg per sample [2]
	PRECISION (ST): See EVALUATION OF METHOD [1]

APPLICABILITY: This method uses a simple desorption and can be used for simultaneous analysis of two or more substances suspected to be present by changing the gas chromatographic conditions (i.e., temperature programmed). High humidity during sampling will prevent organic vapors from being trapped efficiently on the sorbent and greatly decreases breakthrough volume.

INTERFERENCES: None identified. The chromatographic column or separation conditions may be changed to circumvent interference problems.

OTHER METHODS: This method combines and replaces Methods P&CAM 127 [3]; S95, S101, S110, S113, S114, S115, S122, S123 and S133 [4]; and S135, S281, S314, S328 and S351 [5].

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a. Remove and discard back sorbent section of a media blank sampler.

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- b. Inject a known amount of analyte or calibration stock solution directly onto front sorbent section with a microliter syringe.
- c. Cap the tube. Allow to stand overnight.
- d. Desorb (steps 5 through 7) and analyze together with working standards (steps 1] and 12).e. Prepare a graph of DE vs. mg analyte recovered.
- 10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

 Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1003-1. Inject sample aliquot manually using solvent flush technique or with autosampler.

NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.

 Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of analyte found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.

NOTE: If $W_{\rm p} > W_{\rm f}/10$, report breakthrough and possible sample loss.

14. Calculate concentration, C, of analyte in the air volume sampled, V (L):

$$C = \frac{(H_{f} + H_{b} - B_{f} - B_{b}) \cdot 10^{3}}{V}, mg/m^{3}.$$

ENALGATION OF METHOD:

Laboratory testing was performed with spiked samples and generated atmosphere [1]. All analytes are stable at least one week. All methods were validated using SKC Lot 105 coconut shell charcoal. Results were:

1003-3

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METHOD: 1003

HYDROCARBONS, HALOGENATED

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 [9] Criteria for a Recommended Standard...Occupational Exposure to 1,1,1-Trichloroethane, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 76-184 (1976).

[10] Criteria for a Recommended Standard...Occupational Exposure to Carbon Tetrachloride, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 76-133 (1976).

METHOD REVISED BY: G. D. Foley; Y. T. Gagnon; and K. J. Williams, NIOSH/DPSE; methods originally validated under NIOSH Contract CDC-99-74-45.

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Compounds	Formula	M.W.; mg/m ³ <u>w 1 ppm</u>	Synonyms	05HA N105H [6-10] ACG1H	<u> </u>	VP (* 20 °C	Density (g/mL @ 20 °C)
2-Dichlorobenzene	1,4-C ₆ H ₄ C1 ₂	147.00; 6.01	↓ dichlorobenzene; (*#106-46-7	75 ppm 75 ppm, 5TEL 110 ppm	174	50 Pa	1.241
i,1-Dichloroethane	ai ₃ aici ₂ ; c ₂ i14ci2	98.96; 4.05	eth ylidene chioride; Crac #15-34-3	100 ppm 100 ppm 200 ppm, STEL 250 ppm	51	24.3 kPa	1. 174
l,2-Dichloroethylene	c101=04C1; C_11_C1 2_4_2	96.95; 3.96	acetylene dichloride; 1,2-dichloroethene; Cooc#540-59-0	200 ppm 200 ppm 200 ppm, STEL 250 ppm	60 (cis) 47 (trans)	24-35 kPa	1.28
Ethylene dichloride*	c1a1 ₂ a1 ₂ c1; c ₂ 11 ₄ c1 ₂	98.96; 4.05	1,dichloroethane; C #107-06-2	50 ppm, C 100 ppm 5 ppm; 15 ppm/15 min 10 ppm, STEL 15 ppm	83	8.3 kPa	1.255
lexach loroethane#	^{CC1} 3 ^{CC1} 3; ^{C2C1} 6	236.74; 9.68	p.) chloroethane; 19.1 #67-72-1	l ppm (skin) l ppm (skin) 10 ppm	107 (sub]ine s)	30 Pa	2.09
Hethy)chloroform	CH3CCI3; C2H3CI3	133.42; 5.45	1,1,1-trichloroethane; (5 #71-55-6	350 ppm 350 ppm/15 min CAS #71-55-6 STEL 450 ppm	74 350 ppm,	13.3 kPa	1.335
Propylene dichloride	aizaiciaizci; cziięciz	; 112.99; 4.62	1,2-dichloropropane Cour #78-87-5	75 ррм 75 ррм 75 ррм, 75 ррм, 51EL 110 ррм	95	5.3 kPa	1 . 156 (25 °C)

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		Sampl	ina			Heasur	ement	
Compound	Air Sample <u>Volume (L)</u> <u>Min</u>		Breaktle ough <u>in Dr. Air</u>	Working Range (ng/m³)	<u>Column</u> *	<u>t</u> (*C) Column Injector <u>Detector</u>	Interna) Standard	Range (mg per sample)
1,1-Dìchìoroethane	1 (2 100 ppm	10	18.3 L → 33 mg/m ³	40 to 1215 (10 L)	•	50 100 175		0.4 to 12
1,2-Dichloroethylene	0.5 @ 200 ppm	3	5.4 L € 309 mg/m ^a	80 to 2370 (3 L)	۸	60 170 210		.2 to 7
Ethylene dichloride	1 (8 50 ppm	10	29 L 3 ⊨	40 to 1215 (3 L)	A	70 225 250	octane	0.1 to 4
Hexachloroethane	101pm	10	43 L / / kj/m ³	1 to 30 (10 L)	D	110 170 210	n-tridecane	0.01 to 0.3
Methylchloroform	0.5 @ 350 ppm	6	9.5 L √ /08 mg/m³	190 to 5700 (3 L)	۸	10 225 250	octane	0.6 to 17
Propylene dichloride	1 @ 75 ppm	10	18 L 3 ing/m ⁹	35 to 1050 (10 L)	۸	80 170 210 ,	n-undec ane	0.3 to 10

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*A = 3'm x 3 am stainless steel, 10% SP-1000 reco 100 mesh Supelcoport; $B = \delta m \times 3$ in, other. He same as A; C = 3 m x 3 mm stainless steel, 10% OV-101 mm 3-D = 3 m x 6 un glass, .../ SP-2250 on 80/100 mm (

120 mesh Supelcoport; or palcoport.

MT NO

Trichloroethylene

Analyte:	Trichloroethylene	Method No.: S336
Matrix:	Air	Range: 519-2176 mg/cu m
OSHA Standard:	200 ppm (1075 mg/cu m)-Ceiling 100 ppm (535 mg/cu m)-T.W.A.	Precision (\overline{CV}_{T}) : 0.082
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 6/6/75

1. Principle of the Method

- 1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.
- 1.2 The charcoal in the tube is transferred to a small, stoppered sample container and the analyte is desorbed with carbon disulfide.
- 1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.
- 1.4 The area of the resulting peak is determined and compared with areas obtained from injection of standards.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 519-2176 mg/cu m at an atmospheric temperature and pressure of 24.5°C and 759.4 mm Hg, using a 3-liter sample. Under the conditions of sample size (3 liters) the probable useful range of this method is 108-3225 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 9.7 mg sample. This method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.
- 2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of analyte and other substances in the air. The first section of the charcoal tube was found to hold 42 mg of analyte when a test atmosphere containing 2266 mg/cu m of analyte in air was sampled at 0.187 liters per minute for 99 minutes; breakthrough was observed at this time, i.e. the concentration of analyte in the effluent was 5% of that in the influent.

(The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

- 3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.
- 3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.
- 3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.
- 3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation $(\overline{CV_T})$ for the total analytical and sampling method in the range of 519-2176 mg/cu m was 0.082. This value corresponds to an 88.2 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.
- 4.2 On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 6.4 % lower than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result.

These data are based on validation experiments using the internal standard method.

- 5. Advantages and Disadvantages of the Method
 - 5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

- 5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.
- 5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

- 6.1 A calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow rate. (Reference 11.3).
- 6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane form. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane form is placed between the outlat end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.
- 6.3 Gas chromatograph equipped with a flame ionization detector.
- 6.4 Column (10-ft x 1/8-in stainless steel) packed with 10% OV-101 stationary phase on 100/120 mesh Supelcoport.
- 6.5 An electronic integrator or some other suitable method for measuring peak areas.
- 6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated visls may be used.
- 6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.
- 6.8 Pipets: 1.0 ml type graduated in 0.1-ml increments.

S336-3

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

- 7.1 Chromatographic quality carbon disulfide.
- 7.2 Trichloroethylene, resgent grade
- 7.3 Octame, or other suitable internal standard
- 7.4 Purified nitrogen
- 7.5 Prepurified hydrogen.
- 7.6 Filtered compressed air.

8. Procedure

- 8.1 Cleaning of equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.
- 8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.
- 8.3 Collection and Shipping of Samples -

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- 8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).
- 8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.
- 8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.
- 8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.
- 8.3.5 At the ceiling and peak concentrations, a sample size of 3 liters is recommended. Sample for 15 minutes at a flow of 0.2 liters per minute. At the T.W.A. concentration, a sample size of 10 liters is recommended. Sample at a flow of 0.2 liters per minute or less. The flow rates should be known with an accuracy of at least +52.

ารักษณฑิสาราชการที่สาราร สุรารุณณฑิสราชสารริสาราร และสาราราช และการสาราชการสารสารสารสารสารสารสาร (สารา 1555) ซึ่ 8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available. record the elevation. S336-4

- 8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no . circumstances should rubber caps be used.
- 8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.
- 8.3.9 Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.
- 8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

- 8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately.
- 8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 1.0 ml of carbon disulfide containing a known amount of the chosen internal standard.
- 8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

30 ml/min (60 psig) Nitrogen carrier gas flow
 35 ml/min (25 psig) Hydrogen gas flow to detector
 400 ml/min (60 psig) Air flow to detector
 225°C injector temperature
 250°C manifold temperature: (detector) and the second secon

S336-5

- 8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush technique.
- 8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

.

- 8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.
- 8.5.2 Procedure for determining desorption efficiency. Activated ated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of the analyte is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. When using an automatic sample injector, the sample injector vials, capped with Teflon-faced septa, may be used in place of the glass tubes.

S336-6

Six tubes at each of three concentration levels (0.5X,1X and 2X of the standard) are prepared by adding an amount of analyte equivalent to that present in a 3-liter sample at the selected level. The tubes are allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 1.0 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

If the internal standard method is used, prepare calibration standards by using 1.0 ml of carbon disulfide containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

D.E. - Average Weight (mg) recovered Weight (mg) added

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

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It is convenient to express concentration of standards in terms of mg per 1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown sample. Curves are established by plotting concentration in mg per 1.0 ml versus peak area.

For the internal standard method, use carbon disulfide containing a predetermined amount of the internal standard. The internal standard concentration used was approximately 70% of the concentration at 2% the standard. The analyte concentration in mg per ml is plotted versus the area ratio of the analyte to that of the internal standard. Note: Whether the external standard or internal standard method is used, standard solutions should be analyzed at the same time the sample analysis is done. This will minimize the effect of variations in FID response.

10. Calculations

- 10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg per 1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.
- 10.2 Corrections for the blank must be made for each sample.

mg = mg sample - mg blank

where:

mg sample = mg found in front section of sample tube
mg blank = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

- 10.3 Add the amounts present in the front and backup sections of the same sample tube to determine the total weight in the sample.
- 10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

Corrected mg/sample = Total weight

10.5 The concentration of the analyte in the air sampled can be expressed in mg per cu m.

mg/cu m = Corrected mg (Section 10.4) x 1000 (liters/cu m) Air Volume Sampled (liters)

10.6 Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$ppm = mg/cu = x \frac{24.45}{MW} x \frac{760}{P} x \frac{(T+273)}{298}$$

where:

P = pressure (mm Hg) of air sampled T = temperature (°C) of air sampled 24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg MW = molecular weight 760 = standard pressure (mm Hg) 298 = standard temperature (°K)

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S336-8

11. References

- 11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," <u>Amer. Ind. Hyg. Assoc. J.</u>, <u>31</u>: 225 (1970).
- 11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.
- 11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

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FORMULA: CH2=CHC1; C2H3C1

VINYL CHLORIDE

M.W.: 62.50

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METHOD: 1007 ISSUED: 2/15/94

OSHA: 1 ppm; C 5 ppm NIOSH: minimum measurable ACGIH: 5 ppm (human carcinogen) [1] (1 ppm = 2.56 mg/m³ @ NTP) PROPERTIES: BP -14 °C; vapor density 2.2 (air = 1)

SYNONYMS: chloroethylene; chloroethene; CAS #75-01-4.

SAMPLING	MEASUREMENT
SAMPLER: SOLID SORBENT TUBE (2 tandem tubes, each with 150 mg	! !TECHNIQUE: GAS CHROMATOGRAPHY, FID !
activated coconut charcoal)	:ANALYTE: vinyl chloride !
ELO₩ RATE: 0.05 L/min	IDESORPTION: 1 mL carbon disulfide; 30 min 1
VOL-MIN: 0.7 L -MAX: 5 L	INJECTION ALIQUOT: 5 µL
SHIPMENT: separate primary and backup tubes and cap each	COLLUMN: stainless steel, 6.1 m x 3.2 mm, 105 ! SE-30 on 80/100 mesh Chromosorb W ! (AW-DMCS)
SAMPLE STABILITY: 10 days # 25 °C	!CARRIER GAS: He, 40 mL/min
BLANKS: 2 to 10 field blanks per set	: !TEMPERATURE-INJECTOR: 230 °C ! -OETECTOR: 230 °C ! -COLLINN: 60 °C
ACCURACY	
RANGE STUDIED: 1 to 64 mg/m ³ [2]	CALIBRATION: solutions of vinyl chloride in CS2
BIAS: -65 of calculated concentration [2]	<pre>!RANGE: 0.002 to 0.2 mg per sample [2] ! !ESTIMATED LOD: 0.00004 mg per sample [2]</pre>
OVERALL PRECISION (sp): 0.06 [2]	. 1

APPLICABILITY: The working range is 0.4 to 40 mg/m² (0.16 to 16 ppm) for a 5-L air sample. The method is applicable to 15-min samples at concentrations of 1 ppm or higher.

INTERFERENCES: Other than the possibility of loss of sample upon storage of two weeks or more at room temperature, none have been noted.

OTHER METHODS: This is a revision of P&CAN 178 [3].

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VINYL CHLORIDE

REAGENTS:

- Carbon disulfide,* chromatographic quality.
- Vinyl chloride,*, 99.9%, in lecture bottle fitted with valve and septum.
- Calibration stock solution, 0.26 mg/mL.
 - a. Insert the tip of a gas syringe containing 1 mL vinyl chloride gas under the surface of 5 mL CS₂ in a 10-mL volumetric flask.
 - b. Open the value of the syringe and withdraw the plunger to pull CS₂ into the barrel. (As vinyl chloride dissolves, a vacuum will be created, pulling CS₂ into the syringe.)
 - c. Push the solution from the syringe into the flask. Rinse the syringe twice with 1-mL portions of CS₂ and add the washings to the flask.
 - d. Dilute to the mark with CS₂.
- 4. Helium, purified.
- 5. Hydrogen, purified.
- 5. Air, filtered.

*See Special Precautions.

EQUIPMENT:

1. Sampler: two tandem glass tubes, 7 cm long, 6 mm OD, 4 mm ID, flame-sealed ends, each containing 150 mg of 20/40 mesh activated (600 °C) coconut shell charcoal. A silylated glass wool plug precedes the charcoal beds and a 3-mm urethane foam plug follows the charcoal beds. Plastic caps are included for sealing after use. Pressure drop across each tube at 1 L/min airflow must be less than 3.4 kPa.

NOTE: A pair of two-section (100 mg/50 mg) tubes may be used.

- Personal sampling pump, 0.05 L/min, with flexible connecting tubing.
- Gas chromatograph, flame ionization detector, integrator and column (page 1007-1).
- 4. File.
- 5. Bent wire for removing plugs from sampling tube.
- Vials, 2-mL, glass with PTFE-lined septa and crimp-on seals.
- Volumetric flasks, 10-mL, with polyethylene stoppers.
- Pipettes, delivery, 1.0-mL, graduated in 0.1-mL increments, 2- and 5-mL, with pipet bulb.
- 9. Air sampling bags, Tedlar, 10-L.
- 10. Gas syringe, with gas-tight valve, 0.1- and 1-mL.
- 11. Syringe, 10-uL, with 0.1-uL graduations.

SPECIAL PRECAUTIONS: Carbon disulfide is toxic and an acute fire and explosion hazard (flash point x = -30 °C); work with it only in a hood.

Vinyl chloride is a human carcinogen [1].

SAMPLING:

- 1. Calibrate each personal sampling pump with a representative sampler in line.
- Break the ends of the tubes immediately before sampling. Attach two tubes, with ends touching, with a short piece of tubing. Label one tube as the back tube and insert the back tube into the flexible tubing attached to the personal sampling pump.
- 3. Sample at 0.05 L/min for 15 to 100 min. Do not sample more than 5 L of air.
- 4. Separate the primary and backup tubes and cap each tube for shipment.

SAMPLE PREPARATION:

- 5. Add 1.0 mL CS₂ to an empty vial. Loosely cap the vial.
- Score each sampler tube with a file in front of the glass wool plug. Break the tube at the score line.

HETHOD: 1007

- 7. Transfer the charcoal from the front and back tubes to separate vials. Discard the glass wool and foam plugs. Seal the vials with septum caps immediately.
- 8. Allow to stand for 30 min, with occasional agitation. Analyze the sample within the next 30-min period.

CALIBRATION AND QUALITY CONTROL:

- 9. Calibrate with at least five working standards covering the range 0.0002 to 0.2 mg per sample.
 - a. Add known amounts of calibration stock solution to CS2 in 10-mL volumetric flasks and dilute to the marks, using serial dilution as appropriate.

NOTE: Working standards can be stored at -20 °C for at least three days.

- b. Analyze together with samples and blanks (steps 12 and 13).
- c. Prepare calibration graphs of peak area vs. quantity (mg) of vinyl chloride per tube and peak area vs. quantity (ng) per injection.
- Determine desorption efficiency (DE) at least once for each lot of charcoal used in the calibration range (step 9). Prepare three tubes at each of five levels plus three media blanks.
 - a. Prepare three atmospheres of vinyl chloride in air by injecting 0.01, 0.08, and 0.2 mL vinyl chloride gas into 10 L air in Tedlar bags. The resulting concentrations are approximately 2.6, 21 and 52 mg/m³.
 - b. Following steps 1 through 4, sample these atmospheres according to the following scheme:

Concentration in Bag (mg/m ³)	Volume Sampled (L)	Quantity of Vinyl Chloride (mg)
2.6	0.8	0.002
	2.2	0.006
21	0.8	0.017
	2.2	0.046
52	2.5	0.13

Obtain three samples at each level.

- c. Desorb (steps 6 through 8) and analyze together with working standards (steps 12 and 13). No vinyl chloride should be found on the back tubes.
- d. Analyze the atmospheres in the bags (steps 12 and 13) using 1-mL gas samples. Read from the calibration graph the quantity (ng) per injection, which for a 1-mL injection of gas is numerically equal to the concentration in mg/m^3 .
- e. Calculate DE from the mass (mg) of vinyl chloride on the front tube ($M_{\rm F}$), the average blank (B), the concentration of vinyl chloride in the synthetic atmospheres ($C_{\rm S}$, mg/m³), and the volume of air sampled (V, L):

$$DE = \frac{(W_F - B) \cdot 10^3}{(C_e) (V)}$$

f. Prepare a graph of DE vs. mass found (Wg - B).

11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

VINYL CHLORIDE

MEASUREMENT:

12. Set the gas chromatogrph according to manufacturer's instructions and to conditions given on page 1007-1. Inject sample aliquot manually using solvent flush technique or with autosampler. The retention time of vinyl chloride is about 1.7 min.

NOTE: If peak area is above the linear range of the working standards, dilute with CS₂, reanalyze and apply the appropriate dilution factor in calculations.

13. Heasure peak area.

CALCULATIONS:

- 14. Determine the mass, mg (corrected for DE) of vinyl chloride found in the sample front $(W_{\rm F})$ and back $(W_{\rm D})$ tubes, and in the average media blank (B).
- NOTE: If $W_{\rm b} > W_{\rm F}/10$, report breakthrough and possible sample loss.

15. Calculate concentration, C, of vinyl chloride in the air volume sampled, V (L):

$$C = \frac{(H_{f} + H_{b} - 2B) \cdot 10^{3}}{V}, mg/m^{3}$$

EVALUATION OF METHOD:

The method was evaluated using single 150-mg sampling tubes with 100-mg front beds and 50-mg back beds [2]. At four concentrations between 1 and 64 mg/m^3 , the pooled relative standard deviation was 0.06 and the measurements averaged 94% of the concentrations calculated from the volumes of vinyl chloride and air used for the atmospheres sampled; samples at the 3-ug level should no loss of vinyl chloride when stored for 12 days at room temperature or 19 days at -20 °C. There may be significant loss of vinyl chloride from samples stored for 14 days at room temperature [4]. The 1% breakthrough capacity for a 150-mg bed of coconut charcoal challenged at 100 mL/min with vinyl chloride in air at 16 mg/m³ and a relative humidity of 70% was 4.6 L [5].

REFERENCES:

 <u>TLVs - Threshold Limit Values for Chemical Substances and Physical Agents in the Work</u> <u>Environment with Intended Changes for 1983-84</u>, ACGIH, Cincinnati, OH (1983).

[2] Hill, R. H., Jr., C. S. McCannon, A. T. Saalwaechter, A. W. Teass, and W. J. Woodfin. <u>Anal. Chem.</u>, <u>48</u>, 1395-1398 (1976).

- [3] NIOSH Hanual of Analytical Methods, 2nd. ed., V. 1, PSCAM 178, U.S. Department of Health and Human Services, Publ. (NIOSH) 77-157-A (1977).
- [4] Cuddeback, J. E., W. R. Burg, and S. R. Birch, <u>Environ</u>. <u>Sci</u>. <u>Technol</u>., <u>9</u>, 1168-1171 (1975).

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[5] Matsumura, Y. Ind. Health, 18, 61-67 (1980).

HETHOD REVISED BY: A. W. Teass, Ph.D., NIOSH/DPSE.

VELSICOL CHEMICAL CORPORATION ST. LOUIS, MICHIGAN PROJECT Nº 1524

GAS VENT SAMPLING

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DATE OF COLLECTION 14	SEPTEMBER 1985	SAMPLER	CA	CULL	BAROME1 PRESSUR	RIC						30	. 1	7	
TEMPERATURE	68°F	RELATIVE		50%	GAUGE	1	2	3 4	5	6	7	8	9	10	11
CHARCOAL LOT Nº	120	TENAX LOT Nº	220		READING	00	70)0	O	0	0	0	0	0	ø

GAS VENT	PUMP	SAMPLE		SAMPLING RATE	SAMPLE		
NUMBER	NUMBER	NUMBER	START	FINISH	· ELAPSED	(cc/min.)	VOLUME (1)
1	1	4 0	1/6 14:25	14:45	20 min	250	5
2	2	3	14:40	15:00	20	250	.5
3	1	7	14:58	15318	20	250	5
4	2	٩	15:15	15:35	20	250	5
5	1	5	15:32	15:52	20	250	5
6	2	10	15:46	16:06	20	250	5
7	2	8	16:22	16:42	20	250	5
8	l	2	16:04	16:24	20	250	5
9	2	6	4/17 8.35	8:55	20	250	.5
10	1	11	8:50	9:10	20	250	5
	2	12	9:09	9:29	20	250	5
DUPLICATE	1	1	9:17	9:34	20	250	5
BLANK		13					.5
DATE OF SAMPLE SHI	PMENT 9	117/85	METH Shipm	OD OF Federal	Express	· · · · · · · · · · · · · · · · · · ·	

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VELSICOL CHEMICAL CORPORATION ST. LOUIS, MICHIGAN PROJECT Nº 1524

GAS VENT SAMPLING PUMPS CALIBRATION LOG

DATE	16 SEPT	EMBE	R 19	85	CALIB	RATED	BY (2 A	CULL							
[AMPLING				AFTER SAMPLING				AV	ERAGE		
PUMP NUMBER	PUMP TYPE	TEMP. (°F)	HUMIDITY	BAROM. PRESSURE (Inches Hg)	INITIAL FLOW (cc/min.)	CAL. FLOW (cc/min.)	24-HR. TIME	TEMP. (°F)	HUMIDITY	BAROM. PRESSURE (Inches Hg)	FLOW (cc/min.)	24-HR. TIME	TEMP. (°F)	HUMIDITY (%)	BAROM. PRESSURE (Inches Hg)	FLOW (cc/min.)
	GIUAN(A)	69	42	30.24	250	250	12:50	59	3-467	1.080	250	10:5	68'	50	30.17	
	(8)				240	250	2:53	 			250	10:17		<u> </u>		250
2	GILIAN (A)				250	250	12:56				250	10:20				250
	(6)				260	250	12:55				250	10:23				250
			}													
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VELSICOL CHEMICAL CORPORATION

POST - CONSTRUCTION QUARTERLY MONITORING REPORT

DECEMBER 14-15 , 1985

Plant Site, St. Louis Michigan

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	DECEMBER 15, 1985	

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1. 1

1.0 INTRODUCTION

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1.1 GENERAL

In accordance with the terms of the technical appendix to the Consent Judgment entered into by Velsicol Chemical Corporation (Velsicol), the United States Environmental Protection Agency, (USEPA) and the Michigan Department of Natural Resources (MDNR), Velsicol is required to perform specified monitoring activities at quarterly intervals following closure of its St. Louis, Michigan plant site. The monitoring program is designed to address the following:

- 1. Performance of gas vents
- 2. Performance of the site perimeter containment wall
- 3. Determination of site groundwater elevations

This report details the site monitoring which occured during the period December 14 to December 15, 1985.

1.2 PARTICIPATION BY REGULATORY AGENCIES

The regulatory agencies did not participate in or attend this monitoring event.

1.3 MONITORING AND SAMPLING PERSONNEL

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The monitoring and sampling program was carried out by Mr D. Robinson (Conestoga-Rovers and Associates) assisted by Mr. Gene DeGeer, the Velsicol site custodian.

2.0 GAS VENT MONITORING

2.1 GENERAL

The gas vent monitoring began on December 14, 1985 and was completed December 15, 1985.

2.1.1 Equipment

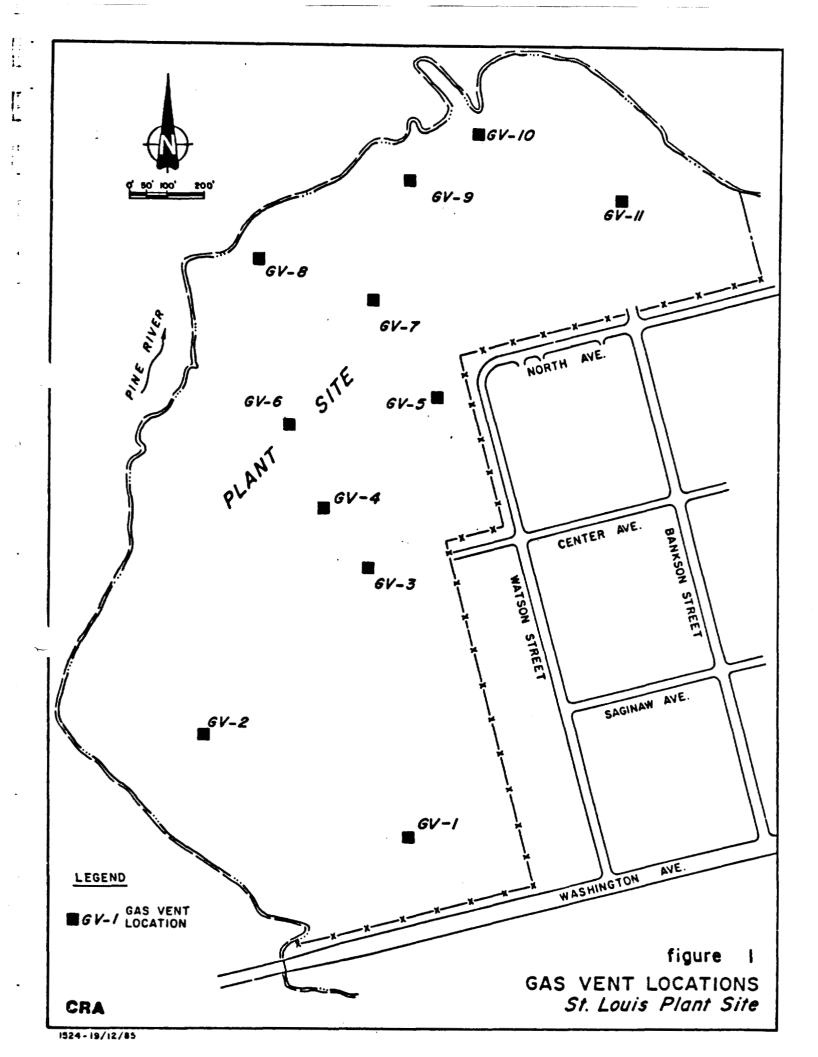
Two Gilian model HFS 113 hi flow samplers were used to collect gas vent samples. The samplers were field calibrated using a rotometer prior to sampling. The calibration data is presented within Appendix B. Samples from each gas vent were collected in two 6-mm diameter x 70-mm long Tenax tubes and two charcoal tubes of similar dimensions. The samples were collected simultaneously using dual parallel/series tube holder sets.

2.2 SAMPLE COLLECTION

Samples were obtained at each of the 11 gas vents. The location of the gas vents within the closed plant site is detailed on Figure 1. One blank set and one duplicate set of samples were also collected.

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Sampling was conducted at the downstream sampling port on each gas vent as detailed on Figure 2. The tube holder was attached directly to the gas vent sampling port using a copper manifold assembly which was environmentally cleaned prior to use. Tygon tubing was used to connect the tube holder to the sampler and was connected between the base of the tube holder and suction port of the sampler. The sampler which was pre-calibrated to 250cc/min/tube set, was operated for a period of 20 minutes for each sampling event, resulting in a collected sample volume of five liters per tube set.

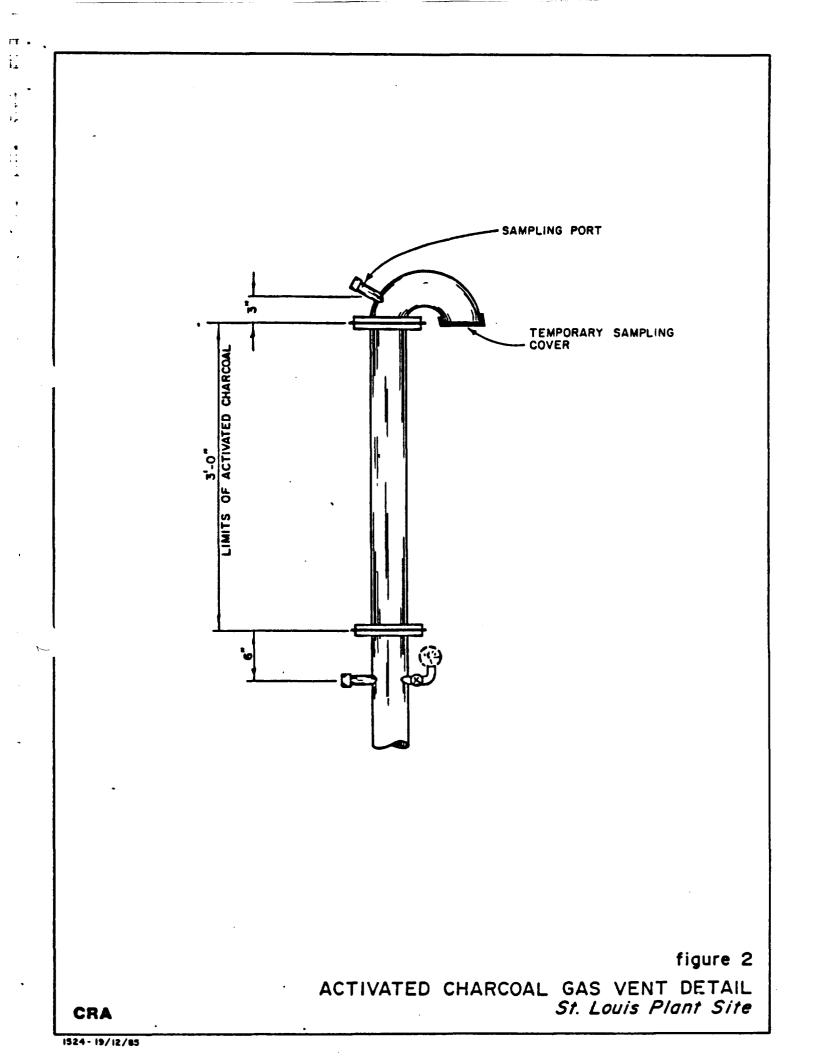
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Prior to sample collection, the gas vent upper chamber was purged by pumping at 500 cc/minute for a period of ten minutes. This precluded the possiblity of sampling retained atmospheric air from the gas vent upper chamber. During the purging and sampling operations, the open end of the gas vent was capped using a 4-inch diameter plastic cover to prevent atmospheric air being drawn into the sample.

At the conclusion of each gas vent sampling, the set of four sample tubes were capped, labelled and stored in a cooler maintained at 0° C.



2.2.1 Sample Storage and Shipment

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On the Morning of December 16, 1985 the samples were transferred to a cooler containing frozen cold packs and styrofoam packing materials. The cooler was shipped under chain of custody protocol, to Velsicol's Memphis, Tennessee laboratory by overnight courier for analysis. A copy of the chain of custody is provided in Appendix A.

2.2.2 Sample Analysis

Analyses were conducted in accordance with NIOSH protocols as follows:

Compound	NIOSH Method
Carbon Tetrachloride	1003
Trichloroethylene	S-336
Vinyl Chloride	1007

Results have been reported verbally by the laboratory as non-detectable for all parameters at all sampling points. A hard copy of the laboratory report will be forwarded to USEPA and MDNR within seven days after receipt of final laboratory data by CRA.

2.2.3 Sampling Protocol

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All sampling was performed in accordance with the methodology detailed within the St. Louis plant site Post-Closure Maintenance and Monitoring Plan, as approved by USEPA and MDNR. A copy of the sampling protocol is contained in Appendix B.

3.0 SITE PERIMETER CONTAINMENT WALL MONITORING

3.1 GENERAL

The monitoring program consisting of the collection of an undisturbed sample of the containment wall with subsequent permeability testing was initiated on December 15, 1983. Subsequent sampling events occurred on March 15, 1984, June 15, 1984, September 14, 1984, December 14, 1985, March 16, 1985, June 19, 1985 and September 16, 1985. The current sampling event occured December 14, 1985. All testing completed to date has confirmed the permeability of the site perimeter containment wall to be less than 1.0 x 10^{-7} cm/sec.

3.2 EQUIPMENT

A Mobil Truck mounted drill rig equipped with rotary head and 4-inch diameter augers was utilized to advance the borehole into the containment wall. A 3-inch diameter Shelby tube, hydraulically pushed and retrieved, was used to collect the samples.

3.3 SAMPLE COLLECTION

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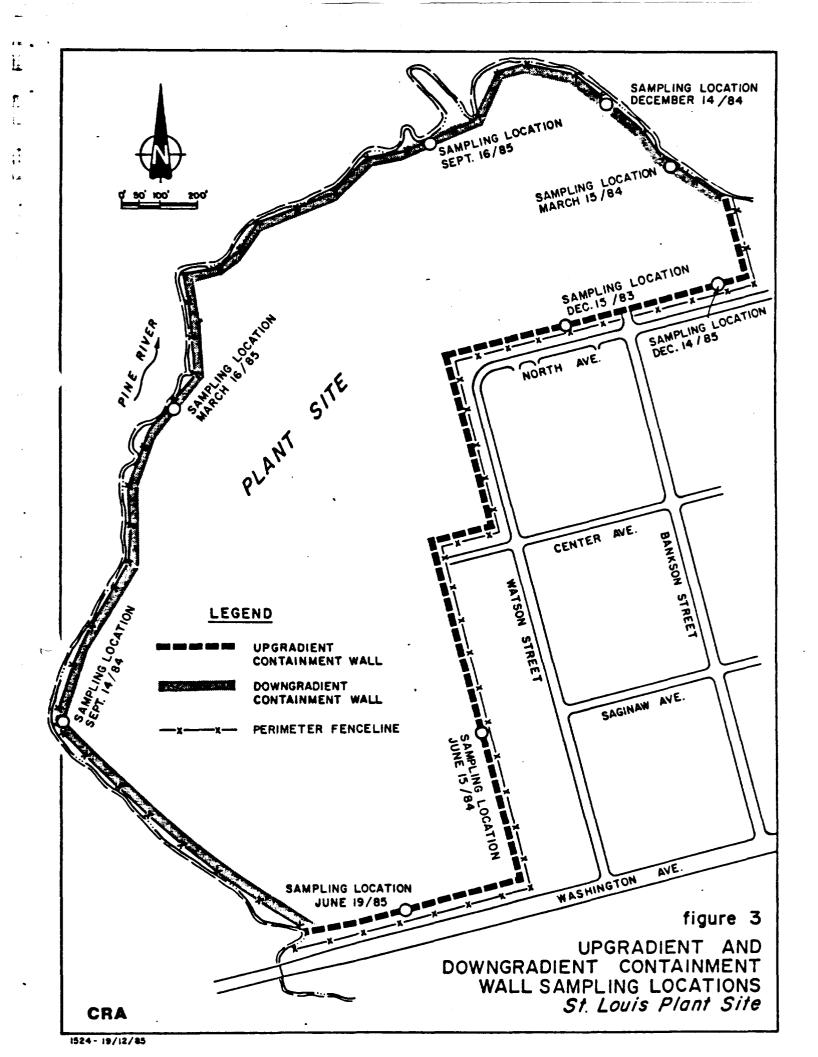
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The containment wall was located by field survey on December 14, 1985. The sampling borehole was begun at Station 0+50, Baseline B by augering through the clay cap into the underlying material.

The presence of soil/bentonite backfill material was confirmed by examination of cuttings on the auger flights. A borehole was advanced to a depth of seven feet below grade. A Shelby tube was introduced into the borehole and a sample was withdrawn. Examination of material in the base of the tube confirmed that the sample was obtained from the containment wall. The locations of this and prior sampling events are detailed on Figure 3. The boreholes were backfilled with bentonite and abandoned.

3.3.1 Sample Preparation and Shipping

The Shelby tube was capped and taped at both ends to prevent sample loss and drying. The sample was hand delivered to the Michigan Testing Engineer's laboratory in Detroit, Michigan for permeability testing.



3.3.2 Sample Testing

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The undisturbed sample is to be tested for permeability using a falling head permeameter set up in accordance with ASTM D 2434. Results of the testing will be provided in written form to USEPA and MDNR within seven days after receipt of final laboratory data by CRA. A summary data report will be prepared and presented to both Agencies following completion of the containment wall monitoring program in the fall of 1986.

4.0 GROUNDWATER TABLE MONITORING

4.1 GENERAL

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The monitoring of plant site groundwater elevation was performed and the elevation of the St. Louis reservoir was determined on December 15, 1985.

4.2 WATER LEVEL DETERMINATION

The elevation of the groundwater was determined by measuring the distance from the top of each site monitoring well to the watertable. This distance was measured by lowering a chalked, weighted surveyors tape into the monitoring well. Readings of the tape, which was graduated in increments of one one-hundredth of a foot, were taken at the water level and at the top of the well casing. The former reading was deducted from the latter and the resultant dimension was subtracted from the previously established top of well casing elevation. Well head and watertable elevations are presented on Table 1.

The elevation of the St. Louis reservoir was determined by level and rod survey.

TABLE 1

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WATER LEVEL MEASUREMENTS DECEMBER 15, 1985

MONITORING WELL	WELL HEAD ELEVATION (AMSL)	MEASURED DISTANCE TO WATER TABLE (ft.)	WATERTABLE ELEVATION (AMSL)
1	735.91	14.42	721.49
2	742.06	19.25	722.81
3	749.91	27.42	722.49
4	736.00	13.79	722.21
5	739.35	17.79	721.56
6	734.48	13.25	721.23
7	733.98	12.76	721.22
8	734.30	13.17	721.13
9	734.60	13.33	721.27
10	733.48	12.27	721.21
11	734.47	13.21	721.26
12	730.78	9.56	721.22
13	734.49	13.23	721.26
14	736.00	14.69	721.31

Water level elevation, St. Louis Reservoir (December 15, 1985) 719.60

4.3 GROUNDWATER CONTOUR MAP

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The groundwater elevation data were used to construct a site groundwater elevation contour map which is presented in Figure 4.

4.4 SITE MEAN GROUNDWATER ELEVATION

The mean elevation of site groundwater is calculated to be 721.55. The maximum allowable site groundwater elevation stipulated by the Consent Judgment is 724.13.

