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VELSICOL CHEMICAL CORPORATION

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

Plant Site, St. Louis, Michigan

Ref. No. 1524

CONESTOGA-ROVERS & ASSOCIATES LIMITED

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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.

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

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

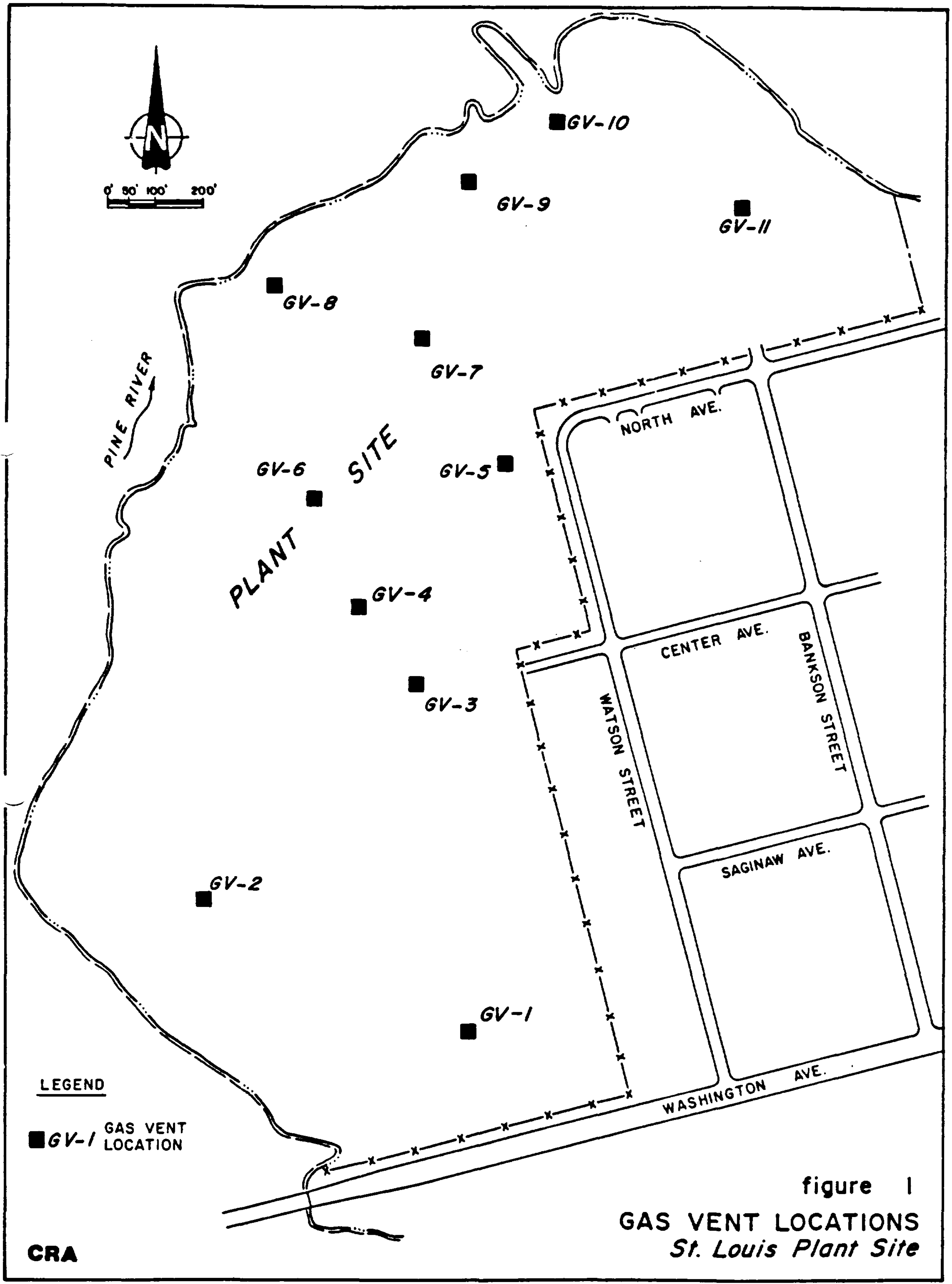

figure 1

GAS VENT LOCATIONS

St. Louis Plant Site

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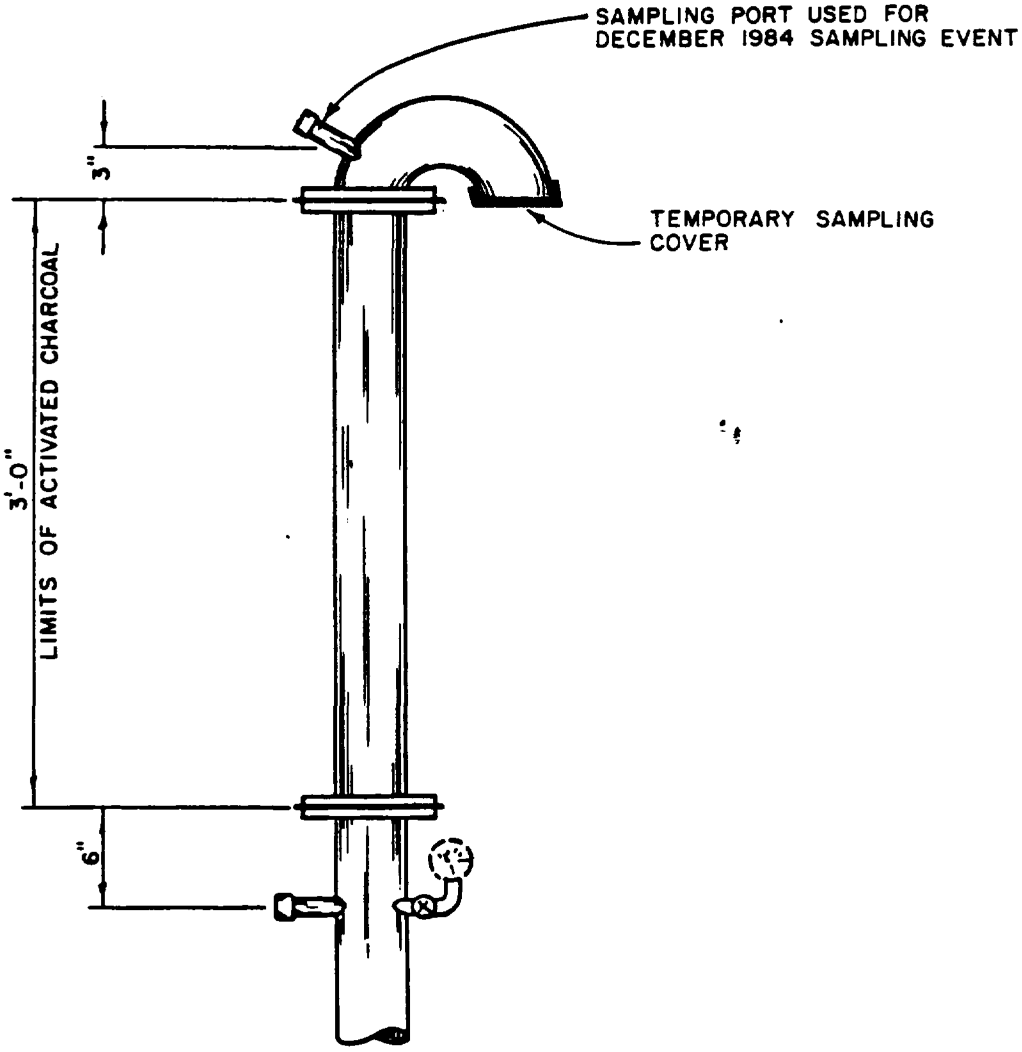

figure 2

ACTIVATED CHARCOAL GAS VENT DETAIL

St. Louis Plant Site

CRA

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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:

COMPOUND	NIOSH 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.

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.

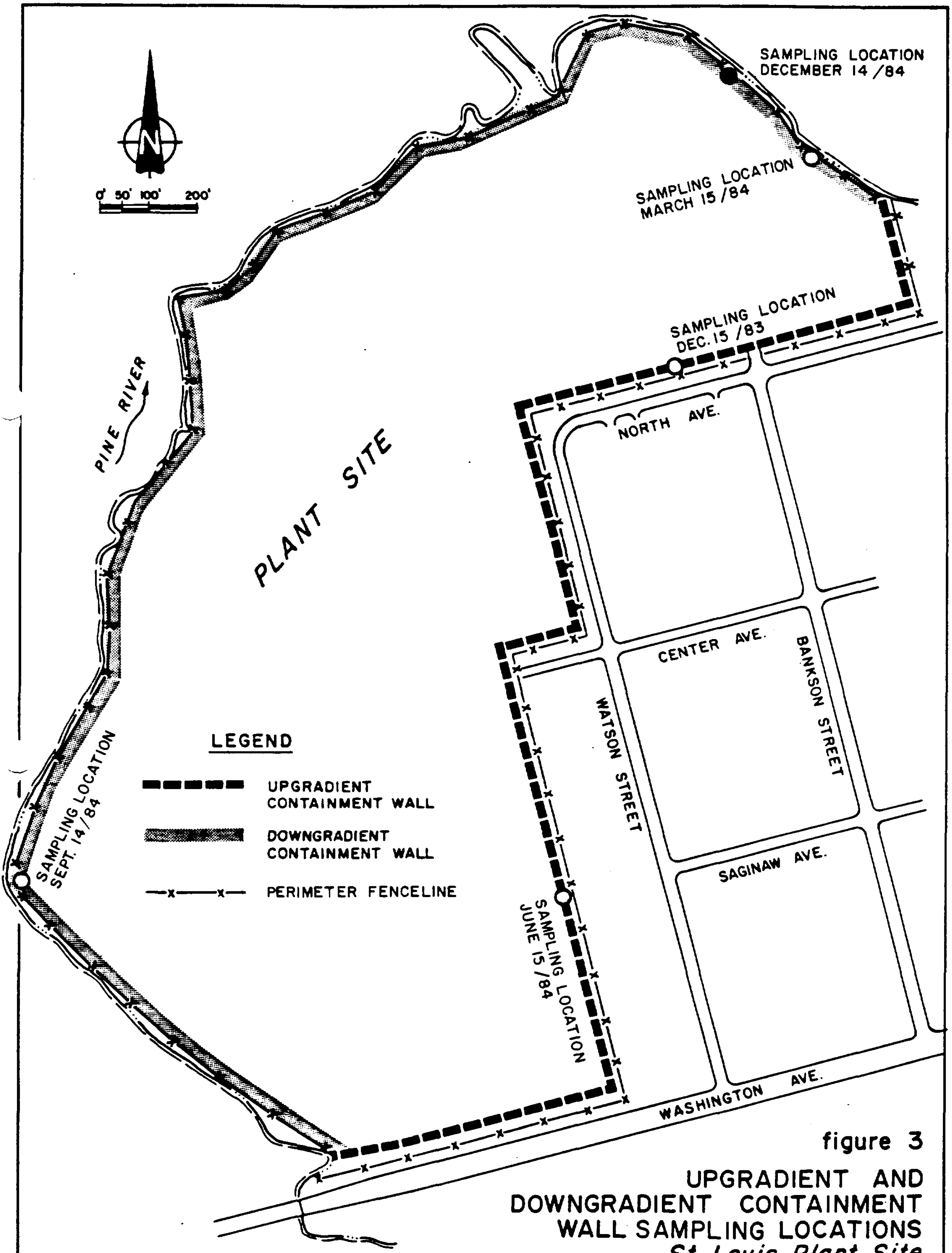

figure 3

UPGRADIENT AND DOWNGRADIENT CONTAINMENT WALL SAMPLING LOCATIONS

St. Louis Plant Site

CRA

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.

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

WATER LEVEL MEASUREMENTS
DECEMBER 12, 1984

MONITORING WELL	WELL HEAD ELEVATION (AMSL)	MEASURED DISTANCE TO WATER TABLE (ft.)	WATERTABLE 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.

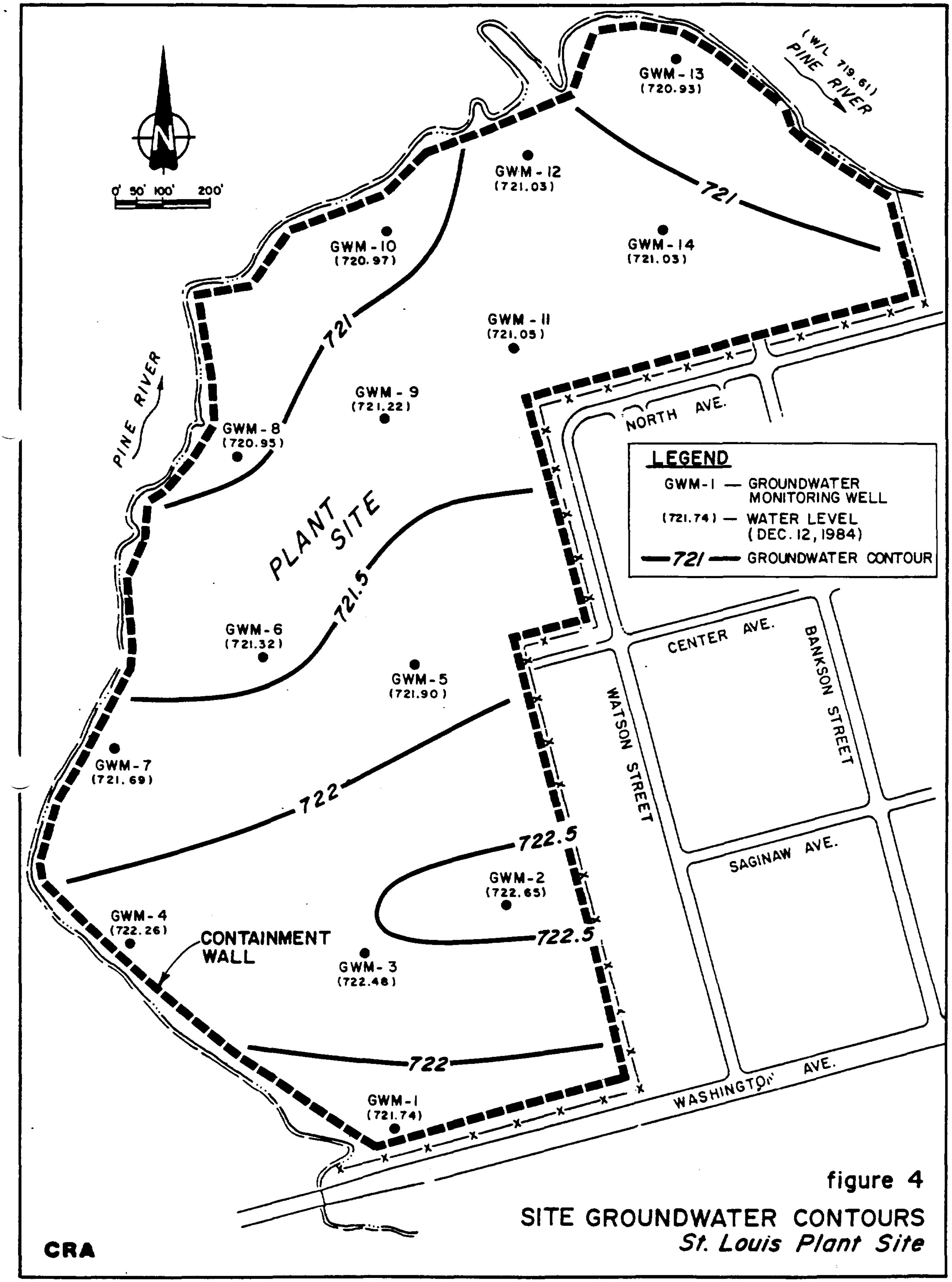

figure 4

SITE GROUNDWATER CONTOURS

St. Louis Plant Site

1524-18/12/84

5.0 SUMMARY

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

CHAIN OF CUSTODY

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.

   $$\text{corrected mg/sample} = \frac{\text{total weight}}{\text{DE}}$$

4. Calculate the concentration of the analyte in air

   $$\text{mg/m}^3 = \frac{\text{Corrected mg} \times 1000 \text{ liters/m}^3}{\text{Air volume Sampled (liters)}}$$

5. Concentration will be reported as ppm, corrected to standard conditions of 25°C and 760 mm Hg

   $$\text{ppm} = \text{mg/m}^3 \times \frac{24.45}{\text{MW}} \times \frac{760}{\text{P}} \times \frac{(\text{T}+273)}{298}$$

   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)

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.

FORMULA: Table 1

HYDROCARBONS, HALOGENATED

METHOD: 1003
ISSUED: 2/14/84

M.W.: Table 1

COMPOUNDS: (synonyms in Table 1)

benzyl chloride	chlorobromomethane	1,1-dichloroethane	hexachloroethane
bromoform	chloroform	1,2-dichloroethylene	methylchloroform
carbon tetrachloride	o-dichlorobenzene	ethylene dichloride	propylene dichloride
chlorobenzene	p-dichlorobenzene		

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: Table 2
-MAX: Table 2

SHIPMENT: routine

SAMPLE STABILITY: at least 1 week @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

[illegible]

BIAS: not significant [1]

OVERALL PRECISION (s_r): see EVALUATION OF METHOD [1]

MEASUREMENT

!TECHNIQUE: GAS CHROMATOGRAPHY, FID

!ANALYTE: compounds above

!DESORPTION: 1 mL CS_2, stand 30 min

!INJECTION VOLUME: 5 µL

!TEMPERATURES: Table 2

!CARRIER GAS: N_2 or He, 30 mL/min

!COLUMN: Table 2; alternates are SP-2100, SP-2100 with 0.1% Carbowax 1500 or DB-1 fused silica capillary column

!CALIBRATION: solutions of analyte in CS_2 with [illegible]

!RANGE: Table 2

!ESTIMATED LOD: 0.01 mg per sample [2]

!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.
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 $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of analyte in the air volume sampled, V (L):

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

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:

[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 NIOSH [6-10] ACGIH	BP (°C)	VP @ 20 °C	Density (g/mL @ 20 °C)
p-Dichlorobenzene	1,4-$C_6H_4Cl_2$	147.00; 6.01	1,4-dichlorobenzene; CAS #106-46-7	75 ppm — 75 ppm, STEL 110 ppm	174	50 Pa	1.241
1,1-Dichloroethane	CH_3CHCl_2; $C_2H_4Cl_2$	98.96; 4.05	ethylidene chloride; CAS #75-34-3	100 ppm 100 ppm 200 ppm, STEL 250 ppm	57	24.3 kPa	1.174
1,2-Dichloroethylene	ClCH=CHCl; $C_2H_4Cl_2$	96.95; 3.96	acetylene dichloride; 1,2-dichloroethene; CAS #540-59-0	200 ppm 200 ppm 200 ppm, STEL 250 ppm	60 (cis) 47 (trans)	24-35 kPa	1.28
Ethylene dichloride*	$ClCH_2CH_2Cl$; $C_2H_4Cl_2$	98.96; 4.05	1,2-dichloroethane; CAS #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*	CCl_3CCl_3; C_2Cl_6	236.74; 9.68	perchloroethane; CAS #67-72-1	1 ppm (skin) 1 ppm (skin) 10 ppm	187 (sublimes)	30 Pa	2.09
Methylchloroform	CH_3CCl_3; $C_2H_3Cl_3$	133.42; 5.45	1,1,1-trichloroethane; CAS #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	$CH_3CHClCH_2Cl$; $C_3H_6Cl_2$	112.99; 4.62	1,2-dichloropropane CAS #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.

	Sampling			Measurement				
	Air Sample Volume (L)					t (°C)		
Compound	Min	Max	Breakthrough in [illegible] Air	Working Range (mg/m³)	Column*	Column Injector Detector	Internal Standard	Range (mg per sample)
1,1-Dichloroethane	1 @ 100 ppm	10	18.3 L [illegible]3 mg/m³	40 to 1215 (10 L)	A	50 100 175	--	0.4 to 12
1,2-Dichloroethylene	0.5 @ 200 ppm	3	5.4 L [illegible]09 mg/m³	80 to 2370 (3 L)	A	60 170 210	--	0.2 to 7
Ethylene dichloride	1 @ 50 ppm	10	29 L [illegible] mg/m³	40 to 1215 (3 L)	A	70 225 250	octane	0.1 to 4
Hexachloroethane	1 @ 1 ppm	10	43 L [illegible] mg/m³	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 [illegible]88 mg/m³	190 to 5700 (3 L)	A	70 225 250	octane	0.6 to 17
Propylene dichloride	1 @ 75 ppm	10	18 L [illegible] mg/m³	35 to 1050 (10 L)	A	80 170 210	n-undecane	0.3 to 10

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*A = 3 m x 3 mm stainless steel, 10% SP-1000 [illegible] 100 mesh Supelcoport;
B = 6 m x 3 mm, otherwise same as A;
C = 3 m x 3 mm stainless steel, 10% OV-101 [illegible] 120 mesh Supelcoport; or
D = 3 m x 6 mm glass, [illegible] SP-2250 on 80/100 [illegible]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

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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:

1. 30 ml/min (60 psig) Nitrogen carrier gas flow
2. 35 ml/min (25 psig) Hydrogen gas flow to detector
3. 400 ml/min (60 psig) Air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 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

$$\text{D.E.} = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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 2X 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.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

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.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

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

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liters/cu m)}}{\text{Air Volume Sampled (liters)}}$$

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

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

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," 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.

FORMULA: $CH_2=CHCl$; C_2H_3Cl

M.W.: 62.50

VINYL CHLORIDE

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

SAMPLER: SOLID SORBENT TUBE (2 tandem tubes, each with 150 mg activated coconut charcoal)

FLOW RATE: 0.05 L/min

VOL-MIN: 0.7 L
-MAX: 5 L

SHIPMENT: separate primary and backup tubes and cap each

SAMPLE STABILITY: 10 days @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 1 to 64 mg/m³ [2]

BIAS: -6% of calculated concentration [2]

OVERALL PRECISION (s_r): 0.06 [2]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: vinyl chloride

DESORPTION: 1 mL carbon disulfide; 30 min

INJECTION ALIQUOT: 5 µL

COLUMN: stainless steel, 6.1 m x 3.2 mm, 10% SE-30 on 80/100 mesh Chromosorb W (AW-DMCS)

CARRIER GAS: He, 40 mL/min

TEMPERATURE-INJECTOR: 230 °C
-DETECTOR: 230 °C
-COLUMN: 60 °C

CALIBRATION: solutions of vinyl chloride in CS_2

RANGE: 0.002 to 0.2 mg per sample [2]

ESTIMATED LOD: 0.00004 mg per sample [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].

REAGENTS:

1. Carbon disulfide,* chromatographic quality.
2. Vinyl chloride,*, 99.9%, in lecture bottle fitted with valve and septum.
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 CS_2 in a 10-mL volumetric flask.
   b. Open the valve of the syringe and withdraw the plunger to pull CS_2 into the barrel. (As vinyl chloride dissolves, a vacuum will be created, pulling CS_2 into the syringe.)
   c. Push the solution from the syringe into the flask. Rinse the syringe twice with 1-mL portions of CS_2 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 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.
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.

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.

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/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.

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 CS_2, 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 $W_b > W_f/10$, report breakthrough and possible sample loss.
15. Calculate concentration, C, of vinyl chloride in the air volume sampled, V (L):

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

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:

[1] TLVs - Threshold Limit Values for Chemical Substances and Physical Agents in the Work Environment with Intended Changes for 1983-84, 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.

PROJECT No. 1524

GAS VENT SAMPLING

VELSICOL CHEMICAL CORPORATION

ST. LOUIS, MICHIGAN

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 (ℓ)	TIME
1			
2			
3			
4			
5			
6			
7			
8			
9			
10			
11			
DUPLICATE			

DATE OF SAMPLE SHIPMENT:

COMMENTS:

1524 - 10/12/84

VELSICOL CHEMICAL CORPORATION

SUMMARY OF POST-CONSTRUCTION CONTAINMENT WALL MONITORING

December, 1983 to September, 1986

St. Louis, Michigan

PRINTED ON
FEB 12 1987

VELSICOL CHEMICAL CORPORATION

SUMMARY OF POST-CONSTRUCTION CONTAINMENT WALL MONITORING

December, 1983 to September, 1986

St. Louis, Michigan

February 1987
Ref. No. 1524

CONESTOGA-ROVERS & ASSOCIATES

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LIST OF APPENDICES

1.0 INTRODUCTION

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.

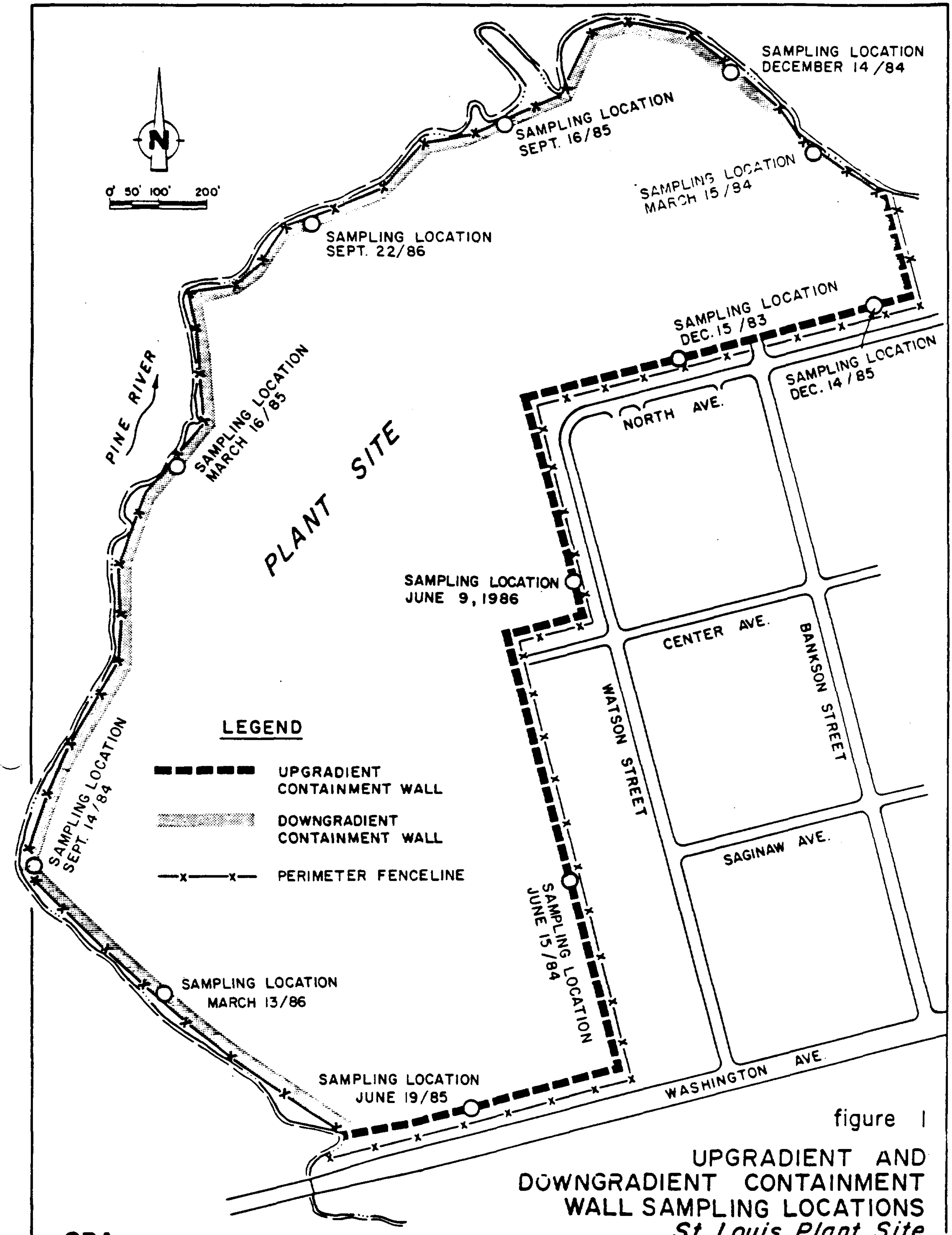

figure 1

UPGRADIENT AND DOWNGRADIENT CONTAINMENT WALL SAMPLING LOCATIONS
St. Louis Plant Site

CRA

1524 - 6/02/87

TABLE 1

SUMMARY OF QUARTERLY PERMEABILITY TESTING
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	1.1×10^{-7}
UGW 19+50	6'-8'	06/15/84	5.3×10^{-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	3×10^{-8}
UGW 31+00	7'-9'	06/19/85	9.9×10^{-8}
DWG 63+25	8'-10'	09/16/85	3.9×10^{-8}
UGW 2+60	5'-7'	12/14/85	6.5×10^{-8}
DWG 38+10	6'-8'	03/13/86	5.8×10^{-8}
UGW 15+00	5'-7'	06/09/86	7×10^{-8}
DGW 58+25	4'-6'	09/22/86	3.3×10^{-8}

3.0 CONCLUSIONS

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 x 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

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 1×10^{-7} cm/sec., or less. Analysis of the data shall be carried out as specified in subparagraph 8.a.4, above.

APPENDIX B

ANALYTICAL RESULTS FOR
POST CONSTRUCTION
CONTAINMENT WALL TESTING

PERMEABILITY RESULTS OF CONTAINMENT WALL AND CLAY CAP SAMPLES

TABLE NO. 2

CONTAINMENT WALL SAMPLES

Sample Number	Time In-Place	Sample Location	Sample Depth	Permeability (cm/s)
UGW-R1	3-months	Station 7+70	4.0'	2.2×10^{-8}
DGW-R2	6-months	Station 71+25	5.0'	1.1×10^{-7}
UGW-R4	9-months	Station 19+50	6.0'	5.3×10^{-8}
DGW-R5	12-months	Station 42+50	12.0'	3.8×10^{-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	7.2×10^{-8}
CC-9	Station 12+00A & 250 Feet Left	Grade	3.5×10^{-8}
CC-10	Station 5+00 & 700 Feet Left	Grade	6.2×10^{-8}

RESULTS OF PERMEABILITY TEST

(Triaxial Cell With Back Pressure Saturation)

Project St. Louis, Michigan

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 Differential	5	p.s.i.
Top Pressure	45	p.s.i.
Bottom Pressure	50	p.s.i.
Cell Pressure	55	p.s.i.
Specific Gravity	--	

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

psi **Professional Service Industries, Inc.**
Michigan Testing Engineers Division

TESTED FOR: Conestoga Rovers & Associates, LTD
651 Colby Drive
Waterloo, Ontario
Canada N2V-1C2

PROJECT: St. Louis, Michigan

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 47+50 8' - 10'
Height of Sample: 4.0 in.
Dia. of Sample: 2.8 in.
Initial Weight of Sample: 920.7g
Initial Moisture Content: ---
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
651 Colby Drive
Waterloo, Ontario
Canada N2V-1C2

PROJECT: St. Louis, Michigan

DATE: July 12, 1985

OUR REPORT NO.: 406-55004

R[illegible]ARKS:

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 JUNE [illegible]
Sample Location: ~~DGW 47 + 50 8' to 10'~~ UGW 31+00 7'-9'
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: 62 psi
Saturation Pressure: 50 psi
Bottom Pressure: 60 psi
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: 9.9×10^{-8} cm/sec

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 9/16/85
Sample Location: DGW 63 + 25
Height of Sample: 4.925" Dia. of Sample: 2.91"
Initial Weight of Sample: 1124 grams Initial Moisture Content: 6.0
Confining Pressure: 72 psi Saturation Pressure: 60 psi
Bottom Pressure: 70 psi Top Pressure: 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: 3.9×10^{-8} cm/sec

TESTED FOR: Conestoga Rovers & Associates, LTD
651 Colby Drive
Waterloo, Ontario
Canada, N2V-1C2

PROJECT: St. Louis, Michigan

DATE: January 6, 1986

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.: 5'-7'
Date Sampled: by CRA 12/14/85
Sample Location: Baseline "B" Station 0+50 UGW 2+60
Height of Sample: 4.652"
Dia. of Sample: 2.877"
Initial Weight of Sample: 1161 grams
Initial Moisture Content: 10.8%
Confining Pressure: 72 psi
Saturation Pressure: 60 psi
Bottom Pressure: 70 psi
Top 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

DATE: March 26, 1986

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.: 6' - 8' Depth **Date Sampled:** by CRA MARCH 13, 1986

Sample Location: Station 38 + 10

Height of Sample: 5.19" **Dia. of Sample:** 2.94"

Initial Weight of Sample: 1292 grams **Initial Moisture Content:** 17.5%

Confining Pressure: 72.0 psi **Saturation Pressure:** 61.5 psi

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: 5.8×10^{-8} cm/sec

Professional Service Industries, Inc.
Michigan Testing Engineers Division

TESTED FOR: Conestoga Rovers & Associates, LTD
651 Colby Drive
Waterloo, Ontario
Canada N2V-1C2

PROJECT: St. Louis, Michigan

DATE:

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.: #1524 5'-7'
Date Sampled: JUNE 9, 1986
Sample Location: UGW 15+00
Height of Sample: 5.223"
Dia. of Sample: 2.954"
Initial Weight of Sample: 1453.4 grams
Initial Moisture Content: 23.0
Confining Pressure: 73 psi
Saturation Pressure: 60 psi
Bottom Pressure: 70 psi
Top Pressure: 60 psi

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

Permeability: 7.0×10^{-8} cm/sec

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

DATE: **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.: 4'-6' Date Sampled: September 22/86 By CRA DGW 58+25
Sample Location: STATION 58+25
Height of Sample: 4.785 inches Dia. of Sample: 2.96 inches
Initial Weight of Sample: 1200 grams Initial Moisture Content: 20.3%
Confining Pressure: 73 psi Saturation Pressure: 60 psi
Bottom Pressure: 70 psi Top Pressure: 60 psi

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

Permeability: 3.3 x 10^{-8} cm/sec

™ VELSICOL CHEMICAL CORPORATION

POST - CONSTRUCTION QUARTERLY MONITORING REPORT

March 13 - 16, 1985

Plant Site, St. Louis, Michigan

March 1985
Ref. No. 1524

CONESTOGA-ROVERS & ASSOCIATES LIMITED

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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 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.

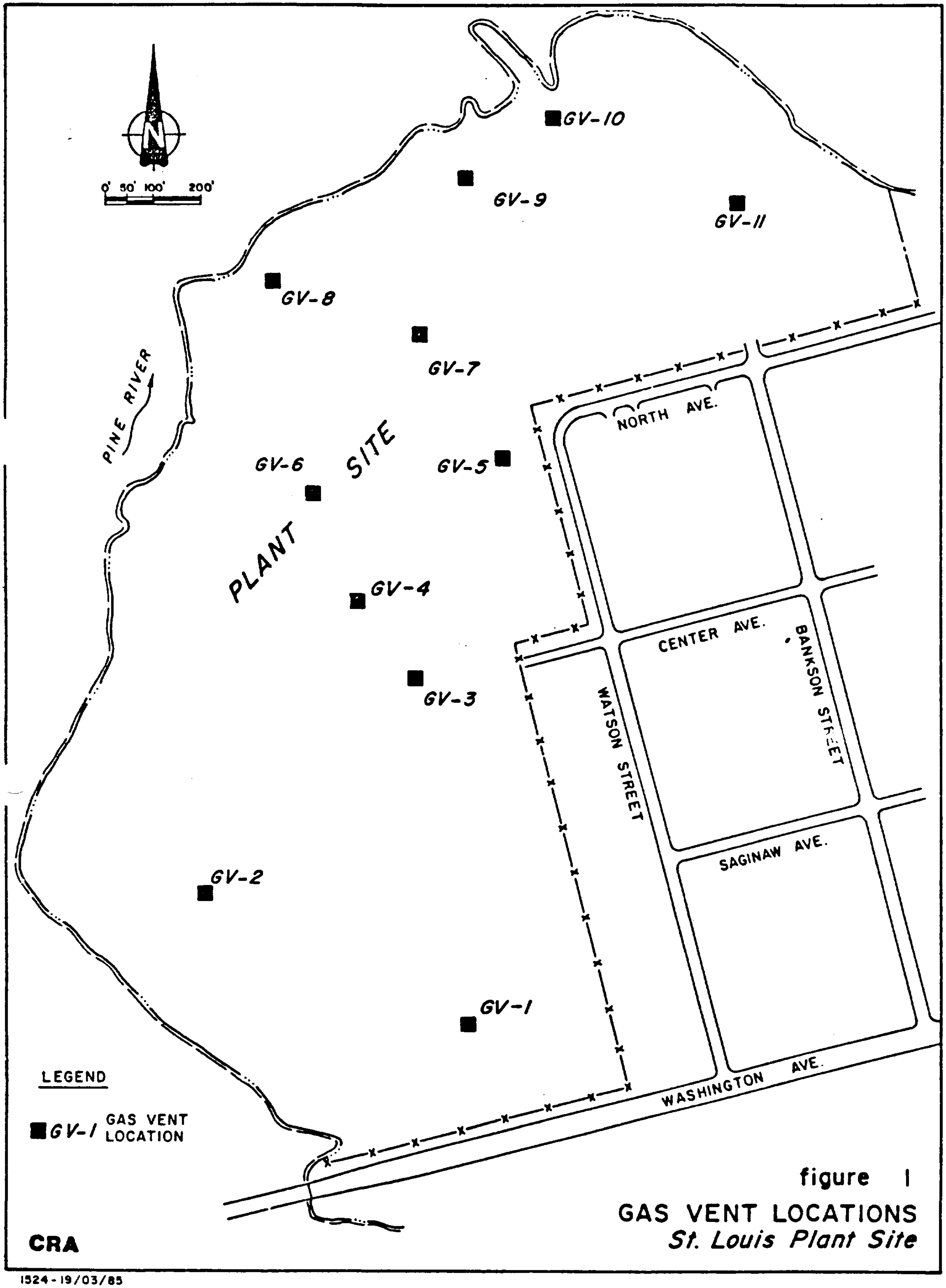

figure 1

GAS VENT LOCATIONS

St. Louis Plant Site

1524-19/03/85

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.

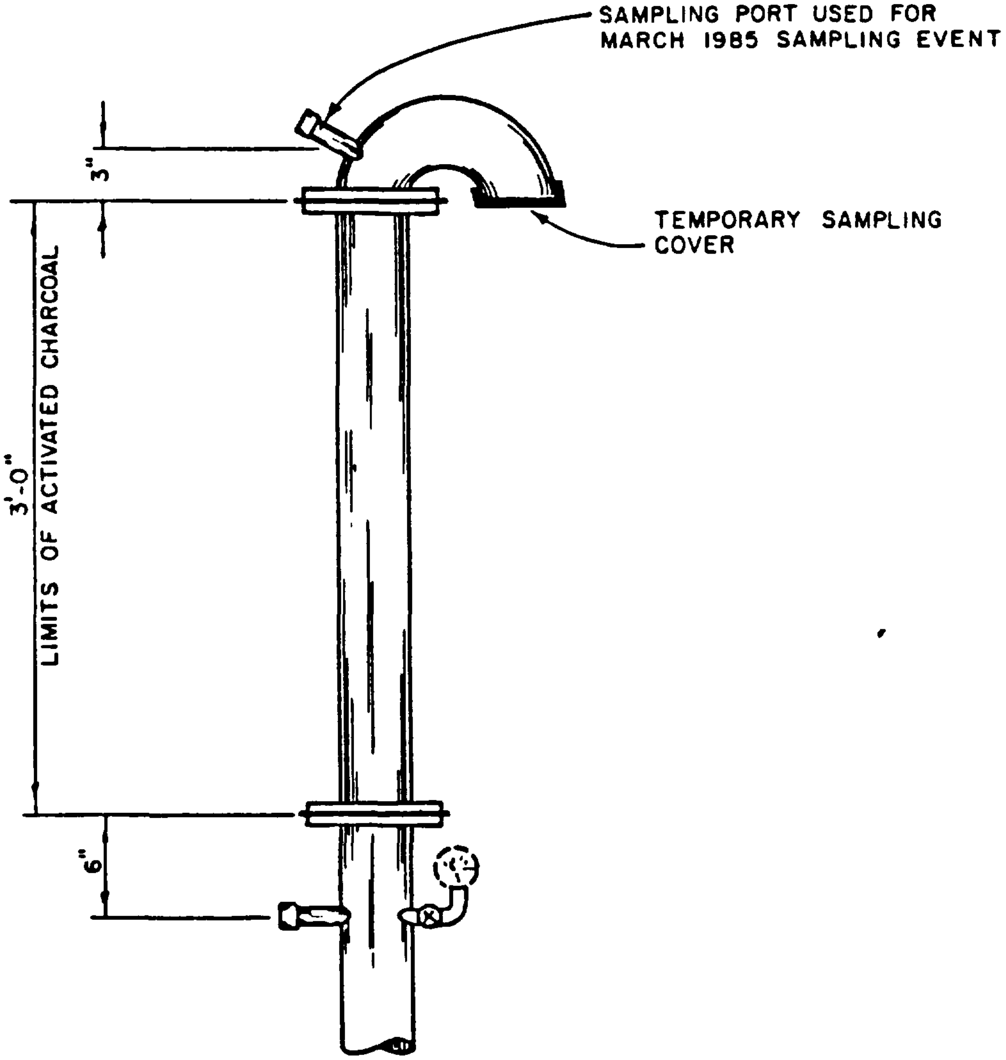

figure 2

ACTIVATED CHARCOAL GAS VENT DETAIL

St. Louis Plant Site

CRA

1524-19/03/85

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

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.

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.

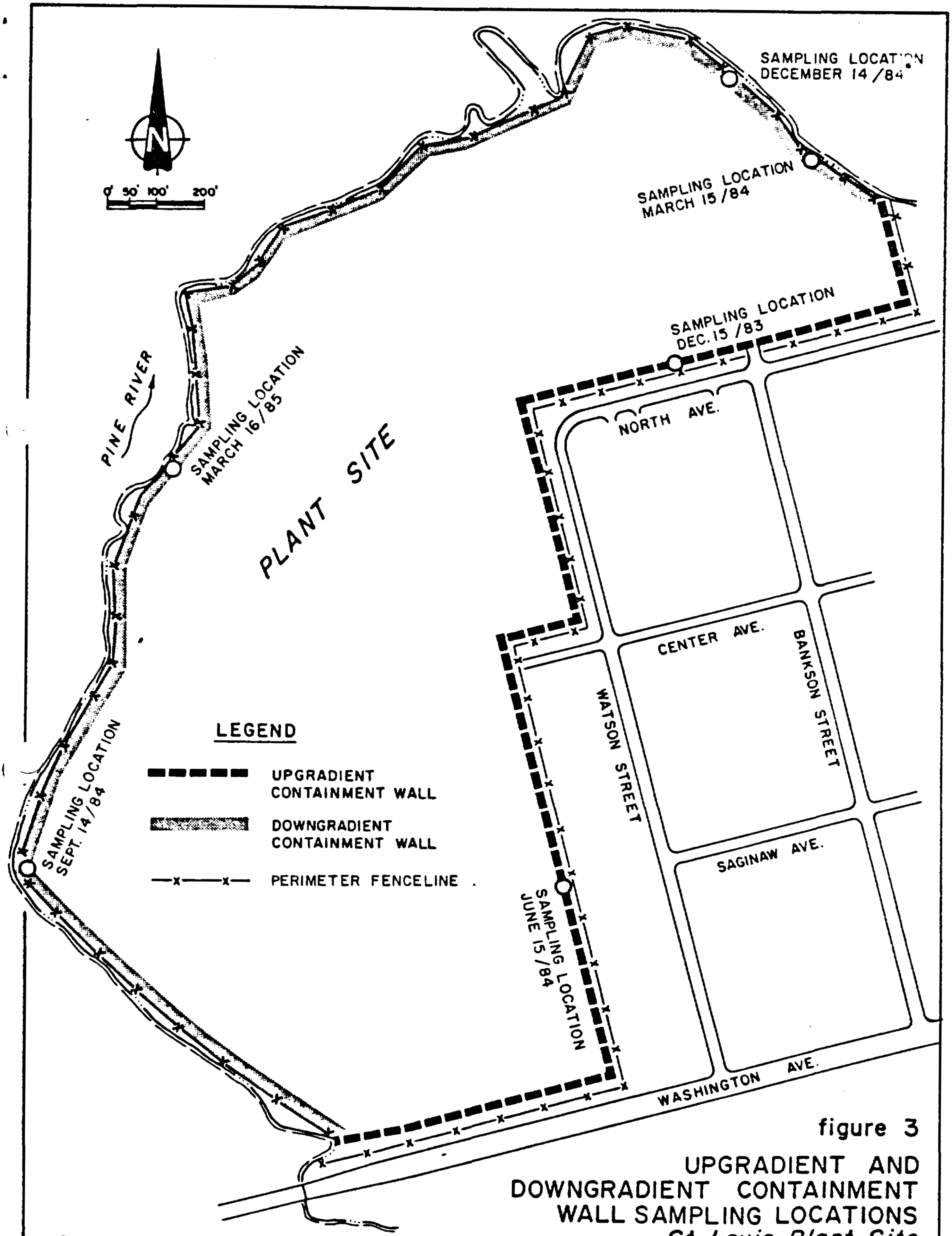

figure 3

UPGRADIENT AND DOWNGRADIENT CONTAINMENT WALL SAMPLING LOCATIONS

St. Louis Plant Site

1524-19/03/85

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 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.

TABLE 1

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

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.

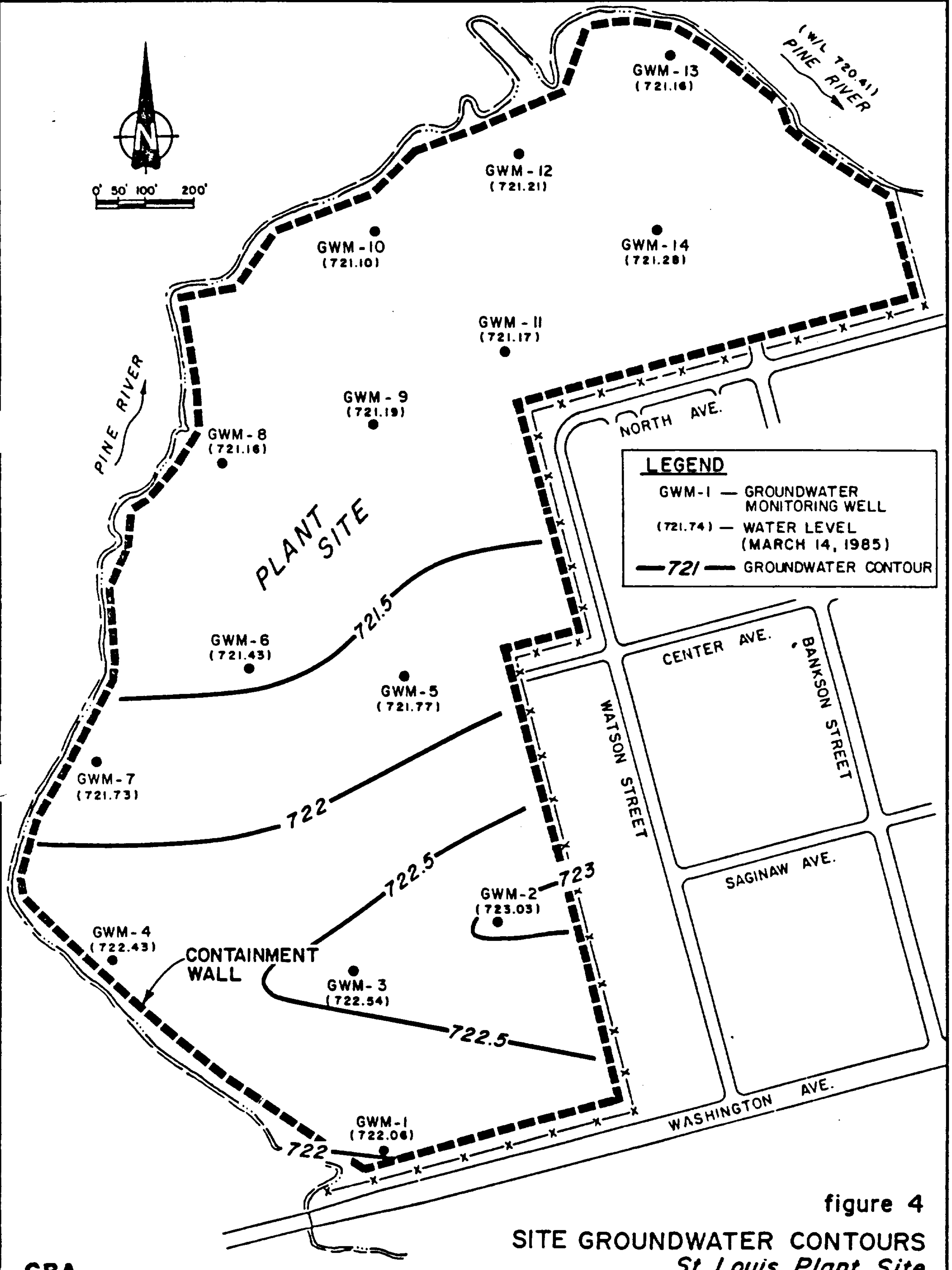

figure 4

SITE GROUNDWATER CONTOURS
St. Louis Plant Site

CRA

1524-19/03/85

5.0 SUMMARY

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.

APPENDIX A

CHAIN OF CUSTODY

SHEET 1 OF 5

CHAIN OF CUSTODY RECORD	PROJECT NO. 1524	PROJECT NAME: GAS VENT MONITORING PLANT SITE ST. LOUIS, MICHIGAN	VELSICOL CHEMICAL CORPORATION 701 W. WASHINGTON STREET ST. LOUIS, MICHIGAN 48880

SAMPLER'S SIGNATURE ______ (SIGN)

SAMPLE NO	SEQ NO	DATE	TIME	FRONT / REAR	TENAX / CHARCOAL	SAMPLE TYPE	NO OF CONTAINERS	REMARKS
1	1	3/15	8:36	F	T	Gas Vent Sample Tube	1	
1	1			R	C		1	
1	1			F	C		1	
1	1		9:13	R	T		1	
2	2			F	T		1	
2	2			R	C		1	
2	2			F	C		1	
2	2			R	T		1	
3	3		9:50	F	T		1	
3	3			R	C		1	
3	3			F	C		1	
3	3			R	T		1	
						TOTAL NO. OF CONTAINERS	12	

RELINQUISHED BY: 1 (SIGN)	DATE/TIME 3/15 1425	RECEIVED BY: 2 (SIGN)	RELINQUISHED BY: 2 (SIGN)	DATE/TIME	RECEIVED BY: 3 (SIGN)
RELINQUISHED BY: 3 (SIGN)	DATE/TIME	RECEIVED BY: 4 (SIGN)	RELINQUISHED BY: 4 (SIGN)	DATE/TIME	RECEIVED BY: 5 (SIGN)
RELINQUISHED BY: 5 (SIGN)	DATE/TIME	RECEIVED BY: 6 (SIGN)	RELINQUISHED BY: 6 (SIGN)	DATE/TIME	RECEIVED BY: 7 (SIGN)

METHOD OF SHIPMENT: Fed Ex	SHIPPED BY:	RECEIVED FOR LABORATORY: (SIGN)	DATE/TIME

SHEET 2 OF 5

CHAIN OF CUSTODY RECORD

PROJECT NO. 1524

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

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

SAMPLER'S SIGNATURE ______ (SIGN)

SAMPLE NO	SEQ NO	DATE	TIME	FRONT / REAR	TENAX / CHARCOAL	SAMPLE TYPE	NO OF CONTAINERS	REMARKS
4	4	3/15	10.27	F	T	Gas Vent Sampling Tube	1	
4	4			R	C		1	
4	4			F	C		1	
4	4			R	T		1	
5	5		11.05	F	T		1	
5	5			R	C		1	
5	5			F	C		1	
5	5			R	T		1	
6	6		11.15	F	T		1	
6	6			R	C		1	
6	6			F	C		1	
6	6			R	T		1	
						TOTAL NO. OF CONTAINERS		

RELINQUISHED BY: 1 (SIGN)	DATE/TIME 3/15 1425	RECEIVED BY: 2 (SIGN)	RELINQUISHED BY: 2 (SIGN)	DATE/TIME	RECEIVED BY: 3 (SIGN)
RELINQUISHED BY: 3 (SIGN)	DATE/TIME	RECEIVED BY: 4 (SIGN)	RELINQUISHED BY: 4 (SIGN)	DATE/TIME	RECEIVED BY: 5 (SIGN)
RELINQUISHED BY: 5 (SIGN)	DATE/TIME	RECEIVED BY: 6 (SIGN)	RELINQUISHED BY: 6 (SIGN)	DATE/TIME	RECEIVED BY: 7 (SIGN)

METHOD OF SHIPMENT: Fed Ex

SHIPPED BY:

RECEIVED FOR LABORATORY: (SIGN)

DATE/TIME

SHEET 3 OF 5

CHAIN OF CUSTODY RECORD	PROJECT NO. 1524	PROJECT NAME: GAS VENT MONITORING PLANT SITE ST. LOUIS, MICHIGAN	VELSICOL CHEMICAL CORPORATION 701 W. WASHINGTON STREET ST. LOUIS, MICHIGAN 48880

SAMPLER'S SIGNATURE (SIGN)

SAMPLE NO	SEQ NO	DATE	TIME	FRONT / REAR	TENAX / CHARCOAL	SAMPLE TYPE	NO OF CONTAINERS	REMARKS
7	7	3/15	11.46	F	T	Gas Vent Sampling Tube	1	
7	7			R	C		1	
7	7			F	C		1	
7	7			R	T		1	
12	1	3/15	8.53	F	T		1	
12	1			R	C		1	
12	1			F	C		1	
12	1			R	T		1	
11	2	3/15	9.29	F	T		1	
11	2			R	C		1	
11	2			F	C		1	
11	2			R	T		1	
						TOTAL NO. OF CONTAINERS	12	

RELINQUISHED BY: ① (SIGN)	DATE/TIME 3/15 14[illegible]	RECEIVED BY: ② (SIGN)	RELINQUISHED BY: ② (SIGN)	DATE/TIME	RECEIVED BY: ③ (SIGN)
RELINQUISHED BY: ③ (SIGN)	DATE/TIME	RECEIVED BY: ④ (SIGN)	RELINQUISHED BY: ④ (SIGN)	DATE/TIME	RECEIVED BY: ⑤ (SIGN)
RELINQUISHED BY: ⑤ (SIGN)	DATE/TIME	RECEIVED BY: ⑥ (SIGN)	RELINQUISHED BY: ⑥ (SIGN)	DATE/TIME	RECEIVED BY: ⑦ (SIGN)

METHOD OF SHIPMENT: Fed Ex	SHIPPED BY:	RECEIVED FOR LABORATORY: (SIGN)	DATE/TIME

SHEET 4 OF 5

CHAIN OF CUSTODY RECORD

PROJECT Nº. 1524

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

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

SAMPLER'S SIGNATURE ______ (SIGN)

SAMPLE Nº	SEQ Nº	DATE	TIME	FRONT / REAR	TENAX / CHARCOAL	SAMPLE TYPE	Nº OF CONTAINERS	REMARKS
10	3	3/15	8.53	F	T	Gas Vent Sampling Tube	1	
10	3			R	C		1	
10	3			F	C		1	
10	3			R	T		1	
9	4	3/15	10.50	F	T		1	
9	4			R	C		1	
9	4			F	C		1	
9	4			R	T		1	
8	5	3/15	11.32	F	T		1	
8	5			R	C		1	
8	5			F	C		1	
8	5			R	T		1	
						TOTAL Nº. OF CONTAINERS	12	

RELINQUISHED BY:	DATE/TIME	RECEIVED BY:	RELINQUISHED BY:	DATE/TIME	RECEIVED BY:
1 (SIGN)	3/15, 1427	② (SIGN)	2 (SIGN)		③ (SIGN)
RELINQUISHED BY: 3 (SIGN)	DATE/TIME	RECEIVED BY: ④ (SIGN)	RELINQUISHED BY: 4 (SIGN)	DATE/TIME	RECEIVED BY: ⑤ (SIGN)
RELINQUISHED BY: 5 (SIGN)	DATE/TIME	RECEIVED BY: ⑥ (SIGN)	RELINQUISHED BY: 6 (SIGN)	DATE/TIME	RECEIVED BY: ⑦ (SIGN)

METHOD OF SHIPMENT: FED EX

SHIPPED BY:

RECEIVED FOR LABORATORY: ______ (SIGN)

DATE/TIME

SHEET 2 OF 2

CHAIN OF CUSTODY RECORD

PROJECT NO. 1524

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

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

SAMPLER'S SIGNATURE (SIGN)

SAMPLE NO	SEQ NO	DATE	TIME	FRONT / REAR	TENAX / CHARCOAL	SAMPLE TYPE	NO OF CONTAINERS	REMARKS
13	6	3/15	11.55	F	T		1	
13	6			R	C		1	
13	6			F	C		1	
13	6			R	T		1	
						TOTAL SHIPMENT 52 TUBES		
						TOTAL NO. OF CONTAINERS	4	

RELINQUISHED BY:	DATE/TIME	RECEIVED BY:	RELINQUISHED BY:	DATE/TIME	RECEIVED BY:
1 (SIGN)	3/15 1425	2 (SIGN)	2 (SIGN)		3 (SIGN)
3 (SIGN)		4 (SIGN)	4 (SIGN)		5 (SIGN)
5 (SIGN)		6 (SIGN)	6 (SIGN)		7 (SIGN)

METHOD OF SHIPMENT:	SHIPPED BY:	RECEIVED FOR LABORATORY:	DATE/TIME
FED EXP		(SIGN)	

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.

   $$\text{corrected mg/sample} = \frac{\text{total weight}}{\text{DE}}$$

4. Calculate the concentration of the analyte in air

   $$\text{mg/m}^3 = \frac{\text{Corrected mg} \times 1000\ \text{liters/m}^3}{\text{Air volume Sampled (liters)}}$$

5. Concentration will be reported as ppm, corrected to standard conditions of 25°C and 760 mm Hg

   $$\text{ppm} = \text{mg/m}^3 \times \frac{24.45}{\text{MW}} \times \frac{760}{\text{P}} \times \frac{(\text{T}+273)}{298}$$

   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)

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.

FORMULA: Table 1

M.W.: Table 1

HYDROCARBONS, HALOGENATED

METHOD: 1003
ISSUED: 2/14/84

COMPOUNDS: (synonyms in Table 1)	benzyl chloride bromoform carbon tetrachloride chlorobenzene	chlorobromomethane chloroform o-dichlorobenzene p-dichlorobenzene	1,1-dichloroethane 1,2-dichloroethylene ethylene dichloride	hexachloroethane methylchloroform propylene dichloride

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: Table 2
-MAX: Table 2

SHIPMENT: routine

SAMPLE STABILITY: at least 1 week @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

[illegible]

BIAS: not significant [1]

OVERALL PRECISION (s_r): see EVALUATION OF METHOD [1]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: compounds above

DESORPTION: 1 mL CS_2, stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURES: Table 2

CARRIER GAS: N_2 or He, 30 mL/min

COLUMN: Table 2; alternates are SP-2100, SP-2100 with 0.1% Carbowax 1500 or DB-1 fused silica capillary column

CALIBRATION: solutions of analyte in CS_2 with [illegible]

RANGE: Table 2

ESTIMATED LOD: 0.01 mg per sample [2]

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.
   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 $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of analyte in the air volume sampled, V (L):

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

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:

[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 NIOSH [6-10] ACGIH	BP (°C)	VP @ 20 °C	Density (g/mL @ 20 °C)
p-Dichlorobenzene	1,4-$C_6H_4Cl_2$	147.00; 6.01	1,4-dichlorobenzene; CAS #106-46-7	75 ppm --- 75 ppm, STEL 110 ppm	174	50 Pa	1.241
1,1-Dichloroethane	CH_3CHCl_2; $C_2H_4Cl_2$	98.96; 4.05	ethylidene chloride; CAS #75-34-3	100 ppm 100 ppm 200 ppm, STEL 250 ppm	57	24.3 kPa	1.174
1,2-Dichloroethylene	ClCH=CHCl; $C_2H_4Cl_2$	96.95; 3.96	acetylene dichloride; 1,2-dichloroethene; CAS #540-59-0	200 ppm 200 ppm 200 ppm, STEL 250 ppm	60 (cis) 47 (trans)	24-35 kPa	1.28
Ethylene dichloride*	$ClCH_2CH_2Cl$; $C_2H_4Cl_2$	98.96; 4.05	1,2-dichloroethane; CAS #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*	CCl_3CCl_3; C_2Cl_6	236.74; 9.68	perchloroethane; CAS #67-72-1	1 ppm (skin) 1 ppm (skin) 10 ppm	187 (sublimes)	30 Pa	2.09
Methylchloroform	CH_3CCl_3; $C_2H_3Cl_3$	133.42; 5.45	1,1,1-trichloroethane; CAS #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	$CH_3CHClCH_2Cl$; $C_3H_6Cl_2$	112.99; 4.62	1,2-dichloropropane CAS #78-87-5	75 ppm 75 ppm 75 ppm, STEL 110 ppm	95	5.3 kPa	1.156 (25 °C)

*Suspect carcinogen.

	Sampling			Measurement				
	Air Sample Volume (L)					t (°C)		
Compound	Min	Max	Breakthrough in Dry Air	Working Range (mg/m³)	Column*	Column Injector Detector	Internal Standard	Range (mg per sample)
1,1-Dichloroethane	1 @ 100 ppm	10	18.3 L [illegible] mg/m³	40 to 1215 (10 L)	A	50 100 175	--	0.4 to 12
1,2-Dichloroethylene	0.5 @ 200 ppm	3	5.4 L [illegible]09 mg/m³	80 to 2370 (3 L)	A	60 170 210	---	0.2 to 7
Ethylene dichloride	1 @ 50 ppm	10	29 L [illegible] mg/m³	40 to 1215 (3 L)	A	70 225 250	octane	0.1 to 4
Hexachloroethane	1 @ 1 ppm	10	43 L [illegible] mg/m³	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 [illegible]08 mg/m³	190 to 5700 (3 L)	A	70 225 250	octane	0.6 to 17
Propylene dichloride	1 @ 75 ppm	10	18 L [illegible] mg/m³	35 to 1050 (10 L)	A	80 170 210	n-undecane	0.3 to 10

---

*A = 3 m x 3 mm stainless steel, 10% SP-1000 [illegible] 100 mesh Supelcoport;
B = 6 m x 3 mm, otherwise same as A;
C = 3 m x 3 mm stainless steel, 10% OV-101 on [illegible]20 mesh Supelcoport; or
D = 3 m x 6 mm glass, [illegible] SP-2250 on 80/100 [illegible]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 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:

1. 30 ml/min (60 psig) Nitrogen carrier gas flow
2. 35 ml/min (25 psig) Hydrogen gas flow to detector
3. 400 ml/min (60 psig) Air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 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

$$\text{D.E.} = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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 2X 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.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

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.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

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

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liters/cu m)}}{\text{Air Volume Sampled (liters)}}$$

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

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

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," 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.

FORMULA: $CH_2=CHCl$; C_2H_3Cl

M.W.: 62.50

VINYL CHLORIDE

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

SAMPLER: SOLID SORBENT TUBE
(2 tandem tubes, each with 150 mg activated coconut charcoal)

FLOW RATE: 0.05 L/min

VOL-MIN: 0.7 L
-MAX: 5 L

SHIPMENT: separate primary and backup tubes and cap each

SAMPLE STABILITY: 10 days @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 1 to 64 mg/m³ [2]

BIAS: -6% of calculated concentration [2]

OVERALL PRECISION (s_r): 0.06 [2]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: vinyl chloride

DESORPTION: 1 mL carbon disulfide; 30 min

INJECTION ALIQUOT: 5 µL

COLUMN: stainless steel, 6.1 m x 3.2 mm, 10% SE-30 on 80/100 mesh Chromosorb W (AW-DMCS)

CARRIER GAS: He, 40 mL/min

TEMPERATURE-INJECTOR: 230 °C
-DETECTOR: 230 °C
-COLUMN: 60 °C

CALIBRATION: solutions of vinyl chloride in CS_2

RANGE: 0.002 to 0.2 mg per sample [2]

ESTIMATED LOD: 0.00004 mg per sample [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].

REAGENTS:

1. Carbon disulfide,* chromatographic quality.
2. Vinyl chloride,*, 99.9%, in lecture bottle fitted with valve and septum.
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 CS_2 in a 10-mL volumetric flask.
   b. Open the valve of the syringe and withdraw the plunger to pull CS_2 into the barrel. (As vinyl chloride dissolves, a vacuum will be created, pulling CS_2 into the syringe.)
   c. Push the solution from the syringe into the flask. Rinse the syringe twice with 1-mL portions of CS_2 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 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.
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.

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.

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/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/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.

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 CS_2, 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 $W_b > W_f/10$, report breakthrough and possible sample loss.
15. Calculate concentration, C, of vinyl chloride in the air volume sampled, V (L):

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

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:

[1] TLVs - Threshold Limit Values for Chemical Substances and Physical Agents in the Work Environment with Intended Changes for 1983-84, 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.

VELSICOL CHEMICAL CORPORATION
ST. LOUIS, MICHIGAN
PROJECT Nº 1524

GAS VENT SAMPLING PUMPS CALIBRATION LOG

DATE 14-15 1955	CALIBRATED BY [illegible]

PUMP NUMBER	PUMP TYPE	BEFORE SAMPLING 3/14/85						AFTER SAMPLING 3/15/85					AVERAGE 3/15/85			
		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.)
1	charcoal a)	42	55	29.96	255	[illegible]	[illegible]	33	59	30.33	[illegible]	12:30	37.5	57	30.145	250
	[illegible] b)	42	55	29.96	250	250	"	33	59	30.33	255	"	37.5	57	30.145	252.5
2	[illegible] a)	42	55	29.96	[illegible]	250	"	33	59	30.33	250	12:35	37.5	57	30.145	250
	[illegible] b)	42	55	29.96	[illegible]	250	"	33	59	30.33	[illegible]	"	37.5	57	30.145	250
		a) charcoal			b) tenax											

COMMENTS

VELSICOL CHEMICAL CORPORATION
ST. LOUIS, MICHIGAN
PROJECT Nº 1524

GAS VENT SAMPLING

DATE OF COLLECTION 3/15/85	SAMPLER Robinson	BAROMETRIC PRESSURE 30.145
TEMPERATURE ~~25~~0 37.5	RELATIVE HUMIDITY 57%	
CHARCOAL LOT Nº 120	TENAX LOT Nº 271	

GAUGE	1	2	3	4	5	6	7	8	9	10	11
READING	0	0	0	0		0					0

GAS VENT NUMBER	PUMP NUMBER	SAMPLE NUMBER	SAMPLING TIME START	SAMPLING TIME FINISH	SAMPLING TIME ELAPSED	SAMPLING RATE (cc/min.)	SAMPLE VOLUME (l)
1	1	7	11.44	12.04	20	250	5 0
2	1	5	1105	11.25	20	250	5 0
3	1	4	10.27	10.47	20	250	5.0
4	1	3	9.50	10.10	20	250	5 0
5							
6	1	2	9 13	9 33	20	250	5 0
7							
8							
9							
10							
11	1	1	8 36	8.56	20	250cc	5.0
DUPLICATE							
BLANK		6	11.15				

DATE OF SAMPLE SHIPMENT 3/15/85	METHOD OF SHIPMENT F.E. AWB# 611891626 3/15/85

COMMENTS Carbon Charged 3/14/85

VELSICOL CHEMICAL CORPORATION
ST. LOUIS, MICHIGAN
PROJECT Nº 1524

GAS VENT SAMPLING

DATE OF COLLECTION 3-15-85	SAMPLER Coll	BAROMETRIC PRESSURE 30.145											
TEMPERATURE 37.5	RELATIVE HUMIDITY 57%	GAUGE	1	2	3	4	5	6	7	8	9	10	11
CHARCOAL LOT Nº 120	TENAX LOT Nº 211	READING					0		0	0	0	0	

GAS VENT NUMBER	PUMP NUMBER	SAMPLE NUMBER	SAMPLING TIME			SAMPLING RATE (cc/min.)	SAMPLE VOLUME (ℓ)
			START	FINISH	ELAPSED		
1							
2							
3							
4							
5	2	9	10:50	11:10	20	250	5.0
6							
7	2	10	10:09	10:29	20	250	5.0
8	2	8 *	11.32	11:52	20	250	5.0
9	2	11	09:29	09.49	20	250	5.0
10	2	12	08:53	09:13	20	250	5.0
11							
DUPLICATE	2 (#8)	13 *	11:55	12:15	20	250	5.0
BLANK							

DATE OF SAMPLE SHIPMENT 3/15/85
METHOD OF SHIPMENT F.E. A.W.B. 611 891 626 3/15/85

COMMENTS Carbon Changed 3/14/85

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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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.

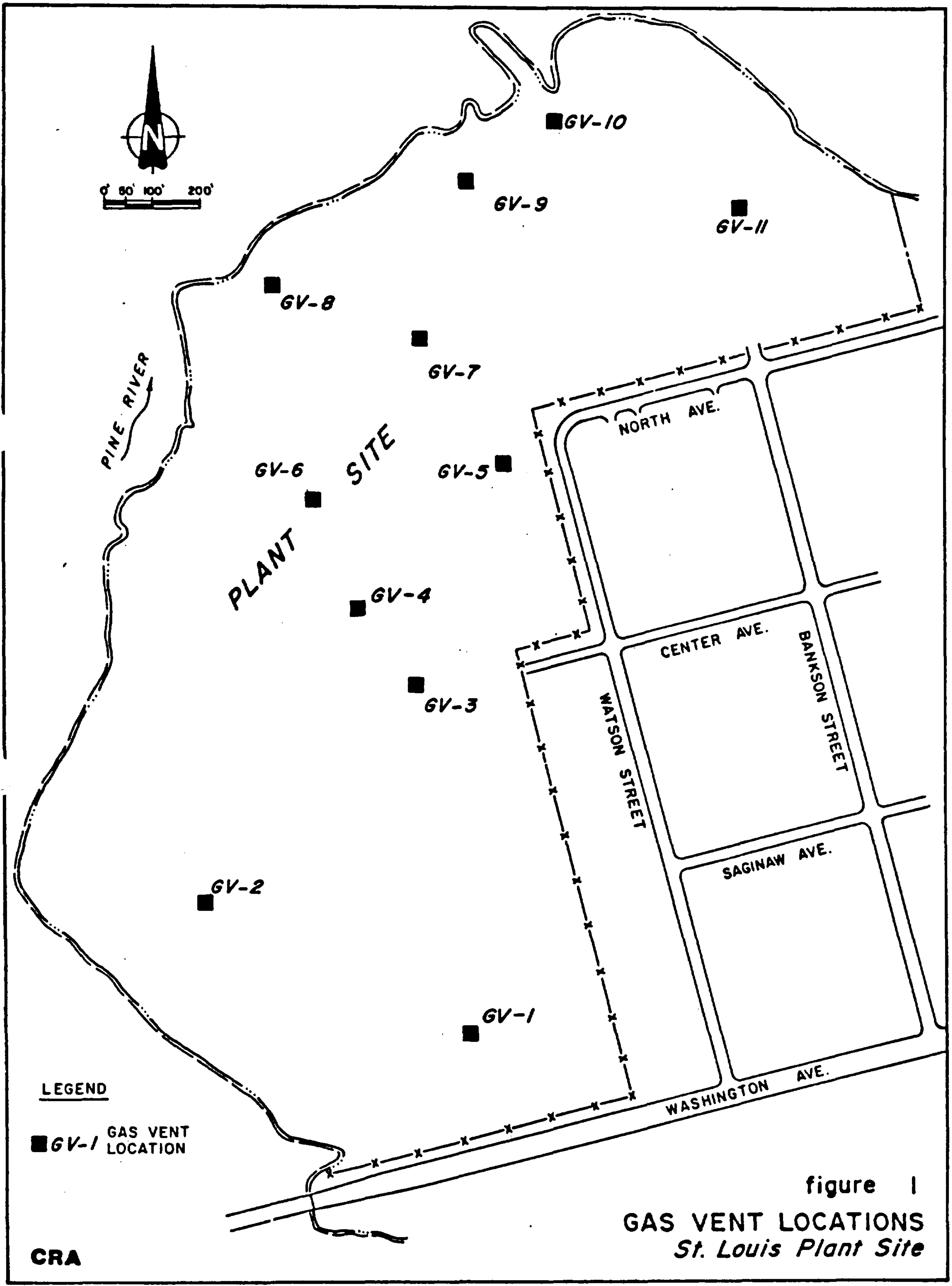

figure 1

GAS VENT LOCATIONS

St. Louis Plant Site

1524 - 19/03/85

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.

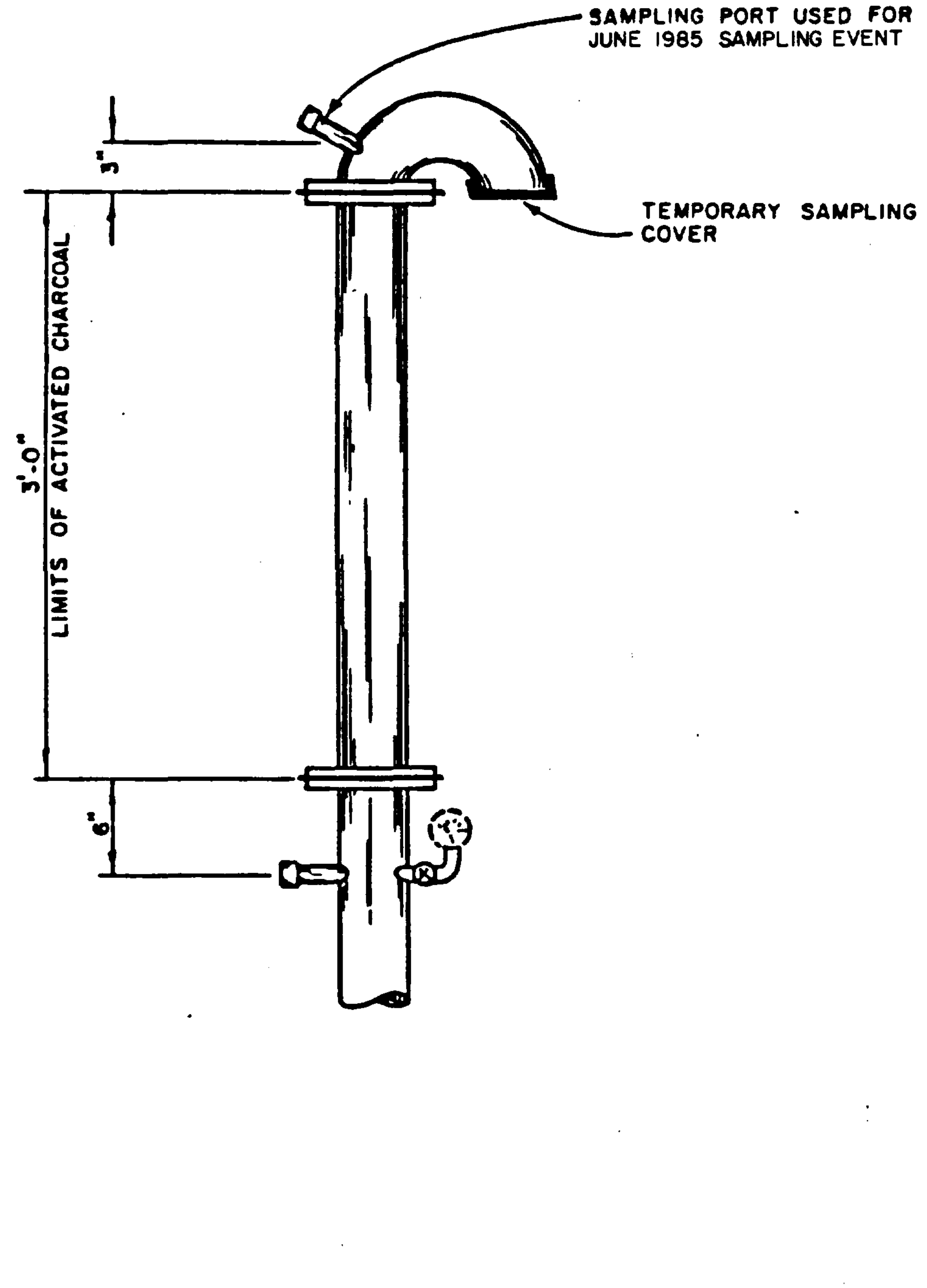

figure 2

ACTIVATED CHARCOAL GAS VENT DETAIL
St. Louis Plant Site

CRA

1624-25/06/85

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.

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 1.0×10^{-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.

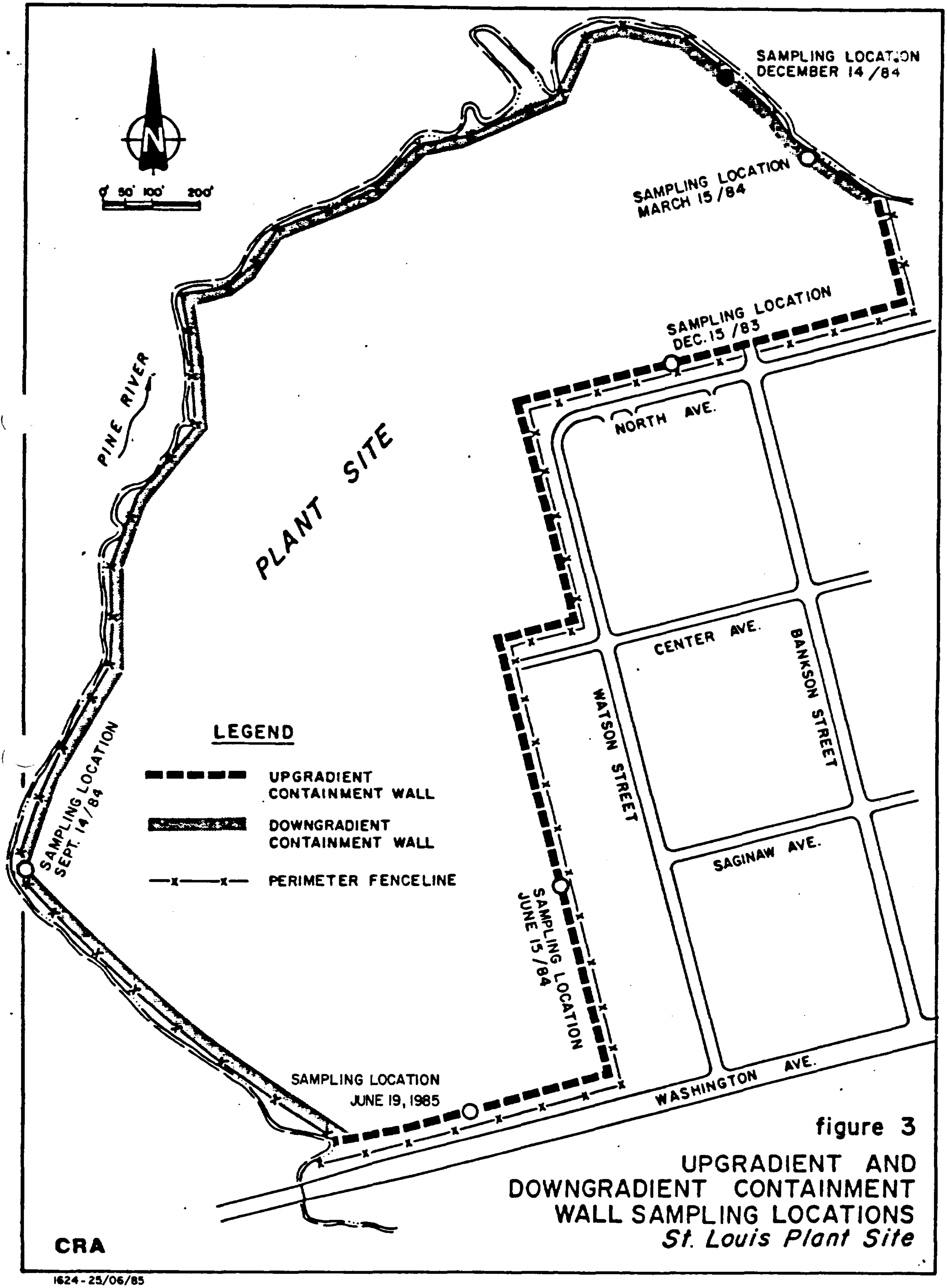

figure 3

UPGRADIENT AND DOWNGRADIENT CONTAINMENT WALL SAMPLING LOCATIONS
St. Louis Plant Site

CRA

1624-25/06/85

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.

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, 1985)	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.

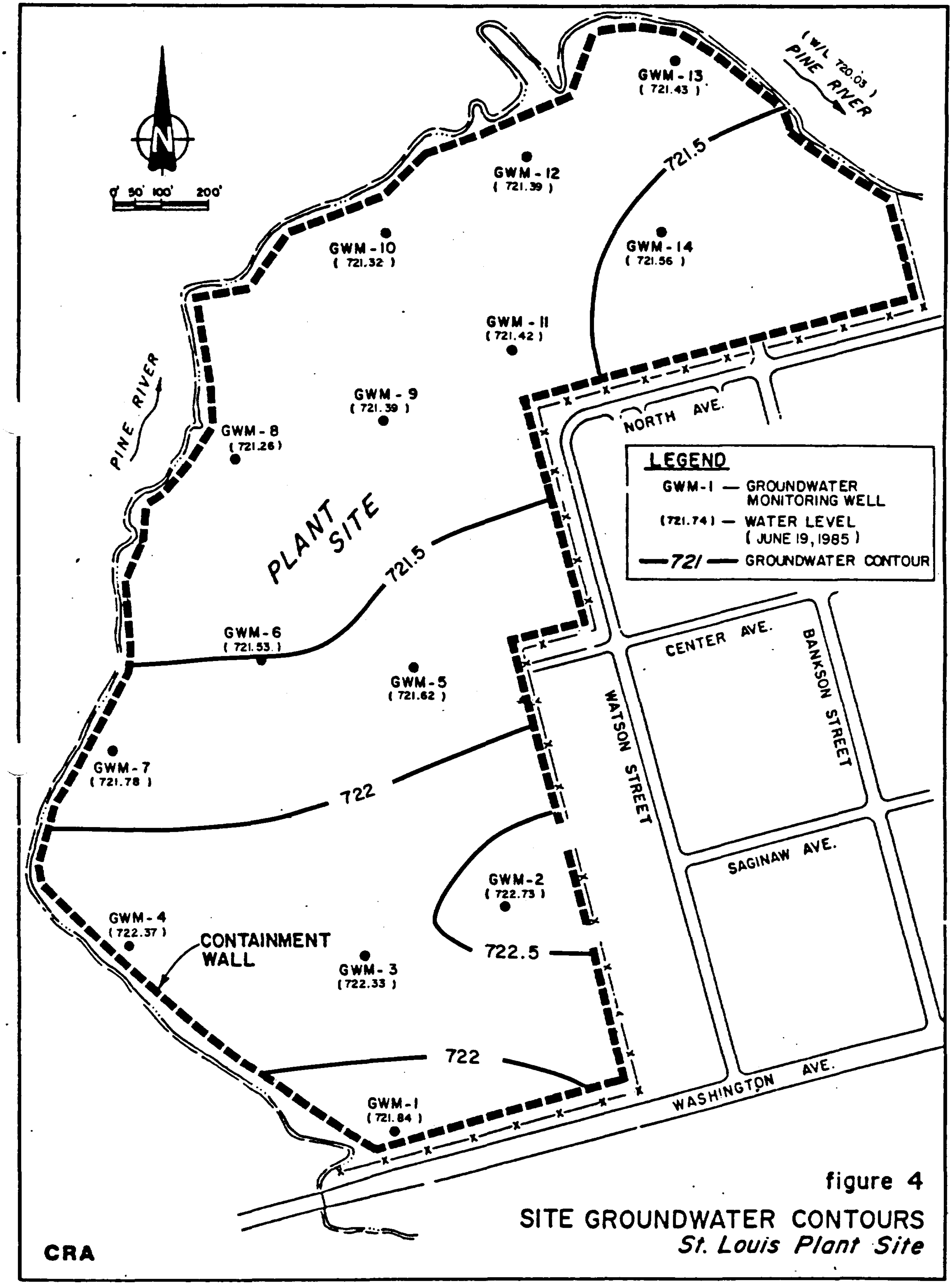

figure 4

SITE GROUNDWATER CONTOURS

St. Louis Plant Site

CRA

1624-25/06/85

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.

APPENDIX A

CHAIN OF CUSTODY

SHEET 1 OF 1

CHAIN OF CUSTODY RECORD	PROJECT NO. 1524	PROJECT NAME: GAS VENT MONITORING PLANT SITE ST. LOUIS, MICHIGAN	VELSICOL CHEMICAL CORPORATION 701 W. WASHINGTON STREET ST. LOUIS, MICHIGAN 48880

SAMPLER'S SIGNATURE (SIGN)

SAMPLE NO.	SEQ NO.	DATE	TIME	FRONT / REAR	TENAX / CHARCOAL	SAMPLE TYPE	NO. OF CONTAINERS	REMARKS
1	1	6/20/81	1040	F	T & C	GAS VENT	2	ANALYSIS:
1	1	6/20	1040	R	T & C	" "	2	CARBON TETRACHLORIDE
2	2	6/20	11.03	F	T & C	" "	2	VINYL CHLORIDE
2	2	6/20	11.03	R	T & C	" "	2	TRICHLOROETHYLENE
3	3	6/20	13.06	F	T & C	" "	2	
3	3	6/20	13.06	R	T & C	" "	2	
4	4	6/20	1345	F	T & C	" "	2	
4	4	6/20	1345	R	T & C	" "	2	
5	5	6/20	1423	F	T & C	" "	2	
5	5	6/20	1423	R	T & C	" "	2	
6	6	6/20	1356	F	T & C	" "	2	
6	6	6/20	1356	R	T & C	" "	2	
						TOTAL NO. OF CONTAINERS	24	

RELINQUISHED BY:	DATE/TIME	RECEIVED BY:	RELINQUISHED BY:	DATE/TIME	RECEIVED BY:
① (SIGN)	6/21, 1400	② (SIGN)	② (SIGN)		③ (SIGN)

RELINQUISHED BY:	DATE/TIME	RECEIVED BY:	RELINQUISHED BY:	DATE/TIME	RECEIVED BY:
③ (SIGN)		④ (SIGN)	④ (SIGN)		⑤ (SIGN)

RELINQUISHED BY:	DATE/TIME	RECEIVED BY:	RELINQUISHED BY:	DATE/TIME	RECEIVED BY:
⑤ (SIGN)		⑥ (SIGN)	⑥ (SIGN)		⑦ (SIGN)

METHOD OF SHIPMENT:	SHIPPED BY:	RECEIVED FOR LABORATORY:	DATE/TIME
FED EXPP.!	Robinson	(SIGN)	

AWB 611891593

SHEET — OF —

CHAIN OF CUSTODY RECORD

PROJECT No. 1524

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

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

SAMPLER'S SIGNATURE (SIGN)

SAMPLE No	SEQ No	DATE	TIME	FRONT / REAR	TENAX / CHARCOAL	SAMPLE TYPE	No OF CONTAINERS	REMARKS
7	7	6/20	1502	F	T & C	GAS VENT	2	Analysis:
7	7	6/20	1502	R	T & C	" "	2	Carbon Tetrachloride
8	8	6/20	1620	F	T & C	" "	2	Vinyl Chloride
8	8	6/20	1620	R	T & C	" "	2	Trichloroethylene
9	9	6/21	1134	F	T & C	" "	2	
9	9	6/21	1134	R	T & C	" "	2	
10	10	6/21	0849	F	T & C	" "	2	
10	10	6/21	0849	R	T & C	" "	2	
11	11	6/21	1009	F	T & C	" "	2	
11	11	6/21	1009	R	T & C	" "	2	
12	12	6/21	1223	F	T & C	" "	2	
12	12	6/21	1223	R	T & C	" "	2	
						TOTAL No. OF CONTAINERS	24	

RELINQUISHED BY:	DATE/TIME	RECEIVED BY:	RELINQUISHED BY:	DATE/TIME	RECEIVED BY:
1 (SIGN)	6/21, 1400	2 (SIGN)	2 (SIGN)		3 (SIGN)
3 (SIGN)		4 (SIGN)	4 (SIGN)		5 (SIGN)
5 (SIGN)		6 (SIGN)	6 (SIGN)		7 (SIGN)

METHOD OF SHIPMENT: Fed Ex P.1

SHIPPED BY: Robinson

RECEIVED FOR LABORATORY: (SIGN)

DATE/TIME

AWB611 891593

SHEET 1 OF 1

# CHAIN OF CUSTODY RECORD	PROJECT NO. 1524	PROJECT NAME: GAS VENT MONITORING PLANT SITE ST. LOUIS, MICHIGAN	VELSICOL CHEMICAL CORPORATION 701 W. WASHINGTON STREET ST. LOUIS, MICHIGAN 48880

SAMPLER'S SIGNATURE ______ (SIGN)

SAMPLE NO.	SEQ NO.	DATE	TIME	FRONT / REAR	TENAX / CHARCOAL	SAMPLE TYPE	NO. OF CONTAINERS	REMARKS
13	13	6/21	1346	F	T & C	Gas Vent	2	Analysis:
13	13	6/21	1346	R	T & C		2	Carbon Tetrachloride
								Vinyl Chloride
								Trichloroethylene
						TOTAL NO. OF CONTAINERS		

RELINQUISHED BY: 1 ______ (SIGN)	DATE/TIME 6/21 / 1400	RECEIVED BY: 2 ______ (SIGN)	RELINQUISHED BY: 2 ______ (SIGN)	DATE/TIME	RECEIVED BY: 3 ______ (SIGN)
RELINQUISHED BY: 3 ______ (SIGN)	DATE/TIME	RECEIVED BY: 4 ______ (SIGN)	RELINQUISHED BY: 4 ______ (SIGN)	DATE/TIME	RECEIVED BY: 5 ______ (SIGN)
RELINQUISHED BY: 5 ______ (SIGN)	DATE/TIME	RECEIVED BY: 6 ______ (SIGN)	RELINQUISHED BY: 6 ______ (SIGN)	DATE/TIME	RECEIVED BY: 7 ______ (SIGN)
METHOD OF SHIPMENT: Fed Exp P.1		SHIPPED BY: Robinson	RECEIVED FOR LABORATORY: ______ (SIGN)		DATE/TIME

AWB 611891593

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.

   $$\text{corrected mg/sample} = \frac{\text{total weight}}{\text{DE}}$$

4. Calculate the concentration of the analyte in air

   $$\text{mg/m}^3 = \frac{\text{Corrected mg} \times 1000 \text{ liters/m}^3}{\text{Air volume Sampled (liters)}}$$

5. Concentration will be reported as ppm, corrected to standard conditions of 25°C and 760 mm Hg

   $$\text{ppm} = \text{mg/m}^3 \times \frac{24.45}{\text{MW}} \times \frac{760}{\text{P}} \times \frac{(\text{T}+273)}{298}$$

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)

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.

FORMULA: Table 1

M.W.: Table 1

HYDROCARBONS, HALOGENATED

METHOD: 1003
ISSUED: 2/14/84

COMPOUNDS: (synonyms in Table 1)	benzyl chloride bromoform carbon tetrachloride chlorobenzene	chlorobromomethane chloroform o-dichlorobenzene p-dichlorobenzene	1,1-dichloroethane 1,2-dichloroethylene ethylene dichloride	hexachloroethane methylchloroform propylene dichloride

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: Table 2
-MAX: Table 2

SHIPMENT: routine

SAMPLE STABILITY: at least 1 week @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: see EVALUATION OF METHOD [1]

BIAS: not significant [1]

OVERALL PRECISION (s_r): see EVALUATION OF METHOD [1]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: compounds above

DESORPTION: 1 mL CS_2, stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURES: Table 2

CARRIER GAS: N_2 or He, 30 mL/min

COLUMN: Table 2; alternates are SP-2100,
SP-2100 with 0.1% Carbowax 1500
or DB-1 fused silica capillary column

CALIBRATION: solutions of analyte in CS_2 with
[illegible]

RANGE: Table 2

ESTIMATED LOD: 0.01 mg per sample [2]

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.
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 $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of analyte in the air volume sampled, V (L):

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

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:

[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 NIOSH [6-10] ACGIH	BP (°C)	VP @ 20 °C	Density (g/mL @ 20 °C)
p-Dichlorobenzene	1,4-$C_6H_4Cl_2$	147.00; 6.01	1,4-dichlorobenzene; CAS #106-46-7	75 ppm — 75 ppm, STEL 110 ppm	174	50 Pa	1.241
1,1-Dichloroethane	CH_3CHCl_2; $C_2H_4Cl_2$	98.96; 4.05	ethylidene chloride; CAS #75-34-3	100 ppm 100 ppm 200 ppm, STEL 250 ppm	57	24.3 kPa	1.174
1,2-Dichloroethylene	ClCH=CHCl; $C_2H_4Cl_2$	96.95; 3.96	acetylene dichloride; 1,2-dichloroethene; CAS #540-59-0	200 ppm 200 ppm 200 ppm, STEL 250 ppm	60 (cis) 47 (trans)	24-35 kPa	1.28
Ethylene dichloride*	$ClCH_2CH_2Cl$; $C_2H_4Cl_2$	98.96; 4.05	1,2-dichloroethane; CAS #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*	CCl_3CCl_3; C_2Cl_6	236.74; 9.68	perchloroethane; CAS #67-72-1	1 ppm (skin) 1 ppm (skin) 10 ppm	187 (sublimes)	30 Pa	2.09
Methylchloroform	CH_3CCl_3; $C_2H_3Cl_3$	133.42; 5.45	1,1,1-trichloroethane; CAS #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	$CH_3CHClCH_2Cl$; $C_3H_6Cl_2$	112.99; 4.62	1,2-dichloropropane CAS #78-87-5	75 ppm 75 ppm 75 ppm, STEL 110 ppm	95	5.3 kPa	1.156 (25 °C)

*Suspect carcinogen.

	Sampling			Measurement				
	Air Sample Volume (L)					t (°C)		
Compound	Min	Max	Breakthrough in Dry Air	Working Range (mg/m³)	Column*	Column Injector Detector	Internal Standard	Range (mg per sample)
1,1-Dichloroethane	1 @ 100 ppm	10	18.3 L [illegible]3 mg/m³	40 to 1215 (10 L)	A	50 100 175	--	0.4 to 12
1,2-Dichloroethylene	0.5 @ 200 ppm	3	5.4 L [illegible]09 mg/m³	80 to 2370 (3 L)	A	60 170 210	---	0.2 to 7
Ethylene dichloride	1 @ 50 ppm	10	29 L [illegible] mg/m³	40 to 1215 (3 L)	A	70 225 250	octane	0.1 to 4
Hexachloroethane	1 @ 1 ppm	10	43 L [illegible] mg/m³	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 [illegible]08 mg/m³	190 to 5700 (3 L)	A	70 225 250	octane	0.6 to 17
Propylene dichloride	1 @ 75 ppm	10	18 L [illegible] mg/m³	35 to 1050 (10 L)	A	80 170 210	n-undecane	0.3 to 10

---

*A = 3 m x 3 mm stainless steel, 10% SP-1000 on [illegible] 100 mesh Supelcoport;
B = 6 m x 3 mm, otherwise same as A;
C = 3 m x 3 mm stainless steel, 10% OV-101 on [illegible] 120 mesh Supelcoport; or
D = 3 m x 6 mm glass, [illegible] SP-2250 on 80/100 [illegible]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 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:

1. 30 ml/min (60 psig) Nitrogen carrier gas flow
2. 35 ml/min (25 psig) Hydrogen gas flow to detector
3. 400 ml/min (60 psig) Air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 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

$$\text{D.E.} = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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 2X 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.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

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.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

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

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liters/cu m)}}{\text{Air Volume Sampled (liters)}}$$

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

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

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," 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.

FORMULA: $CH_2{=}CHCl$; C_2H_3Cl

VINYL CHLORIDE

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/m^3 @ NTP)

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

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

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(2 tandem tubes, each with 150 mg activated coconut charcoal)

FLOW RATE: 0.05 L/min

VOL-MIN: 0.7 L
-MAX: 5 L

SHIPMENT: separate primary and backup tubes and cap each

SAMPLE STABILITY: 10 days @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 1 to 64 mg/m^3 [2]

BIAS: -6% of calculated concentration [2]

OVERALL PRECISION (s_r): 0.06 [2]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: vinyl chloride

DESORPTION: 1 mL carbon disulfide; 30 min

INJECTION ALIQUOT: 5 µL

COLUMN: stainless steel, 6.1 m x 3.2 mm, 10% SE-30 on 80/100 mesh Chromosorb W (AW-DMCS)

CARRIER GAS: He, 40 mL/min

TEMPERATURE-INJECTOR: 230 °C
-DETECTOR: 230 °C
-COLUMN: 60 °C

CALIBRATION: solutions of vinyl chloride in CS_2

RANGE: 0.002 to 0.2 mg per sample [2]

ESTIMATED LOD: 0.00004 mg per sample [2]

PRECISION (s_r): not determined

APPLICABILITY: The working range is 0.4 to 40 mg/m^3 (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].

REAGENTS:

1. Carbon disulfide,* chromatographic quality.
2. Vinyl chloride,*, 99.9%, in lecture bottle fitted with valve and septum.
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 CS_2 in a 10-mL volumetric flask.
   b. Open the valve of the syringe and withdraw the plunger to pull CS_2 into the barrel. (As vinyl chloride dissolves, a vacuum will be created, pulling CS_2 into the syringe.)
   c. Push the solution from the syringe into the flask. Rinse the syringe twice with 1-mL portions of CS_2 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 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.
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.

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.

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/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/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.

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 CS_2, 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 $W_b > W_f/10$, report breakthrough and possible sample loss.
15. Calculate concentration, C, of vinyl chloride in the air volume sampled, V (L):

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

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:

[1] TLVs - Threshold Limit Values for Chemical Substances and Physical Agents in the Work Environment with Intended Changes for 1983-84, 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.

VELSICOL CHEMICAL CORPORATION
ST. LOUIS, MICHIGAN
PROJECT Nº 1524

GAS VENT SAMPLING

DATE OF COLLECTION June 21 /85	**SAMPLER** Robinson	**BAROMETRIC PRESSURE** 29.955														
TEMPERATURE 70.5	**RELATIVE HUMIDITY** 60%	**GAUGE**	1	2	3	4	5	6	7	8	9	10	11
CHARCOAL LOT Nº 120	**TENAX LOT Nº** 271	**READING**							0	0	0	0	0

GAS VENT NUMBER	PUMP NUMBER	SAMPLE NUMBER	SAMPLING TIME START	SAMPLING TIME FINISH	SAMPLING TIME ELAPSED	SAMPLING RATE (cc/min.)	SAMPLE VOLUME (ℓ)
1							
2							
3							
4							
5							
6							
7	9370	9	11.14	1134	20	250	5.0
8	9370	10	8.29	849	20	250	5.0
9	9370	11	9 49	10.09	20	250	5.0
10	9370	12	12.03	12.23	20	250	5.0
11	9370	13	13 26	13 46	20	250	5.0
DUPLICATE							
BLANK							

DATE OF SAMPLE SHIPMENT June 21 1985
METHOD OF SHIPMENT FED. Express AWB 611 891 593

COMMENTS

VELSICOL CHEMICAL CORPORATION
ST. LOUIS, MICHIGAN
PROJECT Nº 1524

GAS VENT SAMPLING

DATE OF COLLECTION June 20/85	SAMPLER D. Robinson	BAROMETRIC PRESSURE 29 935										
TEMPERATURE 63.5	RELATIVE HUMIDITY 58.5	GAUGE	1	2	3	4	5	6	7	8	9	10	11
CHARCOAL LOT Nº 120	TENAX LOT Nº 271	READING	0	0	0	0	0	0					

GAS VENT NUMBER	PUMP NUMBER	SAMPLE NUMBER	SAMPLING TIME START	FINISH	ELAPSED	SAMPLING RATE (cc/min.)	SAMPLE VOLUME (l)
1	9369	1	10.20	10.40	20	250	5.0
2	9369	3	12.46	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							
10							
11							
DUPLICATE	9369	2 (GV1)	10.43	11.03	20	250	5.0
BLANK	9369	6	13.56	1356	20	250	50

DATE OF SAMPLE SHIPMENT June 21 1985

METHOD OF SHIPMENT FED EXPRESS AWB 611 891 593

COMMENTS

VELSICOL CHEMICAL CORPORATION
ST. LOUIS, MICHIGAN
PROJECT Nº 1524

GAS VENT SAMPLING PUMPS CALIBRATION LOG

DATE June 21 1985

CALIBRATED BY D Robinson

PUMP NUMBER	PUMP TYPE	BEFORE SAMPLING						AFTER SAMPLING					AVERAGE			
		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	29.98	250	250	0800	80	53	29.93	250	14.00	70.5	60	29.955	250
9369		61	67	29.98	250	250	0814	80	53	29.93	250	14.10	70.5	60	29.955	250

COMMENTS

VELSICOL CHEMICAL CORPORATION
ST. LOUIS, MICHIGAN
PROJECT Nº 1524

GAS VENT SAMPLING PUMPS CALIBRATION LOG

DATE June 20 1985

CALIBRATED BY D Robinson

PUMP NUMBER	PUMP TYPE	BEFORE SAMPLING						AFTER SAMPLING					AVERAGE			
		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	29.94	250	1710	63.5	58.5	29.935	250
9369		55	83	29 93	250	250	0850	72	34	29.94	250	1725	63.5	58.5	29 935	250

COMMENTS

9-8

VELSICOL CHEMICAL CORPORATION

POST - CONSTRUCTION QUARTERLY MONITORING REPORT

SEPTEMBER 16-17, 1985

Plant Site, St. Louis Michigan

September 1985
Ref. No. 1524

CONESTOGA-ROVERS & ASSOCIATES LIMITED

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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

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

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.

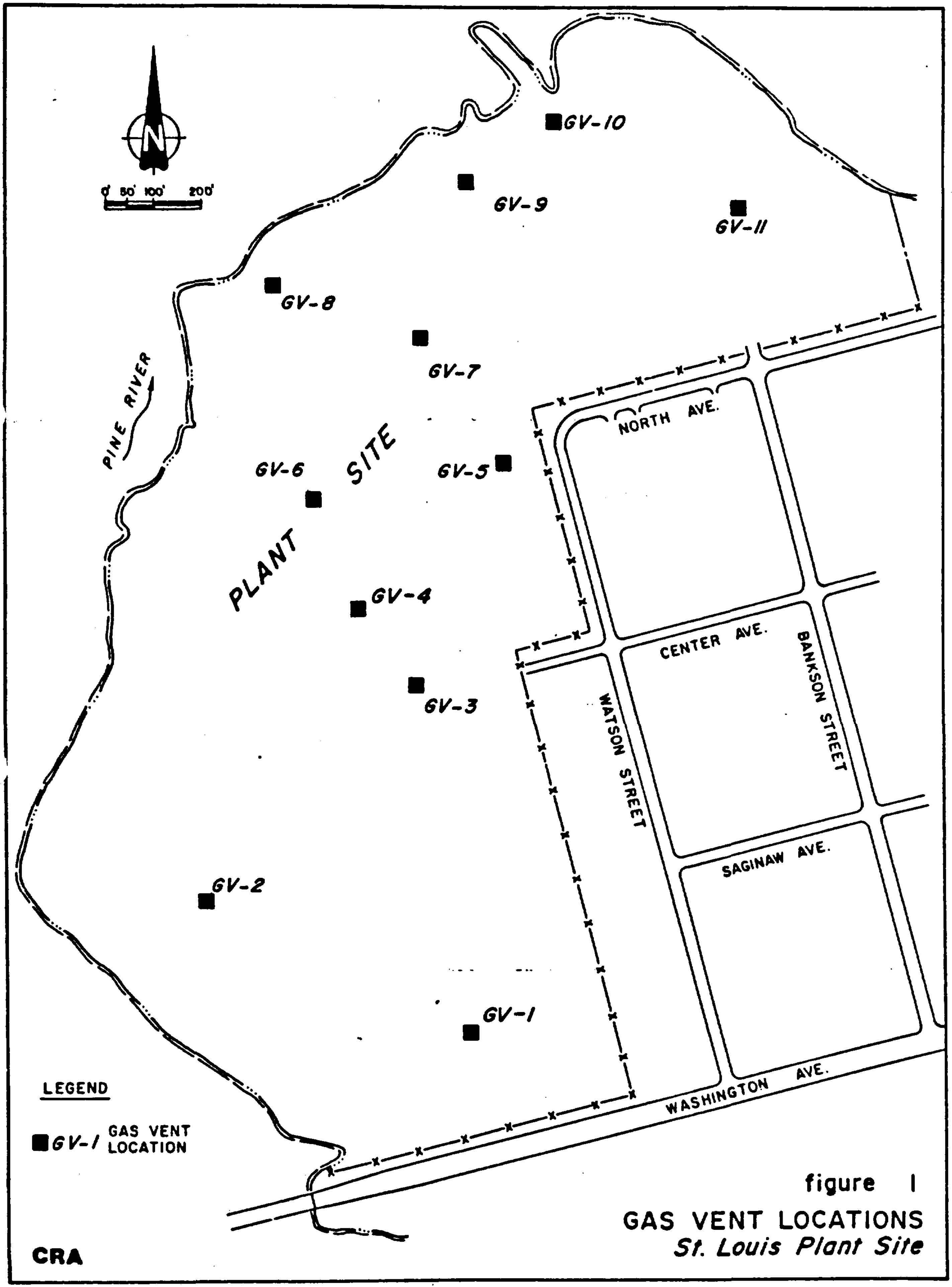

figure 1
GAS VENT LOCATIONS
St. Louis Plant Site

1524-19/03/85

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.

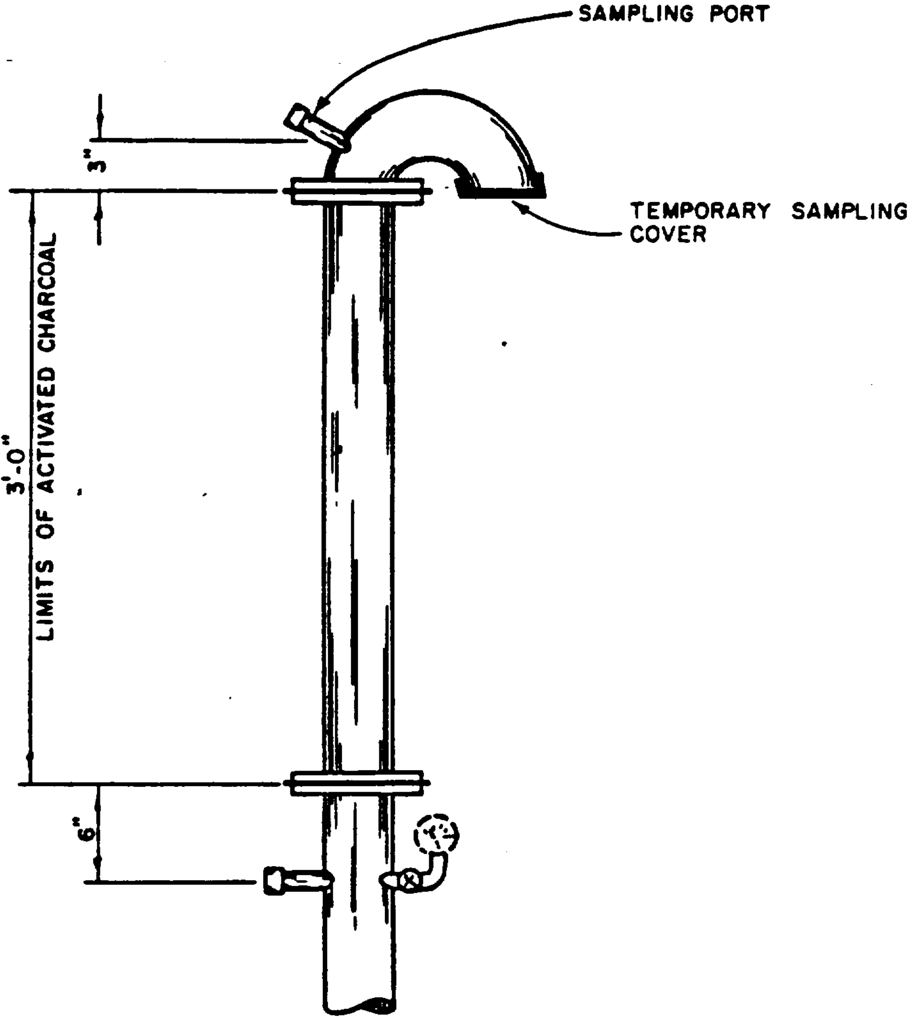

figure 2

ACTIVATED CHARCOAL GAS VENT DETAIL

St. Louis Plant Site

CRA

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.

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 1.0×10^{-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

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

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.

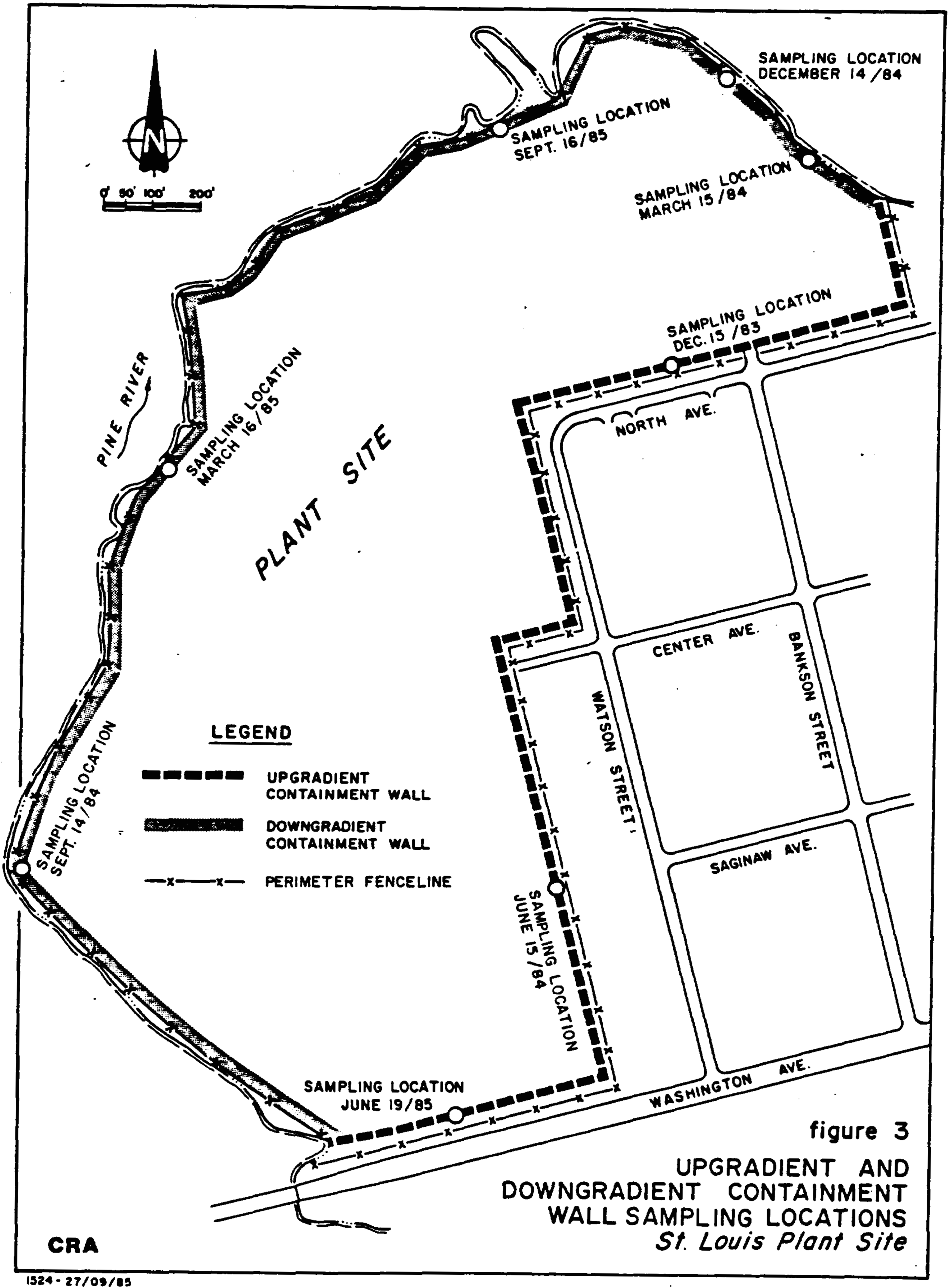

figure 3

UPGRADIENT AND DOWNGRADIENT CONTAINMENT WALL SAMPLING LOCATIONS
St. Louis Plant Site

1524-27/09/85

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 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.

TABLE 1

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

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.

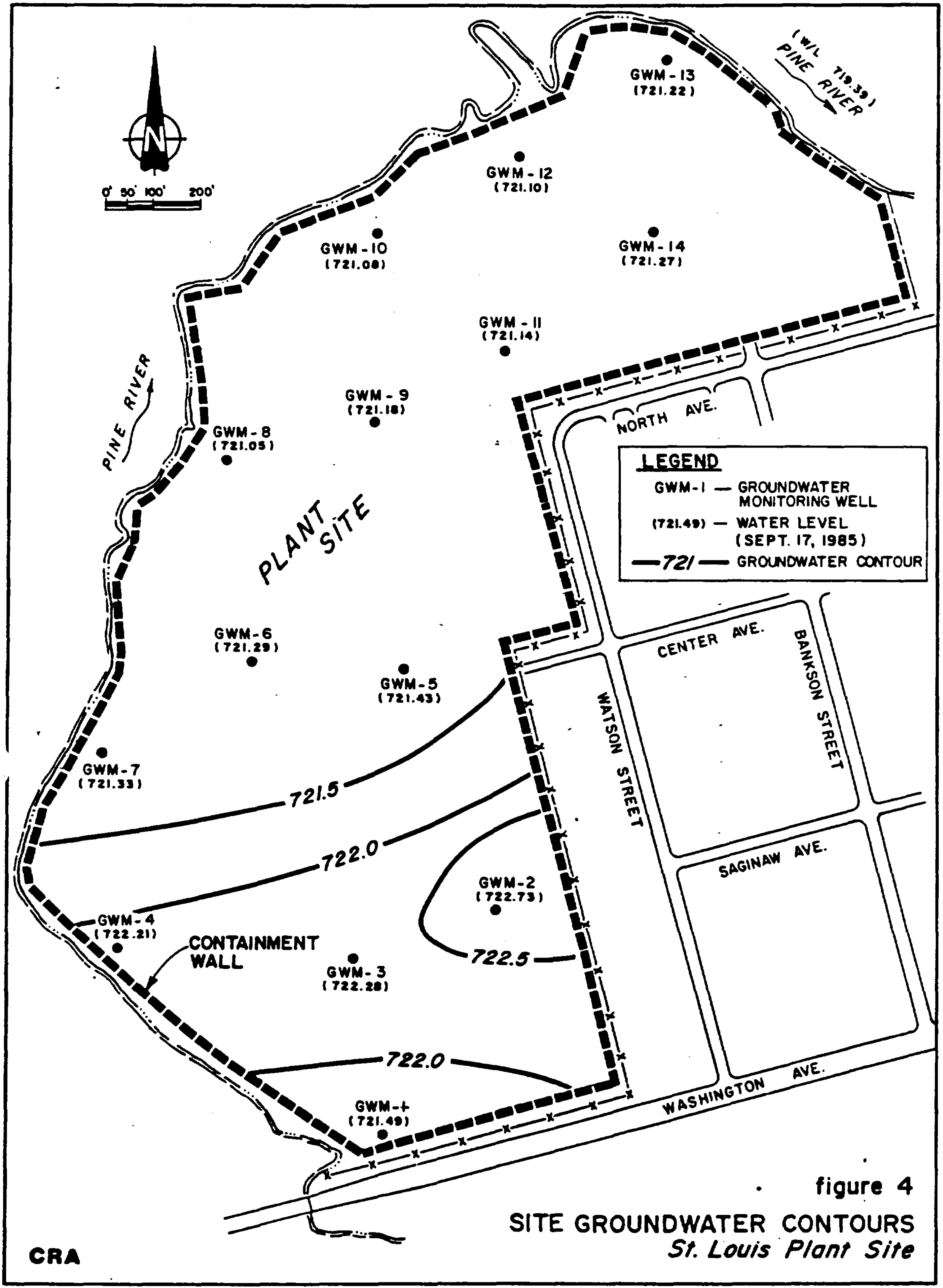

figure 4

SITE GROUNDWATER CONTOURS
St. Louis Plant Site

1524-27/09/85

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 Cull

C. Cull, B.Sc.

R.G. Shepherd, P. Eng.

APPENDIX A

CHAIN OF CUSTODY

SHEET OF

CHAIN OF CUSTODY RECORD	PROJECT NO.	PROJECT NAME:	VELSICOL CHEMICAL CORPORATION
	1524	GAS VENT MONITORING PLANT SITE ST. LOUIS, MICHIGAN	701 W. WASHINGTON STREET ST. LOUIS, MICHIGAN 48880

SAMPLER'S SIGNATURE Catherine A Cull (SIGN)

SAMPLE NO.	SEQ NO.	DATE	TIME	FRONT / REAR	TENAX / CHARCOAL	SAMPLE TYPE	NO. OF CONTAINERS	REMARKS
4	1	9/16	20 min	2@	2@	gas vent samples	4	Desorb w/in
3	2					for TCE vinyl		10 days
7	3					Chloride & carbon		and
9	4					tetrachloride.		analyze
5	5							w/in 30
10	6							days
2	7							
8	8							Keep
6	9	9/17						samples
11	10							refrigerated
12	11							
1	12							
13	13					TOTAL NO. OF CONTAINERS 52		

RELINQUISHED BY:	DATE/TIME	RECEIVED BY:	RELINQUISHED BY:	DATE/TIME	RECEIVED BY:
1 Catherine A Cull (SIGN)		2 E. McGrath (SIGN)	2 (SIGN)		3 (SIGN)
RELINQUISHED BY:	DATE/TIME	RECEIVED BY:	RELINQUISHED BY:	DATE/TIME	RECEIVED BY:
3 (SIGN)		4 (SIGN)	4 (SIGN)		5 (SIGN)
RELINQUISHED BY:	DATE/TIME	RECEIVED BY:	RELINQUISHED BY:	DATE/TIME	RECEIVED BY:
5 (SIGN)		6 (SIGN)	6 (SIGN)		7 (SIGN)

METHOD OF SHIPMENT:	SHIPPED BY:	RECEIVED FOR LABORATORY:	DATE/TIME
		(SIGN)	

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

   $$\text{mg} = \text{mg sample} - \text{mg blank}$$

   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.

   $$\text{corrected mg/sample} = \frac{\text{total weight}}{\text{DE}}$$

4. Calculate the concentration of the analyte in air

   $$\text{mg/m}^3 = \frac{\text{Corrected mg} \times 1000 \text{ liters/m}^3}{\text{Air volume Sampled (liters)}}$$

5. Concentration will be reported as ppm, corrected to standard conditions of 25°C and 760 mm Hg

   $$\text{ppm} = \text{mg/m}^3 \times \frac{24.45}{\text{MW}} \times \frac{760}{\text{P}} \times \frac{(\text{T}+273)}{298}$$

   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)

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.

FORMULA: Table 1

M.W.: Table 1

HYDROCARBONS, HALOGENATED

METHOD: 1003
ISSUED: 2/14/84

COMPOUNDS: (synonyms in Table 1)

benzyl chloride
bromoform
carbon tetrachloride
chlorobenzene
chlorobromomethane
chloroform
o-dichlorobenzene
p-dichlorobenzene
1,1-dichloroethane
1,2-dichloroethylene
ethylene dichloride
hexachloroethane
methylchloroform
propylene dichloride

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: Table 2
-MAX: Table 2

SHIPMENT: routine

SAMPLE STABILITY: at least 1 week @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

[illegible] [1]

BIAS: not significant [1]

OVERALL PRECISION (s_r): see EVALUATION OF METHOD [1]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: compounds above

DESORPTION: 1 mL CS_2, stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURES: Table 2

CARRIER GAS: N_2 or He, 30 mL/min

COLUMN: Table 2; alternates are SP-2100, SP-2100 with 0.1% Carbowax 1500 or DB-1 fused silica capillary column

CALIBRATION: solutions of analyte in CS_2 with [illegible]

RANGE: Table 2

ESTIMATED LOD: 0.01 mg per sample [2]

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.
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 $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of analyte in the air volume sampled, V (L):

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

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:

[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 NIOSH [6-10] ACGIH	BP (°C)	VP @ 20 °C	Density (g/mL @ 20 °C)
p-Dichlorobenzene	1,4-$C_6H_4Cl_2$	147.00; 6.01	1,4-dichlorobenzene; CAS #106-46-7	75 ppm --- 75 ppm, STEL 110 ppm	174	50 Pa	1.241
1,1-Dichloroethane	CH_3CHCl_2; $C_2H_4Cl_2$	98.96; 4.05	ethylidene chloride; CAS #75-34-3	100 ppm 100 ppm 200 ppm, STEL 250 ppm	57	24.3 kPa	1.174
1,2-Dichloroethylene	ClCH=CHCl; $C_2H_4Cl_2$	96.95; 3.96	acetylene dichloride; 1,2-dichloroethene; CAS #540-59-0	200 ppm 200 ppm 200 ppm, STEL 250 ppm	60 (cis) 47 (trans)	24-35 kPa	1.28
Ethylene dichloride*	$ClCH_2CH_2Cl$; $C_2H_4Cl_2$	98.96; 4.05	1,2-dichloroethane; CAS #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*	CCl_3CCl_3; C_2Cl_6	236.74; 9.68	perchloroethane; CAS #67-72-1	1 ppm (skin) 1 ppm (skin) 10 ppm	187 (sublimes)	30 Pa	2.09
Methylchloroform	CH_3CCl_3; $C_2H_3Cl_3$	133.42; 5.45	1,1,1-trichloroethane; CAS #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	$CH_3CHClCH_2Cl$; $C_3H_6Cl_2$	112.99; 4.62	1,2-dichloropropane CAS #78-87-5	75 ppm 75 ppm 75 ppm, STEL 110 ppm	95	5.3 kPa	1.156 (25 °C)

*Suspect carcinogen.

	Sampling				Measurement				
	Air Sample Volume (L)		Breakthrough in Air				t (°C)		
Compound	Min	Max			Working Range (mg/m³)	Column*	Column Injector Detector	Internal Standard	Range (mg per sample)
1,1-Dichloroethane	1 @ 100 ppm	10	18.3 L [illegible]	[illegible] mg/m³	40 to 1215 (10 L)	A	50 100 175	--	0.4 to 12
1,2-Dichloroethylene	0.5 @ 200 ppm	3	5.4 L [illegible]	[illegible]09 mg/m³	80 to 2370 (3 L)	A	60 170 210	---	0.2 to 7
Ethylene dichloride	1 @ 50 ppm	10	29 L [illegible]	[illegible] mg/m³	40 to 1215 (3 L)	A	70 225 250	octane	0.1 to 4
Hexachloroethane	1 @ 1 ppm	10	43 L [illegible]	[illegible] mg/m³	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 [illegible]	[illegible]08 mg/m³	190 to 5700 (3 L)	A	70 225 250	octane	0.6 to 17
Propylene dichloride	1 @ 75 ppm	10	10 L [illegible]	[illegible] mg/m³	35 to 1050 (10 L)	A	80 170 210	n-undecane	0.3 to 10

---

*A = 3 m x 3 mm stainless steel, 10% SP-1000 on [illegible] 100 mesh Supelcoport;
B = 6 m x 3 mm, otherwise same as A;
C = 3 m x 3 mm stainless steel, 10% OV-101 on [illegible] 120 mesh Supelcoport; or
D = 3 m x 6 mm glass, [illegible] SP-2250 on 80/100 mesh Supelcoport.

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:

1. 30 ml/min (60 psig) Nitrogen carrier gas flow
2. 35 ml/min (25 psig) Hydrogen gas flow to detector
3. 400 ml/min (60 psig) Air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 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

$$\text{D.E.} = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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 2X 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.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

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.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

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

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liters/cu m)}}{\text{Air Volume Sampled (liters)}}$$

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

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

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," 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.

VINYL CHLORIDE

FORMULA: $CH_2=CHCl$; C_2H_3Cl

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

SAMPLER: SOLID SORBENT TUBE
(2 tandem tubes, each with 150 mg activated coconut charcoal)

FLOW RATE: 0.05 L/min

VOL-MIN: 0.7 L
-MAX: 5 L

SHIPMENT: separate primary and backup tubes and cap each

SAMPLE STABILITY: 10 days @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 1 to 64 mg/m³ [2]

BIAS: -6% of calculated concentration [2]

OVERALL PRECISION (s_r): 0.06 [2]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: vinyl chloride

DESORPTION: 1 mL carbon disulfide; 30 min

INJECTION ALIQUOT: 5 µL

COLUMN: stainless steel, 6.1 m x 3.2 mm, 10% SE-30 on 80/100 mesh Chromosorb W (AW-DMCS)

CARRIER GAS: He, 40 mL/min

TEMPERATURE-INJECTOR: 230 °C
-DETECTOR: 230 °C
-COLUMN: 60 °C

CALIBRATION: solutions of vinyl chloride in CS_2

RANGE: 0.002 to 0.2 mg per sample [2]

ESTIMATED LOD: 0.00004 mg per sample [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].

REAGENTS:

1. Carbon disulfide,* chromatographic quality.
2. Vinyl chloride,*, 99.9%, in lecture bottle fitted with valve and septum.
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 CS_2 in a 10-mL volumetric flask.
   b. Open the valve of the syringe and withdraw the plunger to pull CS_2 into the barrel. (As vinyl chloride dissolves, a vacuum will be created, pulling CS_2 into the syringe.)
   c. Push the solution from the syringe into the flask. Rinse the syringe twice with 1-mL portions of CS_2 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 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.
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.

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.

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/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/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.

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 CS_2, 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 $W_b > W_f/10$, 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-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] TLVs - Threshold Limit Values for Chemical Substances and Physical Agents in the Work Environment with Intended Changes for 1983-84, 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.

VELSICOL CHEMICAL CORPORATION
ST. LOUIS, MICHIGAN
PROJECT Nº 1524

GAS VENT SAMPLING

DATE OF COLLECTION 16 SEPTEMBER 1985	SAMPLER CA CULL	BAROMETRIC PRESSURE 30.17
TEMPERATURE 68°F	RELATIVE HUMIDITY 50%	
CHARCOAL LOT Nº 120	TENAX LOT Nº 220	

GAUGE	1	2	3	4	5	6	7	8	9	10	11
READING	0	0	0	0	0	0	0	0	0	0	0

GAS VENT NUMBER	PUMP NUMBER	SAMPLE NUMBER	SAMPLING TIME START	SAMPLING TIME FINISH	SAMPLING TIME ELAPSED	SAMPLING RATE (cc/min.)	SAMPLE VOLUME (ℓ)
1	1	4	9/16 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	9	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	1	2	16:04	16:24	20	250	5
9	2	6	9/17 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 SHIPMENT Federal Express

COMMENTS

VELSICOL CHEMICAL CORPORATION
ST. LOUIS, MICHIGAN
PROJECT Nº 1524

GAS VENT SAMPLING PUMPS CALIBRATION LOG

DATE 16 SEPTEMBER 1985 **CALIBRATED BY** C A CULL

PUMP NUMBER	PUMP TYPE	BEFORE SAMPLING TEMP. (°F)	HUMIDITY (%)	BAROM. PRESSURE (Inches Hg)	INITIAL FLOW (cc/min.)	CAL. FLOW (cc/min.)	24-HR. TIME	AFTER SAMPLING TEMP. (°F)	HUMIDITY (%)	BAROM. PRESSURE (Inches Hg)	FLOW (cc/min.)	24-HR. TIME	AVERAGE TEMP. (°F)	HUMIDITY (%)	BAROM. PRESSURE (Inches Hg)	FLOW (cc/min.)
1	GILIAN (A)	69	42	30.24	250	250	12:50	59	~~3~~ 67	30.11	250	10:15	68°	50	30.17	250
	(B)				240	250	12:53				250	10:17				250
2	GILIAN (A)				250	250	12:56				250	10:20				250
	(B)				260	250	12:58				250	10:23				250

COMMENTS

VELSICOL CHEMICAL CORPORATION

POST - CONSTRUCTION QUARTERLY MONITORING REPORT

DECEMBER 14-15 , 1985

Plant Site, St. Louis Michigan

December 1985
Ref. No. 1524

CONESTOGA-ROVERS & ASSOCIATES LIMITED

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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

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.

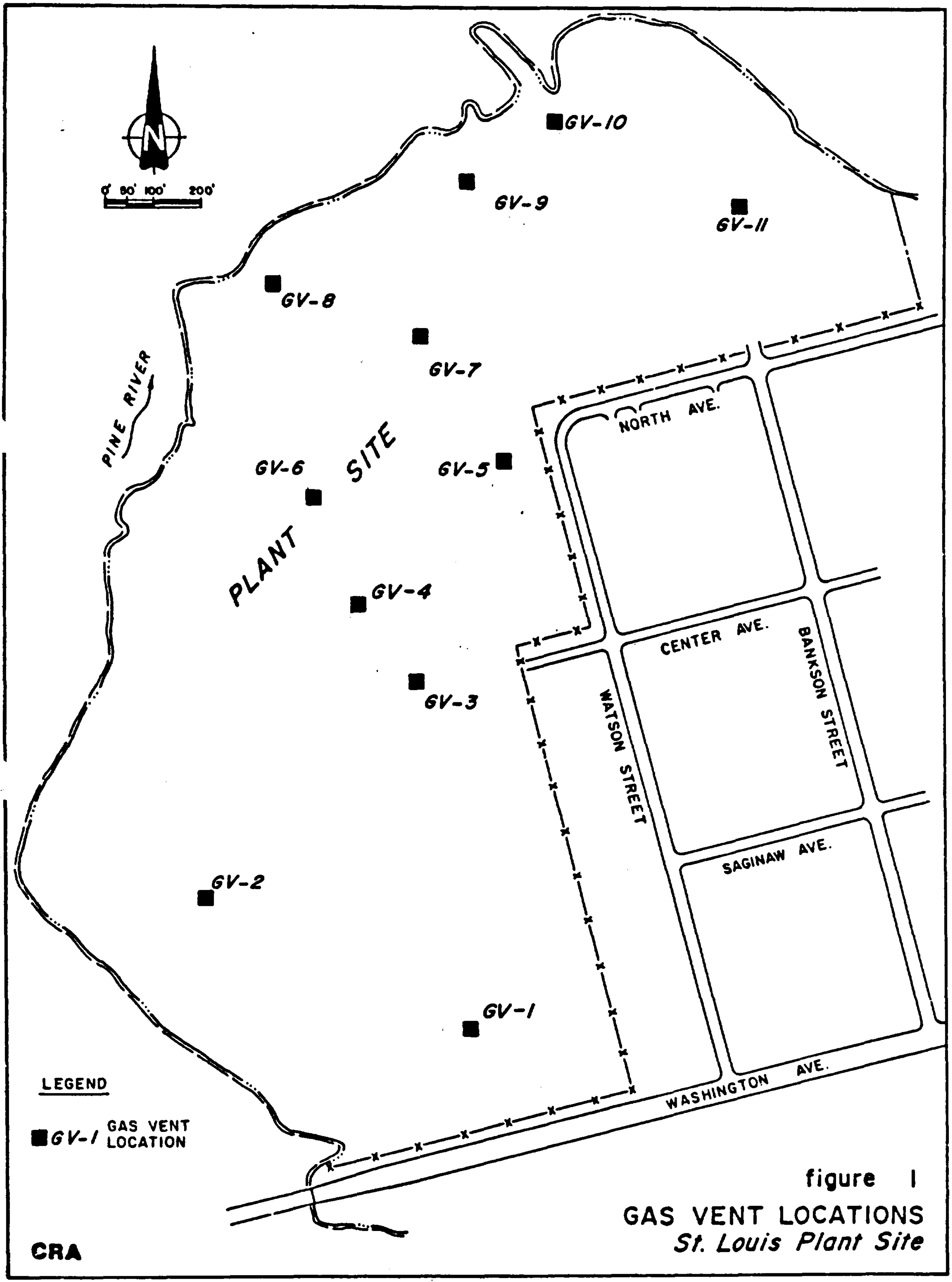

figure 1

GAS VENT LOCATIONS

St. Louis Plant Site

1524-19/12/85

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.

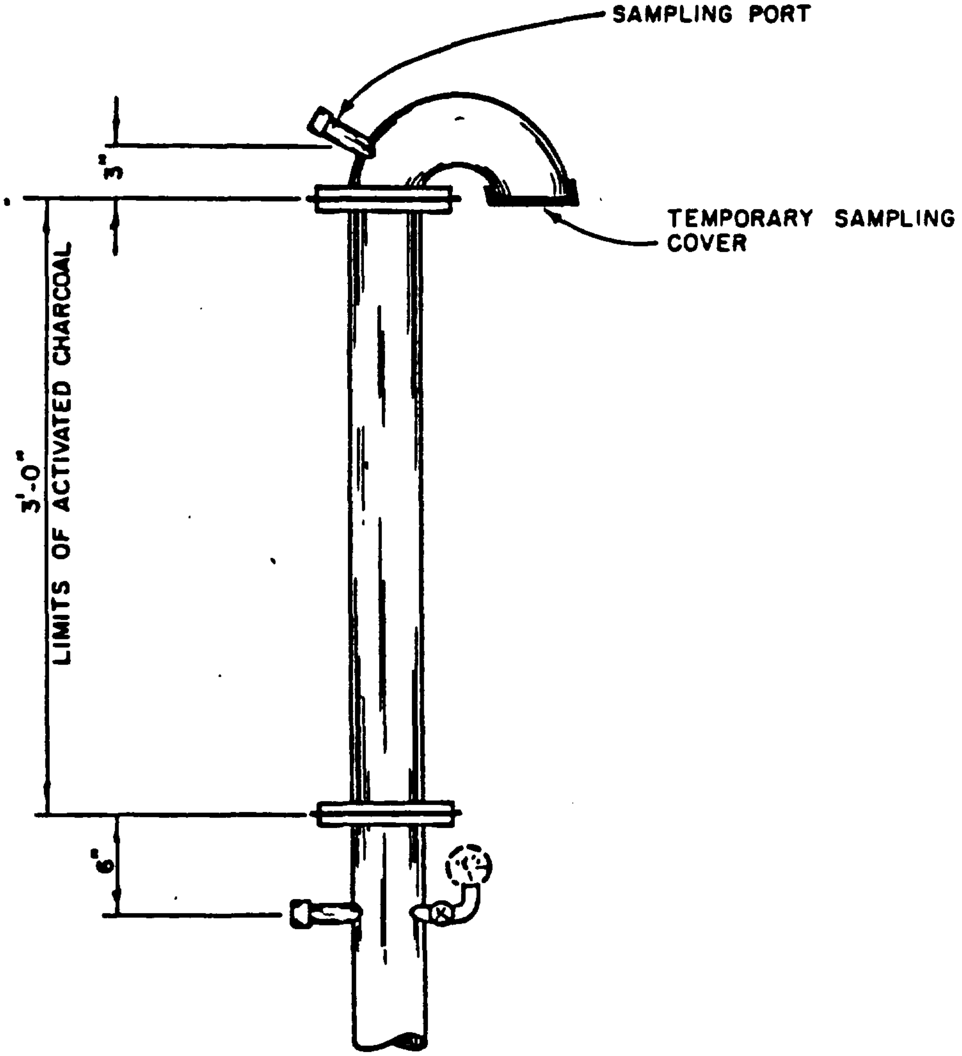

figure 2

ACTIVATED CHARCOAL GAS VENT DETAIL

St. Louis Plant Site

CRA

2.2.1 Sample Storage and Shipment

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

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

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.

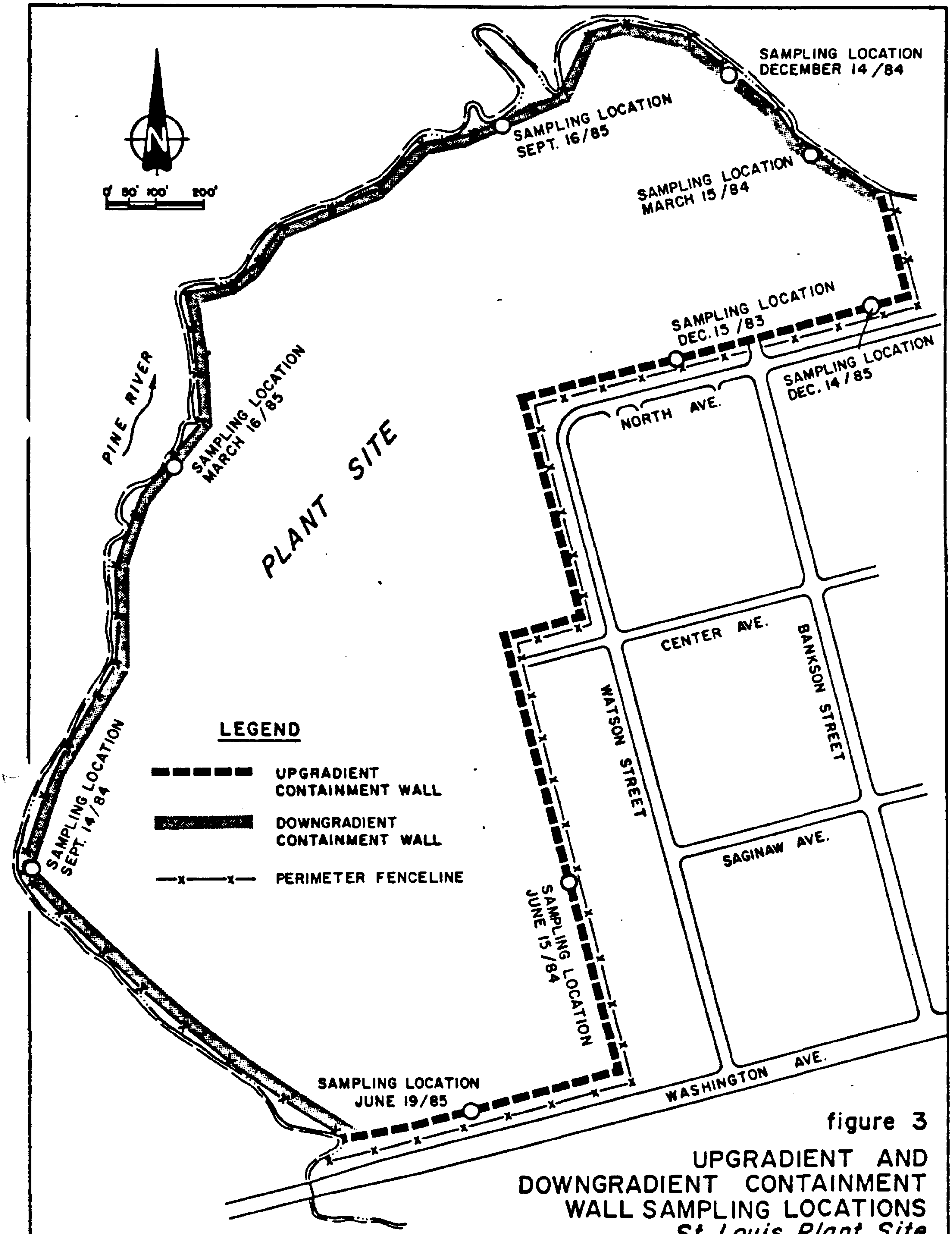

figure 3

UPGRADIENT AND DOWNGRADIENT CONTAINMENT WALL SAMPLING LOCATIONS *St. Louis Plant Site*

CRA

1524- 19/12/85

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 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

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

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.

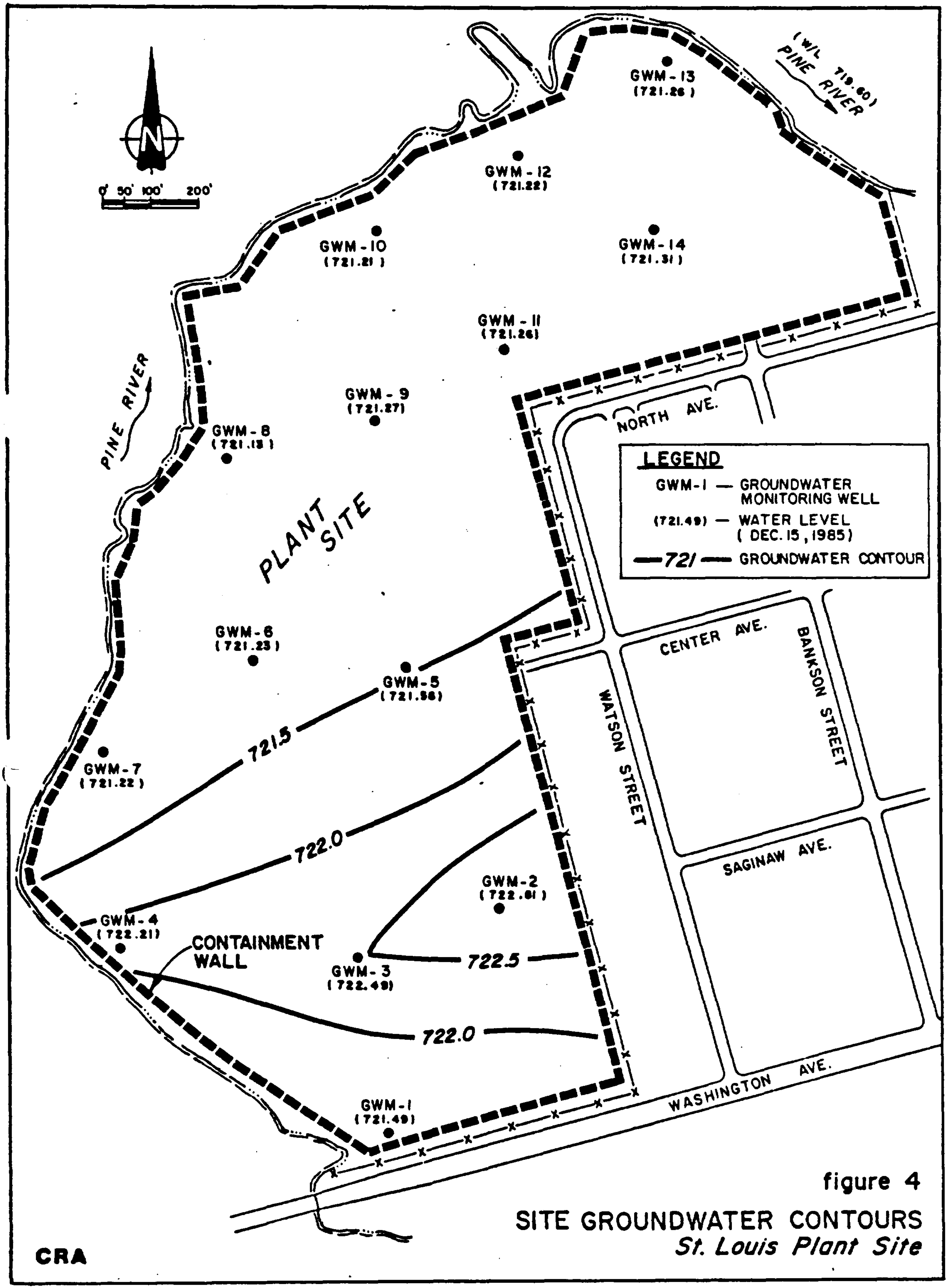

figure 4

SITE GROUNDWATER CONTOURS
St. Louis Plant Site

1524-19/12/85

5.0 SUMMARY

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

D. Robinson

R.G. Shepherd, P. Eng.

APPENDIX A

CHAIN OF CUSTODY

SHEET 1 OF 2

CHAIN OF CUSTODY RECORD	PROJECT NO. 1524	PROJECT NAME: GAS VENT MONITORING PLANT SITE ST. LOUIS, MICHIGAN	VELSICOL CHEMICAL CORPORATION 701 W. WASHINGTON STREET ST. LOUIS, MICHIGAN 48880

SAMPLER'S SIGNATURE (SIGN)

SAMPLE NO	SEQ NO	DATE	TIME	FRONT / REAR	TENAX / CHARCOAL	SAMPLE TYPE	NO OF CONTAINERS	REMARKS
1	1	12/14	3.29	2/2	2/2	GAS VENT	4	
2	2	12/14	3.46	2/2	2/2	" "	4	
3	3	12/14	4.06	2/2	2/2	" "	4	
4	4	12/14	4-31	2/2	2/2	" "	4	
5	5	12/15	1.00	2/2	2/2	" "	4	
6	6	12/15	1.04	2/2	2/2	" "	4	
7	8	12/15	1.37	2/2	2/2	" "	4	
8	7	12/15	1.45	2/2	2/2	" "	4	
9	9	2.15	12/15	2/2	2/2	" "	4	
10	10	12/15	2.22	2/2	2/2	" "	4	
11	11	12/15	2.26	2/2	2/2	" "	4	
12	12	12/15	2.42	2/2	2/2	" "	4	
						TOTAL NO. OF CONTAINERS		

RELINQUISHED BY: 1 (SIGN)	DATE/TIME 12/15/85	RECEIVED BY: ② (SIGN)	RELINQUISHED BY: 2 (SIGN)	DATE / TIME	RECEIVED BY: ③ (SIGN)
RELINQUISHED BY: 3 (SIGN)	DATE/TIME	RECEIVED BY: ④ (SIGN)	RELINQUISHED BY: 4 (SIGN)	DATE/TIME	RECEIVED BY: ⑤ (SIGN)
RELINQUISHED BY: 5 (SIGN)	DATE/TIME	RECEIVED BY: ⑥ (SIGN)	RELINQUISHED BY: 6 (SIGN)	DATE/TIME	RECEIVED BY: ⑦ (SIGN)

METHOD OF SHIPMENT:	SHIPPED BY:	RECEIVED FOR LABORATORY: (SIGN)	DATE/TIME

7

SHEET ___ OF ___

CHAIN OF CUSTODY RECORD

PROJECT Nº 1524

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

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

SAMPLER'S SIGNATURE ______________________ (SIGN)

SAMPLE Nº	SEQ Nº	DATE	TIME	FRONT / REAR	TENAX / CHARCOAL	SAMPLE TYPE	Nº OF CONTAINERS	REMARKS
13	13	12/15	3.00	2/2	2/2	Gas Vent	4.	
						TOTAL Nº. OF CONTAINERS	52	

RELINQUISHED BY:	DATE/TIME	RECEIVED BY:	RELINQUISHED BY:	DATE/TIME	RECEIVED BY:
1 ______ (SIGN)		② ______ (SIGN)	2 ______ (SIGN)		③ ______ (SIGN)
RELINQUISHED BY:	DATE/TIME	RECEIVED BY:	RELINQUISHED BY:	DATE/TIME	RECEIVED BY:
3 ______ (SIGN)		④ ______ (SIGN)	4 ______ (SIGN)		⑤ ______ (SIGN)
RELINQUISHED BY:	DATE/TIME	RECEIVED BY:	RELINQUISHED BY:	DATE/TIME	RECEIVED BY:
5 ______ (SIGN)		⑥ ______ (SIGN)	6 ______ (SIGN)		⑦ ______ (SIGN)

METHOD OF SHIPMENT: FED Exp.

SHIPPED BY: G. DeGear

RECEIVED FOR LABORATORY: ______ (SIGN)

DATE/TIME

AWB 650-405-221

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.

   $$\text{corrected mg/sample} = \frac{\text{total weight}}{\text{DE}}$$

4. Calculate the concentration of the analyte in air

   $$\text{mg/m}^3 = \frac{\text{Corrected mg} \times 1000 \text{ liters/m}^3}{\text{Air volume Sampled (liters)}}$$

5. Concentration will be reported as ppm, corrected to standard conditions of 25°C and 760 mm Hg

   $$\text{ppm} = \text{mg/m}^3 \times \frac{24.45}{\text{MW}} \times \frac{760}{\text{P}} \times \frac{(\text{T}+273)}{298}$$

   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)

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.

FORMULA: Table 1

M.W.: Table 1

HYDROCARBONS, HALOGENATED

METHOD: 1003
ISSUED: 2/14/84

COMPOUNDS: (synonyms in Table 1)

- benzyl chloride
- bromoform
- carbon tetrachloride
- chlorobenzene
- chlorobromomethane
- chloroform
o-dichlorobenzene
p-dichlorobenzene
- 1,1-dichloroethane
- 1,2-dichloroethylene
- ethylene dichloride
- hexachloroethane
- methylchloroform
- propylene dichloride

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: Table 2
-MAX: Table 2

SHIPMENT: routine

SAMPLE STABILITY: at least 1 week @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

[illegible]

BIAS: not significant [1]

OVERALL PRECISION (s_r): see EVALUATION OF METHOD [1]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: compounds above

DESORPTION: 1 mL CS_2, stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURES: Table 2

CARRIER GAS: N_2 or He, 30 mL/min

COLUMN: Table 2; alternates are SP-2100, SP-2100 with 0.1% Carbowax 1500 or DB-1 fused silica capillary column

CALIBRATION: solutions of analyte in CS_2 with [illegible]

RANGE: Table 2

ESTIMATED LOD: 0.01 mg per sample [2]

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.
   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 $W_b > W_f/10$, report breakthrough and possible sample loss.

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

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

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:

[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 NIOSH [6-10] ACGIH	BP (°C)	VP @ 20 °C	Density (g/mL @ 20 °C)
p-Dichlorobenzene	1,4-$C_6H_4Cl_2$	147.00; 6.01	1,4-dichlorobenzene; CAS #106-46-7	75 ppm --- 75 ppm, STEL 110 ppm	174	50 Pa	1.241
1,1-Dichloroethane	CH_3CHCl_2; $C_2H_4Cl_2$	98.96; 4.05	ethylidene chloride; CAS #75-34-3	100 ppm 100 ppm 200 ppm, STEL 250 ppm	57	24.3 kPa	1.174
1,2-Dichloroethylene	ClCH=CHCl; $C_2H_4Cl_2$	96.95; 3.96	acetylene dichloride; 1,2-dichloroethene; CAS #540-59-0	200 ppm 200 ppm 200 ppm, STEL 250 ppm	60 (cis) 47 (trans)	24-35 kPa	1.28
Ethylene dichloride*	$ClCH_2CH_2Cl$; $C_2H_4Cl_2$	98.96; 4.05	1,2-dichloroethane; CAS #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*	CCl_3CCl_3; C_2Cl_6	236.74; 9.68	perchloroethane; CAS #67-72-1	1 ppm (skin) 1 ppm (skin) 10 ppm	187 (sublimes)	30 Pa	2.09
Methylchloroform	CH_3CCl_3; $C_2H_3Cl_3$	133.42; 5.45	1,1,1-trichloroethane; CAS #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	$CH_3CHClCH_2Cl$; $C_3H_6Cl_2$	112.99; 4.62	1,2-dichloropropane CAS #78-87-5	75 ppm 75 ppm 75 ppm, STEL 110 ppm	95	5.3 kPa	1.156 (25 °C)

*Suspect carcinogen.

	Sampling			Measurement				
	Air Sample Volume (L)					t (°C)		
Compound	Min	Max	Breakthrough in [illegible] Air	Working Range (mg/m³)	Column*	Column Injector Detector	Internal Standard	Range (mg per sample)
1,1-Dichloroethane	1 @ 100 ppm	10	18.3 L [illegible]3 mg/m³	40 to 1215 (10 L)	A	50 100 175	--	0.4 to 12
1,2-Dichloroethylene	0.5 @ 200 ppm	3	5.4 L [illegible]09 mg/m³	80 to 2370 (3 L)	A	60 170 210	---	0.2 to 7
Ethylene dichloride	1 @ 50 ppm	10	29 L [illegible] mg/m³	40 to 1215 (3 L)	A	70 225 250	octane	0.1 to 4
Hexachloroethane	1 @ 1 ppm	10	43 L [illegible] mg/m³	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 [illegible]08 mg/m³	190 to 5700 (3 L)	A	70 225 250	octane	0.6 to 17
Propylene dichloride	1 @ 75 ppm	10	18 L [illegible] mg/m³	35 to 1050 (10 L)	A	80 170 210	n-undecane	0.3 to 10

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*A = 3 m x 3 mm stainless steel, 10% SP-1000 [illegible] 100 mesh Supelcoport;
B = 6 m x 3 mm, otherwise same as A;
C = 3 m x 3 mm stainless steel, 10% OV-101 [illegible] 120 mesh Supelcoport; or
D = 3 m x 6 mm glass, [illegible] SP-2250 on 80/100 [illegible]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 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:

1. 30 ml/min (60 psig) Nitrogen carrier gas flow
2. 35 ml/min (25 psig) Hydrogen gas flow to detector
3. 400 ml/min (60 psig) Air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 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

$$\text{D.E.} = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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 2X 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.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

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.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

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

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liters/cu m)}}{\text{Air Volume Sampled (liters)}}$$

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

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

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," 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.

VINYL CHLORIDE

FORMULA: $CH_2{=}CHCl$; C_2H_3Cl

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

SAMPLER: SOLID SORBENT TUBE
(2 tandem tubes, each with 150 mg activated coconut charcoal)

FLOW RATE: 0.05 L/min

VOL-MIN: 0.7 L
-MAX: 5 L

SHIPMENT: separate primary and backup tubes and cap each

SAMPLE STABILITY: 10 days @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 1 to 64 mg/m³ [2]

BIAS: -6% of calculated concentration [2]

OVERALL PRECISION (s_r): 0.06 [2]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: vinyl chloride

DESORPTION: 1 mL carbon disulfide; 30 min

INJECTION ALIQUOT: 5 µL

COLUMN: stainless steel, 6.1 m x 3.2 mm, 10% SE-30 on 80/100 mesh Chromosorb W (AW-DMCS)

CARRIER GAS: He, 40 mL/min

TEMPERATURE-INJECTOR: 230 °C
-DETECTOR: 230 °C
-COLUMN: 60 °C

CALIBRATION: solutions of vinyl chloride in CS_2

RANGE: 0.002 to 0.2 mg per sample [2]

ESTIMATED LOD: 0.00004 mg per sample [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].

REAGENTS:

1. Carbon disulfide,* chromatographic quality.
2. Vinyl chloride,*, 99.9%, in lecture bottle fitted with valve and septum.
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 CS_2 in a 10-mL volumetric flask.
   b. Open the valve of the syringe and withdraw the plunger to pull CS_2 into the barrel. (As vinyl chloride dissolves, a vacuum will be created, pulling CS_2 into the syringe.)
   c. Push the solution from the syringe into the flask. Rinse the syringe twice with 1-mL portions of CS_2 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 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.
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.

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.

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/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.

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 CS_2, 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 $W_b > W_f/10$, report breakthrough and possible sample loss.
15. Calculate concentration, C, of vinyl chloride in the air volume sampled, V (L):

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

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:

[1] TLVs - Threshold Limit Values for Chemical Substances and Physical Agents in the Work Environment with Intended Changes for 1983-84, 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.

VELSICOL CHEMICAL CORPORATION
ST. LOUIS, MICHIGAN
PROJECT Nº 1524

GAS VENT SAMPLING PUMPS CALIBRATION LOG

DATE DEC 14-15, 1985	**CALIBRATED BY** D. ROBINSON

PUMP NUMBER	PUMP TYPE	BEFORE SAMPLING 12/14/85						AFTER SAMPLING 12/15/85					AVERAGE			
		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	GILIAN 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	250	1530	19	31.5	30.03	250
9370	GILIAN 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	250	1530	19	31.5	30.03	250

a) CHARCOAL
b) TENAX

COMMENTS

VELSICOL CHEMICAL CORPORATION
ST. LOUIS, MICHIGAN
PROJECT Nº 1524

GAS VENT SAMPLING

DATE OF COLLECTION 12/14 - 12/15	SAMPLER Robinson	BAROMETRIC PRESSURE 29.90
TEMPERATURE 20°	RELATIVE HUMIDITY 30 %	
CHARCOAL LOT Nº 120	TENAX LOT Nº 271	

GAUGE	1	2	3	4	5	6	7	8	9	10	11
READING	0	0	0	0	0	0	0	0	0	0	0

GAS VENT NUMBER	PUMP NUMBER	SAMPLE NUMBER	SAMPLING TIME START	SAMPLING TIME FINISH	SAMPLING TIME ELAPSED	SAMPLING RATE (cc/min.)	SAMPLE VOLUME (ℓ)
1	9370	1	3.29	3.49	20	250	5.0
2	9369	2	3.46	4.06	20	250	5.0
3	9370	3	4.06	4.26	20	250	5.0
4	9369	4	4.31	4.51	20	250	5.0
5	9370	5	1.00	1.20	20	250	5.0
6	9369	6	1.04	1.24	20	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
11	9369	13	3.00	3.20	20	250	5.0
DUPLICATE	# 9	12	2.42	3.02			
BLANK		11	2.26				

DATE OF SAMPLE SHIPMENT 12/16/81	METHOD OF SHIPMENT FED EX AWB 650-405-221

COMMENTS

7-80

VELSICOL CHEMICAL CORPORATION

POST - CONSTRUCTION QUARTERLY MONITORING REPORT

July 1988

Plant Site, St. Louis Michigan

PRINTED ON
AUG 09 1988

VELSICOL CHEMICAL CORPORATION

POST - CONSTRUCTION
QUARTERLY MONITORING REPORT

July 1988

Plant Site, St. Louis Michigan

Ref. No. 1524

CONESTOGA-ROVERS & ASSOCIATES

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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 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 July 8, 1988.

1.2 MONITORING AND SAMPLING PERSONNEL

The monitoring program was carried out by D. Robinson of Conestoga-Rovers & Associates (CRA) assisted by Mr. Gene DeGeer, Site Custodian under Contract to Velsicol.

2.0 GROUNDWATER TABLE MONITORING

2.1 GENERAL

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. 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

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.

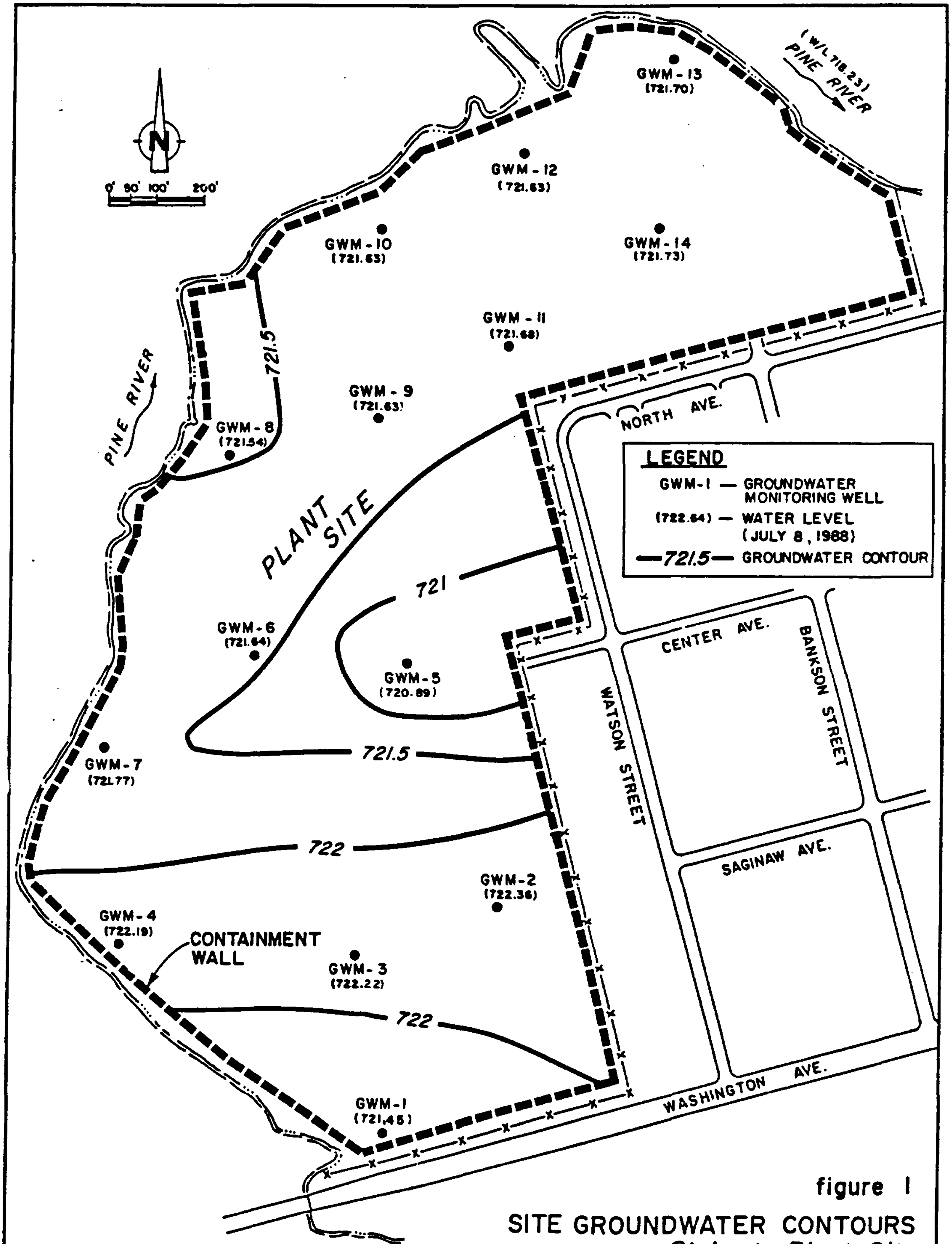

figure 1

SITE GROUNDWATER CONTOURS

St. Louis Plant Site

CRA

1524-26/07/88-19-D-0

9-8

VELSICOL CHEMICAL CORPORATION

POST - CONSTRUCTION QUARTERLY MONITORING REPORT

SEPTEMBER, 1989

Plant Site, St. Louis Michigan

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OCT 5 1989

VELSICOL CHEMICAL CORPORATION

POST - CONSTRUCTION QUARTERLY MONITORING REPORT

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1.1 GENERAL

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

Monitoring Well	*Well Head Elevation (AMSL)*	*Measured Distance to Water Table (feet)*	*Water Table Elevation (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 GENERAL

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 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 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.

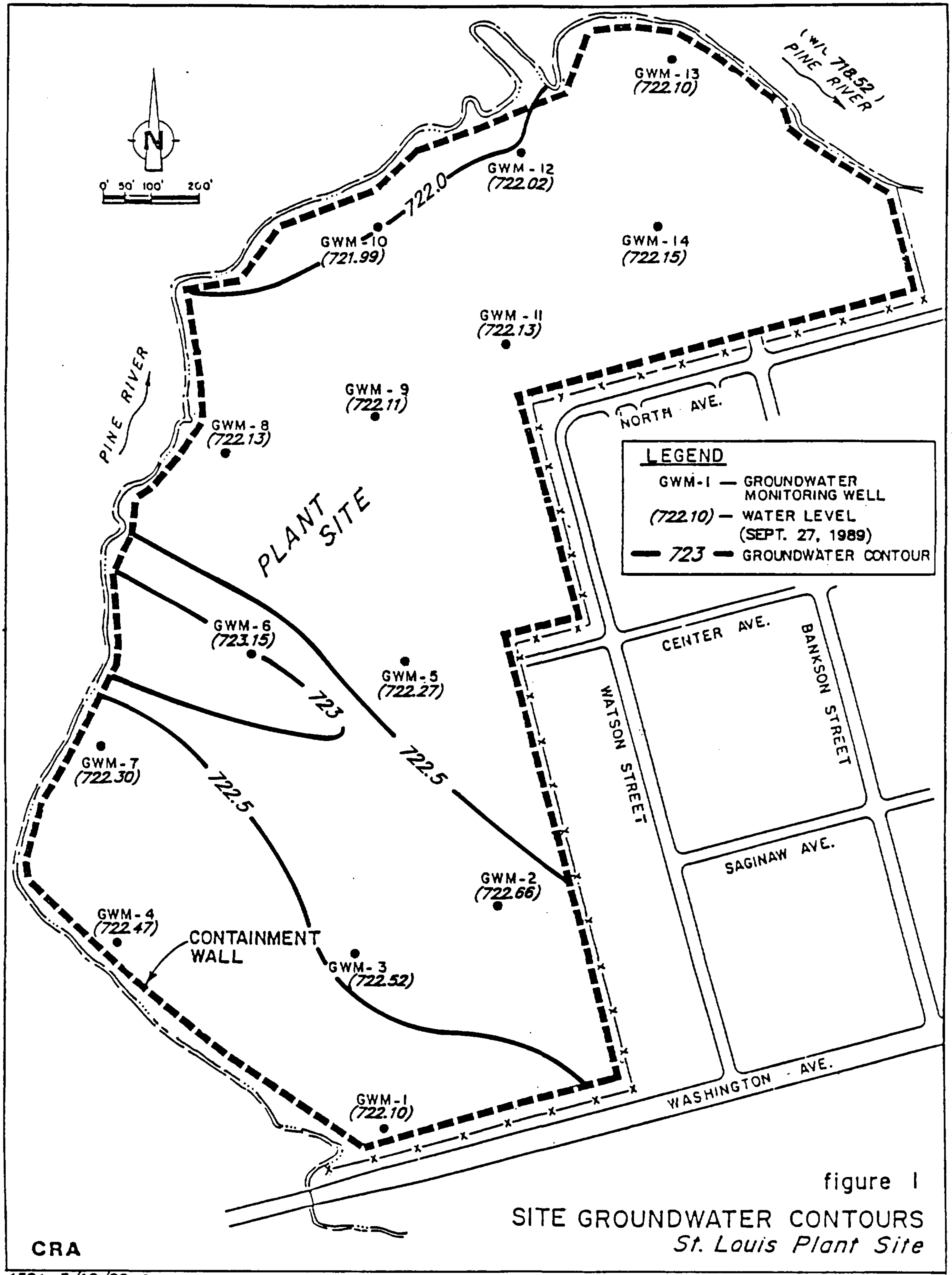

figure 1

SITE GROUNDWATER CONTOURS

St. Louis Plant Site

1524—5/10/89—24—0

VELSICOL CHEMICAL CORPORATION

POST - CONSTRUCTION
QUARTERLY MONITORING REPORT

MARCH 11-14, 1986

Plant Site, St. Louis Michigan

March 1986
Ref. No. 1524

CONESTOGA-ROVERS & ASSOCIATES LIMITED

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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 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.

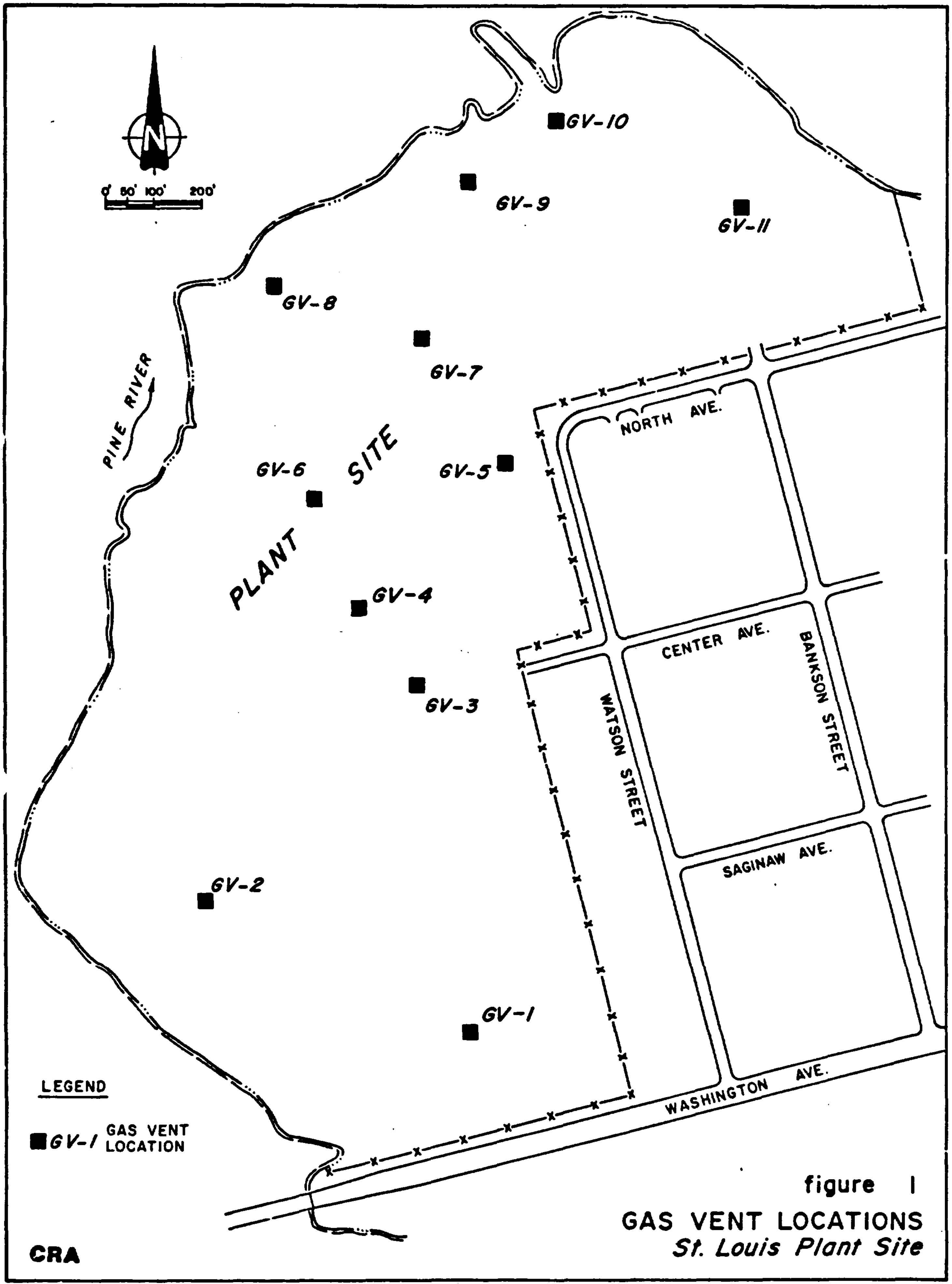

figure 1

GAS VENT LOCATIONS

St. Louis Plant Site

1524-19/03/86

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.

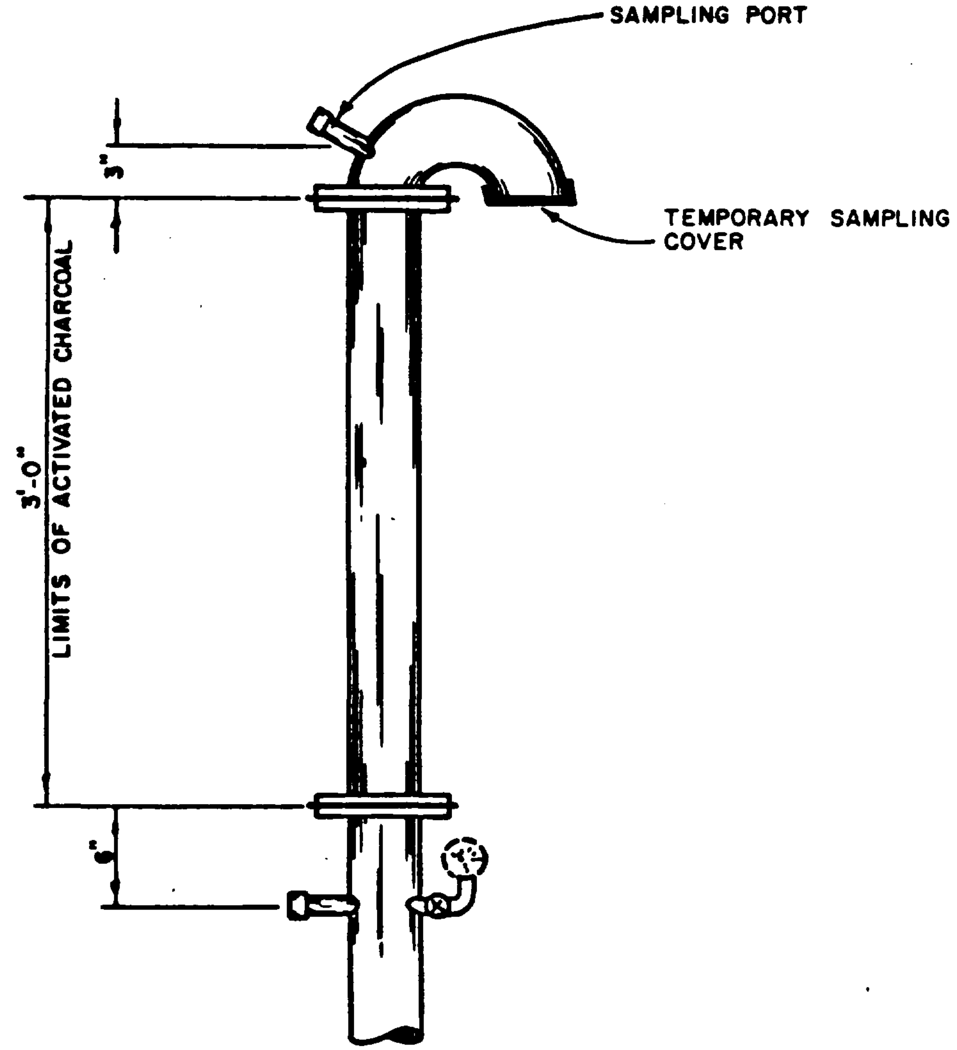

figure 2

ACTIVATED CHARCOAL GAS VENT DETAIL

St. Louis Plant Site

CRA

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 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 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 1.0×10^{-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.

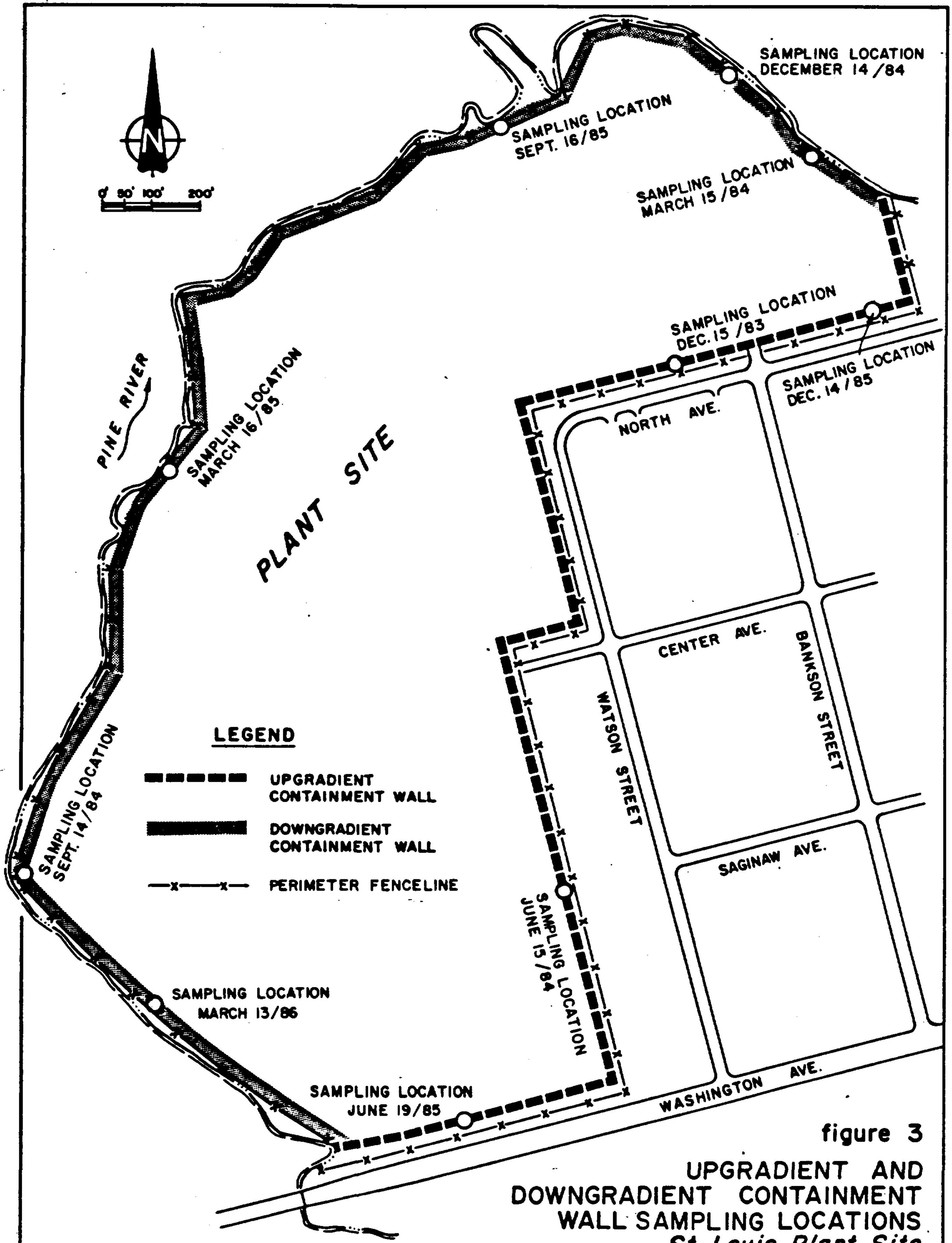

figure 3

UPGRADIENT AND DOWNGRADIENT CONTAINMENT WALL SAMPLING LOCATIONS
St. Louis Plant Site

CRA

1824 - 19/03/86

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

WATER LEVEL MEASUREMENTS
MARCH 13, 1986

MONITORING WELL	WELL HEAD ELEVATION (AMSL)	MEASURED DISTANCE TO WATER TABLE (ft.)	WATERTABLE 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.

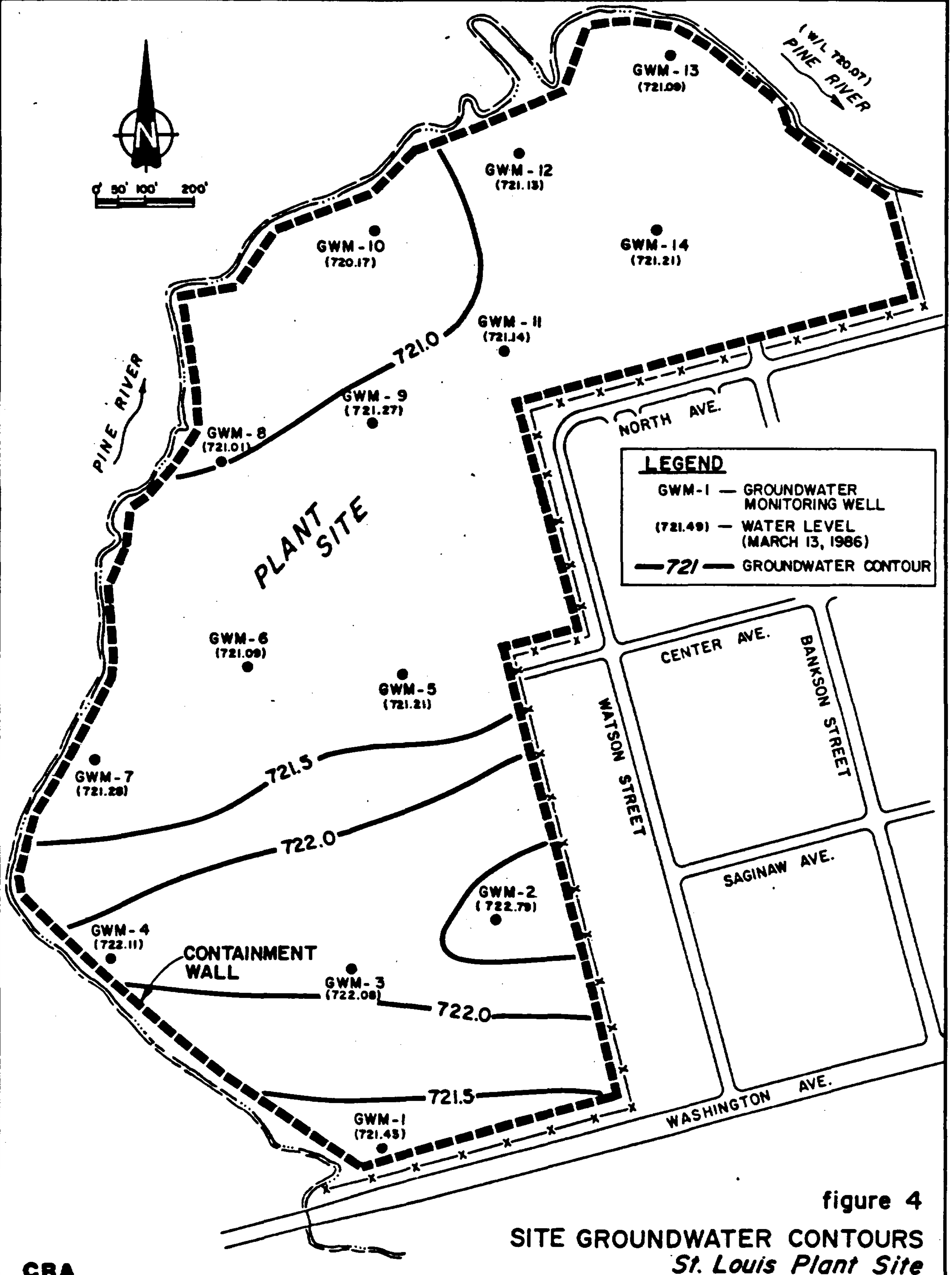

figure 4

SITE GROUNDWATER CONTOURS
St. Louis Plant Site

CRA

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.

6.0 SUMMARY

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 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.

   $$\text{corrected mg/sample} = \frac{\text{total weight}}{\text{DE}}$$

4. Calculate the concentration of the analyte in air

   $$\text{mg/m}^3 = \frac{\text{Corrected mg} \times 1000 \text{ liters/m}^3}{\text{Air volume Sampled (liters)}}$$

5. Concentration will be reported as ppm, corrected to standard conditions of 25°C and 760 mm Hg

   $$\text{ppm} = \text{mg/m}^3 \times \frac{24.45}{\text{MW}} \times \frac{760}{\text{P}} \times \frac{(\text{T}+273)}{298}$$

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)

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.

FORMULA: Table 1

M.W.: Table 1

HYDROCARBONS, HALOGENATED

METHOD: 1003
ISSUED: 2/14/84

COMPOUNDS: (synonyms in Table 1)
- benzyl chloride
- bromoform
- carbon tetrachloride
- chlorobenzene
- chlorobromomethane
- chloroform
- o-dichlorobenzene
- p-dichlorobenzene
- 1,1-dichloroethane
- 1,2-dichloroethylene
- ethylene dichloride
- hexachloroethane
- methylchloroform
- propylene dichloride

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: Table 2
-MAX: Table 2

SHIPMENT: routine

SAMPLE STABILITY: at least 1 week @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: see EVALUATION OF METHOD [1]

BIAS: not significant [1]

OVERALL PRECISION (s_r): see EVALUATION OF METHOD [1]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: compounds above

DESORPTION: 1 mL CS_2, stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURES: Table 2

CARRIER GAS: N_2 or He, 30 mL/min

COLUMN: Table 2; alternates are SP-2100,
SP-2100 with 0.1% Carbowax 1500
or DB-1 fused silica capillary column

CALIBRATION: solutions of analyte in CS_2 with [illegible]

RANGE: Table 2

ESTIMATED LOD: 0.01 mg per sample [2]

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.
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 $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of analyte in the air volume sampled, V (L):

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

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:

[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 NIOSH [6-10] ACGIH	BP (°C)	VP @ 20 °C	Density (g/mL @ 20 °C)
p-Dichlorobenzene	1,4-$C_6H_4Cl_2$	147.00; 6.01	1,4-dichlorobenzene; CAS #106-46-7	75 ppm --- 75 ppm, STEL 110 ppm	174	50 Pa	1.241
1,1-Dichloroethane	CH_3CHCl_2; $C_2H_4Cl_2$	98.96; 4.05	ethylidene chloride; CAS #75-34-3	100 ppm 100 ppm 200 ppm, STEL 250 ppm	57	24.3 kPa	1.174
1,2-Dichloroethylene	$ClCH=CHCl$; $C_2H_4Cl_2$	96.95; 3.96	acetylene dichloride; 1,2-dichloroethene; CAS #540-59-0	200 ppm 200 ppm 200 ppm, STEL 250 ppm	60 (cis) 47 (trans)	24-35 kPa	1.28
Ethylene dichloride*	$ClCH_2CH_2Cl$; $C_2H_4Cl_2$	98.96; 4.05	1,2-dichloroethane; CAS #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*	CCl_3CCl_3; C_2Cl_6	236.74; 9.68	perchloroethane; CAS #67-72-1	1 ppm (skin) 1 ppm (skin) 10 ppm	187 (sublimes)	30 Pa	2.09
Methylchloroform	CH_3CCl_3; $C_2H_3Cl_3$	133.42; 5.45	1,1,1-trichloroethane; CAS #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	$CH_3CHClCH_2Cl$; $C_3H_6Cl_2$	112.99; 4.62	1,2-dichloropropane CAS #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.

	Sampling			Measurement				
	Air Sample Volume (L)							
Compound	Min	Max	Breakthrough in Air	Working Range (mg/m³)	Column*	t (°C) Column Injector Detector	Internal Standard	Range (mg per sample)
1,1-Dichloroethane	1 @ 100 ppm	10	18.3 L [illegible] mg/m³	40 to 1215 (10 L)	A	50 100 175	--	0.4 to 12
1,2-Dichloroethylene	0.5 @ 200 ppm	3	5.4 L [illegible]09 mg/m³	80 to 2370 (3 L)	A	60 170 210	---	0.2 to 7
Ethylene dichloride	1 @ 50 ppm	10	29 L [illegible] mg/m³	40 to 1215 (3 L)	A	70 225 250	octane	0.1 to 4
Hexachloroethane	1 @ 1 ppm	10	43 L [illegible] mg/m³	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 [illegible]08 mg/m³	190 to 5700 (3 L)	A	70 225 250	octane	0.6 to 17
Propylene dichloride	1 @ 75 ppm	10	18 L [illegible] mg/m³	35 to 1050 (10 L)	A	80 170 210	n-undecane	0.3 to 10

*A = 3 m x 3 mm stainless steel, 10% SP-1000 [illegible] 100 mesh Supelcoport;
B = 6 m x 3 mm, otherwise same as A;
C = 3 m x 3 mm stainless steel, 10% OV-101 [illegible] 120 mesh Supelcoport; or
D = 3 m x 6 mm glass, [illegible] SP-2250 on 80/100 [illegible] Supelcoport.

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:

1. 30 ml/min (60 psig) Nitrogen carrier gas flow
2. 35 ml/min (25 psig) Hydrogen gas flow to detector
3. 400 ml/min (60 psig) Air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 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

$$\text{D.E.} = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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 2X 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.

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 CS_2, 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 $W_b > W_f/10$, report breakthrough and possible sample loss.
15. Calculate concentration, C, of vinyl chloride in the air volume sampled, V (L):

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

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:

[1] TLVs - Threshold Limit Values for Chemical Substances and Physical Agents in the Work Environment with Intended Changes for 1983-84, 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.

VELSICOL CHEMICAL CORPORATION
ST. LOUIS, MICHIGAN
PROJECT Nº 1524

GAS VENT SAMPLING PUMPS CALIBRATION LOG

DATE [illegible]

CALIBRATED BY [illegible]

PUMP NUMBER	PUMP TYPE	BEFORE SAMPLING						AFTER SAMPLING					AVERAGE			
		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.)
1	[illegible] (C)	[illegible]	[illegible]	[illegible]	[illegible]	250	[illegible]	3/13	—	---	250	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	(–)				[illegible]	250	[illegible]				250	[illegible]				[illegible]
2	[illegible] (C)				250	250					[illegible]	[illegible]				[illegible]
	(–)				250	250	[illegible]				250	[illegible]				[illegible]

COMMENTS

VELSICOL CHEMICAL CORPORATION
ST. LOUIS, MICHIGAN
PROJECT Nº 1524

GAS VENT SAMPLING

DATE OF COLLECTION 3-12-86	SAMPLER CAC / EDG	BAROMETRIC PRESSURE 30.05
TEMPERATURE 33°F	RELATIVE HUMIDITY [redacted] 91%	
CHARCOAL LOT Nº 120	TENAX LOT Nº 271	

GAUGE	1	2	3	4	5	6	7	8	9	10	11
READING	0	0	0	0	0	0	0	0	0	0	0

GAS VENT NUMBER	PUMP NUMBER	SAMPLE NUMBER	SAMPLING TIME START	FINISH	ELAPSED	SAMPLING RATE (cc/min.)	SAMPLE VOLUME (ℓ)
1	1	5	~~822~~ 8.33	8:53	20 min	250 cc/min	5 ℓ
2	2	2	~~836~~ 8:48	9:08	20 min	↓	5 ℓ
3	1	7	~~9:02~~ 9:12	9:32	20 min		5 ℓ
4	2	9	~~9:15~~ 9:25	9:45	20 min		5 ℓ
5	1	1	137 9:47	10:07	20 min		5 ℓ
6	2	12	~~956~~ 11:14	11:34	20 min		5 ℓ
7	2	13	~~11:38~~ 11:49	12:09	20 min		5 ℓ
8	1	11	~~10:14~~ 11:21	11:41	20 min		5 ℓ
9	1	6	~~11:45~~ 11:55	12:15	20 min		5 ℓ
10	2	4	~~1212~~ 12 28	12.51	23 min		5.75 ℓ
11	1	10	~~1244~~ 13 00	13 20	20 min		5 ℓ
DUPLICATE	1 (#9)	8	~~1227~~ 12:21	12.41	20 min		5 ℓ
BLANK	—	3	12:00	—	—	↓	5 ℓ

DATE OF SAMPLE SHIPMENT 3-12-86	METHOD OF SHIPMENT Federal Express

COMMENTS

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.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

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

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liters/cu m)}}{\text{Air Volume Sampled (liters)}}$$

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

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

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," 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.

FORMULA: $CH_2=CHCl$; C_2H_3Cl

M.W.: 62.50

VINYL CHLORIDE

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

SAMPLER: SOLID SORBENT TUBE
(2 tandem tubes, each with 150 mg activated coconut charcoal)

FLOW RATE: 0.05 L/min

VOL-MIN: 0.7 L
-MAX: 5 L

SHIPMENT: separate primary and backup tubes and cap each

SAMPLE STABILITY: 10 days @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 1 to 64 mg/m³ [2]

BIAS: -6% of calculated concentration [2]

OVERALL PRECISION (s_T): 0.06 [2]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: vinyl chloride

DESORPTION: 1 mL carbon disulfide; 30 min

INJECTION ALIQUOT: 5 µL

COLUMN: stainless steel, 6.1 m x 3.2 mm, 10% SE-30 on 80/100 mesh Chromosorb W (AW-DMCS)

CARRIER GAS: He, 40 mL/min

TEMPERATURE-INJECTOR: 230 °C
-DETECTOR: 230 °C
-COLUMN: 60 °C

CALIBRATION: solutions of vinyl chloride in CS_2

RANGE: 0.002 to 0.2 mg per sample [2]

ESTIMATED LOD: 0.00004 mg per sample [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].

REAGENTS:

1. Carbon disulfide,* chromatographic quality.
2. Vinyl chloride,*, 99.9%, in lecture bottle fitted with valve and septum.
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 CS_2 in a 10-mL volumetric flask.
   b. Open the valve of the syringe and withdraw the plunger to pull CS_2 into the barrel. (As vinyl chloride dissolves, a vacuum will be created, pulling CS_2 into the syringe.)
   c. Push the solution from the syringe into the flask. Rinse the syringe twice with 1-mL portions of CS_2 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 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.
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.

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.

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/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/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.

APPENDIX B

CHAIN OF CUSTODY

CHAIN OF CUSTODY RECORD

PROJECT NO. 1524

PROJECT NAME ST LOUIS, MI - QUARTERLY MONITORING

CRA Consulting Engineers
CONESTOGA-ROVERS & ASSOCIATES LIMITED

SAMPLER'S SIGNATURE Catherine A Cull

SAMPLE NO.	SEQ. NO.	DATE	TOTAL TIME (LITERS)	SAMPLE LOCATION	SAMPLE TYPE	NUMBER OF CONTAINERS	REMARKS
5	1	3/12/86	5.0	[illegible] wells @ ST.	2 carbon tubes + 2 tenax tubes	4	ANALYZE FOR
2	2		5.0	Louis, MI		4	TRIS,
7	3		5.0			4	CARBON TET
9	4		5.0			4	VINYL CHLORIDE
[illegible]	5		5.0			4	
12	6		5.0			4	
13	7		5.0			4	
11	8		5.0			4	
[illegible]	9		5.0			4	
4	10		5.75			4	
10	11		5.0			4	
6	12		5.0			4	
3	13		5.0		TOTAL NO. OF CONTAINERS	4	52 total

RELINQUISHED BY (Sign) 1 Catherine A Cull	DATE/TIME 3/12/86	RECEIVED BY (Sign) ②	RELINQUISHED BY (Sign) 2	DATE/TIME	RECEIVED BY (Sign) ③
RELINQUISHED BY (Sign) 3	DATE/TIME	REC'D BY MOBILE LAB (Sign) ④	REL'D BY MOBILE LAB (Sign) 4	DATE/TIME	RECEIVED BY (Sign) ⑤
METHOD OF SHIPMENT		SHIPPED BY (Sign)	RECEIVED FOR LABORATORY (Sign)		DATE/TIME

APPENDIX C

MECHANICAL INTEGRITY TESTING

ANNULAR PRESSURE TEST

1524

OPERATOR Velsicol Chemical Corp.

STATE PERMIT NO.

ADDRESS

EPA PERMIT NO

DATE OF TEST 3-14-86

WELL NAME Disposal #2

TYPE 1W

LOCATION ____ QUARTER OF THE ____ QUARTER OF THE ____ QUARTER.

SECTION 15 TOWNSHIP 12N

RANGE 2W

TOWNSHIP NAME Bethany

COUNTY NAME Gratiot

COMPANY REPRESENTATIVE Don Robinson

FIELD INSPECTOR Novakowsk.

TYPE PRESSURE GAUGE 4 1/2 INCH FACE, 600 PSI FULL SCALE, 5 PSI INCREMENTS

NEW GAUGE YES ☑ NO ☐ IF NO, DATE OF TEST CALIBRATION

CALIBRATION CERTIFICATION SUBMITTED: YES ☐ NO ☐

RESULTS:

TIME	PRESSURE (PSIG) ANNULUS	PRESSURE (PSIG) TUBING
9:35	320	Vacuum
9:40	319	
9:45	318	
9:50	318	
9:55	317	
10:00	316	
10:05	316	

TEST PRESSURE:

MAX. ALLOWABLE PRESSURE CHANGE: TEST PRESSURE X .03 9 PSI

HALF HOUR PRESSURE CHANGE 4 PSI

TEST PASSED ☑ TEST FAILED ☐ (CHECK ONE)

IF FAILED, NO INJECTION MAY OCCUR UNTIL CORRECTIONS HAVE BEEN MADE AND WELL PASSES.

SIGNATURE OF COMPANY REPRESENTATIVE

DATE 3-14-86

SIGNATURE OF ~~COMPANY REPRESENTATIVE~~

Iuskul.

DATE 3-14-86

LIST OF FIGURES

LIST OF TABLES

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.

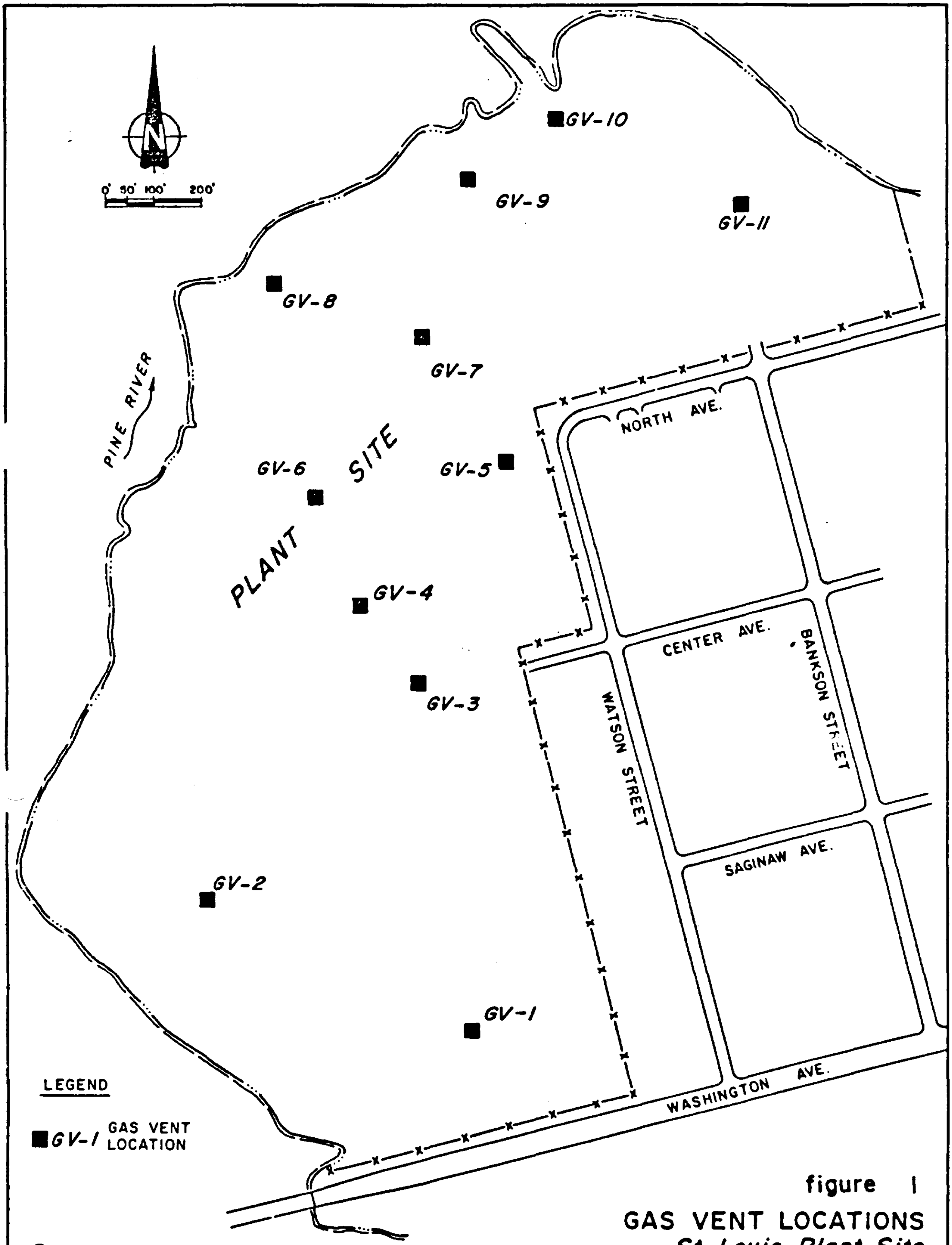

figure 1

GAS VENT LOCATIONS

St. Louis Plant Site

CRA

1524-19/03/85

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.

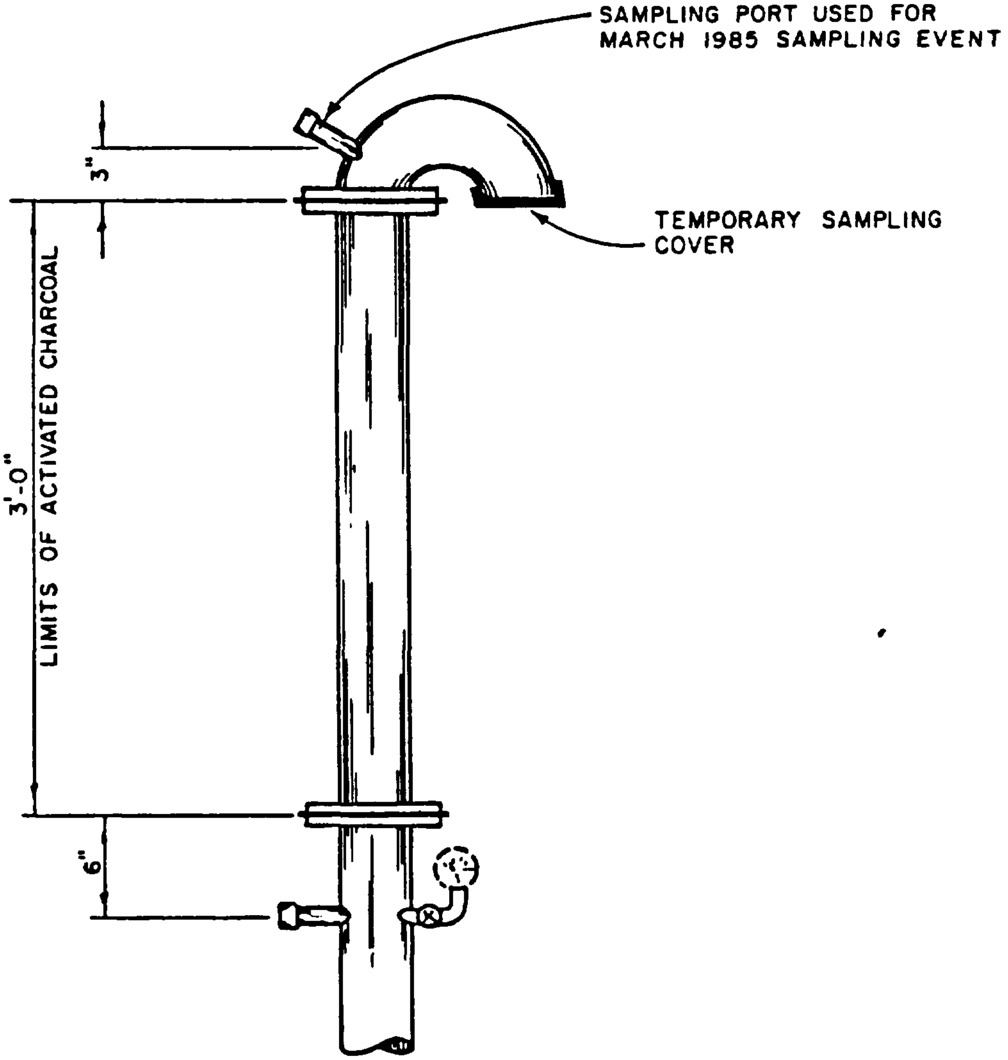

figure 2

ACTIVATED CHARCOAL GAS VENT DETAIL
St. Louis Plant Site

CRA

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

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.

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.

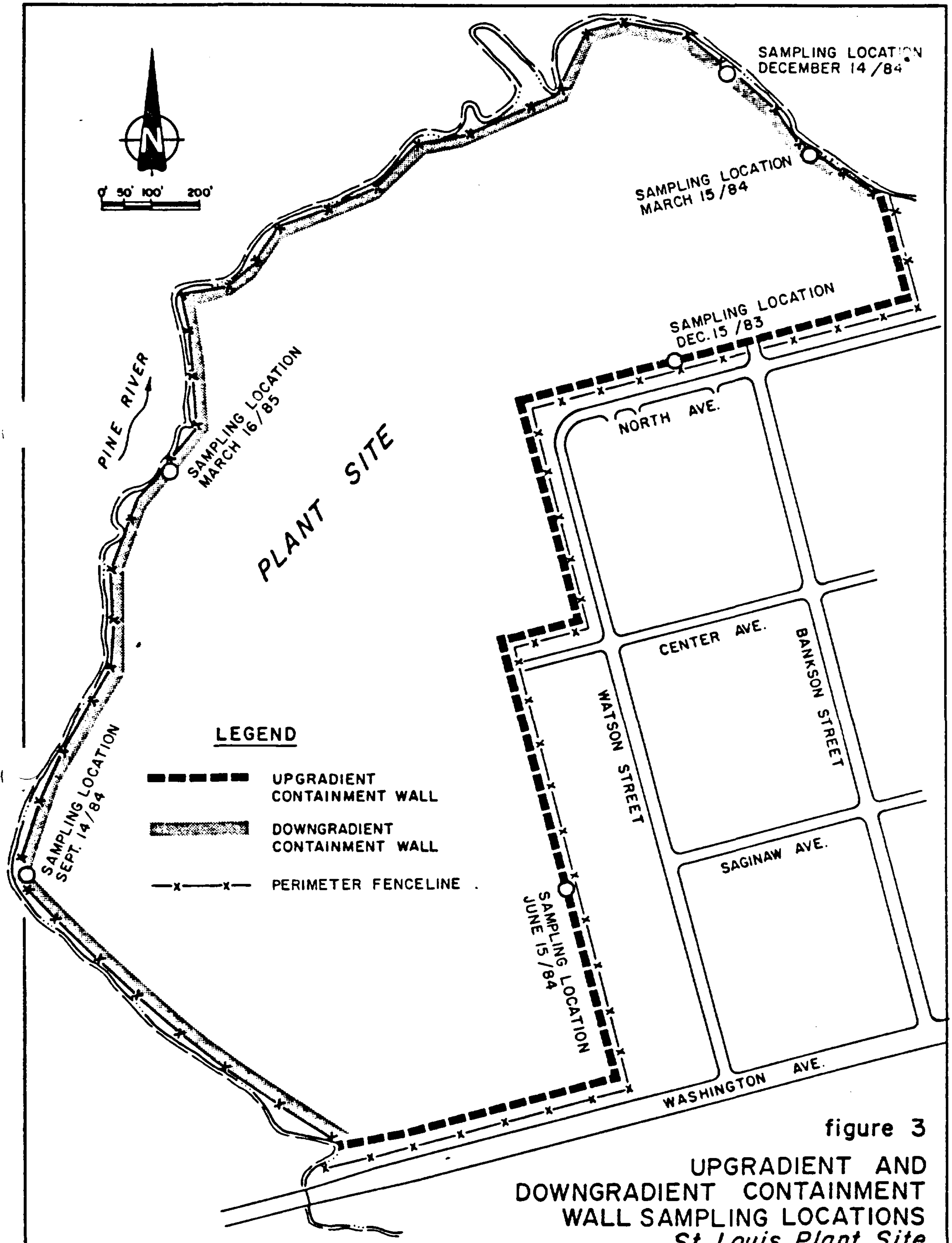

figure 3

UPGRADIENT AND DOWNGRADIENT CONTAINMENT WALL SAMPLING LOCATIONS
St. Louis Plant Site

CRA

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 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.

TABLE 1

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

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.

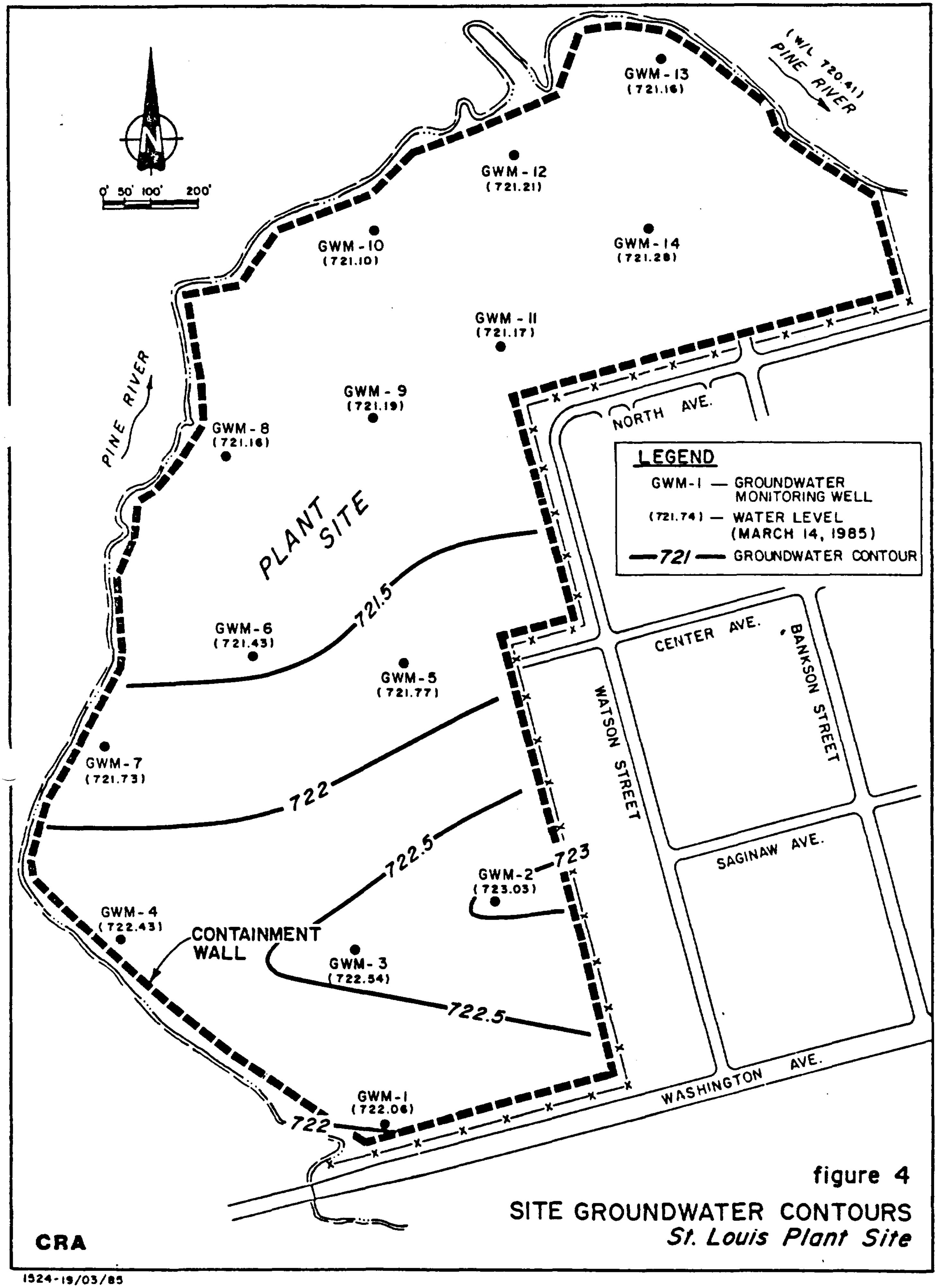

figure 4

SITE GROUNDWATER CONTOURS

St. Louis Plant Site

1524-19/03/85

5.0 **SUMMARY**

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.

APPENDIX A

CHAIN OF CUSTODY

SHEET 1 OF 5

CHAIN OF CUSTODY RECORD

PROJECT NO. 1524

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

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

SAMPLER'S SIGNATURE ______ (SIGN)

SAMPLE NO	SEQ NO	DATE	TIME	FRONT / REAR	TENAX / CHARCOAL	SAMPLE TYPE	NO OF CONTAINERS	REMARKS
1	1	3/15	8:36	F	T	Gas Vent Sample Tube	1	
1	1			R	C		1	
1	1			F	C		1	
1	1		9:13	R	T		1	
2	2			F	T		1	
2	2			R	C		1	
2	2			F	C		1	
2	2			R	T		1	
3	3		9:50	F	T		1	
3	3			R	C		1	
3	3			F	C		1	
3	3			R	T		1	
						TOTAL NO. OF CONTAINERS	12	

RELINQUISHED BY:	DATE/TIME	RECEIVED BY:	RELINQUISHED BY:	DATE/TIME	RECEIVED BY:
1 ______ (SIGN)	3/15 1420	2 ______ (SIGN)	2 ______ (SIGN)		3 ______ (SIGN)
3 ______ (SIGN)		4 ______ (SIGN)	4 ______ (SIGN)		5 ______ (SIGN)
5 ______ (SIGN)		6 ______ (SIGN)	6 ______ (SIGN)		7 ______ (SIGN)

METHOD OF SHIPMENT: Fed Ex

SHIPPED BY:

RECEIVED FOR LABORATORY: ______ (SIGN)

DATE/TIME

SHEET 2 OF 5

CHAIN OF CUSTODY RECORD

PROJECT NO.	PROJECT NAME:
1524	GAS VENT MONITORING PLANT SITE ST. LOUIS, MICHIGAN

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

SAMPLER'S SIGNATURE ______ (SIGN)

SAMPLE NO	SEQ NO	DATE	TIME	FRONT / REAR	TENAX / CHARCOAL	SAMPLE TYPE	NO OF CONTAINERS	REMARKS
4	4	3/15	10.27	F	T	Gas Vent Sampling Tube	1	
4	4			R	C		1	
4	4			F	C		1	
4	4			R	T		1	
5	5		11.05	F	T		1	
5	5			R	C		1	
5	5			F	C		1	
5	5			R	T		1	
6	6		11.15	F	T		1	
6	6			R	C		1	
6	6			F	C		1	
6	6			R	T		1	
						TOTAL NO. OF CONTAINERS		

RELINQUISHED BY:	DATE/TIME	RECEIVED BY:	RELINQUISHED BY:	DATE/TIME	RECEIVED BY:
1 (SIGN)	3/15 14/25	2 (SIGN)	2 (SIGN)		3 (SIGN)
3 (SIGN)		4 (SIGN)	4 (SIGN)		5 (SIGN)
5 (SIGN)		6 (SIGN)	6 (SIGN)		7 (SIGN)

METHOD OF SHIPMENT:	SHIPPED BY:	RECEIVED FOR LABORATORY:	DATE/TIME
Fed Ex		(SIGN)	

SHEET 3 OF 5

CHAIN OF CUSTODY RECORD

PROJECT NO. 1524

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

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

SAMPLER'S SIGNATURE (SIGN)

SAMPLE NO	SEQ NO	DATE	TIME	FRONT / REAR	TENAX / CHARCOAL	SAMPLE TYPE	NO OF CONTAINERS	REMARKS
7	7	3/15	11.46	F	T	Gas Vent Sampling Tube	1	
7	7			R	C		1	
7	7			F	C		1	
7	7			R	T		1	
12	1	3/15	8.53	F	T		1	
12	1			R	C		1	
12	1			F	C		1	
12	1			R	T		1	
11	2	3/15	9.29	F	T		1	
11	2			R	C		1	
11	2			F	C		1	
11	2			R	T		1	
						TOTAL NO. OF CONTAINERS	12	

RELINQUISHED BY: 1 (SIGN)	DATE/TIME 3/15 1427	RECEIVED BY: 2 (SIGN)	RELINQUISHED BY: 2 (SIGN)	DATE/TIME	RECEIVED BY: 3 (SIGN)
RELINQUISHED BY: 3 (SIGN)	DATE/TIME	RECEIVED BY: 4 (SIGN)	RELINQUISHED BY: 4 (SIGN)	DATE/TIME	RECEIVED BY: 5 (SIGN)
RELINQUISHED BY: 5 (SIGN)	DATE/TIME	RECEIVED BY: 6 (SIGN)	RELINQUISHED BY: 6 (SIGN)	DATE/TIME	RECEIVED BY: 7 (SIGN)

METHOD OF SHIPMENT: Fed Ex	SHIPPED BY:	RECEIVED FOR LABORATORY: (SIGN)	DATE/TIME

SHEET 1 OF 5

CHAIN OF CUSTODY RECORD

PROJECT NO. 1524

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

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

SAMPLER'S SIGNATURE ______ (SIGN)

SAMPLE NO	SEQ NO	DATE	TIME	FRONT / REAR	TENAX / CHARCOAL	SAMPLE TYPE	NO OF CONTAINERS	REMARKS
10	3	3/15	8.53	F	T	Gas Vent Sampling Tube	1	
10	3			R	C		1	
10	3			F	C		1	
10	3			R	T		1	
9	4	3/15	10.50	F	T		1	
9	4			R	C		1	
9	4			F	C		1	
9	4			R	T		1	
8	5	3/15	11.32	F	T		1	
8	5			R	C		1	
8	5			F	C		1	
8	5			R	T		1	
						TOTAL NO. OF CONTAINERS	12	

RELINQUISHED BY:	DATE/TIME	RECEIVED BY:	RELINQUISHED BY:	DATE/TIME	RECEIVED BY:
1 (SIGN)	3/15, 1421	② (SIGN)	2 (SIGN)		③ (SIGN)
RELINQUISHED BY: 3 (SIGN)	DATE/TIME	RECEIVED BY: ④ (SIGN)	RELINQUISHED BY: 4 (SIGN)	DATE/TIME	RECEIVED BY: ⑤ (SIGN)
RELINQUISHED BY: 5 (SIGN)	DATE/TIME	RECEIVED BY: ⑥ (SIGN)	RELINQUISHED BY: 6 (SIGN)	DATE/TIME	RECEIVED BY: ⑦ (SIGN)

METHOD OF SHIPMENT: FED EX

SHIPPED BY:

RECEIVED FOR LABORATORY: ______ (SIGN)

DATE/TIME

SHEET 5 OF 5

CHAIN OF CUSTODY RECORD

PROJECT Nº. 1524

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

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

SAMPLER'S SIGNATURE (SIGN)

SAMPLE Nº	SEQ Nº	DATE	TIME	FRONT / REAR	TENAX / CHARCOAL	SAMPLE TYPE	Nº OF CONTAINERS	REMARKS
13	6	3/15	11.55	F	T		1	
13	6			R	C		1	
13	6			F	C		1	
13	6			R	T		1	
						TOTAL SHIPMENT 52 TUBES		
						TOTAL Nº. OF CONTAINERS	4	

RELINQUISHED BY:	DATE/TIME	RECEIVED BY:	RELINQUISHED BY:	DATE/TIME	RECEIVED BY:
1 (SIGN)	3/15 1425	② (SIGN)	2 (SIGN)		③ (SIGN)
3 (SIGN)		④ (SIGN)	4 (SIGN)		⑤ (SIGN)
5 (SIGN)		⑥ (SIGN)	6 (SIGN)		⑦ (SIGN)

METHOD OF SHIPMENT: FED EXP

SHIPPED BY:

RECEIVED FOR LABORATORY: (SIGN)

DATE/TIME

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.

   $$\text{corrected mg/sample} = \frac{\text{total weight}}{\text{DE}}$$

4. Calculate the concentration of the analyte in air

   $$\text{mg/m}^3 = \frac{\text{Corrected mg} \times 1000 \text{ liters/m}^3}{\text{Air volume Sampled (liters)}}$$

5. Concentration will be reported as ppm, corrected to standard conditions of 25°C and 760 mm Hg

   $$\text{ppm} = \text{mg/m}^3 \times \frac{24.45}{\text{MW}} \times \frac{760}{\text{P}} \times \frac{(\text{T}+273)}{298}$$

   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)

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.

FORMULA: Table 1

HYDROCARBONS, HALOGENATED

METHOD: 1003
ISSUED: 2/14/84

M.W.: Table 1

COMPOUNDS: (synonyms in Table 1)				
	benzyl chloride	chlorobromomethane	1,1-dichloroethane	hexachloroethane
	bromoform	chloroform	1,2-dichloroethylene	methylchloroform
	carbon tetrachloride	o-dichlorobenzene	ethylene dichloride	propylene dichloride
	chlorobenzene	p-dichlorobenzene		

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: Table 2
-MAX: Table 2

SHIPMENT: routine

SAMPLE STABILITY: at least 1 week @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

[illegible] [1]

BIAS: not significant [1]

OVERALL PRECISION (s_r): see EVALUATION OF METHOD [1]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: compounds above

DESORPTION: 1 mL CS_2, stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURES: Table 2

CARRIER GAS: N_2 or He, 30 mL/min

COLUMN: Table 2; alternates are SP-2100,
SP-2100 with 0.1% Carbowax 1500
or DB-1 fused silica capillary column

CALIBRATION: solutions of analyte in CS₂ with
[illegible]

RANGE: Table 2

ESTIMATED LOD: 0.01 mg per sample [2]

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.
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 $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of analyte in the air volume sampled, V (L):

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

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:

[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 NIOSH [6-10] ACGIH	BP (°C)	VP @ 20 °C	Density (g/mL @ 20 °C)
p-Dichlorobenzene	1,4-$C_6H_4Cl_2$	147.00; 6.01	1,4-dichlorobenzene; CAS #106-46-7	75 ppm --- 75 ppm, STEL 110 ppm	174	50 Pa	1.241
1,1-Dichloroethane	CH_3CHCl_2; $C_2H_4Cl_2$	98.96; 4.05	ethylidene chloride; CAS #75-34-3	100 ppm 100 ppm 200 ppm, STEL 250 ppm	57	24.3 kPa	1.174
1,2-Dichloroethylene	ClCH=CHCl; $C_2H_4Cl_2$	96.95; 3.96	acetylene dichloride; 1,2-dichloroethene; CAS #540-59-0	200 ppm 200 ppm 200 ppm, STEL 250 ppm	60 (cis) 47 (trans)	24-35 kPa	1.28
Ethylene dichloride*	$ClCH_2CH_2Cl$; $C_2H_4Cl_2$	98.96; 4.05	1,2-dichloroethane; CAS #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*	CCl_3CCl_3; C_2Cl_6	236.74; 9.68	perchloroethane; CAS #67-72-1	1 ppm (skin) 1 ppm (skin) 10 ppm	187 (sublimes)	30 Pa	2.09
Methylchloroform	CH_3CCl_3; $C_2H_3Cl_3$	133.42; 5.45	1,1,1-trichloroethane; CAS #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	$CH_3CHClCH_2Cl$; $C_3H_6Cl_2$	112.99; 4.62	1,2-dichloropropane CAS #78-87-5	75 ppm 75 ppm 75 ppm, STEL 110 ppm	95	5.3 kPa	1.156 (25 °C)

---

*Suspect carcinogen.

	Sampling			Measurement				
Compound	Air Sample Volume (L) Min	Max	Breakthrough in Dry Air	Working Range (mg/m³)	Column*	t (°C) Column Injector Detector	Internal Standard	Range (mg per sample)
1,1-Dichloroethane	1 @ 100 ppm	10	18.3 L [illegible]3 mg/m³	40 to 1215 (10 L)	A	50 100 175	--	0.4 to 12
1,2-Dichloroethylene	0.5 @ 200 ppm	3	5.4 L [illegible]09 mg/m³	80 to 2370 (3 L)	A	60 170 210	---	0.2 to 7
Ethylene dichloride	1 @ 50 ppm	10	29 L [illegible] mg/m³	40 to 1215 (3 L)	A	70 225 250	octane	0.1 to 4
Hexachloroethane	1 @ 1 ppm	10	43 L [illegible] mg/m³	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 [illegible]88 mg/m³	190 to 5700 (3 L)	A	70 225 250	octane	0.6 to 17
Propylene dichloride	1 @ 75 ppm	10	18 L [illegible] mg/m³	35 to 1050 (10 L)	A	80 170 210	n-undecane	0.3 to 10

---

*A = 3 m x 3 mm stainless steel, 10% SP-1000 [illegible] 100 mesh Supelcoport;
B = 6 m x 3 mm, otherwise same as A;
C = 3 m x 3 mm stainless steel, 10% OV-101 on [illegible] 120 mesh Supelcoport; or
D = 3 m x 6 mm glass, [illegible] SP-2250 on 80/100 m[illegible]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 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:

1. 30 ml/min (60 psig) Nitrogen carrier gas flow
2. 35 ml/min (25 psig) Hydrogen gas flow to detector
3. 400 ml/min (60 psig) Air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 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

$$\text{D.E.} = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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 2X 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.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

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.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

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

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000\ \text{(liters/cu m)}}{\text{Air Volume Sampled (liters)}}$$

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

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

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," 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.

FORMULA: $CH_2=CHCl$; C_2H_3Cl

M.W.: 62.50

VINYL CHLORIDE

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

SAMPLER: SOLID SORBENT TUBE (2 tandem tubes, each with 150 mg activated coconut charcoal)

FLOW RATE: 0.05 L/min

VOL-MIN: 0.7 L
-MAX: 5 L

SHIPMENT: separate primary and backup tubes and cap each

SAMPLE STABILITY: 10 days @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 1 to 64 mg/m³ [2]

BIAS: -6% of calculated concentration [2]

OVERALL PRECISION (s_r): 0.06 [2]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: vinyl chloride

DESORPTION: 1 mL carbon disulfide; 30 min

INJECTION ALIQUOT: 5 µL

COLUMN: stainless steel, 6.1 m x 3.2 mm, 10% SE-30 on 80/100 mesh Chromosorb W (AW-DMCS)

CARRIER GAS: He, 40 mL/min

TEMPERATURE-INJECTOR: 230 °C
-DETECTOR: 230 °C
-COLUMN: 60 °C

CALIBRATION: solutions of vinyl chloride in CS_2

RANGE: 0.002 to 0.2 mg per sample [2]

ESTIMATED LOD: 0.00004 mg per sample [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].

REAGENTS:

1. Carbon disulfide,* chromatographic quality.
2. Vinyl chloride,*, 99.9%, in lecture bottle fitted with valve and septum.
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 CS_2 in a 10-mL volumetric flask.
   b. Open the valve of the syringe and withdraw the plunger to pull CS_2 into the barrel. (As vinyl chloride dissolves, a vacuum will be created, pulling CS_2 into the syringe.)
   c. Push the solution from the syringe into the flask. Rinse the syringe twice with 1-mL portions of CS_2 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 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.
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.

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.

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/m^3.
    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 (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.

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 CS_2, 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 $W_b > W_f/10$, report breakthrough and possible sample loss.

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

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

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:

[1] TLVs - Threshold Limit Values for Chemical Substances and Physical Agents in the Work Environment with Intended Changes for 1983-84, 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.

VELSICOL CHEMICAL CORPORATION
ST. LOUIS, MICHIGAN
PROJECT Nº 1524

GAS VENT SAMPLING PUMPS CALIBRATION LOG

DATE : 14-15 1985

CALIBRATED BY [illegible]

PUMP NUMBER	PUMP TYPE	BEFORE SAMPLING 3/14/85						AFTER SAMPLING 3/15/85					AVERAGE 3/15/85			
		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.)
1	charcoal a)	42	55	29.96	255	[illegible]	[illegible]	33	59	30.33	[illegible]	12:30	37.5	57	30.145	250
	[illegible] b)	42	55	29.96	250	250	[illegible]	33	59	30.33	255	[illegible]	37.5	57	30.145	252.5
2	charcoal a)	42	55	29.96	[illegible]	250	[illegible]	33	59	30.33	250	12:35	37.5	57	30.145	250
	[illegible] b)	42	55	29.96	[illegible]	250	[illegible]	33	59	30.33	[illegible]	"	37.5	57	30.145	250
		a) charcoal			b) [illegible]											

COMMENTS

VELSICOL CHEMICAL CORPORATION
ST. LOUIS, MICHIGAN
PROJECT Nº 1524

GAS VENT SAMPLING

DATE OF COLLECTION 3/15/85	SAMPLER Robinson	BAROMETRIC PRESSURE 30.145
TEMPERATURE ~~25~~ 37.5	RELATIVE HUMIDITY 57%	
CHARCOAL LOT Nº 120	TENAX LOT Nº 271	

GAUGE	1	2	3	4	5	6	7	8	9	10	11
READING	0	0	0	0		0					0

GAS VENT NUMBER	PUMP NUMBER	SAMPLE NUMBER	SAMPLING TIME START	FINISH	ELAPSED	SAMPLING RATE (cc/min.)	SAMPLE VOLUME (ℓ)
1	1	7	11.44	12.04	20	250	5.0
2	1	5	1105	11.25	20	250	5.0
3	1	4	10.27	10.47	20	250	5.0
4	1	3	9.50	10.10	20	250	5.0
5							
6	1	2	9 13	9 33	20	250	5.0
7							
8							
9							
10							
11	1	1	8 36	8.56	20	250cc	5.0
DUPLICATE							
BLANK		6	11 15				

DATE OF SAMPLE SHIPMENT 3/15/85

METHOD OF SHIPMENT F.E. A.W.B.# 611891626 3/15/85

COMMENTS Carbon Changed 3/14/85

VELSICOL CHEMICAL CORPORATION
ST. LOUIS, MICHIGAN
PROJECT Nº 1524

GAS VENT SAMPLING

DATE OF COLLECTION 3-15-85	SAMPLER Coll	BAROMETRIC PRESSURE 30.145
TEMPERATURE 37.5	RELATIVE HUMIDITY 57%	
CHARCOAL LOT Nº 120	TENAX LOT Nº 211	

GAUGE	1	2	3	4	5	6	7	8	9	10	11
READING					0		0	0	0	0	

GAS VENT NUMBER	PUMP NUMBER	SAMPLE NUMBER	SAMPLING TIME START	SAMPLING TIME FINISH	SAMPLING TIME ELAPSED	SAMPLING RATE (cc/min.)	SAMPLE VOLUME (ℓ)
1							
2							
3							
4							
5	2	9	10:50	11:10	20	250	5.0
6							
7	2	10	10:09	10:29	20	250	5.0
8	2	8 *	11.32	11:52	20	250	5.0
9	2	11	09:29	09.49	20	250	5.0
10	2	12	08:53	9:13	20	250	5.0
11							
DUPLICATE	2 (#8)	13 *	11:55	12:15	20	250	5.0
BLANK							

DATE OF SAMPLE SHIPMENT 3/15/85
METHOD OF SHIPMENT F.E. Airbill 611891626 3/15/85

COMMENTS Chain Changed 3/14/85

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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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.

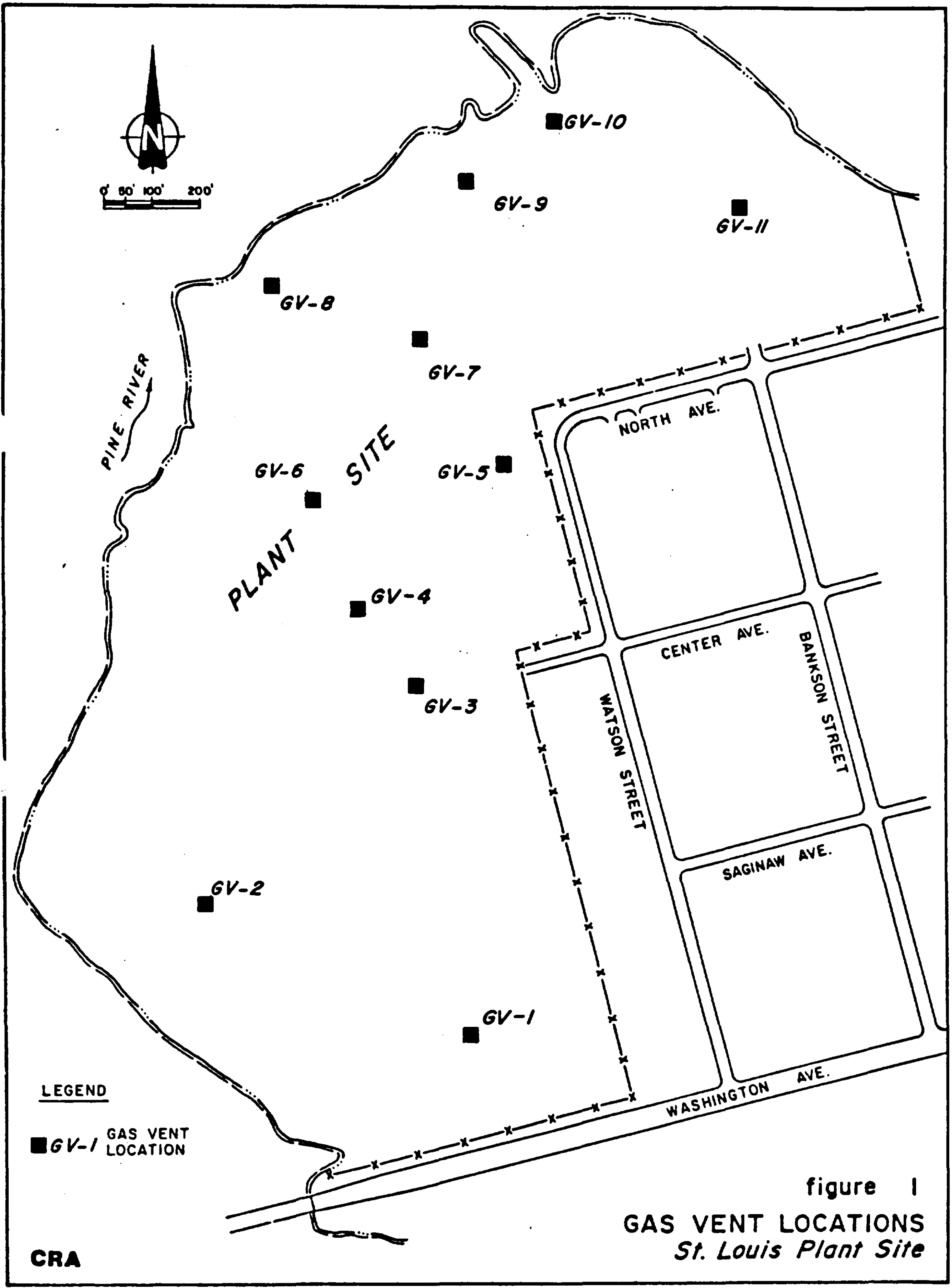

figure 1

GAS VENT LOCATIONS

St. Louis Plant Site

1524-19/03/85

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.

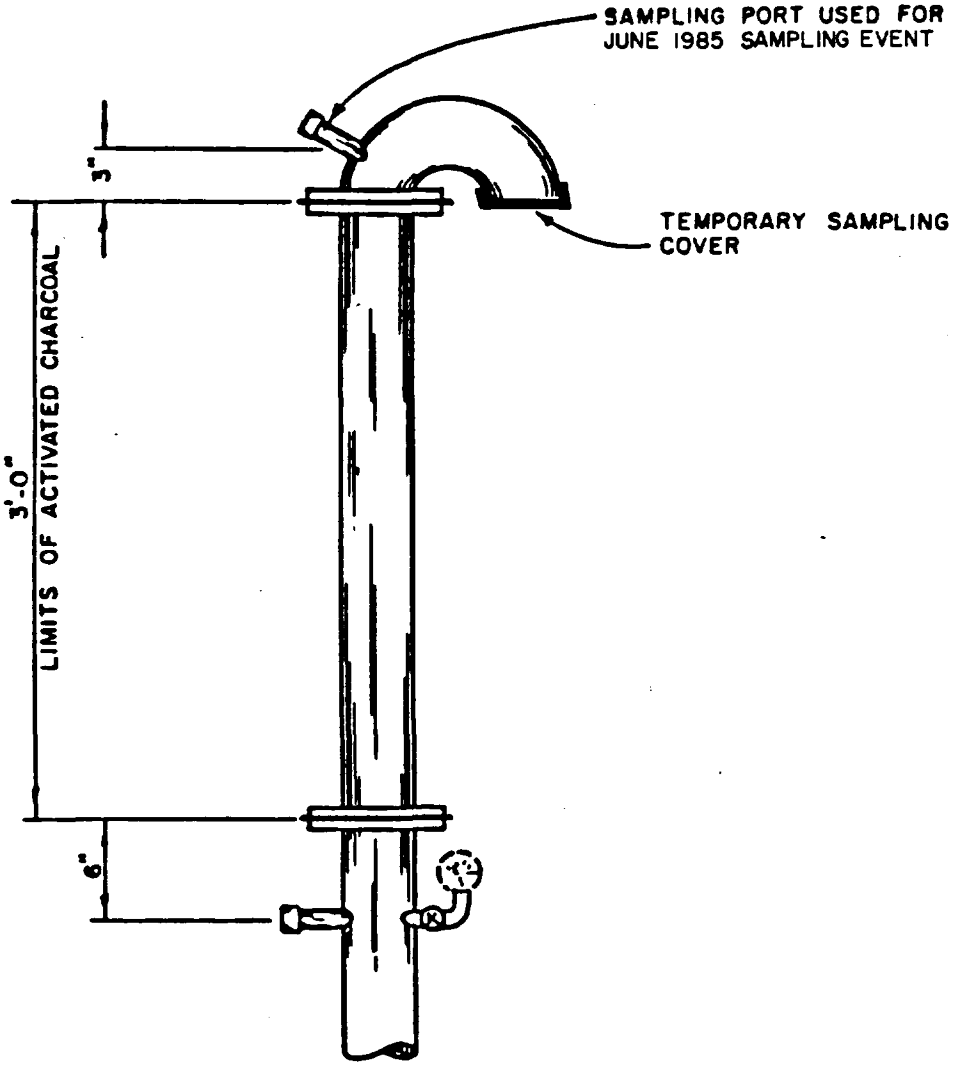

figure 2

ACTIVATED CHARCOAL GAS VENT DETAIL
St. Louis Plant Site

CRA

1624-25/06/85

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.

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.

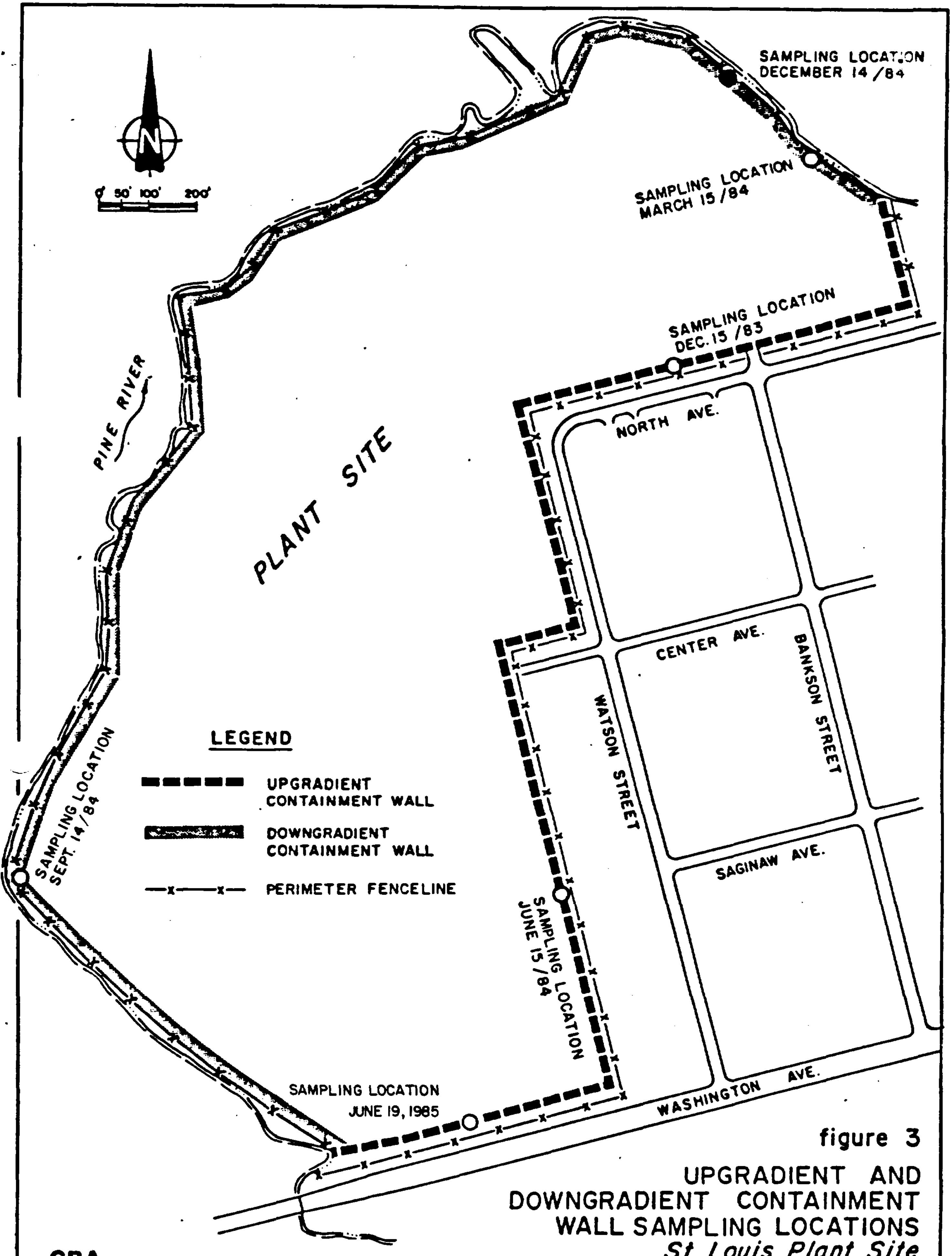

figure 3

UPGRADIENT AND DOWNGRADIENT CONTAINMENT WALL SAMPLING LOCATIONS
St. Louis Plant Site

CRA

1624-25/06/85

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.

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, 1985)	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.

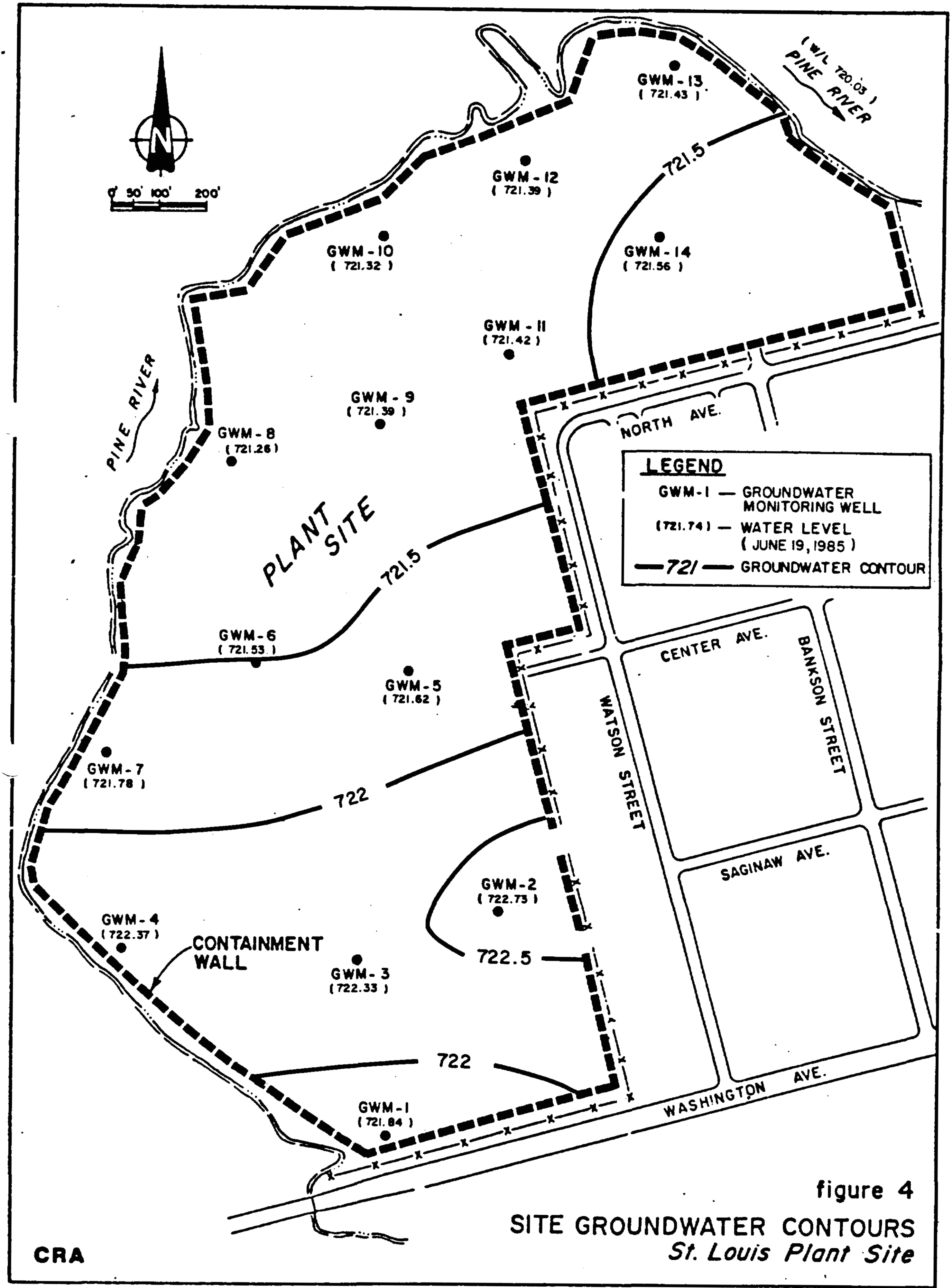

figure 4

SITE GROUNDWATER CONTOURS

St. Louis Plant Site

CRA

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.

APPENDIX A

CHAIN OF CUSTODY

SHEET 1 OF 1

CHAIN OF CUSTODY RECORD

CHAIN OF CUSTODY RECORD	PROJECT NO. 1524	PROJECT NAME: GAS VENT MONITORING PLANT SITE ST. LOUIS, MICHIGAN	VELSICOL CHEMICAL CORPORATION 701 W. WASHINGTON STREET ST. LOUIS, MICHIGAN 48880

SAMPLER'S SIGNATURE ______ (SIGN)

SAMPLE NO	SEQ NO	DATE	TIME	FRONT / REAR	TENAX / CHARCOAL	SAMPLE TYPE	NO OF CONTAINERS	REMARKS
1	1	6/20/87	1040	F	T & C	GAS VENT	2	ANALYSIS:
1	1	6/20	1040	R	T & C	" "	2	CARBON TETRACHLORIDE
2	2	6/20	11.03	F	T & C	" "	2	VINYL CHLORIDE
2	2	6/20	11.03	R	T & C	" "	2	TRICHLOROETHYLENE
3	3	6/20	13.06	F	T & C	" "	2	↕
3	3	6/20	13.06	R	T & C	" "	2	
4	4	6/20	1345	F	T & C	" "	2	
4	4	6/20	1345	R	T & C	" "	2	
5	5	6/20	1423	F	T & C	" "	2	
5	5	6/20	1423	R	T & C	" "	2	
6	6	6/20	1356	F	T & C	" "	2	
6	6	6/20	1356	R	T & C	" "	2	
						TOTAL NO. OF CONTAINERS	24	

RELINQUISHED BY: 1 (SIGN)	DATE / TIME 6/21, 1400	RECEIVED BY: 2 (SIGN)	RELINQUISHED BY: 2 (SIGN)	DATE / TIME	RECEIVED BY: 3 (SIGN)
RELINQUISHED BY: 3 (SIGN)	DATE / TIME	RECEIVED BY: 4 (SIGN)	RELINQUISHED BY: 4 (SIGN)	DATE / TIME	RECEIVED BY: 5 (SIGN)
RELINQUISHED BY: 5 (SIGN)	DATE / TIME	RECEIVED BY: 6 (SIGN)	RELINQUISHED BY: 6 (SIGN)	DATE / TIME	RECEIVED BY: 7 (SIGN)
METHOD OF SHIPMENT: FED EXP P.1		SHIPPED BY: Robinson	RECEIVED FOR LABORATORY: (SIGN)		DATE / TIME

AWB 611891593

SHEET __ OF _

CHAIN OF CUSTODY RECORD

PROJECT NO. 1524

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

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

SAMPLER'S SIGNATURE: (SIGN)

SAMPLE NO	SEQ NO	DATE	TIME	FRONT / REAR	TENAX / CHARCOAL	SAMPLE TYPE	NO OF CONTAINERS	REMARKS
7	7	6/20	1502	F	T & C	GAS VENT	2	ANALYSIS:
7	7	6/20	1502	R	T & C	" "	2	CARBON TETRACHLORIDE
8	8	6/20	1620	F	T & C	" "	2	VINYL CHLORIDE
8	8	6/20	1620	R	T & C	" "	2	TRICHLOROETHYLENE
9	9	6/21	1134	F	T & C	" "	2	
9	9	6/21	1134	R	T & C	" "	2	
10	10	6/21	0849	F	T & C	" "	2	
10	10	6/21	0849	R	T & C	" "	2	
11	11	6/21	1009	F	T & C	" "	2	
11	11	6/21	1009	R	T & C	" "	2	
12	12	6/21	1223	F	T & C	" "	2	
12	12	6/21	1223	R	T & C	" "	2	
						TOTAL NO. OF CONTAINERS	24	

RELINQUISHED BY:	DATE/TIME	RECEIVED BY:	RELINQUISHED BY:	DATE/TIME	RECEIVED BY:
1 (SIGN)	6/21, 1400	2 (SIGN)	2 (SIGN)		3 (SIGN)
RELINQUISHED BY: 3 (SIGN)	DATE/TIME	RECEIVED BY: 4 (SIGN)	RELINQUISHED BY: 4 (SIGN)	DATE/TIME	RECEIVED BY: 5 (SIGN)
RELINQUISHED BY: 5 (SIGN)	DATE/TIME	RECEIVED BY: 6 (SIGN)	RELINQUISHED BY: 6 (SIGN)	DATE/TIME	RECEIVED BY: 7 (SIGN)

METHOD OF SHIPMENT:	SHIPPED BY:	RECEIVED FOR LABORATORY:	DATE/TIME
Fed Ex P.1	ROBINSON	(SIGN)	

AWB611 891593

SHEET 1 OF 1

CHAIN OF CUSTODY RECORD

PROJECT NO. 1524

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

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

SAMPLER'S SIGNATURE (SIGN)

SAMPLE NO	SEQ NO	DATE	TIME	FRONT / REAR	TENAX / CHARCOAL	SAMPLE TYPE	NO OF CONTAINERS	REMARKS
13	13	6/21	1346	F	T & C	Gas Vent	2	Analysis:
13	13	6/21	1346	R	T & C		2	Carbon Tetrachloride
								Vinyl Chloride
								Trichloroethylene
						TOTAL NO. OF CONTAINERS		

RELINQUISHED BY:	DATE / TIME	RECEIVED BY:	RELINQUISHED BY:	DATE / TIME	RECEIVED BY:
1 (SIGN)	6/21 1400	2 (SIGN)	2 (SIGN)		3 (SIGN)
RELINQUISHED BY:	DATE / TIME	RECEIVED BY:	RELINQUISHED BY:	DATE / TIME	RECEIVED BY:
3 (SIGN)		4 (SIGN)	4 (SIGN)		5 (SIGN)
RELINQUISHED BY:	DATE / TIME	RECEIVED BY:	RELINQUISHED BY:	DATE / TIME	RECEIVED BY:
5 (SIGN)		6 (SIGN)	6 (SIGN)		7 (SIGN)

METHOD OF SHIPMENT:	SHIPPED BY:	RECEIVED FOR LABORATORY:	DATE / TIME
Fed Exp P.1	Robinson	(SIGN)	

AWB 611891593

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

   $$\text{mg} = \text{mg sample} - \text{mg blank}$$

   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.

   $$\text{corrected mg/sample} = \frac{\text{total weight}}{\text{DE}}$$

4. Calculate the concentration of the analyte in air

   $$\text{mg/m}^3 = \frac{\text{Corrected mg} \times 1000 \text{ liters/m}^3}{\text{Air volume Sampled (liters)}}$$

5. Concentration will be reported as ppm, corrected to standard conditions of 25°C and 760 mm Hg

   $$\text{ppm} = \text{mg/m}^3 \times \frac{24.45}{\text{MW}} \times \frac{760}{\text{P}} \times \frac{(\text{T}+273)}{298}$$

   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)

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.

FORMULA: Table 1

M.W.: Table 1

HYDROCARBONS, HALOGENATED

METHOD: 1003
ISSUED: 2/14/84

COMPOUNDS: (synonyms in Table 1)
benzyl chloride
bromoform
carbon tetrachloride
chlorobenzene
chlorobromomethane
chloroform
o-dichlorobenzene
p-dichlorobenzene
1,1-dichloroethane
1,2-dichloroethylene
ethylene dichloride
hexachloroethane
methylchloroform
propylene dichloride

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: Table 2
-MAX: Table 2

SHIPMENT: routine

SAMPLE STABILITY: at least 1 week @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

[illegible] see EVALUATION OF METHOD [1]

BIAS: not significant [1]

OVERALL PRECISION (s_r): see EVALUATION OF METHOD [1]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: compounds above

DESORPTION: 1 mL CS_2, stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURES: Table 2

CARRIER GAS: N_2 or He, 30 mL/min

COLUMN: Table 2; alternates are SP-2100,
SP-2100 with 0.1% Carbowax 1500
or DB-1 fused silica capillary column

CALIBRATION: solutions of analyte in CS_2 with
[illegible]

RANGE: Table 2

ESTIMATED LOD: 0.01 mg per sample [2]

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.
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 $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of analyte in the air volume sampled, V (L):

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

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:

[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 NIOSH [6-10] ACGIH	BP (°C)	VP @ 20 °C	Density (g/mL @ 20 °C)
p-Dichlorobenzene	1,4-$C_6H_4Cl_2$	147.00; 6.01	1,4-dichlorobenzene; CAS #106-46-7	75 ppm — 75 ppm, STEL 110 ppm	174	50 Pa	1.241
1,1-Dichloroethane	CH_3CHCl_2; $C_2H_4Cl_2$	98.96; 4.05	ethylidene chloride; CAS #75-34-3	100 ppm 100 ppm 200 ppm, STEL 250 ppm	57	24.3 kPa	1.174
1,2-Dichloroethylene	$ClCH=CHCl$; $C_2H_4Cl_2$	96.95; 3.96	acetylene dichloride; 1,2-dichloroethene; CAS #540-59-0	200 ppm 200 ppm 200 ppm, STEL 250 ppm	60 (cis) 47 (trans)	24-35 kPa	1.28
Ethylene dichloride*	$ClCH_2CH_2Cl$; $C_2H_4Cl_2$	98.96; 4.05	1,2-dichloroethane; CAS #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*	CCl_3CCl_3; C_2Cl_6	236.74; 9.68	perchloroethane; CAS #67-72-1	1 ppm (skin) 1 ppm (skin) 10 ppm	187 (sublimes)	30 Pa	2.09
Methylchloroform	CH_3CCl_3; $C_2H_3Cl_3$	133.42; 5.45	1,1,1-trichloroethane; CAS #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	$CH_3CHClCH_2Cl$; $C_3H_6Cl_2$	112.99; 4.62	1,2-dichloropropane CAS #78-87-5	75 ppm 75 ppm 75 ppm, STEL 110 ppm	95	5.3 kPa	1.156 (25 °C)

*Suspect carcinogen.

	Sampling			Measurement				
	Air Sample Volume (L)					t (°C)		
Compound	Min	Max	Breakthrough in Air	Working Range (mg/m³)	Column*	Column Injector Detector	Internal Standard	Range (mg per sample)
1,1-Dichloroethane	1 @ 100 ppm	10	18.3 L [illegible]3 mg/m³	40 to 1215 (10 L)	A	50 100 175	--	0.4 to 12
1,2-Dichloroethylene	0.5 @ 200 ppm	3	5.4 L [illegible]09 mg/m³	80 to 2370 (3 L)	A	60 170 210	---	0.2 to 7
Ethylene dichloride	1 @ 50 ppm	10	29 L [illegible] mg/m³	40 to 1215 (3 L)	A	70 225 250	octane	0.1 to 4
Hexachloroethane	1 @ 1 ppm	10	43 L [illegible]g/m³	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 [illegible]08 mg/m³	190 to 5700 (3 L)	A	70 225 250	octane	0.6 to 17
Propylene dichloride	1 @ 75 ppm	10	18 L [illegible] mg/m³	35 to 1050 (10 L)	A	80 170 210	n-undecane	0.3 to 10

---

*A = 3 m x 3 mm stainless steel, 10% SP-1000 on [illegible] 100 mesh Supelcoport;
B = 6 m x 3 mm, otherwise same as A;
C = 3 m x 3 mm stainless steel, 10% OV-101 on [illegible]20 mesh Supelcoport; or
D = 3 m x 6 mm glass, [illegible] SP-2250 on 80/100 [illegible]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 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:

1. 30 ml/min (60 psig) Nitrogen carrier gas flow
2. 35 ml/min (25 psig) Hydrogen gas flow to detector
3. 400 ml/min (60 psig) Air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 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

$$\text{D.E.} = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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 2X 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.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

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.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

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

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liters/cu m)}}{\text{Air Volume Sampled (liters)}}$$

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

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

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," 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.

VINYL CHLORIDE

FORMULA: $CH_2=CHCl$; C_2H_3Cl

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

SAMPLER: SOLID SORBENT TUBE (2 tandem tubes, each with 150 mg activated coconut charcoal)

FLOW RATE: 0.05 L/min

VOL-MIN: 0.7 L
-MAX: 5 L

SHIPMENT: separate primary and backup tubes and cap each

SAMPLE STABILITY: 10 days @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 1 to 64 mg/m³ [2]

BIAS: -6% of calculated concentration [2]

OVERALL PRECISION (s_r): 0.06 [2]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: vinyl chloride

DESORPTION: 1 mL carbon disulfide; 30 min

INJECTION ALIQUOT: 5 µL

COLUMN: stainless steel, 6.1 m x 3.2 mm, 10% SE-30 on 80/100 mesh Chromosorb W (AW-DMCS)

CARRIER GAS: He, 40 mL/min

TEMPERATURE-INJECTOR: 230 °C
-DETECTOR: 230 °C
-COLUMN: 60 °C

CALIBRATION: solutions of vinyl chloride in CS_2

RANGE: 0.002 to 0.2 mg per sample [2]

ESTIMATED LOD: 0.00004 mg per sample [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].

REAGENTS:

1. Carbon disulfide,* chromatographic quality.
2. Vinyl chloride,*, 99.9%, in lecture bottle fitted with valve and septum.
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 CS_2 in a 10-mL volumetric flask.
    b. Open the valve of the syringe and withdraw the plunger to pull CS_2 into the barrel. (As vinyl chloride dissolves, a vacuum will be created, pulling CS_2 into the syringe.)
    c. Push the solution from the syringe into the flask. Rinse the syringe twice with 1-mL portions of CS_2 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 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.
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.

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.

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/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/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.

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 CS_2, 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 $W_b > W_f/10$, report breakthrough and possible sample loss.
15. Calculate concentration, C, of vinyl chloride in the air volume sampled, V (L):

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

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:

[1] TLVs - Threshold Limit Values for Chemical Substances and Physical Agents in the Work Environment with Intended Changes for 1983-84, 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.

VELSICOL CHEMICAL CORPORATION
ST. LOUIS, MICHIGAN
PROJECT Nº 1524

GAS VENT SAMPLING

DATE OF COLLECTION June 21 /85	**SAMPLER** Robinson	**BAROMETRIC PRESSURE** 29.955
TEMPERATURE 70.5	**RELATIVE HUMIDITY** 60%	
CHARCOAL LOT Nº 120	**TENAX LOT Nº** 271	

GAUGE	1	2	3	4	5	6	7	8	9	10	11
READING							0	0	0	0	0

GAS VENT NUMBER	PUMP NUMBER	SAMPLE NUMBER	SAMPLING TIME START	SAMPLING TIME FINISH	SAMPLING TIME ELAPSED	SAMPLING RATE (cc/min.)	SAMPLE VOLUME (ℓ)
1							
2							
3							
4							
5							
6							
7	9370	9	11.14	1134	20	250	5.0
8	9370	10	8.29	8 49	20	250	5 0
9	9370	11	9 49	10.09	20	250	5.0
10	9370	12	12.03	12.23	20	250	5.0
11	9370	13	13 26	13 46	20	250	5.0
DUPLICATE							
BLANK							

DATE OF SAMPLE SHIPMENT June 21 1985

METHOD OF SHIPMENT FED. Express AWB 611 891 593

COMMENTS

VELSICOL CHEMICAL CORPORATION
ST. LOUIS, MICHIGAN
PROJECT Nº 1524

GAS VENT SAMPLING

DATE OF COLLECTION June 20/85	SAMPLER D. Robinson	BAROMETRIC PRESSURE 29.935
TEMPERATURE 63.5	RELATIVE HUMIDITY 58.5	
CHARCOAL LOT Nº 120	TENAX LOT Nº 271	

GAUGE	1	2	3	4	5	6	7	8	9	10	11
READING	0	0	0	0	0	0					

GAS VENT NUMBER	PUMP NUMBER	SAMPLE NUMBER	SAMPLING TIME START	SAMPLING TIME FINISH	SAMPLING TIME ELAPSED	SAMPLING RATE (cc/min.)	SAMPLE VOLUME (ℓ)
1	9369	1	10.20	10.40	20	250	5.0
2	9369	3	12.46	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							
10							
11							
DUPLICATE	9369	2 (GV1)	10.43	11.03	20	250	5.0
BLANK	9369	6	13.56	1356	20	250	50

DATE OF SAMPLE SHIPMENT June 21 1985

METHOD OF SHIPMENT FED Express AWB 611 891 593

COMMENTS

VELSICOL CHEMICAL CORPORATION
ST. LOUIS, MICHIGAN
PROJECT Nº 1524

GAS VENT SAMPLING PUMPS CALIBRATION LOG

DATE JUNE 21 1985

CALIBRATED BY D ROBINSON

PUMP NUMBER	PUMP TYPE	BEFORE SAMPLING						AFTER SAMPLING					AVERAGE			
		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	29.98	250	250	0800	80	53	29.93	250	14.00	70.5	60	29.955	250
936.9		61	67	29.98	250	250	0814	80	53	29.93	250	14.10	70.5	60	29.955	250

COMMENTS

VELSICOL CHEMICAL CORPORATION
ST. LOUIS, MICHIGAN
PROJECT Nº 1524

GAS VENT SAMPLING PUMPS CALIBRATION LOG

DATE June 20 1985	CALIBRATED BY D Robinson

PUMP NUMBER	PUMP TYPE	BEFORE SAMPLING						AFTER SAMPLING					AVERAGE			
		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	29.94	250	1710	63.5	58.5	29.935	250
9369		55	83	29.93	250	250	0850	72	34	29.94	250	1725	63.5	58.5	29.935	250

COMMENTS

9-8

VELSICOL CHEMICAL CORPORATION

POST - CONSTRUCTION QUARTERLY MONITORING REPORT

SEPTEMBER 16-17 , 1985

Plant Site, St. Louis Michigan

September 1985
Ref. No. 1524

CONESTOGA-ROVERS & ASSOCIATES LIMITED

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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

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

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.

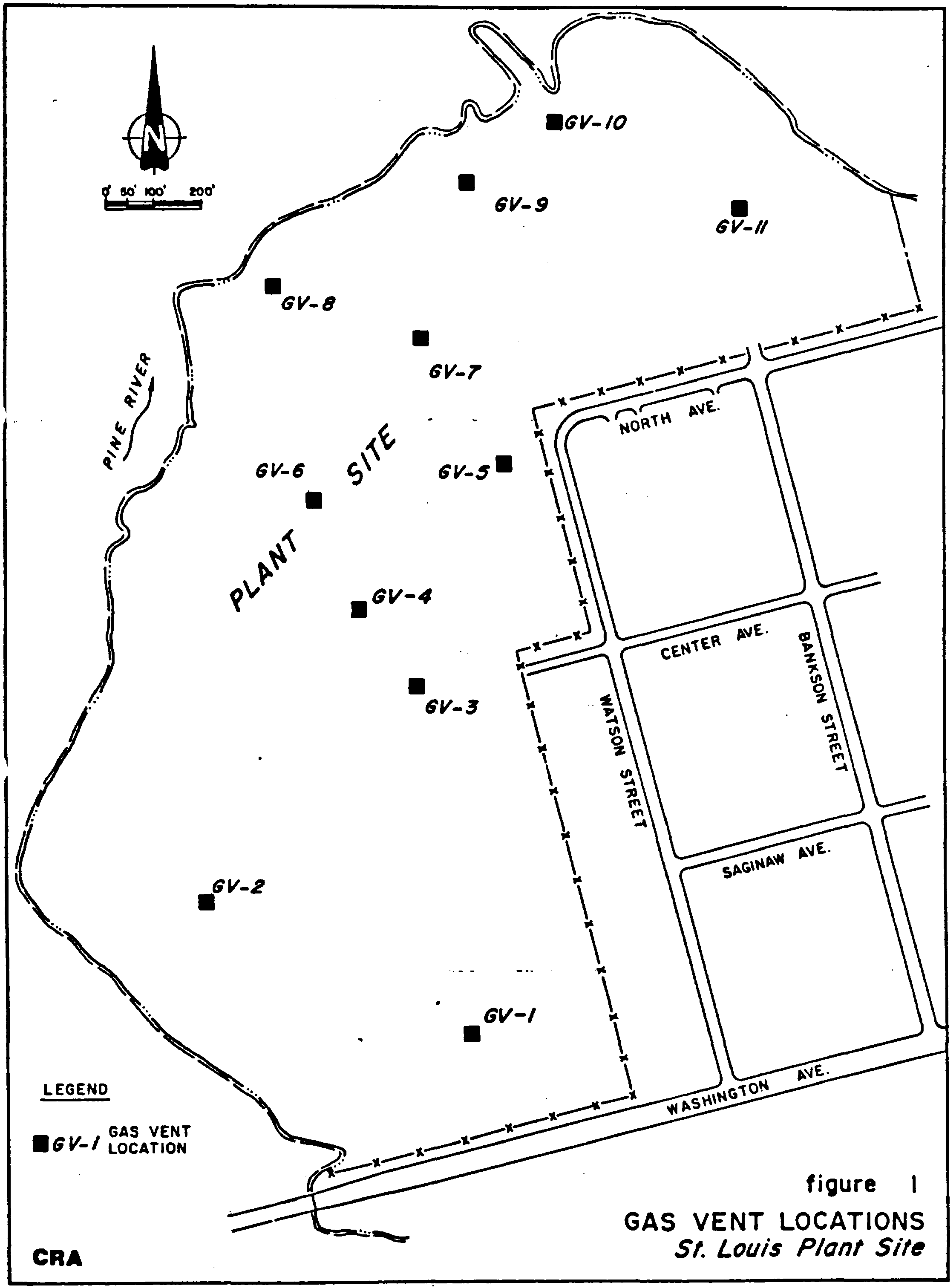

figure 1

GAS VENT LOCATIONS

St. Louis Plant Site

1524-19/03/85

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.

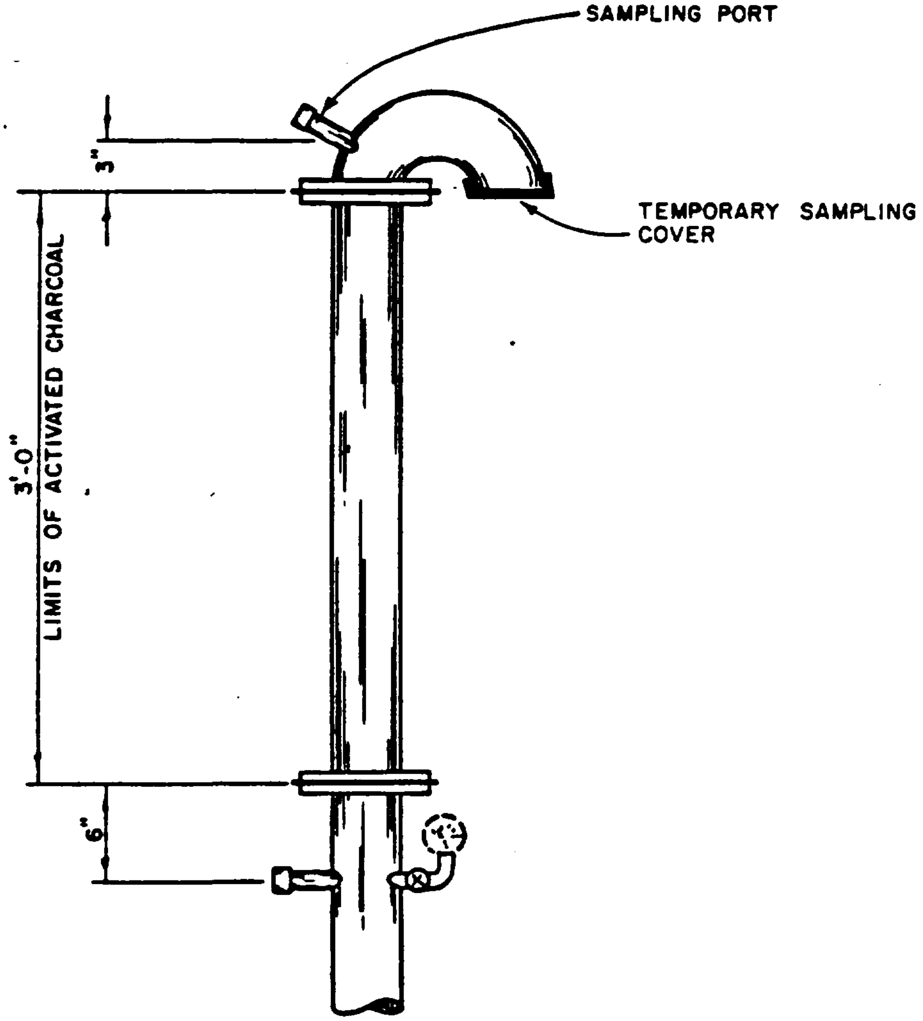

figure 2

ACTIVATED CHARCOAL GAS VENT DETAIL

St. Louis Plant Site

CRA

1524- 27/09/85

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.

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 1.0×10^{-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

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

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.

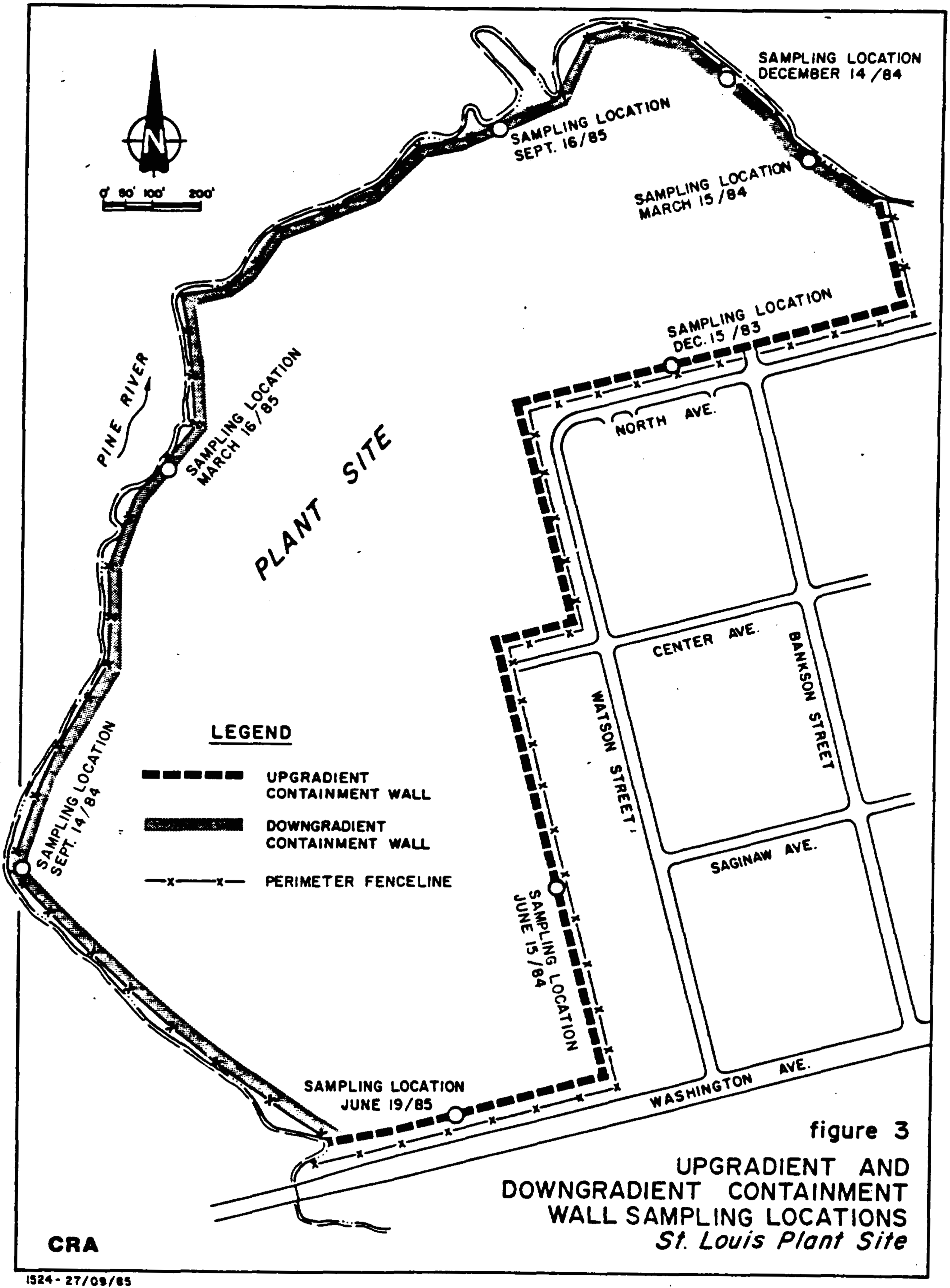

figure 3

UPGRADIENT AND DOWNGRADIENT CONTAINMENT WALL SAMPLING LOCATIONS
St. Louis Plant Site

1524-27/09/85

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 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.

TABLE 1

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

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.

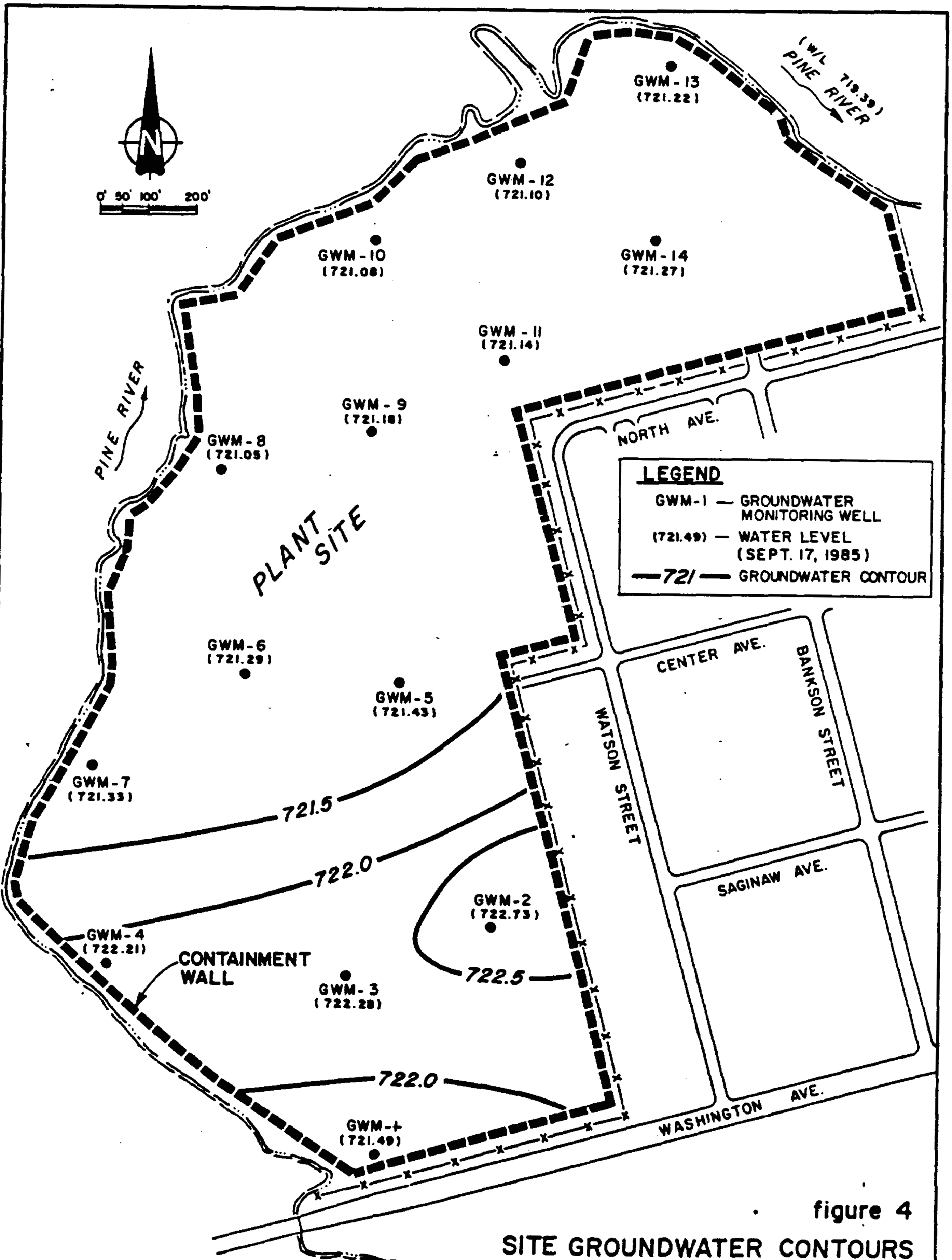

figure 4

SITE GROUNDWATER CONTOURS

St. Louis Plant Site

CRA

1524-27/09/85

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 Cull

C. Cull, B.Sc.

R.G. Shepherd, P. Eng.

APPENDIX A

CHAIN OF CUSTODY

SHEET OF

CHAIN OF CUSTODY RECORD	PROJECT NO. 1524	PROJEC ME: GAS VENT MONITORING PLANT SITE ST. LOUIS, MICHIGAN	VELSICOL CHEMICAL CORPORATION 701 W. WASHINGTON STREET ST. LOUIS, MICHIGAN 48880

SAMPLER'S SIGNATURE Catherine A Cull (SIGN)

SAMPLE NO.	SEQ NO.	DATE	TIME	FRONT / REAR	TENAX / CHARCOAL	SAMPLE TYPE	NO. OF CONTAINERS	REMARKS
4	1	9/16	20 min	2@	2@	gas vent samples	4	Desorb w/in
3	2					for TCE vinyl		10 days)
7	13					Chloride & carbon		and
9	4					tetrachloride.		analyze
5	5							w/in 30
10	6							days
2	7							
8	8							Keep
6	9	9/17						samples
11	10							refrigerated
12	11							
1	12							
13	13					TOTAL NO. OF CONTAINERS 52		

RELINQUISHED BY: 1 Catherine A Cull (SIGN)	DATE/TIME	RECEIVED BY: 2 E. M[illegible] (SIGN)	RELINQUISHED BY: 2 (SIGN)	DATE/TIME	RECEIVED BY: 3 (SIGN)
RELINQUISHED BY: 3 (SIGN)	DATE/TIME	RECEIVED BY: 4 (SIGN)	RELINQUISHED BY: 4 (SIGN)	DATE/TIME	RECEIVED BY: 5 (SIGN)
RELINQUISHED BY: 5 (SIGN)	DATE/TIME	RECEIVED BY: 6 (SIGN)	RELINQUISHED BY: 6 (SIGN)	DATE/TIME	RECEIVED BY: 7 (SIGN)

METHOD OF SHIPMENT:	SHIPPED BY:	RECEIVED FOR LABORATORY: (SIGN)	DATE/TIME

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.

   $$\text{corrected mg/sample} = \frac{\text{total weight}}{\text{DE}}$$

4. Calculate the concentration of the analyte in air

   $$\text{mg/m}^3 = \frac{\text{Corrected mg} \times 1000 \text{ liters/m}^3}{\text{Air volume Sampled (liters)}}$$

5. Concentration will be reported as ppm, corrected to standard conditions of 25°C and 760 mm Hg

   $$\text{ppm} = \text{mg/m}^3 \times \frac{24.45}{\text{MW}} \times \frac{760}{\text{P}} \times \frac{(\text{T}+273)}{298}$$

   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)

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.

HYDROCARBONS, HALOGENATED

FORMULA: Table 1

M.W.: Table 1

METHOD: 1003
ISSUED: 2/14/84

COMPOUNDS: (synonyms in Table 1)	benzyl chloride	chlorobromomethane	1,1-dichloroethane	hexachloroethane
	bromoform	chloroform	1,2-dichloroethylene	methylchloroform
	carbon tetrachloride	o-dichlorobenzene	ethylene dichloride	propylene dichloride
	chlorobenzene	p-dichlorobenzene		

SAMPLING

SAMPLER: SOLID SORBENT TUBE
(coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.2 L/min

VOL-MIN: Table 2
-MAX: Table 2

SHIPMENT: routine

SAMPLE STABILITY: at least 1 week @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

[illegible] [1]

BIAS: not significant [1]

OVERALL PRECISION (s_r): see EVALUATION OF METHOD [1]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: compounds above

DESORPTION: 1 mL CS_2, stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURES: Table 2

CARRIER GAS: N_2 or He, 30 mL/min

COLUMN: Table 2; alternates are SP-2100, SP-2100 with 0.1% Carbowax 1500 or DB-1 fused silica capillary column

CALIBRATION: solutions of analyte in CS_2 with [illegible]

RANGE: Table 2

ESTIMATED LOD: 0.01 mg per sample [2]

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.
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 $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of analyte in the air volume sampled, V (L):

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

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:

[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 NIOSH [6-10] ACGIH	BP (°C)	VP @ 20 °C	Density (g/mL @ 20 °C)
p-Dichlorobenzene	1,4-$C_6H_4Cl_2$	147.00; 6.01	1,4-dichlorobenzene; CAS #106-46-7	75 ppm — 75 ppm, STEL 110 ppm	174	50 Pa	1.241
1,1-Dichloroethane	CH_3CHCl_2; $C_2H_4Cl_2$	98.96; 4.05	ethylidene chloride; CAS #75-34-3	100 ppm 100 ppm 200 ppm, STEL 250 ppm	57	24.3 kPa	1.174
1,2-Dichloroethylene	ClCH=CHCl; $C_2H_4Cl_2$	96.95; 3.96	acetylene dichloride; 1,2-dichloroethene; CAS #540-59-0	200 ppm 200 ppm 200 ppm, STEL 250 ppm	60 (cis) 47 (trans)	24-35 kPa	1.28
Ethylene dichloride*	$ClCH_2CH_2Cl$; $C_2H_4Cl_2$	98.96; 4.05	1,2-dichloroethane; CAS #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*	CCl_3CCl_3; C_2Cl_6	236.74; 9.68	perchloroethane; CAS #67-72-1	1 ppm (skin) 1 ppm (skin) 10 ppm	187 (sublimes)	30 Pa	2.09
Methylchloroform	CH_3CCl_3; $C_2H_3Cl_3$	133.42; 5.45	1,1,1-trichloroethane; CAS #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	$CH_3CHClCH_2Cl$; $C_3H_6Cl_2$	112.99; 4.62	1,2-dichloropropane CAS #78-87-5	75 ppm 75 ppm 75 ppm, STEL 110 ppm	95	5.3 kPa	1.156 (25 °C)

*Suspect carcinogen.

	Sampling			Measurement				
	Air Sample Volume (L)					t (°C)		
Compound	Min	Max	Breakthrough in Air	Working Range (mg/m³)	Column*	Column Injector Detector	Internal Standard	Range (mg per sample)
1,1-Dichloroethane	1 @ 100 ppm	10	18.3 L [illegible] mg/m³	40 to 1215 (10 L)	A	50 100 175	--	0.4 to 12
1,2-Dichloroethylene	0.5 @ 200 ppm	3	5.4 L [illegible]09 mg/m³	80 to 2370 (3 L)	A	60 170 210	---	0.2 to 7
Ethylene dichloride	1 @ 50 ppm	10	29 L 3[illegible] mg/m³	40 to 1215 (3 L)	A	70 225 250	octane	0.1 to 4
Hexachloroethane	1 @ 1 ppm	10	43 L [illegible] mg/m³	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 [illegible]08 mg/m³	190 to 5700 (3 L)	A	70 225 250	octane	0.6 to 17
Propylene dichloride	1 @ 75 ppm	10	18 L [illegible] mg/m³	35 to 1050 (10 L)	A	80 170 210	n-undecane	0.3 to 10

---

*A = 3 m x 3 mm stainless steel, 10% SP-1000 on [illegible] 100 mesh Supelcoport;
B = 6 m x 3 mm, otherwise same as A;
C = 3 m x 3 mm stainless steel, 10% OV-101 on [illegible] 120 mesh Supelcoport; or
D = 3 m x 6 mm glass, [illegible] SP-2250 on 80/100 mesh Supelcoport.

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:

1. 30 ml/min (60 psig) Nitrogen carrier gas flow
2. 35 ml/min (25 psig) Hydrogen gas flow to detector
3. 400 ml/min (60 psig) Air flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 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

$$\text{D.E.} = \frac{\text{Average Weight (mg) recovered}}{\text{Weight (mg) added}}$$

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 2X 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.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

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.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

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

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liters/cu m)}}{\text{Air Volume Sampled (liters)}}$$

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

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

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," 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.

VINYL CHLORIDE

METHOD: 1007
ISSUED: 2/15/84

FORMULA: $CH_2=CHCl$; C_2H_3Cl

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

SAMPLER: SOLID SORBENT TUBE
(2 tandem tubes, each with 150 mg activated coconut charcoal)

FLOW RATE: 0.05 L/min

VOL-MIN: 0.7 L
-MAX: 5 L

SHIPMENT: separate primary and backup tubes and cap each

SAMPLE STABILITY: 10 days @ 25 °C

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 1 to 64 mg/m³ [2]

BIAS: -6% of calculated concentration [2]

OVERALL PRECISION (s_r): 0.06 [2]

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: vinyl chloride

DESORPTION: 1 mL carbon disulfide; 30 min

INJECTION ALIQUOT: 5 µL

COLUMN: stainless steel, 6.1 m x 3.2 mm, 10% SE-30 on 80/100 mesh Chromosorb W (AW-DMCS)

CARRIER GAS: He, 40 mL/min

TEMPERATURE-INJECTOR: 230 °C
-DETECTOR: 230 °C
-COLUMN: 60 °C

CALIBRATION: solutions of vinyl chloride in CS_2

RANGE: 0.002 to 0.2 mg per sample [2]

ESTIMATED LOD: 0.00004 mg per sample [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].

REAGENTS:

1. Carbon disulfide,* chromatographic quality.
2. Vinyl chloride,*, 99.9%, in lecture bottle fitted with valve and septum.
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 CS_2 in a 10-mL volumetric flask.
    b. Open the valve of the syringe and withdraw the plunger to pull CS_2 into the barrel. (As vinyl chloride dissolves, a vacuum will be created, pulling CS_2 into the syringe.)
    c. Push the solution from the syringe into the flask. Rinse the syringe twice with 1-mL portions of CS_2 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 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.
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.

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.

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/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/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.

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 CS_2, 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 $W_b > W_f/10$, report breakthrough and possible sample loss.
15. Calculate concentration, C, of vinyl chloride in the air volume sampled, V (L):

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

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:

[1] TLVs - Threshold Limit Values for Chemical Substances and Physical Agents in the Work Environment with Intended Changes for 1983-84, 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.

VELSICOL CHEMICAL CORPORATION
ST. LOUIS, MICHIGAN
PROJECT Nº 1524

GAS VENT SAMPLING

DATE OF COLLECTION 16 SEPTEMBER 1985	SAMPLER CA CULL	BAROMETRIC PRESSURE 30.17											
TEMPERATURE 68°F	RELATIVE HUMIDITY 50%	GAUGE	1	2	3	4	5	6	7	8	9	10	11
CHARCOAL LOT Nº 120	TENAX LOT Nº 220	READING	0	0	0	0	0	0	0	0	0	0	0

GAS VENT NUMBER	PUMP NUMBER	SAMPLE NUMBER	SAMPLING TIME			SAMPLING RATE (cc/min.)	SAMPLE VOLUME (ℓ)
			START	FINISH	ELAPSED		
1	1	4	9/16 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	9	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	1	2	16:04	16:24	20	250	5
9	2	6	9/17 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 SHIPMENT Federal Express

COMMENTS

VELSICOL CHEMICAL CORPORATION
ST. LOUIS, MICHIGAN
PROJECT Nº 1524

GAS VENT SAMPLING PUMPS CALIBRATION LOG

DATE 16 SEPTEMBER 1985 **CALIBRATED BY** C A CULL

PUMP NUMBER	PUMP TYPE	BEFORE SAMPLING						AFTER SAMPLING					AVERAGE			
		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.)
1	GILIAN (A)	69	42	30.24	250	250	12:50	59	~~3~~ 67	30.11	250	10:15	68°	50	30.17	250
	(B)				240	250	12:53				250	10:17				250
2	GILIAN (A)				250	250	12:56				250	10:20				250
	(B)				260	250	12:58				250	10:23				250

COMMENTS

VELSICOL CHEMICAL CORPORATION

POST - CONSTRUCTION QUARTERLY MONITORING REPORT

DECEMBER 14-15 , 1985

Plant Site, St. Louis Michigan

December 1985
Ref. No. 1524

CONESTOGA-ROVERS & ASSOCIATES LIMITED

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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

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.

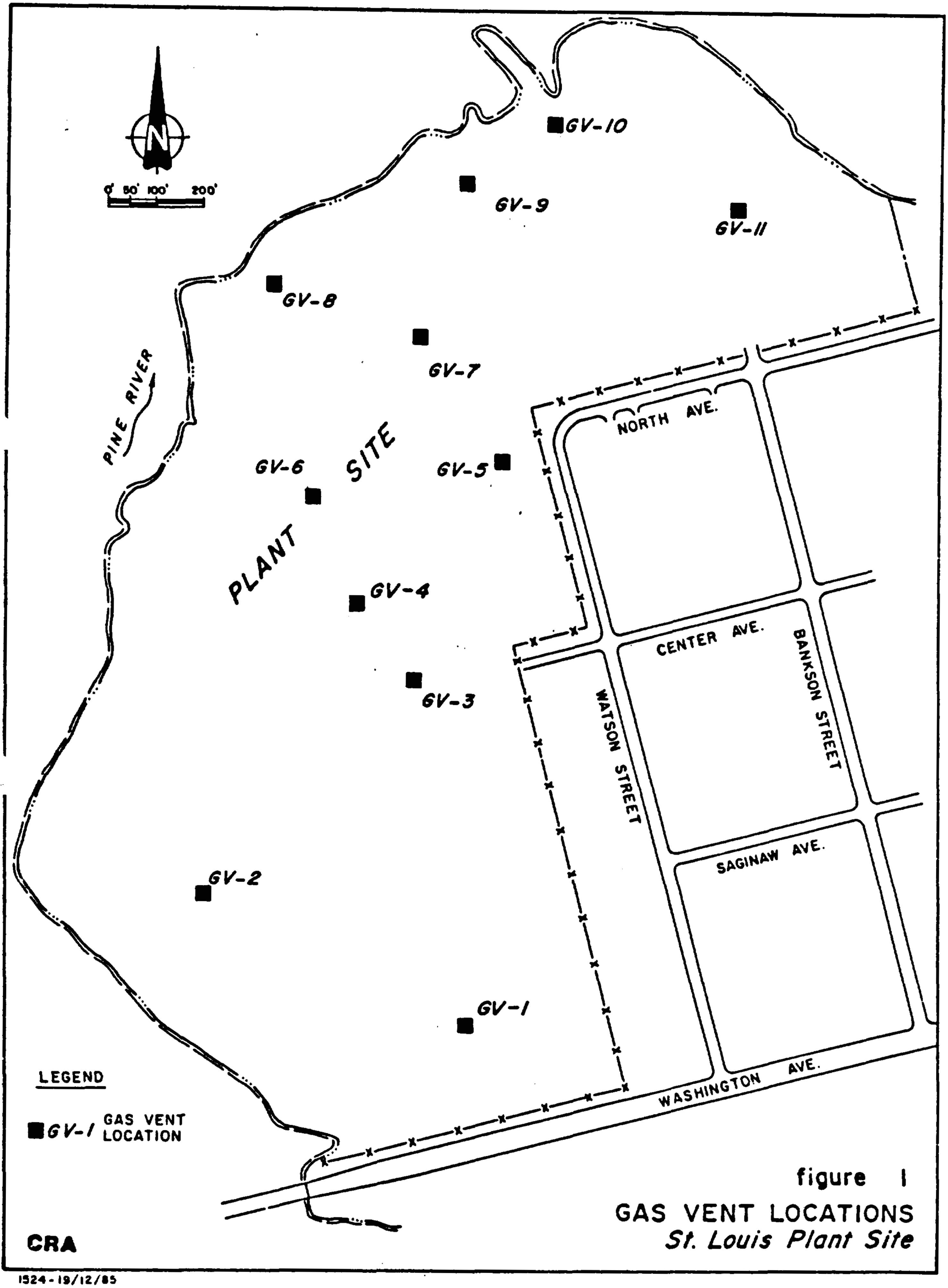

figure 1

GAS VENT LOCATIONS

St. Louis Plant Site

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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.

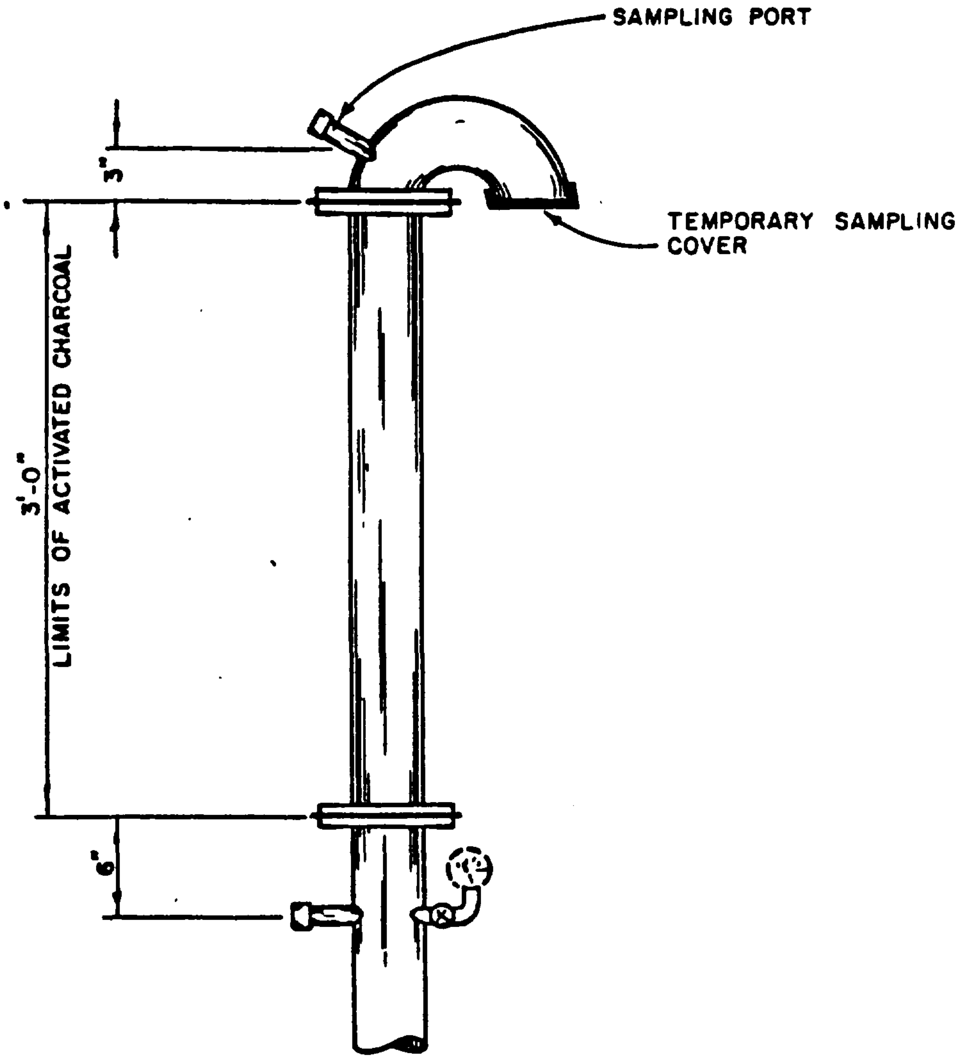

figure 2

ACTIVATED CHARCOAL GAS VENT DETAIL

St. Louis Plant Site

CRA

2.2.1 Sample Storage and Shipment

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

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

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.

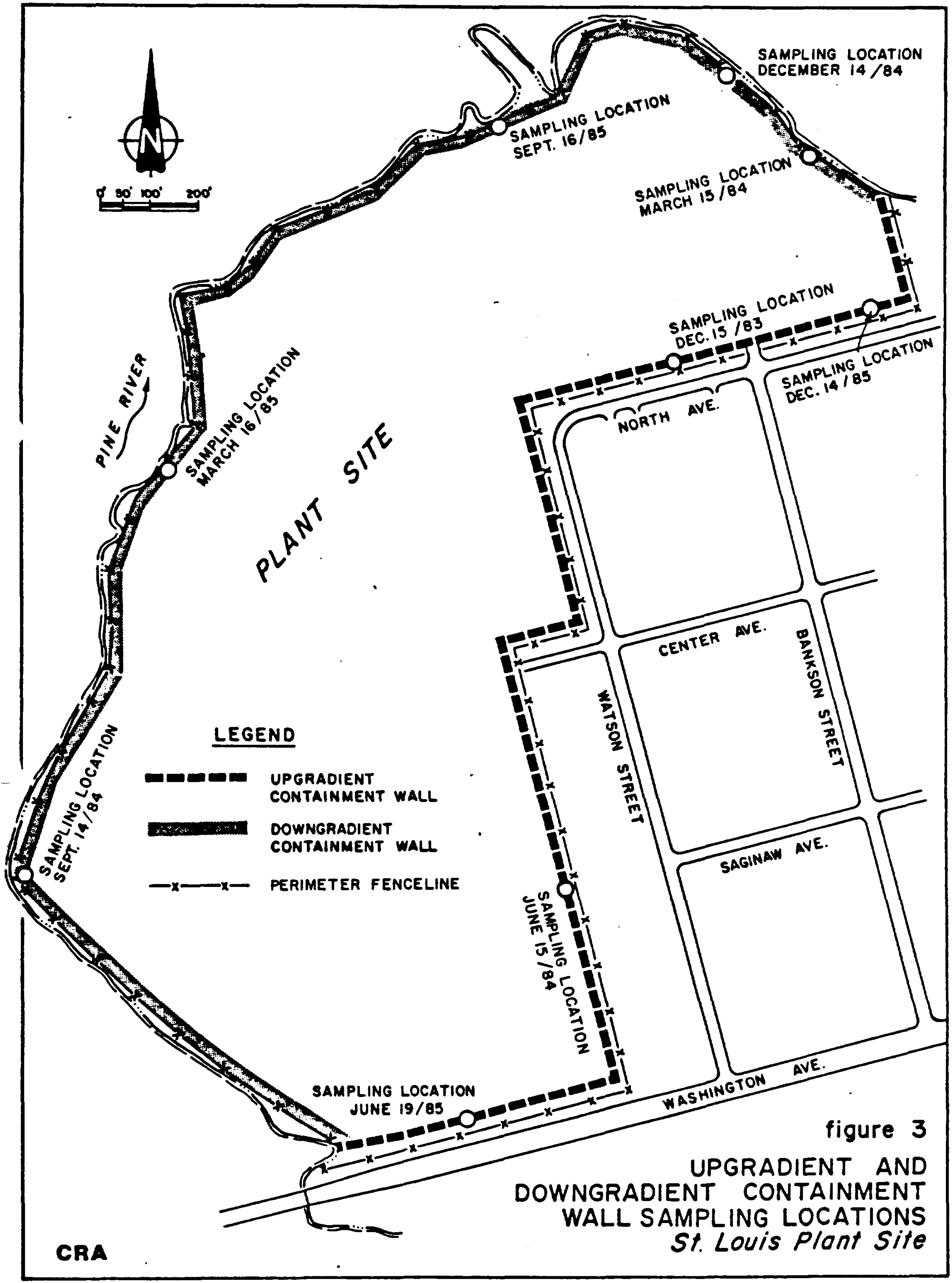

figure 3

UPGRADIENT AND DOWNGRADIENT CONTAINMENT WALL SAMPLING LOCATIONS
St. Louis Plant Site

1524-19/12/85

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 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

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

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.

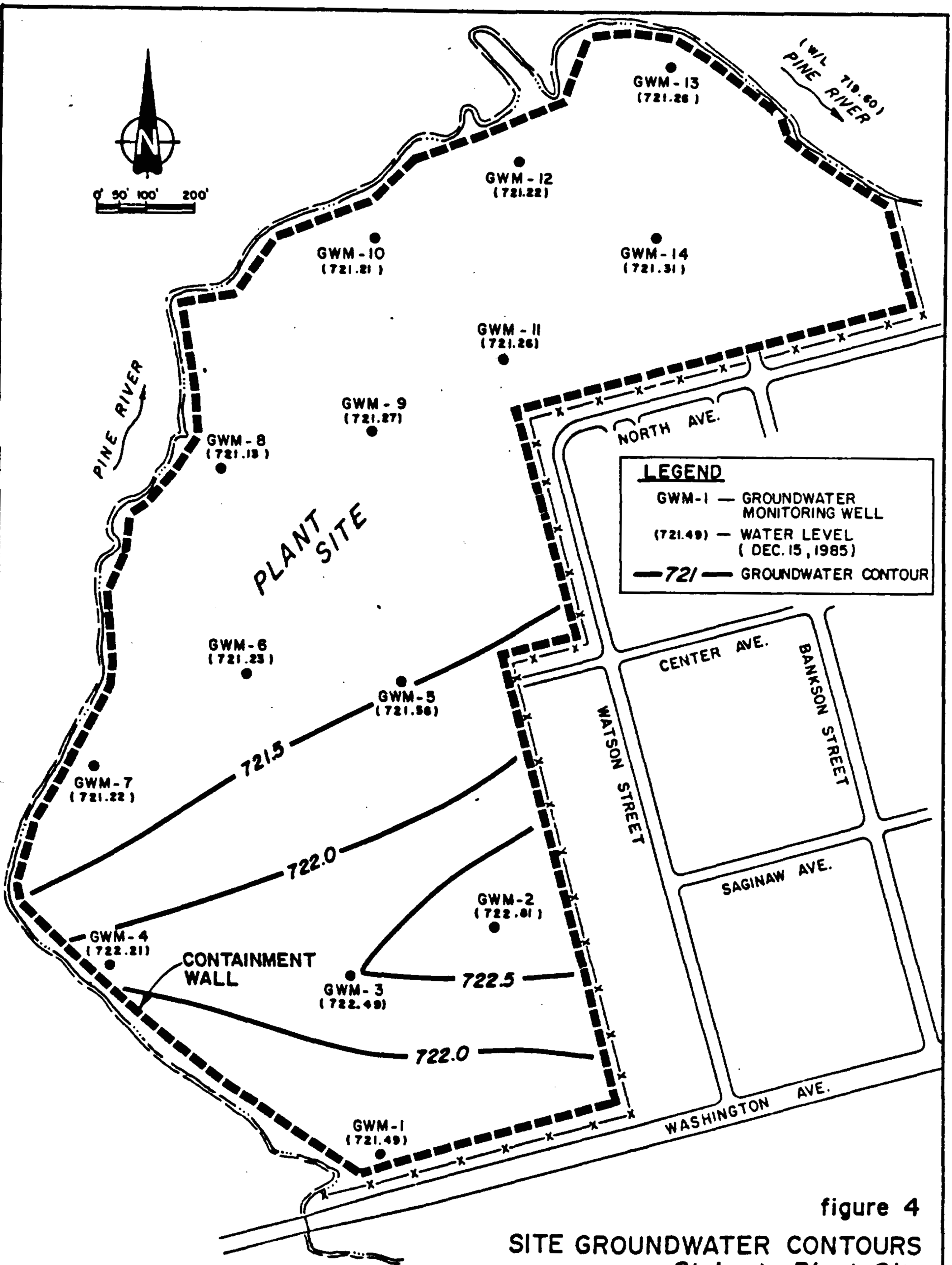

figure 4

SITE GROUNDWATER CONTOURS

St. Louis Plant Site

CRA

1524-19/12/85