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Methylene Chloride



Method no.:	80
Matrix:	Air
Target concentrations:	500 ppm (1736 mg/m ³) OSHA PEL 10 ppm (34.7 mg/m ³)
Procedure:	Samples are collected by drawing air through glass sampling tubes containing Carbosieve S-III (carbon based molecular sieve) adsorbent. Samples are desorbed with a mixture of 99:1 (v/v) carbon disulfide (CS ₂)/dimethylformamide (DMF) in the presence of anhydrous sodium sulfate and are analyzed by GC using a flame ionization detector.
Recommended air volume and sampling rate:	3 L at 0.05 L/min
Reliable quantitation limit:	0.201 ppm (0.697 mg/m ³)
Standard error of estimate at the target concentration: (Section 4.7)	5.8% (10 ppm) 6.5% (10 ppm)
Status of method:	Evaluated method. This method has been subjected to the established evaluation procedures of the Organic Methods Evaluation Branch.

Date: February 1990

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1. General Discussion

1.1 Background

1.1.1 History

This procedure allows the use of a single standard size (6-mm o.d. x 4-mm i.d. x 7 cm) adsorbent tube for the collection of methylene chloride. Because methylene chloride readily migrates on charcoal, earlier methods required the use of two standard size charcoal tubes connected in series, which could be isolated from each other after sampling, (Ref. 5.1) or the use of a custom designed jumbo size adsorbent tube containing an inconveniently large amount of charcoal (Ref. 5.2). These two procedures overcome the effects of migration by either isolating the backup section from the sampling section so that it would not be contaminated by the migrating methylene chloride or by using such a large quantity of charcoal that migration is slowed to an acceptable rate. The benefit of a single standard size adsorbent tube is made possible by the use of an adsorbent material, Carbosieve S-III, which demonstrates negligible methylene chloride migration. Carbosieve S-III, available through Supelco, Inc., is a spherical carbon molecular sieve and has a surface area of about 800 m²/g, about the same as charcoal.

This evaluation was performed at two target concentrations because the current OSHA PEL for methylene chloride is 500 ppm (TC-500) and OSHA is now in the process of 6(b) rule-making to reduce the occupational exposure to methylene chloride. For the purpose of this evaluation, 10 ppm was selected as the lower target concentration (TC-10). A goal of this evaluation was to develop a sampling procedure that will accommodate both the current PEL and a new lower limit if one is promulgated. The current ACGIH TLV is 50 ppm and the current NIOSH REL states that exposure to methylene chloride be controlled to the lowest feasible level. (Refs. 5.3-5.5)

1.1.2 Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy.)

Methylene chloride can affect the body if it is inhaled, swallowed or comes in contact with the eyes or skin. Methylene chloride is an anesthetic and inhaling the vapor may cause mental confusion, light-headedness, nausea, vomiting, and headache. Continued exposure may cause increased light-headedness, staggering, unconsciousness, and death. High vapor concentrations may cause irritation of the eyes and respiratory tract. Exposure to the liquid may cause irritation to the skin and eyes. Extended exposure to the liquid by the skin may cause skin burns. (Ref. 5.6)

Carbon monoxide is a metabolite of methylene chloride in animals and humans. NIOSH has recommended that if the carbon monoxide concentration is above 9 ppm, either the concentration of methylene chloride or carbon monoxide should be reduced. (Ref. 5.5)

On the basis of carcinogenic and tumorigenic responses in rats and mice, NIOSH recommends that methylene chloride be regarded as a potential occupational carcinogen. (Ref. 5.3)

1.1.3 Workplace exposure

Methylene chloride is used mainly as a solvent in paint removers, aerosol mixtures, chemical reaction processes and as a blowing agent for flexible foams. Photography, metal-work, refrigeration, chemical processing, pharmaceutical, flexible foam, and food industries use methylene chloride. (Ref. 5.8) Methylene chloride has been used to extract heat-sensitive naturally occurring substances, such as cocoa, edible fats, spices, and beer hops. It has also been used in the decaffeination of coffee. (Ref. 5.7)

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Approximately 230 million kilograms of methylene chloride were produced in the United States in 1988. (Ref. 5.9) In 1986, NIOSH estimated that 1 million workers were potentially exposed to methylene chloride. (Ref. 5.5)

1.1.4 Physical properties and other descriptive information (Ref. 5.10, unless otherwise stated)

CAS no.:	75-09-2
molecular weight:	84.93
molecular formula:	CH ₂ Cl ₂
melting point:	-97 °C
boiling point:	39.8 °C
vapor pressure:	53.3 kPa (400 mmHg) at 24.1 °C
vapor density:	2.93 (air = 1)
specific gravity:	1.3266 (water = 1)
explosive limit:	12% (lower) 19% (upper) (Ref. 5.11)
self-ignition temperature:	640 °C (Ref. 5.11)
odor:	penetrating ether-like
odor threshold:	205-307 ppm
appearance:	colorless liquid
solubility:	1-2 g/100 mL of water; soluble in most common organic liquids
synonyms:	dichloromethane; Aerothene MM; methylene dichloride; Narkotil; R30; Solaesthin; Solmethine; DCM; methane dichloride; methylene bichloride; NCI-C50102; UN 1593 (Ref. 5.11)

The analyte air concentrations throughout this method are based on the recommended sampling and analytical parameters. Air concentrations listed in ppm are referenced to 25°C and 101.3 kPa (760 mmHg).

1.2 Limit defining parameters

1.2.1 Detection limit of the analytical procedure

The detection limit of the analytical procedure is 0.0746 ng per injection (1.0- μ L injection with a 28:1 split). This is the amount of analyte that will give a peak whose height is approximately 5 times the height of the baseline noise. (Section 4.1)

1.2.2 Detection limit of the overall procedure

The detection limit of the overall procedure is 2.09 μ g per sample (0.201 ppm or 0.697 mg/m³). This is the amount of analyte spiked on the sampling device that allows recovery of an amount of analyte equivalent to the detection limit of the analytical procedure. (Section 4.2)

1.2.3 Reliable quantitation limit

The reliable quantitation limit is 2.09 μ g per sample (0.201 ppm or 0.697 mg/m³). This is the smallest amount of analyte spiked on the sampling device that can be quantitated within the requirements of a recovery of at least 75% and a precision (± 1.96 SD) of $\pm 25\%$ or better. (Section 4.3)

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The reliable quantitation limit and detection limits reported in the method are based upon optimization of the instrument for the smallest possible amount of analyte. When the target concentration of analyte is exceptionally higher than these limits, they may not be attainable at the routine operating parameters.

1.2.4 Instrument response to the analyte

The instrument response over the concentration range of 0.5 to 2 times the TC-10 and TC-500 target concentrations is linear. (Section 4.4)

1.2.5 Recovery

The recovery of methylene chloride from samples used in 17-day storage tests remained above 99.6% and 97.3% at the TC-10 and TC-500 levels, respectively, when the samples were stored at about 22°C. The recovery of analyte from the collection medium during storage must be 75% or greater. (Section 4.5, regression lines of Figures 4.5.1.1 and 4.5.2.1)

1.2.6 Precision (analytical procedure only)

The pooled coefficients of variation obtained from replicate determinations of analytical standards at 0.5, 1 and 2 times the target concentrations are 0.0330 and 0.0267 at the TC-10 and TC-500 levels respectively. (Section 4.6)

1.2.7 Precision (overall procedure)

The precisions at the 95% confidence level for the 17-day ambient temperature storage tests are $\pm 11.3\%$ and $\pm 12.7\%$ at the TC-10 and TC-500 levels respectively. (Section 4.7) These each include an additional $\pm 5\%$ for pump error. The overall procedure must provide results at the target concentration that are $\pm 25\%$ or better at the 95% confidence level.

1.2.8 Reproducibility

Six samples (TC-10) collected from a controlled test atmosphere and a draft copy of this procedure were given to a chemist unassociated with this evaluation. The samples were analyzed after 11 days of refrigerated storage. No individual sample result deviated from its theoretical value by more than the precision reported in Section 1.2.7. (Section 4.8)

1.3 Advantages

Because methylene chloride does not readily migrate on Carbosieve S-III, a single standard size Carbosieve S-III sampling tube may be used. This is not permissible with activated charcoal due to the migration of methylene chloride from the front section to the back section.

1.4 Disadvantages

1.4.1 The fine mesh size of Carbosieve S-III (60/80) results in a greater pressure drop across the sample tube than occurs with the conventional coconut shell charcoal sampling tube. This results in the need for the 0.05 L/min sampling rate.

1.4.2 The recommended sample size is 3 L as opposed to the 10 L sample size of previous methods.

2. Sampling Procedure

2.1 Apparatus

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- 2.1.1 Samples are collected using a personal sampling pump calibrated to within $\pm 5\%$ of the recommended flow rate with the sampling device attached
 - 2.1.2 Samples are collected with 4-mm i.d. x 6-mm o.d. x 70 mm glass sampling tubes packed with two sections of 60/80 mesh Carbosieve S-III. The front section contains 130 mg and the back section contains 65 mg of adsorbent. The sections are held in place with glass wool plugs. For this evaluation, Supelco's ORBO-91 Carbosieve S-III tubes (catalog no. 2-0360) were used.
- 2.2 Reagents
- 2.2.1 No sampling reagents are required.
 - 2.2.2 Technique
 - 2.2.3 Immediately before sampling, break off the ends of the Carbosieve S-III sampler. All samplers should be from the same lot.
 - 2.2.4 Attach the sampler to the sampling pump with plastic tubing such that the large front section of the sampler is exposed directly to the atmosphere. Do not place any tubing in front of the sampler.
 - 2.2.5 Attach the sampler vertically in the worker's breathing zone in such a manner that it does not impede work performance or safety.
 - 2.2.6 After sampling for the appropriate time, remove the sampler and seal the tube with plastic end caps. Wrap each sample end-to-end with a Form OSHA-21 seal.
 - 2.2.7 Submit at least one blank sampler with each set of samples. Handle the blank sampler in the same manner as the other samples except draw no air through it.
 - 2.2.8 Ship any bulk samples in a container separate from the air samples.
- 2.3 Sampler capacity
- The sampling capacity of the front section of a Carbosieve S-III sampling tube was determined by sampling a test atmosphere containing 20 ppm (69.5 mg/m³, 80% relative humidity) methylene chloride at ambient temperature. The sampling rate was 0.0503 L/min. The 5% breakthrough air volume was 7.6 L. (Section 4.9)
- The 5% breakthrough air volume was 3.34 L when sampling a test atmosphere containing 1018 ppm (3535 mg/m³, 83% relative humidity) of methylene chloride at 0.053 L/min. (Section 4.9)
- 2.4 Desorption efficiency
- 2.4.1 The average desorption efficiencies for methylene chloride from Carbosieve S-III adsorbent were quantitative over the range of 0.5 to 2 times the TC-10 and TC-500 target concentrations. (Section 4.10)
 - 2.4.2 Desorbed samples remain relatively stable for at least 24 h. (Section 4.10)
- 2.5 Recommended air volume and sampling rate
- 2.5.1 For time-weighted average samples collect 3 L at 0.05 L/min.
 - 2.5.2 For ceiling or peak samples (Table Z-2 of Title 29 CFR Part 1910.1000) collect the sample for at least 5 min at 0.05 L/min.
 - 2.5.3 When ceiling or peak samples are required, the reliable quantitation limit becomes larger. For example, the reliable quantitation limit is 2.41 ppm (8.36 mg/m³) for methylene chloride when 0.25 L is collected.

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- 2.6 Interferences (sampling)
- 2.6.1 It is not known if any compounds will severely interfere with the collection of methylene chloride on Carbosieve S-III. In general, the presence of other contaminant vapors in the air will reduce the capacity of Carbosieve S-III to collect methylene chloride.
- 2.6.2 Suspected interferences should be reported to the laboratory with submitted samples.
- 2.7 Safety precautions (sampling)
- 2.7.1 The sampling equipment should be attached to the worker in such a manner that it will not interfere with work performance or safety.
- 2.7.2 All safety practices that apply to the work area being sampled should be followed.
3. Analytical Procedure
- 3.1 Apparatus
- 3.1.1 A GC equipped with a flame ionization detector (FID). A Hewlett-Packard 5890 Gas Chromatograph equipped with a 7673A Autosampler, split/splitless injection port and an FID was used in this evaluation.
- 3.1.2 A GC column capable of separating methylene chloride from the desorbing solvent, the internal standard and any potential interferences. A 30-m × 0.32-mm i.d. SUPELCOWAX 10 (0.25 µm film thickness) capillary column (Supelco Inc.) was used in this evaluation.
- 3.1.3 An electronic integrator or some other suitable means of measuring detector response. A Hewlett-Packard 5895A GC ChemStation was used in this evaluation.
- 3.1.4 Two-milliliter vials with PTFE-lined caps.
- 3.1.5 A dispenser capable of delivering 1.0 mL of desorbing solution is used to prepare standards and samples. If a dispenser is not available, a 1.0-mL volumetric pipet may be used.
- 3.2 Reagents
- 3.2.1 Methylene chloride. Reagent grade or better should be used. The methylene chloride (b&j brand HIGH PURITY SOLVENT) used in this evaluation was purchased from American Burdick & Jackson (Muskegon, MI).
- 3.2.2 Carbon disulfide, CS₂. Reagent grade or better CS₂ should be used. The CS₂ (REAGENT ACS) was purchased from Fisher Scientific (Fair Lawn, NJ). In this evaluation, benzene-free CS₂ was used. The CS₂ had been passed through Molecular Sieve 13X (45/60 mesh) to remove the benzene contamination. Fifty grams of molecular sieve should remove the benzene from 1 L of carbon disulfide.
- 3.2.3 Dimethylformamide, DMF. Reagent grade or better should be used. The DMF (b&j brand HIGH PURITY SOLVENT) used in this evaluation was purchased from American Burdick & Jackson (Muskegon, MI).
- 3.2.4 Sodium sulfate, anhydrous. Sodium sulfate is used as a drying agent. The sodium sulfate (AR grade) used in this evaluation was purchased from Mallinckrodt (Paris, KY).
- 3.2.5 Desorbing solution. This consists of a solution of 99:1 (v/v) benzene-free CS₂/DMF. An internal standard such as ethyl benzene can be used.
- 3.2.6 Ethyl benzene. This was used as the internal standard in the desorbing solution. The solution is prepared by adding 250 µL of ethyl benzene to 1 L of desorbing solution. The ethyl benzene (reagent grade) used in this evaluation was purchased from Eastman Kodak (Rochester, NY).

Withdrawn
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3.3 Standard preparation

3.3.1 Prepare concentrated stock standards by diluting the methylene chloride with DMF. Prepare working analytical standards by injecting microliter amounts of concentrated stock standards into 2-mL vials containing 1 mL of desorbing solution delivered from the same dispenser used to desorb samples. For example, to prepare a TC-10 standard, inject 10 μ L of a stock solution containing 10.42 mg/mL methylene chloride in DMF into 1 mL of desorbing solution.

3.3.2 Prepare at least three standards at different concentrations to generate a calibration curve. Ensure that the amount of methylene chloride found in the samples is within the range of the standards. Prepare additional standards if necessary.

3.4 Sample preparation

3.4.1 Remove the plastic caps from the sample tube and carefully transfer each section of the adsorbent to separate vials. Discard the glass tube and glass wool plugs.

3.4.2 Add approximately 150 mg of anhydrous sodium sulfate to each sample.

3.4.3 Add 1.0 mL of desorbing solution to each vial and immediately seal the vials with PTFE-lined caps.

3.4.4 Shake the vials vigorously by hand several times during the next 30 min.

3.5 Analysis

3.5.1 Analytical conditions

GC conditions

temperatures: 40°C (column)
200°C (injector)
220°C (detector)

temp program: hold initial temp 1.0 min, increase temp at 5°C/min to 65°C, then increase temp at 25°C/min to 190°C.

column gas flow: 1.20 mL/min (hydrogen)

septum purge: 1.5 mL/min (hydrogen)

injection size: 1.0 μ L (with an appropriate split)

column: 30 m \times 0.32-mm i.d. capillary SUPELCOWAX 10 (0.25 μ m film thickness) column

retention times: 4.3 min (methylene chloride)
7.2 min (ethyl benzene)

FID conditions

hydrogen flow: 34 mL/min
air flow: 450 mL/min
nitrogen makeup flow: 33 mL/min

chromatogram: Figure 3.5.1

3.5.2 Measure detector response using a suitable method such as electronic integration.

3.5.3 An internal standard (ISTD) calibration method is used. A calibration curve can be constructed by plotting micrograms of methylene chloride per sample versus ISTD-corrected response of standard injections. Bracket the samples with freshly prepared analytical standards over a range of concentrations.

Withdrawn
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3.6 Interferences (analytical)

- 3.6.1 Any compound that responds on an FID and has a similar retention time as the analyte or internal standard is a potential interference. Generally, chromatographic conditions can be altered to separate an interference from the analyte.
- 3.6.2 Retention time on a single column is not considered proof of chemical identity. Analysis by an alternate GC column or confirmation by mass spectrometry are additional means of identification.

3.7 Calculations

The analyte concentration for samples is obtained from the appropriate calibration curve in terms of micrograms per sample, uncorrected for desorption efficiency. The air concentration is calculated using the following formulae. The back (65-mg) section is analyzed to determine if there was any breakthrough from the front (130-mg) section during sampling. If any analyte is found on the back section, it is added to the amount on the front section. This total amount is then corrected by subtracting the total amount (if any) found on the blank. If a significant amount of analyte is found on the back section (e.g., greater than 25% of the amount found on the front section), this should be reported with sample results.

$$mg/m^3 = \frac{(\text{micrograms of analyte per sample})}{(\text{liters of air sampled})(\text{desorption efficiency})}$$

where desorption efficiency is 1.05 for TC-10 or 0.989 for TC-500.

$$ppm = \frac{mg/m^3 (24.46)}{(\text{molecular weight of analyte})}$$

Where 24.46 is the molar volume (liters) at 101.3 kPa (760 mmHg) and 25°C, and the molecular weight is 84.93.

3.8 Safety precautions (analytical)

- 3.8.1 Restrict the use of all chemicals to a fume hood if possible.
- 3.8.2 Avoid skin contact and inhalation of all chemicals.
- 3.8.3 Wear safety glasses and a lab coat at all times while in the laboratory areas.

4. Backup Data

4.1 Detection limit of the analytical procedure

The detection limit of the analytical procedure is 0.0746 ng per injection, based on a 1.0- μ L injection (with a 28:1 split) of a 2.09 μ g/mL standard. This amount produced a methylene chloride peak whose height is about 5 times the height of the baseline noise in the chromatogram. A chromatogram of the detection limit of the analytical procedure is shown in Figure 4.1.

4.2 Detection limit of the overall procedure

The detection limit of the overall procedure is 2.09 μ g per sample (0.201 ppm or 0.697 mg/m³). The injection size listed in the analytical procedure (1.0 μ L) was used in the determination of the detection limit of the overall procedure. Eight vials containing 130 mg of Carbosieve S-III resin were spiked with 10 μ L of a solution containing 0.209 μ g/ μ L. The samples were desorbed about 24 h after being spiked.

Withdrawn
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Table 4.2. Detection Limit of the Overall Procedure for Methylene Chloride.

Sample no.	µg spiked	µg recovered
1	2.09	2.40
2	2.09	2.28
3	2.09	2.29
4	2.09	2.31
5	2.09	2.33
6	2.09	2.31
7	2.09	2.25
8	2.09	2.13

4.3 Reliable quantitation limit data

The reliable quantitation limit is 2.09 µg per sample (0.201 ppm or 0.697 mg/m³). The injection size listed in the analytical procedure (1.0 µL) was used in the determination of the reliable quantitation limit. Eight vials containing 130 mg of Carbosieve S-III resin were liquid-spiked with 10 µL of a solution containing 0.209 µg/µL or 2.09 µg of methylene chloride. Because the recovery of methylene chloride from the spiked samples was greater than 75% and had a precision of ±25 or better, the detection limit of the overall procedure and reliable quantitation limit are the same. The mean recovery was 109.5%, the standard deviation was 3.7%, and the precision was ±7.3% (1.96 × 3.7%)

Table 4.3. Reliable Quantitation Limit (Based on samples and data of Table 4.2).

Sample no.	µg spiked	% recovered
1	2.09	114.8
2	2.09	109.1
3	2.09	109.6
4	2.09	110.5
5	2.09	111.5
6	2.09	110.5
7	2.09	107.7
8	2.09	101.9

4.4 Instrument response to methylene chloride

The instrument response to methylene chloride over the range of 0.5 to 2 times the TC-10 and TC-500 target concentrations is linear with a slope of 5132 and 1474 respectively (in ISTD-corrected area counts per microgram per milliliter). The precision of the response to methylene chloride was determined by multiple injections of methylene chloride standards. The data below is presented graphically in Figure 4.4.1 and 4.4.2.

Withdrawn
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Table 4.4.1. Instrument Response to Methylene Chloride (Injection Split = 8:1).

x target concn (µg/mL)	0.5x (52.1)	1.0x (104.2)	2.0x (208.4)
	261	550	1073
	278	520	1105
	277	581	1055
area counts	276	532	1063
	276	542	1033
	266	539	1030
	264	535	1159
	272	530	1074
mean	271.3	541.1	1074.0

Table 4.4.2. Instrument Response to Methylene Chloride (Injection Split = 28:1).

x target concn (mg/mL)	0.5x (2.65)	1.0x (5.30)	2.0x (10.6)
	2935	8105	15786
	4005	7750	15637
	3977	7685	15354
area counts	3944	7801	15846
	4191	8191	15392
	4188	8151	16088
	4116	8119	15395
	4070	8190	16638
mean	4053.3	7999.0	15767.0

4.5 Storage data

4.5.1 Storage test at 10 ppm

Thirty-six storage samples were collected by sampling a dynamically generated atmosphere containing 57.4 mg/m³ or 16.5 ppm of methylene chloride and 80% relative humidity for 30 min at 0.05 L/min. One-half of the tubes was stored in a freezer (-20°C) and the other half was stored in a closed drawer at ambient temperature (about 22°C). At 3-4 day intervals, three samples were selected from each of the two storage sets and analyzed. The results are listed below and shown graphically in Figures 4.5.1.1. and 4.5.1.2.

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Table 4.5.1.1 Ambient storage test at TC-10.

time (days)	sample 1 (%)	sample 2 (%)	sample 3 (%)
0	101.1	101.1	98.9
0	99.4	100.1	100.0
4	98.5	98.4	99.5
7	101.2	99.6	99.5
11	106.3	103.9	101.2
14	104.9	96.9	101.2
17	109.4	99.1	98.7

Table 4.5.1.2. Refrigerated storage test at TC-10.

time (days)	sample 1 (%)	sample 2 (%)	sample 3 (%)
0	101.1	101.1	98.9
0	99.4	100.1	100.0
4	98.5	98.4	99.5
7	101.2	99.6	99.5
11	106.3	103.9	101.2
14	104.9	96.9	101.2
17	109.4	99.1	98.7

4.5.2 Storage test at 500 ppm

Thirty-six storage samples were collected by sampling a dynamically generated atmosphere containing 3516 mg/m³ or 1013 ppm of methylene chloride and 86% relative humidity for 30 min at 0.05 L/min. one-half of the tubes was stored in a freezer (-20°C) and the other half was stored in a closed drawer at ambient temperature (about 22°C). At 3-5 day intervals, three samples were selected from each of the two storage sets and analyzed. The results are listed below and shown graphically in Figures 4.5.2.1 and 4.5.2.2.

Table 4.5.2.1 Ambient storage test at TC-500.

time (days)	sample 1 (%)	sample 2 (%)	sample 3 (%)
0	99.8	98.3	104.4
0	96.8	97.9	102.9
4	94.7	103.6	90.4
7	93.6	96.3	97.4
11	93.4	92.3	94.7
14	102.9	94.0	96.5
17	100.3	102.7	98.9

Withdrawn
Provided for Historical Reference Only

Table 4.5.2.2. Refrigerated storage test at TC-10.

time (days)	sample 1 (%)	sample 2 (%)	sample 3 (%)
0	99.8	98.3	104.4
0	96.8	97.9	102.9
4	95.7	96.0	97.9
7	99.6	92.2	89.4
11	89.3	97.2	94.1
14	87.5	95.5	87.8
17	94.3	92.9	100.3

4.6 Precision (analytical method)

The precision of the analytical procedure is defined as the pooled coefficient of variation determined from replicate injections of methylene chloride standards at 0.5, 1 and 2 times the TC-10 and TC-500 target concentrations. Based on the data of Tables 4.4.1 and 4.4.2, the coefficients of variation (CV) for the three levels and the pooled coefficient of variation (CV) were calculated and are listed below.

Table 4.6.1. Precision of the analytical method (based on data of Table 4.4.1, SD in area counts).

x target concn (µg/mL)	0.5x (52.1)	1.0x (104.2)	2.0x (208.4)
SD	6.64	18.38	41.89
CV	0.02451	0.03397	0.03901
\overline{CV}	0.0330		

Table 4.6.2. Precision of the analytical method (based on data of Table 4.4.2, SD in area counts).

x target concn (mg/mL)	0.5x (2.65)	1.0x (5.30)	2.0x (10.6)
SD	103.8	214.4	436.7
CV	0.02561	0.02681	0.02770
\overline{CV}	0.0267		

4.7 Precision (overall procedure)

The precision of the overall procedure is determined from the storage data. The determination of the standard error of estimate (SEE) for a regression line plotted through the graphed storage data allows the inclusion of storage time as one of the factors affecting overall precision. The SEE is similar to the standard deviation except it is a measure of dispersion of data about a regression line instead of about a mean. It is determined with the following equation:

$$SEE = \sqrt{\frac{\sum(Y_{obs} - Y_{est})^2}{n - k}}$$

where n = total number of data points, k = 2 for linear regression or 3 for quadratic regression, Y_{obs} = observed percent recovery at a given time, Y_{est} = estimated percent recovery from the regression line at the same given time

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An additional 5% for pump error is added to the SEE by the addition of variances. The precision at the 95% confidence level is obtained by multiplying the SEE (with pump error included) by 1.96 (the z-statistic from the standard normal distribution at the 95% confidence level). The 95% confidence intervals are drawn about their respective regression lines in the storage graphs as shown in Figure 4.5.1.1. The data for Figures 4.5.1.1 and 4.5.2.1 was used to determine the SEE of $\pm 5.75\%$ and $\pm 6.48\%$ at the TC-10 and TC-500 levels respectively.

4.8 Reproducibility data

Six samples, collected from a dynamically generated atmosphere containing methylene chloride, were given to a chemist unassociated with this study. The samples were generated by drawing the 20-ppm test atmosphere through sampling tubes for 30-45 min at approximately 0.050 L/min. The samples were analyzed after being stored for 11 days at 5°C. No sample result had a deviation greater than the precision of the overall procedure, which is $\pm 11.3\%$.

4.9 Sampler capacity

4.9.1 Breakthrough for TC-10

Sampler capacity was determined by sampling from a dynamically generated atmosphere of 20 ppm (69.5 mg/m^3) methylene chloride with a Carbosieve S-III sampling tube that contained only the front section. The tube was followed by a whole Carbosieve S-III sampling tube. The backup tube was periodically changed over a 4 h time. The relative humidity of the test atmosphere was 80%. The sampling rate was 0.0503 L/min. The air volumes listed below are the midpoints of each sampling interval. The data is graphically shown in Figure 4.9.1.

Table 4.9.1. Breakthrough on the Carbosieve S-III Tube.

Air volume (L)	amt found (μg)	downstream (mg/m^3)	breakthrough (%)
0.75	2.56	1.696	2.44
2.26	0	0	0
3.77	0	0	0
4.91	0	0	0
5.66	0	0	0
6.41	2.39	3.162	4.55
7.17	0	0	0
7.92	2.5	3.308	4.76
8.68	4.32	5.720	8.23
9.43	6.99	9.244	13.3
10.2	8.49	11.26	16.2
10.9	12.6	16.61	23.9
11.7	14.5	19.25	27.7

4.9.2 Breakthrough for TC-500

Sampler capacity was determined by sampling from a dynamically generated atmosphere of 1018 ppm (3535 mg/m^3 , 83% relative humidity) methylene chloride with a Carbosieve S-III sampling tube that contained only the 130-mg front section. The sampling rate was 0.053 L/min. The air passing through the sampler was monitored with a GC equipped with a gas sampling valve. An injection was made every three minutes. After sampling for 63 min or 3.34 L, the concentration of methylene chloride in the air

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downstream of the sampler became greater than 5% of the upstream concentration. The data was collected (but not retained) by a computer that produced Figure 4.9.2.

4.10 Desorption efficiency and stability of desorbed samples

4.10.1 Desorption efficiency

The desorption efficiency (DE) of methylene chloride was determined by liquid-spiking 130-mg portions of Carbosieve S-III adsorbent with methylene chloride at 0.5 to 2 times the TC-10 and TC-500 target concentrations. These samples were stored overnight and then desorbed with desorbing solution and analyzed. The average desorption efficiency over the studied range was 105.4% and 98.9% at the TC-10 and TC-500 levels respectively.

Table 4.10.1.1. Desorption Efficiency of Methylene Chloride.

x TC-10 (µg/sample)	0.5x (52.1)	1.0x (104.2)	2.0x (208.4)
	101.9	103.0	108.4
	106.7	112.9	105.4
	108.6	103.2	109.6
DE, %	100.5	108.9	106.5
	97.1	106.2	105.0
	104.6	99.7	106.2
	105.9	101.0	107.7
	108.7	108.0	102.9
mean	104.3	105.4	106.4

Table 4.10.1.2. Desorption Efficiency of Methylene Chloride.

x TC-500 (mg/sample)	0.5x (2.65)	1.0x (5.30)	2.0x (10.6)
	101.2	103.2	99.6
	98.9	101.5	96.7
	100.9	98.4	95.4
DE, %	100.6	99.2	93.6
	99.3	98.8	99.7
	96.8	94.9	97.7
	102.9	98.2	99.1
	95.6	104.6	95.5
mean	99.5	99.9	97.2

4.10.2 Stability of desorbed samples

The stability of desorbed samples was investigated by reanalyzing the TC-10 samples (10 ppm) 24 h after initial analysis. The original analysis was performed and the vials were recapped after injection. The samples were reanalyzed with fresh standards. The average recovery, compared to the average recovery of the original analysis, was 100.4 or a +6.1% change.

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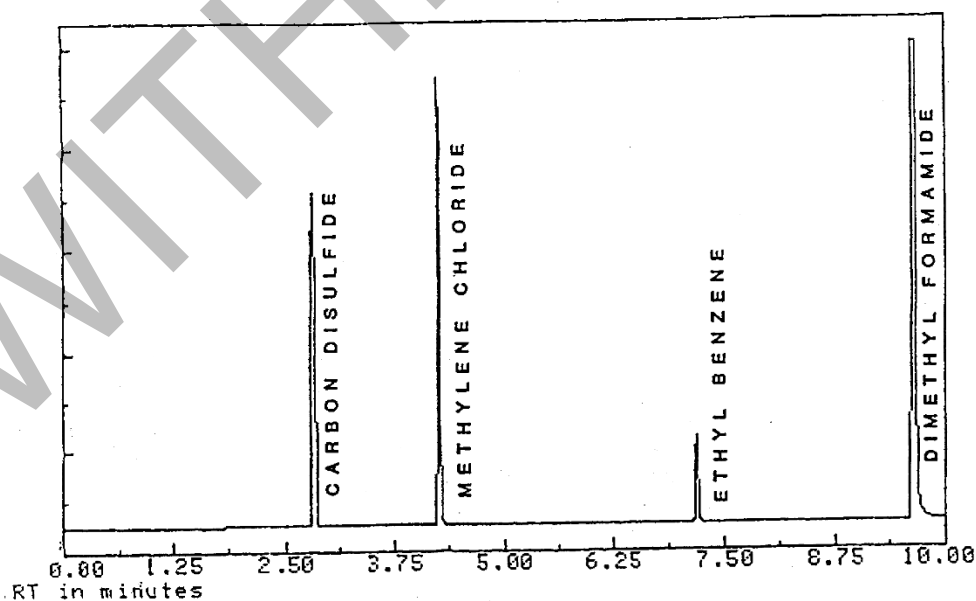
The stability of desorbed samples was investigated by reanalyzing the TC-500 samples (500 ppm) 24 h after initial analysis. The original analysis was performed and the vials were recapped after injection. The samples were reanalyzed with fresh standards. The average recovery, compared to the average recovery of the original analysis, was 101.2% or a +2.7% change.

Table 4.10.2.1. Stability of Desorbed TC-10 Samples.

Initial recovery (%)	recovery after 24 h (%)	percent change (%)
93.9	102.0	36.8
105.1	101.1	
94.7	97.6	
86.8	102.6	
91.4	98.4	
93.7	100.7	

Table 4.10.2.2. Stability of Desorbed TC-500 Samples.

Initial recovery (%)	recovery after 24 h (%)	percent change (%)
95.8	103.6	16.1
100.8	100.3	
97.9	101.5	
99.0	102.4	
98.5	94.8	
98.9	104.4	



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Figure 3.5.1. Chromatogram of methylene chloride at the TC-10 target concentration.

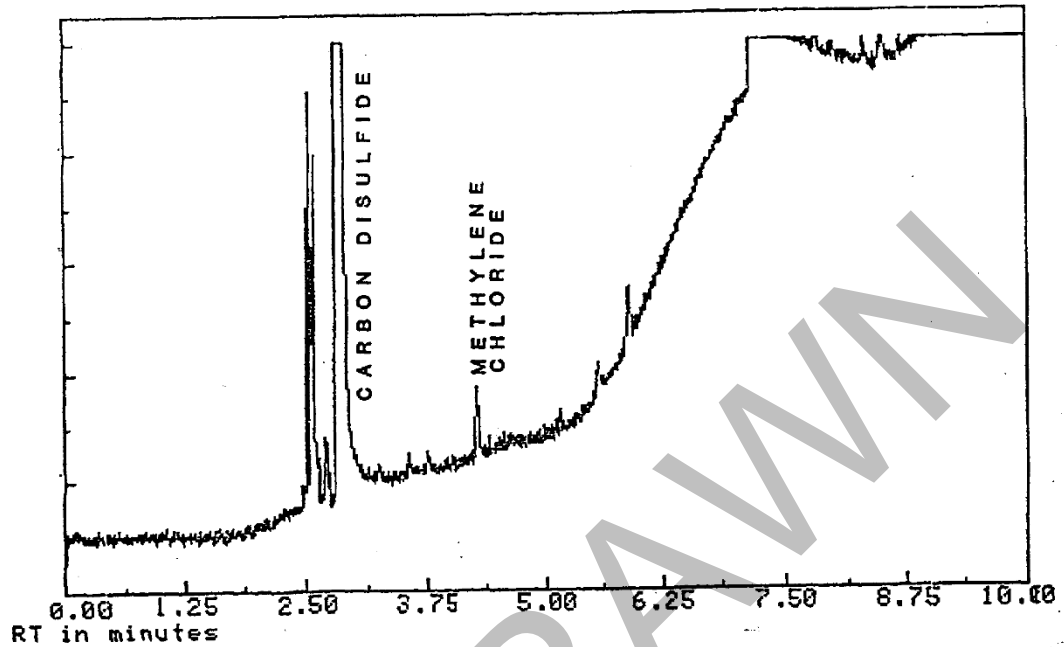


Figure 4.1. Chromatogram of methylene chloride at the detection limit, 0.0746 ng per injection, injection split = 28:1.

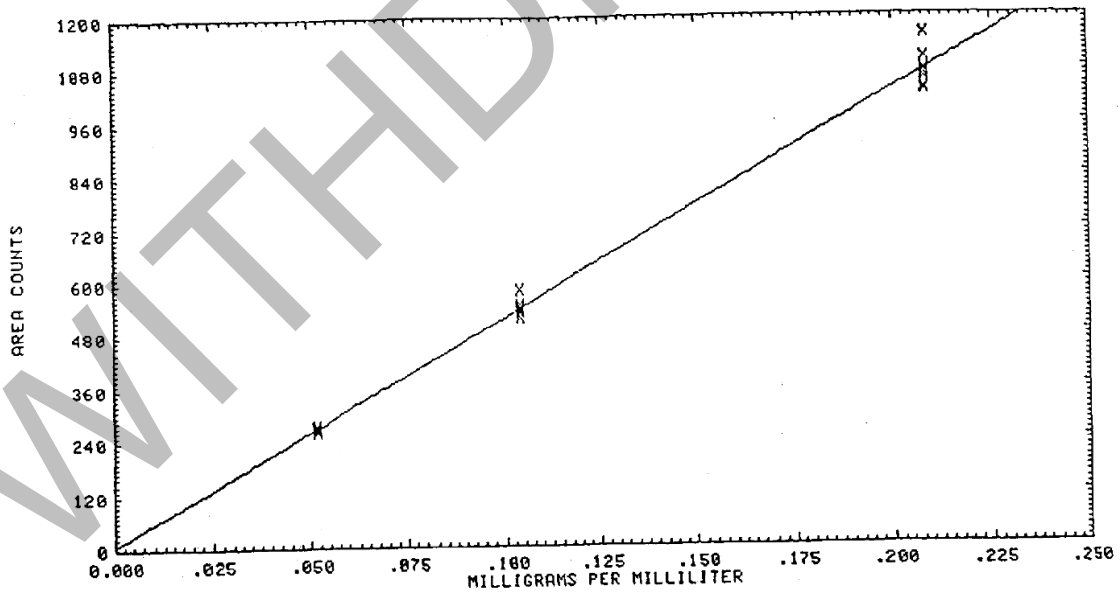


Figure 4.4.1. Instrument response curve for methylene chloride at 10 ppm, slope = 322 area counts per micrograms per milliliter, injection split = 8:1

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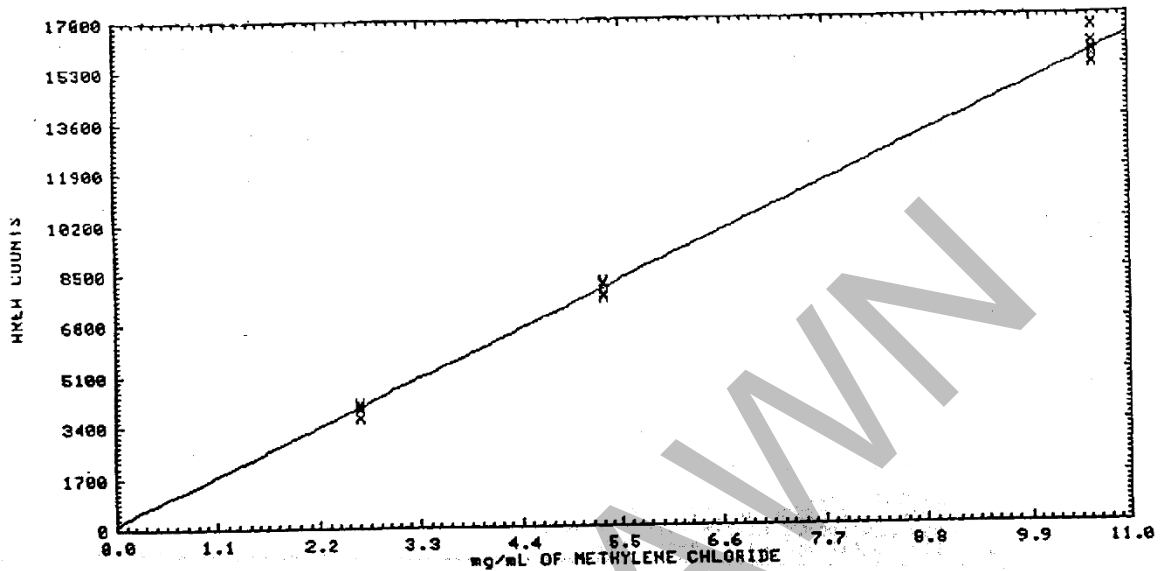


Figure 4.4.2. Instrument response curve for methylene chloride at 500 ppm, slopes = 1474 area counts per micrograms per milliliter, injection split = 28:1.

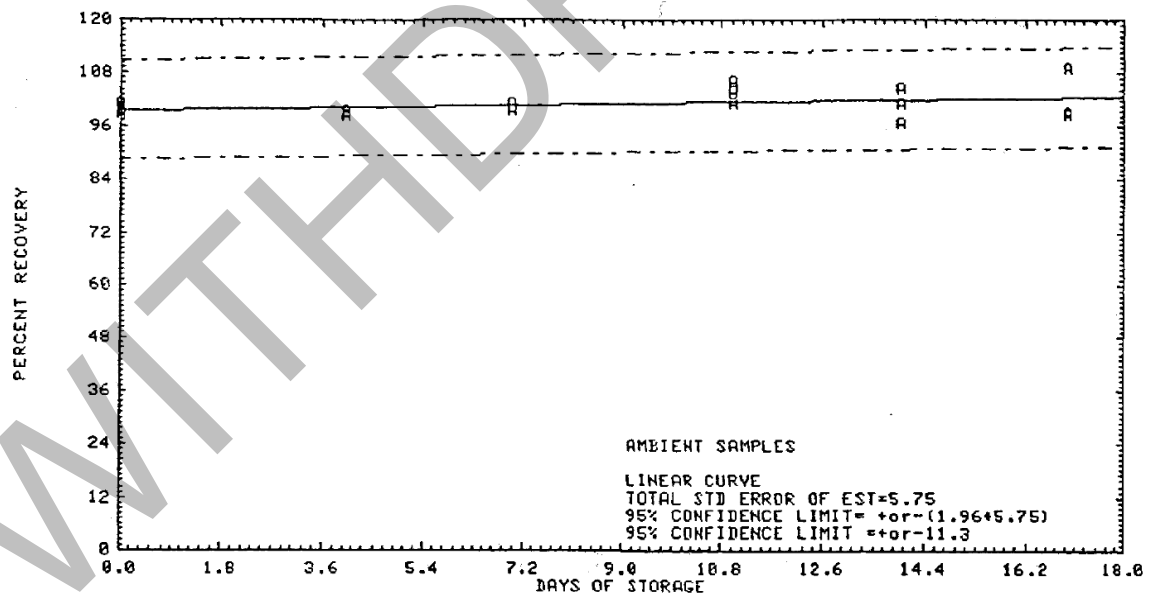


Figure 4.5.1.1. Ambient storage test for methylene chloride at 10 ppm.

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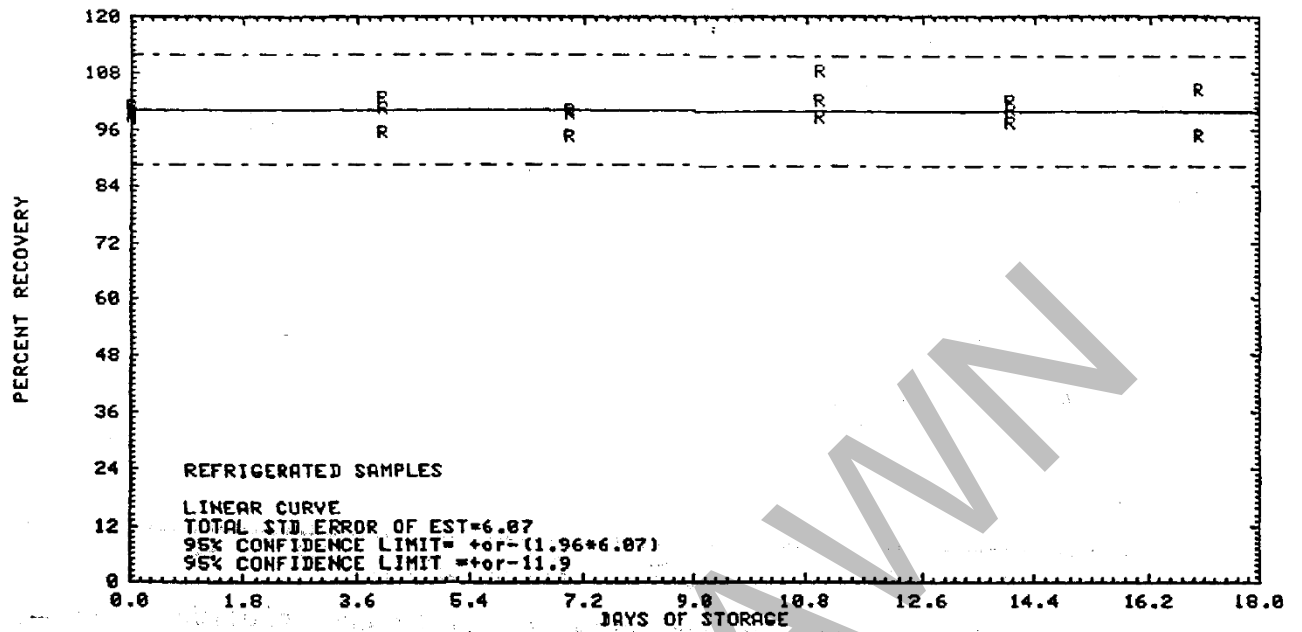


Figure 4.5.1.2. Refrigerated storage test for methylene chloride at 10 ppm.

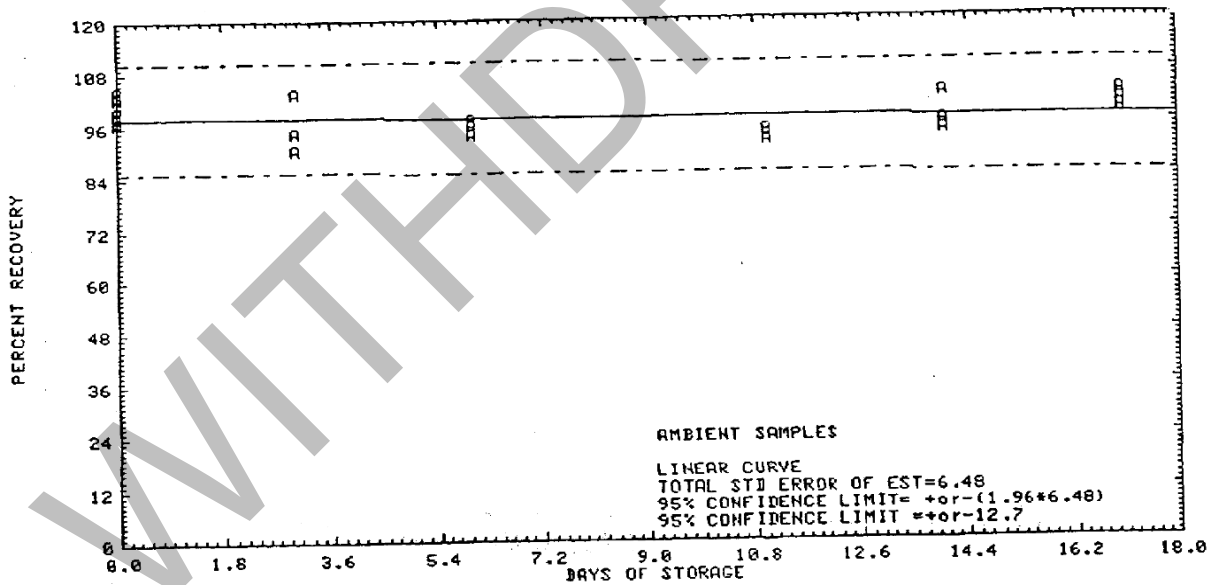


Figure 4.5.2.1. Ambient storage test for methylene chloride at 500 ppm.

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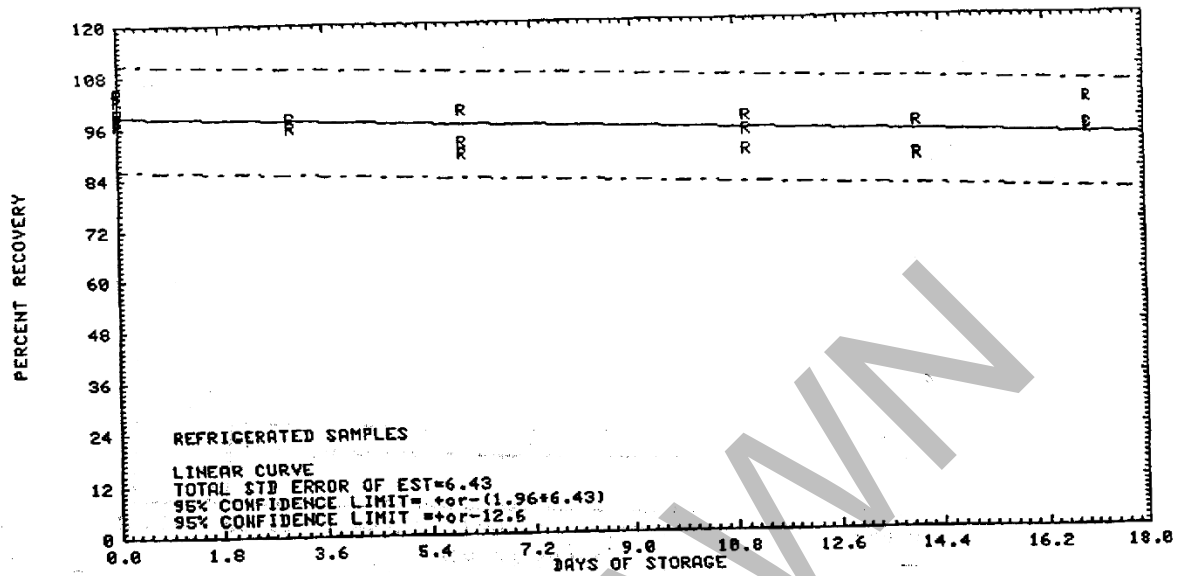


Figure 4.5.2.2. Refrigerated storage test for methylene chloride at 500 ppm.

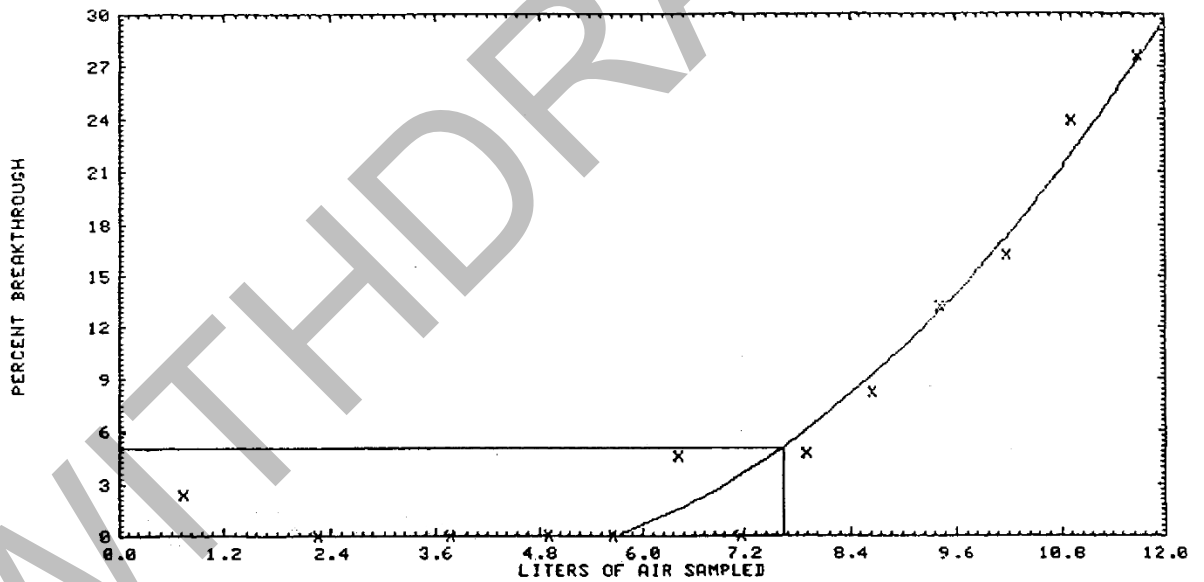


Figure 4.9.1. Determination of the 5% breakthrough air volume at 10 ppm.

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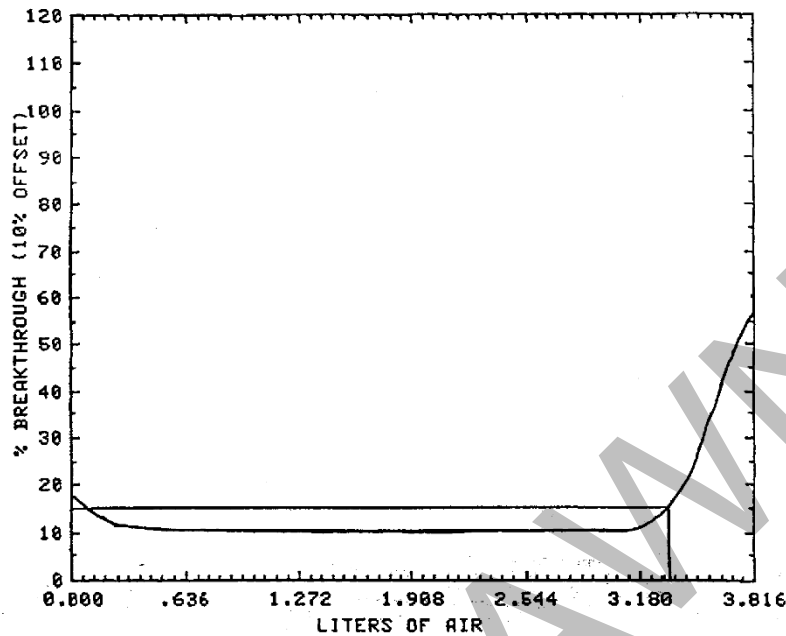


Figure 4.9.2. Determination of the 5% breakthrough air volume at 500 ppm.

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