

1,1,1-TRICHLOROETHANE



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Method no.: 14

Matrix: Air

Target Concentration: 350 ppm (1900 mg/m<sup>3</sup>) OSHA PEL

Procedure: Collection on charcoal adsorbent, desorption with carbon disulfide, analysis by GC using a flame ionization detector.

Recommended air volume and sampling rate: 3 L at 0.2 L/min

Reliable quantitation limit: 0.07 ppm (0.4 mg/m<sup>3</sup>)

Standard error of estimate at the PEL concentration: (Section 4.4) 5.2%

Status of method: Evaluated method, This method has been subjected to the established evaluation procedures of the Organic Methods Evaluation Branch.

Date: January 1980

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## 1. General Discussion

### 1.1 Background

#### 1.1.1 History

Outdated methods for the sampling and analysis of 1,1,1-trichloroethane called for collection of the sample in a gas sampling bag and analysis by infrared spectroscopy or GC. (Ref. 5.1) The use of gas sampling bags is awkward and impractical when they must be transported to a central laboratory for the analysis. Infrared absorption analysis is subject to serious interferences from other components collected in the sample. GC offers an efficient and specific mode of analysis when air samples are collected on charcoal, as in the NIOSH method. (Ref. 5.2) This procedure was evaluated in order to obtain additional data on storage stability of collected samples and collection capacity in humid atmospheres.

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

The following information is taken directly from Reference 5.3.

1,1,1,-Trichloroethane causes central nervous system depression.

A number of human fatalities related to industrial exposure in closed spaces have been reported, some of which may have been "sudden deaths" due to sensitization of the myocardium to epinephrine.

Based on effects caused in monkeys and rats, the following effects are expected in humans: 20,000 ppm for 60 min, coma and possibly death; 10,000 ppm for 30 min, marked incoordination; 2000 ppm for 5 min, disturbance of equilibrium. Human subjects exposed to 900 to 1000 ppm for 20 min experienced lightheadedness, incoordination, and impaired equilibrium; transient eye irritation has also been reported at similar concentrations.

A few scattered reports have indicated mild kidney and liver injury in humans from severe exposure; animal experiments have confirmed the potential for liver, but not for kidney, injury. Skin irritation has occurred from experimental skin exposure to the liquid and from occupational use. The liquid can be absorbed to a moderate degree through the skin.

In dogs, myocardial sensitization to epinephrine occurred at concentrations of 5000 to 10,000 ppm. In a carcinogenicity study, rats and mice were given the liquid orally at two different dose levels, five days a week for 78 weeks. Both female and male test animals exhibited early mortality compared with untreated controls, and a variety of neoplasms was found in both treated animals and controls. Although rats of both sexes demonstrated a positive dose-related trend, no relationship was established between the dosage groups, the species, sex, type of neoplasm, or the sites of occurrence.

The odor threshold has been described by various investigators as ranging from 16 to 400 ppm.

The TLV was set at a level to prevent mild irritation.

#### 1.1.3 Worker exposure

NIOSH estimates that there were 2.9 million workers exposed to 1,1,1-trichloroethane. (Ref. 5.4)

#### 1.1.4 Use and operations where exposure occur

1,1,1,-Trichloroethane is mainly used as a solvent for cleaning and other solvent applications. There were 630 million pounds produced in 1976. (Ref. 5.5)

Industries where 1,1,1-trichloroethane is used include: medical and other health services, automotive dealers and service stations, wholesale trade, printing and publishing, eating and drinking places, communications, chemicals and allied products, electrical equipment and supplies, fabricated metal products, and others. (Ref. 5.4)

### 1.1.5 Physical properties (Refs. 5.6 and 5.7)

molecular weight: 133.42  
specific gravity: 1.3249 (26°C/4°C)  
melting point: -32.62°C  
boiling point: 74.1°C  
vapor density: 4.6 (air = 1)  
vapor pressure: 127 mm Hg (25°C)  
color: colorless liquid  
refractive index: 1.43765 (21°C)  
saturated air: 16.7% (25°C)  
saturated air density: 1.6 (air = 1)  
solubility: insoluble in water; soluble in ethanol and ethyl ether  
molecular formula:  $\text{CCl}_3\text{CH}_3$

synonyms: (Ref. 5.4) Aerothene TT; Chloroethene NU; Chlorothene; Chlorothene NU; Chlorothene VG; Chlorten; Inhibisol; methyl chloroform; methyltrichloromethane; NCI-C04626; Alpha-T; trichlorethane;  $\alpha$ -trichloroethane.

## 1.2 Limit defining parameters

### 1.2.1 Detection limit of the analytical procedure

The detection limit of the analytical procedure is 1.2 ng per injection. This is the amount of analyte which will give a well defined peak on the tail from the solvent peak. (Section 4.1)

### 1.2.2 Detection limit of the overall procedure

The detection limit of the overall procedure is 1.2  $\mu\text{g}$  per sample (0.07 ppm or 0.4  $\text{mg}/\text{m}^3$ ). This is the amount of analyte spiked on the sampling device which allows recovery of an amount of analyte equivalent to the detection limit of the analytical procedure. (Section 4.1)

### 1.2.3 Reliable quantitation limit

The reliable quantitation limit is 1.2  $\mu\text{g}$  per sample (0.07 ppm or 0.4  $\text{mg}/\text{m}^3$ ). This is the smallest amount of analyte which can be quantitated within the requirements of 75% recovery and 95% confidence limits of  $\pm 25\%$ . (Section 4.2)

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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 an analyte is exceptionally higher than these limits, they may not be attainable at the routine operating parameters.

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### 1.2.4 Sensitivity

The sensitivity of the analytical procedure over a concentration range representing 0.1 to 2.1 times the PEL concentration based on the recommended air volume is 53430 area units per  $\text{mg}/\text{mL}$ . The sensitivity is determined by the slope of the calibration curve. (Section 4.3) The sensitivity will vary somewhat with the particular instrument used in the analysis.

### 1.2.5 Recovery

The recovery of analyte from the collection medium must be 75% or greater. The average recovery over the range of 0.5 to 2 times the PEL is 99.6%. (Section 4.1)

### 1.2.6 Precision (analytical method only)

The pooled coefficient of variation obtained from replicate determinations of analytical standards at 0.5, 1 and 2 times the PEL concentration is 0.0086. (Section 4.3)

### 1.2.7 Precision (overall procedure)

The overall procedure must provide results at the PEL concentration that are  $\pm 25\%$  or better at the 95% confidence level. The precision at the 95% confidence level for the

15-day storage test is  $\pm 11.0\%$  (Section 4.4). This includes an additional 5% for sampling error.

### 1.3 Advantages

1.3.1 The sampling procedure is convenient.

1.3.2 The analytical procedure is quick, sensitive, and reproducible.

1.3.3 Reanalysis of the samples is possible.

### 1.4 Disadvantages

If other compounds are present, the GC run time must be lengthened so the late eluting peaks will not interfere with the next sample.

## 2. Sampling Procedure

### 2.1 Apparatus

2.1.1 An approved and calibrated personal sampling pump whose flow can be determined within  $\pm 5\%$  at the recommended flow.

2.1.2 Charcoal tubes: Glass tube, with both ends heat sealed, 7.0 cm  $\times$  6-mm i.d.  $\times$  4-mm i.d., containing 100-mg front and 50-mg backup sections of 20/40 mesh charcoal SKC tubes or equivalent.

### 2.2. Reagents

None required.

### 2.3 Sampling technique

2.3.1 Immediately before sampling, break open the ends of the charcoal tube. All tubes must be from the same lot.

2.3.2 Connect the charcoal tube to the sampling pump with flexible tubing. The short section of the charcoal tube is used as a backup and should be positioned nearer the sampling pump.

2.3.3 The tube should be placed in a vertical position during sampling to minimize channeling.

2.3.4 Air being sampled should not pass through any hose or tubing before entering the charcoal tube.

2.3.5 Seal the charcoal tube with plastic caps immediately after sampling. Also, seal each sample with OSHA sealing tape lengthwise.

2.3.6 With each batch of samples, submit at least one blank tube from the same lot used for samples. This tube should be subjected to exactly the same handling as the samples (break, seal, transport) except that no air is drawn through it.

2.3.7 Transport the samples (and corresponding paperwork) to the lab for analysis.

2.3.8 If bulk samples are submitted for analysis, they should be transported in glass containers with Teflon-lined caps. These samples must not be put in the same container used for the charcoal tubes.

## 2.4 Breakthrough

Breakthrough tests were run on the primary portion of a charcoal tube (SKC Lot 107) at a sampling rate of 0.2 L/min from a generated test atmosphere. The test atmosphere was 708 ppm 1,1,1-trichloroethane with an average relative humidity of 81.4% at 24.6°C. The 5% breakthrough volume was 3.7 L. This was determined by monitoring the downstream effluent for 1,1,1-trichloroethane.

## 2.5 Desorption efficiency

The desorption efficiency from liquid injections on charcoal tubes (SKC Lot 107), averaged 99.6% for 2.98 to 11.9 mg per tube, which is 182 to 728 ppm for a 3-L air volume (Section 4.1).

## 2.6 Recommended air volume and sampling rate

2.6.1 The recommended air volume is 3 L.

2.6.2 The recommended sampling rate is 0.2 L/min.

2.6.3 If a longer sampling time is required, the sampling rate should be lowered to 0.1 L/min or 0.05 L/min.

## 2.7 Interferences (sampling)

2.7.1 At the present time, it is unknown if any compound would severely interfere with the collection of 1,1,1-trichloroethane on charcoal. In general, the presence of other solvents will decrease the breakthrough volume for a particular solvent.

2.7.2 Any compound which is suspected of interfering in the collection or analysis should be listed on the sampling data sheet.

## 2.8 Safety precautions

2.8.1 Safety glasses should be worn when breaking the ends of the tubes.

2.8.2 The broken ends of the tubes should be protected to avoid injury to the person being sampled.

2.8.3 When working in environments containing flammable vapors, do not provide any spark source from equipment used or pumps.

2.8.4 Observe all safety practices for working in hazardous areas.

# 3. Analytical Procedure

## 3.1 Apparatus

3.1.1 A GC equipped with a flame ionization detector.

3.1.2 A number of GC columns are available and adequate. The column used for this study was a 10-ft × 1/8-in. stainless steel 7% Penta 100/120 Chrom P AW.

3.1.3 An electronic integrator or other suitable method of measuring peak area.

3.1.4 Two-milliliter vials with Teflon-lined caps.

3.1.5 Microliter syringes, 50- $\mu$ L for preparing standards, 1- $\mu$ L for sample injections.

3.1.6 Pipets for diluting standards. A 1-mL pipet for dispensing solvent for desorption, or a 1-mL dispenser pipet.

3.1.7 Volumetric flasks, convenient sizes for preparing standards.

## 3.2 Reagents

- 3.2.1 Carbon disulfide, chromatographic grade.
- 3.2.2 1,1,1-Trichloroethane, reagent grade.
- 3.2.3 Purified GC grade helium, hydrogen, and air.

## 3.3 Standard preparation

- 3.3.1 Standards are prepared by diluting pure 1,1,1-trichloro- ethane with carbon disulfide.
- 3.3.2 Forty-five microliters of 1,1,1-trichloroethane per 10 mL of carbon disulfide equals 364 ppm for a 3-L air sample desorbed with 1 mL of carbon disulfide.

## 3.4 Sample preparation

- 3.4.1 The front and backup sections of each sample are transferred to separate 2-mL vials.
- 3.4.2 Each section is desorbed with 1.0 mL of carbon disulfide.
- 3.4.3 The vials are sealed immediately and allowed to desorb for 30 min with intermittent shaking.

## 3.5 Analysis

### 3.5.1 GC conditions

helium (carrier gas) flow rate: 25.1 mL/min  
injector temperature: 150°C  
detector temperature: 200°C  
column temperature: 80°C  
detector: flame ionization  
hydrogen flow rate: 43 mL/min  
air flow rate: 248 mL/min  
injection size: 1 µL

### 3.5.2 Chromatogram (Section 3.5.2)

- 3.5.3 Peak areas are measured by an electronic integrator or other suitable means.
- 3.5.4 An external standard procedure is used. The integrator is calibrated to report results in ppm for a 10-L air sample after correction for desorption efficiency.

## 3.6 Interferences (analytical)

- 3.6.1 Any compound having the same general retention time of 1,1,1-trichloroethane is an interference.
- 3.6.2 GC parameters may be changed to circumvent most interferences.
- 3.6.3 Retention time on a single column is not considered proof of chemical identity. Samples should be confirmed by GC/MS or other suitable means.

## 3.7 Calculations

Usually the integrator is programmed to report results in ppm (corrected for desorption efficiency) for a 3-L air sample. The following calculation is used:

$$\text{ppm} = (A)(3)/B$$

where A = ppm on report  
B = air volume, L

### 3.8 Safety precautions

- 3.8.1 All work using solvents (preparation of standards, desorption of samples, etc.) should be done in a hood.
- 3.8.2 Avoid any skin contact with all of the solvents.
- 3.8.3 Safety glasses should be worn throughout the procedure.

## 4. Backup Data

### 4.1 Detection limit data

#### 4.1.1 Analytical detection limit

A small amount of analyte (1.2 ng/injection) which still produced a well defined peak on the tail of the solvent peak was designated as the analytical detection limit. This was determined with an analytical standard which contained 0.009  $\mu\text{L}$  of 1,1,1-trichloroethane per milliliter of carbon disulfide or 1.2  $\mu\text{g}/\text{mL}$ . The chromatogram is shown in Figure 4.1.1.

Reproducibility of the peak, produced by replicate 1.2-ng injections, was good. Twelve injections gave an average analyte peak height of 35 mm with coefficient of variation of 2.4%.

A sample collected from 3 L of air which contained 1.2 ng/ $\mu\text{L}$  after desorption with 1 mL of carbon disulfide would represent an air concentration of 0.07 ppm.

#### 4.1.2 Desorption efficiencies for determining the overall detection limit and the reliable quantitation limit

Liquid injections were made on the front portion of charcoal tubes (SKC Lot 107) at 0.0012 to 11.92 mg. These charcoal tubes were refrigerated overnight and desorbed and analyzed the following day. These results are presented in Table 4.1.2 and in Figures 4.1.2.1 and 4.1.2.2. The overall detection limit was determined to be 1.2  $\mu\text{g}/\text{sample}$  in Figure 4.1.2.1.

Table 4.1.2  
Desorption Efficiencies for Various Sampler Loadings

$\mu\text{g}/\text{sample}$	11920	5960	2980	1484	296.8	59.4	11.9	2.37	1.187
desorption	98.2	99.6	101.7	99.8	100.4	97.2	101.1	99.7	100.7
efficiency,	98.5	99.5	99.4	99.0	100.2	98.0	101.0		100.0
%	96.4	94.7	100.1	99.1	100.2	101.0	100.4	99.0	102.0
	97.3	98.6	99.2						
	98.2	99.5	100.3						
	98.5	98.3	100.1						
	102.2	102.2	104.5						
	101.3	102.1	102.4						
$\bar{X}$	98.8	99.3	101.0						

The average desorption efficiency over the range of 2980 to 11920  $\mu\text{g}$  (0.5 to 2 times the target concentration) is 99.6%.

### 4.2 Reliable quantitation limit

The reliable quantitation limit was verified to be the same as the overall detection limit by liquid spiking six samples with loadings equivalent to the overall detection limit (1.187  $\mu\text{g}/\text{sample}$ ). These samples were analyzed to assure the requirements of at least 75% recovery with a precision (1.96 SD) of at least  $\pm 25\%$  were met.

Table 4.2  
Reliable Quantitation Limit

sample no.	% recovered
1	98.6
2	94.3
3	99.3
4	100.0
5	100.0
6	98.6
$\bar{X}$	98.5
SD	2.135
1.96(SD)	4.2

#### 4.3 Precision data

Multiple injections were made of standards that were prepared over a range of 0.1 to 2.1 times the OSHA standard. A standard deviation was determined at each concentration. The pooled coefficient of variation was determined for the range.

Table 4.3  
Analytical Precision

× target concn µg/sample	0.1× 596	0.2× 1190	0.5× 2980	1.0× 5960	2.1× 11920
area	33828	67545	166773	327123	647551
counts	33747	66599	165396	327763	643296
	34117	66413	167897	328157	642360
	33516	68164	164153	325401	635031
	33586	67086	163483	322931	634452
	33650	67182	163222	324246	633876
$\bar{X}$				323908	
SD				323029	
CV	33742	67165	165150	325319	639427
$\overline{CV}$	216	638	1882	2117	5735
	0.0064	0.0095	0.0114	0.0065	0.0090
	0.0086				

#### 4.4 Storage data

Samples were collected on charcoal tubes (SKC Lot 107) from a generated atmosphere containing 354 ppm 1,1,1-trichloroethane with an average relative humidity of 81% at 23.5°C. A storage study was then conducted in which the collected samples were divided into two groups; one stored at ambient temperature and the other under refrigeration. Every few days, three samples from each group were analyzed. The results are shown in Table 4.4 and in Figures 4.4.1 and 4.4.2.

Table 4.4  
Storage Tests

storage time (days)	% recovery (18.2 °C to 21 °C)			% recovery (-4 °C to 3 °C)		
1	106.0	103.1	104.4	102.8	104.7	102.5
3	101.0	103.2	102.8	100.6	99.8	100.8
6	101.8	101.5	103.3	104.2	101.6	102.0
9	105.4	102.6	100.9	102.0	99.3	101.6
12	104.3	103.0	102.1	102.2	101.0	101.5
15	100.9	100.0	101.6	102.3	100.8	101.1



Figure 3.5.2. Chromatogram of a standard of 1,1,1-trichloroethane.





Figure 4.1.1. Chromatogram of the analytical detection limit of 1,1,1-trichloroethane.

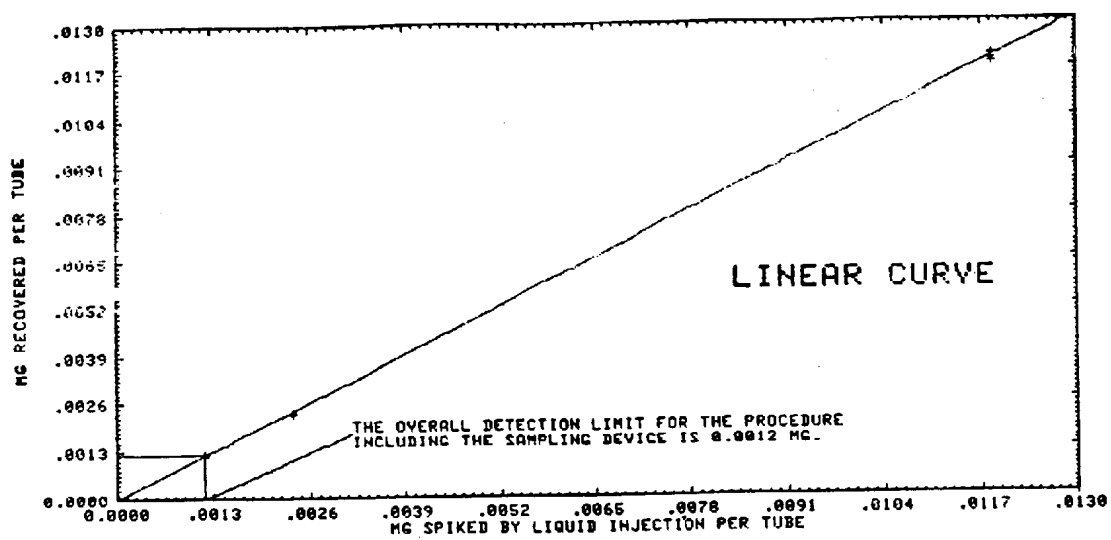


Figure 4.1.2.1. The detection limit of the overall procedure of 1,1,1-trichloroethane.

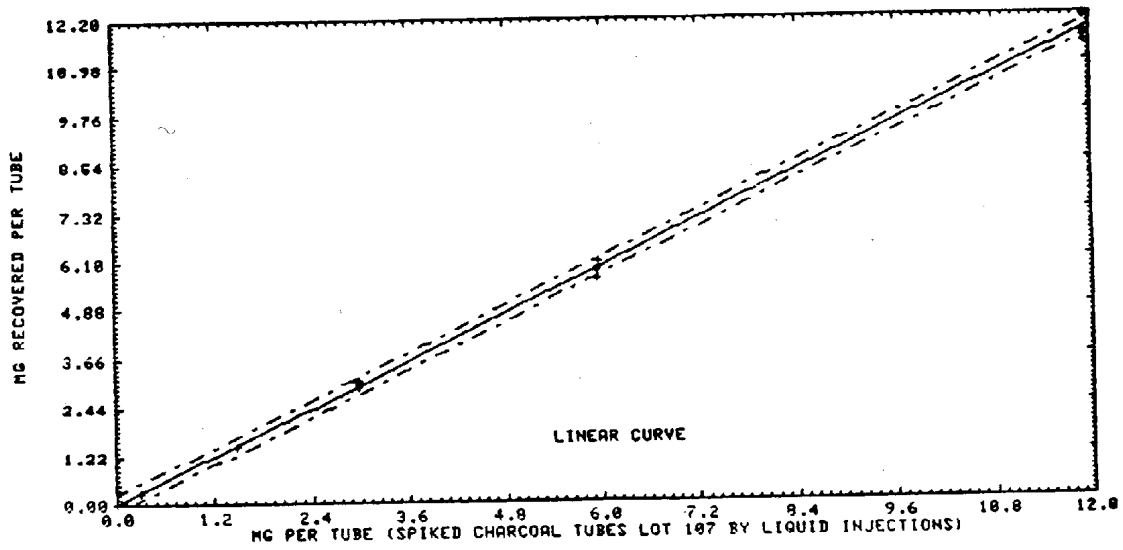


Figure 4.1.2.2. Desorption efficiency data for 1,1,1-trichloroethane.

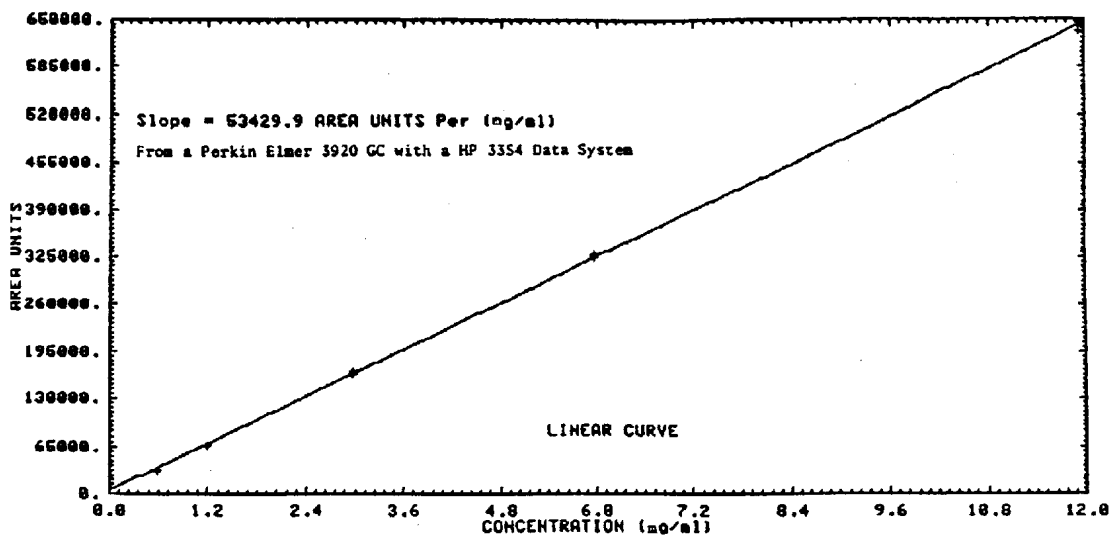


Figure 4.3. Calibration curve of instrument response to 1,1,1-trichloroethane.

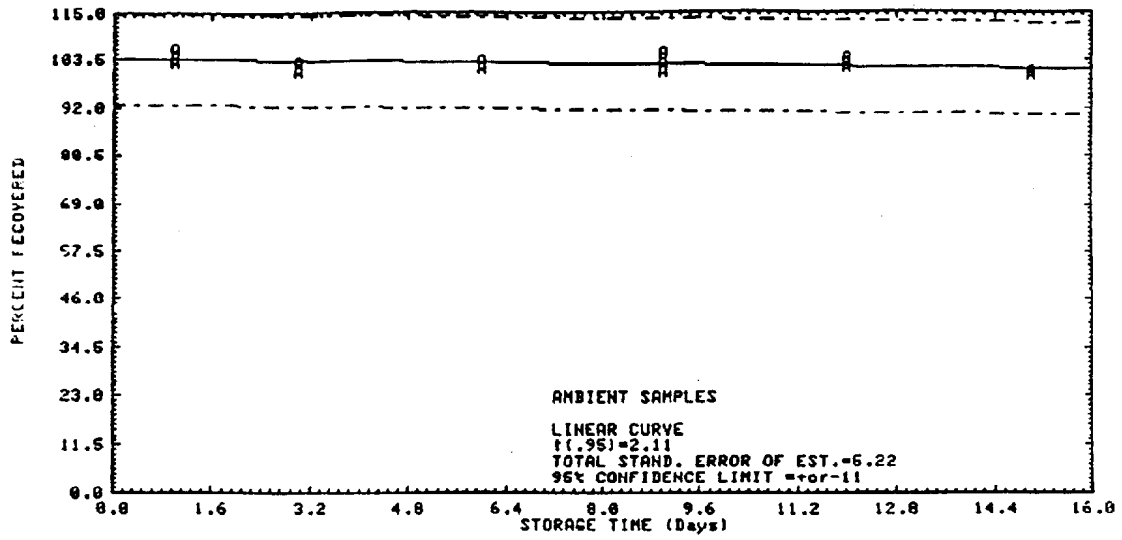


Figure 4.4.1. Ambient storage test of 1,1,1-trichloroethane.

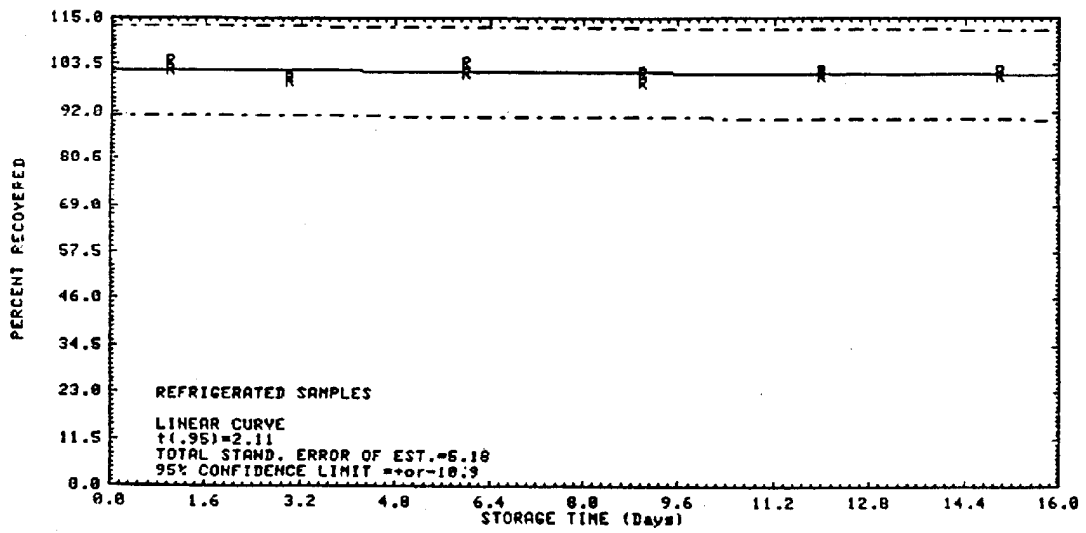


Figure 4.4.2. Refrigerated storage test of 1,1,1-trichloroethane.

## 5. References

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