β-Chloroprene

Method number:	112
Matrix:	Air
Target concentration:	25 ppm (90.5 mg/m^3) TWA, (skin)
OSHA PEL:	25 ppm (90.5 mg/m^3) TWA, (skin)
ACGIH TLV:	10 ppm (36.2 mg/m^3) (skin)
Procedure:	Samples are collected by drawing known volumes of air through sampling tubes containing 600 mg of Chromosorb 106 in the front section and 300 mg in the back section. Keep the samples in a refrigerator to help minimize analyte migration. Samples are desorbed with toluene and analyzed by GC using an electron capture detector.
Recommended air volume and sampling rate:	6 L at 50 mL/min (120 min)
Reliable quantitation limit:	22 ppb (80 µg/m^3)
Standard error of estimate at the target concentration:	7.9%
Status of method:	Evaluated method. This method has been subjected to the established evaluation procedures of the Organic Methods Evaluation Branch.

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1. General Discussion

1.1 Background

1.1.1 History

For monitoring occupational exposure to chloroprene, NIOSH specifies sampling with coconut shell charcoal tubes, desorption with carbon disulfide, and analysis by GC with a flame ionization detector (FID) (Ref. 5.1). Work at OSHA SLTC, however, has shown that the coconut shell charcoal tube does not retain chloroprene well (Ref. 5.2). Also, the method is not very sensitive. The present work was undertaken to develop a sampling and analytical method that is more sensitive.

Chloroprene auto-oxidizes easily, polymerizes spontaneously at room temperature, and forms cyclic dimers on prolonged standing even in the presence of polymerization inhibitors (Ref. 5.3). Attempts were made to convert chloroprene to a stable derivative. The reagents investigated included bromine, hydrogen bromide, tetracyanoethylene, and 7,7,8,8-tetracyanoquinonedimethane. None were successful because the reactions were not quantitative. The chlorine atom on the 1,3-butadiene strongly enhances the free-radical activity (polymerization) of the molecule and decreases its activity in ionic and Diels-Alder reactions.

In 1987, a Chinese scientist reported a method of determining the concentration of chloroprene in air down to 0.01 mg/m^3 (3 ppb) (Ref. 5.4). He sampled with tubes containing Chromosorb 101 and thermally desorbed the analyte directly into a GC column. Because the sample is not diluted with solvents, sensitivity is greatly enhanced – 1000-fold, assuming 1-mL extraction and 1-µL injection. Unfortunately SLTC does not have a thermal desorption unit equipped with an autosampler at this time. We decided on a conventional solvent desorption method. The target concentration was set at 25 ppm, the current OSHA PEL.

Chromosorb 106 was selected as the sampling media for its high surface area (700 to 800 m^2/g versus less than 50 m^2/g for Chromosorb 101). The selection was also based on the consideration that the method may be adapted to thermal desorption in the future. The sensitivity was increased 400-fold by using an electron capture detector (ECD) instead of an FID.

There was concern for the purity of chloroprene used to prepare analytical standards because chloroprene is unstable. NIOSH used freshly distilled chloroprene in their method. (Ref. 5.1) We recommend the same. There are two commercially available sources of chloroprene: Chem Service (45% in xylene) and Alfa/Aeser (50% in xylene). When materials from these two suppliers were compared with freshly distilled chloroprene, their nominal concentrations were within experimental error. They were found to be stable when stored in a freezer (-13 °C) during the time of this work (two months).

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

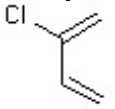
Chloroprene is much more toxic to rodents than butadiene or isoprene. Toxic effects in humans from acute, high-level, chloroprene exposures have been reported for the liver, circulatory system, hematopoietic system, central and peripheral nervous systems, immune system, reproductive system, and the periodontia. Symptoms include headache, irritability, cardiac palpitations, dizziness, insomnia, fatigue, respiratory irritations, chest pains, gastrointestinal disorders, dermatitis, temporary hair loss, conjunctivitis, and corneal necrosis. There are marked disparities between the studies reported by U.S. and Russian investigators of the toxicity and hazards posed by exposure to chloroprene. Although two Russian epidemiological studies suggested that exposure to chloroprene was related to increased incidences of skin and lung cancer, both the International Agency for Research

on Cancer (Ref. 5.5) and the American Conference of Governmental Industrial Hygienist (Ref. 5.6) have concluded that chloroprene is not classifiable as to its carcinogenicity to humans. The NIOSH criteria document also stated "The presently available data appear to be insufficient to formulate firm conclusions on the carcinogenicity of chloroprene." (Ref. 5.7)

1.1.3 Workplace exposure

Most chloroprene is polymerized to make polychloroprene (neoprene), a synthetic rubber used in wire and cable covers, gaskets, automotive parts, adhesives, caulks, flame-resistant cushioning, and other applications requiring chemical, oil, and weather resistance, or high gum strength. (Ref. 5.3) The major worker exposure to chloroprene occurs in the manufacture of the monomer and during the polymerization to neoprene latex. It occurs chiefly by inhalation of the vapor and skin contact with the liquid. (Ref. 5.7)

1.1.4 Physical properties and other descriptive information (Ref. 5.2)

CAS no.:	126-99-8
synonyms:	2-chloro-1,3-butadiene; chloroprene
formula:	C_4H_5Cl
formula weight:	88.54
appearance:	clear liquid
boiling point:	59.4 °C
melting point:	-128 to -132 °C
density:	0.9585 g/mL at 20 °C
	0.9591 g/mL at -12 °C
	0.9148 g/mL (50% in xylene, at -12 °C)
	0.9106 g/mL (calculated for 45% in xylene, at -12 °C)
flash point:	-20 °C (ASTM open cup)
solubility:	slightly soluble in water (<1%) and miscible with most organic solvents
vapor pressure (p):	$\log_{10} p = 6.652 - 1545/T$ (T in K, p in kPa)
reactivity:	readily forms dimers and oxidizes at room temperature
structure:	

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 2.4 pg. This is the amount of analyte that will give a response that is significantly different from the background response of reagent blank. (Sections 4.1 and 4.2)

1.2.2 Detection limit of the overall procedure

The detection limit of the overall procedure is 0.14 µg per sample (6.6 ppb, 24 µg/m^3). This is the amount of analyte spiked on the sampler that will give a response that is significantly different from the background response of a sampler blank. (Sections 4.1 and 4.3)

1.2.3 Reliable quantitation limit

The reliable quantitation limit is 0.48 µg per sample (22 ppb, 80 µg/m^3). This is the amount of analyte spiked on a sampler that will give a signal that is considered the lower limit for precise quantitative measurements. (Section 4.4)

1.2.4 Precision (analytical procedure)

The precision of the analytical procedure, measured as the pooled relative standard deviation over a concentration range equivalent to 0.5 to 2 times the target concentration, is 0.32%. (Section 4.5)

1.2.5 Precision (overall procedure)

The precision of the overall procedure at the 95% confidence level for the ambient 15-day storage test (at the target concentration) is ±16%. This includes an additional 5% for sampling error. (Section 4.6)

1.2.6 Recovery

The recovery of chloroprene from samples used in a 15-day storage test remained above 95%, when the samples were stored at ambient temperature. (Section 4.7)

1.2.7 Reproducibility

Six samples, collected from a controlled test atmosphere of chloroprene, with a draft copy of this procedure, were submitted for analysis by an SLTC Service Branch. The samples were analyzed after 2 days of storage at 5 °C. No individual sample result deviated from its theoretical value by more than the precision reported in Section 1.2.5. (Section 4.8)

2. Sampling Procedure

2.1 Apparatus

2.1.1 A personal sampling pump calibrated to ±5% of the recommended flow rate with the sampling device attached.

2.1.2 Glass sampling tubes (150 mm × 10 mm o.d.) packed with two sections of Chromosorb 106. The front section contains 600 mg and the back section contains 300 mg. The sections are held in place with glass wool plugs. For this evaluation, commercially prepared sampling tubes were purchased from SKC, Inc. (Catalog no. 226-111).

2.2 Reagents

None required.

2.3 Technique

2.3.1 Immediately before sampling, break off the ends of the sampling tube. All tubes should be from the same lot.

2.3.2 Attach the sampling tube to the sampling pump with flexible tubing.

2.3.3 Air should not pass through any hose or tubing before entering the sampling tube.

2.3.4 Cap both ends after sampling. Wrap each sample with a Form OSHA-21 seal.

2.3.5 Record the air volume for each sample.

2.3.6 Submit at least one blank with each set of samples. Blanks should be handled in the same manner as samples, except no air is drawn through them.

2.3.7 List any compounds that could be considered potential interferences.

2.4 Sampler capacity

The capacity of the front section of the SKC 226-111 sampling tube was tested by sampling from a test atmosphere of chloroprene (181 mg/m^3, 80% RH, 22°C) at 50 mL/min. The 5% breakthrough volume was determined to be 8.57 L. (Section 4.9)

2.5 Desorption efficiency

2.5.1 The average desorption efficiency for chloroprene from Chromosorb 106 over the range of 0.5 to 2.0 times the target concentration was 101.9%. (Section 4.10.1)

2.5.2 The desorption efficiencies at 0.05, 0.1, and 0.2 times the target concentration were found to be 100.8%, 101.0%, and 101.1%, respectively. (Section 4.10.1)

2.5.3 Desorbed samples remain stable for at least 24 h. (Section 4.10.2)

2.6 Recommended air volume and sampling rate

2.6.1 The recommended air volume is 6 L at 50 mL/min.

2.6.2 For short-term sampling the recommended air volume is 1.5 L at 100 mL/min.

2.6.3 When short-term samples are collected, the air concentrations equivalent to the reliable quantitation limits become larger. For example, the reliable quantitation limit is 84 ppb or 0.30 mg/m^3 for chloroprene when 1.5 L is collected.

2.7 Interferences (sampling)

There is no known interference for sampling.

2.8 Safety precautions (sampling)

2.8.1 The sampling equipment should be attached to the worker in such a manner that it will not interfere with work performance or safety.

2.8.2 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 an electron capture detector (ECD). An HP 5890 equipped with an ECD and an autosampler were used in this evaluation.

3.1.2 A capillary column capable of separating chloroprene and the internal standard (trichloroethylene) from any interferences. An Rtx-1 column (60 m × 0.32 mm i.d., df 1.0 µm) was used in this evaluation.

3.1.3 An electronic integrator or other suitable means of measuring detector response. The Millennium Chromatography Manager System (Waters) was used in this evaluation.

3.1.4 Glass vials, 4-mL and 2-mL, with poly(tetrafluoroethylene)-lined caps for desorbing samples and for use in the autosampler.

3.1.5 A dispenser capable of delivering 2.00 mL of desorbing solvent.

3.2 Reagents

3.2.1 Chloroprene. Chloroprene, 50% in xylene, was obtained from Alfa/Aesar. Chloroprene, 45% in xylene, was obtained from Chem Service. They were stored in a freezer at -13 °C.

3.2.2 Toluene. Toluene, b&j high purity solvent grade, was obtained from Baxter.

3.2.3 Trichloroethylene. Trichloroethylene, 99.5+%, was obtained from Aldrich Chemical.

3.2.4 Desorbing solvent. Dilute 5.0 µL of trichloroethylene with 1000 mL of toluene.

3.3 Standard preparation

3.3.1 Distill chloroprene from its xylene solution (Section 4.12). Determine the concentration (w/w) of the 50% chloroprene in xylene using the freshly distilled chloroprene as reference. The 50% chloroprene solution should be stored in a freezer and its concentration checked within a month of analysis. Determine the density of the solution if it is measured by volume instead of weight. Alternatively, use the reference standard of chloroprene supplied by Chem Service whose concentration is guaranteed to be within ±0.5% prior to the expiration date.

3.3.2 Prepare analytical standards by diluting the reference standards with the desorbing solvent. Prepare fresh analytical standards daily. A 272-µg/mL standard solution corresponds to the target concentration.

3.4 Sample preparation

3.4.1 Transfer the sorbent of the front and the back section to separate 4-mL glass vials.

3.4.2 Add 2.00 mL of the desorbing solvent to each vial.

3.4.3 Cap the vials and shake them on a shaker for 30 min.

3.4.4. Pour the solution into a 2-mL autosampler vial.

3.5 Analysis

3.5.1 GC conditions

column:	Rtx-1 (60 m × 0.32-mm i.d., 1.0-µm df)
oven temperature:	70 °C for 8 min, 30°/min to 250 °C, hold for 5 min at 250 °C.
inlet temperature:	250 °C
detector temperature:	250 °C
injection size:	1.0 µL
retention time:	4.8 min (chloroprene)
	7.0 min (trichloroethylene)
carrier gas (H_2):	1.8 mL/min
make-up gas (N_2):	45.3 mL/min
split vent:	22.7 mL/min
split ratio:	13.7 : 1

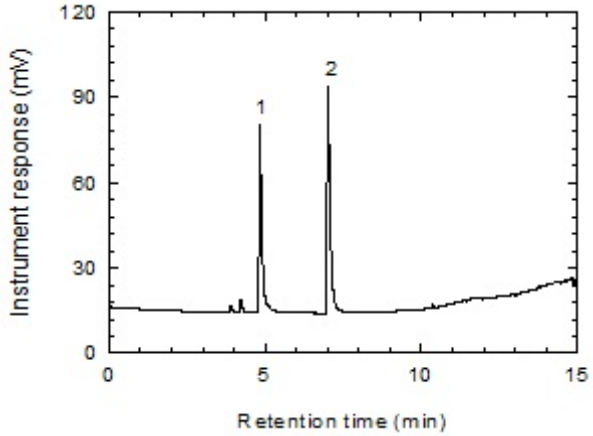


Figure 3.5.1. Chromatogram at target concentration.
1 = chloroprene, 2 = internal standard.

3.5.2 An internal standard calibration method is used. A calibration curve can be constructed by plotting concentration of the analyte versus ISTD-corrected response of standard injections. Bracket the samples with freshly prepared standards.

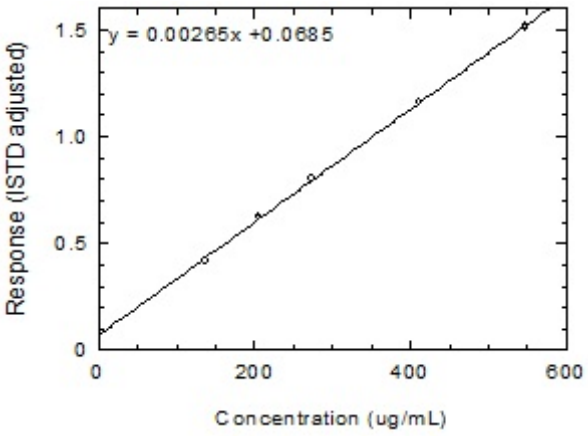


Figure 3.5.2. Calibration curve of chloroprene from the data of Table 4.5.

3.6 Interferences (analytical)

3.6.1 Any compound that produces an ECD response and has a similar retention time as the analyte or the internal standard is a potential interference. If any potential interferences are reported, they should be considered before samples are desorbed. Generally, chromatographic conditions can be altered to separate an interference from the analyte.

3.6.2 Any compound that affects the ECD response is a potential interference. The oven temperature program in Section 3.5.1 should be followed to remove any late eluting peak after each injection.

3.6.3 When necessary, the identity or the purity of an analyte peak may be confirmed with additional analytical data (Section 4.11).

3.7 Calculations

The amount (in micrograms) of chloroprene per milliliter is obtained from the calibration curve. This amount is corrected by subtracting the amount (if any) found in the blank. The air concentration is calculated using the following formula.

$$mg/m^3 = \frac{(\text{microgram per mL}) \times (\text{desorption volume, mL})}{(\text{liters of air sampled}) \times (\text{desorption efficiency})}$$

$$ppm = (mg/m^3) \times \frac{24.46}{MW}$$

where: desorption volume = 2.00 mL
desorption efficiency = 1.05
MW = 88.54

3.8 Safety precautions (analytical)

3.8.1 Follow the rules set down in your Chemical Hygiene Plan.

3.8.2 Wear appropriate gloves. Avoid skin contact and inhalation of all chemicals.

3.8.3 Wear safety glasses and a lab coat at all times while in the lab area.

4. Backup Data

4.1 Determination of detection limits

Detection limits (DL), in general, are defined as the amount (or concentration) of analyte that gives a response (Y_{DL}) that is significantly different (three standard deviations (SD_{BR})) from the background response (Y_{BR}).

$$Y_{DL} - Y_{BR} = 3(SD_{BR})$$

The direct measurement of Y_{BR} and SD_{BR} in chromatographic methods is typically inconvenient and difficult because Y_{BR} is usually extremely low. Estimates of these parameters can be made with data obtained from the analysis of a series of analytical standards or samples whose responses are in the vicinity of the background response. The regression curve obtained for a plot of instrument response versus concentration of analyte will usually be linear. Assuming SD_{BR} and the precision of data about the curve are similar, the standard error of estimate (SEE) for the regression curve can be substituted for SD_{BR} in the above equation. The following calculations derive a formula for DL:

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

Y_{obs} = observed response
Y_{est} = estimated response from regression curve
n = total no. of data points
k = 2 for a linear regression curve

At point Y_{DL} on the regression curve

$Y_{DL} = A(DL) + Y_{BR}$ A = analytical sensitivity (slope)

therefore

$$DL = \frac{(Y_{DL} - Y_{BR})}{A}$$

Substituting 3(SEE) + Y_{BR} for Y_{DL} gives

$$DL = \frac{3(SEE)}{A}$$

4.2 Detection limit of the analytical procedure (DLAP)

The DLAP is measured as the mass of analyte actually introduced into the chromatographic column. Ten analytical standards of chloroprene whose concentrations were equally spaced from 0 to 0.532 µg/mL were prepared. The standard containing 0.532 µg/mL represented approximately 10 times the baseline noise. These solutions were analyzed with the recommended analytical parameters (1-µL injection, 13.7 : 1 split). The data obtained were used to determine the required parameters (A and SEE) for the calculation of the DLAP. Values of 4.92×10^{-5} and 1.19×10^{-4} were obtained for A and SEE respectively. DLAP was calculated to be 2.4 pg on column or 0.033 µg/mL.

Table 4.2
Detection Limit of the Analytical Procedure
for chloroprene

concentration (µg/mL)	mass on column (pg)	response $\times 10^{-6}$
0.000	0.0	0
0.053	3.9	370
0.106	7.7	544
0.159	11.6	612
0.213	15.5	875
0.266	19.4	1103
0.319	23.3	1550
0.372	27.2	1351
0.425	31.0	1623
0.478	34.9	1739
0.532	38.8	2024

* response = (peak area $_{chloroprene}$)/(peak area $_{ISTD}$)

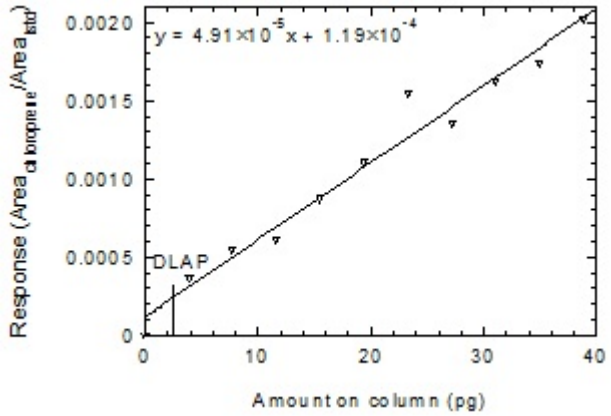


Figure 4.2. Plot of data to determine the DLAP.

4.3 Detection limit of the overall procedure (DLOP)

The DLOP is measured as mass per sample and expressed as equivalent air concentration, based on the recommended sampling parameters. Ten samplers were spiked with chloroprene ranging from 0 to 1.06 µg. The latter amount, when spiked on a sampler, would produce a peak approximately 10 times the baseline noise for a sample blank. These samples were analyzed with the recommended analytical parameters, and the data obtained used to calculate the required parameters (A and SEE) for the calculation of the DLOP. Values of 1.94×10^{-3} and 9.32×10^{-5} were obtained for A and SEE respectively. DLOP was calculated to be 0.14 µg/sample (24 µg/m^3 or 6.6 ppb).

Table 4.3
Detection Limit of the Overall Procedure for Chloroprene

mass per sample (µg)	response $\times 10^{-6}$
0.000	0
0.106	0
0.213	379
0.319	567
0.425	819
0.532	913
0.638	1108
0.744	1561
0.851	1532
0.957	1716
1.06	2017

* response = (peak area $_{chloroprene}$)/(peak area $_{ISTD}$)

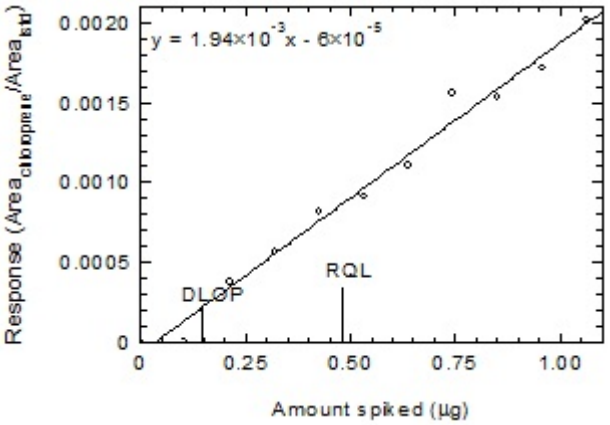


Figure 4.3. Plot of data to obtain DLOP and RQL.

4.4 Reliable quantitation limit

The RQL is considered the lower limit for precise quantitative measurements. It is determined from the regression line data obtained for the calculation of the DLOP (Section 4.3), providing at least 75% of the analyte is recovered. The RQL is defined as the amount of analyte that gives a response (Y_{RQL}) such that

$$Y_{RQL} - Y_{BR} = 10(SD_{BR})$$

therefore

$$RQL = \frac{10(SEE)}{A}$$

RQL = 0.48 µg per sample (80 µg/m^3 or 22 ppb)

Recovery at this level is 88%.

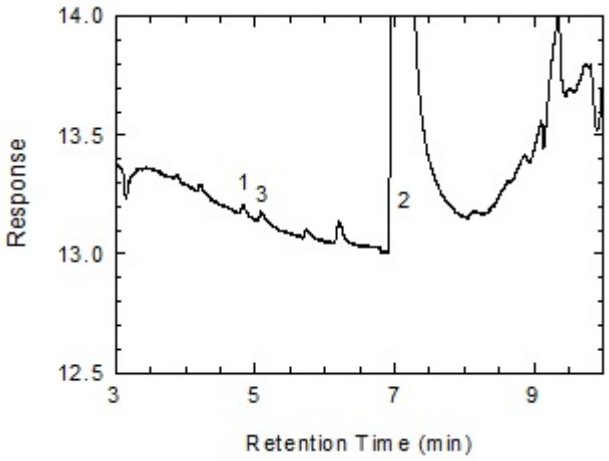


Figure 4.4. Chromatogram near RQL. 1 = chloroprene, 2 = trichloroethylene, 3 = unknown impurity.

4.5 Precision (analytical method)

The precision of the analytical procedure is defined as the pooled relative standard deviation (RSD_P). Relative standard deviations were determined from six replicate injections of analytical standards at 0.5, 0.75, 1, 1.5, and 2 times the target concentration. After assuring that the RSDs satisfy the Cochran test for homogeneity at the 95% confidence level, RSD_p was calculated.

Table 4.5
Instrument Response to Chloroprene

× target concn µg/mL	0.5 × 137	0.75 × 205	1 × 274	1.5 × 411	2 × 548
Response*	0.4174	0.6209	0.7990	1.1582	1.5048
	0.4173	0.6210	0.7982	1.1585	1.5091
	0.4177	0.6230	0.7997	1.1562	1.5225
	0.4171	0.6217	0.8051	1.1555	1.5224
	0.4177	0.6218	0.8065	1.1602	1.5121
	0.4177	0.6220	0.8063	1.1599	1.5130
$\bar{X}$	0.4175	0.6217	0.8025	1.1581	1.5140
SD	0.0003	0.0008	0.0039	0.0019	0.0072
RSD %	0.06	0.12	0.49	0.16	0.47

* response = (peak area $_{chloroprene}$)/(peak area $_{ISTD}$)

The Cochran test for homogeneity requires the calculation of the g statistics according to the following formula:

$$g = \frac{\text{largest RSD}^2}{RSD_{0.5\times}^2 + RSD_{0.75\times}^2 + RSD_{1\times}^2 + RSD_{1.5\times}^2 + RSD_{2\times}^2} = 0.4758$$

The critical value of the *g* statistic, at the 95% confidence level, for five variances, each associated with six observations, is 0.5065. Because the *g* statistic obtained (0.4758) does not exceed this value, the RSDs within each level can be considered equal and they can be pooled (RSD_P) to give an estimated RSD for the concentration range studied.

$$RSD_p = \sqrt{\frac{5(RSD_{0.5\times}^2+RSD_{0.75\times}^2+RSD_{1\times}^2+RSD_{1.5\times}^2+RSD_{2\times}^2)}{5+5+5+5+5}} = 0.32\%$$

4.6 Precision (overall procedure)

The precision of the overall procedure is determined from the storage data in Section 4.7. The determination of the standard error of estimate (SEE_R) 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_R 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:

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

n = total no. of data points
k = 2 for linear regression
k = 3 for quadratic regression
Y_{obs} = observed % recovery at a given time
Y_{est} = estimated % recovery from the regression line at the same given time

An additional 5% for pump error (SP) is added to the SEE_R by the addition of variances to obtain the total standard error of estimate.

$$SEE = \sqrt{(SEE_R)^2 + (SP)^2}$$

The precision at the 95% confidence level is obtained by multiplying the standard error of estimate (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 Figures 4.7.1 and 4.7.2. The precision of the overall procedure of ±16% was obtained from Figure 4.7.1.

4.7 Storage test

Storage samples were prepared by drawing a controlled test atmosphere (80% relative humidity and 22°C) through samplers at 50 mL/min for 120 min. The concentration of chloroprene was approximately at the target concentration. Thirty-six samples were prepared. Six samples were analyzed on the day of preparation. One-half of the remaining samples were stored in a refrigerator (5°C), and the other half were stored at ambient temperature (about 22°C) in a closed drawer. At 2-4 day intervals, three samples were selected from each of the two sets and analyzed. The results were compared to those of day 0. Because a few of the samples were lost, the experiment was repeated with another batch of 18 samples. Some amount of analyte (up to ~15%) was found in the back section of the day-15 and day-13 samples stored at ambient temperature. No chloroprene was detected in the back sections of the samples stored in a refrigerator.

Table 4.7
Storage Test for Chloroprene

time (days)	percent recovery (ambient)			percent recovery (refrigerated)		
0	lost	100.7	99.3	lost	100.7	99.3
0	100.1	99.9	lost	100.1	99.9	lost
0	100.4	99.3	100.3	100.4	99.3	100.3
3	101.3	103.8	100.1	102.2	lost	102.9
4	96.8			99.5	99.4	
6	97.5	97.0	74.6*	100.3	100.9	98.6
7	95.1	96.8		101.0		
9	97.5	89.9	95.5	100.6	53.5*	101.9
11	83.4			96.8	89.2	
13	87.4	83.7	81.1	92.0	93.1	92.2
13	100.1	100.8		95.7		
15	105.1	102.2	104.0	99.7	104.1	99.1
15	99.0			96.3	98.0	

Lost = tube broken or tubing came off during sampling
*outlier, not used

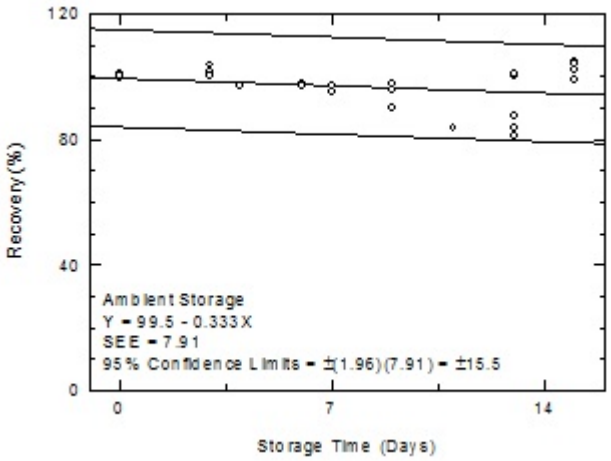


Figure 4.7.1. Ambient storage test for chloroprene.

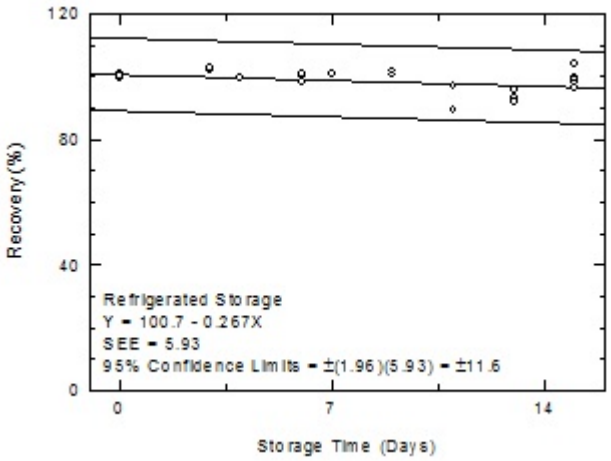


Figure 4.7.2. Refrigerated storage test for chloroprene.

4.8 Reproducibility

Reproducibility samples were prepared by collecting them from a controlled test atmosphere similar to that used in the storage test. The samples were submitted to an SLTC Service Branch for analysis. The samples were analyzed after being stored for 2 days at 5°C. No sample result had a deviation greater than the precision of the overall procedure determined in Section 4.7.

Table 4.8
Reproducibility Data for Chloroprene

ppm expected	ppm found	percent found	percent deviation
26.7	25.6	95.9	-4.1
26.7	26.0	97.4	-2.6
26.7	26.0	97.4	-2.6
26.7	25.4	95.1	-4.9
26.7	25.6	95.9	-4.1
26.7	26.4	98.9	-1.1

4.9 Sampler capacity

The capacity of the front section of a Chromosorb 106 tube (SKC 226-111) was tested by sampling from a test atmosphere of chloroprene at two times the target concentration (181 mg/m^3, 80% relative humidity at 22°C). The flow rate was 0.05 L/min. The downstream air was monitored at 10-minute interval with a GC equipped with a gas sampling valve. The 5% breakthrough point was determined to be 8.57 L.

Table 4.9
Breakthrough of Chloroprene
with Chromosorb 106 Sampling Tubes

Tube 1		Tube 2	
air volume (L)	break-through (%)	air volume (L)	break-through (%)
5.93	0.00	6.15	0.00
6.44	0.00	6.66	0.00
6.95	0.00	7.18	0.00
7.47	0.00	7.69	0.00
7.98	4.49	8.20	1.55
8.49	6.46	8.71	4.90
9.00	12.20	9.22	11.41

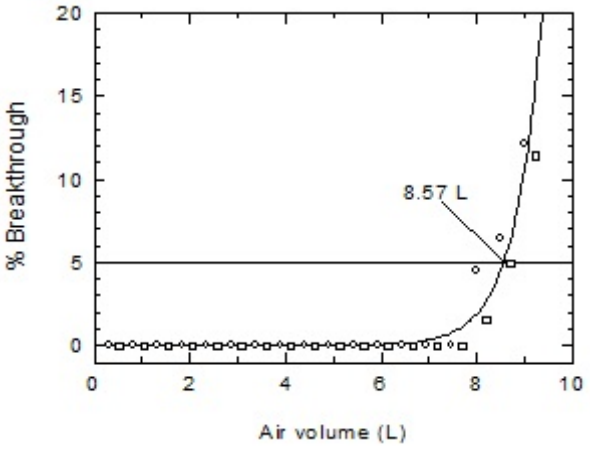


Figure 4.9. Breakthrough curve for chloroprene on Chromosorb 106 at two times the target concentration.

4.10 Desorption efficiency and stability of desorbed samples

4.10.1 Desorption efficiency

The desorption efficiencies (DE) test samples were prepared by liquid-spiking the 600-mg portions of Chromosorb 106 with chloroprene at 0.05 to 2 times the target concentration. These samples were stored overnight at ambient temperature, desorbed, and analyzed. The average desorption efficiency over the working range of 0.5 to 2 times the target concentration was 101.9%.

Table 4.10.1
Desorption Efficiency of Chloroprene

× target concn (µg/sample)	0.05 × 26.6	0.1 × 53.2	0.2 × 106	0.5 × 266	1.0 × 532	2.0 × 1063
DE (%)	101.0	100.5	100.8	101.3	101.0	102.4
	101.2	100.5	101.4	100.9	103.5	102.7
	100.8	100.3	101.8	101.1	101.8	102.5
	100.7	101.4	101.3	101.1	102.0	102.8
	100.3	101.7	101.2	100.9	102.2	103.0
	100.8	101.5	99.9	100.5	102.0	103.0
Average	100.8	101.0	101.1	101.0	102.1	102.7

4.10.2 Stability of desorbed samples

The stability of the desorbed samples was investigated by re-analyzing the one times the target concentration samples 24 hours later. After the desorption efficiency analysis was performed, three vials were recapped with new septa while the remaining three retained their punctured septa. The samples were re-analyzed with fresh standards. The average percent change was −2.7 for the re-capped samples and −3.7 for those that were not recapped.

Table 4.10.2
Stability of Desorbed Samples of Chloroprene

punctured septa replaced			punctured septa retained		
initial DE (%)	DE after one day (%)	difference	initial DE (%)	DE after one day (%)	difference
101.0	99.0	−2.0	102.0	98.2	−3.8
103.5	99.2	−4.3	102.2	98.5	−3.7
101.8	99.9	−1.9	102.0	98.4	−3.5
	average			average	
102.1	99.4	−2.7	102.1	98.4	−3.7

4.11 Qualitative analysis

Chloroprene may be confirmed by GC/MS using GC conditions similar to those in Section 3.5.1.

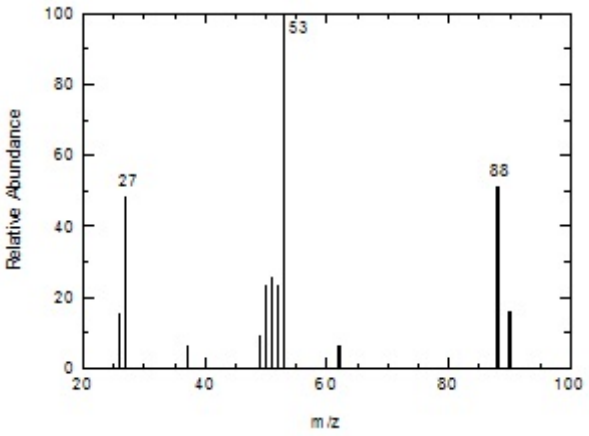


Figure 4.11. Mass spectrum of 2-chloro-1,3-butadiene.

4.12 Distillation of chloroprene

Chloroprene was distilled at atmospheric pressure (650 mmHg). The cut boiling between 62 °C and 66 °C was collected. Freshly distilled chloroprene was stored at -15 °C and used within two days. Chloroprene can also be distilled at reduced pressure (Ref. 1).

5. References

5.1. *NIOSH Manual of Analytical Methods*, Fourth Edition, U.S. Department of Health and Human Services, Center for Disease Control, National Institute for Occupational Safety and Health, Cincinnati, OH, DHHS (NIOSH) Publication No. 94-113, **1994**.

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