CHLOROACETALDEHYDE

Method no.:	76
Matrix:	Air
Target concentration:	1.0 ppm (3.21 mg/m^3) (OSHA ceiling PEL)
Procedure:	Air samples are collected by drawing known volumes of air through 6-mm i.d. glass sampling tubes, each containing 520 mg of silica gel adsorbent in the front section and 260 mg in the backup section. The samples are desorbed with acetonitrile and analyzed by GC using an electron capture detector.
Recommended air volume and sampling rate:	7.5 L at 0.5 L/min
Reliable quantitation limit:	21.3 ppb (68.4 µg/m^3)
Standard error of estimate at the target concentration: (Section 4.7.)	7.67%
Special requirement:	Store collected samples in a freezer upon receipt at the laboratory.
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

This method is similar to NIOSH Method S11 (Ref. 5.1.) for chloroacetaldehyde. The sampling rate was increased to better monitor ceiling exposures. Some of the recommended analytical parameters were changed to be consistent with OSHA analytical practices and techniques.

Chloroacetaldehyde can exist in combinations of four forms: the monomer, the monomer hydrate, the dimer hydrate and the cyclic trimer. The monomer and dimer hydrates are formed instantly when the anhydrous monomer is added to water. The cyclic trimer is formed from the anhydrous monomer upon standing. The cyclic trimer is only slightly soluble in water, but the monomer and dimer hydrates are formed when the cyclic trimer is heated in water. The anhydrous monomer is obtained by cracking the cyclic trimer. (Ref. 5.2.)

Commercial aqueous chloroacetaldehyde solution contains a 50/50 mixture of the two hydrates. When the aqueous mixture is analyzed by GC, only a single peak at the same retention time as chloroacetaldehyde monomer is observed. The two hydrates are dehydrated and converted to the monomer during GC analysis. (Ref. 5.2.)

This method, like the NIOSH method, cannot distinguish between chloroacetaldehyde monomer and its monomer and dimer hydrates. Considering the ubiquitous nature of water in the environment, this issue is probably meaningless because chloroacetaldehyde monomer reacts instantly with water to form its monomer and dimer hydrates.

Chloroacetaldehyde, unlike some aldehydes, is sufficiently stable to permit its direct collection on silica gel and subsequent storage before analysis. Collected samples should be stored in a freezer upon receipt at the laboratory to prevent excessive migration from the front section to the backup section of the sampling tube.

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

Chloroacetaldehyde vapor is a severe irritant of the eyes, skin and mucous membranes. Direct contact with a 40% aqueous solution of chloroacetaldehyde can cause severe eye and skin burns. Chloroacetaldehyde was found to be acutely toxic to rats, mice, rabbits, and guinea pigs following various routes of administration which included oral, intraperitoneal, and skin applications. (Ref. 5.3.)

Chloroacetaldehyde has been reported to be mutagenic by the Ames test. Hundreds of known carcinogens and noncarcinogens have been subjected to this test and about 85% of the known carcinogens were found to be mutagenic while less than 10% of the noncarcinogens gave a positive test. The fact that chloroacetaldehyde is a mutagen is of special interest because chloroacetaldehyde is a possible metabolic product of the human carcinogen vinyl chloride. It has been suggested that a metabolite of vinyl chloride may be the active carcinogenic form of the chemical. Chloroacetaldehyde is also a possible metabolic product of ethylene dichloride, ethylene chlorohydrin, and cyclophosphamide. (Ref. 5.4.)

1.1.3. Workplace exposure

The following are some common uses of chloroacetaldehyde during which exposure may occur: (1) in the production of 2-aminothiazole and in other chemical syntheses which utilize chloroacetaldehyde, (2) in the control of algae, bacteria, and fungi in water, (3) when used in a spinning solution of poly β-alanine, (4) in tree trunk debarking operations, and (5) in analytical chemistry as a fluorescent label. (Refs. 5.4. and 5.5.)

Chloroacetaldehyde may be inadvertently released and exposure may occur when chloroacetaldehyde diethyl acetal is used in acid media during chemical syntheses (Ref. 5.5.).

1.1.4. Physical properties and other descriptive information (Ref. 5.3. unless otherwise indicated)

CAS no.:	107-20-0
molecular weight:	78.50
synonyms:	2-chloro-1-ethanal; monochloroacetaldehyde (Ref. 5.6.)
formula:	$ClCH_2CHO$

Chloroacetaldehyde is combustible and forms an insoluble hemihydrate at aqueous concentrations above 50%.

The following data are for a 40% aqueous solution:

boiling point:	90 to 100°C
vapor pressure:	13 kPa (100 mm Hg) at 20°C
flash point:	190°F (closed cup)
solubility:	water, acetone and methanol

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 760 mm Hg.

1.2. Limit defining parameters

1.2.1. Detection limit of the analytical procedure

The detection limit of the analytical procedure is 17.1 pg per injection. This is the amount of analyte which gave a chloroacetaldehyde peak whose height was about 5 times the height of a nearby trace contaminant peak. (Section 4.1.)

1.2.2. Detection limit of the overall procedure

The detection limit of the overall procedure is 0.513 µg per sample (21.3 ppb or 68.4 µg/m^3). This is the amount of analyte spiked on the sampling device which allows recovery of an amount equivalent to the detection limit of the analytical procedure. (Section 4.2.)

1.2.3. Reliable quantitation limit

The reliable quantitation limit is 0.513 µg per sample (21.3 ppb or 68.4 µg/m^3). This is the smallest amount of chloroacetaldehyde spiked on the sampling device which can be quantitated within the requirements of a recovery of at least 75% and a precision (±1.96 SD) of ±25% or better. (Section 4.3.)

The reliable quantitation limit and detection limits reported in the method are based upon optimization of the instrument for the smallest possible amount of the analyte. When the target concentration of the 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 target concentration is linear. (Section 4.4.)

1.2.5. Recovery

The recovery of chloroacetaldehyde from samples used in a 17-day storage test remained above 90.4% when the samples were stored in the dark at about 22°C. (Section 4.5.) The recovery of an analyte from the collection medium during storage must be 75% or greater.

1.2.6. Precision (analytical procedure only)

The pooled coefficient of variation obtained from replicate injections of analytical standards at 0.5, 1, and 2 times the target concentration is 0.0063. (Section 4.6.)

1.2.7. Precision (overall procedure)

The precision at the 95% confidence level for the refrigerated 17-day storage test is ±15.0% (Section 4.7.). This includes an additional ±5% for sampling error. The overall procedure must provide results at the target concentration that are ±25% or better at the 95% confidence level.

1.2.8. Reproducibility

Six samples, spiked with chloroacetaldehyde, and a draft copy of this procedure were given to a chemist unassociated with this evaluation. The samples were analyzed after 11 days of storage at about 5°C. 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. Advantage

This sampling and analytical method provides a simple and convenient means to monitor occupational exposure to chloroacetaldehyde.

1.4. Disadvantage

None

2. Sampling Procedure

2.1. Apparatus

2.1.1. Samples are collected by use of a personal sampling pump that can be calibrated to within ±5% of the recommended flow rate with the sampling device in line.

2.1.2. Samples are collected on 6-mm i.d. × 8-mm o.d. × 110-mm glass sampling tubes each packed with a 520-mg front section and a 260-mg backup section of 20/40 mesh silica gel. The two sections of silica gel are separated and retained with small plugs of foam and glass wool. The ends of the sampling tubes are flame-sealed. Silica gel sampling tubes were obtained from SKC, Inc. (catalog no. 226-15, Lot 300) for use in this evaluation.

2.2. Reagents

No sampling reagents are required.

2.3. Sampling technique

2.3.1. Break open both ends of the sampling tube so that the holes in the tube ends are at least one-half the i.d. of

the tube. Attach the sampling tube to the sampling pump with flexible, plastic tubing such that the large, front section of the sampling tube is exposed directly to the atmosphere. Do not place any tubing in front of the sampler. Attach the sampler vertically in the worker's breathing zone in such a manner that it does not impede work performance or safety. Be certain that the sharp end of the sampling tube does not injure the worker.

2.3.2. Remove the sampling device after sampling for the appropriate time and then seal the tube with plastic end caps. Wrap the tube lengthwise with an official OSHA seal (Form 21).

2.3.3. Submit at least one blank sample with each set of samples. Handle the blank in the same manner as the other samples with the exception of drawing air through it.

2.3.4. List any potential interferences on the sample data sheet.

2.4. Sampler capacity

Five-percent breakthrough occurred after sampling a controlled test atmosphere containing 6.3 mg/m^3 chloroacetaldehyde (2 times the OSHA PEL) for 33.6 min at 0.5 L/min. At the end of this time 16.8 L of air had been sampled and 105.8 µg of chloroacetaldehyde had been collected. Breakthrough data were obtained by sampling the test atmosphere for increasing periods of time with several of the recommended two-section silica gel tubes. Five-percent breakthrough was defined as the point at which 5% of the total amount of chloroacetaldehyde collected on the entire tube was found on the backup section. (Section 4.9.)

2.5. Desorption efficiency

2.5.1. The average desorption efficiency for chloroacetaldehyde from 520 mg of silica gel (SKC, Inc., Lot 300) over the range of 0.5 to 2 times the target concentration was 91.0%. (Section 4.10.)

2.5.2. Desorbed samples remain stable for at least 16 h. (Section 4.10.)

2.6. Recommended air volume and sampling rate

2.6.1. The recommended air volume is 7.5 L.

2.6.2. The recommended air sampling rate is 0.5 L/min.

2.6.3. When longer-term air samples are required, reduce the sampling rate but do not exceed the recommended air volume.

2.7. Interferences (sampling)

Report suspected interferences to the laboratory with submitted samples.

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). A Hewlett-Packard 5890 Gas Chromatograph equipped with a 7673A Autosampler and an ECD was used in this evaluation.

3.1.2. A GC column capable of separating chloroacetaldehyde from potential interferences. A 30-m × 0.32-mm i.d. fused-silica capillary column coated with SP-2250 (0.20-µm film thickness) was obtained from Supelco, Inc. for use in this evaluation.

3.1.3. An electronic integrator or other suitable means of measuring detector response. A Hewlett-Packard 5895A GC Chem-Station was used in this evaluation.

3.1.4. Four- and two-milliliter vials with PTFE-lined caps were used for sample and standard preparations.

3.2. Reagents

3.2.1. Chloroacetaldehyde. Chloroacetaldehyde, nominally 50% in water, was obtained from Aldrich Chemical Co. and used in this evaluation. The actual concentration of this solution must be determined as described in Section 4.12.

3.2.2. Acetonitrile, reagent grade or better. American B&J brand acetonitrile was used in this evaluation.

3.2.3. 1,1,2-Trichloroethane, reagent grade or better. 1,1,2-Trichloroethane was obtained from Fisher Scientific Co. for use in this evaluation.

3.2.4. The desorbing solution is acetonitrile containing 10 µL/L of 1,1,2-trichloroethane for use as an internal standard. The use of the internal standard is optional but its employment will improve precision.

3.3. Standard preparation

3.3.1. The concentration of the aqueous chloroacetaldehyde solution must be determined as described in Section 4.12.

3.3.2. Prepare stock standards by diluting known amounts of the aqueous chloroacetaldehyde solution with desorbing solution. Store the stock standards in a refrigerator. Prepare fresh stock standards every two weeks.

3.3.3. Prepare analytical standards by further diluting stock standards with desorbing solution. Prepare fresh analytical standards each day.

3.3.4. Prepare a sufficient number of standards to generate a calibration curve. Analytical standard concentrations must bracket sample concentrations. Prepare additional standards if necessary.

3.4. Sample preparation

3.4.1. Transfer the 520-mg front section of silica gel to a 4-mL glass vial. Place the 260-mg backup section in a separate 4-mL vial. Discard the glass wool and foam plugs.

3.4.2. Add 3.0 mL of desorbing solution to each vial.

3.4.4. Seal the vials with PTFE-lined caps and allow them to desorb for 1 h. Mix the contents of the vials vigorously by hand several times during the desorption time.

3.4.5. Transfer some of the desorbed sample to autosampler vials. This step is necessary only if an autosampler is used.

3.5. Analysis

3.5.1. Analytical conditions

GC conditions

temperatures:	40°C (column) 250°C (injector) 300°C (detector)
temperature program:	hold initial temp 5.0 min, increase temp at 15°C/min to 230°C and hold until all peaks have eluted
column head pressure:	31 kPa (hydrogen)
column flow rate:	1.7 mL/min (hydrogen)
septum purge flow rate:	4.8 mL/min (hydrogen)

split vent flow rate:	15.7 mL/min (hydrogen)
detector make-up flow rate:	70 mL/min (nitrogen)
injection volume:	1.0 µL
split ratio:	1 to 10
column:	A 30-m x 0.32-mm i.d. fused-silica capillary column coated with SP-2250 (0.20-µm film thickness)
chromatogram:	Section 4.11.

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

3.5.3. Use an internal standard procedure to prepare a calibration curve using several freshly prepared standards over a range of concentrations. Bracket the samples with analytical standards.

3.6. Interferences (analytical)

3.6.1. Any compound having a similar retention time as chloroacetaldehyde or the internal standard is a potential interference. Generally, chromatographic conditions can be altered to separate an interference.

3.6.2. Retention time on a single column is not proof of chemical identity. Confirmation by GC/MS is a useful means of identification.

3.7. Calculations

3.7.1. Prepare calibration curves from analytical standards by plotting detector response for chloroacetaldehyde versus the analytical standard concentrations (in terms of micrograms chloroacetaldehyde per milliliter). Determine the best-fit line through the data points.

3.7.2. Determine the concentration, in micrograms of chloroacetaldehyde per milliliter, of a sample by comparing its detector response to the calibration curve. Perform blank corrections for each section before adding the results together. If any chloroacetaldehyde is found on the back-up section, add that amount to the amount found on the front section.

3.7.3. The air concentration of chloroacetaldehyde can be expressed in mg/m^3 by using the following equation:

$$mg/m^3 = [(A)(B)]/[(C)(D)]$$

where A = µg/mL of chloroacetaldehyde from Section 3.7.2.
B = desorption volume (3.0 mL)
C = liters of air sampled
D = desorption efficiency, decimal form (0.910)

3.7.4. Convert chloroacetaldehyde results in mg/m^3 to ppm using the following equation:

$$ppm = (mg/m^3)(24.46)/(78.50)$$

where mg/m^3 = results from Section 3.7.3.
24.46 = molar volume at 760 mm Hg and 25°C
78.50 = molecular weight of chloroacetaldehyde

3.8. Safety precautions (analytical)

3.8.1. Avoid skin contact and inhalation of all chemicals.

3.8.2. Restrict the use of all chemicals to a fume hood.

3.8.3. Wear safety glasses in all laboratory areas.

4. Backup Data

4.1. Detection limit of the analytical procedure

The detection limit of the analytical procedure is 17.1 pg per injection. It is based on a 1.0-µL injection (with a 1 to 10 split) of a 0.171 µg/mL standard. This amount produced a chloroacetaldehyde peak whose height is about 5 times the height of a nearby trace contaminant peak 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 0.513 µg per sample (21.3 ppb or 68.4 $µg/m^3$). The injection size recommended in the analytical procedure (1.0 µL with a 1 to 10 split) was used in the determination of the detection limit of the overall procedure. Six vials containing 520 mg of silica gel were each liquid spiked with 0.513 µg of chloroacetaldehyde. The samples were desorbed about 16 h after being spiked.

Table 4.2.
Detection Limit of the Overall Procedure

sample number	theoretical amount (µg)	amount recovered (µg)
1	0.513	0.483
2	0.513	0.472
3	0.513	0.493
4	0.513	0.452
5	0.513	0.463
6	0.513	0.473

4.3. Reliable quantitation limit data

The reliable quantitation limit is also 0.513 µg per sample (21.3 ppb or 68.4 µg/m^3). The injection size recommended in the analytical procedure (1.0 µL with a 1 to 10 split) was used in the determination of the reliable quantitation limit. Six vials containing 520 mg of silica gel were each liquid spiked with 0.513 µg of chloroacetaldehyde. Because the recovery of chloroacetaldehyde from the spiked samples was greater than 75% and because the precision (1.96 SD) was less than ±25%, the detection limit of the overall procedure and reliable quantitation limit are the same.

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

percent recovered	statistics
94.2	
92.0	$\bar{X}$ = 92.1
96.1	SD = ± 2.83
88.1	Precision = (1.96)(±2.83)
90.2	= ± 5.5
92.2	

4.4. Instrument response to chloroacetaldehyde

The instrument response to chloroacetaldehyde over the range of 0.5 to 2 times the target concentration is linear with a slope of 1405 area counts per microgram per milliliter. The response to chloroacetaldehyde was determined by multiple injections of standards. The data in Table 4.4. is presented graphically in Figure 4.4.

Table 4.4.
Instrument Response to Chloroacetaldehyde

× target conc. µg/mL	0.5× 4.17	1× 8.33	2× 16.67
area counts	7578	14290	25268
	7590	14245	25502
	7635	14350	25469
	7644	14298	25385
	7749	14269	25244
	7744	14351	25446
$\bar{X}$	7656.7	14300.5	25385.7

4.5. Storage data

Thirty-six samples were generated by sampling a test atmosphere containing 3.18 mg/m³ chloroacetaldehyde for 15 min at 0.5 L/min. The relative humidity of the atmosphere was 76% at 24°C. One-half of the tubes was stored in a freezer (0°C) and the other half was stored in the dark at ambient temperature (about 22°C). Every few days, three samples were selected from each of the two storage sets and then analyzed. Some migration from the front to the backup section of the sampling tubes was observed following ambient storage. No significant loss of chloroacetaldehyde was noted following ambient storage. No migration was observed following refrigerated storage. The storage data are also presented graphically in Figures 4.5.1. and 4.5.2.

Table 4.5.
Storage Test

storage time (days)	ambient (% recovery)			refrigerated (% recovery)		
0	88.6	87.9	89.0	91.6	98.6	101.6
0	91.6	98.6	101.6	88.6	87.9	89.0
3	91.0	97.6	89.7	95.0	94.6	105.4
8	90.9	100.4	97.2	97.7	102.1	106.2
10	88.0	88.5	86.5	93.4	95.0	98.3
14	86.5	86.5	94.7	94.2	105.4	89.8
17	87.3	90.1	98.4	96.3	89.8	100.0

4.6. Precision (analytical method only)

The precision of the analytical procedure is defined as the pooled coefficient of variation determined from replicate injections of chloroacetaldehyde standards at 0.5, 1, and 2 times the PEL.

Table 4.6.
Precision of the Analytical Method
(based on the data of Table 4.4.)

x target conc. µg/mL	0.5x 4.17	1x 8.33	2x 16.67
SD[1]	74.07	42.93	107.73
CV	0.00967	0.00300	0.00424

$\overline{CV}$ = 0.0063

[1] standard deviation is in area counts

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:

$$SEE = \left[\frac{\Sigma(Y_{obs} - Y_{est})^2}{n - k}\right]^{1/2}$$

where 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 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 4.5.2. The data for Figure 4.5.2. was used to determine the SEE of ±7.67% for chloroacetaldehyde.

4.8. Reproducibility data

Six samples, liquid spiked with chloroacetaldehyde, were given to a chemist unassociated with this study. The samples were analyzed after being stored for 11 days at about 5°C. No sample result had a percent deviation greater than the precision of the overall procedure, which was ±15.0%.

Table 4.8.
Reproducibility Data

µg spiked	µg recovered	% recovered	% deviation
25.65	24.21	94.4	-5.6
25.65	23.92	93.2	-6.8
25.65	24.45	95.3	-4.7
25.65	23.97	93.4	-6.6
25.65	23.43	91.3	-8.7
25.65	23.97	93.4	-6.6

4.9. Sampler capacity

Five-percent breakthrough occurred after sampling a controlled test atmosphere containing 6.3 mg/m³ chloroacetaldehyde at 67% relative humidity and 27°C for 33.6 min at 0.5 L/min. At the end of this time 16.8 L of air had been sampled and 105.8 µg of chloroacetaldehyde had been collected. Breakthrough data were obtained by sampling the test atmosphere for increasing periods of time with several of the recommended two section silica gel tubes. Breakthrough was defined as the amount of chloroacetaldehyde found on the backup section relative to the total amount found on the entire tube. The results of the breakthrough test are also presented in Figure 4.9.

Table 4.9.
Breakthrough Data

air volume (L)	breakthrough (%)
7.14	0.0
7.26	0.0
14.13	0.67
14.75	2.41
21.95	17.64
23.48	22.25

4.10. Desorption efficiency and stability of desorbed samples

4.10.1. Desorption efficiency

The desorption efficiency (DE) of chloroacetaldehyde was determined by liquid-spiking 520-mg portions of silica gel with chloroacetaldehyde at 0.5, 1, and 2 times the target concentration. These samples were stored at room temperature overnight and then desorbed and analyzed. The average desorption efficiency over the studied range was 91.0%.

Table 4.10.1.
Desorption Efficiency

× target conc. µg/sample	0.5× 12.5	1× 25.0	2× 50.0
DE, %	91.9	91.4	90.2
	92.1	89.5	91.1
	93.2	90.1	92.3
	91.5	88.8	91.7
	91.5	89.8	91.2
	92.1	88.8	92.1
$\bar{X}$	92.0	89.7	91.4

4.10.2. Stability of desorbed samples

The stability of desorbed samples was investigated by re-analyzing the "1×" target concentration desorption samples about 16 h after the original analysis. The samples were resealed immediately following the first analysis, stored at ambient temperature, and were reanalyzed with fresh standards. The average of the reanalyzed samples relative to the average of the original analysis was 100.8%.

Table 4.10.2.
Stability of Desorbed Samples

original result (%)	reanalyzed result (%)	reanalyzed relative to original (%)
91.4	91.2	99.8
89.5	90.0	100.6
90.1	90.6	100.6
88.8	90.0	101.4
89.8	91.1	101.4
88.8	89.5	100.8

4.11. Chromatogram

A chromatogram at the target concentration is shown in Figure 4.11.

4.12. A procedure to determine chloroacetaldehyde by titration

This procedure was taken from Reference 5.1. It is based on the reaction of chloroacetaldehyde with hydrazine sulfate to convert chemically bound chlorine to chloride. Silver nitrate, in excess of the amount required to react with the liberated chloride, is

added to the sample. The excess silver is titrated with ammonium thiocyanate using ferric ammonium sulfate as an indicator.

4.12.1. Apparatus

Miscellaneous glassware. A 25-mL burette, 250-mL Erlenmeyer flasks, 100-mL volumetric flask, weighing bottle, pipets, etc.

4.12.2. Reagents

4.12.2.1. Hydrazine sulfate, 99% A.C.S. reagent. Hydrazine sulfate was purchased from Aldrich. Prepare a 2.5% (by weight) solution in deionized water. **CAUTION.** Hydrazine sulfate is a cancer suspect agent.

4.12.2.2. Ferric ammonium sulfate, 99% A.C.S. reagent. Ferric ammonium sulfate was purchased from Aldrich. Prepare a saturated solution in 1 M aqueous nitric acid.

4.12.2.3. Nitric acid, 69.0-71.0%. "Baker Analyzed" reagent grade was purchased from VWR Scientific. Prepare a 50/50 (v/v) solution in deionized water and boil until colorless to remove nitrous acid.

4.12.2.3. Ammonium thiocyanate, 0.100 N, volumetric solution. "Mallinckrodt StandARd" grade 0.100 N solution was purchased from Baxter Scientific.

4.12.2.4. Silver nitrate, 0.1000 N, volumetric standard. A standardized 0.1002 N solution was purchased from Aldrich.

4.12.2.5. Nitrobenzene, reagent grade. "Baker Analyzed" reagent grade was purchased from VWR Scientific.

4.12.3. Procedure

4.12.3.1. Weigh (using a weighing bottle) 1 mL of the 50% chloroacetaldehyde (Section 3.2.1.) into a 100-mL volumetric flask containing about 75 mL of deionized water. Dilute to the mark with deionized water.

4.12.3.2. Pipet two 5-mL aliquots of the diluted chloroacetaldehyde solution into separate 250-mL Erlenmeyer flasks. Pipet 10 mL of the 2.5% hydrazine sulfate solution into one flask. The other flask will serve as the blank. Swirl the flasks and allow them to stand for 10 min.

4.12.3.3. Add 10.0 mL of the 0.1000 N silver nitrate solution, 5 mL of the 50/50 nitric acid solution and 2 mL of the saturated ferric ammonium sulfate solution to each flask. Swirl the contents of the flasks and then add 2 mL of nitrobenzene to each flask. The nitrobenzene serves to prevent the reaction of the precipitated silver chloride with ammonium thiocyanate.

4.12.3.4. Titrate the contents of each flask with 0.100 N ammonium thiocyanate solution to a permanent faint orange/brown endpoint.

4.12.4. Calculations

Calculate, using the following equation, the volumes of standard silver nitrate required to react with the chloride liberated from the sample (V_s) and also the amount present in the blank (V_b).

$$V_s \text{ or } V_b = 10-(A(B/C))$$

where A = volume of ammonium thiocyanate required for titration in Section 4.12.3.4., mL
B = normality of ammonium thiocyanate solution
C = normality of silver nitrate solution

Calculate, using the following equation, the percent of chloroacetaldehyde (CAA) present in the original solution.

$$\text{CAA, \% wt} = [(V_s-V_b)(C)(7.85)(20)]/D$$

where 7.85 = chloroacetaldehyde equivalent factor
20 = dilution factor
D = weight from Section 4.12.3.1., g

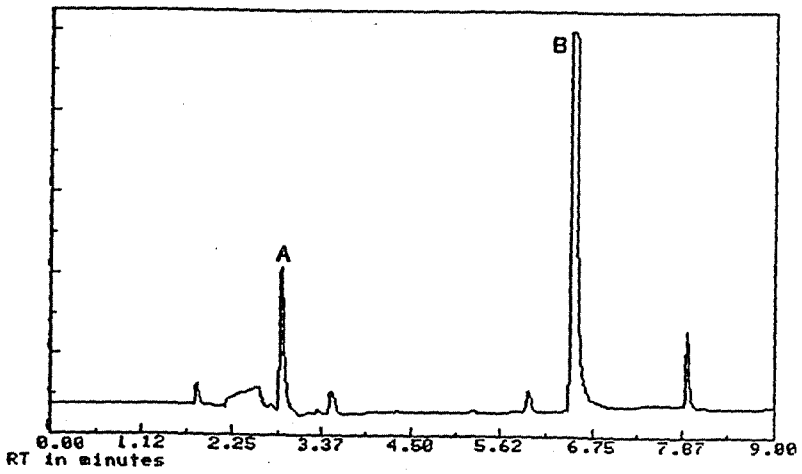

Figure 4.1. Detection limit of the analytical procedure. Peak identification was as follows: A, chloroacetaldehyde; B, 1,1,2-trichloroethane.

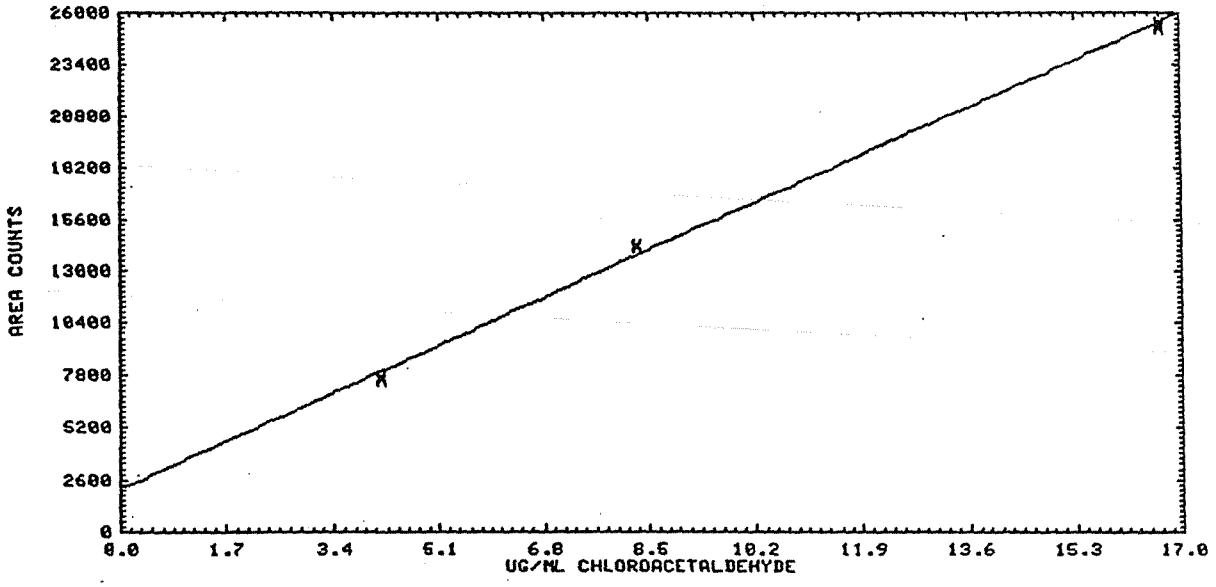

Figure 4.4. Chloroacetaldehyde calibration curve.

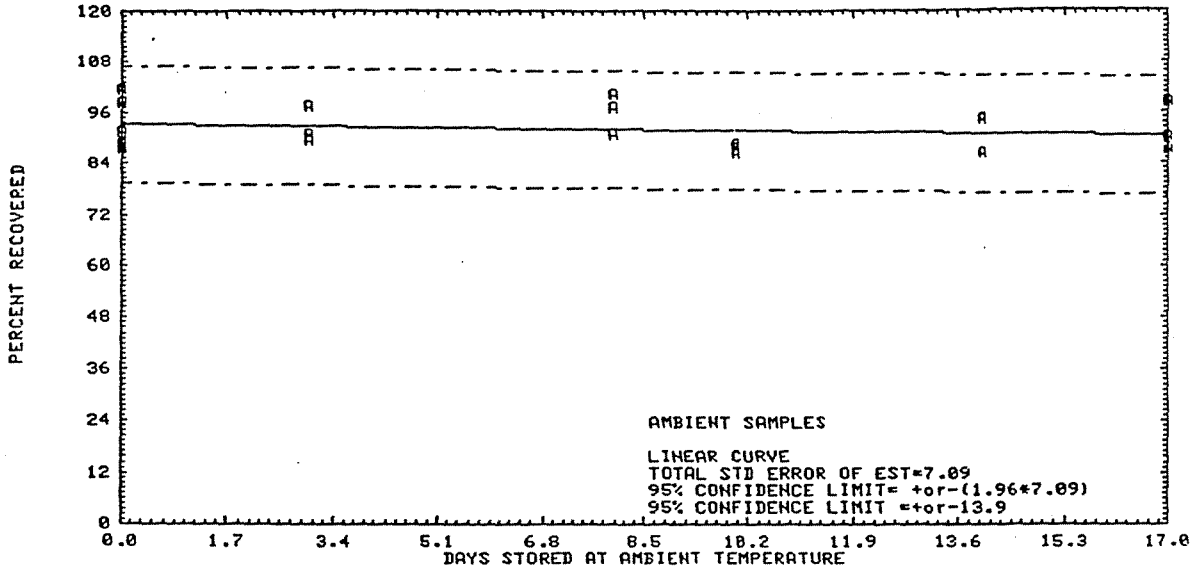

Figure 4.5.1. Ambient temperature storage test for chloroacetaldehyde.

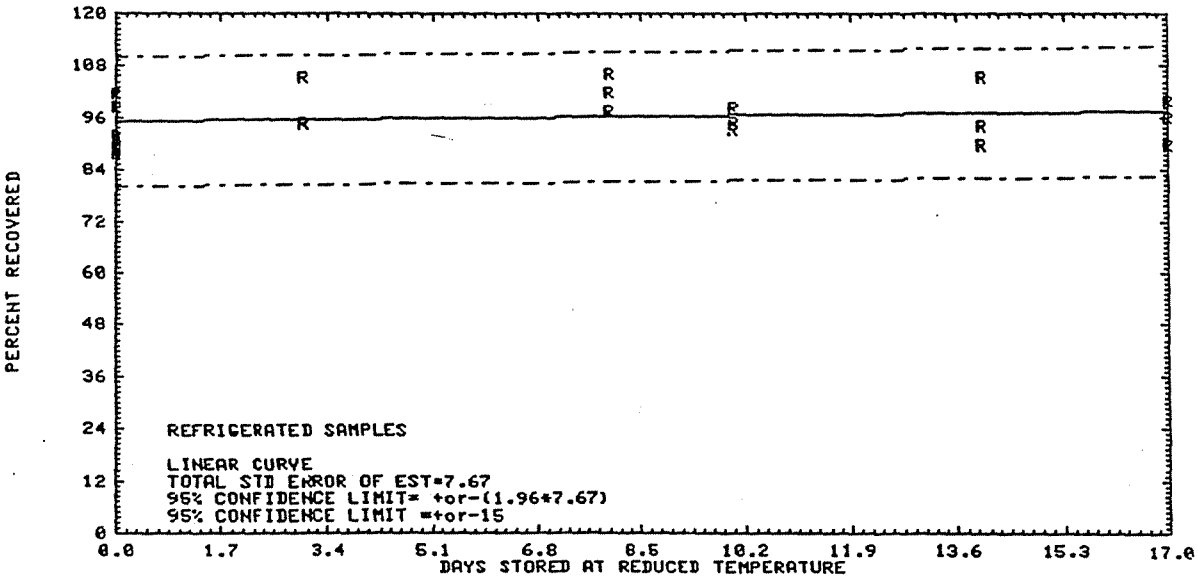

Figure 4.5.2. Refrigerated temperature storage test for chloroacetaldehyde.

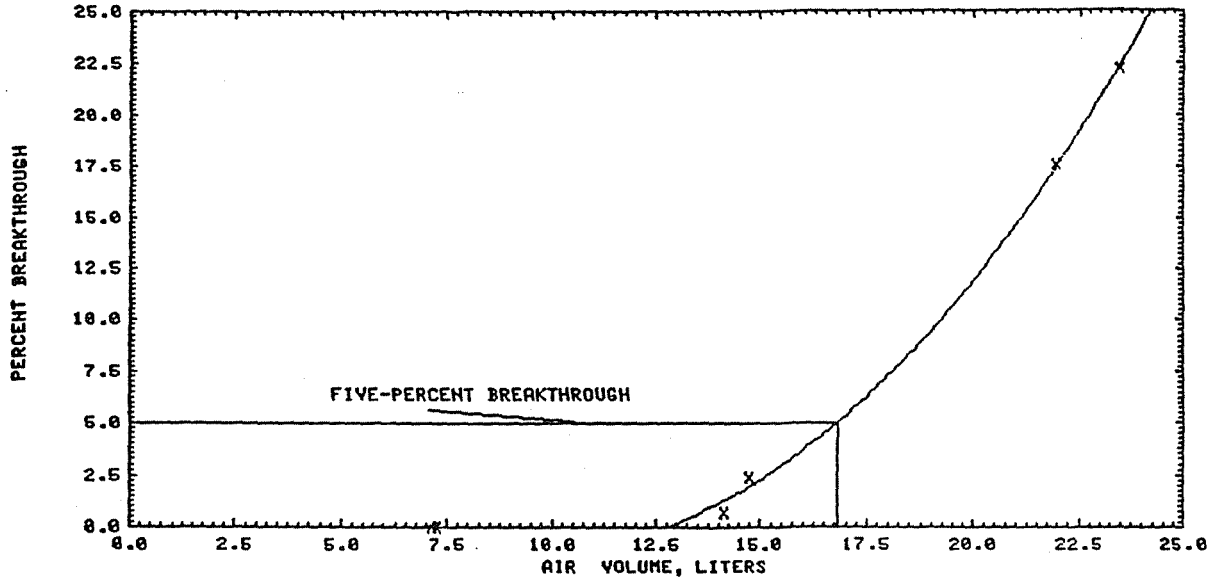

Figure 4.9. Sampler capacity test.

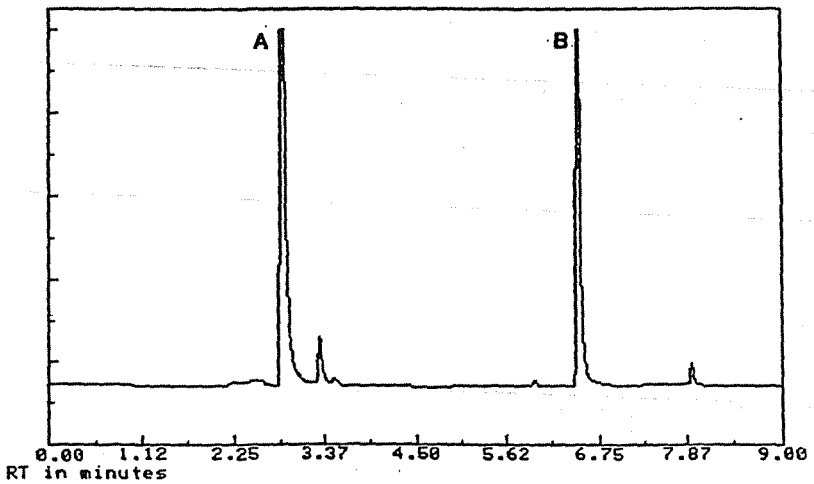

Figure 4.11. Chromatogram at the target concentration. Peak identification was as follows: A, chloroacetaldehyde; B, 1,1,2-trichloroethane.

5. References

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