ACETALDEHYDE

Method no.:	68
Matrix:	Air
Target concentration:	200 ppm (360 mg/m^3) (OSHA PEL)
Procedure:	Air samples are collected by drawing known volumes of air through 8-mm o.d. sampling tubes containing XAD-2 adsorbent which has been coated with 2-(hydroxymethyl) piperidine. Each sampling tube contains a 450-mg sampling section and a 225-mg backup section. The samples are desorbed with toluene and the derivatized acetaldehyde is analyzed by gas chromatography using a nitrogen selective detector.
Recommended air volume and sampling rate:	3 L at 0.05 L/min
Reliable quantitation limit:	580 ppb (1050 µg/m^3)
Standard error of estimate at the target concentration: (Section 4.7)	6.1%
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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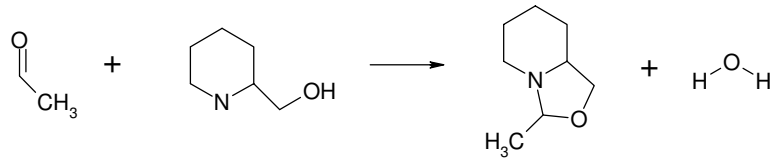
1. General Discussion

1.1 Background

1.1.1 History

This work was performed because the existing NIOSH sampling and analytical method for acetaldehyde is too impractical for use by OSHA. The NIOSH method (Ref. 5.1) requires air sample collection using a bubbler containing Girard T reagent. Analysis of the resulting derivative is performed by HPLC with UV detection. Girard T reagent must be used within 2 weeks of preparation and specially treated glassware must be used to store the reagent and to collect the samples.

XAD-2 adsorbent coated with 2-(hydroxymethyl)piperidine (2-HMP) is used to collect phosgene (Ref. 5.2), acrolein, and formaldehyde (Ref. 5.3). Acetaldehyde was also found to react with 2-HMP when the aldehyde was spiked on the coated adsorbent. Gas chromatographic analysis revealed the presence of two derivative peaks. The ratio of the two derivative peaks is reasonably constant and is independent of the technique (liquid spike or collection from a controlled test atmosphere) used to prepare the derivatives on coated XAD-2 adsorbent. Mass spectrometric analysis showed that the two derivative peaks have the same molecular formula. The two acetaldehyde derivatives are probably due to the relative positions of the methyl group and the hydrogen atom which are bonded to the carbon atom indicated by the asterisk in the proposed derivatization reaction shown below. The proposed names of the derivatives are syn- and anti- 9-methyl-l-aza-8-oxabicyclo[4.3.0]nonane.



A larger tube containing more coated adsorbent must be used for acetaldehyde than for phosgene, formaldehyde, and acrolein because a greater amount of acetaldehyde is collected. Attempts to use the OSHA Versatile Sampler (OVS) tube containing the coated adsorbent were unsuccessful because of excessive migration of the derivatives to the backup section during storage. This effect was not observed with the sampling tube recommended in this method because of its longer adsorbent bed length. The length of the 450-mg bed in an OVS tube is 1.3 cm while that in the recommended tube is 4 cm.

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

Acetaldehyde vapor is an irritant of the eyes, nose, and throat. Inhalation of high concentrations may cause drowsiness, dizziness, and unconsciousness. Acetaldehyde has a penetrating fruity odor. The odor threshold for acetaldehyde is reported to be between 0.031 and 2.3 ppm. Ingestion of acetaldehyde may cause drowsiness, dizziness, unconsciousness, kidney damage, and respiratory problems. The onset of respiratory symptoms may be delayed. Eye contact with acetaldehyde may cause a burning sensation, lacrimation, and blurred vision. Skin contact with acetaldehyde may cause erythema and burns. Repeated skin contact may result in dermatitis which can be caused either by primary irritation or by sensitization. (Ref. 5.4)

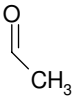
The International Agency for Research on Cancer (IARC) reports that acetaldehyde is an animal teratogen, mutagen, and carcinogen. IARC also reports that there is inadequate evidence of the carcinogenicity of acetaldehyde to humans. IARC states that in the absence of adequate human data, it is reasonable to treat chemicals for which sufficient evidence of animal carcinogenicity exists as if they were carcinogenic to humans. (Ref. 5.5)

1.1.3 Workplace exposure

In 1982, the U.S. production of acetaldehyde was 281,000 metric tons. Most of this amount was produced by the liquid-phase oxidation of ethylene using a catalytic solution of palladium and copper chlorides. In that year, 61% of the acetaldehyde production was used to produce acetic acid, 9% to produce pyridine and pyridine bases, 8% to produce peracetic acid, 7% to produce pentaerythritol, 2% to produce 1,3-butylene glycol, 1% to produce chloral, and 12% for other applications which include food additives and exports. (Ref. 5.5)

NIOSH estimated in 1974 that 1700 workers were potentially exposed to acetaldehyde. Occupational exposure to acetaldehyde occurs primarily in the manufacture of organic chemicals from acetaldehyde. Examples of such chemical manufacturing operations include: production of acetic acid, acetic anhydride, aldol compounds, synthetic resins, pesticides, pharmaceuticals, and rubber processing chemicals. Exposure may also occur in industrial operations where acetaldehyde is used. Uses for acetaldehyde include: coating of mirrors, hardening agent in photography, preservative for food and leather products and manufacture of gelatin, glue, and casein products. (Ref. 5.4)

1.1.4 Physical properties (Ref. 5.5 unless otherwise noted)

CAS no.:	75-07-0
molecular weight:	44.1
appearance:	colorless liquid
melting point:	-123.5°C
boiling point at 1 atm:	20.16°C
vapor pressure at 20°C:	100.6 kPa (755 mm Hg)
density at 20°C:	0.7780 g/mL
solubility:	miscible with water and most organic solvents
flash point (closed cup):	-38°C
structural formula:	
autoignition temperature:	175°C (Ref. 5.4)
flammable limits:	lower 4 (Ref. 5.4)
(% by volume in air)	upper 60
synonyms:	acetic aldehyde; "aldehyde"; ethanal; ethyl aldehyde; ethylaldehyde; NCIC56326

1.2 Limit defining parameters (The analyte air concentrations listed throughout this method are based on an air volume of 3 L and a solvent desorption volume of 5.0 mL. Air concentrations listed in ppm are referenced to 25°C and 760 mm Hg. The analyte concentrations are listed as acetaldehyde even though the derivatives are the actual species analyzed.)

1.2.1 Detection limit of the analytical procedure

The ratio of the two derivative peaks is about 14 to 1 and the smaller derivative peak is just visible at the detection limit. The detection limit of the analytical procedure is based on the peak height of the larger derivative peak. The detection limit of the analytical procedure is 565 pg per injection. This is the amount of analyte which will give a peak whose height is about 5 times the height of a nearby contaminant peak. (Section 4.1)

1.2.2 Detection limit of the overall procedure

The detection limit of the overall procedure is 3.14 µg per sample (580 ppb or 1050 µg/m^3). This is the amount of acetaldehyde spiked on the sampling device which 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 3.14 µg per sample (580 ppb or 1050 µg/m^3). This is the smallest amount of analyte 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 4.2)

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 was not linear. (Section 4.4)

1.2.5 Recovery

The recovery of acetaldehyde from samples used in a 23-day storage test remained above 92.8% when the samples were stored at about 23°C. (Section 4.7) The recovery of the analyte from the collection medium during storage must be 75% or greater.

1.2.6 Precision (analytical procedure)

The pooled coefficient of variation obtained from replicate determinations of analytical standards at 0.5, 1, and 2 times the target concentration is 0.0065. (Section 4.3)

1.2.7 Precision (overall procedure)

The precision at the 95% confidence level for the 23-day ambient temperature storage test is ±11.9%. (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 by liquid injection, and a draft copy of this procedure were given to a chemist unassociated with this evaluation. The samples were analyzed after 41 days of storage at 10°C. No individual sample 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 procedure provides a simple, convenient and precise means to monitor occupational exposure to acetaldehyde.

1.4 Disadvantage

The sampling tubes are not currently commercially available.

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 attached.

2.1.2 Samples are collected with 11-cm x 6-mm i.d. x 8-mm o.d. silane-treated glass tubes which are packed with a 225-mg backup section and a 450-mg sampling section of pretreated XAD-2 adsorbent coated with 2-HMP. The two sections of coated adsorbent are separated and retained with small plugs of silanized glass-wool. Instructions for the pretreatment and the coating of XAD-2 adsorbent are given in Section 4.10 of this method.

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 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 the same 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

When controlled test atmospheres containing 840 mg/m^3 of acetaldehyde (2.3 times the OSHA PEL) in air at 78% relative humidity and 28°C were sampled using the recommended sampling method, 5% breakthrough occurred after sampling for 304 min at 0.05 L/min. At the end of this time 15.2 L of air had been sampled and 12.8 mg of acetaldehyde had been collected. Five-percent breakthrough was defined as the point at which 5% of the total amount of acetaldehyde collected on the entire tube was found on the backup section. (Section 4.5)

At the 5% breakthrough point, 74% of the theoretically available 2-HMP on the front section of the sampling tube had been consumed. Other chemicals with carbonyl groups may also deplete available 2-HMP. Clearly, a safety margin is necessary and this is the basis of the recommended 3-L air volume. After sampling an atmosphere containing 2 times the OSHA PEL of acetaldehyde for 3 L, only 15% of the theoretically available 2-HMP will be consumed.

An additional sampler capacity experiment was performed to determine if the amount of water in the sampled air could affect the ability of the sampler to collect acetaldehyde. When a controlled test atmosphere containing 823 mg/m^3 acetaldehyde (2.3 times the OSHA PEL) in air at 19% relative humidity and 27°C was sampled using the recommended sampling method, 14% breakthrough occurred after sampling for 3 L. Even though the breakthrough was excessive, the amount of acetaldehyde recovered was 99.7% of theoretical. The high breakthrough observed when sampling essentially dry air further supports the recommended 3-L air volume. (Section 4.5)

2.5 Desorption efficiency

2.5.1 No desorption efficiency corrections are necessary to compute results because analytical standards are prepared using coated adsorbent. However, desorption efficiencies were determined to investigate the recovery of acetaldehyde from the sampling device. The average desorption efficiency for acetaldehyde from XAD-2 adsorbent coated with 2-HMP over the range of 0.3 to 2 times the target concentration was essentially 100%. (Section 4.6)

2.5.2 Desorbed samples are stable for at least 72 h. (Section 4.6)

2.6 Recommended air volume and sampling rate

2.6.1 The recommended air volume is 3 L and the recommended sampling rate is 0.05 L/min.

2.6.2 When short-term air samples are required, the recommended sampling rate is 0.05 L/min. A 15-min sample at the reliable quantitation limit is equivalent to 2.3 ppm acetaldehyde.

2.7 Interferences (sampling)

2.7.1 Any collected substance that is capable of reacting with 2-HMP is a potential interference. Mineral acids may neutralize 2-HMP and chemicals which contain a carbonyl group (such as acetone) may be capable of reacting with 2-HMP.

2.7.2 Suspected interferences should be reported to the laboratory with submitted samples.

2.8 Safety precautions

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 gas chromatograph (GC) equipped with a nitrogen selective detector. A Hewlett-Packard 5840A GC fitted with a nitrogen-phosphorus detector (NPD) was used in this evaluation. Injections were performed using a Hewlett-Packard 7671A automatic sampler.

3.1.2 A GC column capable of resolving the acetaldehyde derivative from potential interferences. A 6-ft × 1/4-in. o.d. (2-mm i.d.) glass GC column containing 10% UCON 50-HB-5100 with 2% KOH on 80/100 mesh Chromosorb W-AW was used in this evaluation. Injections were performed on-column.

3.1.3 Vials, 7-mL and 2-mL glass with Teflon-lined caps.

3.1.4 Volumetric flasks, pipets, and syringes for preparing standards, making dilutions, and performing injections.

3.1.5 Vortex mixer, a S/P Deluxe Mixer, obtained from American Scientific Products, was used in this evaluation.

3.2 Reagents

3.2.1 Toluene and dimethylformamide, reagent grade or better. American Burdick and Jackson solvents were used in this evaluation.

3.2.2 Helium, hydrogen, and air, GC grade.

3.2.3 Acetaldehyde, of known high purity. Aldrich Chemical Co. acetaldehyde (99%) was used in this evaluation. Store the acetaldehyde in a freezer at approximately -20°C. CAUTION! ACETALDEHYDE IS AN ANIMAL CARCINOGEN.

3.2.4 Amberlite XAD-2 adsorbent coated with 10%, by weight, 2-(hydroxymethyl)piperidine. (Section 4.10)

3.2.5 Desorbing solution. This solution is prepared by adding 20 µL of dimethylformamide which is used as an internal standard to 100 mL of toluene. This is the same solution used to desorb phosgene, formaldehyde, and acrolein air samples.

3.3 Standard preparation

3.3.1 Prepare stock standards by diluting a known amount of 99% acetaldehyde with toluene. CAUTION! ACETALDEHYDE IS AN ANIMAL CARCINOGEN. Use of the following technique to prepare stock standards is strongly recommended: Determine the weight of a sealed 25-mL volumetric flask containing about 15 mL of toluene. Place the sealed volumetric flask and a 1-mL pipet in the same freezer as used to store the 99% acetaldehyde. After waiting 30 min, remove the sealed volumetric flask, 1-mL pipet, and 99% acetaldehyde from the freezer. Immediately pipet 1 mL of 99% acetaldehyde into the cold flask, reseal the flask, and then allow the flask to warm to room temperature. Reweigh the flask and subtract the tare weight from the weight of the reweighed flask to determine the weight of the added acetaldehyde. Dilute the contents of the volumetric flask to the mark with toluene. A stock standard containing 31.20 mg/mL acetaldehyde was prepared using this technique. Store the stock standards in a freezer. Prepare fresh stock standards every 10 days.

3.3.2 Prepare analytical standards about 16 h before the air samples are to be analyzed in order to ensure that the reaction between acetaldehyde and 2-HMP is complete.

3.3.3 Place 450-mg portions of coated XAD-2 adsorbent, from the same lot number as used to collect the air samples, into each of several 7-mL glass vials. Seal each vial with a Teflon-lined cap. Standards are prepared with coated adsorbent to ensure that analytical standards are similar to air samples.

3.3.4 Prepare standards by injecting appropriate volumes of acetaldehyde onto the coated adsorbent contained in the sealed 7-mL vials. A standard containing 1092 µg (target concentration) of acetaldehyde was prepared by injecting 35.0 µL of a standard containing 31.20 mg/mL acetaldehyde into a vial containing 450 mg of coated adsorbent.

3.3.5 Prepare a sufficient number of standards to generate a calibration curve. Analytical standard concentrations must bracket sample concentrations.

3.3.6 Desorb the standards in the same manner as the samples following the 16-h reaction time.

3.4 Sample preparation

3.4.1 Transfer the 450-mg section of the sampling tube and the front glass-wool plug to a 7-mL glass vial. Place the 225-mg section and the center glass-wool plug in a separate vial. Discard the rear glass-wool plug.

3.4.2 Add 5.0 mL of desorbing solution to each vial.

3.4.3 Seal the vials with Teflon-lined caps and allow them to desorb for 1 h. Mix the contents of the vials using a vortex mixer several times during the desorption time.

3.4.4 Dilute samples containing high amounts of acetaldehyde with desorbing reagent. When samples are not in the concentration range of the prepared standards, additional standards must be prepared to determine detector response.

3.5 Analysis

3.5.1 GC Conditions

column temperature:	bi-level temperature program
first level:	100 to 140°C at 4°C/min upon injection
second level:	140 to 180°C at 20°C/min following completion of the first level
isothermal period:	hold column at 180°C until the recorder pen returns to baseline (usually about 25 min after injection)
injector temperature:	180°C
helium flow rate:	30 mL/min (detector response will be reduced if nitrogen is substituted for helium carrier gas)
injection volume:	0.90 µL
GC column:	6-ft × 1/4-in. o.d. (2-mm i.d.) glass GC column containing 10% UCON 50-HB-5100 + 2% KOH on 80/100 Chromosorb W-AW

NPD conditions

hydrogen flow rate:	3 mL/min
air flow rate:	50 mL/min
detector temperature:	275°C

3.5.2 Retention times: 5.8 and 7.7 min (two peaks)

3.5.3 Chromatogram: Figure 3.5.3

3.5.4 Use a suitable method, such as electronic integration, to measure detector response.

3.5.5 Analyze a standard at the target concentration. Determine the relative concentration (µg/sample) for each of the two acetaldehyde peaks by multiplying the factor, which is obtained by dividing the area of each peak by the total area for both peaks, times the concentration (µg/sample) of the standard. For example: The area of the 5.8-min peak was 186700 and the area of the 7.7-min peak was 12110. The total area was 198810 and the standard concentration was 1092 µg/sample. The relative concentration of the 5.8-min peak is [(186700/198810)](1092) = 1025.48 µg/sample and for the 7.7-min peak, [(12110/198810)](1092) = 66.52 µg/sample. Calibrate the integrator using the appropriate amounts and an internal standard procedure. An internal standard is used to compensate for minor variations in injection volume and detector response.

3.5.6 Analyze several standard solutions of different concentration to generate the calibration curve. A calibration curve must be used to compensate for possible nonlinear detector response. Prepare the calibration curve daily.

3.5.7 Bracket sample concentrations with standards.

3.6 Interferences

3.6.1 Any compound having a similar retention time as the acetaldehyde derivatives is a potential interference.

3.6.2 GC parameters (temperature, column, etc.) may be changed to circumvent Interferences.

3.6.3 Retention time on a single column is not proof of chemical identity.

3.6.4 GC/MS is a useful means of structure determination. It is recommended that this procedure be used to confirm samples whenever possible.

3.7 Calculations

3.7.1 Add the integrator results for both peaks to obtain total µg/sample. A calibration curve must be applied to these results to compensate for possible nonlinear detector response.

3.7.2 Prepare a calibration curve by plotting total µg/sample against the actual concentration for each standard. Determine the best line through the data points by curve fitting.

3.7.3 Determine the actual concentration, in µg/sample, for a particular sample by comparing its summed integrator results to the calibration curve. If acetaldehyde is found on the backup section, add it to the amount found on the front section. Perform blank corrections before adding the results for the front and backup sections together.

3.7.4 Express acetaldehyde air concentration using the following equation:

$$mg/m^3 = (A)/(B)$$

where: A = µg/sample from Section 3.7.3
B = liters of air sampled

No desorption efficiency correction is required because analytical standards are prepared using coated adsorbent.

3.7.5 Convert acetaldehyde results in mg/m^3 to ppm using the following equation:

$$ppm = (mg/m^3)(24.46)/(44.1)$$

where: mg/m^3 = result from Section 3.7.4
24.46 = molar volume at 760 mm Hg and 25°C
44.1 = molecular weight of acetaldehyde

3.8 Safety precautions

3.8.1 Acetaldehyde is an animal carcinogen. Treat it as if it were a human carcinogen.

3.8.2 Avoid skin contact and inhalation of all chemicals.

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

3.8.4 Wear safety glasses and a lab coat in laboratory areas.

4. Backup Data

4.1 Detection limit of the analytical procedure

The injection size recommended in the analytical procedure (0.90 µL) was used in the determination of the detection limit of the analytical procedure. The ratio of the two derivative peaks is about 14 to 1 and the smaller derivative peak is just visible at the detection limit. Therefore, the detection limit of the analytical procedure is based on the peak height of the larger derivative peak. The detection limit of the analytical procedure was 565 pg per injection. This is the amount of analyte which will give a peak whose height is about five times the height of a nearby contaminant peak. This detection limit was determined by the analysis of a standard containing 0.628 µg/mL acetaldehyde. Figure 4.1.1 is a chromatogram of a blank sample and Figure 4.1.2 is a chromatogram of the detection limit of the analytical procedure. A small acetaldehyde peak is present in the blank sample. The acetaldehyde elution times for the blank sample are indicated with arrows. The formaldehyde derivative, which is a contaminant of the coated adsorbent, is present in both chromatograms.

4.2 Detection limit of the overall procedure and reliable quantitation limit data

The injection size recommended in the analytical procedure (0.90 µL) was used in the determination of the detection limit of the overall procedure and in the determination of the reliable quantitation limit. Samples were prepared by the liquid injection of 10 µL of a solution containing 314 µg/mL acetaldehyde in toluene onto 450-mg portions of coated XAD-2 adsorbent. Standards were prepared by injecting acetaldehyde into several 7-mL glass vials, each containing 5 mL of a solution containing 9 mg/mL of 2-HMP in toluene. The samples and standards were stored for about 16 h at room temperature before analysis. Since the recoveries of acetaldehyde from the samples were high and approximately equivalent to the detection limit of the analytical procedure, the detection limit of the overall procedure and the reliable quantitation limit were 3.14 µg/sample (580 ppb or 1050 µg/m^3).

Table 4.2
The Detection Limit of the Overall Procedure and the Reliable Quantitation Limit

sample number	theoretical amount (µg)	amount recovered (µg)	percent recovered
1	3.14	33.28	104
2	3.14	2.89	92.0
3	3.14	3.42	109
4	3.14	3.28	104
5	3.14	3.04	96.8
6	3.14	3.00	95.5
			$\bar{X}$ = 100.2
			SD = 6.4
			1.96 SD = 12.5

4.3 Precision (analytical method only)

The precision of the analytical method was evaluated by performing multiple injections of analytical standards. The standards were prepared by injecting appropriate amounts of acetaldehyde into sealed 7-mL glass vials containing 450 mg of coated adsorbent. The standards were allowed to stand 16 h prior to desorption and analysis. The results of this study are presented in Tables 4.3.1 to 4.3.3 Tables 4.3.1 and 4.3.3 contain peak area data which have not been corrected by the internal standard. Tables 4.3.2 and 4.3.3 contain peak concentration data which has been corrected by the internal standard. The peak area data is presented for use in Figure 4.4 and the precision of the analytical method was evaluated using the combined peak concentration data.

Table 4.3.1
Acetaldehyde Individual Peak Area Data

0.5 x TC 542.5 µg/sample 100 ppm		1 x TC 1085 µg/sample 201 ppm		2 x TC 2170 µg/sample 401 ppm	
peak 1	peak 2	peak 1	peak 2	peak 1	peak 2
574600	34250	*1051000	69120	1739000	136200
550900	33170	1023000	66760	1866000	147200
536600	31990	1044000	68800	1840000	144600
560100	33090	1066000	70140	1803000	139700
555900	33040	1042000	68540	1760000	135000
540700	31800	1036000	68380	1738000	133200

TC = Target Concentration
* Areas from this standard were used to calibrate the integrator

Table 4.3.2
Acetaldehyde Individual Peak Concentration Data

0.5 x TC 542.5 µg/sample 100 ppm		1 x TC 1085 µg/sample 201 ppm		2 x TC3 2170 µg/sample 401 ppm	
peak 1	peak 2	peak 1	peak 2	peak 1	peak 2
542.0	32.3	1018.0	67.0	1766.8	137.9
539.5	32.5	1012.0	66.0	1748.3	137.9
541.6	32.3	1013.1	66.8	1761.5	138.4
540.7	32.0	1014.5	66.8	1797.6	139.3
541.6	32.2	1013.9	66.7	1791.8	137.4
541.3	31.8	1014.9	67.0	1796.2	137.7

TC = Target Concentration

Table 4.3.3
Acetaldehyde Combined Peak Area
and Combined Peak Concentration Data

0.5 x TC 542.5 µg/sample 100 ppm		1 x TC 1085 µg/sample 200 ppm		2 x TC 2170 µg/sample 400 ppm	
area	µg/sample	area	µg/sample	area	µg/sample
608850	574.3	1120120	1085.0	1875200	1904.7
584070	572.0	1089760	1078.0	2013200	1886.2
568590	573.9	1112800	1079.9	1984600	1899.9
593190	572.7	1136140	1081.3	1942700	1936.9
588940	573.8	1110540	1080.6	1895000	1929.2
572500	573.1	1104380	1081.9	1871200	1933.9
$\bar{X}$ = 573.3 SD = 0.860 CV = 0.00150 $\overline{CV}$ = 0.0065		$\bar{X}$ = 1081.1 SD = 2.33 CV = 0.00216		$\bar{X}$ = 1915.1 SD = 20.98 CV = 0.0110	

TC = Target Concentration

4.4 Instrument response to the analyte

The combined area data in Table 4.3.3 are presented graphically in Figure 4.4. This figure shows instrument response over the concentration range of 0.5 to 2 times the target concentration. The instrument response was not linear over this range.

4.5 Breakthrough data

4.5.1 Breakthrough studies were performed using several of the recommended two-section collection devices to sample controlled test atmospheres containing acetaldehyde in air for increasing periods of time. The average acetaldehyde concentration was 840 mg/m³ (2.3 times the OSHA PEL) and the average relative humidity was 78% at 28°C. The sampling rate was 0.05 L/min. Breakthrough was defined as the amount of acetaldehyde found on the backup section divided by the total amount of acetaldehyde collected on the entire sampling tube. Five-percent breakthrough occurred after sampling for 304 min. At the end of this time, 15.2 L of air had been sampled and 12.8 mg of acetaldehyde had been collected. The results of these studies are presented in Table 4.5.1 and Figure 4.5.

Table 4.5.1
Acetaldehyde Breakthrough Data

air volume (L)	breakthrough (percent)
8.6	0.17
15.0	0.80
15.0	1.2
16.3	4.8
16.4	3.5
16.7	3.6
20.2	23.1
20.8	32.0
23.9	42.8

4.5.2 An additional sampler capacity experiment was performed as in Section 4.5.1 to determine if the amount of water in the sampled air could affect the ability of the sampler to collect acetaldehyde. A controlled test atmosphere containing 823 mg/m^3 acetaldehyde (2.3 times the OSHA PEL) in air at 19% relative humidity and 27°C was sampled using the recommended sampling method. The dilution air used in this experiment was not humidified. The humidity was due to the water with which the acetaldehyde was diluted. Even though the observed breakthrough was excessive, the amount of acetaldehyde recovered was high in all cases.

Table 4.5.2
Acetaldehyde Breakthrough Data

air volume (L)	breakthrough (percent)	amount recovered (%)
2.7	13.3	104
3.0	14.0	99.7
4.7	15.1	91.0
5.1	16.1	92.5
6.4	16.0	91.3
6.5	14.6	91.2

4.6 Desorption efficiency and stability of desorbed samples

4.6.1 Desorption efficiency

No desorption efficiency corrections are required to calculate air sample results because standards are prepared using coated adsorbent. However, the desorption efficiency of acetaldehyde from XAD-2 adsorbent coated with 2-HMP was investigated by liquid spiking acetaldehyde into sealed 7-mL glass vials containing 450-mg portions of coated XAD-2 adsorbent. Analytical standards were prepared by injecting equivalent amounts of acetaldehyde into 5-mL aliquots of toluene containing 9 mg/mL of 2-HMP. The samples and standards were stored at room temperature overnight before analysis.

Table 4.6.1
The Desorption Efficiency of Acetaldehyde
From XAD-2 Coated with 10% 2-HMP

amount spiked (µg)	% of PEL	amount recovered (µg)	desorption efficiency (%)
310.0	29.0	316.2	102
620.0	57.4	652.0	105
930.0	86.1	952.3	102
1240	115	1277	103
1550	144	1604	103
1860	172	1971	106
2170	201	2282	105
			$\bar{X}$ = 104

4.6.2 Stability of desorbed samples

The stability of desorbed samples was investigated by reanalyzing desorbed air samples following 72 to 120 h storage at room temperature. Fresh standards were used and the sample vials were resealed immediately after the first analysis. The average recovery, relative to the original analysis, was 103%.

Table 4.6.2
The Stability of Desorbed Samples

original analysis (µg)	storage time (hours)	reanalysis (µg)	% of original analysis
1166	120	1185	102
1226	120	1270	104
1134	120	1156	102
1184	120	1198	101
1177	72	1211	104
1130	72	1173	103
			$\bar{X}$ = 103

4.7 Storage data

Samples stored at approximately 23°C were collected from a controlled test atmosphere containing 231 ppm acetaldehyde in air at 80% relative humidity and 28°C. Samples stored at -20°C were collected from a controlled test atmosphere containing 211 ppm acetaldehyde in air at 81% relative humidity and 27°C. All of the storage samples were generated by sampling the controlled test atmosphere for 60 min at 0.05 L/min. The results of the storage tests are shown graphically in Figures 4.7.1 and 4.7.2.

Table 4.7.1
Ambient Storage Data

storage time (days)	recovery (percent)		
0	95.0	91.8	97.4
5	91.7	92.9	88.1
8	92.4	96.6	94.7
12	94.6	98.2	100
15	89.8	91.1	90.1
23	99.3	96.6	98.8

Table 4.7.2
Refrigerated Storage Data

storage time (days)	recovery (percent)		
0	95.3	91.0	94.5
2	94.0	95.9	93.9
6	87.3	95.4	99.0
9	101	96.1	95.7
13	101	98.7	99.7
16	95.4	92.4	98.4

4.8 Reproducibility data

Reproducibility samples were prepared by the liquid injection of acetaldehyde on the sampling sections of coated XAD-2 tubes. The samples and a draft copy of this evaluation were given to a chemist unassociated with this evaluation. The samples were analyzed after 41 days of storage at about 10°C. No individual sample deviated from its theoretical value by more than the precision (±11.9%) at the 95% confidence level for the 23-day storage test (Section 4.7)

Table 4.8
Reproducibility Results

sample no.	theoretical amount (µ)	analytical results (µ)	percent recovery
1	1022	1048	102
2	1022	1044	102
3	1022	1077	105
4	1022	1026	100
5	1022	997.2	97.6
6	1022	1083	106

4.9 Generation of controlled test atmospheres

The controlled test atmospheres which were used in this evaluation were generated by pumping an acetaldehyde/water solution into a heated glass manifold with a Sage Instruments Model 355 Syringe Pump. The acetaldehyde/water solution was volatilized and then diluted with heated air. The dilution air was metered into the heated glass manifold using a calibrated precision rotameter. The air was humidified, if desired, by passing it through a water bubbler prior to its entering the

heated glass manifold. The water bubbler was contained in a temperature-controlled water bath. The relative humidity of the dilution air could be varied by changing the temperature of the water bath. If dry dilution air was required, the water bubbler was not used. The relative humidity of the test atmosphere was monitored, after mixing, with a YSI Model 91 Dew Point Hygrometer. The test atmosphere passed through a manifold from which samples could be collected. The acetaldehyde concentration of the test atmosphere was adjusted to the desired level by varying the aldehyde concentration of the acetaldehyde/water solution.

The theoretical acetaldehyde concentrations of the test atmospheres were calculated using the concentration of the acetaldehyde/water solution, the flowrate of the syringe pump, and the volume of the dilution air. Air sample results agreed with the theoretical concentrations. The theoretical concentrations were used throughout this evaluation.

4.10 Procedure to coat XAD-2 adsorbent with 2-HMP

4.10.1 Apparatus

a) Soxhlet extractor

b) Rotary evaporator

c) Miscellaneous glassware: One-liter vacuum flask, 1-L round-bottomed evaporative flask, 1-L Erlenmeyer flask, 250-mL Buchner funnel with a coarse fritted disc, etc.

4.10.2 Reagents

a) Methanol, isooctane, and toluene, reagent grade or better. American Burdick and Jackson solvents were used in this evaluation.

b) 2-(hydroxymethyl)piperidine. Technical grade 2-HMP, obtained from Aldrich Chemical Company, was recrystallized from isooctane for use in this evaluation.

c) Amberlite XAD-2 non-ionic polymeric adsorbent, 20 to 60 mesh. Aldrich Chemical XAD-2 adsorbent was used in this evaluation.

4.10.3 Procedure

This procedure is similar to the one described in Section 4.10 of OSHA Method 61: Phosgene (Ref. 5.2) and in Section 4.8 of OSHA Method 52: Acrolein and/or Formaldehyde (Ref. 5.3). Coated adsorbent prepared by the procedure described below can be used for Method 61 and for Method 52 if the formaldehyde blank level is determined to be acceptably low.

Weigh 125 g of crude XAD-2 adsorbent into a 1-L Erlenmeyer flask. Add about 200 mL of water to the flask and then swirl the mixture to wash the adsorbent. Discard any adsorbent that floats to the top of the water and then filter the mixture using a fritted-Buchner funnel. Transfer the adsorbent back to the Erlenmeyer flask and repeat the water wash and the filtration. Air dry the adsorbent for about 2 min. Transfer the adsorbent back to the Erlenmeyer flask and then add about 200 mL of methanol to the flask. Swirl and then filter the mixture as before. Transfer the washed adsorbent to a 1-L evaporative flask and remove the methanol using the rotary evaporation apparatus. Cool the flask to room temperature and then add 13 g of 2-HMP and 200 mL of toluene to the flask. Swirl the mixture and then allow it to stand for 1 h. Remove the toluene using rotary evaporation. Seal the evaporative flask and allow the coated adsorbent to stand overnight at ambient temperature.

Transfer the coated adsorbent to a Soxhlet extractor and then extract the material with toluene for about 24 h. Replace the contaminated toluene with fresh toluene and continue

the extraction for an additional 24 h. Replace the second aliquot of contaminated toluene with methanol and continue the Soxhlet extraction for 4 h. Transfer the adsorbent to a weighed 1-L round-bottomed evaporative flask and remove the methanol using the rotary evaporation apparatus. Determine the weight of the adsorbent and then add an amount of 2-HMP, which is 10%, by weight, of the adsorbent. Add 200 mL of toluene and then swirl the mixture. Allow the flask to stand for 1 h. Remove the toluene using rotary evaporation. If the last traces of toluene are difficult to remove, add about 100 mL of methanol to the flask, swirl the mixture, and then remove the solvents using rotary evaporation.

XAD-2 adsorbent treated in this manner will often contain residual formaldehyde derivative levels of about 0.5 µg/150 mg of adsorbent. The formaldehyde blank level and potential acrolein and acetaldehyde chromatographic interferences should be determined at this time. If the formaldehyde blank and/or any interference is determined to be excessive the batch should be returned to the Soxhlet extractor, extracted with toluene again and then recoated with 2-HMP. This process can be repeated until an acceptable blank and/or level of chromatographic interferences are attained.

The coated adsorbent is now ready to be packed into sampling tubes. The sampling tubes should be stored in the dark and segregated by lot number. A sufficient amount of each lot of coated adsorbent should be retained to prepare analytical standards for use with air samples from that lot number.

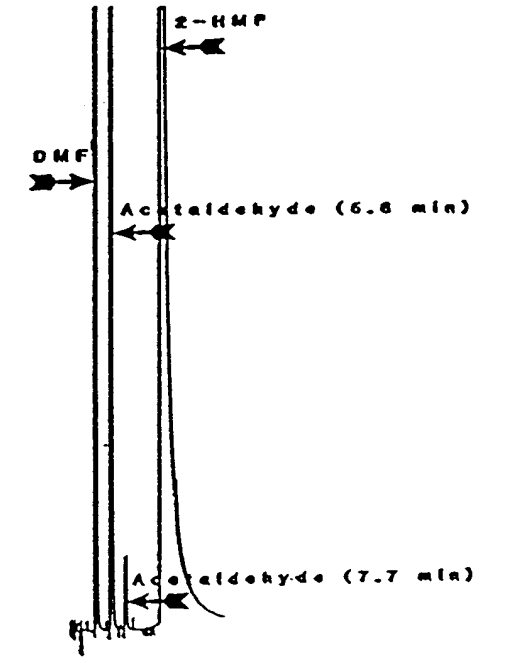


Figure 3.5.3 Acetaldehyde chromatogram.

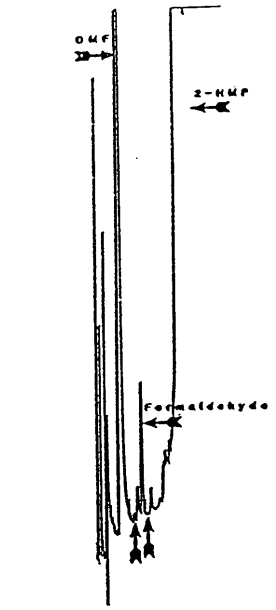


Figure 4.1.1 Blank sample chromatogram.

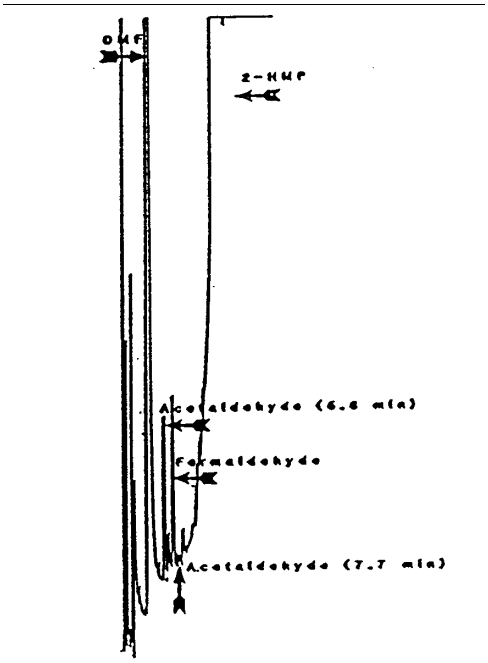


Figure 4.1.2 Detection limit of the analytical procedure chromatogram for acetaldehyde.

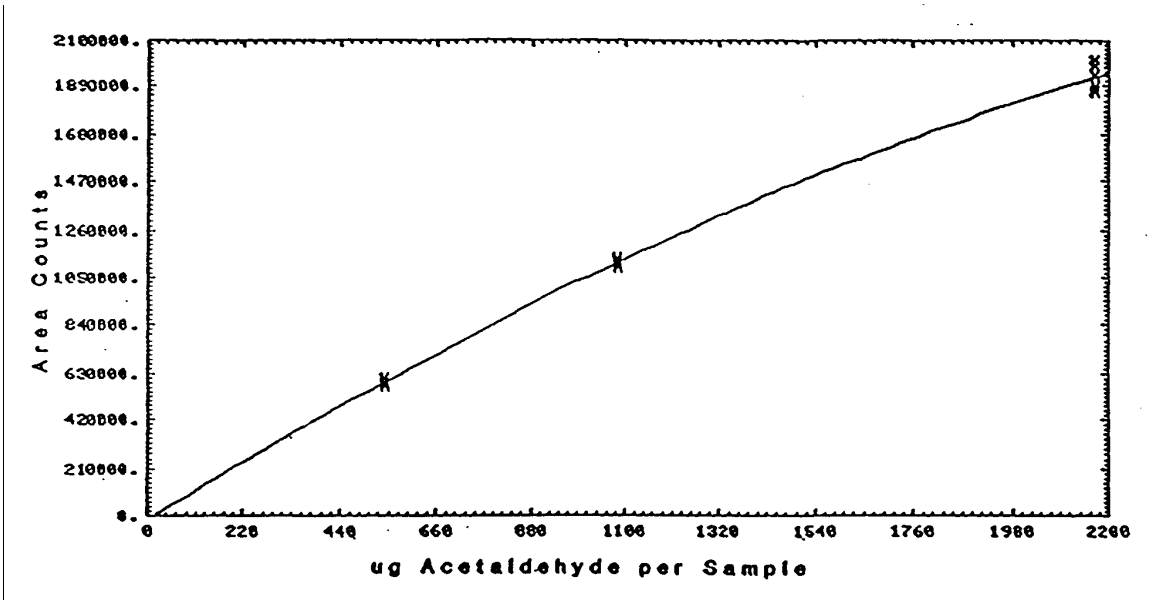


Figure 4.4 Instrument response to acetaldehyde.

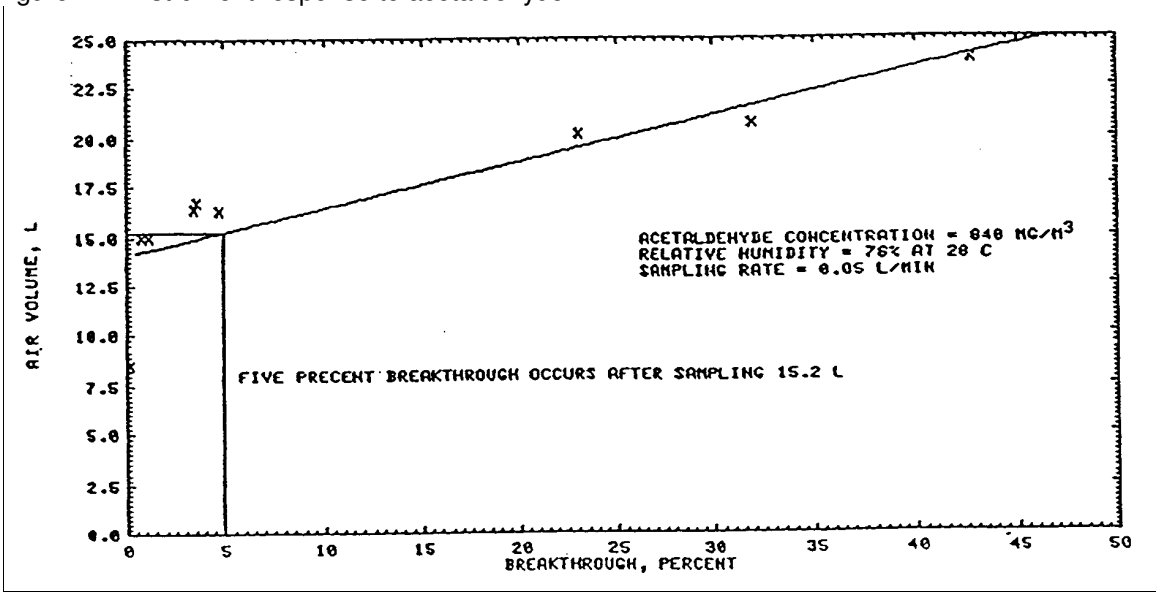


Figure 4.5 Sampler capacity for acetaldehyde.

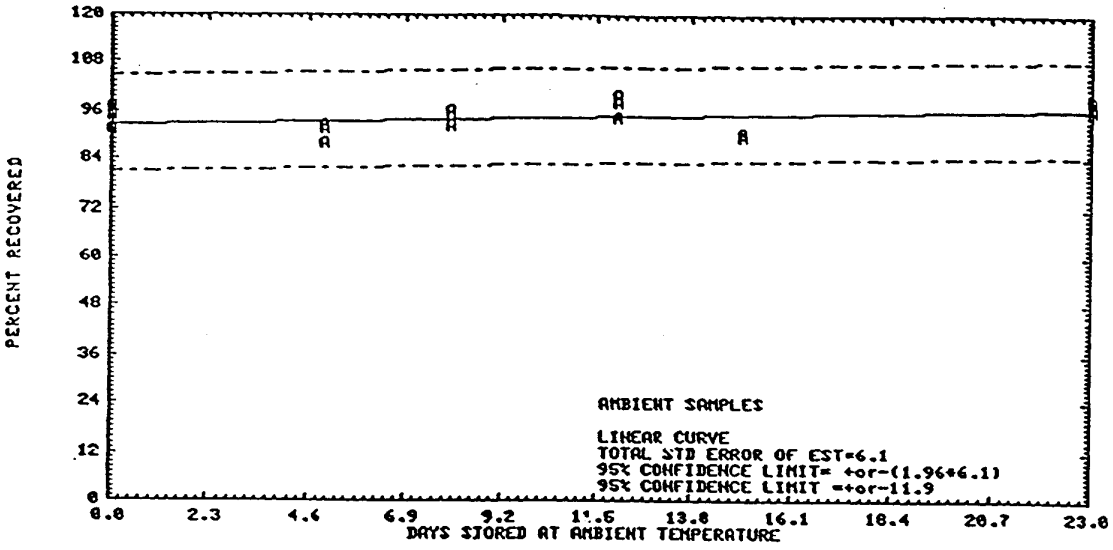


Figure 4.7.1 Ambient temperature storage study for acetaldehyde.

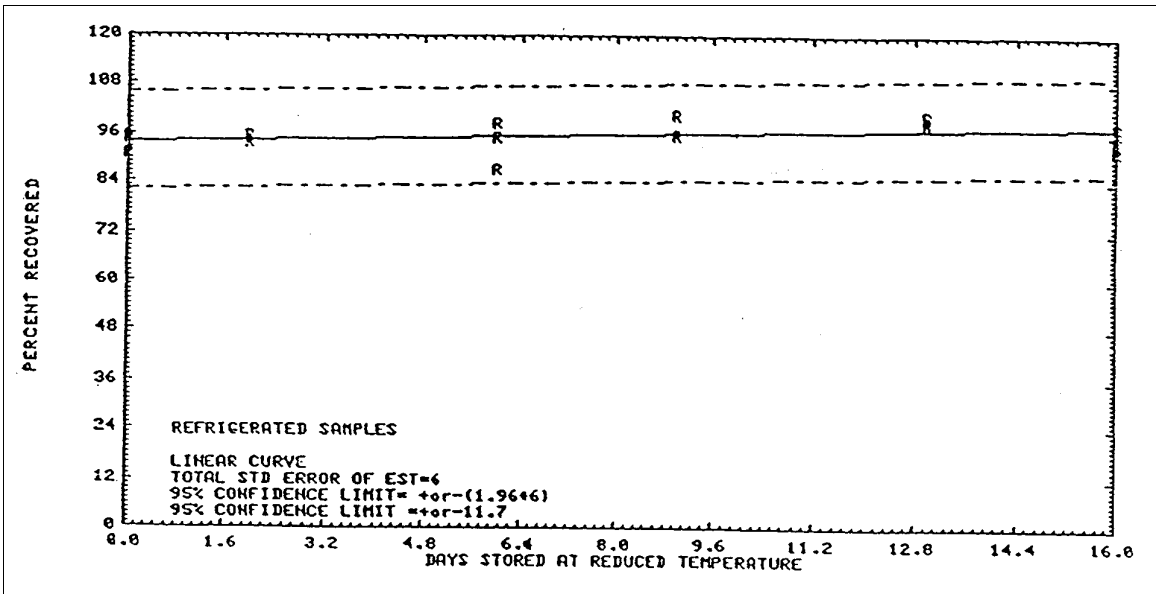


Figure 4.7.2 Refrigerated temperature storage study for acetaldehyde.

5 References

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