Method no.: 52

Matrix: Air

Target concentrations: Acrolein - 0.1 ppm (0.23 mg/m^3)
Formaldehyde - 3 ppm (3.7 mg/m^3)

Procedure: Air samples are collected by drawing known volumes of air through sampling tubes containing XAD-2 adsorbent which has been coated with 2-(hydroxymethyl) piperidine. The samples are desorbed with toluene and then analyzed by gas chromatography using a nitrogen selective detector.

Recommended air volumes and sampling rates
Acrolein (TWA): 48 L at 0.1 L/min
Formaldehyde (TWA): 24 L at 0.1 L/min
Formaldehyde (STEL): 3 L at 0.2 L/min

	acrolein	formaldehyde
Reliable quantitation limit (for TWA samples):	2.7 ppb (6.1 µg/m^3)	16 ppb (20 µg/m^3)
Standard error of estimate at the target concentration: (Section 4.6.)	7.1%	7.3%

Status of method: Evaluated method. This method has been subjected to the established evaluation procedures of the Organic Methods Evaluation Branch. Additional evaluation data was collected because of the 1988 reduction of the formaldehyde PEL.

Date: March 1985
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1. General Discussion

1.1 Background

1.1.1 History

The current OSHA method for collecting acrolein vapor recommends the use of activated 13X molecular sieves. The samples must be stored in an ice bath during and after sampling and they must be analyzed within 48 h of collection. The current OSHA method for collecting formaldehyde vapor recommends the use of bubblers containing 10% methanol in water as the trapping solution (Ref. 5.1).

This work was undertaken to resolve the sample stability problems associated with acrolein and also to eliminate the need to use bubblers to sample formaldehyde. A goal of this work was to develop and evaluate a common sampling and analytical procedure for acrolein and formaldehyde. The simultaneous determination of these aldehydes was an appropriate goal because they can be found together in industrial environments. Further, common sampling and analytical procedures can reduce both field and laboratory workloads.

NIOSH has developed independent methodologies for acrolein (Ref. 5.2) and formaldehyde (Ref. 5.3) which recommend the use of reagent-coated adsorbent tubes to collect the aldehydes as stable derivatives. The formaldehyde sampling tubes contain Chromosorb 102 adsorbent coated with N-benzylethanolamine (BEA) which reacts with formaldehyde vapor to form a stable oxazolidine compound. The acrolein sampling tubes contain XAD-2 adsorbent coated with 2-(hydroxymethyl) piperidine (2-HMP) which reacts with acrolein vapor to form a different, stable oxazolidine derivative. Acrolein does not appear to react with BEA to give a suitable reaction product (Ref. 5.2), therefore, the formaldehyde procedure cannot provide a common method for both aldehydes. However, formaldehyde does react with 2-HMP to form a very suitable reaction product. It is the quantitative reaction of acrolein and formaldehyde with 2-HMP that provides the basis for this evaluation.

This sampling and analytical procedure is very similar to the method recommended by NIOSH for acrolein. Some changes in the NIOSH methodology were necessary to permit the simultaneous determination of both aldehydes and also to accommodate OSHA Laboratory equipment and analytical techniques.

This successfully evaluated method recommends the collection of acrolein and formaldehyde vapors on pretreated XAD-2 adsorbent which has been coated with 2-HMP. The goals of this work were attained in that both aldehydes can be simultaneously determined without the need to use bubblers and there are no sample stability problems.

In June of 1989, this method was updated with additional data which verified it would adequately accommodate the new PELs for formaldehyde which went into effect in 1988. The new PELs for formaldehyde are 1 ppm for the TWA and 2 ppm for the STEL. The acrolein PEL remains a TWA of 0.1 ppm. The report for the update work has been incorporated into the "Backup Data" section of this method as Section 4.11.

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

Acrolein: Human exposure to acrolein can occur through inhalation of the vapors or percutaneous absorption of the liquid. The results of exposure are intense irritation of the eyes, the respiratory tract mucous membranes and finally pulmonary edema or bronchitis. Skin and eye burns may result from prolonged and repeated exposure or splashes of acrolein. Sensitization has been reported to occur in some individuals. (Ref. 5.4)

Acrolein has induced mutagenic effects in various test systems. There is no evidence that acrolein has carcinogenic or co-carcinogenic activity. Acrolein has not been shown to have teratogenic or fetotoxic effects. (Refs. 5.4 and 5.5)

The International Agency for Research on Cancer (IARC) did not make an evaluation regarding the mutagenicity of acrolein because of the preliminary and conflicting nature of the available data. Also, the absence of human data precluded an evaluation of the carcinogenicity of acrolein by IARC. (Ref. 5.6)

Formaldehyde: Symptoms of human exposure to formaldehyde include irritation of the eyes, the nose and the throat which lead to lachrymation, sneezing, shortness of breath, sleeplessness, tight chest, nausea and excess phlegm. Formaldehyde has been shown to cause dermatitis. Formaldehyde is an allergen and susceptible persons can become sensitized to the agent. Formaldehyde has been reported to cause menstrual disorders and secondary sterility in women. Formaldehyde is mutagenic in a variety of test systems. IARC reports that there is sufficient evidence that formaldehyde gas is carcinogenic to rats. IARC also reports that epidemiological studies provide inadequate evidence to assess the carcinogenicity of formaldehyde to man. (Ref. 5.7)

Formaldehyde can react with hydrogen chloride to form bis-chloromethyl ether (BCME). IARC reports that exposure to BCME may constitute a serious human lung cancer hazard. (Ref. 5.8)

NIOSH recommends that formaldehyde be handled in the work-place as a potential occupational carcinogen. The basis of this recommendation are two inhalation studies that resulted in the same rare form of cancer in rats and in mice. Formaldehyde has also demonstrated mutagenic activity in several test systems. (Ref. 5.9)

The Federal Panel on Formaldehyde has concluded that formaldehyde should be presumed to pose a carcinogenic risk to humans. The panel consisted of scientists from within the federal government and was formed under the authority of the National Toxicology Program. (Ref. 5.10)

1.1.3 Potential workplace exposure

Acrolein: Acrolein is produced by the catalytic vapor phase oxidation of propylene with air. Acrolein production in the United States was estimated to be 61 million pounds in 1974. This figure does not include an additional 99 to 150 million pounds used as a captive intermediate in the production of acrylic acid. The main uses for acrolein are: fifty percent for the production of glycerin, 25% for the production of methionine (a poultry feed supplement) and 25% for other applications. Some of these applications are: manufacturing of chemicals and chemical products including glutaraldehyde and 1,2,6-hexanetriol, modification of food starch and use as an aquatic herbicide, biocide and slimicide. Acrolein has been used as a war gas and as a slimicide in the manufacture of paper and paperboard for use to package food products. (Ref. 5.6)

In 1979, acrolein production was estimated to be 85 to 90 million pounds. Approximately 7500 workers are occupationally exposed to acrolein annually. (Ref. 5.4)

Formaldehyde: Formaldehyde is produced by the catalytic vapor phase oxidation of methanol with air. Most formaldehyde is marketed in a aqueous solution, called formalin, which contains 37 to 50% formaldehyde by weight. The United States produced about 6.4 billion pounds of aqueous formaldehyde in 1978 and most of this amount was used domestically. The United States consumption of formaldehyde was estimated to exceed 7.5 billion pounds in 1983. About half of the formaldehyde produced in the U.S. is used to manufacture synthetic resins. These resins are often used to produce particle board, fiberboard and plywood. Urea-formaldehyde resins are used to coat materials, to produce paper products and to make foams for insulation. Other important uses include textile

treating and molding of plastic materials. Formaldehyde is used in some medicines and also in embalming fluids. It is used in fur and leather tanning and also in the photographic industry. (Ref. 5.9)

NIOSH estimated that 1.6 million workers were exposed to formaldehyde in a survey conducted from 1972 to 1974. About one-third of this total was employed in medical and health services occupations. Another one-third of the total was employed in miscellaneous occupations which included: chemicals and chemical products, printing and publishing, paper, machinery, retail stores, eating and drinking places, automotive dealers and service stations, funeral services and crematories, photographic studios and dry cleaning plants. (Ref. 5.9)

Other jobs and/or occupations in which exposure to formaldehyde may occur include: formaldehyde production workers, seamstresses, hairdressers, glue workers, foundry employees, resin manufacturing workers, wood laminating workers and fabric workers. (Ref. 5.7)

1.1.4 Physical properties

Acrolein (Ref. 5.6)

CAS no.:	107-02-8
molecular weight:	56.1
appearance:	colorless liquid
boiling point:	52.5 to 53.5°C
density:	0.841 at 20°C
vapor pressure:	200 mm Hg at 17.5°C
flash point:	-26.1°C
molecular formula:	CH_2=CHCHO
synonyms:	2-propenal; acraldehyde; acrylaldehyde; acrylic aldehyde; allylaldehyde; prop-2-en-1-al; 2-propen-1-one; Aqualin; NSC 8819; propenal

Acrolein polymerizes spontaneously, particularly in the presence of light, alkali or strong acid.

Formaldehyde (Ref. 5.7)

CAS no.:	50-00-0
molecular weight:	30.0
appearance:	colorless gas
boiling point:	-19°C
density:	0.8153 at -20°C; 1.067 (air = 1.000)
vapor pressure:	400 mm Hg at -33°C
ignition temp.:	430°C
molecular formula:	HCHO
synonyms: (including polymeric forms from which formaldehyde can be generated)	formaldehyde; formaldehyde gas; formaldehyde solution; formalin 40 formalin 100%; formic aldehyde; methaldehyde; methanal; methyl aldehyde; methylene glycol; methylene oxide; oxomethane; oxymethylene; paraform; paraformalde-hyde; polyoxymethylene glycols; α-polyoxymethylene; α-trioxane; β-trioxymethylene; tetraoxymethylene; α- polyoxymethylene; trioxane

Formaldehyde polymerizes rapidly, especially under alkaline conditions.

1.2 Limit defining parameters (The analyte air concentrations reported in this method are based on the recommended air volume for each analyte collected separately and a desorption volume of 1 mL. The amounts are presented as acrolein and/or formaldehyde, even though the derivatives are the actual species analyzed.)

1.2.1 Detection limits of the analytical procedure

The detection limit of the analytical procedure was 233 pg per injection for acrolein. This was the amount of acrolein which gave a measurable response relative to the interferences present in a standard. The detection limit of the analytical procedure was 386 pg per injection for formaldehyde. This was the amount of analyte which gave a peak whose height was about 5 times the height of the peak given by the residual formaldehyde derivative (Section 4.8) in a typical blank front section of the recommended sampling tube (Section 4.1).

1.2.2 Detection limits of the overall procedure

The detection limits of the overall procedure were 291 ng per sample (2.7 ppb or 6.1 µg/m^3) for acrolein and 482 ng per sample (16 ppb or 20 µg/m^3) for formaldehyde. These were the amounts of analyte spiked on the sampling device which allowed recoveries approximately equal to the detection limits of the analytical procedure (Section 4.2).

1.2.3 Reliable quantitation limits

The reliable quantitation limits were 291 ng per sample (2.7 ppb or 6.1 µg/m^3) for acrolein and 482 ng per sample (16 ppb or 20 µg/m^3) for formaldehyde. These were the smallest amounts of analyte which could be quantitated within the limits of a recovery of at least 75% and a precision ($\pm$1.96 SD) of $\pm$25% or better (Section 4.2).

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

1.2.4 Sensitivity

The sensitivities of the analytical procedure over concentration ranges representing 0.4 to 2 times the target concentration, based on the recommended air volumes, were 9443 area units per µg/mL for acrolein and 7589 area units per µg/mL for formaldehyde. These values were determined from the slope of the calibration curves (Section 4.3). The sensitivity may vary with the particular instrument used in the analysis.

1.2.5 Recovery

The recovery of acrolein from samples used in a 19-day storage test remained above 88% when the samples were stored at ambient temperature. The recovery of formaldehyde from samples used in an 18-day storage test remained above 92% when the samples were stored at ambient temperature. These values were determined from regression lines which were calculated from the storage data (Section 4.6). The recovery of the analyte from the collection device must be at least 75% following storage.

1.2.6 Precision (analytical method only)

The pooled coefficients of variation obtained from replicate determinations of analytical standards over the range of 0.4 to 2 times the target concentration were 0.034 for acrolein and 0.0052 for formaldehyde (Section 4.3).

1.2.7 Precision (overall procedure)

The precisions at the 95% confidence level for the ambient temperature storage tests were $\pm$13.8% for acrolein and $\pm$14.3% for formaldehyde (Section 4.6). These values each include an additional $\pm$5% for sampling error. The overall procedure must provide results at the target concentrations that are $\pm$25% at the 95% confidence level.

1.2.8 Reproducibility

Samples collected from controlled test atmospheres and a draft copy of this procedure were given to a chemist unassociated with this evaluation. The acrolein samples were analyzed following 7 days of storage at ambient temperature. The average recovery was 99.0% and the standard deviation was 10.5%. The formaldehyde samples were analyzed following 15 days of storage. The average recovery was 96.3% and the standard deviation was 1.7% (Section 4.7).

1.3 Advantages

1.3.1 The sampling and analytical procedures permit the simultaneous determination of acrolein and formaldehyde.

1.3.2 Samples are stable following storage at ambient temperature for at least 18 days.

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 sampling rate with the sampling tube in line.

2.1.2 Samples are collected with laboratory prepared sampling tubes. The sampling tube is constructed of silane-treated glass and is about 8-cm long. The i.d. is 4 mm and the o.d. is 6 mm. One end of the tube is tapered so that a glass wool end plug will hold the contents of the tube in place during sampling. The other end of the sampling tube is open to its full 4-mm i.d. to facilitate packing of the tube. Both ends of the tube are fire-polished for safety. The tube is packed with a 75-mg backup section, located nearest the tapered end and a 150-mg sampling section of pretreated XAD-2 adsorbent which has been coated with 2-HMP. The two sections of coated adsorbent are separated and retained with small plugs of silanized glass wool. Following packing, the sampling tubes are sealed with two 7/32-in. o.d. plastic end caps. Instructions for the pretreatment and the coating of XAD-2 adsorbent are presented in Section 4.8 of this method.

2.1.3 Sampling tubes, similar to those recommended in this method, are marketed by Supelco, Inc. These tubes were not available when this work was initiated, therefore, they were not evaluated.

2.2 Reagents

None required

2.3 Technique

2.3.1 Properly label the sampling tube before sampling and then remove the plastic end caps.

2.3.2 Attach the sampling tube to the pump using a section of flexible, plastic tubing such that the large, front section of the sampling tube is exposed directly to the atmosphere. Do not place any tubing ahead of the sampling tube. The sampling tube should be attached in the worker's breathing zone in a vertical manner such that it does not impede work performance.

2.3.3 After sampling for the appropriate time, remove the sampling from the pump and then seal the tube with plastic end caps. Wrap the tube lengthwise with an official OSHA seal (Form 21).

2.3.4 Include at least one blank for each sampling set. The blank should be handled in the same manner as the samples with the exception that air is not drawn through it.

2.3.5 List any potential interferences on the sample data sheet.

2.4 Breakthrough (Breakthrough was defined as the relative amount of analyte found on a backup sample in relation to the total amount of analyte collected on the sampling train.)

2.4.1 Acrolein: When a test atmosphere containing 3 times the PEL was sampled for 2 times the recommended air volume, the breakthrough was 1% (Section 4.4). No breakthrough of acrolein from the 150-mg to the 75-mg adsorbent bed was observed when the recommended sampling method was followed.

2.4.2 Formaldehyde: For formaldehyde collected from test atmospheres containing 2 times the PEL, the average 5% breakthrough air volume was 41 L. The sampling rate was 0.1 L/min and the average mass of formaldehyde collected was 250 µg (Section 4.4).

2.5 Desorption efficiency

No desorption efficiency corrections are necessary to compute air sample results because analytical standards are prepared using coated adsorbent. Desorption efficiencies were determined, however, to investigate the recoveries of the analyses from the sampling device. The average recoveries, over the range of 0.4 to 2 times the target concentration, based on the recommended air volumes, were 102% for acrolein and 96.2% for formaldehyde. The desorption efficiencies were essentially constant over the ranges studied (Section 4.5).

2.6 Recommended air volumes and sampling rate

2.6.1 The recommended air volume for acrolein is 48 L collected at 0.1 L/min.

2.6.2 The recommended air volumes for formaldehyde are 24 L collected at 0.1 L/min for the TWA and 3 L collected at 0.2 L/min for the STEL.

2.6.3 The recommended air volume to be used when both aldehydes are sampled together is 24 L collected at 0.1 L/min.

2.7 Interferences (sampling)

2.7.1 Any collected substance that is capable of reacting with, and depleting the derivatizing reagent is a potential interference. Chemicals which contain a carbonyl group, such as acetone, may be capable of reacting with 2-HMP.

2.7.2 There are no other known interferences to the sampling method.

2.8 Safety precautions (sampling)

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

2.8.2 Follow all safety practices that apply to the work area being sampled.

3. Analytical Procedure

3.1 Apparatus

3.1.1 A gas chromatograph (GC), equipped with a nitrogen selective detector. A Hewlett-Packard Model 5840A GC fitted with a nitrogen phosphorus flame ionization detector

(NPD) was used for this evaluation. Injections were performed using a Hewlett-Packard Model 7671A automatic sampler.

3.1.2 A GC column capable of resolving the analytes from potential interferences. A 6-ft x 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 for this evaluation. Injections were performed on-column.

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

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

3.2 Reagents

3.2.1 Toluene and dimethylformamide. Burdick and Jackson solvents were used in this evaluation.

3.2.2 Helium, hydrogen and air, GC grade.

3.2.3. Acrolein, of known high purity. Aldrich Chemical, Gold Label Grade acrolein was used in this study.

3.2.4. Formaldehyde, 37% by weight in water. Aldrich Chemical, A.C.S. Reagent Grade formaldehyde was used in this evaluation.

3.2.5. Amberlite XAD-2 adsorbent coated with 10%, by weight, 2-(hydroxymethyl) piperidine (2-HMP) (Section 4.8.).

3.2.6. Desorbing solution with internal standard. This solution was prepared by adding 20 µL of dimethylformamide to 100 mL of toluene.

3.3 Standard preparation

3.3.1 Acrolein: Prepare stock standards by diluting known amounts of the aldehyde with methanol. A standard containing 1 mg/mL acrolein was prepared by diluting 12 µL of the 99% reagent to 10 mL with methanol.

3.3.2 Formaldehyde: Prepare stock standards by diluting known volumes of 37% formaldehyde solution with methanol. A procedure to determine the formaldehyde content of these standards is presented in Section 4.9. A standard containing 7.7 mg/mL formaldehyde was prepared by diluting 1 mL of the 37% reagent to 50 mL with methanol.

3.3.3 It is recommended that analytical standards be prepared about 16 h before the air samples are to be analyzed in order to ensure the complete reaction of the analytes with 2-HMP. However, rate studies have shown the reaction to be greater than 95% complete after 4 h. Therefore, one or two standards can be analyzed after this reduced time if sample results are outside the concentration range of the prepared standards.

3.3.4 Place 150-mg portions of coated XAD-2 adsorbent, from the same lot number as used to collect the air samples, into each of several glass 2-mL vials. Seal each vial with a Teflon-lined cap.

3.3.5 Prepare fresh analytical standards each day by injecting appropriate amounts of the diluted analytes directly onto 150-mg portions of coated adsorbent. It is permissible to inject both acrolein and formaldehyde on the same adsorbent portion. Allow the standards to stand at room temperature. A standard, approximating the target levels, was prepared by

injecting 11 µL of the acrolein and 12 µL of the formaldehyde stock standards onto a single coated XAD-2 adsorbent portion.

3.3.6 Prepare a sufficient number of standards to generate the calibration curves. Analytical standard concentrations should bracket sample concentrations. Thus, if samples are not in the concentration range of the prepared standard additional standards must be prepared to determine detector response.

3.3.7 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 150-mg section of the sampling tube to a 2-mL vial. Place the 75-mg section in a separate vial. If the glass wool plugs contain a significant number of adsorbent beads, place them with the appropriate sampling tube section. Discard the glass wool plugs if they do not contain a significant number of adsorbent beads.

3.4.2 Add 1 mL of desorbing solution to each vial.

3.4.3 Seal the vials with Teflon-lined caps and then allow them to desorb for 1 h. Shake the vials by hand with vigorous force several times during the desorption time.

3.4.4 Save the used sampling tubes to be cleaned and recycled.

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:	0.8 µL
GC column:	6-ft x 1/4-in. o.d. (2-mm i.d.) glass GC column containing 10% UCON 50-HB-5100 with 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 Chromatogram Figure 4.11.

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

3.5.4 Use an internal standard method to prepare the calibration curve with several standard solutions of different concentrations. Prepare the calibration curve daily. Program the integrator to report results in µg/mL.

3.5.5 Bracket sample concentrations with standards.

3.6 Interferences (analytical)

3.6.1 Any compound with the same general retention time as the analytes and which also gives a detector response is a potential interference. Possible interferences should be reported to the laboratory with submitted samples by the industrial hygienist.

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

3.6.3 A useful means of structure designation is GC/MS. It is recommended this procedure be used to confirm samples whenever possible.

3.6.4 The coated adsorbent usually contains a small amount of residual formaldehyde derivative (Section 4.8).

3.7 Calculations

3.7.1 Results are obtained by use of calibration curves. Calibration curves are prepared by plotting detector response against concentration for each standard. The best line through the data points is determined by curve fitting.

3.7.2 The concentration, in µg/mL, for a particular sample is determined by comparing its detector response to the calibration curve. If either of the analytes is found on the backup section, it is added to the amount found on the front section. Blank corrections should be performed before adding the results together. See Section 4.11. for additional information and suggestions on blank determinations and corrections.

3.7.3 The acrolein and/or formaldehyde air concentration can be expressed using the following equation:

$$mg/m^3 = \frac{A\ B}{C}$$

where A is µg/mL from Section 3.7.2
B is desorption volume
C is liters of air sampled

No desorption efficiency corrections are required.

3.7.4 The following equation can be used to convert results in mg/m^3 to ppm.

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

where mg/m^3 is result from Section 3.7.3
24.46 is molar volume of an ideal gas at 760 mm Hg and 25°C
MW is molecular weight (acrolein = 56.1, formaldehyde = 30.0)

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 whenever possible.

3.8.3 Wear safety glasses and a lab coat in all laboratory areas.

4. Backup Data

(The analyte concentrations are presented as acrolein and/or formaldehyde even though the derivatives are the actual species analyzed.)

4.1 Detection limit data

The injection size recommended in the analytical procedure (0.8 µL) was used in the determination of the detection limits for the analytical procedure. The detection limit of the analytical procedure was 233 pg per injection for acrolein. This was the amount of acrolein which gave a measurable response relative to interferences present in a standard. The detection limit of the analytical procedure was 386 pg per injection for formaldehyde. This was the amount of formaldehyde which gave a peak whose height was about five times the height of the peak given by the residual formaldehyde derivative in a typical blank front section of the recommended sampling tube. These detection limits were determined by the analysis of a sample containing 291 ng/mL of acrolein and 482 ng/mL of formaldehyde. Figure 4.1. is a chromatogram of the detection limits of the analytical procedure. The analysis was performed using a Hewlett-Packard 5840A GC equipped with a NPD. The NPD offset was 75 mm at attenuation 8. The chart speed was set at 0.25 cm/min.

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

Six samples were used to determine the detection limit of the overall procedure and the reliable quantitation limit. Individual samples were prepared by injecting 291 ng of acrolein and 482 ng of formaldehyde onto a single 150-mg portion of coated XAD-2 adsorbent. Analytical standards were prepared by injecting equivalent amounts of the analytes into 1-mL aliquots of toluene containing 15 mg/mL 2-HMP. The samples and standards were stored about 16 h at room temperature before analysis. Since the recoveries were high and approximately equivalent to the detection limits of the analytical procedure, the detection limits of the overall procedure and the reliable quantitation limit were 291 ng per sample (2.7 ppb or 6.1 µg/m^3) for acrolein and 482 ng per sample (16 ppb or 20 µg/m^3) for formaldehyde.

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

	acrolein		formaldehyde	
sample no.	mass recovered (ng)	recovery (%)	mass recovered (ng)	recovery (%)
1	287	98.6	471	97.7
2	299	103	453	94.0
3	284	97.6	478	99.2
4	269	92.4	464	96.3
5	310	106	477	99.0
6	284	97.6	450	93.4
$\bar{X}$		99.2		96.6
SD		4.7		2.5
1.96SD		9.3		4.9

4.3 Sensitivity and precision (analytical method only)

The sensitivity and precision of the analytical procedure were evaluated by performing multiple injections of analytical standards. The standards were prepared by injecting appropriate amounts of the aldehydes onto coated XAD-2 adsorbent 16 h prior to desorption and analysis. The data are presented in Tables 4.3.1 and 4.3.2 and also in Figures 4.3.1 and 4.3.2. The ISTD data are the results of an internal standard calibration.

Table 4.3.1
Acrolein Sensitivity and Precision Data

× target concn µg/sample	0.4× 4.0		1× 10		2× 20	
	ISTD	area	ISTD	area	ISTD	area

	3.9	38600	10.8	98620	19.6	187400
	4.0	40840	10.2	98820	20.0	190700
	3.8	39260	10.1	98580	20.2	190300
	4.0	40290	10.5	104300	19.9	178800
	4.0	41360	9.2	102900	20.0	20950
	3.9	38650	10.1	108900	20.2	194100
$\overline{X}$	3.93		10.15		19.98	
SD	0.082		0.539		0.223	
CV	0.021		0.053		0.011	
$\overline{CV}$	0.034					

The sensitivity for formaldehyde was 9443 area counts per µg/mL.

Table 4.3.2
Formaldehyde Sensitivity and Precision Data

× target concn	0.4×		1×		2×	
µg/sample	38.8		97		194	
	ISTD	area	ISTD	area	ISTD	area
	38.7	284700	97.4	648800	194.6	1434000
	38.8	292900	97.3	653800	193.8	1458000
	39.0	301000	97.1	636100	192.4	1492000
	38.8	283300	97.0	682200	192.0	1480000
	38.7	289000	96.9	681800	195.5	1429000
	38.6	294200	96.9	672400	195.7	1454000
$\overline{X}$	38.8		97.1		194.0	
SD	0.137		0.210		1.56	
CV	0.0035		0.0022		0.0080	
$\overline{CV}$	0.0052					

The sensitivity for formaldehyde was 7589 area counts per µg/mL.

4.4 Breakthrough data

4.4.1 Acrolein: Acrolein test atmospheres were generated in the manner discussed in Section 4.10. No breakthrough from the 150-mg to the 75-mg adsorbent bed was observed when the recommended sampling procedure was followed. The most concentrated atmosphere studied contained 0.77 mg/m^3 (about 3 times the PEL) acrolein. The relative humidity of this atmosphere was 30% at 24°C. The atmosphere was sampled at 0.2 L/min for 416 min. The total air volume was 83.2 L (1.7 times the recommended volume). The amount of acrolein found on the backup section of the sampling tube was 1% of the total amount found on the tube.

Studies were performed in which the sampling tube was reversed in order to evaluate breakthrough with a reduced adsorbent bed. A short section of silane-treated glass tubing, containing a small plug of silanized glass wool, was connected to the adsorbent tube. Acrolein was injected onto the glass wool plug and then humid air was drawn through the sampling train. The acrolein was volatilized from the glass wool so that the sampling tube was challenged with a vapor. This technique is known as vapor spiking. The relative humidity of the air was 85% at 25°C. Air was drawn through the tube at 0.2 L/min for 7 h. The total air volume was 84 L.

Table 4.4.1
Acrolein Breakthrough with the
Sampling Tube Connected in the Reverse Direction

sample number	amt. on 75 mg section, µg	amt. on 150 mg section, µg	breakthrough %
1	46.4	4.4	8.7
2	48.0	6.4	11.8
3	47.0	4.8	9.3
4	41.6	6.0	12.6

The average breakthrough was 10.6%. The amount of acrolein collected on each sample was more than four times the target concentration based on the recommended air volume. The air volume sampled was 1.8 times the recommended volume. The high relative humidity of the sampled air did not appear to affect breakthrough. These data plus the fact that the recommended sampling tube contains a 150-mg front section show the device to have more than adequate capacity for acrolein.

4.4.2 Formaldehyde: Formaldehyde test atmospheres were generated in the manner discussed in Section 4.10. Two breakthrough studies were performed using test atmospheres. One study was conducted using only 150-mg coated adsorbent sections. Two sections were connected in series. The second section was removed periodically and replaced with a fresh section. The test atmosphere contained 5.3 mg/m^3 formaldehyde, the relative humidity of the air was 49% at 24°C and the sampling rate was 0.1 L/min. Breakthrough was calculated using the amount of formaldehyde found on the second section and the theoretical amount of formaldehyde collected on the first tube. The theoretical amount of formaldehyde was determined from the concentration of the test atmosphere and the air volume sampled.

Table 4.4.2.1
First Formaldehyde Breakthrough Study

elapsed time, min	cumulative breakthrough, %
120	0.0
240	1.2
360	4.0
420	5.8

Five-percent breakthrough occurred at 396 min (6.6 h), after 41.8 L of air had been sampled and 284 µg of formaldehyde had been collected.

The second breakthrough study was conducted using four sampling tubes. The atmosphere was sampled for an appropriate time and then a tube was removed for analysis. Sampling was continued using the remaining tubes which were each removed at various intervals. The test atmosphere contained 6.8 mg/m^3 formaldehyde, the relative humidity of the air was 38% at 24°C and the sampling rate was 0.1 L/min. Breakthrough was calculated using the amount of formaldehyde found on the 75-mg section and the total amount of formaldehyde collected on both sections.

Table 4.4.2.2
Second Formaldehyde Breakthrough Study

sample number	sampling time, min	breakthrough, %
1	247	0.9
2	311	1.5
3	360	3.1
4	427	5.6

Five-percent breakthrough occurred at 407 min (6.8 h), after 40.7 L of air had been sampled and 214 µg of formaldehyde had been collected.

A vapor spiking breakthrough study using formaldehyde and the recommended sampling device was performed. The relative humidity of the sampled air was 75% at 26°C. The sampling rate was 0.1 L/min. Two samples were taken in this manner.

Table 4.4.2.3
Vapor Spiked Formaldehyde Breakthrough Study

sample number	sample time, min	amt. on 150 mg section, µg	amt. on 75 mg section, µg	breakthrough, %
1	240	244.1	4.8	1.9
2	360	262.5	8.8	3.2

This study shows that breakthrough is not a function of the relative humidity of the sampled air. The data in Tables 4.4.2.1 - 4.4.2.3 indicate that the coated adsorbent tube has adequate capacity for formaldehyde when the recommended sampling method is followed.

4.5 Desorption Efficiency

The desorption efficiency of acrolein and formaldehyde was determined by injecting the analytes onto separate 150-mg portions of coated XAD-2 adsorbent. Analytical standards were prepared by injecting equivalent amounts of the analytes into 1-mL aliquots of toluene containing 15 mg/mL 2-HMP. The samples and toluene solutions were spiked with the analytes and then stored at room temperature overnight before analysis.

Table 4.5.1
Desorption Efficiency
of Acrolein from XAD-2 Coated with 10% 2-HMP

× target concn µg/sample	0.4× 4	0.7× 8	0.9× 10	1.1× 12	1.4× 16	1.8× 20
desorption	92.2	96.2	99.6	109	97.4	93.1
efficiency, %	84.9	115	96.0	95.9	97.2	107
	104	114	104	93.4	97.2	92.7
	100	112	109	104	96.9	103
	109	106	110	100	111	108
	103	101	105	105	116	96.8
$\bar{X}$	98.8	107	104	101	103	100

The average desorption efficiency for acrolein was 102% and the standard deviation was 7.3%.

Table 4.5.2
Desorption Efficiency
of Formaldehyde from XAD-2 Coated with 10% 2-HMP

× target concn µg/sample	0.4× 36.4	0.8× 72.8	1.0× 91.0	1.2× 109.2	1.6× 145.6	2.0× 182
desorption	96.2	94.6	96.7	93.8	99.3	106
efficiency, %	93.0	99.3	97.0	101	97.1	97.5
	90.5	94.8	92.7	97.7	98.0	96.5
	99.2	96.4	86.3	99.2	92.1	93.4
	97.8	98.8	91.0	91.0	97.5	95.9
	103	98.7	93.8	93.8	99.7	94.5
$\bar{X}$	96.6	97.1	92.9	96.1	97.3	97.3

The average desorption efficiency for formaldehyde was 96.2% and the standard deviation was 3.8%.

4.6 Storage data

Test atmospheres were generated in the manner discussed in Section 4.10. The acrolein samples were collected from an atmosphere containing 0.35 mg/m^3 acrolein. The relative humidity of the air was 49% at 27°C. The sampling rate was 0.2 L/min and the sampling time was 150 min. The amount of acrolein thus collected was equivalent to sampling a 0.22 mg/m^3 atmosphere for 8 h at 0.1 L/min. The formaldehyde samples were collected from an atmosphere containing 4.4 mg/m^3 formaldehyde. The relative humidity of the air was 45% at 24°C. The sampling rate was 0.1 L/min and the sampling time was 215 min. The amount of formaldehyde thus collected was equivalent

to sampling a 3.9 mg/m^3 atmosphere for 4 h at 0.1 L/min. The data in Tables 4.6.1 and 4.6.2 represent the effects of storage at ambient (21 to 26°C) and reduced (-20°C) temperatures on these samples. These data are presented graphically in Figures 4.6.1 and 4.6.2.

Table 4.6.1
Acrolein Storage Test

storage time, days	ambient recovery, %			storage time, days	refrigerated recovery, %		
0	85.7	95.7	99.0	0	90.8	87.7	97.2
0	89.8	92.9	90.9	0	87.3	87.4	91.5
3	92.3	82.7	90.4	0	90.8	92.9	101
6	94.2	91.6	92.9	3	98.7	104	92.0
10	85.0	86.8	77.6	6	98.0	79.2	93.1
12	86.8	85.9	88.9	9	79.6	91.1	101
16	82.7	86.1	93.8	12	94.7	99.6	98.3
19	93.2	94.7	92.2	15	97.4	95.2	96.2

Table 4.6.2
Formaldehyde Storage Test

storage time, days	ambient recovery, %			storage time, days	refrigerated recovery, %		
0	88.2	98.7	93.4	0	76.2	105	92.0
0	100	95.8	92.0	0	91.2	90.4	91.6
4	89.4	92.6	94.3	3	84.0	87.7	91.3
7	91.0	90.7	90.7	7	95.1	92.2	91.3
10	94.7	97.3	93.7	9	95.7	91.2	93.7
12	90.1	85.3	90.5	14	93.5	93.0	94.2
15	91.8	89.2	78.4	18	94.5	96.1	94.3
18	103	98.3	98.3				

4.7 Reproducibility data

Separate acrolein and formaldehyde samples were collected from test atmospheres which were generated in the manner discussed in Section 4.10. The samples and draft copies of this evaluation were given to chemists unassociated with this work. The acrolein samples were analyzed after 7 days of storage at ambient temperature. The formaldehyde samples were analyzed following 15 days of storage.

Table 4.7
Reproducibility

analyte	acrolein	formaldehyde
µg/sample	10.6	94.6
recovered, %	87.7	97.7
	97.2	96.8
	111	97.3
	97.2	95.2
	112	93.3
	88.7	97.4
$\bar{X}$	99.0	96.3
SD	10.5	1.7

4.8. A procedure to coat XAD-2 adsorbent with 2-HMP

4.8.1 Apparatus

Soxhlet extraction apparatus.

Rotary evaporation apparatus.

Vacuum desiccator.

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

4.8.2 Reagents

Methanol, isooctane and toluene. Burdick and Jackson solvents were used in this evaluation.

2-(Hydroxymethyl) piperidine. The Aldrich Chemical, Technical Grade was recrystallized from isooctane for use in this evaluation.

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

4.8.3 Procedure

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 add about 200 mL of methanol to the flask. Swirl and 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 add 13 g of 2-HMP and 200 mL of toluene to the flask. Swirl the mixture and 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 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 0.1 to 0.5 µg/150 mg of adsorbent. If the formaldehyde blank or any other interference is determined to be too high, then 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 the desired blank and 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 a sealed container to prevent contamination. Sampling tubes should be stored in the dark at room temperature. The sampling tubes should be segregated by coated adsorbent lot number. A sufficient amount of each lot number of coated adsorbent should be retained to prepare analytical standards for use with air samples from that lot number.

4.9 A procedure to determine formaldehyde by acid titration

4.9.1 Apparatus

Miscellaneous glassware. Fifty-milliliter burette, 250-mL Erlenmeyer flasks, 1-L volumetric flasks, pipets, etc.

4.9.2 Reagents

Sodium sulfite, anhydrous. Prepare a 0.1 M solution by dissolving 12.6 g of the salt in 1 L of deionized water.

Hydrochloric acid, reagent grade. Prepare a 0.1 N solution by diluting 7.9 mL of 38% HCl to 1 L with deionized water.

Thymolphthalein indicator. Prepare a 0.1% solution in ethanol.

Methyl orange indicator. Prepare a 0.1% solution in ethanol.

Sodium carbonate, ACS primary standard grade.

4.9.3 Procedure

Standardize the 0.1 N HCl solution using sodium carbonate and methyl orange indicator. A complete procedure for the standardization is presented in Ref. 5.11.

This procedure to determine formaldehyde was adapted from the method presented in Ref. 5.12.

Place 50 mL of 0.1 M sodium sulfite and three drops of thymophthalein indicator into a 250-mL Erlenmeyer flask. Titrate the contents of the flask to a colorless endpoint with 0.1 N HCl (usually one or two drops is sufficient). Transfer 10 mL of the formaldehyde/methanol solution (prepared in Section 3.3.2) into the same flask and titrate the mixture with 0.1 N HCl, again, to a colorless endpoint. The formaldehyde concentration of the standard can be calculated by the following equation:

$$\text{Formaldehyde, mg/mL} = \frac{\text{acid titer} \times \text{acid normality} \times 30.0}{\text{mL of sample}}$$

This method is based on the quantitative liberation of sodium hydroxide when formaldehyde reacts with sodium sulfite to form the formaldehyde-bisulfite addition product. The volume of sample may be varied depending on the formaldehyde content but the solution to be titrated must contain excess sodium sulfite. Formaldehyde solutions containing substantial amounts of acid or base must be neutralized before analysis.

4.10 Generation of test atmospheres

Controlled test atmospheres of acrolein and formaldehyde were separately generated using a Metronics Model 450 Dynacalibrator permeation apparatus. The Metronics apparatus consists of a permeation device, usually a sealed Teflon tube, containing the test material which is maintained at constant temperature in a heated chamber. The permeation device provides a constant flow of the test material into a carrier gas stream. The carrier gas used in this evaluation was clean, dry nitrogen at a fixed flow rate of 0.4 L/min. Certified permeation tubes were purchased from Metronics. The effluent of the permeation chamber was diluted with humid air which was introduced into the chamber stream using a calibrated rotometer. The humid air was generated by bubbling clean, dry air through a temperature controlled water bath. The relative humidity of the combined chamber effluent and dilution air was determined, after mixing, using a YSI Model 91 Dew Point Hygrometer. The relative humidity of the test atmospheres was usually less than 80% because the permeation chamber purge flow rate of dry gas was high in relation to the flow rate of humid dilution air. Sampling was performed at a glass manifold equipped with 6 ports.

The theoretical concentrations of the acrolein test atmospheres were determined from the permeation rate of the acrolein source tube and the sum of the purge flow rate and the dilution air flow rate. The permeation rate of the tube was established by maintaining the device in the constant temperature permeation chamber with a purge flow of dry nitrogen and weighing the device periodically until a constant weight loss per unit time was achieved. The permeation rate of the acrolein tube was 444 ng/min at 30°C. The average assay of "day zero" samples, used in storage tests for this evaluation (Section 4.6), was 92.0% of the theoretical amount based on the gravimetric permeation rate.

The theoretical concentrations of the formaldehyde test atmospheres were also determined from the permeation rate of the formaldehyde source tube and the sum of the purge flow rate and the dilution flow rate. The permeation rate of the tube could not be determined gravimetrically because the tube contained paraformaldehyde, from which formaldehyde was generated by heating the tube. The permeation rate of the tube was established by the use of two independent sampling and analytical methods. One of the methods was the aforementioned NIOSH adsorbent tube procedure for formaldehyde (Ref. 5.2). The other method utilized bubblers containing 2,4-dinitrophenylhydrazine (DNPH) for sampling and then analysis by HPLC (Ref. 5.13). The permeation rate of the formaldehyde tube was 4711 ng/min at 100°C. The average assay of "day zero" samples, used in the storage tests for this evaluation, was 92.9% of the theoretical amount based on the permeation rate as determined by the NIOSH and DNPH methods.

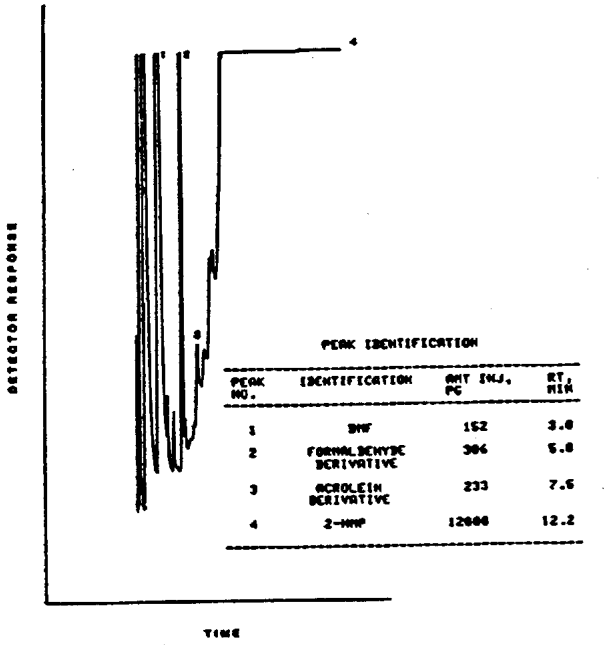

Figure 4.1. The detection limits of the analytical procedure for formaldehyde and acrolein.

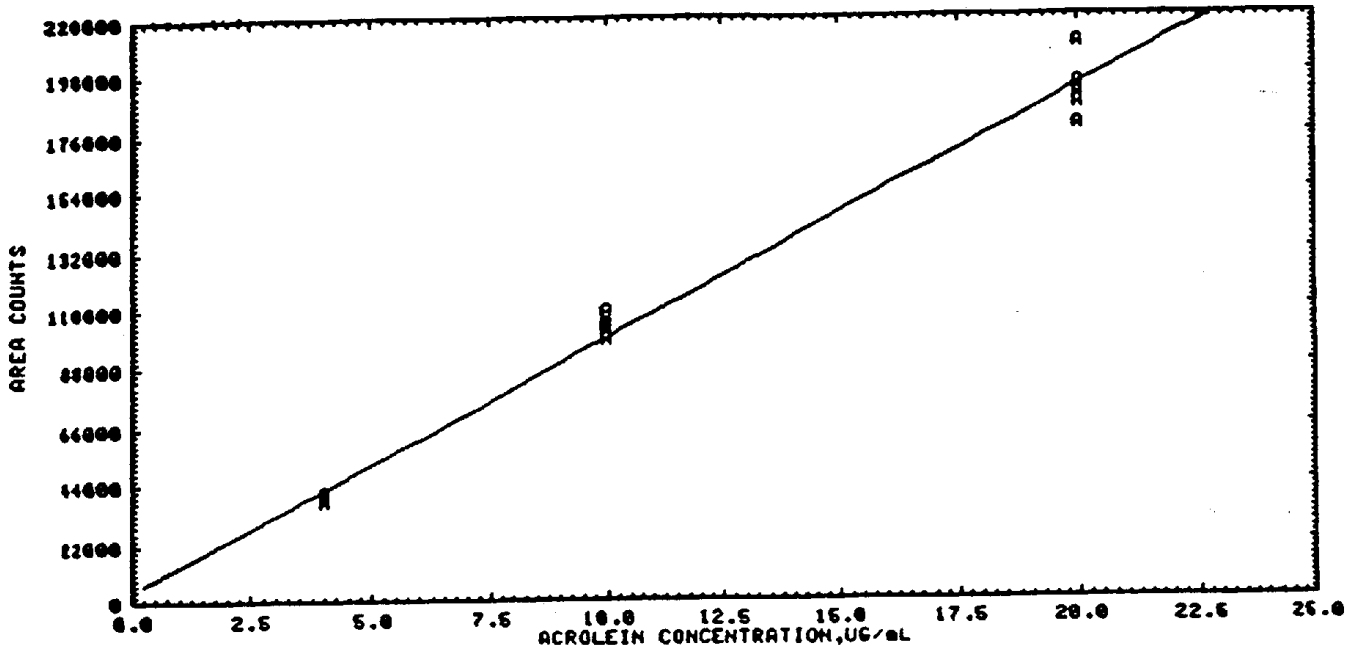

Figure 4.3.1. Calibration curve for acrolein.

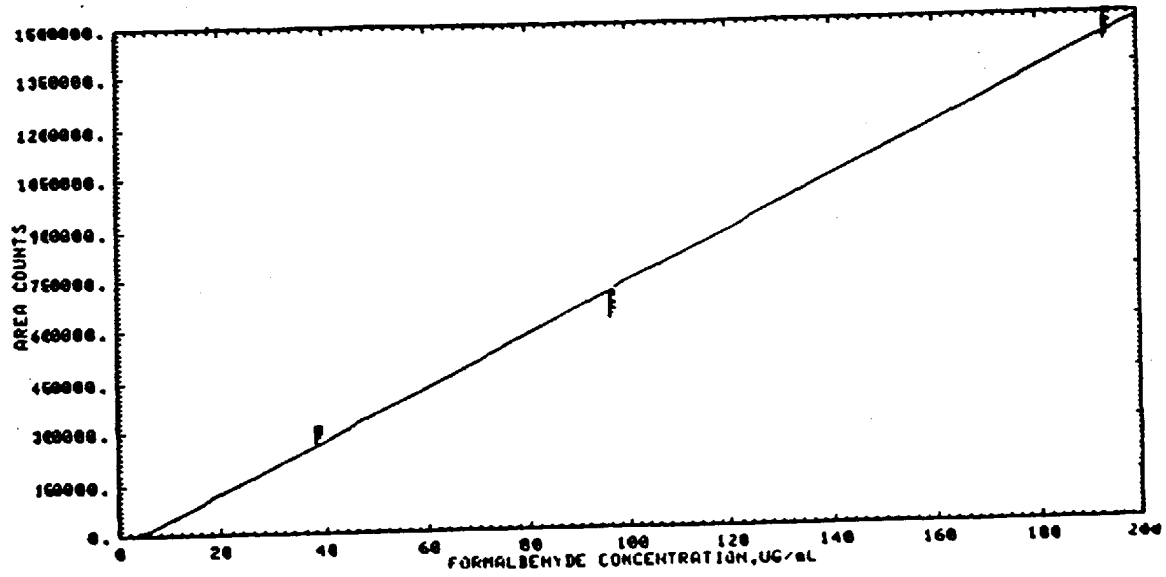

Figure 4.3.2. Calibration curve for formaldehyde.

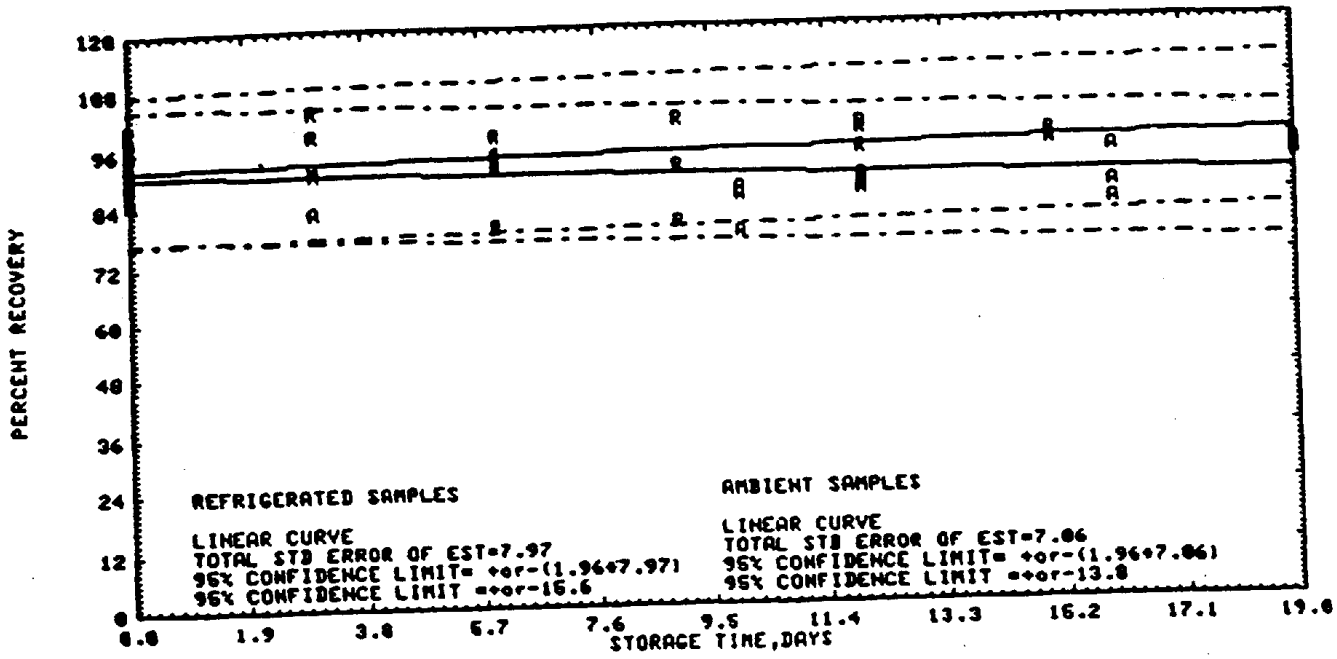

Figure 4.6.1. Storage tests for acrolein.

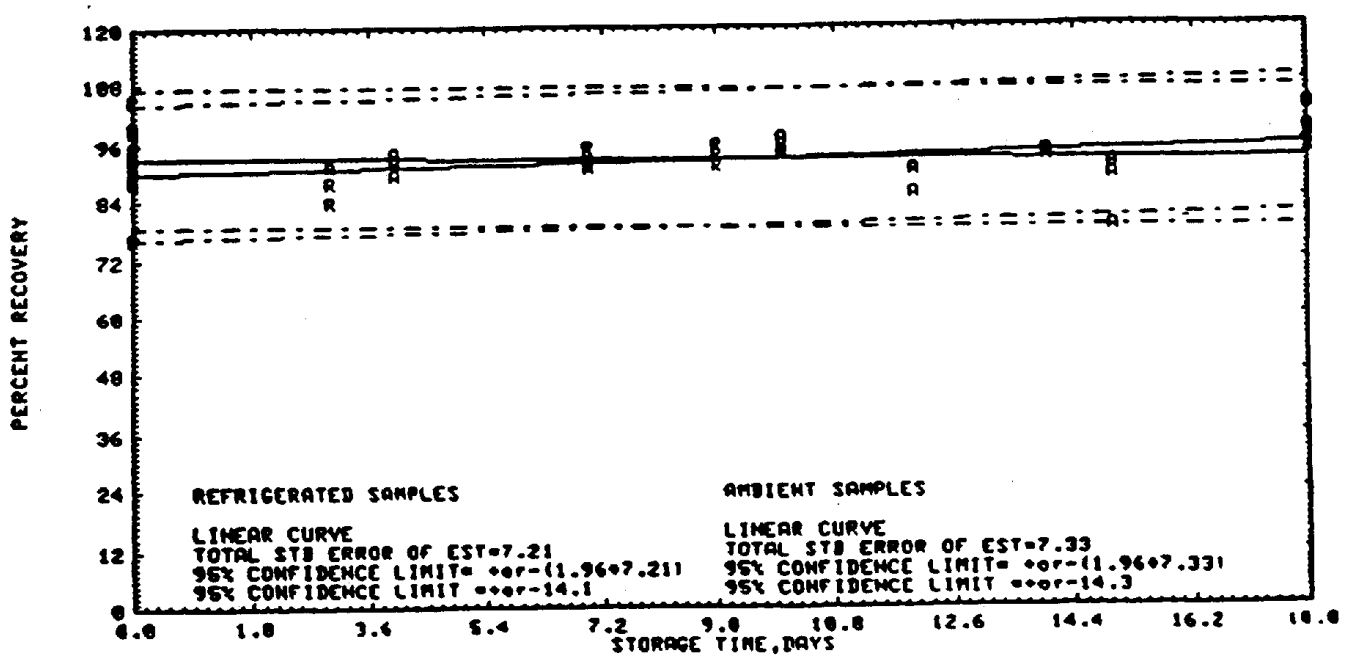

Figure 4.6.2. Storage tests for formaldehyde.

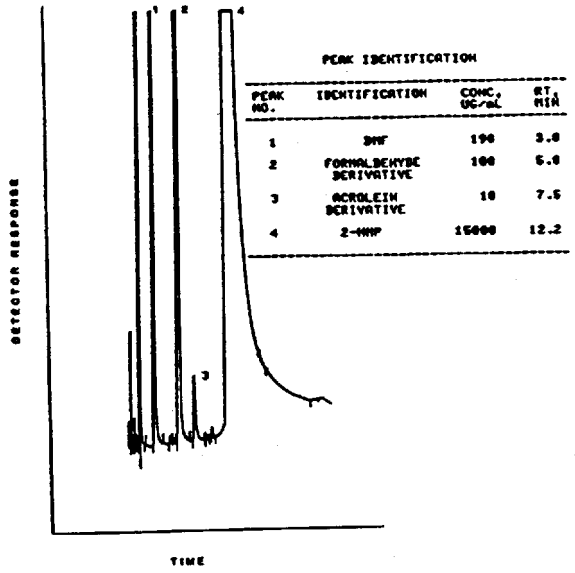

Figure 4.11. Typical chromatogram of a standard containing DMF and the 2-HMP derivatives of acrolein and formaldehyde.

4.11 Additional evaluation data

This work was performed to verify that OSHA Method 52 (Ref. 5.14) is suitable to monitor compliance with the new, reduced OSHA PELs for formaldehyde. The previous PELs included an 8-h TWA of 3 ppm, a ceiling of 5 ppm and a 30 min peak of 10 ppm (Ref. 5.15). The new PELs consist of an 8-h TWA of 1 ppm, a 15-min STEL of 2 ppm and an "action level" of 0.5 ppm (Ref. 5.16). The action level is to be measured as an 8-h TWA. The action level is intended to minimize the compliance burden for employers with workplaces in which exposure to formaldehyde is low.

The areas of interest regarding OSHA Method 52 which are addressed in this report include: (1) The feasibility of increasing the sampling rate to monitor compliance with the new OSHA STEL, (2) the determination of the residual (blank) amount of formaldehyde derivative present in formaldehyde sampling tubes, (3) the desorption efficiency of formaldehyde from samples prepared at 0.5, 1 and 2 times the new OSHA TWA, (4) the sensitivity and precision of the analytical procedure at the new OSHA standard and (5) the ambient temperature storage stability of samples collected at the new OSHA TWA. An additional area of interest is also addressed; Supelco has recently marketed a commercial version of the OSHA formaldehyde air sampling tube. The Supelco sampling tubes were tested to determine if they are suitable for use by OSHA.

EXPERIMENTAL SECTION

Reagents. Formaldehyde sampling tubes, containing XAD-2 adsorbent which has been coated with 2-(hydroxymethyl) piperidine (2-HMP), were obtained from Supelco and also from the OSHA Analytical Laboratory. 2-HMP was purchased from Aldrich Chemical Company and was recrystallized from isooctane prior to use. Toluene, methanol and dimethylformamide were obtained from American Burdick and Jackson. Permeation tubes, 15-cm Teflon, containing paraformaldehyde, were purchased from VICI Metronics. Formaldehyde, 37% by weight in water, ACS Reagent Grade, was purchased from Aldrich Chemical Company. The exact concentration of the Aldrich formaldehyde solution was determined by titration as specified in OSHA Method 52.

Instrumentation. The determinations were performed using a Hewlett-Packard 5840A GC equipped with a nitrogen phosphorus detector (NPD). The NPD was set to give a 75-mm offset at attenuation 8. Injections were made with a Hewlett-Packard Model 7671A automatic sampler. A 6-ft x 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 purchased from Supelco to perform the separations. Injections were made on-column. The GC column was temperature programmed in two stages. First stage: 100°C to 140°C at 4°C/min. Second stage: 140°C to 180°C at 20°C/min. The column was then maintained at 180°C for the balance of the determination. The total GC analysis time was about 30 min. The GC injector temperature was 180°C and the detector temperature was 275°C. The GC carrier gas was helium and the flow rate was 30 mL/min.

Apparatus. Controlled test atmospheres of formaldehyde were generated using a Metronics Model 450 Dynacalibrator permeation apparatus. The apparatus contained a Teflon permeation tube which was maintained at 100°C. The permeation device provided a constant flow of formaldehyde into a carrier gas stream. The carrier gas used in this work was clean, dry nitrogen at a fixed flow rate of 0.4 L/min. The effluent of the permeation chamber was diluted with humid air which was introduced into the chamber stream using a calibrated rotameter. The humid air was generated by bubbling clean, dry air through a temperature-controlled water bath. The relative humidity of the combined chamber effluent and dilution air was determined, after mixing, using a YSI Model 91 Dew Point Hygrometer. Sampling was performed using calibrated, adjustable sampling tube flow holders (SKC, Inc.) at a glass manifold equipped with six sampling ports.

Procedure. Air samples were generated by sampling controlled test atmospheres with either OSHA or Supelco sampling tubes. Formaldehyde stock standards were prepared by diluting aqueous formaldehyde with methanol. Analytical standards and test samples were prepared by spiking 150-mg portions of OSHA lot 12 coated adsorbent with appropriate amounts of formaldehyde stock standards. Additional analytical standards which did not utilize coated adsorbent (solution standards) were prepared by spiking 1-mL aliquots of toluene, which contained 15 mg/mL recrystallized 2-HMP, with appropriate amounts of formaldehyde stock standards. Analytical standards and test samples were prepared about 16 h prior to analysis to ensure the complete reaction of formaldehyde with 2-HMP. Coated adsorbent standards and samples were desorbed with 1-mL toluene for 1 h before analysis. Dimethylformamide internal standard was added to the toluene which was used for the desorption of samples, desorption of coated-adsorbent standards and also for the dilution of recrystallized 2-HMP. Air samples were analyzed using coated-adsorbent standards. Test samples and blanks were analyzed with solution standards. The results are reported as formaldehyde even though the actual analyzed species was the 2-HMP derivative of formaldehyde.

RESULTS AND DISCUSSION

Increasing the sampling rate. The 2-ppm formaldehyde OSHA STEL requires a 15-min sample. OSHA's sampling method specifies a 0.1 L/min sampling rate. A 15-min sample collected at 0.1 L/min from a 2-ppm atmosphere would contain only 4 µg of formaldehyde. An increase in the sampling rate would cause more formaldehyde to be collected and this would result in a potentially more accurate and precise determination.

Sampling tube capacity must be considered when determining a sampling rate. Sampling tube capacity was evaluated by determining breakthrough from the front to the back sections of sampling tubes which were used to sample a test atmosphere for increasing periods of time. Excessive breakthrough could indicate that either the 2-HMP had been depleted or that the formaldehyde residence time was not long enough for the derivatization reaction to be complete. A limited number of samples were collected from a 2-ppm formaldehyde test atmosphere at 0.5 L/min. This sampling rate was found to be unacceptable because of the high breakthrough observed after sampling for only 15 min. Because excess 2-HMP was present in these samples, sampling at 0.5 L/min failed apparently because of inadequate formaldehyde residence time in the sampling tube. Sampling tube capacity was therefore evaluated at 0.2 L/min using OSHA and Supelco tubes by sampling a

test atmosphere. The formaldehyde concentration was 2 ppm and the relative humidity was 64% at 25°C. The results of this study are presented in Table 1.

Table 1
Sampling Tube Capacity

OSHA lot 12		Supelco lot 673-30		Supelco lot 673-40	
air vol (L)	BT (%)	air vol (L)	BT (%)	air vol (L)	BT (%)
24.0	1.9	24.6	1.0	24.9	5.9
27.6	2.1	27.6	1.0	29.4	7.2
37.2	5.4	35.5	1.2	37.1	10.0
41.6	7.3			41.9	12.3
46.8	9.2	46.2	2.6		
50.9	10.8			51.6	15.2
55.8	11.7			56.2	16.9
66.1	12.2	65.6	9.1		

BT = breakthrough

The air volumes at which 5% breakthrough occurred were determined graphically by plotting the data in Table 1. The breakthrough plots are shown in Figures 1, 2 and 3. The 5% breakthrough air volumes were: OSHA lot 12 = 35 L, Supelco lot 673-30 = 50 L and Supelco lot 673-40 = 23 L. The data show that the sampling rate can be increased to 0.2 L/min to monitor compliance with the 15-min OSHA STEL. These data also show that there are capacity variations between lots of formaldehyde sampling tubes. The sampling rate should not be increased from 0.1 L/min to monitor compliance with the TWA.

Blank determinations. The sampling and analytical procedure for formaldehyde is unique in that a significant blank-amount subtraction must be performed. All XAD-2 adsorbent coated with 2-HMP will contain some amount of residual formaldehyde derivative which must be determined so that the blank subtractions can be made. Blank subtract ions should be performed both on standards and on samples. The blank correction is especially important at low formaldehyde levels or when the blank amount is high.

The amount of residual derivative present in the front sections of ten OSHA lot 12 formaldehyde sampling tubes was determined. The ten sampling tubes were selected at random. The results of this study are presented in Table 2.

Table 2
Formaldehyde Blank Determinations

sample no.	amount (µg)	sample no.	amount (µg)
1	0.74	6	0.70
2	0.66	7	0.76
3	0.59	8	0.62
4	0.74	9	0.56
5	0.74	10	0.71

$\overline{X}$ = 0.68, SD = 0.07, CV = 0.10

The blank amounts determined for field-blank samples may be different from those shown in Table 2. This may be due to differences in sampling-tube lots, minor differences in instrument calibration, field-blank sample contamination and other indeterminate causes. The field-blank amount should be used to perform blank subtractions from the associated field samples.

Because of the imprecision of the blank-amount determination, errors can inadvertently be introduced into the analysis of field samples. It is, therefore, essential to take precautions to assure that the presence of formaldehyde is not reported when it is absent. One such precaution to minimize the possibility of this error occurring would be to utilize an arbitrary parameter called the "minimum reportable amount" (MRA). The MRA is based on the assumption that the precision of

all blank-amount determinations is similar to that in Table 2. No field-sample result (after blank subtraction) less than the MRA should be used in subsequent calculations. Field samples containing less formaldehyde than the MRA should be reported simply as "less than MRA". The MRA should not be confused with the reliable quantitation limit. A field-sample result lower than the reliable quantitation limit can be reported with confidence because it is the difference of two sample results which were each larger than the reliable quantitation limit. The MRA is calculated as follows:

$$MRA = 1.96 \times 0.10 \times B$$

where 1.96 is z-statistic from the normal distribution at the 95% confidence level
0.10 is coefficient of variation from Table 2
B is field-blank amount determined from the blank sample submitted with the set of field samples

Because the MRA is a precaution against reporting false positive field-sample results, it has significance only when the field-sample result is similar to the field-blank amount.

Desorption efficiency. No desorption efficiency corrections are necessary to compute sample results because analytical standards are prepared using coated adsorbent. Desorption efficiencies were determined, however, to investigate formaldehyde recovery from the sampling medium. The results of this study are presented in Table 3. The average desorption efficiency over the studied range was 101.4% and the SD was 2.6%.

Table 3
Percent Desorption Efficiency

15.4 µg 0.5×	24.1 µg 0.8×	30.9 µg 1.0×	34.4 µg 1.2×	55.0 µg 1.9×	61.8 µg 2.1×
98.3	99.8	98.2	101.6	102.8	98.5
98.1	101.2	99.6	106.4	102.2	101.8
101.1	101.4	96.9	105.0	105.2	98.7
99.0	104.7	99.9	99.0	103.6	99.5
102.1	104.8	99.0	103.5	106.0	103.5
102.1	103.9	98.8	101.4	102.6	98.4
$\overline{X}$ = 100.1	102.6	98.7	102.8	103.7	100.0

Sensitivity and precision. The sensitivity and precision of the analytical method was evaluated by performing multiple determinations of coated-adsorbent standards which were prepared at 0.5, 1 and 2 ppm. The results of the sensitivity and precision study are presented in Table 4. ISTD data are results from an internal standard calibration.

Table 4
Sensitivity and Precision Data

0.52 ppm 15.4 µg/sample		1.0 ppm 30.9 µg/sample		2.1 ppm 61.8 µg/sample	
ISTD	area	ISTD	area	ISTD	area
15.4	3144000	31.2	6365000	62.2	12690000
15.3	3132000	31.2	6372000	61.9	12631000
15.4	3154000	31.2	6374000	61.8	12614000
15.4	3152000	30.4	6216000	61.9	12645000
15.5	3170000	30.8	6294000	61.5	12559000
15.6	3183000	30.5	6235000	61.5	12563000
$\overline{X}$= 15.43		30.88		61.80	
SD = 0.1033		0.3708		0.2681	
CV = 0.00670		0.01201		0.00433	

The pooled coefficient of variation at the new OSHA standard is 0.0083. It is similar to that obtained at the previous standard which was 0.0052. The sensitivity of the analytical method is defined as the slope of the calibration curve. The calibration curve was prepared by plotting the data in Table 4 and it is shown in Figure 4. The sensitivity of the analytical method is 203936 area units per µg/mL.

Ambient temperature storage stability. Storage samples were generated by sampling a test atmosphere containing 2-ppm formaldehyde at 0.1 L/min for 2 h. The relative humidity of the test atmosphere was 58% at 28°C. The results of the ambient temperature storage study are presented in Table 5 and in Figures 5 and 6.

Table 5
Ambient Temperature Storage Test

storage time (days)	OSHA lot 12 (% recovered)			storage time (days)	Supelco lot 673-30 (% recovered)		
0	100.4	96.8	99.6	0	104.4	106.0	105.2
4	104.8	97.6	101.2	3	102.8	99.2	97.6
7	95.4	100.9	100.0	6	95.1	99.2	97.4
11	98.8	101.2	100.0	10	102.0	98.8	98.4
14	103.2	102.4	100.4	13	102.0	96.8	97.2
19	97.6	98.8	104.4	18	97.6	97.6	99.6

These data show that samples containing the equivalent of 1 ppm formaldehyde are stable for at least 19 days of storage at ambient temperature.

CONCLUSIONS

The present sampling and analytical method used by OSHA to monitor occupational exposure to formaldehyde is suitable for use at the new OSHA TWA and action level. The recommended sampling rate for STEL samples is 0.2 L/min. The sampling tubes which were purchased from Supelco gave acceptable sample results.

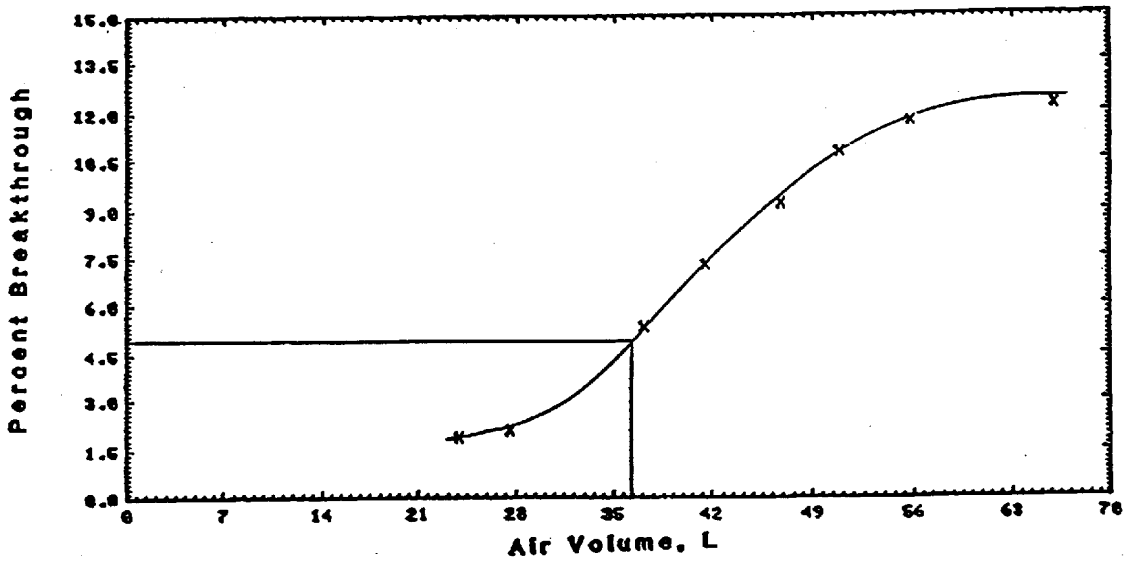

Figure 1. OSHA sampling tubes (lot 12) capacity test.

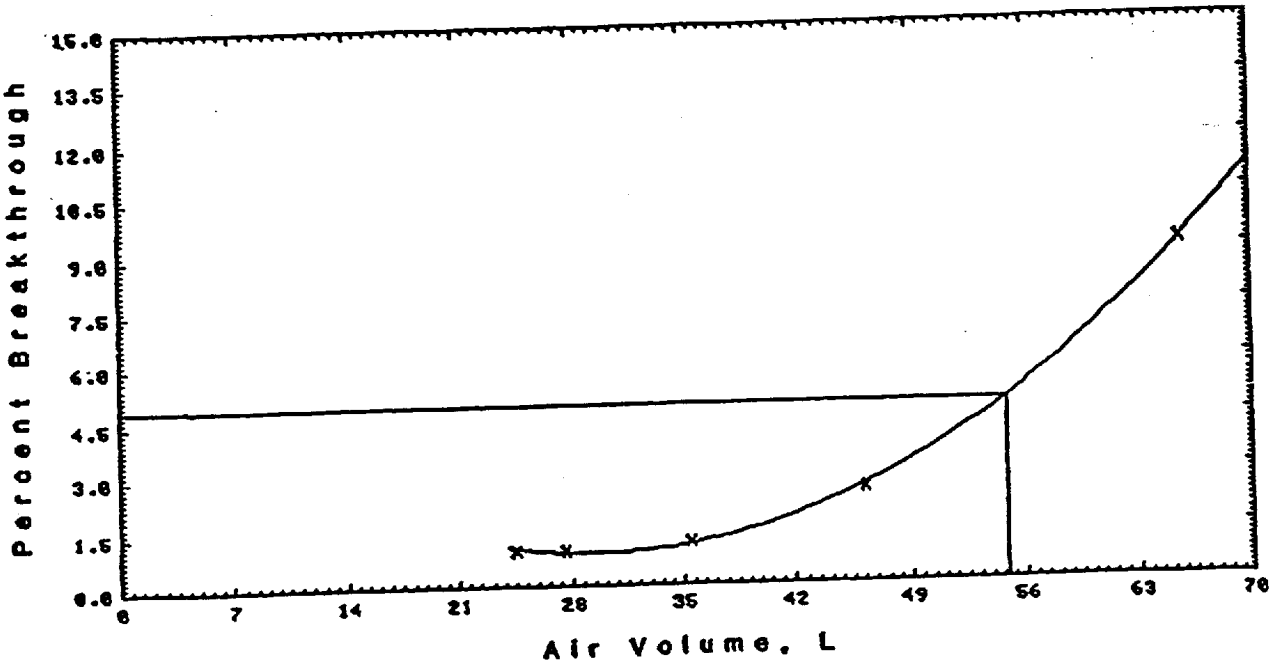

Figure 2. Supelco sampling tubes (lot 673-30) capacity test.

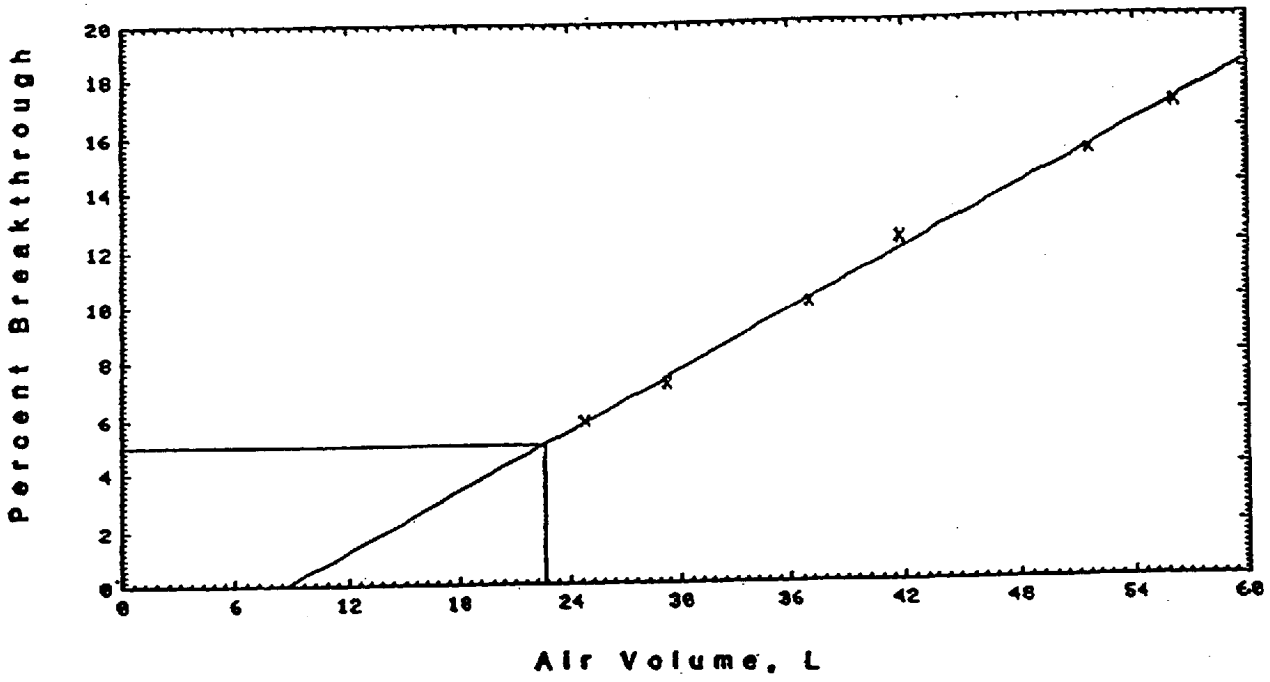

Figure 3. Supelco sampling tubes (lot 673-40) capacity test.

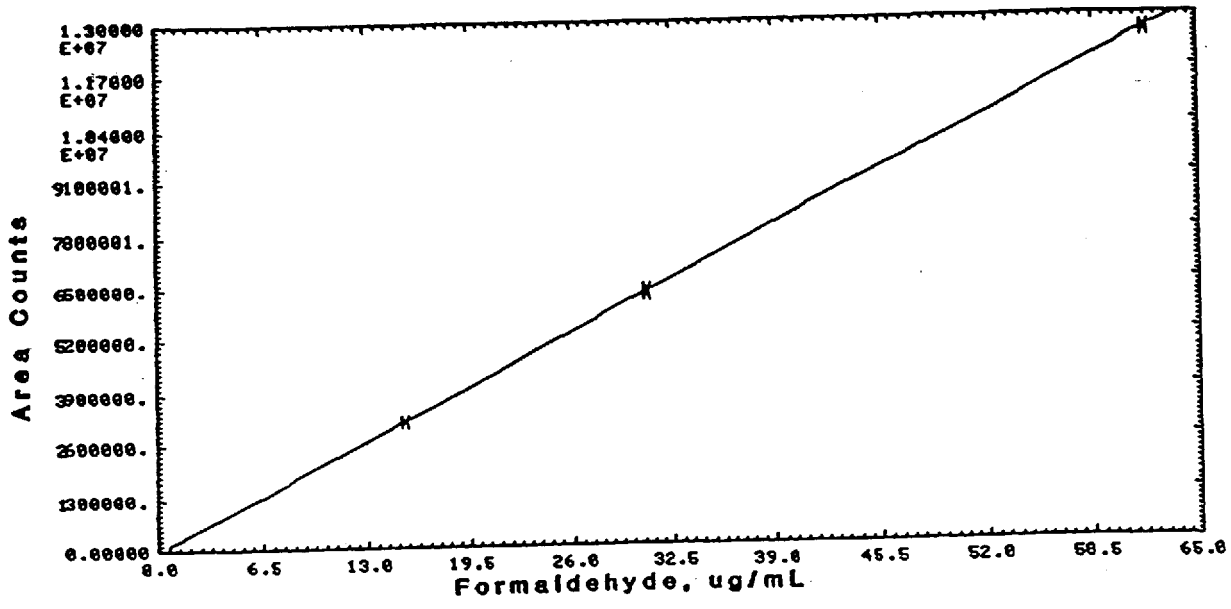

Figure 4. Calibration curve for formaldehyde.

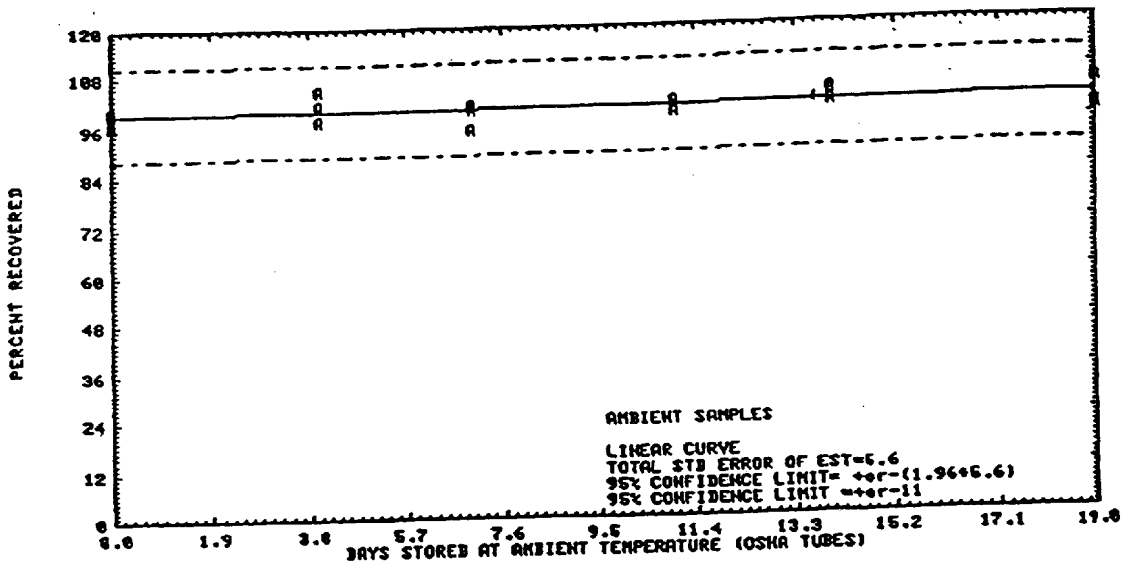

Figure 5. OSHA sampling tubes (lot 12) ambient temperature storage test.

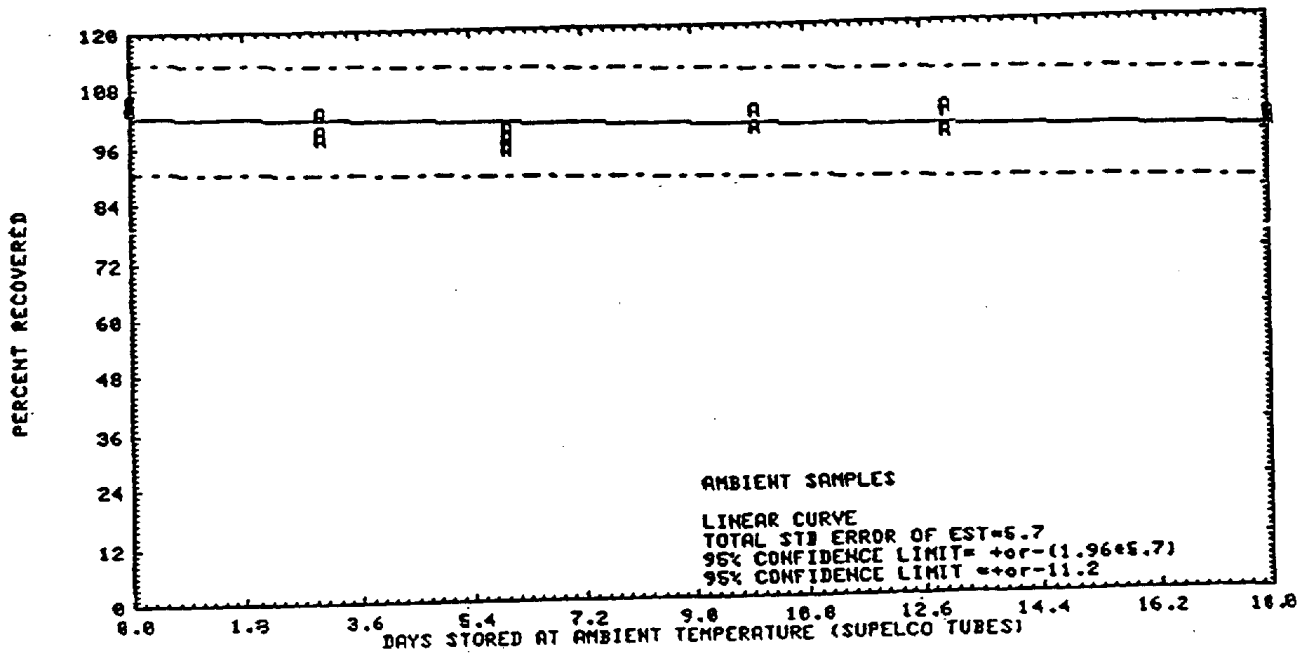

Figure 6. Supelco sampling tubes (lot 673-40) ambient temperature storage test.

5. References

5.1 "Industrial Hygiene Technical Manual", U.S. Department of Labor Occupational Safety and Health Administration, March 30, 1984, Appendix A-Chemical Information Tables.

5.2 Kennedy, E.R.; O'Connor, P.F. and Gagnon, Y.T. Anal. Chem. (1984), (56), 2120-2123.

5.3 Kennedy, E.R. and Hill, R.H. Anal. Chem. (1982,54), 1739-1742.

5.4 "Information Profiles on Potential Occupational Hazards, Vol. I. Single Chemicals. Acrolein", Syracuse Research Corporation, U.S. Dept. of Commerce, NTIS, Springfield, VA., PB 81-147951.

5.5 "Acrolein Health Effects", Midwest Research Inst., U.S. Dept. of Commerce, NTIS, Springfield, VA., PB 82-161282.

5.6 "IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans, Some Monomers, Plastics and Synthetic Elastomers, and Acrolein" International Agency for Research on Cancer: Lyon, 1979, Vol. 19, 479-494.

5.7 "IARC Monograph on the Evaluation of the Carcinogenic Risk of Chemical to Humans, Some Industrial Chemicals and Dyestuffs" International Agency for Research on Cancer: Lyon, 1982, Vol. 29, 345-389.

5.8 "IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man, some Aromatic Amines Hydrazine and Related Substances, N-nitroso Compounds and Miscellaneous Alkylating Agents", International Agency for Research on Cancer: Lyon, 1973, Vol. 4, 231-237.

5.9 "Current Intelligence Bulletin No. 34, Formaldehyde: Evidence of Carcinogenicity", April 15, 1981, U.S. Dept. of Health and Human Services, Public Health Service, Center for Disease Control, NIOSH.

5.10 Environmental Health Perspectives" (1982,43), 139-168.

5.11 Treadwell, F.P. and Hall, W.T. "Analytical Chemistry", John Wiley and Sons, Inc.: New York, 1948, Vol. II, 481-483.

5.12 Walker, J.F. "Formaldehyde", Reinhold Publ. Corp.: New York, 1953, 382.

5.13 Kurvata, K.; Vebori, M.; Yamasaki, H.; Kuge, Y. and Kiso, Y. Anal. Chem. (1983), (55), 2013-2016.

5.14 "OSHA Analytical Methods Manual", U.S. Department of Labor, Occupational Safety and Health Administration, OSHA Analytical Laboratory: Salt Lake City, UT, Method 52, American Conference of Governmental Industrial Hygienists (ACGIH): Cincinnati, 1985, ISBN: 0-936712-66-X.

5.15 "Code of Federal Regulations"; Office of the Federal Register, National Archives and Records Service Administration; U.S. Government Printing Office:, Washington, DC, 1985, 29 CFR 1901.1 Ch. XVII (7-1-85 Edition) 1910.1000, Table Z-2.

5.16 "Fed. Regist.", 1987, 52 (December 4), 46168-46313.