APPENDIX A

METHODS FOR SAMPLING AND ANALYSIS OF EGME, EGEE, EGMEA, AND EGEEA IN AIR*

A.1 General Requirements for Sampling

Air samples are collected that represent the air a worker breathes while performing each job or specific operation. It is advisable to maintain records of the date, time, rate, duration, volume, and location of sampling.

A.2 Collection and Shipping of Samples

1. Immediately before sampling, break the ends of the sampling tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

2. Attach the sampling tube to the sampling pump with flexible tubing. The smaller section of charcoal is used as a backup and should be positioned nearest the sampling pump.

3. The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

4. Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

5. The flow rate of sampling should be known with an accuracy of at least ±5%. Calibrate each sampling pump with a representative charcoal tube in line.

6. The temperature, relative humidity, and pressure of the atmosphere being sampled should be recorded. If a pressure reading is not available, record the elevation.

7. The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

8. One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

*This appendix was reprinted from NIOSH [1984].

9. Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

10. A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

OSHA METHOD NO. 79 FOR EGME, EGMEA, EGEE, AND EGEEA [OSHA 1990]*

2-METHOXYETHANOL (METHYL CELLOSOLVE, 2ME)
2-METHOXYETHYL ACETATE (METHYL CELLOSOLVE ACETATE, 2MEA)
2-ETHOXYETHANOL (CELLOSOLVE, 2EE)
2-ETHOXYETHYL ACETATE (CELLOSOLVE ACETATE, 2EEA)

Method no.: 79

Matrix: Air

Procedure: Samples are collected by drawing air through standard size coconut shell charcoal tubes. Samples are desorbed with 95/5 (v/v) methylene chloride/methanol and analyzed by gas chromatography using a flame ionization detector.

Recommended air volume and sampling rate:
48 liters at 0.1 liters/min for TWA samples
15 liters at 1.0 liters/min for STEL samples

	2ME	2MEA	2EE	2EEA
Target conc.: ppm (mg/m^3)	0.1 (0.3)	0.1 (0.5)	0.5 (1.8)	0.5 (2.7)
Reliable quantitation limit: ppb (μg/m^3)	6.7 (21)	1.7 (8.4)	2.1 (7.8)	1.2 (6.5)
Standard error of estimate at target concentration: (Section 4.7)	6.0%	5.7%	6.2%	5.7%

Special requirements: As indicated in OSHA Method 53 (Ref. 5.1), samples for 2MEA and 2EEA should be refrigerated upon receipt by the laboratory to minimize hydrolysis.

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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*This method was reprinted from OSHA [1990].

1 General Discussion

1.1 Background

1.1.1 History of procedure

An air sampling and analytical procedure for 2ME, 2MEA, 2EE, and 2EEA (OSHA Method 53) was previously evaluated by the Organic Methods Evaluation Branch of the OSHA Analytical Laboratory (Ref. 5.1). The target concentration for all four analytes in that method was 5 ppm. OSHA is now in the process of 6(b) rulemaking to consider reducing occupational exposure to these glycol ethers. Because the proposed exposure limits may be significantly lower than the target concentrations in Method 53, the methodology was re-evaluated at lower levels.

A number of changes were made to Method 53 to accommodate the lower target concentrations.

(1) The recommended air volume for TWA samples was increased from 10 liters to 48 liters. This allows for lower detection limits and increases the TWA sampling time to a more convenient 480 min (8 hr) when sampling at 0.1 liter/min.

(2) A capillary GC column was substituted for a packed column to attain higher resolution. This was especially helpful in achieving better separation of 2ME and methylene chloride, a major component of the desorption solvent.

(3) It was found that the desorption efficiency from wet charcoal was significantly lower for 2ME, and to a lesser extent for 2EE, at these lower concentrations. This problem was overcome by adding about 125 mg of anhydrous magnesium sulfate to each desorption vial to remove the desorbed water. Because charcoal will always collect some water from sampled air, all 2ME and 2EE air samples must be treated in this manner.

Utilizing these three major modifications of Method 53, a successful evaluation was performed for these glycol ethers at the lower target concentrations. Also, a minor modification was made in the determination of desorption efficiencies. Aqueous instead of methanolic stock solutions were used to determine the desorption efficiencies for 2MEA and 2EEA. It was found that at these lower levels, when stock methanolic solutions are spiked on dry Lot 120 charcoal, part of the 2MEA and 2EEA react with the methanol to form methyl acetate and 2ME and 2EE, respectively. The reaction, which is analogous to hydrolysis, is called transesterification (alcoholysis) and is catalyzed by acid or base. The surface of dry Lot 120 charcoal is basic and the reaction was verified to occur by quantitatively

determining methyl acetate and the corresponding alcohol (2ME for 2MEA samples, 2EE for 2EEA samples) from spiked samples. Transesterification was not observed when methanolic stock solutions were spiked onto wet charcoal. Therefore, transesterification is not expected to occur for samples collected from workplace air containing methanol as well as 2MEA or 2EEA because workplace atmospheres are seldom completely dry.

Because of the number of modifications and the extensive amount of data generated in this evaluation, the findings are presented as a separate method instead of a revision of Method 53. This method supersedes Method 53, although Method 53 is still valid at the higher analyte concentrations. Although hydrolysis of 2MEA and 2EEA does not appear to be a problem at lower concentrations, as a precautionary measure, the special requirement that 2MEA and 2EEA samples should be refrigerated upon receipt by the laboratory was retained from Method 53.

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

As reported in the Documentation of Threshold Limit Values (Refs. 5.2 to 5.5), all four analytes were investigated by Nagano et al. (Ref. 5.6) in terms of potency for testicular effects. They concluded that on an equimolar basis, the respective acetate esters were about as potent as 2ME and 2EE in producing testicular atrophy and leukopenia (an abnormally low number of white blood cells) in mice. Based on this study and because 2MEA and 2EEA hydrolyze to 2ME and 2EE respectively in the body, ACGIH suggests lowering the time-weighted TLVs for all four analytes to 5 ppm.

The following is quoted from NIOSH Current Intelligence Bulletin 39 (Ref. 5.7).

> The National Institute for Occupational Safety and Health (NIOSH) recommends that 2-methoxyethanol (2ME) and 2-ethoxyethanol (2EE) be regarded in the workplace as having the potential to cause adverse reproductive effects in male and female workers. These recommendations are based on the results of several recent studies that have demonstrated dose-related embryotoxicity and other reproductive effects in several species of animals exposed by different routes of administration. Of particular concern are those studies in which exposure of pregnant animals to concentrations of 2ME or 2EE at or below their respective Occupational Safety and Health Administration (OSHA) Permissible Exposure Limits (PELs) led to increased incidences of embryonic death, teratogenesis, or growth retardation. Exposure of male animals resulted in

> testicular atrophy and sterility. In each case the animals had been exposed to 2ME or 2EE at concentrations at or below their respective OSHA PELs. Therefore, appropriate controls should be instituted to minimize worker exposure to both compounds.

On May 20, 1986, EPA referred these four analytes to OSHA in accordance with the Toxic Substances Control Act (TSCA). On April 2, 1987, OSHA issued an Advanced Notice of Proposed Rulemaking (ANPR) which summarized the information currently available to OSHA concerning the uses, health effects, estimates of employee exposure and risk determinations for these glycol ethers. OSHA invited comments from interested parties and, based on the gathered information, will decide on appropriate action (Ref. 5.8).

1.1.3 Workplace exposure

2ME—It is used as a solvent for many purposes: cellulose esters, dyes, resins, lacquers, varnishes, and stains; and as a perfume fixative and jet fuel deicing additive (Ref. 5.2).

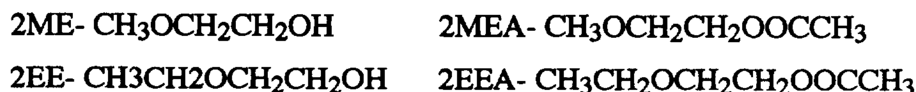
2MEA—It is used in photographic films, lacquers, textile printing, and as a solvent for waxes, oils, various gums and resins, cellulose acetate, and nitrocellulose (Ref. 5.3).

2EE—It is used as a solvent for nitrocellulose, natural and synthetic resins, and as a mutual solvent for the formulation of soluble oils. It is also used in lacquers, in the dyeing and printing of textiles, in varnish removers, in cleaning solutions, in products for the treatment of leather, and as an anti-icing additive for aviation fuels (Ref. 5.4).

2EEA—It is used as a blush retardant in lacquers; as a solvent for nitrocellulose, oils and resins; in wood stains, varnish removers; and in products for the treatment of textiles and leathers (Ref. 5.5).

1.1.4 Physical properties (Refs. 5.2-5.5)

Chemical formulae:



2ME- $CH_3OCH_2CH_2OH$ 2MEA- $CH_3OCH_2CH_2OOCCH_3$

2EE- $CH3CH2OCH_2CH_2OH$ 2EEA- $CH_3CH_2OCH_2CH_2OOCCH_3$

Synonyms: (Ref. 5.9)

2ME—Methyl Cellosolve; glycol monomethyl ether; ethylene glycol monomethyl ether; methyl oxitol; Ektasolve; Jeffersol EM

2MEA—Methyl Cellosolve acetate; glycol monomethyl ether acetate; ethylene glycol monomethyl ether acetate

2EE—Cellosolve solvent; ethylene glycol monoethyl ether

2EEA—Cellosolve acetate; glycol monoethyl ether acetate; ethylene glycol monoethyl ether acetate

Analyte	2ME	2MEA	2EE	2EEA
CAS no.	109-86-4	110-49-6	110-80-5	111-15-9
mol wt	76.09	118.13	90.11	132.16
bp (°C)	124.5	145	135.6	156.4
Color		all are colorless liquids		
sp gr	0.9663	1.005	0.931	0.975
vp [kPa (mm Hg) at 20°C]	0.8(6)	0.3(2)	0.49(3.7)	0.3(2)
Flash pt. (°C, closed cup)	43	49	40	49
Odor (Ref. 5.9)	mild, non-residual	mild, ether-like	sweetish	mild, non-residual
Explosive limits, % (Ref. 5.9):				
Lower	2.5	1.1	1.8	1.7
Upper	19.8	8.2	14	?

The analyte air concentrations throughout this method are based on the recommended TWA-sampling and analytical parameters. Air concentrations listed in ppm and ppb are referenced to 25°C and 101.3 kPa (760 mm Hg).

1.2 Limit-defining parameters

1.2.1 Detection limit of the analytical procedure

The detection limits of the analytical procedure are 0.10, 0.04, 0.04, and 0.03 ng per injection (1.0-μL injection with a 10:1 split) for 2ME, 2MEA, 2EE, and 2EEA respectively. These are the amounts of each analyte that will give peaks with heights approximately 5 times the height of baseline noise (Section 4.1).

1.2.2 Detection limit of the overall procedure

The detection limits of the overall procedure are 1.0, 0.40, 0.37, and 0.31 µg per sample for 2ME, 2MEA, 2EE, and 2EEA respectively. These are the amounts of each analyte spiked on the sampling device that allow recovery of amounts of each analyte equivalent to the detection limits of the analytical procedure. These detection limits correspond to air concentrations of 6.7 ppb (21 µg/m^3), 1.7 ppb (8.4 µg/m^3), 2.1 ppb (7.8 µg/m^3), and 1.2 ppb (6.5 µg/m^3) for 2ME, 2MEA, 2EE, and 2EEA respectively (Section 4.2).

1.2.3 Reliable quantitation limit

The reliable quantitation limits are the same as the detection limits of the overall procedure because the desorption efficiencies are essentially 100% at these levels. These are the smallest amounts of each analyte that can be quantitated within the requirements of recoveries of at least 75% and precisions (±1.96 SD) of ±25% or better (Section 4.3).

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

1.2.4 Instrument response to the analyte

The instrument response over the concentration ranges of 0.5 to 2 times the target concentrations is linear for all four analytes (Section 4.4).

1.2.5 Recovery

The recovery of 2ME, 2MEA, 2EE, and 2EEA from samples used in a 15-day storage test remained above 84, 87, 84, and 85% respectively when the samples were stored at ambient temperatures. The recovery of analyte from the collection medium after storage must be 75% or greater. (Section 4.5, from regression lines shown in Figures 4.5.1.2, 4.5.2.2, 4.5.3.2, and 4.5.4.2)

1.2.6 Precision (analytical procedure)

The pooled coefficients of variation obtained from replicate determinations of analytical standards at 0.5, 1, and 2 times the target concentrations are 0.022, 0.004, 0.002, and 0.002 for 2ME, 2MEA, 2EE, and 2EEA respectively (Section 4.6).

1.2.7 Precision (overall procedure)

The precisions at the 95% confidence level for the ambient temperature 15-day storage tests are ±11.7, ±11.1, ±12.3, and ±11.2% for 2ME, 2MEA, 2EE, and 2EEA respectively. These include 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 (Section 4.7).

1.2.8 Reproducibility

Six samples for each analyte collected from controlled test atmospheres and a draft copy of this procedure were given to a chemist unassociated with this evaluation. The samples were analyzed after 12 days of refrigerated storage. No individual sample result deviated from its theoretical value by more than the precision reported in Section 1.2.7 (Section 4.8).

1.3 Advantages

1.3.1 Charcoal tubes provide a convenient method for sampling.

1.3.2 The analysis is rapid, sensitive, and precise.

1.4 Disadvantage

It may not be possible to analyze co-collected solvents using this method. Most of the other common solvents which are collected on charcoal are analyzed after desorption with carbon disulfide.

2 Sampling Procedure

2.1 Apparatus

2.1.1 Samples are collected using a personal sampling pump calibrated to within ±5% of the recommended flow rate with a sampling tube in line.

2.1.2 Samples are collected with solid sorbent sampling tubes containing coconut shell charcoal. Each tube consists of two sections of charcoal separated by a urethane foam plug. The front section contains 100 mg of charcoal and the back section, 50 mg. The sections are held in place with glass wool plugs in a glass tube 4-mm i.d. × 70-mm length. For this evaluation, SKC Inc. charcoal tubes (catalog number 226-01, Lot 120) were used.

2.2 Reagents

None required

2.3 Technique

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

2.3.2 Connect the sampling tube to the sampling pump with flexible tubing. Position the tube so that sampled air first passes through the 100-mg section.

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

2.3.4 Place the sampling tube vertically (to avoid channeling) in the employee's breathing zone.

2.3.5 After sampling, seal the tubes immediately with plastic caps and wrap lengthwise with OSHA Form 21.

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

2.3.7 Record sample volumes (in liters of air) for each sample, along with any potential interferences.

2.3.8 Ship any bulk sample(s) in a container separate from the air samples.

2.4 Sampler capacity

2.4.1 Sampler capacity is determined by measuring how much air can be sampled before breakthrough of analyte occurs (i.e., the sampler capacity is exceeded). Individual breakthrough studies were performed on each of the four analytes by monitoring the effluent from sampling tubes containing only the 100-mg section of charcoal while sampling at 0.2 liters/min from atmospheres containing 10 ppm analyte. The atmospheres were at approximately 80% relative humidity and 20-25°C. No breakthrough was detected in any of the studies after sampling for at least 6 hr (>70 liters). (These data were collected in the evaluation of OSHA Method 53, Ref. 5.1.)

2.4.2 A similar study as in 2.4.1 was done while sampling an atmosphere containing 10 ppm of all four analytes. The atmosphere was sampled for more than 5 hr (>60 liters) with no breakthrough detected. (These data were collected in the evaluation of OSHA Method 53, Ref. 5.1.)

2.5 Desorption efficiency

2.5.1 The average desorption efficiencies of 2ME, 2MEA, 2EE, and 2EEA from Lot 120 charcoal are 95.8, 97.9, 96.5, and 98.3% respectively over the

range of 0.5 to 2 times the target concentrations. Desorption samples for 2MEA and 2EEA must not be determined by using methanolic stock solutions since a transesterification reaction can occur (Section 4.9).

2.5.2 Desorbed samples remain stable for at least 24 hr (Section 4.10).

2.6 Recommended air volume and sampling rate

2.6.1 For TWA samples, the recommended air volume is 48 liters collected at 0.1 liters/min (8-hr samples).

2.6.2 For short-term samples, the recommended air volume is 15 liters collected at 1.0 liter/min (15-min samples).

2.6.3 When short-term samples are required, the reliable quantitation limits become larger. For example, the reliable quantitation limit is 21 ppb (67 $\mu g/m^3$) for 2ME when 15 liters is sampled.

2.7 Interferences (sampling)

2.7.1 It is not known if any compound(s) will severely interfere with the collection of any of the four analytes on charcoal. In general, the presence of other contaminant vapors in the air will reduce the capacity of charcoal to collect the analytes.

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

2.8 Safety precautions (sampling)

2.8.1 Attach the sampling equipment to the employee so that it will not interfere with work performance or safety.

2.8.2 Wear eye protection when breaking the ends of the charcoal tubes.

2.8.3 Follow all safety procedures that apply to the work area being sampled.

3 Analytical Procedure

3.1 Apparatus

3.1.1 A GC equipped with a flame ionization detector. For this evaluation, a Hewlett-Packard 5890 Series II Gas Chromatograph equipped with a 7673A Automatic Sampler was used.

3.1.2 A GC column capable of separating the analyte of interest from the desorption solvent, internal standard, and any interferences. A thick film, 60-m × 0.32-mm i.d., fused silica RTx-Volatiles column (Cat. no. 10904, Restek Corp., Bellefonte, PA) was used in this evaluation.

3.1.3 An electronic integrator or some other suitable means of measuring peak areas or heights. A Hewlett-Packard 18652A A/D converter interfaced to a Hewlett-Packard 3357 Lab Automation Data System was used in this evaluation.

3.1.4 Two-milliliter vials with Teflon-lined caps.

3.1.5 A dispenser capable of delivering 1.0 mL to prepare standards and samples. If a dispenser is not available, a 1.0-mL volumetric pipet may be used.

3.1.6 Syringes of various sizes for preparation of standards.

3.1.7 Volumetric flasks and pipets to dilute the pure analytes in preparation of standards.

3.2 Reagents

3.2.1 2-Methoxyethanol, 2-methoxyethyl acetate, 2-ethoxyethanol, and 2-ethoxyethyl acetate, reagent grade. Aldrich Lot HBO62777 2ME, Eastman Lot 701-2 2MEA, Aldrich Lot DB040177 2EE, and Aldrich Lot 04916HP 2EEA were used in this evaluation.

3.2.2 Anhydrous magnesium sulfate, reagent grade. Chempure Lot M172 KDHM was used in this evaluation.

3.2.3 Methylene chloride, chromatographic grade. American Burdick and Jackson Lot AQ098 was used in this evaluation.

3.2.4 Methanol, chromatographic grade. American Burdick and Jackson Lot AT015 was used in this evaluation.

3.2.5 A suitable internal standard, reagent grade. "Quant Grade" 3-methyl-3-pentanol from Polyscience Corporation was used in this evaluation.

3.2.6 The desorption solvent consists of methylene chloride/methanol, 95/5 (v/v) containing an internal standard at a concentration of 20 μL/liter.

3.2.7 GC grade nitrogen, air, and hydrogen.

3.3 Standard preparation

3.3.1 Prepare concentrated stock standards by diluting the pure analytes with methanol. Prepare working standards by injecting microliter amounts of concentrated stock standards into vials containing 1.0 mL of desorption solvent delivered from the same dispenser used to desorb samples. For example, to prepare a stock standard of 2ME, dilute 195 μL of pure 2ME (sp gr = 0.9663) to 50.0 mL with methanol. This stock solution would contain 3.769 μg/μL. A working standard of 15.08 μg/sample is prepared by injecting 4.0 μL of this stock into a vial containing 1.0 mL of desorption solvent.

3.3.2 Bracket sample concentrations with working standard concentrations. If samples fall outside of the concentration range of prepared standards, prepare and analyze additional standards to ascertain the linearity of response.

3.4 Sample preparation

3.4.1 Transfer each section of the samples to separate vials. Discard the glass tubes and plugs.

3.4.2 For 2ME and 2EE samples, add about 125 mg of magnesium sulfate to each vial.

3.4.3 Add 1.0 mL of desorption solvent to each vial using the same dispenser as used for preparation of standards.

3.4.4 Immediately cap the vials and shake them periodically for about 30 min.

3.5 Analysis

3.5.1 GC conditions

zone temperatures:	column—80°C for 4 min 10°C/min to 125°C 125°C for 4 min injector—150°C detector—200°C
gas flows (mL/min):	hydrogen (carrier)—2.5 (80 kPa head pressure) nitrogen (makeup)—20 hydrogen (flame)—65 air—400
injection volume:	1.0 µL (with a 10:1 split)
column:	60-m × 0.32-mm i.d. fused silica, RTx-Volatiles, thick film
retention times (min):	2ME-5.0 2MEA-10.0 2EE-6.7 2EEA-11.9 (3-methyl-3-pentanol-7.5)
chromatograms:	Section 4.11

3.5.2 Peak areas (or heights) are measured by an integrator or other suitable means.

3.5.3 An internal standard (ISTD) calibration method is used. Calibration curves are prepared by plotting micrograms of analyte per sample versus ISTD-corrected response of standard injections. Sample concentrations must be bracketed by standards.

3.6 Interferences (analytical)

3.6.1 Any compound that responds on a flame ionization detector and has the same general retention time of the analyte or internal standard is a potential interference. Possible interferences should be reported to the laboratory with submitted samples by the industrial hygienist. These interferences should be considered before samples are desorbed.

3.6.2 GC parameters (i.e., column and column temperature) may be changed to possibly circumvent interferences.

3.6.3 Retention time on a single column is not considered proof of chemical identity. Analyte identity should be confirmed by GC/mass spectrometer if possible.

3.7 Calculations

The analyte concentration for samples is obtained from the appropriate calibration curve in terms of micrograms per sample, uncorrected for desorption efficiency. The air concentration is calculated using the following formulae. The back (50-mg) section is analyzed primarily to determine if there was any breakthrough from the front (100-mg) section during sampling. If a significant amount of analyte is found on the back section (e.g., greater than 25% of the amount found on the front section), this fact should be reported with sample results. If any analyte is found on the back section, it is added to the amount found on the front section. This total amount is then corrected by subtracting the total amount (if any) found on the blank.

$$\text{mg/m}^3 = \frac{\text{(micrograms of analyte per sample)}}{\text{(liters of air sampled) (desorption efficiency)}}$$

where desorption efficiency = 0.958 for 2ME, 0.979 for 2MEA
0.965 for 2EE, 0.983 for 2EEA

$$\text{ppm} = \frac{(\text{mg/m}^3)\ (24.46)}{\text{(molecular weight of analyte)}}$$

where 24.46 = molar volume (liters) at 25°C and 101.3 kPa (760 mm Hg)
molecular weight = 76.09 for 2ME, 118.13 for 2MEA
90.11 for 2EE, 132.16 for 2EEA

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 when possible.

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

4 Backup Data

4.1 Detection limit of the analytical procedure

The injection size listed in the analytical procedure (1.0 µL with a 10:1 split) was used in the determination of the detection limits of the analytical procedure. The detection limits of 0.10, 0.04, 0.04, and 0.03 ng were determined by making injections of 1.00, 0.40, 0.37, and 0.31 ng/µL standards for 2ME, 2MEA, 2EE, and 2EEA respectively. These amounts were judged to produce peaks with heights approximately 5 times the baseline noise. Chromatograms of such injections are shown in Figures 4.1.1 and 4.1.2.

4.2 Detection limit of the overall procedure

Six samples for each analyte were prepared by injecting (from dilute aqueous standards) 1.00 µg of 2ME, 0.40 µg of 2MEA, 0.37 µg of 2EE, and 0.31 µg of 2EEA into the 100-mg section of charcoal tubes. The samples were stored at room temperature and analyzed the next day. The detection limits of the overall procedure correspond to air concentrations of 6.7 ppb (21 $\mu g/m^3$), 1.7 ppb (8.4 $\mu g/m^3$), 2.1 ppb (7.8 $\mu g/m^3$), and 1.2 ppb (6.5 $\mu g/m^3$) for 2ME, 2MEA, 2EE, and 2EEA respectively. The results are given in Tables 4.2.1 to 4.2.4.

Table 4.2.1
Detection Limit of Overall Procedure for 2ME

Sample no.	µg spiked	µg recovered
1	1.00	0.908
2	1.00	0.945
3	1.00	0.957
4	1.00	0.982
5	1.00	1.067
6	1.00	0.969

Table 4.2.2
Detection Limit of Overall Procedure for 2MEA

Sample no.	μg spiked	μg recovered
1	0.40	0.382
2	0.40	0.392
3	0.40	0.385
4	0.40	0.402
5	0.40	0.402
6	0.40	0.408

Table 4.2.3
Detection Limit of Overall Procedure for 2EE

Sample no.	μg spiked	μg recovered
1	0.37	0.347
2	0.37	0.352
3	0.37	0.347
4	0.37	0.388
5	0.37	0.370
6	0.37	0.361

Table 4.2.4
Detection Limit of Overall Procedure for 2EEA

Sample no.	μg spiked	μg recovered
1	0.31	0.301
2	0.31	0.319
3	0.31	0.304
4	0.31	0.322
5	0.31	0.328
6	0.31	0.328

4.3 Reliable quantitation limit

The reliable quantitation limits were determined by analyzing charcoal tubes spiked with loadings equivalent to the detection limits of the analytical procedure. Samples were prepared by injecting 1.0 μg of 2ME, 0.40 μg of 2MEA, 0.37 μg of

2EE, and 0.31 µg of 2EEA into the 100-mg section of charcoal tubes. These amounts correspond to air concentrations of 6.7 ppb (21 µg/m^3), 1.7 ppb (8.4 µg/m^3), 2.1 ppb (7.8 µg/m^3), and 1.2 ppb (6.5 µg/m^3) for 2ME, 2MEA, 2EE, and 2EEA respectively. The results are given in Tables 4.3.1 to 4.3.4.

Table 4.3.1
Reliable Quantitation Limit for 2ME
(Based on samples and data of Table 4.2.1)

Sample no.	Percent recovered	Statistics
1	90.8	$\bar{X}$ = 97.1
2	94.5	
3	95.7	
4	98.2	SD = 5.3
5	106.7	Precision = (1.96)(±5.3)
6	96.9	= ±10.4

Table 4.3.2
Reliable Quantitation Limit for 2MEA
(Based on samples and data of Table 4.2.2)

Sample no.	Percent recovered	Statistics
1	95.5	$\bar{X}$ = 98.8
2	98.0	
3	96.2	
4	100.5	SD = 2.6
5	100.5	Precision = (1.96)(±2.6)
6	102.0	= ±5.1

Table 4.3.3
Reliable Quantitation Limit for 2EE
(Based on samples and data of Table 4.2.3)

Sample no.	Percent recovered	Statistics
1	93.8	$\bar{X}$ = 97.5
2	95.1	
3	93.8	
4	104.9	SD = 4.3
5	100.0	Precision = (1.96)(±4.3)
6	97.6	= ±8.4

Table 4.3.4
Reliable Quantitation Limit for 2EEA
(Based on samples and data of Table 4.2.4)

Sample no.	Percent recovered	Statistics
1	97.1	$\overline{X}$ = 102.3
2	102.9	
3	98.1	
4	103.9	SD = 3.8
5	105.8	Precision = (1.96)(±3.8)
6	105.8	= ±7.4

4.4 Instrument response to the analyte

The instrument response to the analytes over the range of 0.5 to 2 times the target concentrations was determined from multiple injections of analytical standards. These data are given in Tables 4.4.1 to 4.4.4 and Figures 4.4.1 and 4.4.2. The response is linear for all four analytes with slopes (in ISTD-corrected area counts per micrograms of analyte per sample) of 980, 1040, 1300, and 1330 for 2ME, 2MEA, 2EE, and 2EEA respectively.

4.5 Storage test

Storage samples are normally generated by sampling the recommended air volume at the recommended sampling rate from test atmospheres at 80% relative humidity containing the analyte at the target concentration. Because this would require generation of 8-hr samples, in the interest of time, samples were generated by sampling from atmospheres containing the analytes at about 4 times the target concentrations for 60 min at 0.2 liters/min (12-liter samples). (Note: To test the performance of the sampler for 48-liter volumes and to show the validity of collecting 12-liter samples at 4 times the target concentrations instead of 48-liter samples at the target concentrations, a set of six 48-liter samples at the target concentration for each analyte was individually generated and compared to the corresponding Day 0 samples. All samples agreed within the precisions of the method.) 2ME and 2EE were generated in the same atmosphere, and 2MEA and 2EEA were generated together in another atmosphere. For each set of 36 samples, 6 samples were analyzed immediately after generation, 15 were stored in a refrigerator at 0°C and 15 were stored in a closed drawer at ambient temperatures of 20-25°C. Six samples, three from refrigerated and three from ambient storage, were analyzed in 3-day intervals over a period of 15 days. The results are given in Tables 4.5.1 to 4.5.4 and shown graphically in Figures 4.5.1.1, 4.5.1.2, 4.5.2.1, 4.5.2.2, 4.5.3.1, 4.5.3.2, 4.5.4.1, and 4.5.4.2.

Table 4.4.1
Instrument Response to 2ME

× target conc.	0.5×	1×	2×
μg/sample	7.537	15.07	30.15
ppm	0.050	0.101	0.202
area counts	6930.6	14033	29007
	6832.1	14219	28908
	6771.4	14139	28920
	6655.9	14133	28691
	6202.5	14165	28834
	6786.0	14176	28887
$\overline{X}$	6696.4	14144	28874

Table 4.4.2
Instrument Response to 2MEA

× target conc.	0.5×	1×	2×
mg/sample	11.66	23.32	46.63
ppm	0.050	0.101	0.201
area counts	11946	24182	48262
	11772	24108	48302
	11987	24124	48160
	12002	24230	48281
	11954	24168	48116
	11888	24111	48250
$\overline{X}$	11925	24154	48228

Table 4.4.3
Instrument Response to 2EE

× target conc.	0.5×	1×	2×
μg/sample	44.69	89.38	178.8
ppm	0.253	0.505	1.01
area counts	54351	112883	229836
	54263	113321	229797
	53870	113357	229284
	54239	113320	229292
	54102	113176	228496
	54292	113418	229250
$\overline{X}$	54186	113246	229326

Table 4.4.4
Instrument Response to 2EEA

× target conc.	0.5×	1×	2×
µg/sample	64.35	128.7	257.4
ppm	0.248	0.496	0.992
area counts	84793	171546	342651
	84896	171239	343419
	84718	171727	341665
	84795	171787	342505
	84446	171303	341122
	84612	171138	342812
$\overline{X}$	84710	171457	342362

Table 4.5.1
Storage Data for 2ME

Storage time (days)	% recovery (refrigerated)			% recovery (ambient)		
0	97.8	102.0	96.3	97.8	102.0	96.3
0	99.9	104.2	94.8	99.9	104.2	94.8
3	96.8	99.5	95.9	93.7	91.7	94.2
6	96.3	96.6	93.3	92.8	91.4	92.8
9	91.4	88.8	91.4	86.1	88.8	87.5
1	289.9	89.8	88.7	91.3	93.1	86.9
1	587.4	88.8	84.4	87.8	79.8	80.7

Table 4.5.2
Storage Data for 2ME

Storage time (days)	% recovery (refrigerated)			% recovery (ambient)		
0	101.2	103.5	101.8	101.2	103.5	101.8
0	102.0	105.0	103.8	102.0	105.0	103.8
3	96.8	99.2	99.4	94.1	95.0	93.7
6	94.2	93.1	95.9	92.6	93.3	92.0
9	96.9	99.7	98.7	92.0	90.8	90.2
12	95.1	96.2	95.5	88.6	90.5	87.1
15	94.0	95.9	96.1	89.3	89.4	89.8

Table 4.5.3
Storage Data for 2EE

Storage time (days)	% recovery (refrigerated)			% recovery (ambient)		
0	96.4	101.4	95.8	96.4	101.4	95.8
0	99.8	100.2	93.9	99.8	100.2	93.9
3	93.9	100.5	98.3	93.9	95.7	96.2
6	96.4	96.9	96.7	93.4	96.8	94.0
9	92.1	88.2	91.5	81.6	87.9	88.0
12	89.2	89.6	89.1	92.6	92.3	86.1
15	88.6	88.4	84.1	90.1	80.4	80.0

Table 4.5.4
Storage Data for 2EEA

Storage time (day)	% recovery (refrigerated)			% recovery (ambient)		
0	99.7	101.7	101.8	99.7	101.7	101.8
0	100.9	104.1	102.2	100.9	104.1	102.2
3	94.5	96.7	103.6	92.8	94.2	91.6
6	92.7	92.2	95.7	91.4	91.5	90.8
9	96.2	98.7	98.0	90.3	88.9	88.8
12	93.5	94.6	94.7	87.0	88.8	84.9
15	92.9	95.0	95.2	87.6	87.6	87.6

4.6 Precision (analytical procedure)

The precision of the analytical procedure for each analyte is the pooled coefficient of variation determined from replicate injections of standards.

The precision of the analytical procedure for each analyte is given in Tables 4.6.1 to 4.6.4. These tables are based on the data presented in Section 4.4.

Table 4.6.1
Precision of the Analytical Procedure for 2ME
(Based on Table 4.4.1)

× target conc.	0.5×	1×	2×
µg/sample	44.69	89.38	178.8
ppm	0.253	0.505	1.01
SD (area counts)	257.9	62.5	106.0
CV	0.0385	0.0044	0.0037

$\overline{CV}$ = 0.022

Table 4.6.2
Precision of the Analytical for 2MEA
(Based on Table 4.4.2)

× target conc.	0.5×	1×	2×
μg/sample	11.66	23.32	46.63
ppm	0.050	0.101	0.201
SD (area counts)	84.7	48.2	73.6
CV	0.0071	0.0020	0.0015
$\overline{CV}$ = 0.004			

Table 4.6.3
Precision of the Analytical for 2EE
(Based on Table 4.4.3)

× target conc.	0.5×	1×	2×
μg/sample	44.69	89.38	178.8
ppm	0.253	0.505	1.01
SD (area counts)	175.6	194.8	485.7
CV	0.0032	0.0017	0.0021
$\overline{CV}$ = 0.002			

Table 4.6.4
Precision of the Analytical for 2EEA
(Based on Table 4.4.4)

× target conc.	0.5×	1×	2×
μg/sample	64.35	128.7	257.4
ppm	0.248	0.496	0.992
SD (area counts)	160.0	269.3	830.3
CV	0.0019	0.0016	0.0024
$\overline{CV}$ = 0.002			

4.7 Precision (overall procedure)

The precision of the overall procedure is determined from the storage data. The determination of the standard error of estimate (SEE) for a regression line plotted through the graphed storage data allows the inclusion of storage time as one of the factors affecting overall precision. The SEE is similar to the standard deviation,

except it is a measure of dispersion of data about a regression line instead of about a mean. It is determined with the following equation:

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

where

n = total no. of data points
k = 2 for linear regression
k = 3 for quadratic regression
Yobs = observed % recovery at a given time
Yest = estimated % recovery from the regression line at the same given time

An additional 5% for pump error is added to the SEE by the addition of variances. The SEEs are 6.0%, 5.7%, 6.2%, and 5.7% for 2ME, 2MEA, 2EE, and 2EEA respectively. The precision of the overall procedure is the precision at the 95% confidence level, which is obtained by multiplying the SEE (with pump error included) by 1.96 (the z-statistic from the standard normal distribution at the 95% confidence level). The 95% confidence intervals are drawn about their respective regression lines in the storage graphs. The precisions of the overall procedure are ±11.7%, ±11.1%, ±12.3%, and ±11.2% for 2ME, 2MEA, 2EE, and 2EEA respectively. The SEE and precision of the overall procedure for each analyte were obtained from Figures 4.5.1.2, 4.5.2.2, 4.5.3.2, and 4.5.4.2 for 2ME, 2MEA, 2EE, and 2EEA respectively.

4.8 Reproducibility

Six samples for each analyte, collected from controlled test atmospheres (at about 80% R.H., 20-26°C, 86-88 kPa) containing the analytes at about 4 times the target concentrations, were analyzed by chemists unassociated with this evaluation. The samples were generated by drawing the test atmospheres through sampling tubes for 60 min at approximately 0.2 liters/min. The samples were stored in a refrigerator for 12 days before being analyzed. The results are presented in Tables 4.8.1 to 4.8.4.

Table 4.8.1
Reproducibility for 2ME

Sample no.	μg found	μg expected	% found	% deviation
1	14.90	14.59	102.1	+2.1
2	15.21	15.36	99.0	-1.0
3	15.06	14.93	100.9	+0.9
4	15.42	15.38	100.3	+0.3
5	15.41	15.07	102.3	+2.3
6	15.88	15.54	102.2	+2.2

Table 4.8.2
Reproducibility for 2MEA

Sample no.	μg found	μg expected	% found	% deviation
1	21.61	23.35	92.5	-7.5
2	20.33	22.77	89.3	-10.7
3	21.47	23.12	92.9	-7.1
4	21.51	22.84	94.2	-5.8
5	22.44	23.87	94.0	-6.0
6	22.48	24.01	93.6	-6.4

Table 4.8.3
Reproducibility for 2EE

Sample no.	μg found	μg expected	% found	% deviation
1	83.47	85.55	97.6	-2.4
2	88.22	90.07	97.9	-2.1
3	84.10	87.57	96.0	-4.0
4	86.57	90.20	96.0	-4.0
5	84.79	88.40	95.9	-4.1
6	88.90	91.16	97.5	-2.5

Table 4.8.4
Reproducibility for 2EEA

Sample no.	μg found	μg expected	% found	% deviation
1	117.3	129.9	90.3	-9.7
2	118.1	126.7	93.2	-6.8
3	117.5	128.6	91.4	-8.6
4	117.4	127.1	92.4	-7.6
5	122.8	132.8	92.5	-7.5
6	121.9	133.6	91.2	-8.8

4.9 Desorption efficiency

The desorption efficiency for each analyte was determined by injecting microliter amounts of aqueous stock standards onto the front section of charcoal tubes. Aqueous standards were used because it was found that when methanolic standards were injected onto dry charcoal, part of the 2MEA and 2EEA reacted with the methanol via transesterification (alcoholysis). The reaction was presumably catalyzed by the basic surface of the charcoal. Eighteen samples were prepared,

six samples for each concentration level listed in the following tables. The samples were stored in a refrigerator and analyzed the next day.

Table 4.9.1
Desorption Efficiency Data for 2ME and 2MEA

Analyte		**2EE**			**2EEA**	
× target conc.	**0.5×**	**1×**	**2×**	**0.5×**	**1×**	**2×**
µg/sample	**7.537**	**15.07**	**30.15**	**11.66**	**23.32**	**46.63**
ppm	**0.050**	**0.101**	**0.202**	**0.050**	**0.101**	**0.201**
Desorption	92.8	94.5	96.2	97.6	97.6	96.7
efficiency, %	96.8	97.7	97.0	98.8	98.0	98.3
	93.0	94.0	98.0	97.4	98.3	98.0
	97.1	96.4	97.6	97.5	99.6	96.9
	95.8	94.9	96.2	97.9	99.1	96.7
	90.7	97.9	97.3	98.1	98.4	96.9
$\overline{X}$	94.4	95.9	97.0	97.9	98.5	97.2
$\overline{\overline{X}}$		95.8			97.9	

Table 4.9.2
Desorption Efficiency Data for 2EE and 2EEA

Analyte		**2EE**			**2EEA**	
× target conc.	**0.5×**	**1×**	**2×**	**0.5×**	**1×**	**2×**
µg/sample	**44.69**	**89.38**	**178.8**	**64.35**	**128.7**	**257.4**
ppm	**0.2530**	**0.505**	**1.01**	**0.248**	**0.496**	**0.992**
Desorption	94.9	95.4	96.9	97.7	98.5	97.1
efficiency, %	95.3	97.3	97.7	99.1	98.8	98.4
	93.1	94.9	98.4	98.6	98.8	98.2
	97.3	97.2	98.3	98.3	100.2	97.5
	95.4	97.7	96.9	98.5	99.5	96.8
	93.0	98.8	98.1	97.9	98.9	97.3
$\overline{X}$	94.8	96.9	97.7	98.4	99.1	97.6
$\overline{\overline{X}}$		96.5			98.3	

4.10 Stability of desorbed samples

The stability of desorbed samples was checked by reanalyzing the target concentration samples from Section 4.9 one day later using fresh standards. The sample

vials were resealed with new septa after the original analyses and were allowed to stand at room temperature until reanalyzed. The results are given in Table 4.10.

Table 4.10
Stability of Desorbed Samples at the Target Concentration

Sample no.	% desorption after 24 h			
	2ME	2MEA	2EE	2EEA
1	95.0	100.9	98.9	101.6
2	97.7	99.4	99.0	101.0
3	98.5	101.3	99.3	101.6
4	98.4	101.8	99.0	101.9
5	99.7	101.2	100.2	101.4
6	98.5	101.2	100.2	101.7
$\overline{X}$	98.0	101.0	99.4	101.5

4.11 Chromatograms

A chromatogram of the four analytes is shown in Figure 4.11. The chromatogram is from an injection of a standard equivalent to a 48-liter air sample at the target concentrations.

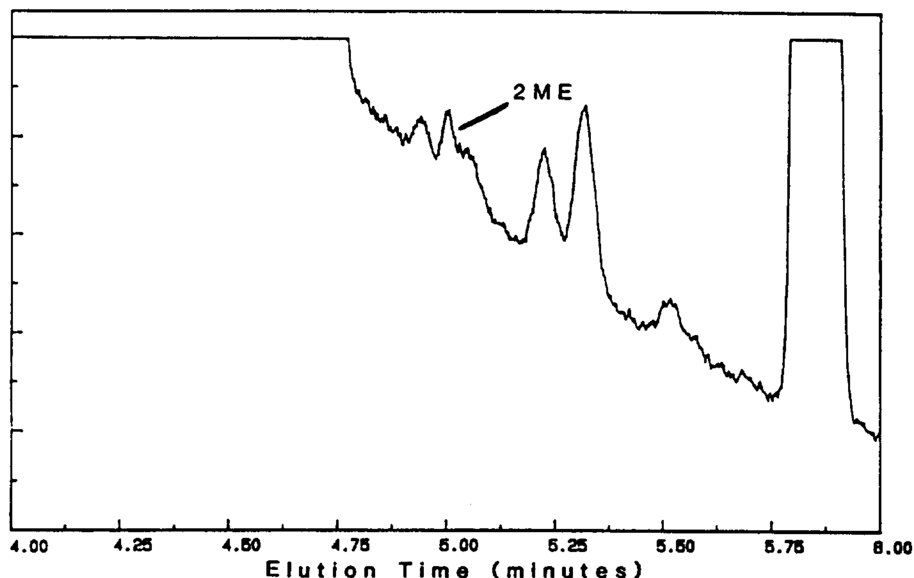


Figure 4.1.1 Detection limit chromatogram for 2ME.

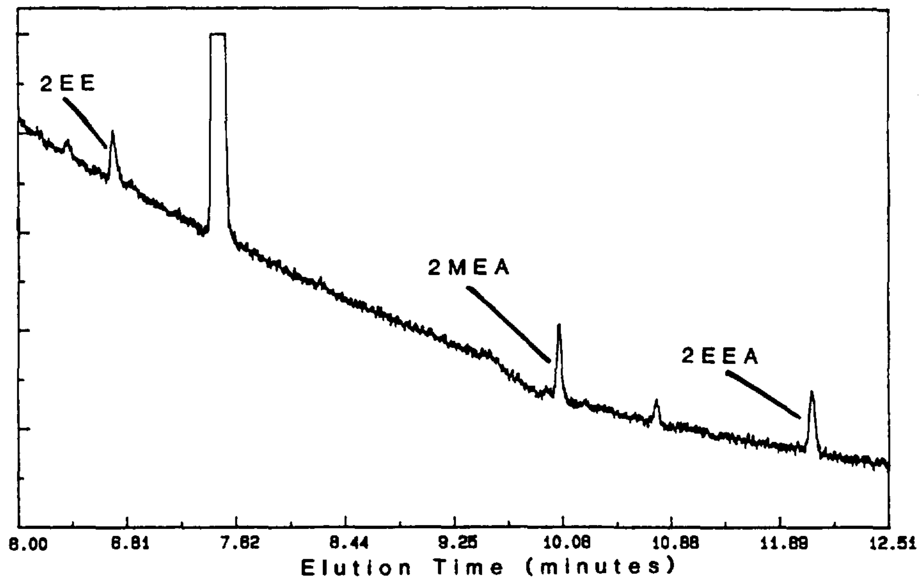


Figure 4.1.2 Detection limit chromatogram for 2MEA, 2EE, and 2EEA.

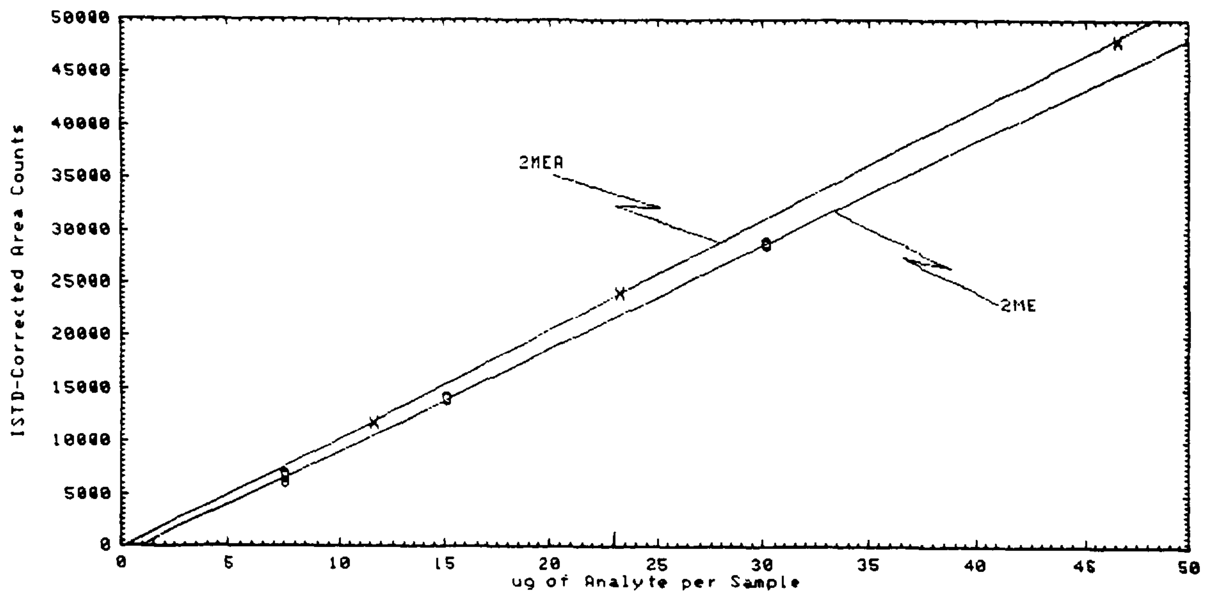


Figure 4.4.1 Instrument response to 2ME and 2MEA.

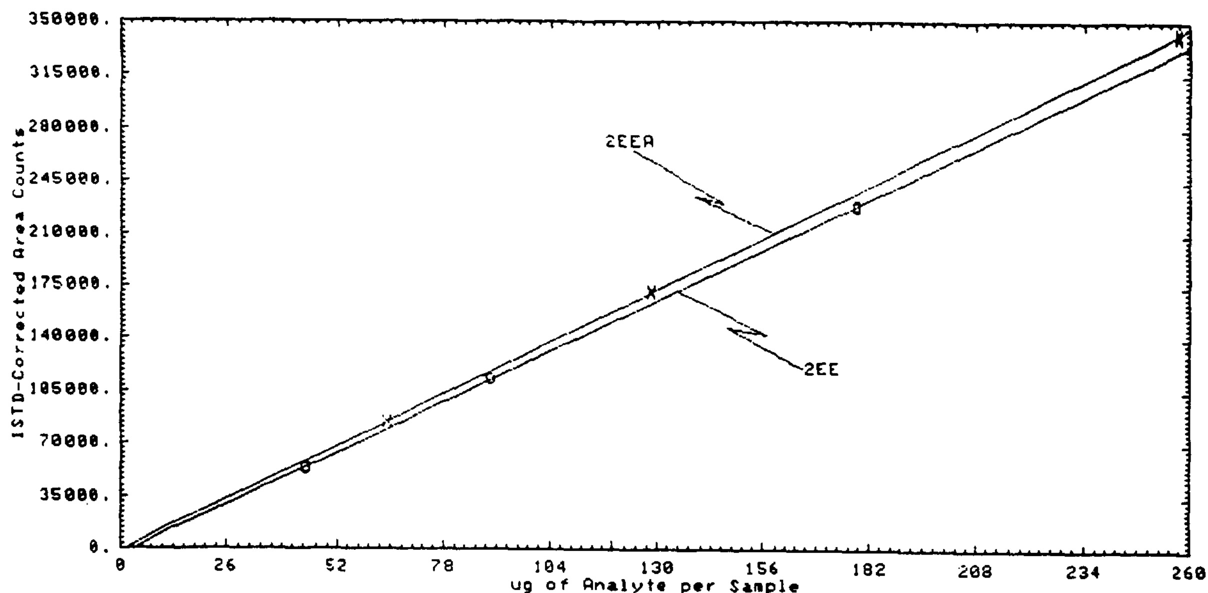


Figure 4.4.2 Instrument response to 2EE and 2EEA.

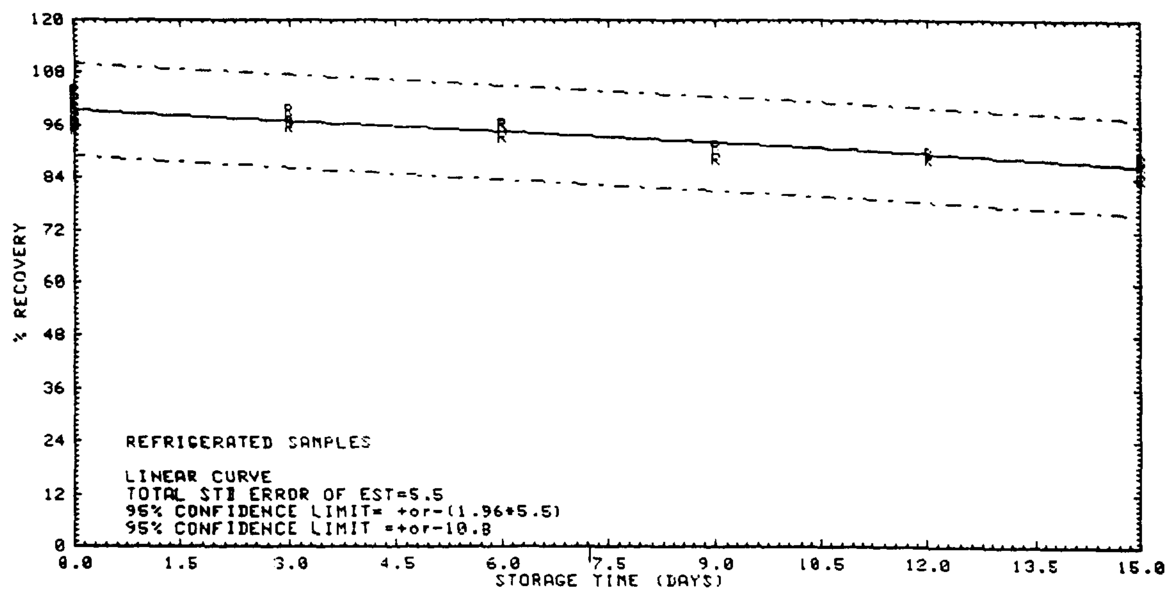


Figure 4.5.1.1 2ME refrigerated storage samples.

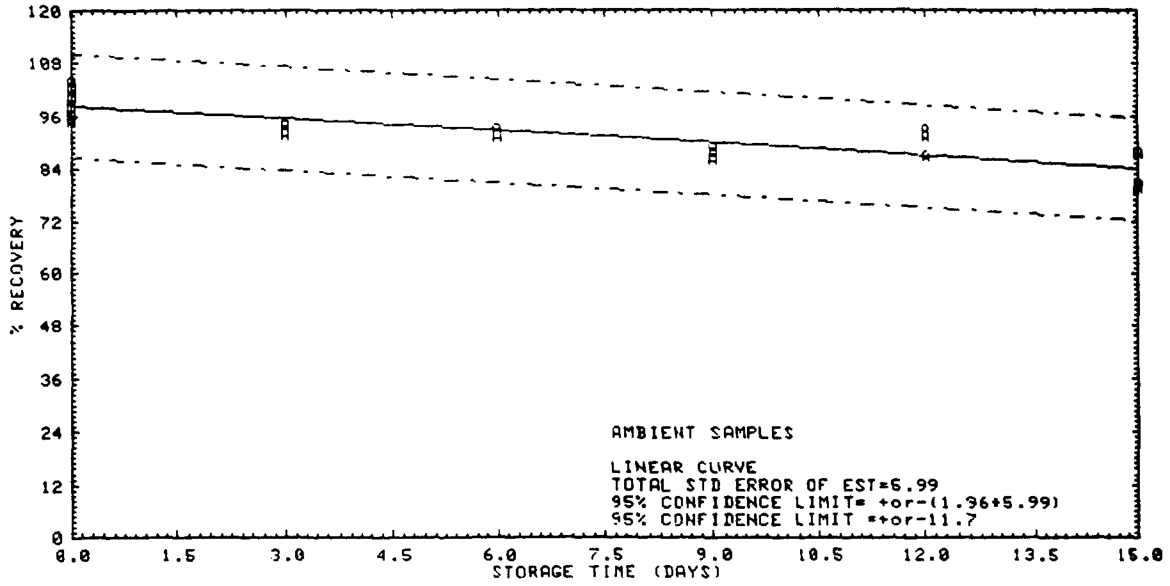


Figure 4.5.1.2 2ME ambient storage samples.

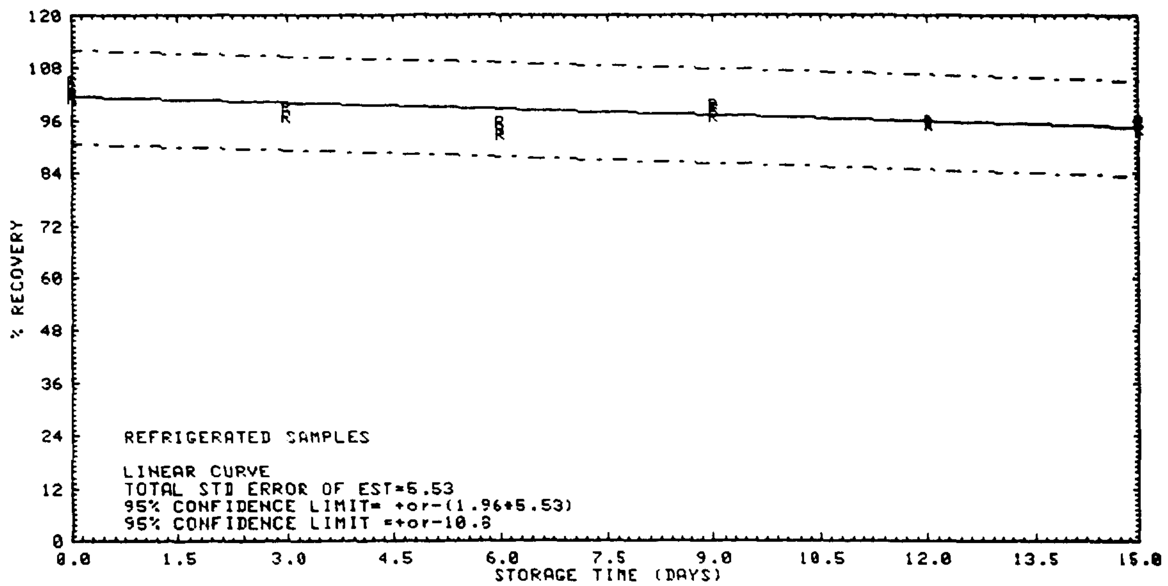


Figure 4.5.2.1 2MEA refrigerated storage samples.

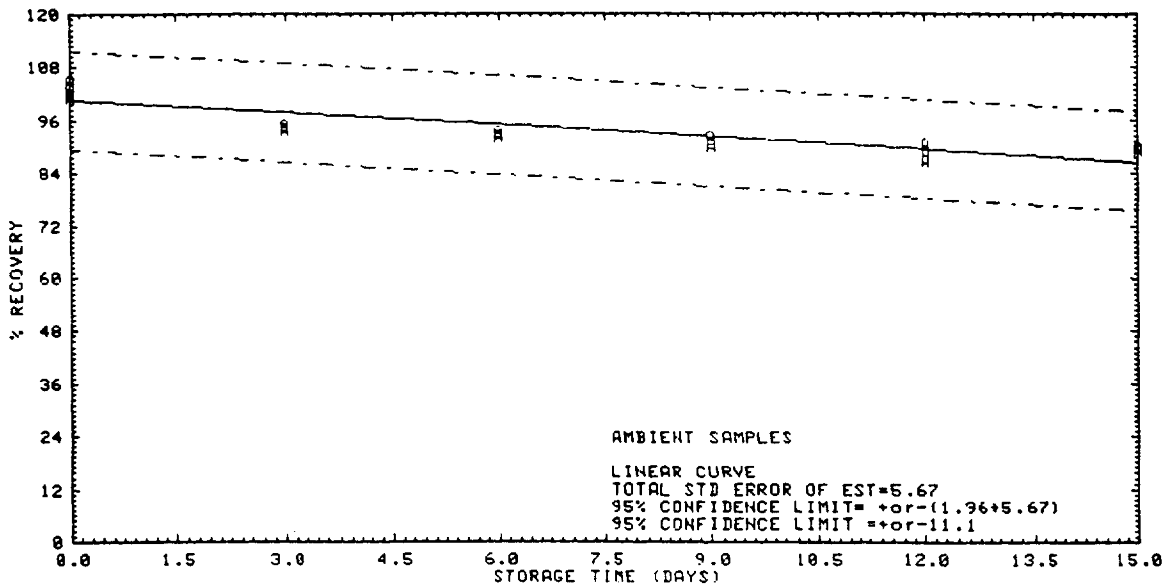


Figure 4.5.2.2 2MEA ambient storage samples.

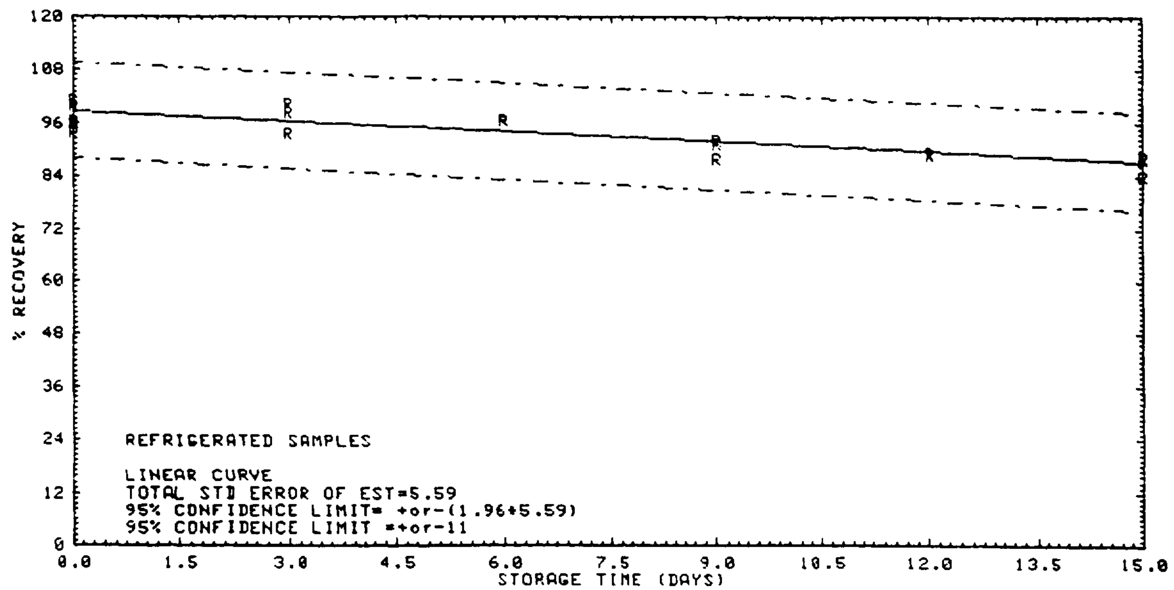


Figure 4.5.3.1 2EE refrigerated storage samples.

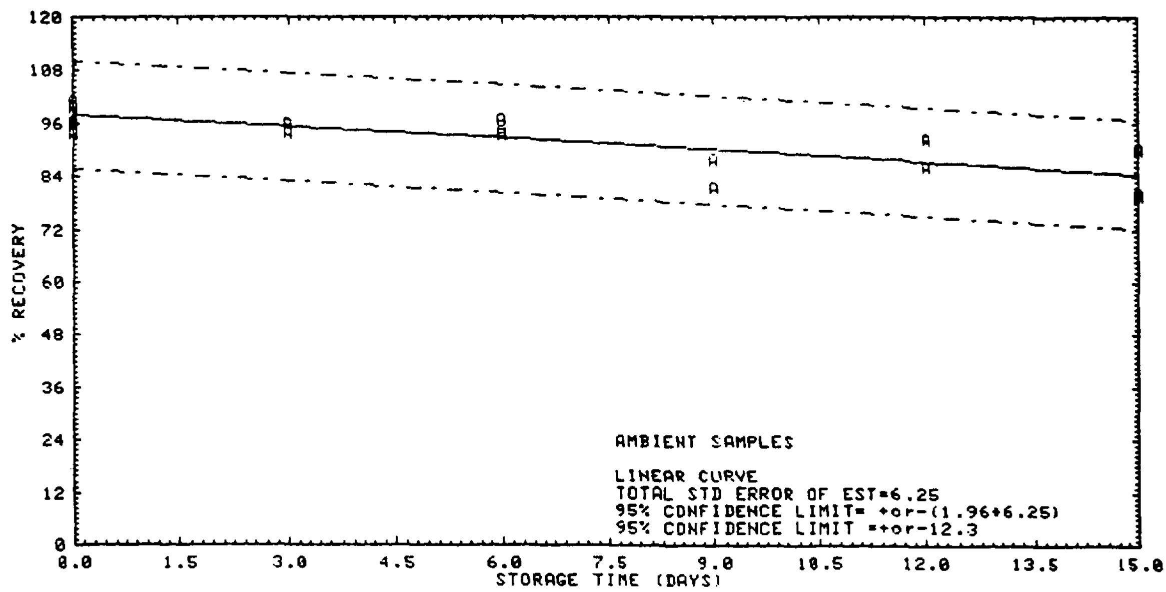


Figure 4.5.3.2 2EE ambient storage samples.

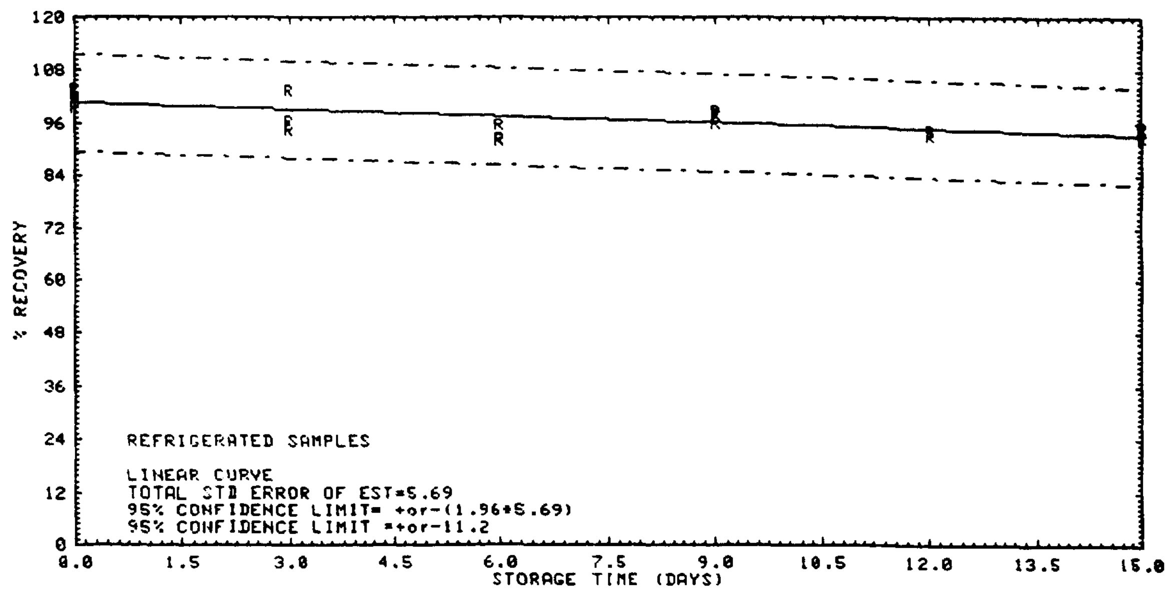


Figure 4.5.4.1 2EEA refrigerated storage samples.

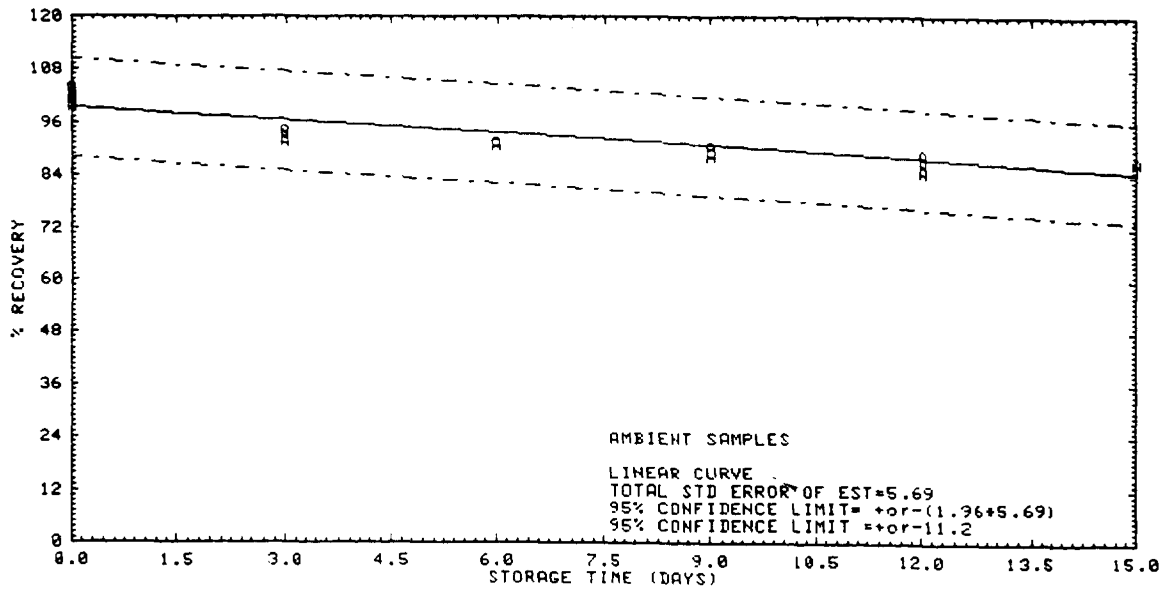


Figure 4.5.4.2 2EEA ambient storage samples.

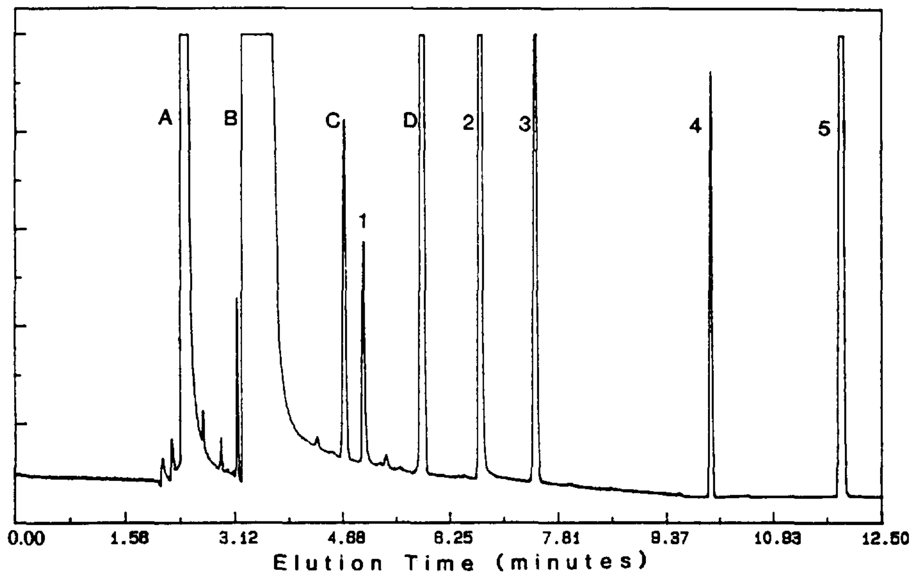


Figure 4.11 Chromatogram of a standard at the target concentrations. Key: (1) 2ME, (2) 2EE, (3) 3-methyl-3-pentanol, (4) 2MEA, (5) 2EEA. Other peaks: (A) methyl alcohol, (B) methylene chloride, (C) chloroform (impurity in methylene chloride), (D) cyclohexene (preservative in methylene chloride).

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UNION CARBIDE METHOD OF AIR MONITORING FOR GLYCOL ETHERS: DETERMINATION OF GLYCOL ETHERS IN AIR BY ADSORPTION ON ACTIVATED CHARCOAL AND PASSIVE DOSIMETERS WITH SUBSEQUENT ANALYSIS BY GAS CHROMATOGRAPHY†

INTRODUCTION

This bulletin details the air monitoring and analytical procedures used by Union Carbide Corporation in obtaining personal air samples to determine the degree of exposure, if any,

†Reprinted from an unpublished bulletin of the Union Carbide Corporation, Tarrytown, NY 10591.

of its employees to glycol ethers and glycol ether acetates. New information has been included in this booklet concerning the use of PASSIVE MONITORS as an alternate method to evaluate employee exposure. These PASSIVE MONITORS have become very popular recently because they are small, light-weight badges that are worn by the employee and do not require sampling pumps or other forms of calibration.

It is the intention of this bulletin to provide those who use glycol ethers or glycol ether acetates with all of the information available within Union Carbide in detecting and defining personal exposure to the chemicals. You are strongly urged to make use of this information to determine the degree of such exposure of your employees to these chemicals. This bulletin is designed as an aid to you in establishing and implementing your exposure limitation and reduction program.

METHOD

The method featured in this booklet can be used to measure several glycol ethers in the work environment. Union Carbide has confirmed the validity of the charcoal tube sampling method for:

Methyl CELLOSOLVE®
Methyl CELLOSOLVE® Acetate
CELLOSOLVE® Solvent
CELLOSOLVE® Acetate

while the Passive Dosimeter part of the method can be used for sampling:

Methyl CELLOSOLVE®
Methyl CELLOSOLVE® Acetate
CELLOSOLVE® Solvent

1. Principle

The sample is collected by drawing air through a glass tube containing activated charcoal (SKC-226-01) or by using a passive dosimeter (3M #3500 Organic Vapor Monitor) containing petroleum based carbon. The adsorbed glycol ethers and/or glycol ether acetates are then desorbed from the adsorbent with a 5% (v/v) methanol in methylene chloride solution and analyzed by gas chromatography with a flame ionization detector.

2. Range, Stability and Interference

This method has been validated for sampling air concentrations of the stated glycol ethers and their acetates from 2 to 25 ppm by volume in air. The method can be used for higher concentrations; however, the higher range has not been validated by Union Carbide.

Because some of the compounds may become hydrolyzed when sampled in high humidity atmospheres, the analysis of the charcoal tube samples must be completed within 24 hours

of the sampling. However, in the case of CELLOSOLVE® solvent, samples can be stored for up to 14 days in a refrigerator but should be analyzed within 90 minutes after desorption.

In the case of passive dosimeters, the sample may be refrigerated for up to five days prior to analysis without any significant loss.

The presence of other glycol ether vapor with similar molecular weights and vapor pressure may result in interference.

3. Instrument Parameters

Chromatograph	Hewlett-Packard 5830A or equivalent
Detector	Flame ionization
Column	3.05 m × 3.2 mm (10-ft × 1/8-inch) stainless steel packed with 5% FFAP on 80/100 mesh, acid washed DMCS Chromosorb W
Alternate column	Same as above except 10% FAPP loading
Temperatures	
Column	100°C
Detector	250°C
Injection Port	250°C
Carrier gas and flow rate	nitrogen at 30 cc per minute
Air flow rate	250 cc per minute
Hydrogen flow rate	20 cc per minute
Sample size	2 µL, solvent flush technique
Approximate retention time	Methyl CELLOSOLVE®: 2.45 min. Methyl CELLOSOLVE® acetate: 3.25 min. CELLOSOLVE® Solvent: 5.6 min. CELLOSOLVE® Acetate: 3.0 min.
Recorder	0-1 mV recorder or electronic integration

4. Apparatus

a) Personal sampling pump. MSA Model S, Sipin SP-2, SKC-222-3 or equivalent.

b) Charcoal tube. Coconut-Base, 150 mg. SKC Catalog, No. 226-01, SKC Inc. RDl, 395 Valley View Road, Eighty Four, PA 15330.

c) 3M Organic Vapor Monitor, #3500 3M Occupational Health and Safety Products Division, P.O. Box 33155, St. Paul, MN 55101.

d) Syringes, 10, 25, 100-µL Hamilton, or equivalent.

e) Pipets, 1 and 2-mL graduated, 1, 2, and 5-mL (Repipet' dispenser may be used to add desorption solvent to vials. Cat. No. 13-687-54, Fisher Scientific Co., or equivalent).

f) Balston DFU Grade B filter. Balston, Inc., P.O. Box C, 703 Massachusetts Ave., Lexington, MA 02173. The same filter is also available from DuPont Company, Applied Technology Division, Room B1275, Wilmington, DE 19898, Part No. P101.

g) Vials, 4.0-mL screw-capped septum, Cat., No. 2-2954, Supelco, Inc., Bellefonte, PA 16823 or equivalent.

h) Flasks, 10 and 100-mL, volumetric.

i) Rotameter, calibrated to measure flows in the 1000 cc per minute range or equivalent.

j) File, 3-corner for scoring sample tubes.

k) Wire, small diameter with hook formed at end to remove charcoal retainers from sample tube.

l) Sample tube holder, Size A, SKC Cat. No. 222-31, SKC, Inc., Eighty Four, PA or equivalent.

m) Soap film flow meter, 0-250 mL and 0-1000 mL to calibrate pumps and rotameter.

n) Developing vibrator, SKC Cat., No. 226-D-03-115, SKC, Inc., Eighty Four, PA or equivalent.

o) Sample tube opener. Tape a 4 × 6-inch piece of 1/2-inch plywood (or equivalent) to the top of a 6 × 6 × 6-inch cardboard box and drill a 7-mm hole through the plywood into the box.

p) 3M Organic Vapor Monitor Badge Sampling Chamber. Available from 3M, Occupational Health and Safety Division, P.O. Box 33155, St. Paul, MN 55101.

5. Reagents

a) Methanol, ACS Grade

b) Methylene Chloride ACS Grade

c) Methyl CELLOSOLVE®

d) Methyl CELLOSOLVE® Acetate

e) CELLOSOLVE® Solvent

f) CELLOSOLVE® Acetate

g) Nitrogen, high purity

h) Hydrogen, high purity

i) Compressed air-filtered

6. Sampling Procedure With Charcoal Tubes

a) Calibration of personal pumps: Each pump must be calibrated with a representative sample tube in line. This will minimize errors associated with uncertainties in the sample volume collected. Use soap film flowmeter to determine the sampling pump flow rate.

b) Immediately before sampling, break the tips of each tube to be used to provide openings of at least 2mm.

c) Attach the tube to a portable pump with the back-up section next to the pump by means of a piece of Tygon tubing of the desired length.

d) Long-term sampling: Set the air flow rate through the charcoal tube for 50 to 200 cc per minute. Collect 15 to 30 liters volume.

e) If a personal sample is to be taken, put the tube in an appropriate holder to protect the individual from the glass tube.

f) Record the stroke count, if using pump with counter, time, temperature, relative humidity, and barometric pressure when the air sampling is started.

g) At the end of the sample time stop the pump, seal the ends of the sample tube, record the stroke count, if required, and the time, temperature, relative humidity, and barometric pressure. Return the tube to the laboratory for analysis.

h) Short-term sampling. Flow rates of up to one liter per minute can be used to collect a sufficient quantity of the analyte to measure quantitatively. Use a MSA Model S personal pump or equivalent to obtain the flow rates.

i) Determine the actual flow rate through the charcoal tube by means of a soap film meter or a calibrated rotameter.

j) Record the flow rate, time, temperature, relative humidity and barometric pressure, when sampling is started.

k) At the end of the sampling period, recheck and record the flow rate, seal the ends of the tube, record the time, temperature, relative humidity, and barometric pressure and return the tube to the laboratory for analysis.

l) Sample tubes must be analyzed within 24 hours if stored at room temperature.

m) Break the tips from a tube at the same time the sample tubes are opened to be used as a blank. Cap, and return to the laboratory with the sample tubes.

7. Sampling Procedure with 3M Organic Vapor Monitors

a) Remove from protective pouch and clip monitor to lapel of worker near the breathing zone.

b) Record the time, temperature, relative humidity, and barometric pressure when the air sampling has started.

c) At the end of the sample time, remove the white face and retaining ring and snap on the elutriation cap. Firmly close both ports. Record the time, temperature, relative humidity, and barometric pressure.

d) Place monitor back in original package and seal.

e) Samples may be stored up to 5 days refrigerated before laboratory analysis.

f) Remove a monitor from the pouch at the same time the sample monitors are removed to be used as a blank. Reseal immediately and return to the laboratory with the sample monitors.

8. Analytical Procedure For Charcoal Adsorption Tubes

a) Wash all glassware with hot soapy water and rinse with distilled water followed by acetone. Air- or oven-dry to remove all traces of acetone.

b) Score the sample tube between the end and the primary section retainer and break off the end of the tube in the tube opener (care must be exercised to prevent loss of the bent wire retainer and possible loss of the glass wood and charcoal).

c) Make a small hook at the end of a piece of wire and remove the glass wool retainer plug and discard. Make sure no charcoal particles adhere to the glass wool plug.

d) Transfer the charcoal from the primary section and back-up section of the tube into separate Supelco desorption vials. Cool in wet ice 5 minutes while capped.

e) Pipet 5 mL of methanol into 95 mL of methylene chloride and mix well. Pipet 1.0 mL of this solvent into each desorption vial and cap securely.

f) Shake or vibrate gently for 30 minutes.

g) Solvent flush injection technique. This injection technique is designed to eliminate difficulties arising from blow-back or distillation within the needle of the microliter syringe.

h) Flush a 10-μL syringe with the methanol-methylene chloride desorption solution several times to wet the barrel and plunger.

i) Draw a 1 μL of methanol-methylene chloride solution into the syringe and remove the tip of the needle from the solution. Withdraw the plunger and additional 0.5 μL to separate the methanol-methylene chloride from the sample with a pocket of air.

j) Dip the needle into the sample solution in the desorption vial and withdraw the plunger until the air bubble between the solvent and the sample has passed the 3-μL mark on the syringe.

k) Remove the top of the needle from the sample solution and adjust the volume in the syringe until the meniscus of the air bubble rests on the 3-μL mark. Remove the excess sample solution from the tip of the needle.

l) Pull the plunger back an additional 0.5 μL to prevent the sample solution from evaporating from the tip of the needle.

m) Inject the entire contents of the syringe into the chromatograph.

n) Measure the peak area or height and determine the organic content from a previously prepared calibration curve.

o) Analyze the backup (small) section of charcoal tube in the same manner as the primary.

p) Analyze the blank tube in the same manner as the sample tube.

9. Analytical Procedure For 3M Organic Vapor Monitors

a) Open the center elutriation port and inject 1.5 mL of 5μ MeOH as CH_2Cl_2 with a syringe.

b) Close the center port and allow to elutriate for 1/2 hour with occasional gentle agitation. Be sure to not let any desorption solvent get on the elutriation cap.

c) Solvent flush injection technique. This injection technique is designed to eliminate difficulties arising from blow-back or distillation within the needle of the microliter syringe.

d) Flush a 10-µL syringe with the methanol-methylene chloride desorption solution several times to wet the barrel and plunger.

e) Draw 1 µL of methanol-methylene chloride solution into the syringe and remove the tip of the needle from the solution. Withdraw the plunger an additional µL to separate the methanol-methylene chloride from the sample with a pocket of air.

f) Dip the needle into the center elutriation port and withdraw the plunger until the air bubble between the solvent and sample has passed the 2-µL mark on the syringe.

g) Remove the top of the needle from the sample solution and adjust the volume in the syringe until the meniscus of the air bubble rests on the 3-µL mark. Remove the excess sample solution from the tip of the needle.

h) Pull the plunger back an additional 0.5 µL to prevent the sample solution from evaporating from the tip of the needle.

i) Inject the entire contents of the syringe into the chromatograph.

j) Measure the peak area or height and determine the organic content from a previously prepared calibration curve.

k) Analyze the blank monitor in the same manner as the sample monitor.

10. Calibration Curve

a) Determine quantities of analyte required to prepare standards in desired range based on a 15 liter sample by referring to Table A.

b) Inject standards in the chromatograph using the solvent flush procedure described in the analytical procedure.

c) Plot peak height or area versus micrograms of analyte per mL.

11. Desorption Efficiency

a) Desorption efficiency (percentage of adsorbed analyte desorbed from the charcoal by the desorbing solution) can vary from one laboratory to another and from one batch of charcoal to another.

b) Make up an analyte (glycol ether or acetate sampled) standard in the desorption solvent that will allow injection of 2 to 10 microliters of standard to cover the range desired. Use a 10 mL syringe to inject the standard in the charcoal and 3M Organic Vapor Monitor.

c) Calculate the microliters of analyte (glycol ether or acetate sampled) standard to be added to the adsorption tube based on a 15 liter sample of 0.5, 1.0 and 2.0 times the TLV-TWA or the expected concentration using the following equation:

$$\frac{\text{TLV or TWA} \times V \times MW}{G \times 24.450} = A_S$$

A_S	= µL of analyte to be added to the selected volume of solvent to produce a solution of the desired ppmv
G	= specific gravity of analyte at temperature being measured (specific gravity at 20/20°C ± Δ sp. gr. / Δ T × temperature difference)
MW	= molecular weight of analyte
TLV or TWA	= threshold limit value - time weighted average in ppm
V	= volume of air sample in liters
24.450	= molar volume (mL per mole) at 25°C and 101.3 kPa (760 mm of Hg)

d) The recommended number of tubes at each level is six plus three blanks for a total of twenty-one tubes. Tubes used for the desorption efficiency study ***must*** be of the same lot that will be used for monitoring the work place. If practical, analyte should be added to the front of the primary section of charcoal in the tube and humidified air (to approximate work place air) pulled across the tube to total twenty liters at flow rates up to 500 cc per minute by personal pumps or a vacuum manifold. Air can be humidified by passing cylinder air through three bubblers in series containing distilled water and directing the eluent into a sampling chamber. Total flow in the chamber must be more than that being withdrawn through the tubes. If this proves impractical, 100 mg of charcoal from the tubes may be transferred to each of a sufficient number of desorption vials (twenty-one), the analyte added, the vials capped and allowed to stand overnight to allow the analyte to permeate the charcoal. Analysis is accomplished using the procedure in Section 10.

e) The recommended number of 3M Organic Vapor Monitors at each level is six plus three blanks for a total of 21 monitors. The monitors used for the desorption efficiency study ***must*** be of the same lot that will be used for monitoring the work place. If practical, analyte should be added to the monitor through the white face onto the charcoal pad. Humidified air (to approximate work place air) is pulled across the monitor to total fifteen liters at flow rates up to 500 cc per minute by a 3M Organic Vapor Monitor Badge Sampling Device. Air can be humidified by passing cylinder air through three bubblers in series containing distilled water and directing the eluent into a sampling chamber. Total flow into the chamber must be more than that being withdrawn through the monitors. Analysis is accomplished using the procedure in Section 11.

f) Calculation of the desorption efficiency

$$\frac{A-B}{S} = DE$$

A = average peak area or peak height of sample
B = average peak area or peak height of blank
DE = desorption efficiency
S = average peak area or peak height of standard

Plot the description efficiency versus the µg/mL found.

12. Calculations

a) Read the weight in µg/mL corresponding to each peak area or height from the calibration curve and convert to total micrograms by multiplying the µg/mL by the desorbant volume in milliliters.

b) Correct each sample weight for the blank.
µg sample - µg blank = µg sample, corrected
µg sample = µg found in front section of sample tube
µg blank = µg found in front section of blank tube

c) Follow a similar procedure for the back-up section.

d) Add the amounts present in front and back-up sections to determine the total weight in the sample.

e) Read the desorption efficiency (DE) from the DEC curve for the amount found in the sample tube. Divide the total weight by the DE to obtain the corrected µg/sample.

$$\frac{\text{Total Weight}}{DE} = \text{corrected µg/sample}$$

DE = desorption efficiency
Total Weight = µg of analyte found in the front section of the sample tube - µg found in the front section of the blank tube + µg of analyte found in the backup section of the sample tube.

f) Correct the volume of air sampled to standard conditions of 25°C and 760 mm of pressure.

$$\frac{V \times P \times 298}{760 \times (T+273)} = \text{volume of sample in liters at 25° C and 760 mm of pressure}$$

P = barometric pressure in mm of mercury
T = temperature (°C) of air sampled
V = volume of air sample in liters as measured
760 = standard pressure in mm of mercury
298 = standard temperature (°K)

NOTE: The sampling rate for the 3M Organic Vapor Monitors has been determined by 3M as being 36.3 cc/min for methyl CELLOSOLVE®, 29.0 cc/min for methyl CELLOSOLVE® acetate, and 32.2 cc/min for CELLOSOLVE® Solvent.

g) The concentration of the analyte in the air sampled can be expressed in milligrams per cubic meter.

$$\frac{\text{Corrected micrograms}}{\text{Air volume samples (liters)}} = \text{mg/m}^3$$

h) Another way of expressing concentration is ppmv.

$$\frac{\text{mg/m}^3 \times 24.45}{\text{MW}} = \text{ppmv}$$

MW = molecular weight (g/mole) of the analyte
24.45 = molar volume (liters/mole) at 25° C and 760 mm of pressure

13. Other Relevant Information

The National Institute for Occupational Safety and Health has published other sampling and analytical methods for glycol ethers. The recently consolidated NIOSH Manual of Analytical Methods, Vol. 1 contains Method #1403, which can be used for Methyl CELLOSOLVE® and CELLOSOLVE® Solvent while Method #1450 can be used for CELLOSOLVE® Acetate. It is also stated in this manual that NIOSH intends to revise their previously published method for Methyl CELLOSOLVE® Acetate (S39).

In addition to the 3M #3500 Organic Vapor Monitoring Badge, passive dosimeter badges from other manufacturers, such as Dupont's Pro-Tek® Organic Badge, may also be used for monitoring glycol ethers. Please contact the manufacturer for information concerning the suitability of their monitors for specific glycol ethers or glycol ether acetates.

Some firms are also known to provide analytical services for these monitors for specific chemicals, including glycol ethers. This may be useful for some of the smaller locations which do not have air sampling equipment and/or on-site analytical capabilities of their own. Further information about the NIOSH methods or passive monitors may be obtained from the NIOSH regional office or equipment manufacturer.

Further information on this subject or the Union Carbide method may be obtained from

Union Carbide Corporation
Saw Mill River Road
Route 100 C
Tarrytown, NY 10591
(914) 789-2232

TABLE A
Calibration Curve Standards

Analyte	Molecular weight	Specific gravity at 25°C	Microliters for 10 mL solvent	Micrograms per mL	Air conc.(ppm), 15-liter sample
CELLOSOLVE® Acetate	132.16	0.9708	1.4	136	1.7
			4.2	408	5.0
			8.4	815	10.0
			21.0	2,039	25.1
CELLOSOLVE® Solvent	90.12	0.9269	1.0	93	1.7
			3.0	278	5.0
			6.0	556	10.1
			15.0	1,390	25.1
Methyl CELLOSOLVE®	76.10	0.9617	0.8	77	1.6
			2.4	231	4.9
			4.8	462	9.9
			12.2	1,173	25.1
Methyl CELLOSOLVE® Acetate	118.13	1.0012	1.2	120	1.7
			3.6	360	5.0
			7.2	721	9.9
			18.0	1,802	24.9