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 L at 0.1 L/min for TWA samples
15 L at 1.0 L/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.

Date: January 1990 Chemist: Carl J. Elskamp

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OSHA Analytical Laboratory
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1. General Discussion

1.1 Background

1.1.1 History

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 L to 48 L. This allows for lower detection limits and increases the TWA sampling time to a more convenient 480 min (8 h) when sampling at 0.1 L/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. 5.2-5.5), 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 embryo-toxicity 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)

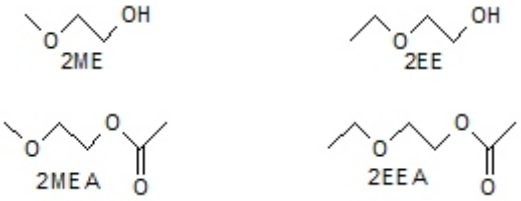
2MEA- It is used in photographic films, lacquers, textile printing, and as a solvent for waxes, oils, various gums and resins, cellulose acetate, and nitrocellulose. (Ref. 5.3)

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, 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:



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:	colorless	colorless	colorless	colorless
sp gr:	0.9663	1.005	0.931	0.975
vp [kPa (mmHg) at 20 °C]:	0.8 (6)	0.3 (2)	0.49 (3.7)	0.3 (2)
flash pt.: (°C, CC)	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
higher:	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.

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 L/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 h (>70 L). (This data was 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 h (>60 L) with no breakthrough detected. (This data was 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 h. (Section 4.10)

2.6 Recommended air volume and sampling rate

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

2.6.2 For short-term samples, the recommended air volume is 15 L collected at 1.0 L/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 µg/m^3) for 2ME when 15 L 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 × O.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 HB062777 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/L.

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

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

where 24.46 = molar volume (L) 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 4.2.1-4.2.4.

Table 4.2.1
Detection Limit of the 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 the 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 the 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 the 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 1O0-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 4.3.1-4.3.4.

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

percent recovered	statistics
90.8	
94.5	mean = 97.1
95.7	SD = 5.3
98.2	Precision = (1.96)(±5.3)
106.7	= ±10.4
96.9	

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

percent recovered	statistics
95.5	
98.0	mean = 98.8
96.2	SD = 2.6
100.5	Precision = (1.96)(±2.6)
100.5	= ±5.1
102.0	

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

percent recovered	statistics
93.8	
95.1	mean = 97.5
93.8	SD = 4.3
104.9	Precision = (1.96)(±4.3)
100.0	= ±8.4
97.6	

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

percent recovered	statistics
97.1	
102.9	mean = 102.3
98.1	SD = 3.8
103.9	Precision = (1.96)(±3.8)
105.8	= ±7.4
105.8	

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 4.4.1-4.4.4 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.

Table 4.4.1
Instrument Response to 2ME

× target concn	0.5×	1.0×	2.0×
µg/sample	7.537	15.07	30.15
ppm	0.050	0.101	0.202
area counts	6930.6	14033	29007
	68.32.1	14219	28908
	6771.4	14139	28920
	6655.9	14133	28691
	6202.5	14165	28834
	6786.0	14176	28887
mean	6696.4	14144	28874

Table 4.4.2
Instrument Response to 2MEA

× target concn	0.5×	1.0×	2.0×
µg/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
mean	11925	24154	48228

Table 4.4.3
Instrument Response to 2EE

× target concn	0.5×	1.0×	2.0×
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
mean	54186	113246	229326

Table 4.4.4
Instrument Response to 2EEA

× target concn	0.5×	1.0×	2.0×
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
mean	84710	171457	342362

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-h 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 L/min (12-L samples). (Note: To test the performance of the sampler for 48-L volumes and to show the validity of collecting 12-L samples at 4 times the target concentrations instead of 48-L samples at the target concentrations, a set of six 48-L 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, six samples were analyzed immediately after generation, fifteen were stored in a refrigerator at 0°C and fifteen 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 three-day intervals over a period of fifteen days. The results are given in Tables 4.5.1-4.5.4 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 4.5.1
Storage Test of 2ME

time (days)	percent recovery (ambient)			percent recovery (refrigerated)		
0	97.8	102.0	96.3	97.8	102.0	96.3
	99.9	104.2	94.8	99.9	104.2	94.8
3	93.7	91.7	94.2	96.8	99.5	95.9
6	92.8	91.4	92.8	96.3	96.6	93.3
9	86.1	88.8	87.5	91.4	88.8	91.4
12	91.3	93.1	86.9	89.9	89.8	88.7
15	87.8	79.8	80.7	87.4	88.8	84.4

Table 4.5.2
Storage Test of 2MEA

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

Table 4.5.3
Storage Test of 2EE

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

Table 4.5.4
Storage Test of 2EEA

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

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 4.6.1-4.6.4. These tables are based on the data presented in Section 4.4.

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

× target concn	0.5×	1.0×	2.0×
µg/sample	7.537	15.07	30.15
ppm	0.050	0.101	0.202
SD[1]	257.9	62.5	106.0
CV	0.0385	0.0044	0.0037
$\overline{CV}$	0.022		

1 - in area counts

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

× target concn	0.5×	1.0×	2.0×
µg/sample	11.66	23.32	46.63
ppm	0.050	0.101	0.201
SD[1]	84.7	48.2	73.6
CV	0.0071	0.0020	0.0015
$\overline{CV}$	0.004		

1 - in area counts

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

× target concn	0.5×	1.0×	2.0×
µg/sample	44.69	89.38	178.8
ppm	0.253	0.505	1.01
SD[1]	175.6	194.8	485.7
CV	0.0032	0.0017	0.0021
$\overline{CV}$	0.002		

1 - in area counts

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

× target concn	0.5×	1.0×	2.0×
µg/sample	64.35	128.7	257.4
ppm	0.248	0.496	0.992
SD[1]	160.0	269.3	830.3
CV	0.0019	0.0016	0.0024
$\overline{CV}$	0.002		

1 - in area counts

4.7 Precision (overall procedure)

The precision of the overall procedure is determined from the storage data. The determination of the standard error of estimate (SEE) for a regression line plotted through the graphed storage data allows the inclusion of storage time as one of the factors affecting overall precision. The SEE is similar to the standard deviation, except it is a measure of dispersion of data about a regression line instead of about a mean. It is determined with the following equation:

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

where n = total number of data points
k = 2 for linear regression
k = 3 for quadratic regression
Y_{obs} = observed percent recovery at a given time
Y_{est} = estimated percent 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 L/min. The samples were stored in a refrigerator for 12 days before being analyzed. The results are presented in Tables 4.8.1-4.8.4.

Table 4.8.1
Reproducibility Data for 2ME

µg spiked	µg recovered	percent recovered	percent deviation
14.59	14.90	102.1	2.1
15.36	15.21	99.0	-1.0
14.93	15.06	100.9	0.9
15.38	15.42	100.3	0.3
15.07	15.41	102.3	2.3
15.54	15.88	102.2	2.2

Table 4.8.2
Reproducibility Data for 2MEA

µg spiked	µg recovered	percent recovered	percent deviation
23.35	21.61	92.5	-7.5
22.77	20.33	89.3	-10.7
23.12	21.47	92.9	-7.1
22.84	21.51	94.2	-5.8
23.87	22.44	94.0	-6.0
24.01	22.48	93.6	-6.4

Table 4.8.3
Reproducibility Data for 2EE

µg spiked	µg recovered	percent recovered	percent deviation
85.55	83.47	97.6	-2.4
90.07	88.22	97.9	-2.1
87.57	84.10	96.0	-4.0
90.20	86.57	96.0	-4.0
88.40	84.79	95.9	-4.1
91.16	88.90	97.5	-2.5

Table 4.8.4
Reproducibility Data for 2EEA

µg spiked	µg recovered	percent recovered	percent deviation
129.9	117.3	90.3	-9.7
126.7	118.1	93.2	-6.8
128.6	117.5	91.4	-8.6
127.1	117.4	92.4	-7.6
132.8	122.8	92.5	-7.5
133.6	121.9	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	2ME			2MEA		
× target concn	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
average		95.8			97.9	

Table 4.9.2
Desorption Efficiency Data for 2EE and 2EEA

analyte	2EE			2EEA		
× target concn	0.5×	1×	2×	0.5×	1×	2×
µg/sample	44.69	89.38	178.8	64.35	128.7	257.4
ppm	0.253	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
average		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

	% desorption after 24 h			
sample no.	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 Figures 4.11. The chromatogram is from an injection of a standard equivalent to a 48-L air sample at the target concentrations.

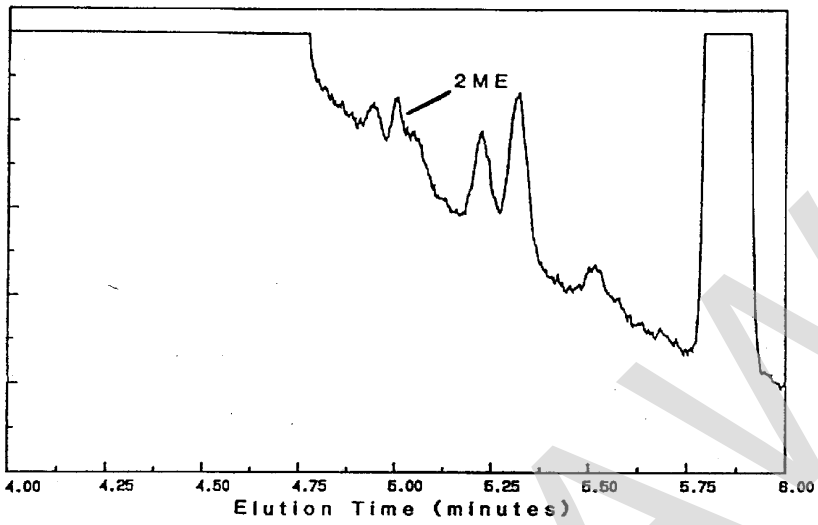


Figure 4.1.1. Detection limit chromatogram for 2ME.

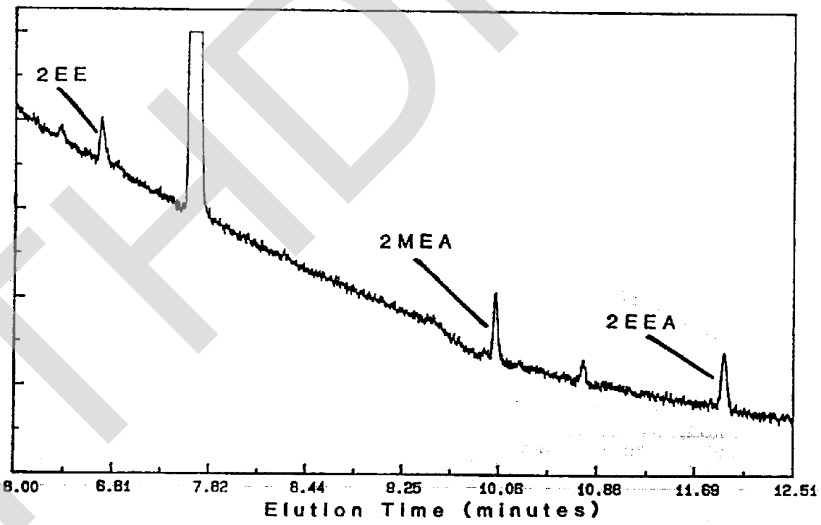


Figure 4.1.2. Detection limit chromatogram for 2MEA, 2EE, and 2EEA.

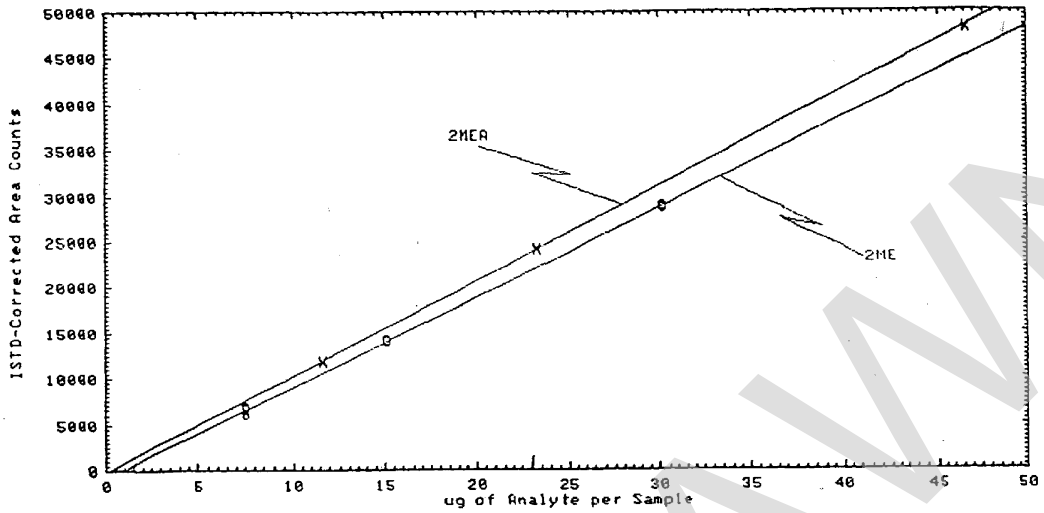


Figure 4.4.1. Instrument response to 2ME and 2MEA.

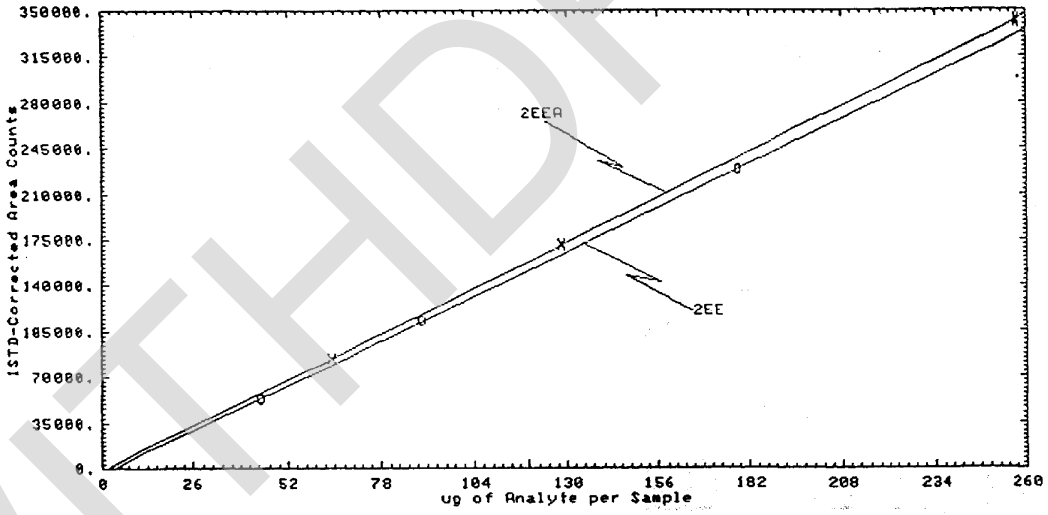


Figure 4.4.2. Instrument response to 2EE and 2EEA.

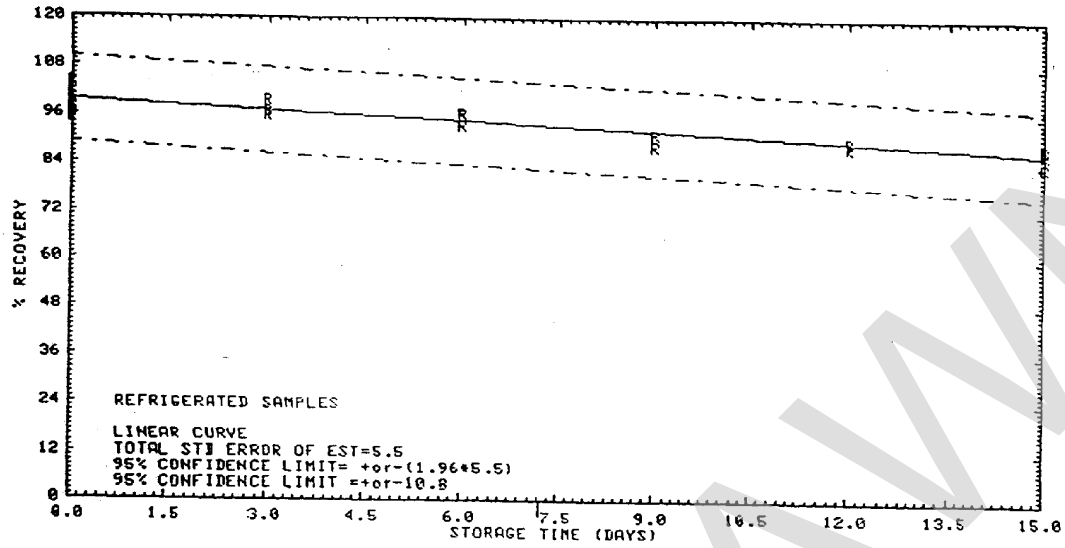


Figure 4.5.1.1. 2ME refrigerated storage samples.

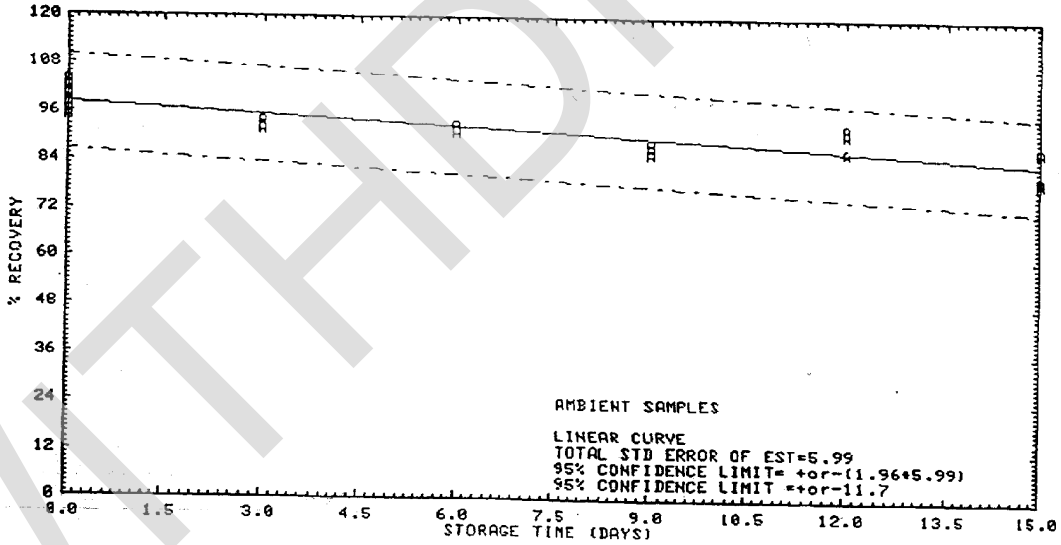


Figure 4.5.1.2. 2ME ambient storage samples.

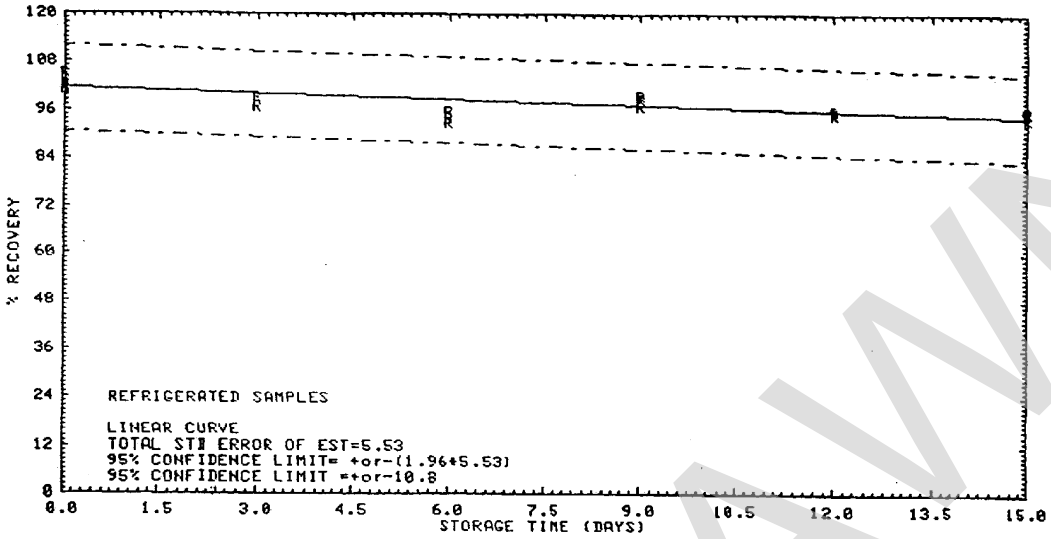


Figure 4.5.2.1. 2MEA refrigerated storage samples.

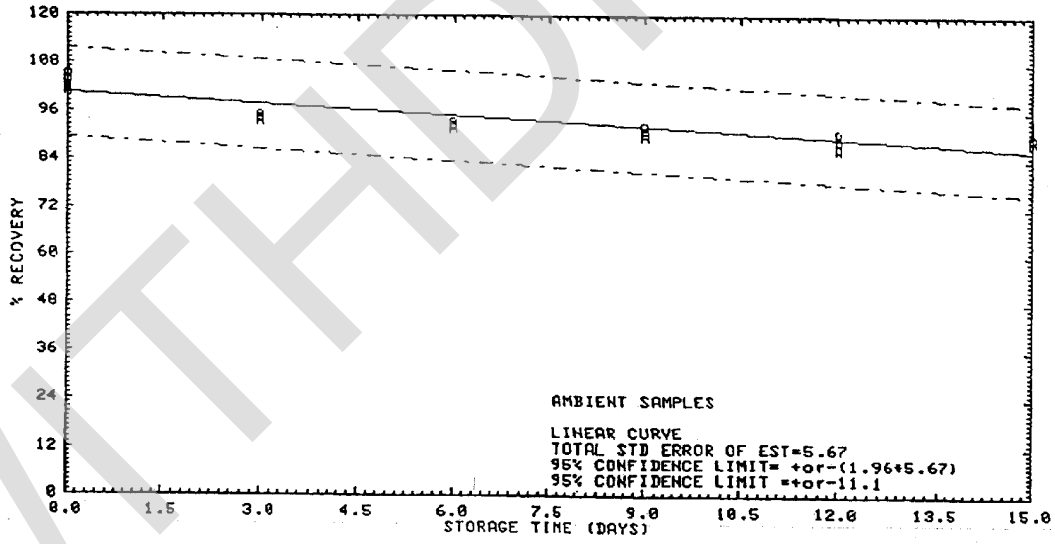


Figure 4.5.2.2. 2MEA ambient storage samples.

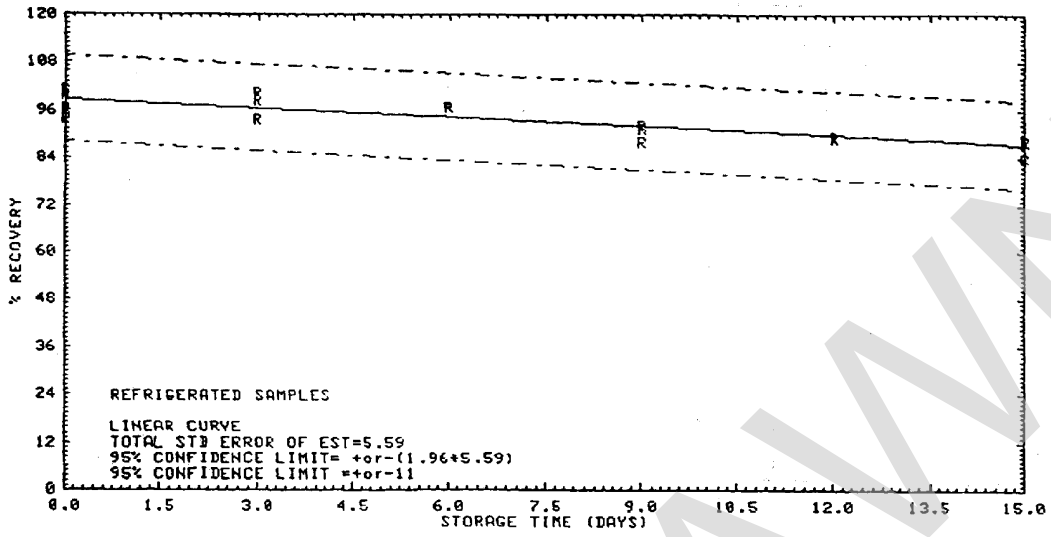


Figure 4.5.3.1. 2EE refrigerated storage samples.

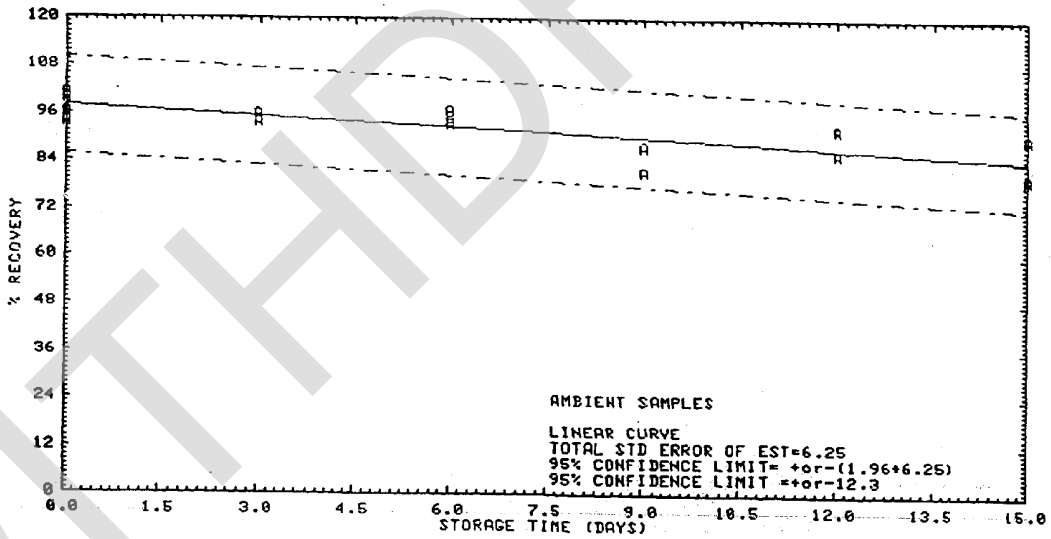


Figure 4.5.3.2. 2EE ambient storage samples.

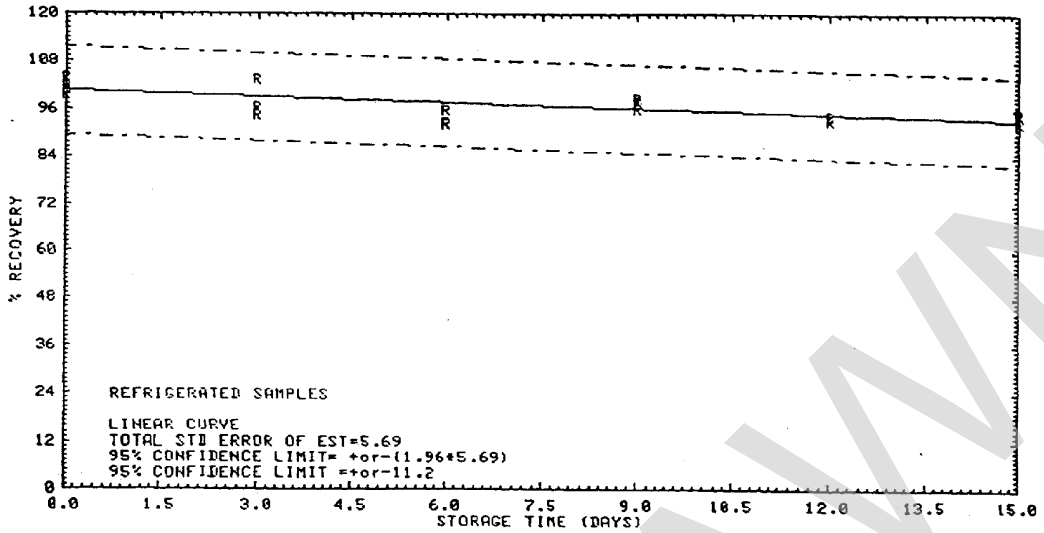


Figure 4.5.4.1. 2EEA refrigerated storage samples.

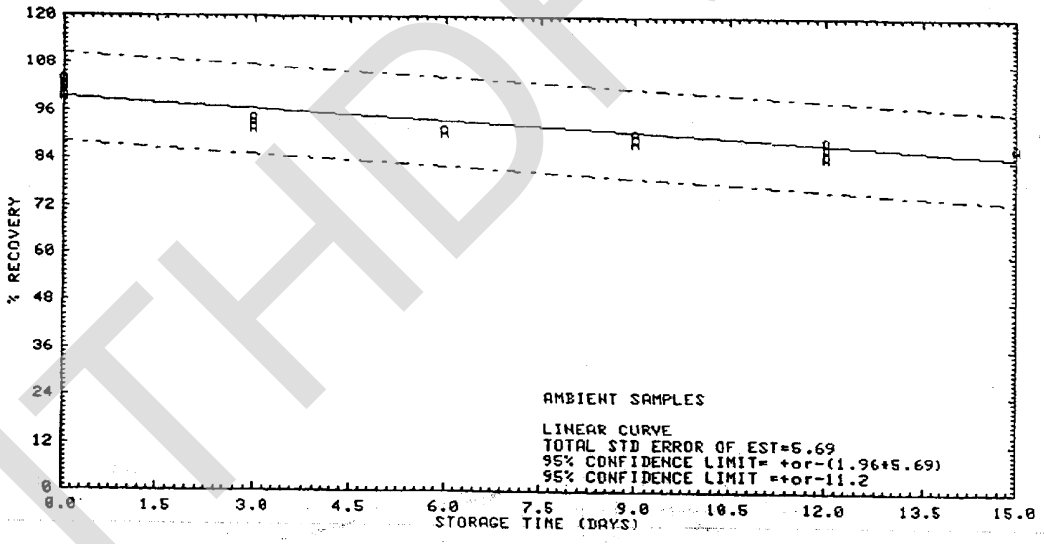


Figure 4.5.4.2. 2EEA ambient storage samples.

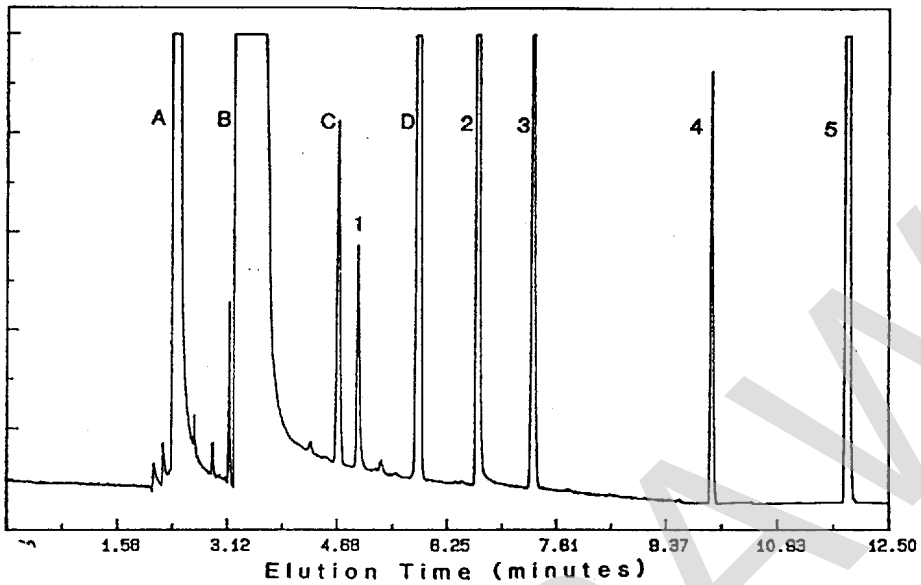


Figure 4.11. Chromatogram of a standard at the target concentrations. Key: (1) 2ME, (2) 2EE, (3) 3-methyl-3-pentanol, (4) 2MEA, (5) 2EEA. Other peaks: (A) methyl alcohol, (B) methylene chloride, (C) chloroform (impurity in methylene chloride), (D) cyclohexene (preservative in methylene chloride).

5. References

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