APPENDIX A

METHODS FOR SAMPLING AND ANALYSIS OF EGBE AND EGBEA IN AIR*

A.1 GENERAL REQUIREMENTS FOR SAMPLING

The air samples collected represent the air a worker breathes while performing each job or 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.

NIOSH METHOD NO. 1403 FOR 2-BUTOXYETHANOL

FORMULA: Table 1 — ALCOHOLS IV

METHOD: 1403

M.W.: Table 1 — ISSUED: 2/15/84

OSHA/NIOSH/ACGIH: Table 1 — PROPERTIES: Table 1

COMPOUND and SYNONYM:
(1) 2-Methoxyethanol: [Methyl Cellosolve; CAS #109-86-4];
(2) 2-Ethoxyethanol: [Cellosolve; CAS #110-80-5]; and
(3) 2-Butoxyethanol: [Butyl Cellosolve; CAS #111-76-21].

SAMPLING

SAMPLER: SOLID SORBENT TUBE (coconut shell charcoal, 100 mg/50 mg)

FLOW RATE: 0.01 to 0.05 L/min

	(1) & (3)	(2)
VOL-MIN:	1 L	1 L
-MAX:	10 L	6 L

SHIPMENT: routine

SAMPLE STABILITY: store in freezer; analyze as soon as possible

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: see EVALUATION OF METHOD

BIAS: not significant [1,2]

OVERALL PRECISION (s_r): see EVALUATION OF METHOD

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, FID

ANALYTE: compounds above

DESORPTION: 1 mL 5% methanol in CH_2Cl_2

INJECTION VOLUME: 5 μL

TEMPERATURE-INJECTION: 200°C
-DETECTOR: 250-300°C
-COLUMN: (1) 95°C;
(2) 140°C;
(3) 145°C

CARRIER GAS: N_2 or He, 30 mL/min

COLUMN: glass, 3 m x 2 mm ID, 10% SP-1000 on 80/100 mesh Chromosorb WHP, or equivalent

CALIBRATION: solutions of analyte in eluent with internal standard

RANGE AND PRECISION: see EVALUATION OF METHOD

ESTIMATED LOD: 0.01 to 0.02 mg per sample [3]

ALCOHOLS IV METHOD: 1403

APPLICABILITY: This method may be used to determine two or more analytes simultaneously by varying GC conditions (e.g., temperature programming).

INTERFERENCES: High humidity reduces sampling capacity. The methods were validated using a 3 m x 3 mm stainless steel column packed with 10% FFAP on Chromosorb W-AW; other columns with equal or better resolution (e.g., capillary) may be used. Less volatile compounds may displace more volatile compounds on the charcoal.

OTHER METHODS: This method combines and replaces Methods S79 [4], S361 [5], and S76 [4].

REAGENTS:

1. Eluent: methylene chloride with 5% (v/v) methanol and 0.2% (v/v) 1-heptanol, 0.1% (v/v) ethyl benzene or other suitable internal standard.
2. Analyte.
3. Nitrogen, purified.
4. Hydrogen, prepurified.
5. Air, compressed, filtered.

EQUIPMENT:

1. Sampler: glass tube, 7 cm long, 6 mm OD, 4 mm ID, flame-sealed ends, containing two sections of activated (600°C) coconut shell charcoal (front=100 mg; back=50 mg) separated by a 2-mm urethane foam plug. A silylated glass wool plug precedes the front section and a 3-mm urethane foam plug follows the back section. Pressure drop across the tube at 1 L/min airflow must be less than 3.4 kPa. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 0.05 L/min, with flexible connecting tubing.
3. Gas chromatograph, FID, integrator and column (page 1403-1).
4. Vials, glass, 2-mL, PTFE-lined crimp caps.
5. Syringe, 10-μL, readable to 0.1 μL.

SPECIAL PRECAUTIONS: None.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 0.05 L/min for a total sample size of 1 to 10 L (2-methoxyethanol and 2-butoxyethanol) or 1 to 6 L (2-ethoxyethanol). NOTE: Maximum flow rate for 2-methoxyethanol and 2-butoxyethanol is 0.2 L/min.
4. Cap the samplers with plastic (not rubber) caps and pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool and foam plugs.
6. Add 1.0 mL eluent to each vial. Attach crimp cap to each vial.
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least five working standards over the range 0.02 to 8 mg analyte per sample.
   a. Add known amounts of analyte to eluent in 10-mL volumetric flasks and dilute to the mark.
   b. Analyze together with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph (ratio of peak area of analyte to peak area of internal standard vs. mg analyte).
9. Determine desorption efficiency (DE) at least once for each batch of charcoal used for sampling in the calibration range (step 8). Prepare three tubes at each of five levels plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount of analyte directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze together with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. mg analyte recovered.
10. Analyze three quality control blind spikes and three analyst spikes to insure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1403-1. Inject sample aliquot manually using solvent flush technique or with autosampler.

NOTE: If peak area is above the linear range of the working standards, dilute with eluent, reanalyze and apply the appropriate dilution factor in calculations.

12. Measure peak area. Divide the peak area of analyte by the peak area of internal standard on the same chromatogram.

CALCULATIONS:

13. Determine the mass, mg (corrected for DE) of analyte found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of analyte in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b) \cdot 10^3}{V}, \text{ mg/m}^3$$

EVALUATION OF METHOD:

Methods S79 (2-methoxyethanol), S361 (2-ethoxyethanol) and S76 (2-butoxy-ethanol) were issued on February 14, 1975 [4], March 17, 1978 [5], and February 14, 1975 [4], and validated using, respectively, 50-, 6- and 10-L air samples of atmospheres generated by calibrated syringe drive. Precision and recovery were as shown below, representing non-significant bias in each method:

Overall method	Precision (S_r)	Recovery (%)	Range studied		Breakthrough @ 2 × OSHA	Measurement	
			mg/m³	mg per sample		Avg. DE	Precision (S_r)
S79 [1,4]	0.068	93	44 to 160	2 to 8	128 L*	0.98	0.008
S361 [2,5,6]	0.059	107	340 to 1460	2 to 7	>10 L**	1.02	0.009
S76 [1,4]	0.060	92	124 to 490	1 to 5	>44 L*	0.99	0.009

*Dry air.
**90% RH.

REFERENCES

1. Documentation of the NIOSH Validation Tests, S76 and S79, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 [1977].
2. Backup Data, S361, available as "Ten NIOSH Analytical Methods, Set 6," Order No. PB 288-629 from NTIS, Springfield, VA 22161.
3. User check, UBTL, NIOSH Sequence #3990-Z [unpublished, November 3, 1983].
4. NIOSH Manual of Analytical Methods, 2nd ed., V. 2., S76 and S79, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-B [1977].
5. Ibid, V. 5, S361, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141 [1979].

6. NIOSH Research Report, Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Dept. of Health and Human Services Publ. (NIOSH) 80-133 [1980].

METHOD REVISED BY: George Williamson, NIOSH/DPSE; methods originally validated under NIOSH Contracts 99-74-45 and 210-76-0123.

Table 1.—General information

Compound	Exposure limits (ppm) OSHA	NIOSH	ACGIH	Formula	mg/m^3 = 1 ppm @ NTP	M.W.	Density @ 20°C (g/mL)	BP (°C)	VP @ 20°C, kPa (mm Hg)
2-Methoxyethanol	25	Lowest feasible	25 (skin)	$HOCH_2CH_2OCH_3$; $C_3H_8O_2$	3.11	76.09	0.966	124	0.8 (6)
2-Ethoxyethanol	20	Lowest feasible	100 (skin)	$HOCH_2CH_2OCH_2CH_3$; $C_4H_{10}O_2$	3.68	90.12	0.931	135	0.5 (4)
2-Butoxyethanol	50	---	25 (skin)	$HOCH_2CH_2O(CH_2)_3\ CH_3$; $C_6H_{14}O_2$	4.83	118.17	0.902	171	0.08 (0.6)

OSHA METHOD NO. 83 FOR 2-BUTOXYETHANOL (BUTYL CELLOSOLVE) AND 2-BUTOXYETHYL ACETATE (BUTYL CELLOSOLVE ACETATE)*

Method no.:	83	
Matrix:	Air	
Procedure:	Samples are collected by drawing air through standard size coconut shell charcoal tubes. The charcoal is desorbed with a 95/5 (v/v) methylene chloride/methanol solution and the desorbate is analyzed by gas chromatography using a flame ionization detector.	
Recommended air volume and sampling rate:	48 L at 0.1 L/min	
	2-butoxyethanol	2-butoxyethyl acetate
Target concentration:	5 ppm (24 mg/m^3)	5 ppm (33 mg/m^3)
Reliable quantitation limit:	31 ppb (150 μg/m^3)	24 ppb (157 μg/m^3)
Standard error of estimate at target concentration: (Section 4.7.)	5.2%	5.5%
Special requirement:	Samples for 2-butoxyethyl acetate should be stored at 0°C or colder to reduce hydrolysis. Reduced temperature shipment of samples to the laboratory is not necessary.	
Status of method:	Evaluated method. This method has been subjected to the established evaluation procedures of the Organic Methods Evaluation Branch.	
Date: May 1990	Chemist: Carl J. Elskamp	

Organic Methods Evaluation Branch
OSHA Analytical Laboratory
Salt Lake City, Utah

*Reprinted from OSHA [1990].

1. General Discussion

1.1. Background

1.1.1. History

Methodologies to determine airborne concentrations of 2-methoxyethanol (methyl Cellosolve), 2-methoxyethyl acetate (methyl Cellosolve acetate), 2-ethoxyethanol (Cellosolve), and 2-ethoxyethyl acetate (Cellosolve acetate) have previously been evaluated by the OSHA Laboratory at two different target concentrations (OSHA Method 53, Ref. 5.1 and OSHA Method 79, Ref. 5.2). These two methods were based on work done by NIOSH where samples are collected by drawing air through coconut shell charcoal and are analyzed by GC after desorption of the charcoal with 95/5 (v/v) methylene chloride/methanol (Ref. 5.3). The NIOSH method also included an evaluation of 2-butoxyethanol at a range of 124 to 490 mg/m^3 for 10-L air samples. NIOSH has no evaluated method for 2-butoxyethyl acetate.

OSHA has adopted a PEL of 25 ppm for 2-butoxyethanol (Ref. 5.4) and currently has no PEL for 2-butoxyethyl acetate. NIOSH is considering issuing recommendations to lower the PEL for 2-butoxyethanol and to establish a PEL at about the same recommended concentration for 2-butoxyethyl acetate, thus a target concentration of 5 ppm was chosen for both analytes in this evaluation. A number of modifications were made to OSHA Method 79 for this evaluation. Although an RTx-Volatiles (Restek Corp.) capillary column is acceptable for analysis of 2-butoxyethanol, there was less peak-tailing when a Nukol (Supelco, Inc.) capillary column was used. There is no significant peak-tailing for 2-butoxyethyl acetate on either of these columns. In OSHA Method 79, solid anhydrous magnesium sulfate was added to the desorption vials for 2-methoxyethanol and 2-ethoxyethanol samples to improve desorption efficiency. This was found to be unnecessary for 2-butoxyethanol samples.

To ascertain the validity of this method at higher concentrations, the collection efficiency of charcoal sampling tubes was confirmed at 50 ppm for each analyte. The stability and desorption efficiency of the analytes should not be affected at these higher loadings.

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

The effects of overexposure to 2-butoxyethanol and 2-butoxyethyl acetate are similar. Inhalation of vapors may be irritating to the respiratory tract and may cause nausea, headaches, vomiting, dizziness, drowsiness, and unconsciousness. The liquid is readily absorbed through the skin and may cause irritation to the skin and eyes. Ingestion may cause nausea, vomiting,

headaches, dizziness, and gastrointestinal irritation. Chronic overexposure may damage the kidneys, liver, and blood (Ref. 5.5).

1.1.3. Workplace exposure

2-Butoxyethanol is used as a solvent for nitrocellulose, natural and synthetic resins, soluble oils, lacquers, varnishes and enamels. It is also used in textile dyeing and printing, in the treatment of leather, in the production of plasticizers, as a stabilizer in metal cleaners and household cleaners, and in hydraulic fluids, insecticides, herbicides and rust removers (Ref. 5.6).

2-Butoxyethyl acetate is used as a high-boiling solvent for nitrocellulose lacquers, epoxy resins, and multicolor lacquers. It is also used as a film coalescing aid for polyvinyl acetate latex (Ref. 5.7).

1.1.4. Physical properties (Ref. 5.6 unless otherwise noted)

chemical formula:

2-butoxyethanol: $CH_3CH_2CH_2CH_2OCH_2CH_2OH$

2-butoxyethyl acetate: $CH_3CH_2CH_2CH_2OCH_2CH_2OOCCH_3$

	2-Butoxyethanol	2-Butoxyethyl acetate
CAS no.:	111-76-2	112-07-2
mol wt:	118.17	160.21
bp at 101.3 kPa, °C:	171.2	192
appearance:	colorless liquid	colorless liquid
sp gr at 20/20°C:	0.9022 (Ref. 5.8)	0.9422
vp at 20°C, Pa:	101	33-40
vapor density, air=1:	4.1	5.5
flash point, °C		
open cup: (Ref. 5.8)	69.4	87.8
closed cup: (Ref. 5.8)	60.0	73.9
autoignition temp., °C	244	340
odor:	mild	pleasant, sweet, fruity
odor threshold, ppm:	approx. 0.4	0.1 (absolute perception limit) 0.35-0.48 (recognition)
explosive limits, %		
lower:	1.1	0.88
upper	10.1	8.54
solubility:	soluble in water, alcohol, ether	moderately soluble (1 g per 100 g at 20°C) in water, soluble in hydrocarbons and other organic solvents

synonyms and trade names:

2-butoxyethanol:

ethylene glycol monobutyl ether; ethylene glycol n-butyl ether; butyl Cellosolve

2-butoxyethyl acetate:

ethylene glycol monobutyl ether acetate; 2-butoxyethanol acetate; acetic acid, 2-butoxyethyl ester; ethylene glycol butyl ether acetate; Ektasolve EB Acetate; butyl Cellosolve acetate

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

1.2. Limit defining parameters

1.2.1. Detection limit of the analytical procedure

The detection limits of the analytical procedure are 0.12 and 0.13 ng per injection (1.0-μL injection with a 58:1 split) for 2-butoxyethanol and 2-butoxyethyl acetate 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 7.22 and 7.54 μg per sample for 2-butoxyethanol and 2-butoxyethyl acetate 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 31 ppb (150 $\mu g/m^3$) and 24 ppb (157 $\mu g/m^3$) for 2-butoxyethanol and 2-butoxyethyl acetate 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 both analytes (Section 4.4).

1.2.5. Recovery

The recovery of 2-butoxyethanol and 2-butoxyethyl acetate from samples used in a 15-day storage test remained above 98 and 86% respectively when the samples were stored at ambient temperatures (Section 4.5, from regression lines shown in Figures 4.5.1.2 and 4.5.2.2).

1.2.6. Precision (analytical procedure)

The pooled coefficients of variation obtained from replicate injections of analytical standards at 0.5, 1 and 2 times the target concentrations are 0.004 and 0.002 for 2-butoxyethanol and 2-butoxyethyl acetate 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 $\pm$10.1 and $\pm$10.8% for 2-butoxyethanol and 2-butoxyethyl acetate respectively. These include an additional $\pm$5% for pump error. The overall procedure must provide results at the target concentration that are $\pm$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 8 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 quantitate certain co-collected solvent vapors using this method because most other common solvents which are collected on charcoal are normally analyzed after desorption with carbon disulfide and may exhibit unacceptably low desorption efficiencies when 95/5 (v/v) methylene chloride/methanol is used.

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. x 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. It is desirable to utilize sampling tube holders that have protective covers to shield the employee from the sharp, jagged end of the sampling tube. Position the tube so that sampled air passes through the 100-mg section first.

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

2.3.4. To avoid channeling, place the sampling tube vertically 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 a list of any other solvents being used in the sampling area.

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

2.4. Sampler capacity

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 analytes by monitoring the effluent from sampling tubes containing only the 100-mg section of charcoal while sampling at 0.1 L/min from atmospheres containing 50 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 more than 8 h (>48 L).

2.5. Desorption efficiency

2.5.1. The average desorption efficiencies of 2-butoxyethanol and 2-butoxyethyl acetate from SKC Inc. Lot 120 charcoal are 99.0 and 101.5% respectively over the range of 0.5 to 2 times the target concentrations (Section 4.9.).

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

2.5.3. Desorption efficiencies should be periodically confirmed because they may change slightly due to variations in charcoal and operator technique.

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 99 ppb (478 $\mu g/m^3$) for 2-butoxyethanol 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 the two analytes on charcoal. In general, the presence of other solvent vapors in the air will reduce the capacity of charcoal to collect the analytes.

2.7.2. Other solvents used in the sampling area should be reported to the laboratory as potential interferences.

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. Use sampling tube holders with protective covers if possible.

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 30-m × 0.25-mm i.d. (0.25-μm film), fused silica Nukol column (Catalog Number 2-4107M, Supelco, Inc., 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 Waters 860 Networking Computer 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-Butoxyethanol and 2-butoxyethyl acetate, reagent grade. Aldrich Lot 01604KT 2-butoxyethanol and Lot 01106KP 2-butoxyethyl acetate were used in this evaluation.

3.2.2. Methylene chloride, chromatographic grade. American Burdick and Jackson Lot AQ553 was used in this evaluation.

3.2.3. Methanol, chromatographic grade. American Burdick and Jackson Lot AW106 was used in this evaluation.

3.2.4. A suitable internal standard, reagent grade. Aldrich Lot 01601HT 2-ethyl-1-hexanol was used in this evaluation.

3.2.5. The desorption solvent consists of methylene chloride/methanol, 95/5 (v/v) containing an internal standard at a concentration of 1.5 mL/L.

3.2.6. GC grade nitrogen, air, and hydrogen.

3.3. Standard preparation

3.3.1. Prepare concentrated stock standards by diluting the pure analytes with methylene chloride. 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 2-butoxyethanol, dilute 3.0 mL of pure 2-butoxyethanol (sp gr = 0.9022) to 10.0 mL with methylene chloride. This stock solution would contain 270.7 μg/μL. A working standard of 1137 μg/sample is prepared by injecting 4.2 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. Add 1.0 mL of desorption solvent to each vial using the same dispenser as used for preparation of standards.

3.4.3. Immediately cap the vials and shake them periodically for about 30 min before analysis.

3.5. Analysis

3.5.1. GC conditions

column:	30-m x 0.25-mm i.d. fused silica, Nukol, 0.25-μm film	
injection volume:	1.0 μL (with a 58:1 split)	
zone temperatures:	column—90°C injector—150°C detector—200°C	
gas flows:	hydrogen (carrier)— (83 kPa head pressure) nitrogen (makeup)— hydrogen (flame)— air—	1.7 mL/min 20 mL/min 65 mL/min 315 mL/min
retention times:	2-butoxyethanol— 2-butoxyethyl acetate— (2-ethyl-1-hexanol—	7.55 min 9.75 min 5 min)
chromatogram:	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 produces a flame ionization detector response and has a similar retention time as the analyte or internal standard is a potential interference. Any potential interferences reported to the laboratory by the industrial hygienist 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.

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

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

where 24.46 = molar volume (L) at 25°C and 101.3 kPa (760 mmHg)
molecular weight = 118.17 for 2-butoxyethanol
160.21 for 2-butoxyethyl acetate

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 58:1 split) was used in the determination of the detection limits of the analytical procedure. The detection limits of 0.12 and 0.13 ng were determined by making injections of 7.22 and 7.54 ng/μL standards for 2-butoxyethanol and 2-butoxyethyl acetate, respectively. These amounts were judged to produce peaks with heights approximately 5 times the baseline noise. A chromatogram of such an injection is shown in Figure 4.1.

4.2. Detection limit of the overall procedure

Six samples for each analyte were prepared by injecting 7.22 µg of 2-butoxyethanol and 7.54 µg of 2-butoxyethyl acetate into the 100-mg section of charcoal tubes. The detection limits of the overall procedure correspond to air concentrations of 31 ppb (150 µg/m^3) and 24 ppb (157 µg/m^3) for 2-butoxyethanol and 2-butoxyethyl acetate, respectively. The results are given in Tables 4.2.1 and 4.2.2.

Table 4.2.1
Detection Limit of Overall Procedure
for 2-Butoxyethanol

Sample no.	µg spiked	µg recovered
1	7.22	6.87
2	7.22	7.03
3	7.22	7.49
4	7.22	7.36
5	7.22	6.98
6	7.22	7.16

Table 4.2.2
Detection Limit of Overall Procedure
for 2-Butoxyethyl Acetate

Sample no.	µg spiked	µg recovered
1	7.54	8.57
2	7.54	8.51
3	7.54	7.76
4	7.54	7.58
5	7.54	7.72
6	7.54	7.34

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 7.22 µg of 2-butoxyethanol and 7.54 µg of 2-butoxyethyl acetate into the 100-mg section of charcoal tubes. These amounts

correspond to air concentrations of 31 ppb (150 $\mu g/m^3$) and 24 ppb (157 $\mu g/m^3$) for 2-butoxyethanol and 2-butoxyethyl acetate, respectively. The results are given in Tables 4.3.1 and 4.3.2.

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

Sample no.	Percent recovered	Statistics
1	95.2	$\overline{X}$ = 99.0
2	97.4	
3	103.7	
4	101.9	SD = 3.25
5	96.7	Precision = (1.96) (±3.25)
6	99.2	= ±6.37

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

Sample no.	Percent recovered	Statistics
1	113.7	$\overline{X}$ = 105.0
2	112.9	
3	102.9	
4	100.5	SD = 6.74
5	102.4	Precision = (1.96) (±6.76)
6	97.3	= ±13.2

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 and 4.4.2 and Figures 4.4.1 and 4.4.2. The response is linear for both analytes with slopes (in ISTD-corrected area counts per micrograms of analyte per sample) of 226.3 and 219.6 for 2-butoxyethanol and 2-butoxyethyl acetate, respectively.

Table 4.4.1
Instrument Response to 2-Butoxyethanol

× target concn	0.5×	1×	2×
µg/sample	568.9	1138	2276
ppm	2.45	4.91	9.81
Area counts	130013	265338	511143
	130843	264851	511543
	130236	266530	510113
	130759	264206	507834
	130483	266271	508070
	130198	265353	514955
$\overline{X}$	130422	265425	510610

Table 4.4.2
Instrument Response to 2-Butoxyethyl Acetate

× target concn	0.5×	1×	2×
µg/sample	791.3	1583	3165
ppm	2.52	5.03	10.07
Area counts	174117	355187	690704
	174715	355740	688825
	173817	355966	690567
	173654	355907	690419
	173498	355731	693114
	173516	354933	692883
$\overline{X}$	173886	355577	691085

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). For each set of 36 samples for each analyte, 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 20–28°C. Six samples, three from refrigerated and three

from ambient storage, were analyzed at intervals over a period of fifteen days. The results are given in Tables 4.5.1 and 4.5.2 and shown graphically in Figures 4.5.1.1, 4.5.1.2, 4.5.2.1 and 4.5.2.2. The loss of analyte on the 2-butoxyethyl acetate samples was due to hydrolysis of the ester to 2-butoxyethanol and acetic acid. This was supported by the fact that amounts of 2-butoxyethanol were found on these samples which corresponded to the loss of 2-butoxyethyl acetate. The loss of analyte in this study after 15 days was about 3% for refrigerated storage and about 10% for ambient storage. If possible, stored 2-butoxyethyl acetate samples should be refrigerated to reduce hydrolysis.

Table 4.5.1
Storage Test for 2-Butoxyethanol

Storage time (days)	% recovery (refrigerated)			% recovery (ambient)		
0	98.5	96.9	98.0	98.5	96.9	98.0
0	97.7	98.2	98.4	97.7	98.2	98.4
2	99.7	99.7	99.2	99.5	98.9	99.7
6	97.9	98.3	99.0	97.5	98.2	99.0
8	95.5	96.0	96.2	95.2	96.4	96.3
13	100.3	100.2	100.8	98.4	99.4	100.0
15	99.1	99.0	100.0	98.2	99.6	98.2

Table 4.5.2
Storage Test for 2-Butoxyethyl Acetate

Storage time (days)	% recovery (refrigerated)			% recovery (ambient)		
0	99.2	98.6	98.9	99.2	98.6	98.9
0	97.7	94.0	99.4	97.7	94.0	99.4
2	98.6	96.4	98.6	93.2	96.5	95.8
6	97.5	97.1	97.9	91.6	86.7	92.4
8	96.0	96.5	97.7	89.3	90.1	90.9
13	97.4	95.1	97.1	88.2	85.2	90.0
15	97.2	93.1	96.8	87.0	89.7	89.1

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 and 4.6.2. These tables are based on the data presented in Section 4.4.

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

× target concn	0.5×	1×	2×
µg/sample	568.9	1138	2276
ppm	2.45	4.91	9.81
SD (area counts)	330.6	867.7	2624
CV	0.0025	0.0033	0.0051

$\overline{CV}$ = 0.004

Table 4.6.2
Precision of the Analytical Procedure
for 2-Butoxyethyl Acetate
(Based on Table 4.4.2)

× target concn	0.5×	1×	2×
µg/sample	791.3	1583	3165
ppm	2.52	5.03	10.07
SD (area counts)	466.2	418.9	1632
CV	0.0027	0.0012	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:

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

where

n = total no. of data points
k = 2 for linear regression
k = 3 for quadratic regression
Y_{obs} = observed % recovery at a given time
Y_{est} = estimated % recovery from the regression line at the same given time

An additional 5% for pump error is added to the SEE by the addition of variances. The SEEs are 5.2% and 5.5% for 2-butoxyethanol and 2-butoxyethyl acetate 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 ±10.1% and ±10.8% for 2-butoxyethanol and 2-butoxyethyl acetate respectively. The SEE and precision of the overall procedure for each analyte were obtained from Figures 4.5.1.2 and 4.5.2.2 for 2-butoxyethanol and 2-butoxyethyl acetate, respectively.

4.8 Reproducibility

Six samples for each analyte, collected from controlled test atmospheres (at about 80% R.H., 24–28°C, 86–88 kPa) containing the analytes at about 4 times the target concentrations, were analyzed by a chemist 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 8 days before being analyzed. The results are presented in Tables 4.8.1 and 4.8.2.

Table 4.8.1
Reproducibility for 2-Butoxyethanol

Sample no.	µg found	µg expected	% found	% deviation
1	1008	1090	92.5	-7.5
2	992.6	1073	92.5	-7.5
3	994.5	1073	92.7	-7.3
4	993.2	1063	93.4	-6.6
5	1007	1091	92.3	-7.7
6	1036	1104	93.8	-6.2

Table 4.8.2
Reproducibility for 2-Butoxyethyl Acetate

Sample no.	µg found	µg expected	% found	% deviation
1	1347	1396	96.5	-3.5
2	1337	1372	97.4	-2.6
3	1315	1371	95.9	-4.1
4	1318	1361	96.8	-3.2
5	1364	1373	99.3	-0.7
6	1380	1414	97.6	-2.4

4.9. Desorption efficiency

The desorption efficiency for each analyte was determined by injecting microliter amounts of stock standards onto the front section of charcoal tubes. Eighteen samples were prepared, six samples for each concentration level listed in the following table.

Table 4.9
Desorption Efficiency Data

Analyte	2-Butoxyethanol			2-Butoxyethyl acetate		
× target concn	0.5×	1×	2×	0.5×	1×	2×
µg/sample	568.9	1138	2276	791.3	1583	3165
ppm	2.45	4.91	9.81	2.52	5.03	10.07
Desorption	99.0	99.4	99.9	101.6	100.6	102.2
efficiency, %	98.7	99.1	99.1	101.6	101.7	101.8
	100.4	98.5	98.4	101.9	101.4	101.3
	99.2	98.9	99.0	101.5	101.2	102.2
	98.5	98.0	99.2	101.4	100.9	101.7
	99.1	98.2	99.3	101.1	100.9	102.4
$\overline{X}$	99.2	98.7	99.2	101.5	101.1	101.9
$\overline{X}$		99.0			101.5	

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	
	2-Butoxyethanol	2-Butoxyethyl acetate
1	101.8	103.4
2	102.7	103.8
3	102.7	103.8
4	101.7	103.8
5	101.0	103.6
6	100.7	103.4
$\overline{X}$	101.8	103.6

4.11. Chromatograms

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

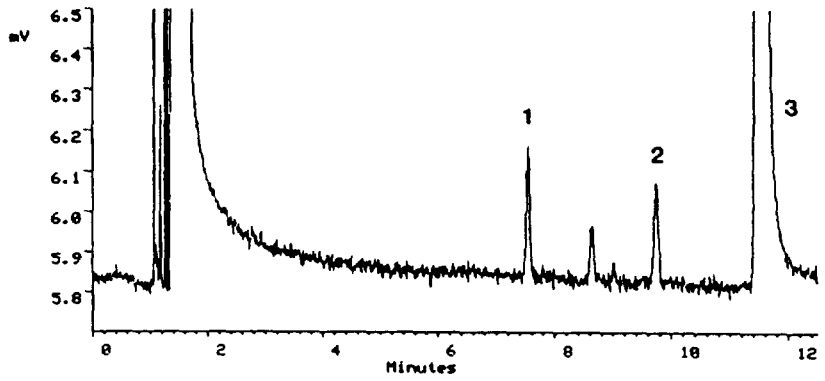

Figure 4.1. Detection limit chromatogram. Key: (1) 2-butoxyethanol, (2) 2-butoxyethyl acetate, (3) 2-ethyl-1-hexanol.

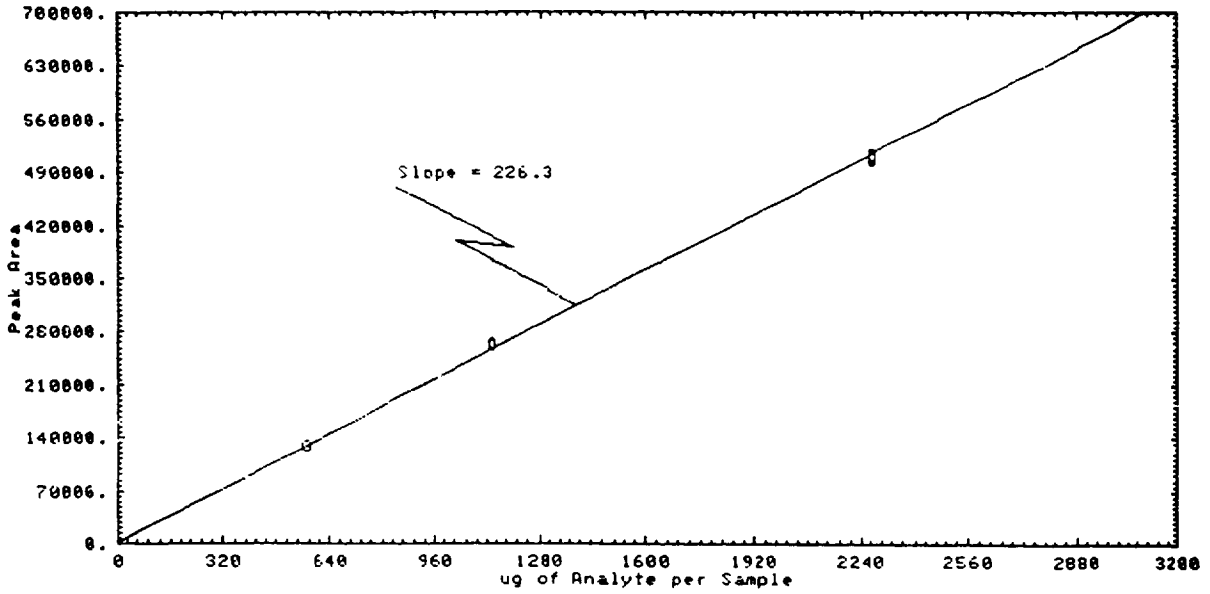

Figure 4.4.1. Instrument response to 2-butoxyethanol.

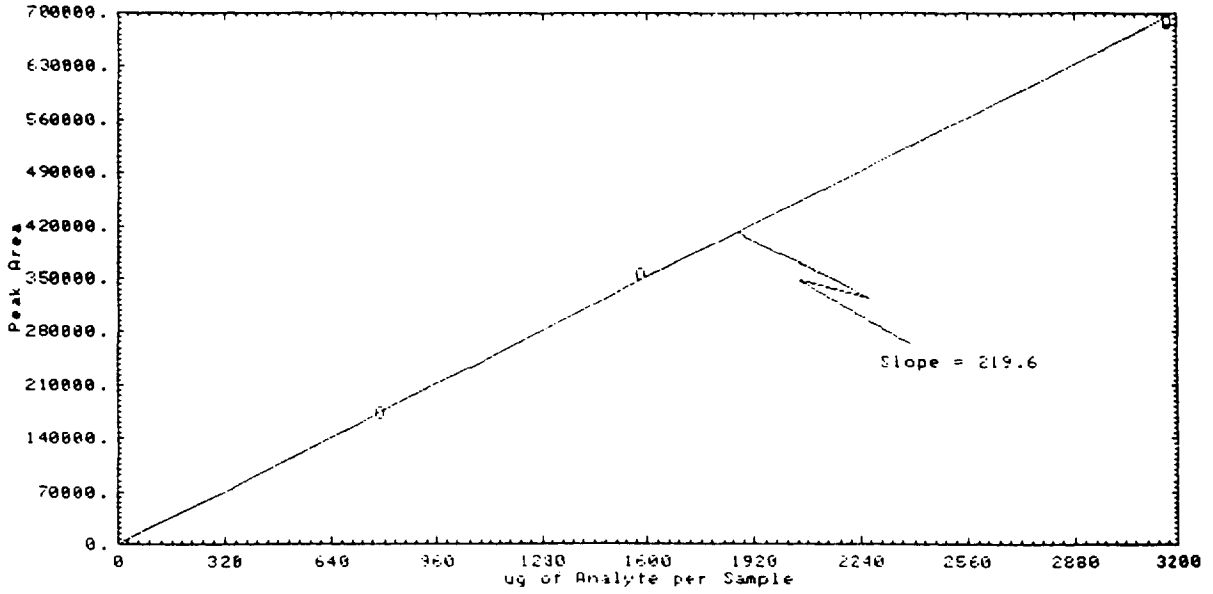

Figure 4.4.2. Instrument response to 2-butoxyethyl acetate.

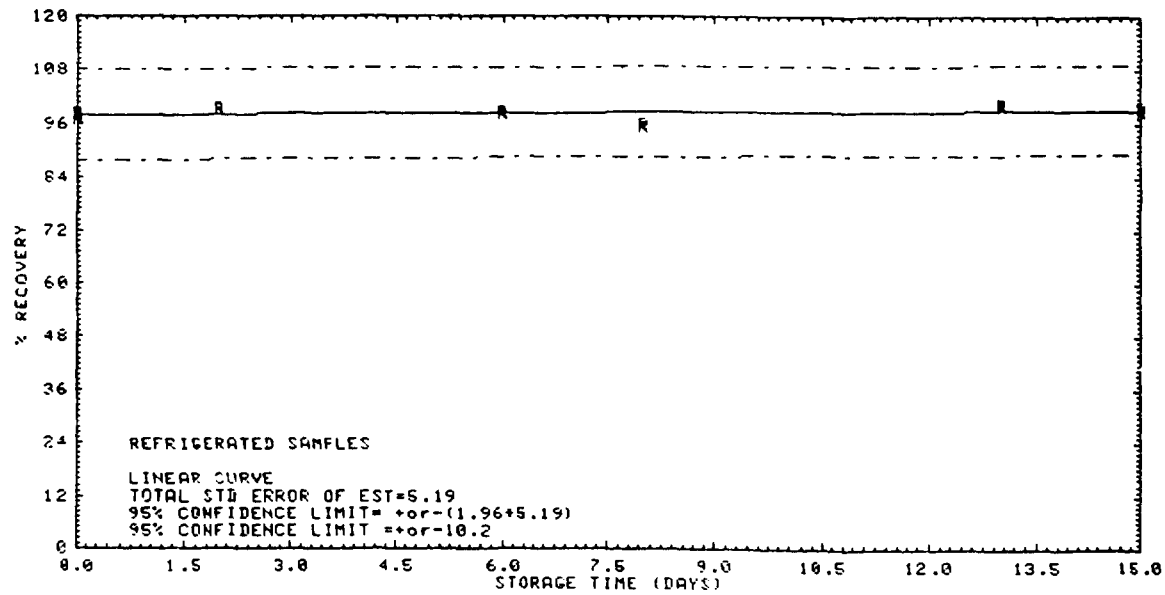

Figure 4.5.1.1. 2-Butoxyethanol refrigerated storage samples.

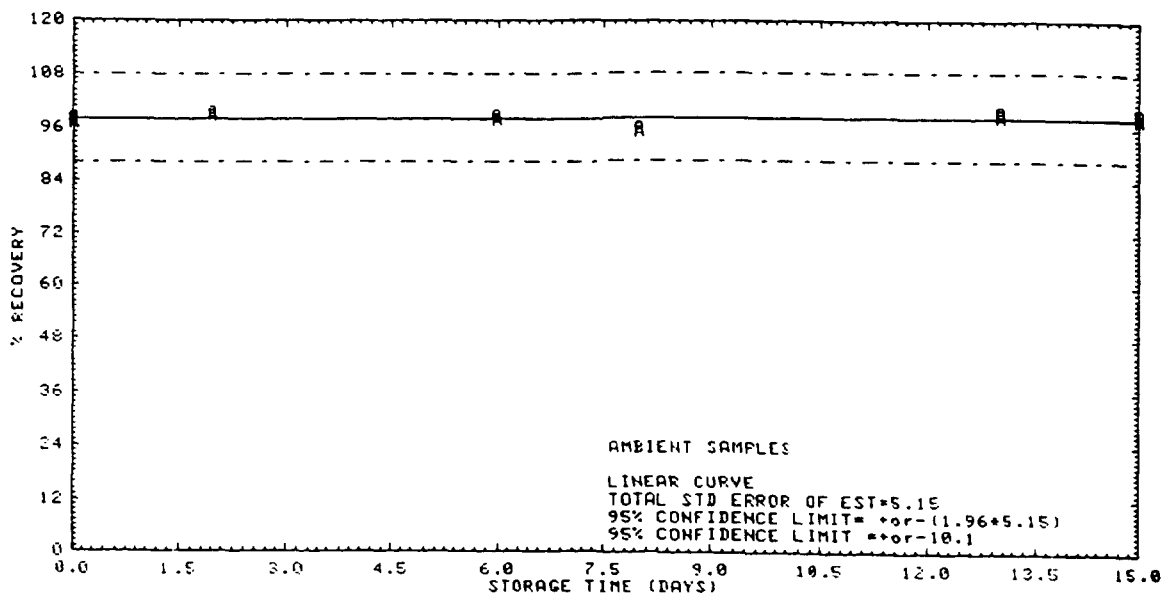

Figure 4.5.1.2. 2-Butoxyethanol ambient storage samples.

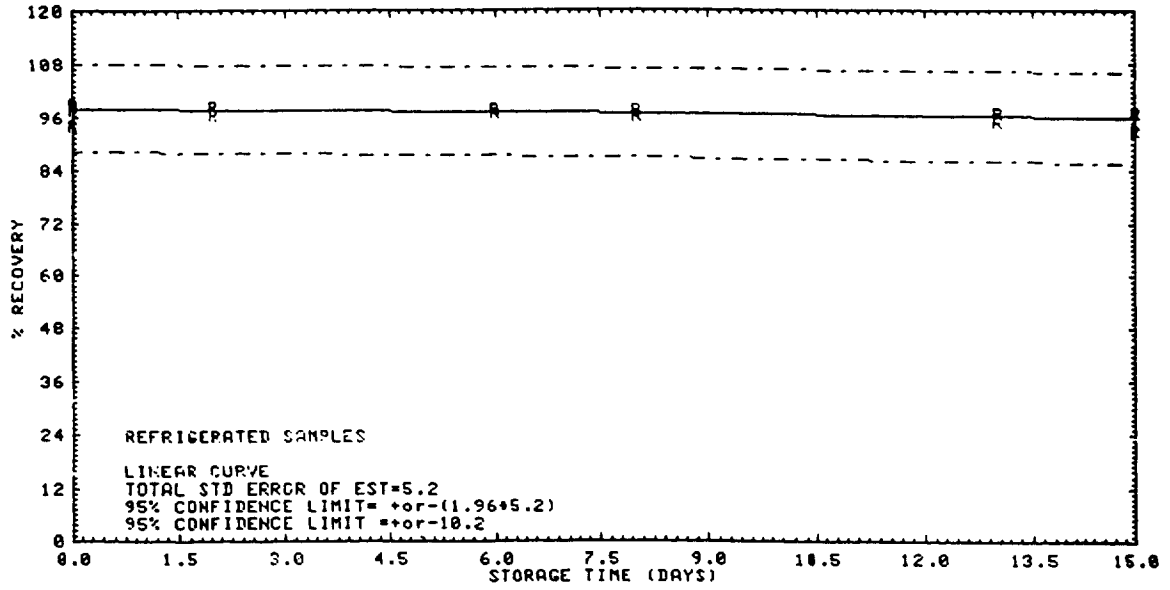

Figure 4.5.2.1. 2-Butoxyethyl acetate refrigerated storage samples.

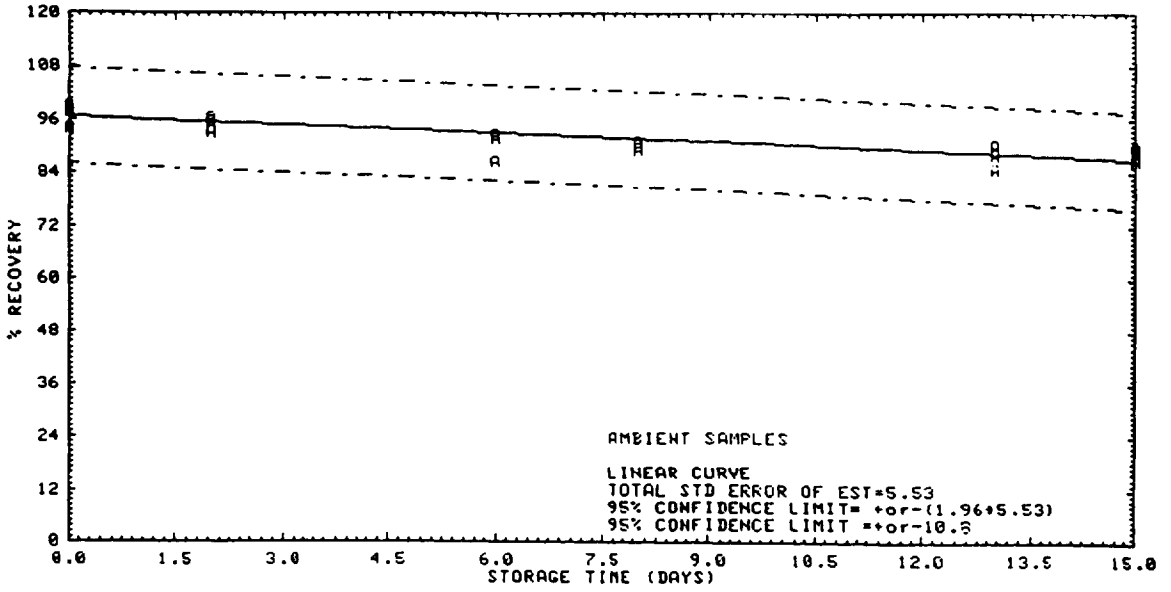

Figure 4.5.2.2. 2-Butoxyethyl acetate ambient storage samples.

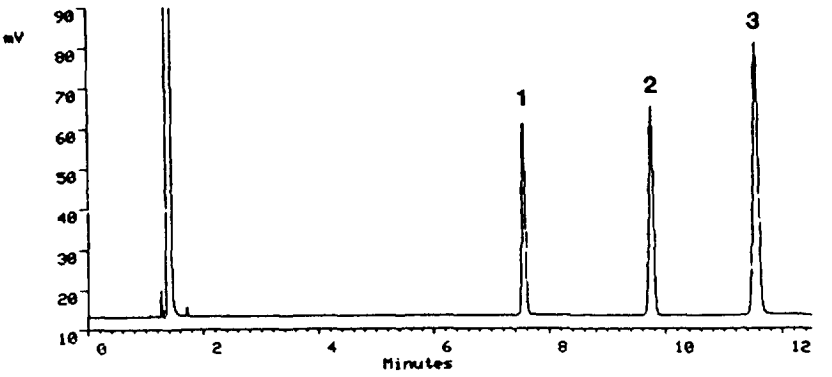

Figure 4.11. Chromatogram of a standard at the target concentrations. Key: (1) 2-butoxyethanol, (2) 2-butoxyethyl acetate, (3) 2-ethyl-1-hexanol.

5. REFERENCES

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