ETHYL ALCOHOL

Method no.:	100
Matrix:	Air
Target concentration:	1000 ppm (1900 mg/m^3)
Procedure:	Samples are collected by drawing air through two 8-mm o.d. (6-mm i.d.) Anasorb 747 sampling tubes connected in series. The front tube contains 400 mg of adsorbent, and the back tube 200 mg. The samples are desorbed with a 60/40 *N,N*-dimethyl-formamide/carbon disulfide solution and analyzed by GC using a flame ionization detector.
Recommended air volume and sampling rate:	12 L at 0.05 L/min
Reliable quantitation limit:	0.68 ppm (1.29 mg/m^3)
Standard error of estimate at the target concentration:	5.17%
Special requirement:	The air sampler must be separated into its component sampling tubes as soon as possible after sampling. This will prevent post-sampling migration.
Status of method:	Evaluated method. This method has been subjected to the established evaluation procedures of the Organic Methods Evaluation Branch.

Date: April 1993
Chemist: Warren Hendricks

Organic Methods Evaluation Branch
OSHA Salt Lake Technical Center
Salt Lake City, UT 84165-0200

1. General Discussion

   1.1 Background

      1.1.1 History

         Previous to this method, OSHA had been using a procedure based on NIOSH Method 1400 (Ref. 5.1) to collect and analyze ethyl alcohol samples. Method 1400 requires sample collection on coconut-shell charcoal, refrigerated sample shipment and storage, and analysis to be performed as soon as possible. Method 1400 utilizes desorption with 99/1 carbon disulfide/2-butanol, and analysis by GC/FID. The maximum air volume is 1 L and the sampling rate is 0.05 L/min (20-min samples).

         A post-sampling migration test for ethyl alcohol was performed using samples collected on the sampling medium recommended in Method 1400. These samples were collected for 20 min at 0.05 L/min from a test atmosphere containing 980 ppm of ethyl alcohol at 78% relative humidity and 26°C. Eighteen percent of the collected ethyl alcohol migrated into the sampling tube back section during two weeks of ambient storage. Much less migration (0.3%) was observed in similar samples stored at 5°C. The shipping restrictions of Method 1400 are inconvenient, but do help alleviate a serious migration problem.

         The purpose of this work was to develop a collection method which permitted ambient temperature sample shipment, and which also utilized a sampler with more capacity for ethyl alcohol than the charcoal sampler in Method 1400. The use of Anasorb 747 to collect methyl alcohol vapors was reported in OSHA Method 91 (Ref. 5.2). Sampler capacity tests showed that Anasorb 747 had ample capacity for ethyl alcohol, however, ethyl alcohol (like methyl alcohol) was found to undergo post-sampling migration on Anasorb 747. The migration problem was avoided by using two one-section sampling tubes as described in Method 91. These sampling tubes are connected in series for sampling, and then separated for shipment to the laboratory.

         This method features sample collection on Anasorb 747, desorption with 60/40 *N,N*-dimethylformamide (DMF)/carbon disulfide, and analysis by GC with FID detection. The large amount of DMF is used to put any collected water into solution, eliminating the possibility of two-phase samples. The recommended air volume is 12 L (12 times the air volume of Method 1400), collected at 0.05 L/min. There are no shipping or storage temperature restrictions.

         Anasorb 747 is a proprietary beaded active carbon marketed by SKC, Inc. It is reported to have a low ash content, a surface more hydrophobic and catalytically less active than coconut-shell charcoal, and capacity for organic vapors similar to SKC Lot 120 coconut-shell charcoal (Ref. 5.3). Anasorb 747, because of its properties, should efficiently collect and retain other solvent vapors. The analytical method is sufficiently versatile to permit the analysis of other solvents which may have been simultaneously collected with ethyl alcohol (Section 4.10).

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

         The lethal dose for ethyl alcohol administered by inhalation to rats is about 13,000 ppm after 22 h; to guinea pigs, about 22,000 ppm after 9 h; and to mice, about 29,000 ppm after 7 h (Ref. 5.4).

         The OSHA PEL for ethyl alcohol is 1000 ppm based on an 8-h TWA (Ref. 5.5). The minimum concentration of ethyl alcohol that can be identified by odor has been reported to be 350 ppm. Exposure to concentrations of 5,000 to 10,000 ppm ethyl alcohol can result in irritation of the eyes and of the upper respiratory tract mucous membranes. Concentrations of this level have an intense odor, but most people become acclimated after a short time. If exposure at these levels continues, the result can be stupor or drowsiness. An air concentration of 15,960 ppm, which could be tolerated only with discomfort, caused continuous lacrimation and marked coughing. An air concentration of 21,280 ppm was described as intolerable, even for short periods. There is disagreement among experts on whether inhalation of ethyl alcohol vapors can cause drunkenness. (Ref. 5.6) Splashes of the liquid in the eyes cause immediate stinging and burning, with reflex closing of the lids and tearing, transitory injury of the cornea, and hyperemia of the conjunctiva (Ref. 5.4). Direct skin contact with the liquid may cause mild redness and

burning. Skin sensitization has been reported. Prolonged or repeated contact with the liquid can cause dermatitis and defatting of the skin (Ref. 5.7).

International Agency for Research on Cancer (IARC), in a monograph that did not consider occupational exposure to ethyl alcohol or exposure other than by drinking, concluded that alcoholic beverages are carcinogenic to humans. IARC further concluded that there is inadequate evidence for the carcinogenicity of ethyl alcohol and of alcoholic beverages in experimental animals. IARC made a distinction between alcoholic beverages and ethyl alcohol. Alcoholic beverages contain many constituents other than ethyl alcohol and water. (Ref. 5.8)

1.1.3   Workplace exposure

Ethyl alcohol can be produced by direct catalytic hydration (or with ethyl sulfate as an intermediate) from ethylene, by fermentation of biomass, and by enzymatic hydrolysis of cellulose (Ref. 5.9).

Several administrative and chemical controls have been implemented to avoid taxation of ethyl alcohol. The administrative controls include bonds, permits and scrupulous recordkeeping. Chemical controls involve the use of denaturants that make the ethyl alcohol unsuitable for beverage use. Some of the denatured ethyl alcohols that may be encountered in the workplace include: denatured ethyl alcohol (unpalatable for beverages), completely denatured ethyl alcohol (unfit for beverages), specially denatured alcohol (unfit for beverages but useful for specific applications), and proprietary solvents and special industrial solvents. (Ref. 5.6. Some of the many chemicals that are used to denature ethyl alcohol include: methyl alcohol, brucine, brucine sulfate, quassin, tert-butyl alcohol, sucrose octa-acetate, and Bitrex (Ref. 5.10).

Ethyl alcohol is used in the manufacture of acetaldehyde, acetic acid, ethylene, butadiene, 2-ethyl hexanol, glycol ethers, ethylamines, ethyl acrylate, ethyl ether, ethyl vinyl ether, ethyl acetate, ethyl chloride, vinegar, dyes, pharmaceuticals, elastomers, detergents, cleaning preparations, surface coatings, cosmetics, explosives, antifreeze, beverages, antisepsis, gasohol, yeast-growth medium, and octane booster in gasoline. It is also used extensively as an extraction solvent. (Refs. 5.6 and 5.9)

The total U.S. industrial production of ethyl alcohol in 1975 was 264 million gallons (Ref. 5.6). The U.S. capacity for fuel ethyl alcohol was reported to be more than 1 billion gallons in 1992 (Ref. 5.11).
No estimate of the number of workers potentially exposed to ethyl alcohol was found.

1.1.4   Physical properties and other descriptive information (Ref. 5.7)

chemical name:	ethyl alcohol
CAS no.:	64-17-5
molecular wt:	46.07
boiling point:	78°C
melting point:	-117°C
specific gravity:	0.7893
vapor pressure:	40 mmHg at 19°C (5 kPa)
vapor density:	1.59
evaporation rate:	1.4 (carbon tetrachloride = 1)
flash point:	55°F
explosive limits:	upper, 19%; lower, 3.3%
description:	a clear, colorless, volatile liquid with a pleasant odor, and a burning taste
solubility:	soluble in water, benzene, ether, acetone, chloroform, methyl alcohol, and many other organic solvents
synonyms:	ethanol; ethyl alcohol, 100%; alcohol; alcohol anhydrous; Algrain; Anhydrol; ethyl hydrate; ethyl hydroxide; Jaysol; Tecsol; PL-1075 Rinse; ethyl alcohol USP 200 proof (USI); methyl carbinol; grain alcohol; ethylic alcohol; STCC 4909159; UN 1170; OHS08700
structural formula:	CH_3CH_2OH

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 limit of the analytical procedure is 40 pg per injection. This is the amount of analyte that will produce a peak with a height that is approximately 5 times the baseline noise. (Section 4.1)

1.2.2   Detection limit of the overall procedure

The detection limit of the overall procedure is 15.52 µg per sample. This is the amount of analyte spiked on the sampling device that, upon analysis, produces a peak similar in size to that of the detection limit of the analytical procedure. This detection limit corresponds to an air concentration of 0.68 ppm (1.29 mg/m^3). (Section 4.2)

1.2.3   Reliable quantitation limit

The reliable quantitation limit is 15.52 µg per sample. This is the smallest amount of analyte which can be quantitated within the requirements of a recovery of at least 75% and a precision (±1.96 SD) of ±25% or better. This reliable quantitation limit corresponds to an air concentration of 0.68 ppm (1.29 mg/m^3). (Section 4.3)

The reliable quantitation limit and detection limits reported in the method are based upon optimization of the instrument for the smallest possible amount of analyte. When the target concentration of 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 concentration ranges representing 0.5 to 2 times the target concentration was linear. (Section 4.4)

1.2.5   Recovery

The recovery of ethyl alcohol from samples used in the 16-day ambient storage test remained above 102%. (Section 4.5, regression line of Figure 4.5.1)

1.2.6   Precision (analytical procedure)

The pooled coefficient of variation obtained from replicate determinations of analytical standards at 0.5, 1 and 2 times the target concentration is 0.014. (Section 4.6)

1.2.7   Precision (overall procedure)

The precision at the 95% confidence level for the 16-day ambient temperature storage test is ±5.17%. (Section 4.7) This includes an additional ±5% for sampling error.

1.2.8   Reproducibility

Six samples, collected from a controlled test atmosphere, and a draft copy of this procedure were submitted to SLTC for analysis. The samples were analyzed after 5 days of storage at about 5°C. No individual sample result deviated from its theoretical value by more than the precision reported in Section 1.2.7. (Section 4.8)

2. Sampling Procedure

2.1   Apparatus

2.1.1   A personal sampling pump that can be calibrated within ±5% of the recommended flow rate with the sampling device in line.

2.1.2   A sample is collected using a 400-mg and a 200-mg Anasorb 747 sampling tube. The sampling tubes (11-cm × 8-mm o.d. × 6-mm i.d.) are connected in series with silicone

tubing prior to sampling. The adsorbent beds are held in place with a glass wool plug at the front, and a foam plug at the rear of the sorbent bed. The sampling tubes are commercially available from SKC, Inc. as catalog no. 226-82.

2.2 Reagents

No reagents are required for sampling.

2.3 Technique

2.3.1 Break off both ends of the sampling tubes immediately before sampling. The holes in the broken ends of the sampling tubes should be approximately one-half of the i.d. of the sampling tube. All tubes should be from the same lot. Connect the outlet end of a 400-mg sampling tube to the inlet end of a 200-mg tube with a 1-in. length of 1/4-in. i.d. silicone rubber tubing. The inlet end of a sampling tube is the end with the glass wool plug. Insure that the connection is secure and that the broken ends of the tubes just touch each other. Be careful not to cut the silicone tubing with the sharp ends of the sampling tubes.

2.3.2 Connect the sampling tube to the sampling pump with flexible tubing so that the sampled air passes through the inlet end of the 400-mg sampling tube first. If possible, use a sampling tube holder with a protective tube shield to cover the sharp, jagged end of the sampling tube.

2.3.3 Sampled air should not pass through any hose or tubing before entering the front sampling tube.

2.3.4 Attach the sampler vertically in the worker's breathing zone, with the 400-mg sampling tube pointing downward, and positioned so it does not impede work performance or safety.

2.3.5 Remove the sampling device after sampling for the appropriate time. Separate the two sampling tubes and seal the tube ends with plastic end caps. Wrap each sample end-to-end with a Form OSHA-21 seal. Silicone tubing is susceptible to cuts from the sharp ends of the sampling tubes and should be discarded after one use.

2.3.6 Submit at least one blank with each set of samples. The blank should be handled the same as the other samples except no air is drawn through it.

2.3.7 Record the sample air volume (in liters of air) for each sample. Note any potential interferences, such as chemicals used to denature the ethyl alcohol.

2.3.8 Ship any bulk sample separate from air samples.

2.4 Sampler capacity

Sampler capacity studies (Section 4.9) were performed using controlled test atmospheres and 400-mg front sampling tubes. The average ethyl alcohol concentration of these test atmospheres was 3640 mg/m^3 (1932 ppm) at 85% relative humidity and 25°C. The sampling rate was 0.05 L/min. The average 5% breakthrough air volume was 15.2 L. Five percent breakthrough was defined as the point at which the effluent from the sampling tube contained ethyl alcohol at a concentration equivalent to 5% of the test atmosphere. The effluent of the sampling tube was monitored with a GC equipped with a gas sampling valve and an FID. The GC was calibrated with the test atmosphere.

Additional sampler capacity tests (Section 4.9.) were performed to determine if the relative humidity of the sampled air had an effect on sampler capacity. The average ethyl alcohol concentration of these test atmospheres was 3656 mg/m^3 (1941 ppm) at 6% relative humidity and 25°C. The sampling rate was 0.05 L/min. The average 5% breakthrough air volume was 18.9 L. Reduced relative humidity did not have a detrimental effect on the capacity of Anasorb 747 for ethyl alcohol as did low relative humidity for methyl alcohol in OSHA Method 91. (Ref. 5.2)

2.5   Desorption efficiency

2.5.1   The average desorption efficiency of ethyl alcohol from Anasorb 747 over the range of from 0.5 to 2 times the target concentration is 104.1%. (Section 4.10.1)

2.5.2   Desorbed samples remain stable for at least 2 days. (Section 4.10.2)

2.5.3   Desorption efficiencies of *m*-xylene, toluene, methyl isobutyl ketone, ethyl acetate, and methyl alcohol from Anasorb 747 were determined using the desorption solvent (60/40 DMF/CS_2) recommended in this method. These desorption efficiencies were high and constant. (Section 4.10.3)

2.5.4   Desorption efficiencies should be confirmed periodically because differences may occur due to variations between sampling media lots, desorption solvent, and operator technique.

2.6   Recommended air volume and sampling rate

2.6.1   Sample 12 L of air at 0.05 L/min for TWA samples.

2.6.2   Sample 0.75 L of air at 0.05 L/min for short-term samples.

2.6.3   The air concentration corresponding to the reliable quantitation limit becomes larger when short-term samples are collected. For example, the reliable quantitation limit is 20.7 mg/m^3 (11 ppm) for a 0.75-L sample.

2.7   Interferences (sampling)

2.7.1   There are no known interferences with the collection of ethyl alcohol on Anasorb 747. Generally, the collection of other chemicals will reduce the capacity of Anasorb 747 for ethyl alcohol.

2.7.2   Suspected interferences, such as chemicals used to denature the ethyl alcohol, should be reported to the laboratory when samples are submitted.

2.8   Safety precautions (sampling)

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

2.8.2   Follow all safety practices applicable to the work area.

2.8.3   Wear protective eyeware when breaking the ends of the glass sampling tubes. Take suitable precautions against cuts when connecting the sampling tubes.

3. Analytical Procedure

3.1   Apparatus

3.1.1   A GC equipped with an flame ionization detector (FID). A Hewlett-Packard 5890 GC, a 7673A automatic sampler, and an FID were used in this evaluation.

3.1.2   A GC column capable of separating ethyl alcohol from the desorbing solvent and potential interferences. A 60-m × 0.32-mm i.d. Restek Corp. Stabilwax (1-μm film thickness) fused silica capillary column (Restek catalog no. 10657) was used in this evaluation.

3.1.3   An electronic integrator or other suitable means of measuring detector response. A Waters 860 Networking Computer System was used in this evaluation.

3.1.4   Sample vials, 2-mL and 4-mL glass, with polytetrafluoroethylene-lined septum caps.

3.1.5   Pipets, disposable, Pasteur-type.

3.2   Reagents

3.2.1   Ethyl alcohol, 95% or better. Pharmco Products, Inc. 190 proof ethyl alcohol was used in this evaluation. The ethyl alcohol content can be expressed in proof or in percent volume. Percent volume is calculated from proof by dividing proof by two. Ninety-five percent volume ethyl alcohol is equivalent to 92.42 percent weight. The specific gravity (20/20°C) of 190 proof ethyl alcohol is 0.816. (Ref. 5.6)

3.2.2   Desorbing solution, 60/40 (v/v) DMF/carbon disulfide, reagent grade or better. EM OMNISOLV carbon disulfide (Lot no. 31132) and Baxter B&J Brand, High Purity Solvent DMF (Lot no. BB087) were used in this evaluation. p-Cymene (1 µL/mL) was added for use as an internal standard for this method. The large amount of DMF is necessary to dissolve water collected in air samples.

3.3   Standard preparation

3.3.1   Prepare analytical standards by injecting microliter amounts of reagent ethyl alcohol into tared 4-mL glass vials (sealed with polytetrafluoroethylene-lined septum caps) containing 3.0 mL of desorbing solution. Reweigh the vials to determine the weight of ethyl alcohol. Multiply this weight by the decimal equivalent of the percent weight of ethyl alcohol in the reagent. An analytical standard equivalent to a 1016 ppm air sample was prepared by weighing 30 µL of 190 proof ethyl alcohol into a sealed vial containing 3.0 mL of desorbing solution.

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

3.4   Sample preparation

3.4.1   Transfer the adsorbent section of each sampling tube to separate 4-mL glass vials. An air sampler is composed of two one-section sampling tubes (front and rear tube). Discard the foam and glass-wool plugs.

3.4.2   Add 3.0 mL of desorbing solution to each vial.

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

3.5   Analysis

3.5.1   Transfer an aliquot of both standards and samples into separate GC autosampler vials if necessary.

3.5.2   GC Conditions

temperatures (°C)
  injector: 250
  detector: 250
  column: 40, hold 1 min, program at 10°C/min to 220, hold temp until column is clear

gas flow rates (mL/min)
  column: 2.0 (H$_2$)
  split: 258 (H$_2$)
  septum purge: 1.8 (H$_2$)
  auxiliary: 38   (N$_2$)
  detector air: 375 (air)
  detector H$_2$:   27   (H$_2$)

miscellaneous
  detector: FID
  column: 60-m × 0.32-mm i.d. Stabilwax (df = 1.0-µm)
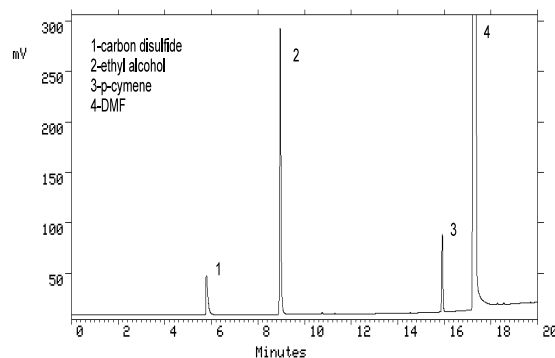 injection size: 1 µL (130:1 split)

Figure 3.5.2. Chromatogram of a standard.

1-carbon disulfide
2-ethyl alcohol
3-p-cymene
4-DMF

GC retention times (min)
ethyl alcohol: 9.0
p-cymene: 15.9 (internal standard)

The total GC run time was 23 min as a precaution to clear the column.

3.5.3   An internal standard (ISTD) calibration method should be used. Construct a calibration curve by plotting the ISTD corrected detector response for each standard solution against its respective concentration in micrograms of ethyl alcohol per sample. Determine the best-fit line through the data by curve fitting. Sample results must be bracketed by standard concentrations.

3.6   Interferences (analytical)

3.6.1   Any compound that gives an FID response and has a similar GC retention time as the analyte or the internal standard is a potential interference. Generally, chromatographic conditions can be altered to separate an interference.

3.6.2   Retention time on a single column is not proof of chemical identity. Confirmation of suspected identity should be performed by GC/mass spectrometry when necessary.

3.7   Calculations

The analyte amount per sample, micrograms of ethyl alcohol per sample, is obtained from the calibration curve. The back tube of the sample is analyzed primarily to determine if there was any breakthrough from the front tube during sampling. If a significant amount of analyte is found on the back tube (e.g., greater than 25% of the amount found on the front tube) this fact should be reported with sample results. If any analyte is found on the back tube it is added to the amount on the front tube. This analyte amount is then corrected by subtracting the total amount found in the blank. The air concentration is obtained by using the following equations.

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

where   A =   total micrograms (blank corrected) of analyte per sample
B =   liters of air sampled
C =   desorption efficiency

$$\text{ppm} = \frac{24.46 \times \text{mg/m}^3}{MW}$$

where   24.46 =   molar volume (liters) at 101.3 kPa (760 mmHg) and 25°C
MW =   46.07 for ethyl alcohol

3.8   Safety precautions (analytical)

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

3.8.2   Avoid skin contact and inhalation of all chemicals.

3.8.3   Wear safety glasses, gloves, and a lab coat at all times while working with chemicals.

4. Backup Data

4.1 Detection limit of the analytical procedure

The injection size recommended in the analytical procedure (1 µL, 130:1 split) was used in the determination of the detection limit of the analytical procedure. The detection limit was 40 pg on-column. It was determined by analyzing a dilute standard containing 15.52 µg/standard. This standard gave an ethyl alcohol peak with a height about 5 times the height of the baseline noise.
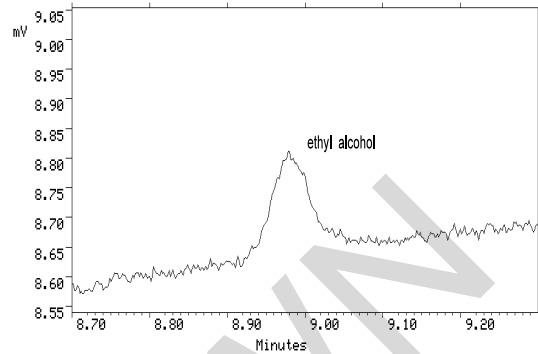

Figure 4.1. Detection limit of the analytical procedure.

4.2 Detection limit of the overall procedure

The detection limit of the overall procedure was determined by analyzing 400-mg portions of Anasorb 747 spiked with 15.52 µg of ethyl alcohol. This amount corresponds to an air concentration of 0.68 ppm (1.29 mg/m^3). The injection size listed in the analytical procedure (1 µL, 130:1 split) was used in the determination of the detection limit of the overall procedure.

Table 4.2
Detection Limit of the
Overall Procedure

sample no.	µg spiked	µg recovered
1	15.52	15.36
2	15.52	15.26
3	15.52	15.69
4	15.52	15.26
5	15.52	16.39
6	15.52	14.37

4.3 Reliable quantitation limit

The reliable quantitation limit was determined by analyzing 400-mg portions of Anasorb 747 spiked with 15.52 µg of ethyl alcohol. This amount corresponds to an air concentration of 0.68 ppm (1.29 mg/m^3). Because the recovery of the analyte from the spiked samples was greater than 75% with a precision of ±25% or better, the detection limit of the overall procedure and reliable quantitation limit are the same.

Table 4.3
Reliable Quantitation Limit
(Based on samples and data of Table 4.2)

percent recovered	statistics
99.0	
98.3	mean = 99.2%
101.1	SD = 4.24%
98.3	precision = (1.96)(±4.24%)
105.6	= ±8.3%
92.6	

4.4 Instrument response to the analyte

The instrument response to ethyl alcohol over the range of 0.5 to 2 times the target concentration was determined from multiple injections of analytical standards. The response was linear with a slope of 30.6.

Table 4.4
Instrument Response

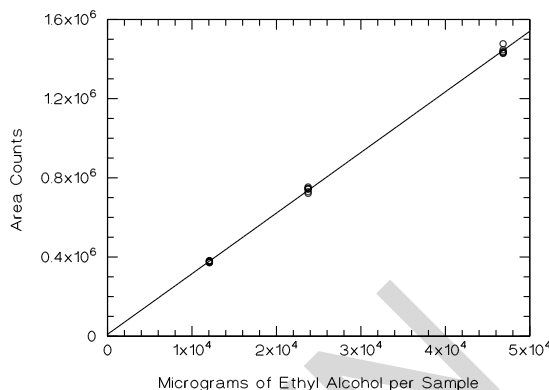| × target concn µg/standard	0.5× 12065	1.0× 23750	2.0× 46835
ISTD corrected areas	372840	747373	1477996
	381097	721669	1435538
	379231	754169	1431093
	381919	730028	1437428
	371549	743159	1428796
	377760	745198	1447001
mean	377399.3	740266.0	1442975.3

Figure 4.4. Calibration curve for ethyl alcohol.

4.5   Storage data

Thirty-six samples were collected using sampling tubes containing Anasorb 747 (Lot 645) over 2 days (18 samples each day) from controlled test atmospheres containing an average of 1979 ppm ethyl alcohol. The high level of ethyl alcohol (twice the target concentration) was used so that a sufficient number of samples to perform a storage test could be collected in a single day's run. Each sample was collected for 2 h at 0.05 L/min. The average relative humidity of the controlled test atmospheres was 75% at 26°C. Six samples (3 each day) were analyzed immediately after collection.   Fifteen samples were stored in a refrigerator at about 5°C, and 15 different samples were stored in the dark at about 23°C. Every few days, 3 samples from each group were selected and analyzed. The recovery of ethyl alcohol from samples stored at ambient temperature remained above 102%.

Table 4.5
Storage Tests

days of amb. storage	% recovery (ambient)			days of ref. storage	% recovery (refrigerated)		
0	105.0	105.4	102.4	0	102.6	104.4	100.3
3	104.2	105.4	103.3	2	104.3	105.7	102.9
7	103.4	101.6	100.7	6	102.5	105.5	102.5
10	104.2	102.9	103.4	9	104.8	103.3	100.4
14	101.3	102.7	101.6	13	106.0	104.9	103.6
16	104.6	102.3	101.7	15	103.4	106.9	102.9

Ambient Samples
Y = -0.117X + 104
Total Standard Error of Estimate = 5.17
95% Confidence Limit = ±(1.96)(5.17) = ±10.13

Figure 4.5.1. Ambient temperature storage test.

Refrigerated Samples
Y = 0.094X + 103
Total Standard Error of Estimate = 5.30
95% Confidence Limit = ±(1.96)(5.30) = ±10.39
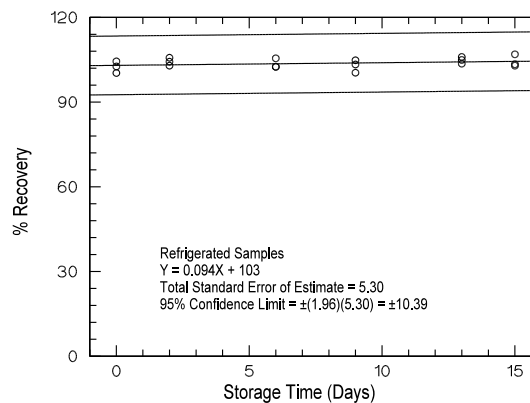
Figure 4.5.2. Refrigerated temperature storage test.

4.6   Precision (analytical method)

The precision of the analytical procedure is defined as the pooled coefficient of variation determined from replicate injections of analytical standards representing 0.5, 1, and 2 times the target concentration. The coefficients of variation are calculated from the data in Table 4.4. The pooled coefficient of variation is 0.014.

Table 4.6
Precision of the Analytical Method
(Based on the Data of Table 4.4)

× target concn	0.5×	1.0×	2.0×
µg/sample	12065	23750	46835
SD[1]	4303.5	12059.5	18281.0
CV	0.0114	0.0163	0.0127

[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 precision at the 95% confidence level 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 line in the storage graph as shown in Figure 4.5.1. The data for Figure 4.5.1 were used to determine the SEE of ±5.17% and the precision of the overall procedure of ±10.13%.

4.8   Reproducibility data

Six samples were collected from a test atmosphere. The ethyl alcohol concentration of the test atmosphere was 1919 ppm. The relative humidity was 82% at 26°C. A draft copy of this method and the samples were submitted for analysis. The samples were analyzed after 5 days of storage at about 5°C. All of the sample results were within the precision of the overall procedure.

Table 4.8
Reproducibility Data

µg collected	µg recovered	percent recovered	percent deviation
20636	21492	104.1	4.1
21323	22276	104.5	4.5
22118	23081	104.4	4.4
20708	22106	106.8	6.8
22515	23392	103.9	3.9
20889	21777	104.3	4.3

4.9   Sampler capacity

Sampler capacity was evaluated by sampling controlled test atmospheres with 400-mg front sampling tubes (Lot 645). The effluent of the sampling tube was monitored with a GC. The GC was calibrated with the test atmosphere. The average ethyl alcohol concentration was 1936 ppm. Two sampler capacity tests were performed under humid conditions, and two under dry conditions.

Table 4.9
Sampler Capacity Tests

80% RH, 25°C		90% RH, 25°C		5.9% RH, 25°C		6.1% RH, 26°C	
air vol, (L)	BT, (%)	air vol, (L)	BT, (%)	air vol, (L)	BT, (%)	air vol, (L)	BT, (%)
11.9	0	5.9	0	13.7	0	7.4	0
12.3	0	8.0	0	14.7	0	8.5	0
12.8	0	9.1	0	15.7	0	9.8	0
13.2	0	10.5	0	16.7	0	14.6	0
13.5	0	12.3	0	17.2	0	15.5	0
13.7	0	13.3	0	17.4	0	16.4	0
14.3	0	14.0	0	17.9	0	16.7	0
14.7	0.1	14.4	0.7	18.4	1.1	17.7	0
15.2	0.8	14.7	2.6	18.9	3.6	17.9	1.3
15.6	3.8	15.2	11.1	19.2	5.9	18.1	1.5
16.1	13.6	15.4	19.1	19.5	8.4	18.6	3.7
16.5	35.1	15.7	29.8	19.7	12.7	18.9	6.5
16.7	44.0	16.2	48.6	19.9	16.0	19.1	8.6
17.4	95.9	17.3	72.3	20.2	21.3	19.6	16.8

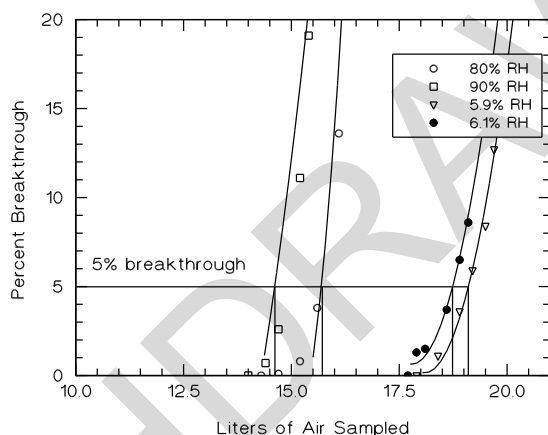RH = relative humidity   BT = breakthrough

Figure 4.9. Sampler capacity tests.

4.10   Desorption efficiency and stability of desorbed samples

   4.10.1   Desorption efficiency

The desorption efficiency of ethyl alcohol from Anasorb 747 was determined by liquid spiking 400-mg portions of adsorbent (Lot 645) with the alcohol at 0.5, 1, and 2 times the target concentration. These samples were stored overnight at ambient temperature and then desorbed and analyzed. The average recovery was 104.1% over the studied range.

Table 4.10.1
Desorption Efficiency

× target concn μg/sample	0.5× 11851	1.0× 23725	2.0× 47405
DE, %	105.8	104.5	105.2
	105.8	101.6	106.7
	104.4	106.0	103.4
	101.0	101.3	103.3
	104.3	104.5	104.3
	106.1	100.6	105.1
mean	104.6	103.1	104.7

   4.10.2   Stability of desorbed samples

The stability of desorbed samples
was verified by reanalyzing the 1.0 times target concentration samples following the original analysis. Samples are considered stable if the average of the percent difference between the initial and the reanalyzed samples is less than ±5% [average(% initial-% reanalyzed)<5%]. The samples were resealed immediately after the original analysis and fresh standards were used in the reanalysis. Both the original desorbed samples (4-mL

vials with Anasorb 747) and the transferred (2-mL vials without Anasorb 747) samples were reanalyzed 5 and 2 days, respectively, after the original analysis. The average of initial recoveries was 103.1%, the average of the reanalysis of the original desorbed samples was 105.6%, and the average for the transferred samples was 106.0%.

Table 4.10.2.1
Stability of Desorbed Samples

initial recovery (percent)	recovery after 5 days (percent)	change
104.5	108.2	+3.7
101.6	106.6	+5.0
106.0	106.1	+0.1
101.3	103.9	+2.6
104.5	104.0	-0.5
100.6	104.8	+4.2

Table 4.10.2.2
Stability of Transferred Samples

initial recovery (percent)	recovery after 2 days (percent)	change
104.5	105.7	+1.2
101.6	105.4	+3.8
106.0	108.5	+2.5
101.3	104.4	+3.1
104.5	105.0	+0.5
100.6	107.2	+6.6

4.10.3   Desorption efficiency of other analytes

The desorption efficiencies of other analytes from Anasorb 747 was determined by liquid spiking 400-mg portions of adsorbent (Lot 645) with the analytes at 0.1, 0.5, 1, and 2 times the OSHA PELs. The spiked amounts were based on 10-L air volumes, except for methyl alcohol which was based on 5 L. OSHA Method 91 for methyl alcohol recommends a 5-L air volume. These spiked samples were stored overnight at ambient temperature and then desorbed and analyzed. The analytes studied were *m*-xylene, toluene, methyl isobutyl ketone, ethyl acetate, and methyl alcohol. The respective average recoveries were 96.9%, 97.3%, 101.5%, 102.6% and 100.3%.

Table 4.10.3.1
Desorption Efficiency of *m*-Xylene

× target concn	0.1×	0.5×	1.0×	2.0×
µg/sample	434	2171	4342	8684
DE, %	104.2	98.8	96.5	97.4
	98.4	96.0	96.5	97.6
	98.2	95.0	96.8	96.8
	96.7	97.0	95.8	96.2
	92.3	97.9	96.6	98.1
	94.2	95.2	94.9	99.1
mean	97.3	96.6	96.2	97.5

average DE over the studied range was 96.9%

Table 4.10.3.2
Desorption Efficiency of Toluene

× target concn	0.1×	0.5×	1.0×	2.0×
µg/sample	346	1732	3464	6928
DE, %	96.0	94.4	101.4	97.6
	94.6	93.8	101.5	95.6
	102.0	97.0	101.4	95.5
	98.9	94.4	96.8	96.1
	101.0	96.0	97.2	95.8
	97.5	94.1	97.8	98.5
mean	98.3	95.0	99.4	96.5

average DE over the studied range was 97.3%

Table 4.10.3.3
Desorption Efficiency
of Methyl Isobutyl Ketone

× target concn	0.1×	0.5×	1.0×	2.0×
µg/sample	201	1005	2010	4021
DE, %	101.0	101.2	101.3	102.0
	102.4	100.2	100.1	102.2
	99.1	101.7	101.4	103.4
	100.8	102.3	100.7	104.4
	100.6	101.5	102.2	101.7
	101.7	100.1	102.0	102.0
mean	100.9	101.2	101.3	102.6

average DE over the studied range was 101.5%

Table 4.10.3.4
Desorption Efficiency
of Ethyl Acetate

× target concn	0.1×	0.5×	1.0×	2.0×
µg/sample	1430	7152	14304	28608
DE, %	103.8	105.2	102.9	98.9
	104.2	103.6	100.8	104.7
	102.9	99.5	102.0	100.8
	103.1	103.6	104.8	99.5
	101.1	103.0	105.7	101.1
	101.6	107.2	100.3	101.3
mean	102.8	103.7	102.8	101.0

average DE over the studied range was 102.6%

Table 4.10.3.5
Desorption Efficiency
of Methyl Alcohol

× target concn	0.1×	0.5×	1.0×	2.0×
µg/sample	122	630	1259	2518
DE, %	103.3	97.3	102.6	98.0
	102.2	102.8	98.6	97.5
	101.8	102.1	99.9	100.2
	99.6	101.9	91.2	99.2
	102.4	103.5	102.1	100.8
	102.8	102.6	99.5	95.6
mean	102.0	101.7	99.0	98.6

average DE over the studied range was 100.3%

5. References

5.1 *NIOSH Manual of Analytical Methods*, 3rd. ed; Eller, P.M., Ed.; U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, Division of Physical Sciences and Engineering: Cincinnati, DHHS (NIOSH) Publication No. 84-100, 1984; Method 1400.

5.2 Hendricks, W. "OSHA Method No. 91, Methyl Alcohol"; OSHA Salt Lake Technical Center, unpublished, Salt Lake City, UT 84165-0200, October 1991.

5.3 Harper, M. Technical Information Sheet: 226-82/83, 1991; SKC, Inc., Eighty Four, PA.

5.4 *Documentation of the Threshold Limit Values and Biological Exposure Indices*, 5th. ed.; American Conference of Governmental Industrial Hygienists, Inc.: Cincinnati, 1986; p 242.2.

5.5 *Code of Federal Regulations*, Title 29, 1910.1000, Table Z-1-A, U.S. Office of the Federal Register National Archives and Records Administration, Washington, DC, 1991.

5.6 *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd ed.; Grayson, M. Ed.; John Wiley & Sons: New York, 1980, Vol. 9; pp 338-373.

5.7 OSHA Computerized Information System Database, Occupational Health Services, Inc. (OHS) MSDS File; Ethyl Alcohol; Revision Date: 06/23/92; OSHA SLTC, Salt Lake City, UT 84165-0200.

5.8 *IARC Monographs on the Evaluation of Carcinogenic Ricks to Humans, Alcohol Drinking*; Volume 44; International Agency for Research on Cancer, Secretariat of the World Health Organization: UK, 1988; ISBN 92 832 1244 4.

5.9 *Hawley's Condensed Chemical Dictionary*; 11th ed.; Revised by Sax, I.N. and Lewis, R.J.; Van Nostrand and Reinhold: New York, 1987; pp 477-478.

5.10. *Hawley's Condensed Chemical Dictionary*; 11th ed.; Revised by Sax, I.N. and Lewis, R.J.; Van Nostrand and Reinhold: New York, 1987; p 31.

5.11 Anderson, E.V. *Chem. Eng. News* **1992,** *70*(44), 7-13.