Designation: D 4413 – 98 (Reapproved 2003)

Standard Test Method for Determination of Ethylene Oxide in Workplace Atmospheres (Charcoal Tube Methodology)[1]

This standard is issued under the fixed designation D 4413; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method describes the determination of ethylene oxide (oxirane) in workplace atmospheres using charcoal tube methodology.

1.2 This test method is compatible with low flow rate personal sampling equipment: 10 to 200 mL/min. It can be used for personnel or area monitoring.

1.3 The sampling method develops a time-weighted average (TWA) sample and can be used to determine short-term excursions (STE).

1.4 The applicable concentration range for the TWA sample is from 0.3 to 20 ppm(v).

1.5 The applicable concentration range for the STE sample ranges from 1 to 1000 ppm(v).

1.6 The values stated in SI units shall be regarded as the standard. Inch-pound units are provided for information only.

1.7 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* (For more specific safety precautionary statements see Section 9 and 10.2.3 and 11.1.3.)

2. Referenced Documents

2.1 *ASTM Standards:*

D 1356 Terminology Relating to Sampling and Analysis of Atmospheres[2]

D 3686 Practice for Sampling Atmospheres to Collect Organic Compound Vapors (Activated Charcoal Tube Adsorption Method)[2]

E 355 Practice for Gas Chromatography Terms and Relationships[3]

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms relating to this test method, refer to Terminology D 1356 and Practice E 355.

4. Summary of Test Method

4.1 A known volume of sample air is passed through a glass tube packed with activated charcoal. Ethylene oxide is removed from the air stream by adsorption on the charcoal.

4.2 A two-section tube containing a front and a backup section of adsorbent is used to collect the sample. The backup section adsorbs vapors that penetrate the front section and is used to determine if the collection capacity of the tube has been exceeded.

4.3 The ethylene oxide is desorbed with carbon disulfide and analyzed with a gas chromatograph equipped with a flame ionization detector.

4.4 Quantitation is based on the comparison of peak heights or peak areas of the samples with those of standard solutions.

4.5 Recovery factors are determined by the same techniques used for the atmospheric analysis applied to known standards.

5. Significance and Use

5.1 Ethylene oxide is a major raw material used in the manufacture of numerous other bulk industrial chemicals as well as a sterilizing agent.

5.2 This test method provides a means of evaluating exposure to ethylene oxide in the working environment at the presently recommended exposure guidelines:

5.2.1 OSHA PEL 1 ppm(v) 8-hr TWA.[4]

5.2.2 ACGIH TLV 1 ppm(v).[5]

6. Interferences

6.1 Organic components that have the same or nearly the same retention time as ethylene oxide during gas chromatographic analysis will interfere.

6.2 Other volatile organic compounds in the area where samples are taken should be considered.

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[1] This test method is under the jurisdiction of ASTM Committee D22 on Sampling and Analysis of Atmospheres and is the direct responsibility of Subcommittee D22.04 on Workplace Atmospheres.

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[2] *Annual Book of ASTM Standards*, Vol 11.03.

[3] *Annual Book of ASTM Standards*, Vol 14.02.

[4] Title 29, Code of Federal Regulation (Section 1910.1047), U.S. Department of Labor, revised 49FR 25797 June 22, 1984.

[5] "Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1997," American Conference of Governmental Industrial Hygienists, P.O. Box 1937, Cincinnati, OH 45201.

6.3 Such interferences can be minimized by proper selection of gas chromatographic columns. A mass spectrometric detector can be used to confirm the presence of ethylene oxide.

6.4 Water mists, high humidity, elevated temperatures, and high concentrations of other compounds affect adsorption efficiencies by reducing the adsorptive capacity of the charcoal for ethylene oxide.

7. Apparatus

7.1 *Charcoal Sampling Tube*:

7.1.1 *Description*—A sampling tube consists of a length of glass tubing containing two sections of activated charcoal that are held in place by nonadsorbent material and sealed at each end. The front section is retained by a plug of glass wool and the back section is retained by a second 2-mm portion of urethane foam or other retainer, such as glass wool. The two charcoal sections are separated by a 2-mm portion of urethane foam. The ends of the tube are flame-sealed (refer to Practice D 3686). The back section of the sample tube adsorbs vapors that penetrate the front section and is used to determine if the collection capacity of the tube has been exceeded. Instead of a single tube, two tubes in series may be used (see 11.1.12).

7.1.2 Sampling tubes containing approximately 1 g of activated charcoal are used for sampling ethylene oxide. Two types of sampling tubes have been found suitable.[6,7]

7.1.2.1 A sampling tube consisting of a glass tube 110-mm long, 10 mm in outside diameter, 8 mm in inside diameter and containing two sections of activated charcoal (Pittsburgh Coconut Base (PCB) 20/40 mesh),[6] 800 and 200 mg, separated by a 2-mm section of urethane foam. This tube is capable of sampling 3 to 20 L of air, depending on the environmental conditions, with no or with minimal breakthrough of ethylene oxide into the back section **(1,2)**.[8]

7.1.2.2 A sampling tube, consisting of a glass tube 150-mm long, 8 mm in outside diameter, 6 mm in inside diameter and containing two sections of activated charcoal (Columbia JXC, 20/48 mesh),[7] 700 and 390 mg, separated by a 2-mm section of urethane foam. This tube is capable of sampling 3 to 8 L of air, depending on the environmental conditions, with no or with minimal breakthrough of ethylene oxide into the back section **(3)**.

7.1.2.3 When sampling under conditions of high humidity, elevated temperatures, or in the presence of high concentrations of other compounds, the lesser volume in 7.1.2.1 and 7.1.2.2 should be used.

7.1.3 The pressure drop across the charcoal tube should be no greater than 3.3 kPa [25 mm Hg] at a flow rate of 1000 mL/min.

7.1.4 Glass tubes shall be held in suitable protective holders to prevent breakage during sampling and to protect workers.

7.1.5 Polyethylene end caps are used to reseal the charcoal tubes. Caps must fit tightly to prevent leakage.

7.2 *Syringes*:

7.2.1 *Gas-Tight Syringe*, 1 and 2-mL capacity with a low dead-volume needle.

7.2.2 *Microlitre Syringes*, 10, 100, and 1000-µL or other convenient sizes for making standards.

7.3 *Vials*, glass, 4, 8, and 12 mL [1, 2, and 3 dram] for desorbing samples and holding standards, polyethylene or TFE-fluorocarbon-lined screw caps and septum-valve caps.

7.4 *Styrene Foam Shipping Container*, seamless polystyrene foam container with a minimum wall thickness of 35 mm [1⅜ in.] and approximately 12-L [⅓-ft^3] capacity. Other containers, such as vacuum bottles, may be suitable as long as they can maintain the samples at dry-ice temperatures during shipping.

7.5 *Mechanical Shaker*, or vibrator that will vigorously agitate the desorbing sample.

7.6 *Sampling Equipment*:

7.6.1 Any pump whose flow rate can be accurately determined and set at the desired sampling rate is suitable.

7.6.2 As a guideline, suitable pumps are those having stable low flow rates, ±10 % of the set flow rate, within the range of 10 to 100 mL/min, for sampling periods of up to 8 h. Flowrates up to 200 mL/min can be used for STE (15 min) monitoring.

7.6.3 All sampling pumps shall be carefully calibrated with a charcoal tube in the proper sampling position (see Fig. A2.1 of Practice D 3686). The accuracy of determining the total air volume sampled should be 100 ± 5 %.

7.6.4 *Tubing*, rubber or plastic, 6-mm [¼-in.] bore, about 90-cm [3-ft] long equipped with a spring clip to hold the tubing and charcoal tube in place on worker's lapel area.

7.6.4.1 **Caution:** Sampling tubes shall not be used with plastic or rubber tubing upstream of the charcoal. Absorption by the tubing may introduce sampling errors.

7.7 *Gas Chromatograph*:

7.7.1 Gas chromatographs that employ either a flame ionization detector or a detector whose specifications are equivalent in sensitivity and selectivity should be used. Detectors shall be capable of determining ethylene oxide concentrations of interest with a signal to noise ratio of at least 10 to 1. Suitable detectors are capable of detecting approximately 1×10^{-10} g of ethylene oxide per injection. For example, 3.2 µg of ethylene oxide will be collected from a 6-L air sample containing 0.3-ppm ethylene oxide and the use of 5 mL of desorption solvent will result in a concentration of 0.65 µg of ethylene oxide per millilitre of CS_2.

7.7.2 A gas chromatographic column capable of separating ethylene oxide from other components is required. A number of suitable columns have been discussed in the literature **(1, 2, 3, 4)**. Table 1 lists columns and the chromatographic conditions used for ethylene oxide determination. Table 2 lists the retention lines of some potential interferences for three chromatographic columns. Column suitability shall be verified by testing two or more columns of dissimilar packings to minimize the possibility of interferences. If the chromatographic

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[6] Activated coconut-shell charcoal (Pittsburgh Coconut Base, 20/40 mesh) has been found to have adequate adsorption capacity and recovery properties. Prepared tubes containing activated coconut-shell charcoal (800 mg/200 mg) are available from a number of sources.

[7] Columbia activated (pelletized) carbon, grade-JXC (20/48 mesh) is no longer available. The sole supplier of JXC carbon (700 mg/390 mg) known to the committee at this time is SKC, Eighty Four, PA. If you are aware of alternate suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend.

[8] The boldface numbers in parentheses refer to the list of references at the end of this test method.

TABLE 1 Gas Chromatographic Columns for Determination of Ethylene Oxide

Column	Length	Diameter	Carrier Flow (mL/min)	Temperature °C Column	Temperature °C Detector	Ethylene Oxide Retention Time (min)	Ref
(1) Chromosorb 102 (60/80 mesh)	2 m [6.6 ft]	3.17 mm [1/8 in.]	30	140	250	1.4	(2)
(2) Phenapiwax 12 %	6.1 m [20 ft]	3.17 mm [1/8 in.]	20	80	300	3.8	(2)
(3) Porapak QS, (100/200 mesh)	2.0 m [6.6 ft]	2 mm [0/078 in.]	30	140	250	1.5	(5)

TABLE 2 Retention Time for Ethylene Oxide and Possible Interfering Compounds

Compound	Retention Time (min) Chromosorb 102	Phenapiwax	Porapak QS
Freon 12	0.88	2.2	1.12
Methyl chloride	0.99	2.8	1.01
Vinyl chloride	1.23	2.9	1.48
Freon 11	3.09	3.7	3.69
Ethyl chloride	1.95	3.8	2.22
Ethylene oxide	1.36	3.8	1.53
Methyl bromide	1.67	3.9	1.76
Propylene oxide	1.88	4.9	2.42
Vinylidene chloride	3.44	5.0	4.07
Carbon disulfide	2.89	7.0	3.08
Butylene oxide	6.10	8.3	7.91
Acrylonitrile	2.74	9.0	3.32
Benzene	3.26	14.8	11.07

peak for ethylene oxide overlaps the peak for other components by no greater than 5 %, the separation is considered to be satisfactory.

7.7.3 Gas chromatographic operating conditions for the instrument being used should be optimized so that the separation required for a successful analysis can be obtained in a reasonable time.

8. Reagents

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise noted, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[9] Other reagents may be used provided it can be demonstrated that they are of sufficiently high purity to permit their use without decreasing the accuracy of determination.

8.2 *Carbon Disulfide* (CS_2), spectroquality, should contain no major interferences at the retention time of ethylene oxide.

8.3 *Ethylene Oxide*, commercially available in lecture bottles at 99 % purity or better.

9. Safety Precautions

9.1 Carbon disulfide vapors are toxic and highly flammable. Usage should be restricted to a well-ventilated hood.

9.2 Small waste quantities of carbon disulfide shall be disposed of only in accordance with local regulations and accepted practices.

9.3 Ethylene oxide may cause irritation and necrosis of the eyes, blistering, edema, and necrosis of the skin.

9.3.1 **Caution:** Ethylene oxide is toxic, highly flammable, and should be handled under a hood.

9.4 Avoid inhalation of, or skin contact with, carbon disulfide, carbon disulfide solutions of ethylene oxide, and ethylene oxide gas.

10. Calibration

10.1 *Pump Calibration*:

10.1.1 Calibrate the sample pump flow in accordance with Practice D 3686, Annex A2.

10.1.2 Calibrate the flow rate of the pump from 10 to 100 mL/min for TWA sampling and 100 to 200 mL/min for short term excursions (STE) sampling depending on the duration of the sample and the volume of the sample needed (see 11.1).

10.2 *Gas Chromatograph Calibration*:

10.2.1 Prepare calibration standards containing micrograms of ethylene oxide per mL of carbon disulfide over the range of interest.

10.2.2 Pipet 10 mL of carbon disulfide into each of two 12-mL [3-dram] vials and seal with septum-valve caps. Place the vials in dry ice or a wet-ice bath to cool.

10.2.3 Adapt a valve on the ethylene oxide cylinder with a 0.25-in. Swagelok tubing nut which contains a chromatographic septum. **Caution:** Ethylene oxide is toxic, highly flammable, and therefore should be handled under a hood.

10.2.4 Place the ethylene oxide cylinder in the hood and insert a hypodermic needle through the septum on the cylinder. Open the valve and allow the ethylene oxide gas to vent through the needle for about 10 s to purge the air from the system. Remove the needle.

10.2.5 Using a 1.0 or 2.0-mL gas syringe (equipped with a low-volume needle), insert the needle through the septum on the cylinder and withdraw ethylene oxide into the syringe. Flush the syringe with ethylene oxide three times (directly into

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[9] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

the exhaust slot at the back of the hood) to remove any air that may have been trapped in the syringe barrel or the needle.

10.2.6 Inject 1.0 mL of ethylene oxide through the septum cap and into the chilled carbon disulfide to prepare Concentrate A. Inject 2.0 mL into a second vial to prepare Concentrate B. Shake for 2 min, label, and allow the contents to warm to room temperature 15 min before use. These concentrates will contain 180 and 360 µg of ethylene oxide per millilitre, respectively.

10.2.7 Pipet 10 mL of carbon disulfide into each of four 12-mL [3-dram] vials and seal with septum valves. Place in dry ice, a wet-ice bath, or equivalent to cool. Momentarily loosen the cap to equalize the pressure in the vial. Inject 1.0 mL of Concentrate A and Concentrate B, prepared in 10.2.6, each into a separate vial. These standards will contain 180 and 360 µg/11 mL (16.36 and 32.72 µg/mL) of ethylene oxide in carbon disulfide. Inject 0.1 mL of Concentrate A and Concentrate B each into separate vials. These standards will contain 18 and 36 µg/10.1 mL (1.78 and 3.56 µg/mL) of ethylene oxide in carbon disulfide.

10.2.8 When it is necessary to cover a broader range, additional standards are prepared by dilution of the above standards or concentrates with carbon disulfide in a similar manner.

10.2.9 When not in use, store the standards in an ice bath or freezer. Allow standards to warm to room temperature for 15 min before use.

10.2.10 The standards may be stored in a freezer up to five days. At least one independent standard shall be prepared each day to verify the response factor.

10.2.11 Analyze each ethylene oxide in carbon disulfide standard in duplicate by gas chromatography. Draw 3 to 4 µL of the solution to be analyzed into a 10-µl syringe and make sure there are no bubbles in the syringe. Adjust the volume in the syringe to 2 µL. After the needle is removed from the sample and prior to injection, the plunger is pulled back approximately 1 µL to minimize evaporation of the sample from the tip of the needle. Inject the contents of the syringe into a gas chromatograph. The same syringe used to inject the standards shall be used for the samples.

10.2.12 An alternative injection procedure (solvent flush technique) may be used to inject samples into the chromatograph. Flush a 10-µL syringe with CS_2 several times to wet the barrel and plunger. Draw 1 µL of CS_2 into the syringe and remove the tip of the needle from the solvent. Withdraw the plunger an additional 0.5 µL to separate the CS_2 from the sample with a small air bubble. Dip the needle into the sample solution in the desorption vial and withdraw the plunger until the bubble between the solvent and the sample has passed the 2-µL mark on the syringe. Remove the tip of the needle from the sample solution and adjust the volume in the syringe until the meniscus of the air bubble rests on the 2-µL mark. Remove the excess sample from the tip of the needle. The amount of sample solution in the syringe is 2 µL plus the amount in the needle. Pull the plunger back an additional 0.5 µL to prevent the sample solution from evaporating from the tip of the needle. Inject the entire contents of the syringe into the chromatograph.

10.2.13 Prepare a calibration curve by plotting micrograms of ethylene oxide per millilitre of carbon disulfide versus peak height or peak area. From the calibration curve, determine the linear range for the analysis. If the plot is linear over the range of the standards, a linear regression equation or an appropriate response factor may be used.

11. Procedure

11.1 *Sampling*:

11.1.1 Break open both ends of the charcoal tube to be used for sampling, ensuring that each opening is at least one-half the inside diameter of the tube. Place identifying labels on each tube.

11.1.2 Attach a sample pump that has been previously calibrated within the flow rate range of 10 to 100 mL/min (10.1), for TWA sampling and 100 to 200 mL/min for STE sampling, to the activated charcoal tube with rubber or plastic tubing, placing the backup section nearest the pump. A protective cover should be placed on the tube.

11.1.3 For a breathing zone sample, fasten the sampling pump to the worker and attach the sampling tube as close to the worker's breathing zone as possible. Position the tube in a vertical position to avoid channeling of air through adsorber sections. **Caution:** Assure that the presence of the sampling equipment is not a safety hazard to the worker.

11.1.4 Turn on the pump, which has previously been adjusted and calibrated as described in 10.1.

11.1.5 A maximum total volume up to 20 L can be collected with the PCB charcoal tube **(1, 2)** and a maximum total volume up to 8 L can be collected with the JXC charcoal tube **(3).**

11.1.6 Under collection conditions of high humidity (>85 % at 22 ± 2°C, 0.014 lb of water/lb of air), elevated temperatures (>35°C), or in the presence of high concentrations of other organic compounds, the maximum sample volume of 10 L for the PCB charcoal tube or 6 L for the JXC charcoal tube should not be exceeded. Attempting to collect larger quantities at high concentrations, high flow rates or long sampling times may result in a breakthrough of ethylene oxide and loss of sample. The breakthrough volume can be determined for these adverse conditions in accordance with A1.2.

11.1.7 At the end of the sampling period, note the flow rate or pump register reading if appropriate, turn the pump off, and note and record the time, temperature, and barometric pressure.

11.1.8 Disconnect the sample tube and seal both ends with polyethylene end caps.

11.1.9 Present at least one charcoal sampling tube for analysis as a blank with every 10 or 20 samples, or for each specific inspection or field study. Break the sealed ends off the tube and cap it with the plastic caps. Do not draw air through the tube, but in all other ways treat it as an air sample.

11.1.10 Ship samples in a dry ice-packed shipping container as soon as possible, store in a freezer (less than −5°C) or in dry ice (−78°C) until they are analyzed, and analyze within 3 weeks.

11.1.11 Do not store samples at room temperature longer than one day during storage or shipment. Migration or equilibration of the sampled material within the sampling tube during prolonged or adverse storage handling could be confused with breakthrough.

11.1.12 If samples cannot be analyzed within 1 day or stored in a freezer, collect samples using two tubes connected in a series; one charcoal tube for the front section and a second charcoal tube for the back section. Separate the tubes immediately after sampling to avoid migration. The precision and bias statements, 13.1 and 13.2, do not apply to samples stored at room temperature more than one day.

11.2 *Analysis*:

11.2.1 Prepare a set of vials by placing appropriate labels on them; indicating the identification number; and designating whether they are the front (F) section of the sample tube or the backup (B) section.

11.2.2 Pipet exactly 5.0 mL of carbon disulfide into each vial, seal and chill in a dry ice or wet-ice bath for at least 10 min.

11.2.3 Remove the plastic caps from the sampling tubes or score and break the tubes just above the plug.

11.2.4 Remove the plug of glass wool that holds the front portion of charcoal and add the glass wool to the vial since some charcoal may be attached. Slowly add the charcoal to the chilled carbon disulfide in the vial (approximately 10 s). Reseal the vial.

11.2.5 Discard the foam spacer and pour the charcoal from the back section into a second vial containing chilled carbon disulfide.

11.2.6 Desorb a previously unopened sample tube in the same manner to serve as a reagent blank.

11.2.7 Agitate at room temperature for 5 to 10 min for complete desorption. Analyze within approximately 30 min or store in dry ice for no longer than 1 h before analysis to minimize loss of ethylene oxide.

11.2.8 Inject the sample mixture into the gas chromatograph as described in 10.2.11 or 10.2.12.

11.2.9 Determine the peak height or peak area for the ethylene oxide peak.

11.2.10 Calculate the concentration of ethylene oxide as directed in Section 12.

11.2.11 Analyze samples, standard solutions used for calibration, and the samples used to determine adsorption/desorption efficiencies in the same manner. Use the same injection technique and injection volume for samples and standards.

12. Calculation

12.1 Subtract the quantity of ethylene oxide found in the reagent blank (see 11.2.6) from the amount found in the sample.

12.2 Determine the micrograms of ethylene oxide (EO) found in the front and backup portions of the sample tube using the calibration curve prepared in 10.2.13 or calculate directly from the standard as follows:

$$\text{EO, µg} = \frac{A \times B \times C}{\text{D}} \quad (1)$$

where:

A = µg of EO/mL of standard solution,
B = mL of CS_2 used to desorb sample,
C = peak height or area of sample, and
D = peak height or area of standard.

12.3 Sum the values of the front and back sections. If the backup section contains more than 15 % of the total amount of ethylene oxide, the loss of ethylene oxide because of breakthrough may have occurred. This would require reevaluation of the sampling and storage conditions and, in most cases, resampling. In cases where the calculated airborne concentration exceeds the exposure guideline, despite breakthrough, it is meaningful to report the results as greater than the calculated value.

12.4 Correct the micrograms EO found for the recovery factor as follows:

$$\text{Corrected EO, µg} = \frac{\text{EO found}}{R} \quad (2)$$

Where R equals the recovery factor for PCB or JXC charcoal written as a decimal (see A1.2).

12.5 Calculate the volume of air collected:

12.5.1 For sample pumps, calibrate with flow-rate meters as follows:

$$V = F \times t \times G \times \frac{\text{Barometric pressure (kPa)}}{101.325\text{ kPa}} \times \frac{298}{°C + 273} \quad (3)$$

where:

V = volume of air sampled, in litres,
F = sampling flow rate, in millilitres per minute,
t = sampling time, in minutes,
G = conversion factor, 0.001, from 1 L/1000 mL, and
$°C$ = sampling temperature.

12.5.2 For sample pumps with digital counters as follows:

$$V = H \times I \times G \times \frac{\text{Barometric pressure (kPa)}}{101.325} \times \frac{298}{°C + 273} \quad (4)$$

where:

V = volume of air sampled, in litres,
H = stroke volume of pump, in millilitres per stroke,
I = net strokes or counts during sampling period, and
G = conversion factor, 0.001, from 1 L/1000 mL.

12.6 Calculate concentration of ethylene oxide in air:

12.6.1 Parts per million (v/v) in air:

$$\text{ppm (v)} = \frac{\text{corrected µg of EO} \times 22.47}{\text{litres of air sampled} \times 44.05} \quad (5)$$

where 44.05 equals the molecular weight of ethylene oxide.

12.6.2 Or milligrams per cubic metre (mg/m^3):

$$\text{mg/m}^3 = \frac{\text{µg}}{\text{L}} = \frac{\text{corrected µg EO}}{\text{litres of air sampled}} \quad (6)$$

12.7 Results from the field blanks (see 11.1.9) shall not be used to correct sample results. If a field blank shows contamination, the samples taken during the test shall be assumed to be contaminated.

13. Precision and Bias

13.1 *TWA*:

13.1.1 For the PCB charcoal tubes, the average recovery of ethylene oxide is reported to be 91.5 % with a standard deviation of 11.7 % over a concentration range from 0.3 to 21 ppm(v), both at high and low humidity **(2).**[10]

13.1.2 For the JXC charcoal tubes, the average recovery of ethylene oxide is reported to be 97 % at the 0.5 and 5.0-ppm(v) level with relative standard deviation and systematic error of 3.76 and 2.9 % respectively **(3).** A round-robin study of six laboratories, for 16 and 179-µg EO added to tubes, produced an average recovery of 92 % with a standard deviation of 12.5 %.

13.1.3 In both studies, 13.1.1 and 13.1.2, the samples were prepared in the laboratory and may not reflect the precision of actual field samples.

13.1.4 In the first part of an extensive collaborative study **(5),** 30 tubes spiked with ethylene oxide were sent to 24 laboratories. The amount of ethylene oxide spiked ranged from 7.35 to 924 µg, which is equivalent to a range 0.4 to 51.3 ppm(v) (based on a 10-L sample). The average recovery was 91 % for PCB charcoal tubes and 100 % for JXC. The average relative standard deviation (precision) for the concentration ranging from 1.7 to 51.3 ppm(v), was 14.9 % for PCB and 15.4 % for JXC, including both within-and-between laboratory variability. The average relative standard deviation (precision) for the lowest concentration (0.4 ppm) was 25.0 and 25.6 % for PCB and JXC respectively.

13.2 *(STE)* — Supporting data are shown in Table 3 and Table 4.

13.2.1 For PCB charcoal tubes, the average recovery of ethylene oxide is reported to be 100 % with a relative standard deviation (95 %) of 11.8 % over a concentration range of 1 to 10 ppm(v) at a humidity of 90 % **(6).**

13.2.2 For the JXC charcoal tubes, the average recovery of ethylene oxide is reported to be 109 % with a relative standard deviation (95 %) of 13.2 % over a concentration range of 1 to 10 ppm(v), at a humidity of 90 % **(6).**

13.2.3 In both studies, 14.1 and 14.2, the samples were prepared in the laboratory and may not reflect the precision of actual field samples.

TABLE 3 Summary of Analysis of JXC and PCB Tubes by Concentration

Actual Concentration: 1 ppm	JXC Tube		PCB Tube	
Flowrate (mL/min)	100	200	100	200
Average (ppm)[A]	1.27	1.11	1.26	0.86
Standard Deviation	0.125	0.139	0.108	0.088
Accuracy (% Recovery)	127	111	126	86
Precision (% RSD[B])	19.3	24.6	16.8	20.0
Bias (%)	+27.0	+11.0	+26.0	−14.2

Actual Concentration: 4.98 ppm	JXC Tube		PCB Tube	
Flowrate (mL/min)	100	200	100	200
Average (ppm)[A]	4.50	5.41	4.40	5.07
Standard Deviation	0.151	0.468	0.272	0.171
Accuracy (% Recovery)	90	109	88	102
Precision (% RSD[B])	6.6	17.0	12.1	6.6
Bias (%)	−10.0	+8.2	−12.0	+1.4

Actual Concentration: 9.95 ppm	JXC Tube		PCB Tube	
Flowrate (mL/min)	100	200	100	200
Average (ppm)[A]	10.20	11.52	9.67	10.15
Standard Deviation	0.316	0.319	0.176	0.594
Accuracy (% Recovery)	102	116	97	102
Precision (% RSD[B])	6.1	5.4	3.6	11.5
Bias (%)	+20	+15.2	−3.3	+1.5

[A] The average is based on 10 samples.

[B] % RSD = Percent relative standard deviation at 95 % confidence interval.

13.2.4 The STE validation study **(6)** consisted of the sampling and analysis of 10 JXC and 10 PCB charcoal tubes at flowrates of 100 and 200 mL/min at a humidity of 90 %. All tests were run for 15-minute sampling periods. Test concentrations of 1, 5, and 10-ppm(v) ethylene oxide were evaluated. The average recovery was 100 % for PCB charcoal tubes and 109 % for JXC charcoal tubes. The average relative standard deviation (95 %) (precision) for the concentration range of 1 to 10 ppm(v) ethylene oxide was 11.8 % for PCB and 13.2 % for JXC charcoal tubes. The average relative standard deviation (95 %) (precision) for the lowest concentration (1.0 ppm(v)) was 18.4 % for PCB and 22 % for JXC charcoal tubes.

14. Keywords

14.1 air monitoring; charcoal tube methodology; ethylene oxide; sampling and analysis; workplace atmosphere

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[10] Supporting data are available from ASTM Headquarters. Request RR: D22-1011.

TABLE 4 Summary of Analyses of JXC and PCB Tubes by Tube Type

Tube Type: JXC

Actual Concentration (ppm)	Flowrate (mL/min)	Average^A (ppm)	Standard Deviation	Accuracy (% Recovery)	Precision (% RSD^B)	Bias (%)
1	100	1.27	0.125	127	19.3	+27.0
	200	1.11	0.139	111	24.6	+11.0
4.98	100	4.50	0.151	90	6.6	−10.0
	200	5.41	0.468	109	17.0	+8.2
9.95	100	10.20	0.316	102	6.1	+2.0
	200	11.52	0.319	116	5.4	+15.2
	Averages:		0.253	109	13.2	

Tube Type: PCB

Actual Concentration (ppm)	Flowrate (mL/min)	Average^A (ppm)	Standard Deviation	Accuracy (% Recovery)	Precision (% RSD^B)	Bias (%)
1	100	1.26	0.108	126	16.8	+26.0
	200	0.86	0.088	86	20.0	−14.2
4.98	100	4.40	0.272	88	12.1	−12.0
	200	5.07	0.171	102	6.6	+1.4
9.95	100	9.67	0.176	97	3.6	−3.3
	200	10.15	0.594	102	11.5	+1.5
	Averages:		0.234	100	11.8	

[A] The average is based on 10 samples.

[B] % RSD = Percent relative standard deviation at 95 % confidence interval.

ANNEX

(Mandatory Information)

A1. PREPARATION OF ETHYLENE OXIDE KNOWNS AND DETERMINATION OF BREAKTHROUGH VOLUME

A1.1 Preparation of Knowns

A1.1.1 Accurate knowns shall be generated determining adsorption/desorption efficiency for new batches of charcoal; for submission with samples for quality control; for determining equivalency of other procedures; and for running field validation experiments.

A1.1.2 Preparation of knowns by injecting a solution containing ethylene oxide is not suitable because the solvent greatly changes the retention properties of charcoal for ethylene oxide and a small volume of air will cause breakthrough and loss.

A1.1.3 Suitable knowns may be prepared by preparing a known concentration of ethylene oxide in an air bag and sampling with calibrated field sampling equipment.

A1.1.3.1 Fill a plastic air bag (see Note A1.1) with a known volume of air. Inject a known volume of ethylene oxide gas using a gas syringe (10.2.4 and 10.2.5) into the bag and mix.

NOTE A1.1—Bags made of TFE-fluorocarbon have been found suitable for preparing known concentrations of ethylene oxide in air. Bags are initially conditioned overnight with ethylene oxide to eliminate possible reactive sites on the surface. Bags made of polyvinylidene chloride are not suitable because of deterioration after 2 or 3 days of use.

A1.1.3.2 Attach a collection tube to a calibrated sampling pump and pull a known volume of sample from the bag.

A1.1.4 When determining recovery factors, the concentration sampled and the volume taken should simulate expected field conditions.

A1.1.4.1 The charcoal tubes shall be from the same lot of tubes to be used for sampling.

A1.1.4.2 The flow rate of the ethylene oxide standard shall be in the range from 10 to 100 mL/min. The total volume shall be less than the breakthrough volume.

A1.1.4.3 Recovery factors for the commercial charcoal tubes usually ranges from 90 to 100 %.

A1.1.4.4 If the field samples are to be collected under high temperatures (>90°F or >35°C) and relative humidity (>85 % RH) conditions, warm the charcoal tube to the same temperature or above, and saturate the gas stream containing the ethylene oxide with water. Breakthrough would show the need to reduce sample volume.

A1.1.4.5 At the end of the sampling period, disconnect the charcoal tube. Seal the tube with polyethylene caps and label them. Prepare five tubes at the same sample volume that will be used to collect field samples. Three samples for each level are sufficient if the adsorption/desorption is to be tested at different levels.

A1.1.4.6 Desorb ethylene oxide from the tubes using the procedure for samples and analyze in exactly the same manner that the samples and standards are analyzed.

A1.1.4.7 The recovery factor (R) is given by:

$$R = \frac{A}{\mathrm{B}}$$

where:

A = milligrams of ethylene oxide found in CS_2 and

B = milligrams of ethylene oxide in the air that passed into the tube.

A1.1.5 When preparing knowns for use in field validation experiments, use a much smaller volume to prepare the knowns since additional air will be sampled in the field.

A1.1.5.1 The amount of ethylene oxide prepared on the tube should be from one-half to three times the amount that will be collected in the field.

A1.1.5.2 The concentration prepared in the air bag should be high enough so that the appropriate amount of ethylene oxide can be loaded onto the tube in approximately 1 L of air.

A1.2 Determination of Breakthrough

A1.2.1 It may be necessary to determine breakthrough volume in the laboratory prior to sampling when extreme environmental conditions are expected.

A1.2.2 The breakthrough volume is the amount of air sample that can be passed through or drawn through the charcoal adsorbent before ethylene oxide begins to be emitted from the exhaust end of the tube. The breakthrough volume is affected by high concentrations of ethylene oxide, high concentrations of other impurities in air, and extreme conditions of humidity and temperature.

A1.2.3 The breakthrough volume can be determined for a specific size tube and type of charcoal. Assemble a gas train consisting of a plastic bag, containing a known concentration of ethylene oxide, a collection tube, and a calibrated sampling pump. Adjust the attenuation on a gas chromatograph so that a concentration of 5 % of the assault concentration can easily be detected in a 1-mL gas sample. The assault concentration of ethylene oxide should be at least as high as the maximum concentration expected.

A1.2.4 Pump the sample air through the collection tube at a known rate from 10 to 100 mL/min. Note the time the flow was initiated. Periodically sample the air at the back end of the tube with a 1-mL gas syringe and inject it into the gas chromatograph.

A1.2.5 When the ethylene oxide begins to emerge, the detector will show a response. Record the time when a concentration of 5 % of the assault concentration is detected in the effluent.

A1.2.6 Calculate the breakthrough volume by multiplying the flow rate expressed as litres per minute by the elapsed time in minutes.

A1.2.7 Breakthrough volumes for activated charcoal are typically in the range from 10 to 20-L sample volume per gram.

A1.2.8 Determine the effect of moisture on the breakthrough volume by humidifying the sample stream to 100 % relative humidity prior to entering the sample tube. A gas scrubbing flask or tube containing water may be used. The breakthrough volume is then determined as described in A1.2.

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(**3**) Qazi, A. H., and Ketcham, N. H., "A New Method for Monitoring Personal Exposure to Ethylene Oxide in the Occupational Environment," *American Journal of Industrial Hygiene Association,* Vol 38, 1977, p. 635.

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(**5**) Opthoff, J. D., and Lieckfield, Jr., R., "Collaborative Study for the Proposed ASTM Monitoring Method for Ethylene Oxide," *Clayton Environmental Consultants, Inc. Report,* (December 1983).[11]

(**6**) Lieckfield, Jr., R., and Shaughnessy, Stephen, J., "Application of ASTM Ethylene Oxide Method to Short-Term Exposure Limit (STEL) Monitoring for the Ethylene Oxide Industry Council, Chemical Manufacturers Association," Clayton Environmental Consultants, Inc. Report, (November, 1987).[11]

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[11] Supporting data are available on loan from ASTM Headquarters. Request RR: D22-1014.