



Designation: D4413 – 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 D4413; 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*:²

D1356 Terminology Relating to Sampling and Analysis of Atmospheres

D3686 Practice for Sampling Atmospheres to Collect Organic Compound Vapors (Activated Charcoal Tube Adsorption Method)

E355 Practice for Gas Chromatography Terms and Relationships

¹ This test method is under the jurisdiction of ASTM Committee D22 on Air Quality and is the direct responsibility of Subcommittee D22.04 on Workplace Atmospheres.

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² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

3. Terminology

3.1 *Definitions*:

3.1.1 For definitions of terms relating to this test method, refer to Terminology **D1356** and Practice **E355**.

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.³

5.2.2 ACGIH TLV 1 ppm(v).⁴

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.

³ Title 29, Code of Federal Regulation (Section 1910.1047), U.S. Department of Labor, revised 49FR 25797 June 22, 1984.

⁴ "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 **D3686**). 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.^{5,6}

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),⁵ 800 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**).⁷

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),⁶ 700 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.

⁵ 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.

⁶ 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.

⁷ The boldface numbers in parentheses refer to the list of references at the end of this test method.

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- μ L 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 [$1\frac{3}{8}$ in.] and approximately 12-L [$\frac{1}{3}$ -ft³] 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, $\pm 10\%$ 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 **D3686**). The accuracy of determining the total air volume sampled should be $100 \pm 5\%$.

7.6.4 *Tubing*, rubber or plastic, 6-mm [$\frac{1}{4}$ -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 μ g 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 μ g of ethylene oxide per millilitre of CS₂.

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

TABLE 1 Gas Chromatographic Columns for Determination of Ethylene Oxide

Column	Length	Diameter	Carrier Flow	Temperature °C		Ethylene Oxide Retention Time	
			(mL/min)	Column	Detector	(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.⁸ 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 *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.

8.2 *Carbon Disulfide* (CS₂), 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 D3686, 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

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 CS₂ several times to wet the barrel and plunger. Draw 1 µL of CS₂ into the syringe and remove the tip of the needle from the solvent. Withdraw the plunger an additional 0.5 µL to separate the CS₂ 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.