Designation: D 5578 – 94 (Reapproved 1999)ε1

Standard Test Method for Determination of Ethylene Oxide in Workplace Atmospheres (HBr Derivatization Method)[1]

This standard is issued under the fixed designation D 5578; 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.

ε[1] NOTE—Editorial corrections were made throughout in December 1999.

1. Scope

1.1 This test method covers a method of collecting and analyzing samples to determine the amount of ethylene oxide (ETO) present in workplace atmospheres.

1.2 This test method can be used to provide a time-weighted average (TWA) over the concentration range from 0.2 to 30 ppm (v).

1.3 This test method can be used to determine 15-min excursions (STEL) ranging from 10 to 500 ppm (v).

1.4 The values stated in SI units are to be regarded as the standard.

1.5 *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.* See Section 9 for specific safety hazards.

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]

D 3687 Practice for Analysis of Organic Compound Vapors Collected by the Activated Charcoal Tube Adsorption Method[2]

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

2.2 *Other Standard:*

Occupational Safety and Health Administration, U.S. Department of Labor, Title 29, *Code of Federal Regulations*, Part 1910, Subpart Z, Section 1910.1047.[4]

3. Terminology

3.1 For definitions of terms used in this test method, refer to Terminology D 1356, and Practice E 355.

4. Summary of Test Method

4.1 A known volume of air is pumped through a glass tube packed with carbon molecular sieve, surface area 400 m^2/g impregnated with hydrogen bromide (HBr) where ETO is adsorbed and converted to 2-bromoethanol.

4.2 The tube contains two reactive sections for sample collection. The backup section collects vapors that pass through the front section and is used to determine if the collection capacity of the front section has been exceeded.

4.3 The resultant derivative, 2-bromoethanol, is desorbed with a mixture of acetonitrile/toluene and analyzed using a gas chromatograph equipped with an electron capture detector.

4.4 Desorption efficiency is determined by spiking tubes with known amounts of 2-bromoethanol and analyzing with the same procedure used for air samples.

4.5 Quantitation is achieved by comparing peak areas from sample solutions with areas from standard solutions.

5. Significance and Use

5.1 Ethylene oxide is a major industrial chemical with production volume ranked in the top 25 chemicals produced in the United States. It is used in the manufacture of a great variety of products as well as being a sterilizing agent and fumigant.

5.2 This test method provides a means of determining exposure levels of ETO in the working environment at the presently recommended exposure guidelines.

[1] This test method is under the jurisdiction of ASTM Committee D-22 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] Available from Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

5.2.1 OSHA Permissible Exposure Limit (PEL) 1 ppm, 15-min excursion limit 5 ppm (CFR, Part 1910, Subpart Z, Section 1910.1047).[4]

5.2.2 ACGIH Threshold Limit Value (TLV) 1 ppm (1.8 mg/m^3), suspected human carcinogen.[5]

6. Interferences

6.1 Derivatives and other compounds that have identical or nearly the same retention time as 2-bromoethanol during the gas chromatographic analysis will interfere.

6.2 Interferences can sometimes be resolved by altering gas chromatographic operating conditions. The presence of 2-bromoethanol under a chromatographic peak can be verified using a mass spectrometer.

7. Apparatus

7.1 *Carbon Molecular Sieve*, surface area 400 m^2/g, HBr sampling tube.

7.1.1 *Preparation of Collection Medium*—Add 20 mL of HBr (24 %) to 70 g of carbon molecular sieve, surface area 400 m^2/g, in a glass jar. Cap the jar and mix the contents thoroughly for 5 min by rotating. Allow to equilibrate and dry overnight or for 12 h.

7.1.2 *Tube Preparation*— Insert a plug of silanized glass wool into a 10-cm by 6-mm outside diameter (4-mm inside diameter) glass tube. Pack the front section of the tube with 400 mg of the reactive adsorbent (7.1.1), using gentle tapping or vibration to promote uniform packing. Insert another plug of silanized wool and pack 200 mg of the adsorbent in the backup section. Hold the backup section in place by firmly inserting an additional glass wool plug. The tubes may be flame-sealed or sealed with polyethylene caps. Provide a numerical identification for each lot of tubes.

7.1.3 *Tube Holder*, capable of preventing breakage and protecting worker during sampling.

7.1.4 *High-Density Polyethylene or Polypropylene Caps*, tight-fitting, for resealing used tubes.

7.2 *Pump and Tubing*:

7.2.1 *Sampling Pumps*, having stable low flow rates (±10 % of set flow rate) within the range from 20 to 100 mL/min for up to 8 h.

7.2.2 *Rubber or Plastic Tubing*, 6-mm inside diameter, for connecting collection tube to pump. All tubing must be downstream (between tube and pump) of collection tube to prevent contamination or loss of sample.

7.3 *Vials*, glass with TFE-fluorocarbon lined caps, 10 mL, for desorbing samples and storing standards.

7.4 *Pipettes*, 5 mL, for adding desorbing solution to samples.

7.5 *Syringes*, 10, 50, and 100-µL syringes, for preparing standards.

7.6 *Gas-Tight Syringe*, 2 µL, with low dead-volume needle.

7.7 *Gas Chromatograph (GC)*:

7.7.1 *Gas Chromatograph*, with an electron capture detector and a suitable readout device.

7.7.2 *Chromatographic Column*, packed or capillary columns in accordance with 7.7.2.1 and 7.7.2.2 have been found suitable for this analysis.

7.7.2.1 *Packed*, 3.7 m by 3 mm (12 ft by ⅛ in.), stainless steel, packed with 10 % diethylene glycol succinate on diatomaceous earth, flux-calcined, silanized, 80/100 mesh.

7.7.2.2 *Capillary*, 30-m by 0.53-mm inside diameter fused silica capillary column with polyethylene glycol phase.

8. Reagents

8.1 *Purity of Reagents*—Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.[6] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *Acetonitrile*, pesticide grade.

8.3 *2-Bromoethanol*, commercially available at 98 % purity or better.

8.4 *Desorbing Solution*, 1+1 (v/v) mixture of acetonitrile and toluene.

8.5 *Sodium Carbonate* (Na_2CO_3).

8.6 *Toluene*, pesticide grade.

9. Hazards

9.1 Minimize exposure to all reagents and solvents by performing all sample and standard preparations as well as tube desorption in a well-ventilated hood.

9.2 Avoid inhalation and skin contact with all reagents and solvents.

9.3 Use suitable protective holders when collecting samples and handle used tubes carefully to prevent injury.

10. Calibration

10.1 *Sample Pump Calibration*:

10.1.1 Calibrate the sample pump flow in accordance with Practice D 3686, with the ETO sampling tube positioned vertically and in line during calibration of the pump.

10.1.2 Calibrate the flow rate of the pump at 20 mL/min for TWA sampling and 100 mL/min for STEL sampling depending on the duration of the sample and the volume of sample needed.

10.2 *Gas Chromatograph Calibration*:

10.2.1 Prepare a 2-bromoethanol stock solution (1 µg/µL) by adding 57 µL of 2-bromoethanol to 100 mL of toluene. If refrigerated, this solution is stable for at least one month.

10.2.2 To a series of four 10-mL vials containing 5.0 mL of desorbing solution, add 0.0, 50, 100, and 200 µL of stock solution, thus, providing calibration standards equivalent to

[5] *Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices*, American Conference of Governmental Industrial Hygienists, 6500 Glenway Avenue, Building D-7, Cincinnati, OH 45211-4438.

[6] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the 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.

0.0, 17.4, 34.5, and 67.7 µg of ETO per 5 mL of desorbing solution. These values take into account volume changes caused by the addition of stock solution.

10.2.3 The 0.0-µg standard described in 10.2.2 constitutes a reagent blank.

10.2.4 Prepare a calibration curve by injecting these standards into the GC following the procedure specified in 11.3.5 and 11.3.6. Plot the peak area (or height) versus micrograms of ETO per 5 mL of desorbing solution.

10.2.5 To cover a broader ETO concentration range, prepare additional standards with the stock and desorbing solutions; however, exercise care by staying within the linear dynamic range of the electron capture detector.

11. Procedure

11.1 *Sample Collection*:

11.1.1 Immediately before sampling, break off the ends of the sampling tube (if flame sealed) or remove end caps to create an opening of at least 2 mm in diameter.

11.1.2 Attach a collection tube to a calibrated sampling pump using a section of plastic tubing, with the backup section nearest the pump.

11.1.3 Place the tube vertically in the tube holder as near to the breathing zone as possible.

11.1.4 Activate the sampling pump that has been calibrated for the flow rate desired (20 mL/min for 8 h; or 100 mL/min for 15 min).

11.1.5 Record the time, flow rate, barometric pressure, and temperature when the pump is started.

11.1.6 When sampling is completed, check the flow rate before deactivating the pump. Immediately record the time, temperature, and barometric pressure again.

11.1.7 Disconnect the sample tube and cap the ends with polyethylene caps. Label the tube with sample identification.

11.1.8 Include at least one blank sampling tube with every 10 to 15 samples, or for each operation or field survey. Treat the field blank the same as air samples with the exception that no air is drawn through the blank tube. The field blank must be from the same tube lot as the air samples.

11.2 *Desorption Efficiency*:

11.2.1 Determine the desorption efficiency on the same lot of tubes as the air samples.

11.2.2 Place 400-mg portions of collection medium (7.1.1) in each of several 10-mL vials.

11.2.3 Add appropriate amounts of 2-bromoethanol stock solution (10.2.1) directly onto the adsorbent prepared in 11.2.2, that correspond to the approximate levels of ETO expected in air samples. Allow the spiked adsorbents to equilibrate overnight (or 12 h) at room temperature.

11.2.4 Analyze replicates of each concentration level along with blank tubes using the procedure indicated in 11.3.5-11.3.6, inclusively. Calibrate gas chromatograph using mass of 2-bromoethanol in calibration standards (10.2.2) instead of ETO equivalent.

11.2.5 Calculate the desorption efficiency (*DE*) for each amount of 2-bromoethanol as follows:

$$DE = \frac{W_r - B}{W_a} \quad (1)$$

where:

W_r = average mass recovered, µg,
B = blank, µg, and
W_a = mass added, µg.

11.3 *Analysis*:

11.3.1 Add 100 mg of Na_2CO_3 and 5.0 mL of desorbing solution to each of the appropriately labeled vials that indicate the tube numbers and front or backup section.

11.3.2 Score and break tubes just above the front glass wool plug, remove plug, and slowly add front portion of adsorbent to the appropriate vial. Seal the vial.

11.3.3 Remove the glass wool separator and add the backup section of adsorbent to the proper vial. Make certain adsorbent particles are not retained on the glass wool plugs and separator before discarding.

11.3.4 Desorb for 30 min at room temperature, shaking the vial occasionally during this period.

11.3.5 Quantitatively inject 2 µL of sample solution into the GC using the solvent flush technique as described in Practice D 3687. Alternatively, samples may be injected using an automated injection system.

11.3.6 Complete the GC analysis following the chromatographic conditions described in 11.3.6.1. The approximate ETO retention time and total chromatographic analysis time is 4.0 and 8.0 min, respectively.

11.3.6.1 *Gas Chromatographic Operating Conditions*—Column temperature, 155°C; injection port and detector temperatures, 240°C; carrier gas (5 % methane/argon) flow rate, 30 mL/min (packed column) or 20 cm/s (capillary column).

11.3.6.2 Determine the peak height or peak area of the 2-bromoethanol.

12. Calculation

12.1 Correct samples for ETO found in the reagent blank (10.2.3).

12.2 Determine the amount (µg) of ethylene oxide in the front and backup sections of the sample tube using the calibration curve generated in 10.2.4. If the backup section contains more than 10 % of the amount of ethylene oxide contained in the front section, report breakthrough and possible sample loss.[7]

12.3 Calculate the concentration of ETO in the air samples as follows:

$$\text{Ethylene Oxide, ppm by volume} = \frac{W \times 24.47 \times 101.3 \times (T + 273)}{DE \times L \times 44.05 \times 298 \times P} \quad (2)$$

where:

DE = desorption efficiency,
L = volume of air sampled, L
P = atmospheric pressure at sampling site, kPa,
T = temperature at sampling site, °C,
W = micrograms of ETO in sample (sum of front and backup section),
44.05 = molecular weight of ethylene oxide, g/mol, and

[7] *NIOSH Manual of Analytical Methods*, Cincinnati, OH 45226.

24.47 = molar volume of an ideal gas, L/mole, at 25°C and 101.3 kPa (760 mm Hg).

12.4 If a field blank shows contamination, the samples collected during the survey must be assumed to be contaminated (see Practice D 3687).

13. Precision and Bias [8]

13.1 *Precision*—Based on limited information from one laboratory, the repeatability standard deviations and the 95 % repeatability limits are approximately ± 9.3 %, as illustrated in Table 1. The reproducibility of this test method is being determined.

13.1.1 The values shown in Table 1 are averages of six replicates obtained for each concentration of ETO generated in a 6920L static chamber. They take into account adsorption/desorption efficiency and the derivatization reaction.

TABLE 1 Precision and Accuracy of Chamber Concentrations

Theoretical ETO Concentration, ppm	Average Recovery, %	Relative Standard Deviation, %
0.5	111.6	1.6
1.0	100.6	2.0
5.0	100.8	3.6
10.0	101.8	5.6
20.0	102.1	2.9

13.2 *Bias*—The Quazi-Ketcham[9] charcoal tube method was used as a reference method for comparison. Forty-one paired sets of charcoal tubes and carbon molecular sieve tubes were collected and analyzed. The two sets of data had a correlation coefficient of 0.95.

14. Keywords

14.1 air monitoring; 2-bromoethanol; carbon molecular sieve; ethylene oxide; gas chromatography; HBr derivatization; sampling and analysis; workplace atmospheres

[8] Supporting data are available from ASTM Headquarters. Request RR:D22-1025.

[9] Quazi, A. H. and Ketcham, N. H., *American Industrial Hygiene Association Journal*, Vol 39, 1977, pp. 635–647.