ETHYLENE OXIDE 1614

$CH_2(O)CH_2$ MW: 44.05 CAS: 75-21-8 RTECS: KX2450000

METHOD: 1614, Issue 2 **EVALUATION: FULL** **Issue 1: 15 August 1987**
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OSHA : 1 ppm
NIOSH: 0.1 ppm; C 5 ppm/10 min; carcinogen; Group I Pesticide
ACGIH: 1 ppm; suspect carcinogen

PROPERTIES: gas; d (liquid) 0.8694 g/mL @ 20 °C; BP 10.7 °C; MP −111 °C; explosive limits 3 to 100% (v/v) in air

SYNONYMS: 1,2-epoxyethane; oxirane

SAMPLING

SAMPLER: SOLID SORBENT TUBE (HBr-coated petroleum charcoal, 100 mg/50 mg)

FLOW RATE: 0.05 to 0.15 L/min

VOL-MIN: 1 L @ 5 ppm
-MAX: 24 L

SHIPMENT: routine

SAMPLE STABILITY: 90% recovery after 17 days @ 25 °C in the dark [3]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.04 to 0.98 ppm (24-L samples) [1]

BIAS: −6.9% [1]

OVERALL PRECISION ($\hat{S}_{rT}$): 0.062 [1]

ACCURACY: ±19%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, ECD

ANALYTE: 2-bromoethylheptafluorobutyrate

DESORPTION: 1 mL dimethylformamide; stand 5 min

INJECTION VOLUME: 1 µL

TEMPERATURE-INJECTION: 200 °C
-DETECTOR: 300 °C
-COLUMN: 100 °C

CARRIER GAS: 5% CH_4 in Ar, 25 mL/min

COLUMN: 3 m x 4 mm glass; 10% SP-1000 on 80/100 Chromosorb WHP

CALIBRATION: standard solutions of 2-bromoethanol in dimethylformamide

RANGE: 2 to 42 µg ethylene oxide per sample

ESTIMATED LOD: 1 µg EtO per sample [2]

PRECISION ($\bar{S}_r$): 0.020 @ 18 to 71 µg EtO per sample [1]

APPLICABILITY: The working range is 0.05 to 4.6 ppm (0.08 to 8.3 mg/m^3) for a 24-L air sample. The method is applicable to short-term (10-min) samples.

INTERFERENCES: 2-Bromoethanol, if present in the sample interferes. No other significant interferences have been found [1].

OTHER METHODS: This is a modification of OSHA Method 50 [1] and replaces NIOSH method 1607, which has smaller sample capacity, and S286 [3], which is useful for higher levels. Method 3702 (Ethylene Oxide by Portable GC) describes field-readable gas chromatography for the determination of ethylene oxide.

REAGENTS:

1. *N*,*N*-Dimethylformamide (DMF), high purity.
2. Isooctane (2,2,4-trimethylpentane), reagent grade.
3. Benzene, reagent grade.*
4. *N*-Heptafluorobutyrylimidazole (HFBI;*N*-heptafluorobutanoylimidazole; Alfa Chemical #31594, Alfa Products, Ward Hill, MA 01835).
5. Water, high purity (e.g., deionized distilled).
6. 2-Bromoethanol (2-FrEt), 95 to 98%.
7. Sodium hydroxide (NaOH), reagent grade.
8. Potassium hydrogen phthalate (KHP), reagent grade, dried at 90°C.
9. HCl, conc., reagent grade.*
10. Pyridine, reagent grade.
11. Phenolphthalein, 1% (w/v) in ethanol or methanol.
12. Hydrobromic acid (HBr), 48%, reagent grade.*
13. Charcoal, petroleum-based (SKC Lot 208 or equivalent, SKC, Eighty-Four, PA).
14. Ethylene oxide (EtO), liquid or gas, 99.7% purity.*
15. Sodium hydroxide, 0.5 N. Dissolve 20 g NaOH in distilled water to make 1 L of solution. Standardize with KHP to a phenolphthalein endpoint (APPENDIX B).
16. HCl in pyridine, 0.2 N. Dissolve 8.5 mL conc. HCl in pyridine to make 500 mL solution. Standardize (APPENDIX C).
17. Ethylene oxide stock solution,* ca. 40 µg/µL. Bubble EtO gas (or pipet 4 mL EtO liquid) into 85 mL benzene in a graduated cylinder until solution volume increases ca. 4 mL. Seal tightly and store in freezer. Standardize weekly (APPENDIX D).
18. HFBI, 2% in isooctane. Dissolve 2 mL HFBI in isooctane to make 100 mL solution. Store in refrigerator.
19. 5% Methane in argon.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: 6-mm OD x 4-mm ID x 45 mm glass tube, flame-sealed, with plastic caps, contaiing HBr-coated charcoal (see APPENDIX A), two sections, 100-mg front, 50-mg back, separated and contained with silanized glass wool plugs. Tubes are commercially available (Supelco Orbo-78, SKC 226-38-03, or equivalent.
2. Gas chromatograph, electron capture detector, integrator, and column (p. 1614-1).
3. Burette, 50-mL, 0.1-mL graduations.
4. Flask, round-bottom, 100-mL, with ground-glass joint.
5. Condenser, reflux, with ground-glass joint to fit round-bottom flask.
6. Heating mantle, with heat control, to fit round bottom flask.
7. Graduated cylinder, glass, 100-mL, with stopper that seals tightly.
8. Vials, glass, 5-mL, with PTFE-lined screw caps.
9. Pipets, volumetric, 2- to 500-µL and 1-, 2-, 4-, and 40-mL, with pipet bulb.
10. Syringes.
11. Vials, glass, 2-mL, with PTFE-lined septum screw caps.
12. Flasks, Erlenmeyer, 125-mL.
13. Gloves.
15. Fume hood.
16. File, triangular.
17. Evaporator, rotary.

SPECIAL PRECAUTIONS: Ethylene oxide and benzene are toxic and serious fire and explosion hazards; they are also suspect carcinogens [4-6]. Hydrobromic and hydrochloric acids are eye, skin, and inhalation hazards [6]. Work with these substances only in a hood. Use protective gloves.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break ends of sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.05 and 0.15 L/min for a total sample size of 1

to 24 L.

4. Cap each tube. Pack securely for shipment.

SAMPLE PREPARATION:

5. Score each sampler with a file. Break sampler at score line.
6. Transfer front sorbent section and first glass wool plug to a 2-mL vial. Transfer middle glass wool plug and back sorbent section to a separate vial.
7. Add 1.0 mL DMF to each vial. Cap each vial.
8. Shake at least 10 sec. Allow to stand at least 5 min.
9. Pipet a 20-µL aliquot of the DMF solution to another 5-mL vial containing 2.0 mL 2% HFBI (v/v) in isooctane.
   NOTE: Pipet 20 µL of each working standard (step 13) into vials containing 2% HFBI at this step.
10. Cap and shake 1 min: Allow to stand at room temperature at least 5 min.
11. Add 2.0 mL high purity water. Mix 1 min to ensure complete hydrolysis of excess HFBI.
12. Transfer at least 1.0 mL of isooctane (top) layer to 2-mL vial.
    NOTE: If the sample concentration is higher than the standards, dilute an aliquot of sample with DMF, reanalyze starting at step 9, and apply the appropriate dilution factor in calculations. The desorbed sample (in DMF) keeps well in a freezer [1].

CALIBRATION AND QUALITY CONTROL:

13. Calibrate daily with at least six working standards over the range 1 to 42 µg EtO per sample. For example:
    a. Pipet 1.0 mL 2-BrEt (density 1.763 g/mL @ 20°C) into a 10-mL volumetric flask. Dilute to volume with DMF. This is stock solution "A." Dilute 3 mL of "A" to 25 mL with DMF to give standard "B." Dilute 1 mL of "B" to 10 mL with DMF to give standard "C."
       NOTE: A sample calculation with 95% pure 2-BrEt (MW = 124.98) expressed as its equivalent weight in EtO (MW = 44.05) is:

       Standard Solution "A":

       $$\frac{1.763\ g\ \ 2\text{-BrEt}}{10\ mL} \cdot 0.95 \cdot \frac{44.05}{124.97} \cdot 10^6\ \mu g = 59{,}036\ \mu g\ EtO/mL.$$

       Standard Solution "B":
       3 mL • 59,030/25 mL = 7084 µg EtO/mL.
       Standard Solution "C":
       1 mL • 7084/10 mL = 708.4 µg EtO mL.

    b. Prepare working standards by injecting microliter volumes of "B" and "C" into vials containing 1.0 mL DMF. The following serial dilution scheme is suggested:

Working Standard	Aliquot added to 1.0 mL DMF	Final µg EtO/mL
D	2.5 µL "C"	1.77
E	5.0 µL "C"	3.54
F	10.0 µL "C"	7.08
G	2.5 µL "B"	17.7
H	3.5 µL "B"	24.8
I	5.0 µL "B"	35.4
J	6.0 µL "B"	42.5

       Higher standards may be used if detector output remains acceptable. (Some detectors may become saturated at higher levels.)
    c. Analyze working standards together with samples and blanks.
    d. Prepare calibration graph (µg EtO per sample vs. peak area). Use a nonlinear (e.g.,

parabolic) least squares fit if necessary to obtain the best fit of the data.

14. Determine recovery (R) at least once for each lot of charcoal used for sampling in the concentration range of interest. Prepare three tubes at each concentration of interest plus three media blanks.
    a. Remove and discard back sorbent section of a media blank sampler.
    b. Inject a known amount (2 to 15 µL) of EtO stock solution or a serial dilution thereof directly onto the charcoal with a microliter syringe.
    c. Cap the tube. Allow to stand overnight.
    d. Desorb (steps 5 through 8) and analyze together with working standards (steps 9 through 12 and 16 and 17).
15. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

16. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 1614-1. Inject sample aliquot manually using solvent-flush technique or with autosampler.
17. Measure peak area.

CALCULATIONS:

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

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

EVALUATION OF METHOD:

This method uses HBr-coated charcoal to collect EtO and rapidly convert it to 2-bromoethanol. This method was evaluated at the OSHA Analytical Laboratory, Salt Lake City, UT, as OSHA Method 50 [1]. Fifteen-min and 30-min air samples were collected from a constant 5-ppm test atmosphere (80% relative humidity, ambient temperature) at 0.1 L/min with observed recoveries in the range 88 to 100%.

Fifteen pairs of side-by-side area samples were collected and analyzed by OSHA using this method and the Qazi-Ketcham method. The sampling rate was ca. 50 mL/min for 4 to 7.5 H. Results showed no statistical difference in the two methods, with no bias over the range 0.3 to 7 ppm EtO. test atmospheres of 0.1, 0.5, 1.0, and 16 ppm at 70 to 80% relative humidity and ambient temperature were sampled for 4 h at 0.1 L/min with no breakthrough. The 5% breakthrough volume for sampling a 16-ppm atmosphere of EtO at 0.15 L/min was 39 L. No significant storage effects were observed for samples in the 0.1 to 16 ppm range at high humidity and stored at ambient temperature for a minimum of two weeks.

The precision, S_r, of chromatographic response of working standards in the range 18 to 71 µg EtO per sample was 0.028 [1]. Recovery of EtO spikes in NIOSH laboratories averaged 75% at 11, 22, 33, and 44 µg EtO per sample.

REFERENCES:

[1] Cummins, K.J. OSHA Method No. 50, "Ethylene Oxide," OSHA Analytical Laboratory, Salt Lake City, UT (unpublished, January, 1985).
[2] User check, DataChem, Inc., NIOSH Seq. #5860-J (unpublished, May 15, 1987).
[3] NOSH Manual of Analytical Methods, 2nd. ed., V. 3, S286, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157C (1977); also cited in NIOSH Special Occupational Hazard

Review with Control Recommendations - Use of Ethylene Oxide as a Sterilant in Medical Facilities, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-200 (1977).
[4] Threshold Limit Values and Biological Exposure Indices for 1993-94, ACGIH, Cincinnati, OH (1993).
[5] NIOSH Testimony to USDOL at OSHA rulemaking hearing for ethylene oxide (July 20, 1983); also see Current Intelligence Bulletin 35, "Ethylene Oxide," U.S. Department of Health and Human Services, Publ. (NIOSH) 81-130 (May 22, 1981).
[6] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services Publ. (NIOSH) 81-123 (1981), available as GPO stock #17-033-00337-8 from Superintendent of Documents, Washington, D.C. 20402.
[7] Siggia, S. and J.G. Hanna. Quantitative Organic Analysis via Functional Groups, 4th ed., Chapter 5, John Wiley & Sons, Inc., New York, NY (1979).

METHOD REVISED BY:

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APPENDIX A: PREPARATION OF SOLID SORBENT

Slowly add a mixture of 25 mL 48% hydrobromic acid and 125 mL acetonitrile to 75 g petroleum-based charcoal (SKC Inc., Lot 208) contained in a 500-mL round-bottom flask. Allow the slurry to cool to room temperature. Dry the coated charcoal by rotary evaporation using gentle heat and keep it overnight under vacuum at ambient temperature. The product is stable for four months when stored in a tightly sealed amber glass jar at room temperature [1]. Recovery may be lower as the sample medium ages.

APPENDIX B: STANDARDIZATION OF NaOH

1. Transfer duplicate, accurately weighed, ca. 1.5-gram portions of KHP (W, mg) to separate 125-mL Erlenmeyer flasks. Dissolve in 20 to 30 mL distilled water, warming if necessary.
2. Add one drop phenolphthalein solution to each flask.
3. Fill the burette with 0.5 N NaOH. Titrate, with constant mixing, to a pink endpoint in each flask. Record the volume, V (mL), of 0.5 N NaOH used.
4. Calculate the normality, N_b, of the NaOH solution.

$$N_b = \frac{W}{(204.22 \cdot V)}.$$

APPENDIX C: STANDARDIZATION OF HCl IN PYRIDINE

1. Pipet 40.0 mL 0.2 N HCl in pyridine into a 100-mL round-bottom flask.
2. Add 4.0 mL benzene.
3. Attach the flask to a water-cooled condenser and heat flask with a heating mantle to boiling. Reflux for 20 min.
4. Cool to near room temperature. Add 5 mL distilled H_2O through condenser and collect washings in the flask.
5. Remove reflux condenser and add a drop of phenolphthalein solution to the flask.
6. Titrate, with mixing, 0.5 N NaOH from the burette to the flask to a pink endpoint. Record volume, V_b (mL), of NaOH used.
7. Repeat steps 1 through 7 and average the results. Calculate the normality, N_o, of the HCl-pyridine solution using N_b from APPENDIX B:

$$N_o = \frac{N_b V_b}{40}.$$

APPENDIX D: STANDARDIZATION OF ETHYLENE OXIDE STOCK SOLUTION [7]

1. Pipet 20.0 mL standardized HCl-pyridine solution into a 100-mL round bottom flask.
2. Add 2.0 mL EtO stock solution.
3. Attach the flask to the condenser. Reflux for 20 min.
   NOTE: The reaction is: EtO + HCl(xs)→ chloroethanol. The excess HCl is back-titrated in step D-6.
4. Cool to near room temperature. Add 5 mL distilled H_2O through the condenser, collecting washings in the flask.
5. Remove the condenser and add a drop of phenolphthalein solution to the flask.
6. Titrate, with mixing, 0.5 N NaOH from the burette to a pink endpoint. Record volume, V_c (mL), of NaOH used.
7. Calculate the normality, N_s, of the excess HCl using N_b from APPENDIX B:

$$N_s = \frac{N_b V_c}{20\ mL}.$$

8. Repeat steps 1 through 7 to obtain an average of two titrations. Results should agree to within 1%. Rinse flask thoroughly before reuse.
9. Calculate the concentration of the EtO stock solution:

$$\frac{mg\ EtO}{mL\ EtO\ stock\ solution} = (N_o - N_s) \cdot \frac{20\ mL}{10^3\ mL} \cdot \frac{44.05\ g}{1\ equivalent} \cdot \frac{1}{2\ mL} \cdot \frac{10^3\ mg}{1\ g} = (N_o - N_s) \cdot 440.5$$