ETHYLENE OXIDE by Portable GC 3702

C_2H_4O MW: 44.05 CAS: 75-21-8 RTECS: KX2450000

METHOD: 3702, Issue 2 **EVALUATION: FULL** **Issue 1: 15 August 1987**
Issue 2: 15 August 1994

OSHA : 1 ppm
NIOSH: 0.1 ppm; C 5 ppm/10 min; carcinogen; Group I Pesticide
ACGIH: 1 ppm; suspect carcinogen
1 ppm = 1.801 mg/m^3 @ NTP

PROPERTIES: gas; d (liq.) 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: AMBIENT AIR OR BAG SAMPLE

FLOW RATE: ≥ 0.02 L/min; spot samples possible (See Step 1)

SHIPMENT: calibration and carrier gas shipment must comply with hazardous materials shipment regulations

SAMPLE STABILITY: bag samples stable 24 h @ 25 °C [1]

FIELD BLANKS: clean air, either in bag or from non-work area

ACCURACY

RANGE STUDIED: 0.1 to 700 ppm [1]

BIAS: not significant

OVERALL PRECISION ($\hat{S}_{rT}$): <0.09 [1]

ACCURACY: ± 17%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY (PORTABLE), PHOTOIONIZATION DETECTOR

ANALYTE: ethylene oxide

COLUMN: 1.2 m x 3 mm OD PTFE, packed with Carbopak BHT 40/100 mesh

CARRIER GAS: ultrapure air, 15 mL/min

CALIBRATION: bag standards or calibrated gas mixtures

RANGE: 0.001 to 1000 ppm

ESTIMATED LOD: 2.5 pg per injection @ .001 ppm (1-mL injection)

PRECISION ($\hat{S}_r$): <0.07 @ 0.05 to 0.2 ppm [1]

APPLICABILITY: The working range is 0.001 to 1000 ppm in relatively non-complex atmospheres (e.g., sterilization facilities).

INTERFERENCES: Freon 12, carbon dioxide, and alcohols do not interfere. Other compounds with similar retention times under the same chromatographic conditions are potential interferences.

OTHER METHODS: This method complements Method 1614 [2] which utilizes solid sorbent collection, derivatization, and gas chromatographic measurement for ethylene oxide.

REAGENTS:

1. Uncontaminated air for preparation of standards and purging samplers.
2. Carrier gas, air, ultra-pure.*
3. Ethylene oxide (EtO) for standards, pure or in known concentration (i.e., 88/12 Freon 12/EtO mixture).*
   NOTE: Commercial sterilant mixtures are sold on a weight/weight ratio. An 88/12 mixture is 27% EtO by volume.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Portable gas chromatograph (GC) with photoionization detector, column (page 3702-1), and (if appropriate) portable strip chart recorder or integrator, and battery chargers, regulators, and other peripherals necessary for individual instruments.
2. Personal sampling pump, 0.02 to 4 L/min or other rate suitable for filling bag, with flexible connecting tubing.
3. Syringes, gas-tight (0.01 to 1-mL, 1-L), for standards preparation, sample collection and sample injection.
4. Bags, inert plastic (e.g., aluminized polyester or Tedlar), 2- to 20-L, for standard preparation, and (if needed) sample collection.
   NOTE: Care must be taken to assure that the pump, bag, and tubing are all inert and impermeable to the analyte (step 3).

SPECIAL PRECAUTIONS: Ethylene oxide is flammable. Shipment of compressed calibration gas and carrier gas must comply with 49 CFR regulations on shipment of hazardous materials.

SAMPLING:

1. Collect samples by one of the following methods:
   NOTE: Other techniques such as liquid displacement or use of an evacuated vessel may be adaptable to this method but have not been evaluated.
   a. **Draw air directly into a syringe.** Collect syringe samples by first purging a gas-tight syringe several times with clean air to remove any residual ethylene oxide from previous samples, then draw air into the syringe at the time and location of interest.
      NOTE: This technique requires less equipment and also has the advantage of allowing for a grab sample. It is not easily applied to TWA measurements. Since this is a one-time analysis, the concentration of the sample must be estimated in advance so that the proper size sample can be collected. An injection volume as small as ten microliters can be used if the concentration is expected to be several hundred ppm, while a 1.0- mL syringe is more appropriate if a concentration on the order of 0.01 ppm is expected.
   b. **Bag samples for TWA.**
      (1) Evacuate the sampling bag.
      (2) Allow the pump to be purged with sample air before opening the valve on the sampling bag. Collect bag sample by using pump to pull air from a point of interest and push it into the bag.
      NOTE: This technique can obtain a sample in a relatively short time (e.g., at 4 L/min, a few seconds sampling time will yield the fraction of a liter necessary for several replicate analyses). By selecting a low flow rate and larger bag (i.e., 10 mL/min flow and 5 L bag), an 8-h TWA sample can be obtained. A few mL will allow for replicate injections of 1 mL or less, although in practice several hundred mL to 1 L is a more reasonable minimum. The maximum volume is limited only by the size of bags available and space in which to store them.

CALIBRATION AND QUALITY CONTROL:

2. Calibrate the GC daily in the field.
   a. Prepare bag standards by adding a known volume of EtO to a known volume of clean air in a bag. This creates a standard of known concentration in ppm (µL EtO/L air).
      (1) Evacuate a 5- to 10-L bag completely by drawing the air out with a large (1- to 2-L) syringe.
      (2) Draw clean air (or oxygen or nitrogen) from a supply cylinder into the syringe for measured transfer into the bag. Alternately, if a clean air supply is not available, draw room air through charcoal sorbent into the syringe. Repeat until the bag contains 5 L of air.
      (3) Add a known amount of pure EtO or standard EtO mixture to the bag by means of gas-tight syringe.
      Example:
      Using a gas-tight syringe, take 50 µL from a cylinder of pure EtO and inject it into 5 L of air to create a 10 ppm standard. Alternately, 200 µL of a 27% v/v EtO mixture (i.e., 88/12 w/w Freon 12 and EtO) can be added to the 5 L of air to obtain a 10.8 ppm standard.
      (4) Allow the bag to equilibrate, with occasional kneading, for at least 5 min.
   b. Analyze aliquots of various sizes to establish a calibration graph (steps 4 and 5). Analyze three or more replicates at each point.
      NOTE: On a high instrument attenuation (low sensitivity), injections of 0.2, 0.4, 0.6, 0.8 and 1.0 mL might be possible. This would correspond to injections of 2, 4, 6, 8, and 10 nL. On a more sensitive attenuation, injections of 0.02, 0.04, 0.06, 0.08 and 0.10 mL would be typical. Results will vary from instrument to instrument, and from time to time on the same instrument.
   c. Plot nL EtO vs. peak height or area. This plot should be a straight line.
   d. Periodically throughout the day, check calibration by repeating some of these injections of standards. Ideally, each sample would be bracketed, before and after, with injections of standards, although this is seldom practical.
3. Check the sampling equipment to prevent contamination.
   a. Use different syringes for sampling and for standard preparation. Identify each syringe with a unique number.
      NOTE 1:
So called gas-tight syringes appear to be so only when new. Leakage results in injections less than indicated, resulting in inaccurate reporting of the actual concentration.
      NOTE 2:
Even after more than a dozen purges, a syringe used to transfer pure ethylene oxide continues to elute small amounts of EtO.
   b. Bag sampling.
      (1) Check inertness and impermeability of the entire sampling train. This is best accomplished in the laboratory before going to the field. Purge a bag of the type to be used for sampling with clean air, and then fill it with clean air and an amount of EtO to create a concentration in the range of interest. Take replicate samples from that bag and inject them into the GC. Measure peak heights. Pump the contents of this bag through a sampling train of the type to be used in the field, into a second bag. Analyze replicate samples from the second bag immediately after transfer and hourly thereafter. If the concentrations found immediately after transfer are equal to those prior to transfer, the sampling train is not altering the EtO concentration (i.e., is inert). If the concentrations do not change over time, the bags are inert.
      (2) Consider any residual analyte which may remain in a bag after use, since practicality dictates reuse of bags. One or two purges with clean air are usually sufficient to remove residual EtO unless the concentration of the previous sample was extremely high. Analyze a sample of "clean" air taken from the bag during its final purge. If no measurable EtO is found, the bag is ready for reuse.
      NOTE: Some bags continue to show traces of analyte, even after several purges, and

these bags should be discarded.

(3) Segregate bags used for sample collection from those used for calibration standards.

MEASUREMENT:

4. Fill a gas-tight syringe, purged several times with sample, from the sample bag. Then empty it to the desired volume, and inject that volume into the chromatograph with a quick firm motion. Record identity of syringe. Use replicate analyses to determine the repeatability of the analysis.

   NOTE 1: If no estimate of concentration is available, use an injection volume of 10 to 25 µL at a high attenuation to reduce the possibility of column and detector overload. Depending on the results of this injection, larger volumes and/or more sensitive attenuations may be selected.

   NOTE 2: The procedure for analysis of samples collected directly in a gas tight syringe is the same as for bag samples, with the obvious elimination of the step where the sample is withdrawn from the bag.

5. Along with the sample identification, record the injection volume (mL), the instrument attenuation, and the resultant peak height or area.

CALCULATIONS:

6. Divide the EtO volume (nL) from the calibration graph, by the injection volume (mL) to calculate sample EtO concentration (ppm):

$$\text{ppm} = \frac{\mu\text{L (gas)}}{\text{L (gas)}} = \frac{\text{nL (gas)}}{\text{mL (gas)}}.$$

EVALUATION OF METHOD:

This method was evaluated in the laboratory where the accuracy and precision were determined by a comparison of measured values with accepted concentrations from a dynamic (permeation tube) generation system with confirmation by lab G.C. with flame ionization detector [1]. Field evaluations were conducted in hospital and manufacturing sterilization facilities which used commercial mixtures of EtO with Freon 12 and carbon dioxide, respectively.

REFERENCES:

[1] Burroughs G. E., and Busch, K. A., "Field Validation of Direct-Reading Instrumental Methods for the Sampling and Analysis of Environmental Contaminants," unpublished NIOSH report (1985).

[2] NIOSH Manual of Analytical Methods, 3rd ed., Vol. 1, Method 1614, Department of Health and Human Services (NIOSH) Publ. No. 84-100 (1984).

METHOD WRITTEN BY:

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