Determination of ethylene oxide in air by gas chromatography

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Determination of Ethylene Oxide in Air by Gas Chromatography

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A method for the collection and analysis of airborne ethylene oxide (ETO) has been developed. This procedure is based on the entrapment of ETO on a chemically impregnated air sampling tube where it is converted to 2-bromoethanol. The 2-bromoethanol is subsequently analyzed by gas–liquid chromatography using an electron capture detector. The method was tested in the 0.5–20 ppm concentration range and was shown to provide recoveries of 92–112%. Statistical treatment of laboratory and field data is presented.

Ethylene oxide (ETO) is an important chemical having wide industrial application for the synthesis of polymers, surfactants, antifreeze, etc. Within health care facilities, ETO provides the only practical means of sterilizing heat-sensitive surgical tools and equipment. The effectiveness of ETO as a sterilant residues in its inherent toxicity; consequently, there is an acute concern regarding its toxic effects on exposed workers. Furthermore, at concentrations below the current limit of 50 ppm as an 8-h time weighted average (TWA), ETO is suspected of being a carcinogen. Recently, the U.S. district court ordered the Occupational Safety and Health Administration (OSHA) to issue an emergency health standard of 1 ppm. If the proposed standard of 1 ppm is adopted, current ETO monitoring techniques will be severely stressed to accurately measure down to that level.

The National Institute for Safety and Health (NIOSH) sampling and analysis method for ETO (*1*) uses activated charcoal and carbon disulfide to collect and desorb ETO. Analysis of the desorbed material is accomplished using gas chromatography (GC) with a flame ionization detector. Other charcoal tube methods have dealt with various parameters such as different charcoal tubes (2) and different equipment (*3*). Coyne and Pilny (*4*) conducted a validation study of the ETO charcoal tube procedure; they studied storage stability, air flow rates, and the effect of relative humidity. The generally accepted method utilizes the large charcoal tube (390/700 mg) based on the procedure recommended by Qazi and Ketcham (2).

Even though the charcoal tube method has found wide acceptance for monitoring ETO, this technique has certain shortcomings. Some of the problems associated with the ETO charcoal tube method are interferences from other organic compounds, limited sample size because of breakthrough, the negative effect of high relative humidity, the need for refrigeration to avoid losses, and the overall complexity of sampling and analysis.

In addition to charcoal tubes, methods using passive monitors (*5*, *6*) have been used for the determination of ETO. These devices offer convenience and ease of operation; however, the cost per sampler is significantly greater than that of a charcoal tube. This cost is offset, to a great extent, by savings in time and labor.

Recently, a new method (*7*) for ETO was developed by OSHA at their Salt Lake City Laboratory. Samples are collected by using two charcoal tubes connected in series and desorbed with 1% CS_2 in benzene. The desorbed ETO is derivatized with HBr and analyzed by GC with an electron capture detector. This method provides good data; however, the limited capacity of the charcoal tubes requires sequential samples be taken to monitor long term exposures. In addition, tube storage is limited to approximately 3 weeks.

The object of this study was to circumvent the shortcomings of the OSHA method by simultaneous adsorption and derivatization of ETO in a collection tube. During the initial stages of the study, several sorbents were tested for their suitability as substrates for the derivatization reagent, HBr. Of the materials evaluated, the one that provided the best results was Ambersorb 347, a spherical carbonaceous material prepared by the controlled pyrolysis of polymeric beads. It is sufficiently retentive to entrain ETO long enough for derivatization to occur; with a mixture of toluene and acetonitrile, the derivative is quantitatively desorbed within 30 min.

In the proposed method, Ambersorb 347 is treated with HBr and packed into glass tubes. Air is drawn through the tubes where ETO is converted to 2-bromoethanol. The tubes are desorbed with a mixture of acetonitrile and toluene and subsequently analyzed by GC using an electron capture de-

tector. Tests were conducted to determine the effect of sampling rate, sampling volume, humidity, and storage on the performance of the new sampling tube. In addition, the new method was tested in the field by comparison to the charcoal tube procedure. A statistical interpretation of laboratory and field data is presented.

EXPERIMENTAL SECTION

Sampling Equipment. Accuhaler 808 (MDA, Park Ridge, IL), Du Pont P-4000 (E. I. du Pont de Nemours & Co., Wilmington, DE), and Gilian HFS-113UT pumps were used to collect samples; pumps were calibrated daily in the field. Qasi-Ketcham tubes, 390/700 mg of charcoal (SKC Inc., Eighty Four, PA), were used when the reference charcoal tube method was applied.

The tubes developed in this laboratory were prepared by adding 10 mL of HBr (24%) to 35 g of Ambersorb XE 347 (Rohm and Haas, Philadelphia, PA) in a 2-oz jar with a screw cap. The impregnated sorbent was thoroughly mixed for about 5 min, tightly sealed, and allowed to equilabrate overnight. Tubes were prepared by adding 0.5 g of packing material into 50 × 5 mm o.d. glass tubes. All sample tube packings were adjusted to give a pressure drop in the range 3.5–4.0 cmHg. Each tube was connected through a flowmeter to a laboratory vacuum source with a mercury manometer in-line. Glass wool plugs were used to hold the packing in place.

Calibration Standards. Ethylene oxide (101 ppm in nitrogen) was purchased from Scott Specialty Gases and 2-bromoethanol was obtained from the OSHA laboratory in Salt Lake City, UT. Pure ETO was purchased from Liquid Carbonic (Baltimore, MD).

Chromatographic Conditions. The chromatographic analysis of the Ambersorb tubes was conducted on a Hewlett-Packard Model 5880 gas chromatograph equipped with an electron capture detector. A 12 ft by $^1/_8$ in. stainless steel column packed with diethylene glycol succinate on Chromosorb WHP (80–100 mesh) was used for the separation of components. The column was operated at 155 °C and the injection port and detector temperatures were set at 250 °C. The carrier gas (5% methane/argon) flow was 30 mL/min.

The charcoal tubes were analyzed on a Chromosorb 102 (6 ft × $^1/_8$ in.) column using a flame ionization detector. The column, injection port, and detector temperatures were set at 140, 240, and 240 °C, respectively. The nitrogen flow rate was 30 mL/min.

Test Atmospheres. Predetermined volumes of pure ETO were injected into a sealed, 6920-L environmental chamger and allowed to equilibrate. A $^1/_{20}$ hp blower was operated within the chamber throughout each experiment to provide constant mixing. Ethylene oxide concentrations (5.0 ppm and above) were monitored with a Miran 103 (Foxboro Co., Foxboro, MA) for verification of ETO concentrations. Pumps were located outside, connected to the sorbent tubes inside the chamber via Tygon tubing.

Laboratory Study. Vapor concentrations ranging from 0.5 to 20 ppm were generated in the 6920-L exposure chamber. In some experiments, Freon-12 was mixed with ETO to test for Freon interference. Air sample collection flow rates were varied from 20 to 100 mL/min. In addition, different volumes of air (6–32 L) were collected to determine the possibility of breakthrough occurring. Storage stability tests, before and after usage, were conducted for periods up to 1 month. All laboratory tests were conducted at ambient temperatures and relative humidity with the exception of two experiments where the relative humidities were established at 60% and 90%.

Field Study. A prototype ETO sterilizer used in an Army mobile hospital was subjected to operational field tests during the summer of 1983. A variety of sampling points were sampled in the proximity of the sterilizer. Moreover, samplers were located at the air intake and exhaust of two operating rooms adjacent to the shelter housing the sterilizer. The ETO charcoal and Ambersorb tubes were placed side-by-side at each location and a Miran 103 was used to spot check concentrations throughout the hospital. The sampling rate for both tubes was 20 mL/min. The charcoal tubes were refrigerated until they were ready for the chromatographic analysis. The Ambersorb tubes were stored at room temperature. Samples were collected on three consecutive days for periods of approximately 4–8 h. Some of the charcoal and Ambersorb tubes were analyzed on site by using a portable gas chromatograph; the rest were brought back to the laboratory and analyzed within 7 days.

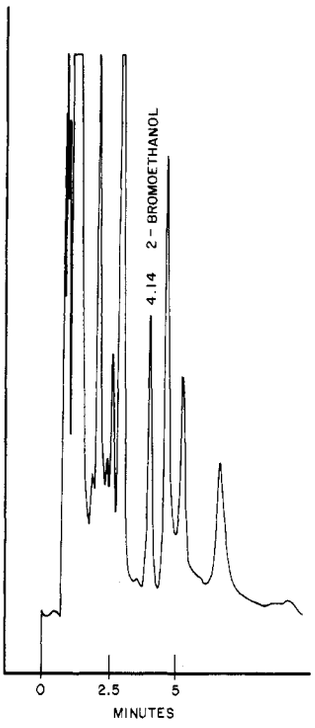

Figure 1. Chromatographic separation of 2-bromoethanol.

Desorption. The Ambersorb-HBr tubes were desorbed in vials containing 100 mg of sodium carbonate with 5 mL of a 1:1 mixture of acetonitrile and toluene for 30 min. For the desorption of charcoal tubes, 5 mL of carbon disulfide was placed in vials and stored in a freezer. The contents of a charcoal tube were added to a vial immediately after removal from the freezer. Vials were allowed to warm to room temperature before being analyzed. All of the samples were stirred occasionally during the desorption period.

RESULTS AND DISCUSSION

Desorption efficiency on the Ambersorb-HBr tubes was determined by using the phase equilibrium method. The DE's ranged from 98.9% to 99.8% for a series of six batches of Ambersorb treated tubes prepared in the laboratory. As a matter of routine, 2-bromoethanol standards were prepared in 5 mL of desorbing solvent containing the contents of an Ambersorb-HBr tube.

Calibration with 2-bromoethanol was accomplished by preparing 1 mg/mL stock solution in toluene. When refrigerated, this solution was stable up to 3 months. Appropriate aliquots of the stock solution were introduced into vials containing 100 mg of Na_2CO_3, 5 mL of desorbing solution, and the contents of a collection tube. The theoretical concentration of each solution was corrected for volume change. A calibration curve was constructed by plotting detector response vs. standard concentration.

For calibration of the charcoal tube method, a unique technique was employed to determine the adsorption–desorption efficiency of ETO on charcoal. The gas standard (101 ppm ETO) was assayed with pure ETO and found to be accurate. This standard was then carefully metered onto charcoal tubes, and the tubes were immediately stored in a freezer. The standard tubes were desorbed as previously described, thus providing a combined adsorption–desorption efficiency for each tube. A calibration curve was then constructed from the analysis of the desorbed tubes.

Figure 1 shows a typical chromatogram obtained from a sample collected for 8 h at 20 mL/min in an atmosphere containing 1 ppm of ETO. As shown in the chromatogram,

Table I. Effect of Flow Rate[a]

nominal flow rate, mL/min	liters (av)	ppm of ETO found[b]	recovery, %
20	2.525	4.65	93.0
50	5.076	4.53	90.6
100	11.103	4.60	92.0

[a] Sampling time, 2 h. [b] Theoretical ETO concentration, 5 ppm.

Table II. Breakthrough at 60% and 90% Relative Humidity (RH)

	ppm of ETO Found	
liters sampled	60% RH	90% RH[a]
6	5.1	5.3
12	4.7	5.0
17	5.0	4.9
22	4.7	4.7
27	4.8	5.1
32	5.0	5.3

[a] Theoretical ETO concentration, 5 ppm.

Table III. Precision and Accuracy of Chamber Concentrations

theoretl concn, ppm	av recovery,[a] ppm	av recovery, %	rel std dev, %
0.5	0.56	111.6	1.61
1.0	1.01	100.9	1.98
5.0	5.04	100.8	3.57
10.0	10.1	101.8	5.64
20.0	20.4	102.1	2.94

[a] Average of six air samples.

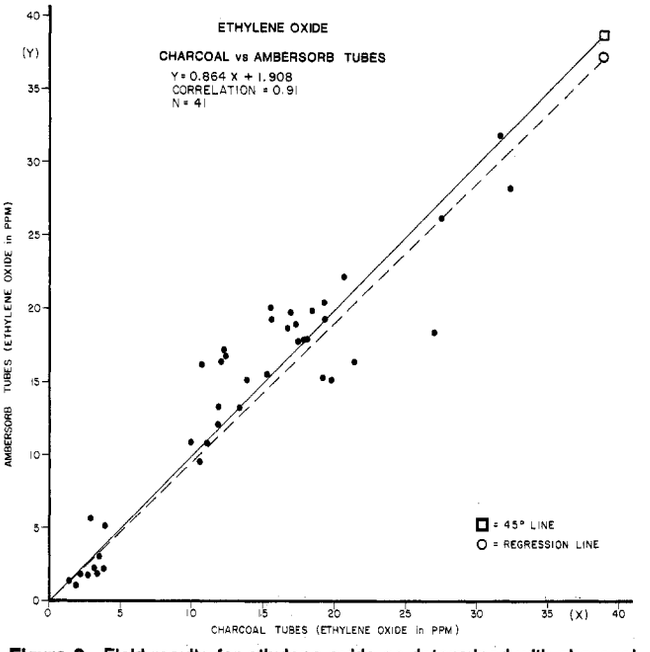

Figure 2. Field results for ethylene oxide as determined with charcoal tubes and Ambersorb tubes.

Table IV. Storage Stability

weeks stored	ppm of ETO found[a]	% recovered
1	5.2	104
2	5.1	102
3	4.7	94.0
4	4.7	94.0

[a] Theoretical concentration, 5 ppm.

the 2-bromoethanol peak was completely resolved from all the other peaks. When an unreacted tube was desorbed and chromatographed under identical conditions, a very small peak with the same retention time as ETO was observed. For a 10-L sample the peak is equivalent to approximately 0.1 ppm. Since the peak size was found to be consistent in different blank determinations, a blank correction can be made to compensate for its presence.

In the flow rate study, the sampling time was kept constant (2 h) and the flow rate was varied 20–100 mL/min. As shown in Table I, recoveries were good at all of the flow rates tested. As will be shown later, these recoveries (93.0%, 90.6%, and 92.0%) were lower than those obtained in subsequent experiments. Limited recovery breakthrough data obtained at different relative humidities and sample volumes are presented in Table II. In order to cover the desired sample volume range in a single day, a sampling rate of 100 mL/min was required. A vaporizer was used in conjunction with the 6920-L test chamber to adjust the relative humidity to desired levels. All tests were conducted at ambient temperature (23 ± 1 °C). As the data illustrate, the Ambersorb-HBr tube has the capacity to efficiently collect and retain ETO at high relative humidity (90%) when challenged with air volumes up to 32 L. Comparable results were obtained at 60% relative humidity.

In order to determine the efficiency of the proposed procedure when applied to a broad range of ETO concentrations, a series of air mixtures equivalent to 0.5, 1.0, 5.0, 10.0, and 20.0 ppm were established in our 6920-L test chamber. To simulate a typical sterilization mixture, 80 ppm of Freon was added to the 20 ppm test atmosphere. Table III presents the precision and accuracy of the combined collection and analytical procedure. Each value in the recovery column represents an average of six Ambersorb-HBr test results. A plot of the data (observed ETO concentrations vs. theoretical value) gave a regression line having a correlation coefficient of 1.0 and slope of 1.018 reflecting good agreement between theoretical and experimental values. Interference from Freon 12 was not detected.

To obtain field comparison data, the Quazi-Ketcham charcoal tube method was used for comparative purposes. Side-by-side samples were collected over a of 2-week period and analyzed by the corresponding analytical procedure. The resulting data for 41 paired sets of charcoal tubes and Ambersorb tubes are illustrated in Figure 2. The new method correlated well with the refernce method, $R^2 = 0.91$, and was significant at the $P = 0.01$ level. The associated best fit line had a slope of 0.864.

To check storage stability of collected samples, a 5-ppm concentration of ETO was sampled with four Ambersorb-HBr tubes, stored at room temperature, and analyzed over a 4-week period. The results are shown in Table IV. The small decrease in recovery after 4 weeks of storage was within the precision limits of the method.

In conclusion, The Ambersorb tubes exhibited excellent analytical efficiency for the collection of ETO over the challenged concentration range of 0.5–20 ppm without adverse effects from humidity or Freon and without the need of refrigeration to maintain stability for extended periods.

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Purge and Trap Chromatographic Method for the Determination of Acrylonitrile, Chlorobenzene, 1,2-Dichloroethane, and Ethylbenzene in Aqueous Samples

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A purge and trap method has been developed for the determination of four priority pollutants in aqueous samples. Water samples are purged at 50 °C with helium and the analytes are trapped on Tenax GC. The trap is thermally desorbed directly into a gas chromatograph equipped with a flame ionization detector. Instrument calibration is performed by direct injection of standard solutions in methanol through a modified purge vessel. The method was laboratory validated for the range of 20–500 ppb for each analyte using a 5-g aqueous sample. Average recoveries (relative standard deviation) were 62% (0.08), 100% (0.07), 99% (0.07), and 92% (0.07), respectively, for acrylonitrile, chlorobenzene, 1,2-dichloroethane, and ethylbenzene.

The purge and trap (PT) technique for the determination of volatile organics in aqueous samples is widely used (*1–3*). The advantages of the method include high sensitivity, simplicity of use, and relatively low cost. A disadvantage is the difficulty in directly calibrating the detector response after installation of the PT sampler. Further, water-soluble analytes often show low recoveries with this technique.

Purge and trap samplers usually bypass the gas chromatograph injection port. Instrument calibration is generally performed one of two ways. In one, standards are injected and a response curve is constructed before sampler installation. Alternatively, aqueous standards are exhaustively purged and analyzed. The first procedure carries the assumption that peaks produced by direct injection have the same retention times and shapes as do those produced using the PT sampler. This calibration technique requires that the PT desorption process and passage of the analytes through the sampler have the same efficiency as does sample vaporization in the injection port during direct injection.

The second procedure carries the assumption that analyte recovery from any aqueous matrix is quantitative and reproducible. For a number of compounds, including many which are water soluble, this is not the case (*4*). Absolute recovery is difficult to determine and relative recoveries of analytes and internal standards from various real-world matrices may differ markedly from those of standard solutions prepared in deionized water.

This work describes a method of instrument calibration using a PT sampler. It also describes a simple system for sample heating which improves analyte recovery. Finally, these procedures are applied in the development and validation of a method for determining acrylonitrile (AN), 1,2-dichloroethane (DCE), ethylbenzene (EB), and chlorobenzene (CB) in water. The method was developed as part of Monsanto Company's continuing efforts to monitor, document, and control priority pollutant levels in wastestreams.

EXPERIMENTAL SECTION

Reagents. Methanol was Matheson, Coleman and Bell distilled in glass OmniSolv. Charcoal-filtered deionized water was obtained with a Continental water system (St. Louis, MO). The priority pollutants AN, CB, DCE, and EB were obtained in 99+% purity from Supelco, Inc. Fisher Certified bromoform was used as an internal standard.

Apparatus. A Hewlett-Packard 5840A gas chromatograph equipped with a flame ionization detector and a Hewlett-Packard 7675A purge and trap sampler were used for all analyses. Separations were performed on a Supelco, Inc., 6 ft × $^1/_8$ in. o.d. stainless steel column packed with Carbowax 1500 on 80/100 Carbopack C using a 20 mL min^{-1} flow of helium carrier gas. The column was conditioned by heating for 3 days at 170 °C with a 20 mL min^{-1} flow of helium. The sampler trap was packed with 60/80 Tenax GC and was conditioned by heating 3 days at 250 °C under a 20 mL min^{-1} flow of helium. A standard 15-mL needle purge vessel was used for analyses of all samples except instrument calibration standards.

Instrument Calibration. The modified purge vessel shown in Figure 1 was used for instrument calibration. Instrument calibration standards were prepared in methanol over the range 5.0–250 $\mu g\ mL^{-1}$ of each analyte. These solutions also contained 202 $\mu g\ mL^{-1}$ of bromoform as an internal standard. For instrument calibration, a modified purge vessel was fitted with a 5-mL size serum stopper over the side arm. The vessel was attached to the purge and trap sampler. Concomitant with the initiation of the purge cycle, 10 μL of a calibration standard was injected through the serum stopper into the empty (dry) vessel. The sample was vaporized with a heat gun and the analysis cycle was continued to completion.

Method Validation. The method was validated by analyzing standard aqueous solutions of AN, DCE, EB, and CB, each at five levels from 20 to 500 ppb (20–500 ng mL^{-1}). These solutions were prepared by first making primary standards in methanol and diluting aliquots of these to known volume with deionized water.

A five-gram aqueous sample was accurately weighed on a balance accurate to five decimal places in grams into a standard 15-mL needle purge vessel. To this weighed sample was added 1.00 mL of a 2.0 $\mu g\ mL^{-1}$ standard solution of bromoform in water as internal standard. The vessel was attached to the sampler and purged with helium at 20 mL min^{-1} for 15 min. The purge vessel

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