

3M COMPANY
OCCUPATIONAL HEALTH & ENVIRONMENTAL SAFETY DIVISION
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DETERMINATION OF ETHYLENE OXIDE IN AIR
Using 3M 3550/3551 Ethylene Oxide Monitors

SCOPE

This procedure covers the method of analyzing samples to determine the amount of ethylene oxide present in air using the 3M Brand 3550/3551 Ethylene Oxide Monitor.

SUMMARY OF THE METHOD

The ethylene oxide (ETO) vapors are adsorbed on chemically treated activated charcoal where they are converted to 2-bromoethanol, desorbed with 10% methylene chloride in methanol and quantitated using a gas chromatograph equipped with an electron capture detector (ECD) and capillary column. Alternate methods using a flame ionization detector (FID) with a capillary column and an ECD with packed column are described in Appendix B.

EQUIPMENT

The following or equivalent equipment is used:

Gas Chromatograph - Hewlett Packard, Model 5880 or 5890 equipped with an electron capture detector.

Analytical Column - J&W DB225 (50% cyanopropylmethyl - 50% methylphenyl-polysiloxane) 0.25 um film thickness, 0.25 mm I.D., 15 m capillary

REAGENTS/SUPPLIES

The following or equivalent reagents and supplies are used:

Methanol - Aldrich HPLC grade

Methylene Chloride - Aldrich HPLC grade

Desorption Solution - 10% (vol./vol.) methylene chloride in methanol

Ethylene Oxide - Lecture Bottle

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Compressed gas cylinders of:

Helium for carrier gas (Linde High Purity).

P5 mixture 5% methane, 95% argon for auxiliary gas (Linde).

Caution: High pressure gas is hazardous and should be handled with care. Do not store in extreme heat.

Ethylene Oxide Monitor - 3M Brand No. 3550/3551

Features: Sampling rate controlled by molecular diffusion.

Collection layer has about 160 milligrams of treated activated carbon in a Teflon matrix.

Microliter Syringes - Hamilton (or equivalent) 1 μ L - 5 mL. These syringes are guaranteed accurate to \pm 1% full scale and are used without further calibration.

Volumetric Flasks - Class A (10 \pm 0.02 mL, 25 \pm 0.03 mL, 50 \pm 0.05 mL, 100 \pm 0.08mL, etc.)

Vials - 2 ml with Teflon lined caps

CALIBRATION

A solution of 4ml ETO gas in 10ml of D.I. water is prepared and spiked on to 3M Brand Ethylene Oxide Monitors. The amounts spiked are 5 μ l(3.59 μ g), 15 μ l(10.77 μ g), 20 μ l(14.36 μ g), 40 μ l(28.72 μ g), & 70 μ l(50.26 μ g). A best fit line is calculated by the regression technique to correlate peak height with the amount spiked on the monitors.

NOTE: The ETO solution is prepared by drawing 4 ml of ETO gas into a 5 ml gas-tight syringe. The needle is submerged in a beaker of DI water and a small amount of water is pulled into the syringe. As the ETO gas dissolves a vacuum is formed which draws additional water to fill the syringe. Dilute this solution to 10 ml in a volumetric flask.

Alternatively, a standard curve can be prepared from dilutions of 2-bromoethanol in 10% methylene chloride in methanol and calculating the equivalent amount of ETO.

$$\text{ETO}(\mu\text{g}) = 2\text{-Bromoethanol}(\mu\text{g}) \times (44.05/124.98)$$

Appropriate quality control samples are run with each set of standards and samples.

ETO Analytical Method
SAMPLE ANALYSIS

Using a repipet or a syringe add 1.5 ml of the desorption solution to each monitor through the center port (the port is immediately resealed). After 30 minutes, with occasional gentle agitation, the eluent is decanted into a marked 2 ml vial and a 1 ul sized sample is automatically injected into the gas chromatograph. The previously prepared standards should be analyzed at the same time as the monitor samples and spread throughout the total run so that standards are run at the beginning, middle and end of the sample set. The syringe is washed with methanol after each sample. The split liner is packed loosely with 2 cm of silanized glass wool and should be changed every 50-250 injections. Specific chromatographic parameters are described in Appendix A.

CALCULATIONS

The time-weighted-average concentration of the environment sampled can be calculated by knowing the length of sampling period, the contaminant weight determined by gas chromatography, the recovery coefficient and the calculation constant either A or B. The calculation constant A is used to calculate the concentration when expressed in units of milligrams per cubic meter (mg/m³) and constant B when expressed in units of parts per million (ppm). The calculation constants A and B have been determined using our experimentally validated sampling rate of 49.3 cc/min:

$$A = \frac{1000}{SR} = 20.28$$

$$B = \frac{1000 \times 24.45}{SR \times MW} = 11.26$$

The time-weighted-average concentration in milligrams per cubic meter (mg/m³) of ethylene oxide in the environment sampled can be calculated from the following expression:

$$C(\text{mg/m}^3) = \frac{W \times A}{r \times t}$$

The time-weighted-average concentration in parts per million (ppm) of the contaminant can be calculated from the following expression:

$$C(\text{ppm}) = \frac{W \times B}{r \times t}$$

where:

- W = equivalent ETO weight recovered (micrograms)
- SR = Sampling Rate

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MW = Molecular Weight

r = recovery coefficient

t = length of sampling period (minutes)

Note: When the standard curve is prepared by spiking ETO gas onto monitors, the recovery is automatically taken into account and r is set to 1.00. If 2-bromoethanol is used for the standard curve, it is necessary for the laboratory to determine and use a recovery correction.

Experiments in our laboratory have shown a recovery of 0.85.

The above expressions calculate the time-weighted-average concentrations at a sampling temperature of 25 °C and pressure of 760 mm Hg. When sampling at other environmental conditions, the previous expressions need to be corrected only for variations in temperature. The previous expressions can be multiplied by the following temperature correction factors (CFt) for samples collected at temperatures other than 25 °C (77 °F).

Sampling Temperature		Correction Factor
(°C)	(°F)	(CFt)
44	111	.97
37	99	.98
31	88	.99
25	77	1.00
19	66	1.01
13	55	1.02
7	45	1.03
2	36	1.04
- 3	27	1.05
- 8	18	1.06

As shown in the above table, every 10-11 degrees above or below 77 °F requires a one percent correction to the calculated time- weighted-average concentration.

Example Calculation:

Length of sampling period (t)= 465 minutes

Temperature = 19 °C

Calculation constant A = 20.28 or B = 11.26

Equivalent Ethylene Oxide weight (W) = 40.7 micrograms

Recovery coefficient = 1.00

Using calculation constant (A):

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$$C(\text{mg}/\text{m}^3) = \frac{(40.7)(20.28)(1.01)}{(1.00)(465)}$$

$$C = 1.8 \text{ mg}/\text{m}^3$$

Using calculation constant (B):

$$C(\text{ppm}) = \frac{(40.7)(11.26)(1.01)}{(1.00)(465)}$$

$$C = 1.0 \text{ ppm}$$

LIMIT OF QUANTITATION

The limit of quantitation in our laboratory has been determined to be 1 ug. This allows detection of 0.75 ppm with a 15 min sample or 0.02 ppm with an 8 hr sample.

SAMPLE STABILITY

Storage stability tests were conducted with monitors which were spiked at a level equal to 75% of their capacity. Half of the monitors were stored at room temperature (25°C) and the other half stored in a hot room maintained at 40°C. After 50 days of storage, the monitors showed respective losses of only 6.4% and 7.2%.

INTERFERENCES

Acetone and isopropanol can both be brominated by the chemistry on the 3550/3551 monitors. Use care to insure that each column has adequate resolution to effectively separate the brominated acetone and isopropanol derivatives.

APPENDIX A

Parameters For HP 5890A Chromatograph:

Oven temp = 60
Equib time = 1.00 min.
Initial time = 6.50 min.
Program Rate = 50.0
Final temp = 180
Final time = 6.00 min.
Inj. A temp = 180
Det. B temp = 300

Times and temperatures may vary depending on instrument or column.

Run parameters:

Zero = 10
Att 2 = 4
Cht sp = .50
Ar rej = 0
Thrsh = 0
Pk wd = 0.04

Timetable Events:

1.100 Intg # = 9
4.500 Intg # = -9
7.500 Intg # = 9

Times may vary depending on instrument or column.

Report Options:

Height% report yes

Detector B = ECD (on)
Purge A = On
Purge B = On
Split Ratio = 40:1 to 20:1 (depending on sensitivity of detector)
Head Pressure = 10 psi
Helium Pressure = 45 psi
P5 Pressure = CONTROLLED BY AUX ON/OFF VALVE

Regulator Settings:

Helium = 50 psi
P5 = 35 psi

APPENDIX B

3M Company - OH&ESD Determination of Ethylene Oxide in Air Alternate Methods - November, 1991

Alternate Method using a Flame Ionization Detector with a Capillary Column

Extraction: 10% Methylene Chloride in Methanol

Column: 5% diphenyl 95% dimethyl polysiloxane 30 M x .25 mm ID x .5 um film

Oven Temperature: 50 °C isothermal

Split Ratio: 30:1

Injection Temperature: 150 °C

Detector Temperature: 250 °C

Although this method does not have the sensitivity of the electron capture detector, it is sensitive and accurate to 0.2 ppm over an eight hour sampling period.

Alternate Method using an Electron Capture Detector with a Packed Column

Extraction: 1.5 ml 10% methylene chloride in methanol

Dilution: Dilute 100ul of the eluent to 1 ml with 1:1 toluene:acetonitrile

Injection: 1ul of the diluted extract

Column: 10' x 2mm ID glass column packed with 10% diethylene glycol succinate (DEGS) on 80/100 mesh Chromosorb W AW.

Injection Temperature: 150-160°C

Detector Temperature: 250-300°C

Oven Temperature: 110-125°C

Carrier Gas Flow: 25-35 cc/min

CAUTION: Acetone and isopropanol can both be brominated by the chemistry on the 3550/3551 monitors. Use care to insure that each column has adequate resolution to effectively separate the brominated acetone and isopropanol derivatives.