

California Environmental Protection Agency



Method 431

**DETERMINATION OF ETHYLENE OXIDE  
EMISSIONS FROM STATIONARY SOURCES**

Adopted: September 12, 1989  
Amended: July 28, 1997  
Amended: November 13, 1998

**PROPERTIES:** gas at room temp

M.W.: 44.05 B.P.: 10.7 °C ; V.P.: 146 kPa (20 °C)

vapor density: 0.98 (air = 1); explosive range: 3% to 80 + % v/v in air

SAMPLING	MEASUREMENT
<p>Actual monitoring at the inlet of control devices, where concentrations of EtO are extremely high and may even be in the explosive range, may pose a significant safety hazard. There have been explosions at several commercial EtO sterilization facilities. These explosions may have been associated with catalytic oxidation control devices. Due to these concerns it is recommended that the estimation calculations (Appendix B) be used instead of actual monitoring measurements to determine the mass of EtO delivered to the inlet of the control unit.</p> <p>The calculations described in Appendix B may be used to estimate the mass of EtO delivered to the inlet of the control device, or; the direct interface sampling and analysis procedure described in Appendix A may be used to continuously monitor ethylene oxide concentrations at the outlet (and inlet) of the control device using a gas chromatograph with flame ionization detector (GC/FID) or photo-ionization detector (PID).</p> <p>OPTION: Where appropriate, integrated Tedlar bag sampling may be used to monitor the ethylene oxide concentrations. Refer to Appendix I for sampling procedures.</p>	<p><b>TECHNIQUE:</b> Gas Chromatography, Flame Ionization detector (PID optional).</p> <p><b>ANALYTE:</b> Ethylene Oxide (EtO)</p> <p><b>INJECTION:</b> 0.5 cc to 2 cc; sampling loop.</p> <p><b>TEMPERATURE:</b> - INJECTION: 100 cc - DETECTOR: 220 cc - COLUMN: isothermal 80 °C</p> <p><b>CARRIER GAS:</b> UHP Helium or Nitrogen 30 cc/minute</p> <p><b>COLUMNS:</b> 6 to 9 foot 1% SP-1000 on 60/80 mesh Carbo-pack B</p> <p><b>CALIBRATION:</b> compressed gas cylinder standard,</p> <p><b>ANALYTICAL RANGE:</b> 0.20 ppmV to 0.50% v/v</p>

**PRINCIPLE:** The mass (or concentration) of ethylene oxide delivered to a control unit (inlet) during a sterilization cycle will be estimated (i.e., calculated) using the procedures in Appendix B or measured using the sampling/analysis procedures described above. The mass (or concentration) of ethylene oxide delivered to the control unit (inlet) during an aeration cycle and the mass (or concentration) of ethylene oxide emitted from the control unit (outlet) during a sterilization or aeration cycle will be determined

using the sampling/analysis procedures described above and the calculations described in Appendix F.

**APPLICABILITY:** This method is applicable to the measurement of ethylene oxide in emissions from hospital equipment sterilization and aeration chambers, and appropriately configured commercial sterilizers.

**LIMITATIONS:** Refer to Appendix H for limitations associated with Tedlar bag and direct interface sampling/analysis of ethylene oxide.

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**INTERFERENCES:** The diluent gas (such as Freon-12, HCFC-124, or others) may interfere with the EtO peak when testing low EtO emissions concentrations. GC operating conditions should be adjusted to provide baseline resolution between EtO and any diluent gas.

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**REFERENCED METHODS:** This method is based on the EPA rule for EtO emissions from sterilizers (December 6, 1994, CFR 40, Part 63.63, pg. 689).

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**REAGENTS:**

1. Ethylene oxide in compressed gas cylinders at levels bracketing the sample concentrations. Sterilant diluent gas may be included in the gas mixtures at levels expected in the emission matrix.
2. Helium, 99.999%, and FID grade hydrogen and air.
3. Air, purified, to be used for dilutions, blank preparation, and standard preparation.

**EQUIPMENT:**

1. Gas chromatograph, flame ionization detector or photo ionization detector, integrator, and columns.
2. Sample loops .50, 1.0, and 2.0 cc.

**\*\* SPECIAL PRECAUTIONS:** Ethylene Oxide is a potential carcinogen. Work should be performed in a well ventilated fume hood. For specific regulatory requirements refer to the California Labor Code, Part 10, Section 9020; Title 8, California Code of Regulations, Section 5220.

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### **CALIBRATION AND QUALITY CONTROL:**

Refer to Appendix E for multipoint and daily calibration and quality control procedures. Refer to Appendix E for calibration procedures specific to the direct-interface gas chromatography.

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### **LIST OF APPENDICES:**

- Appendix A: Testing Procedures for Sterilizers with Catalytic Oxidation or Hydrolytic Scrubber Type Control Units
- Appendix B: Procedures for Estimating Mass of EtO at the Control Unit Inlet
- Appendix C: Testing Procedures for Aeration Chambers
- Appendix D: Documentation of the Probe Position at the Inlet of Catalytic Oxidation Units
- Appendix E: Calibration and Quality Control Procedures
- Appendix F: Calculations
- Appendix G: Reporting Requirements
- Appendix H: Method Limitations
- Appendix I: Tedlar Bag Sampling and Quality Control Procedures
- Appendix J: Definitions
- Appendix K: Testing Procedures for Sterilizers with Joslyn Recovery Type Control Units
- Appendix L: Ethylene Oxide in Water

## APPENDIX A

### TESTING PROCEDURES FOR STERILIZERS WITH CATALYTIC OXIDATION OR HYDROLYTIC SCRUBBER TYPE CONTROL UNITS

The following procedures shall be used to determine the efficiency of catalytic oxidation and hydrolytic scrubber types of control devices used in controlling emissions from an ethylene oxide sterilizer. The following aspects of the ethylene oxide compliance test are discussed below in this Appendix:

- Stack gas moisture determination.
- Stack gas volumetric flow rate determination.
- Determination of ethylene oxide concentration.

The procedures described herein are used to provide control unit inlet and outlet mass or concentration values to be used in calculating a control efficiency, as specified in the Ethylene Oxide Airborne Toxic Control Measure for Sterilizers and Aerators (17 CCR, Section 93108). As described below, stack gas moisture and volumetric flow rate determination may not be required for many control unit configurations. In such cases the control efficiency will be based solely on the concentration reduction across the control device.

#### **Stack Gas Moisture**

For catalytic oxidation units, the atmospheric moisture dominates the resulting average moisture from the sterilization chamber humidification process and of the moisture created by the destruction of EtO. This is due to the fact that ambient air is used in great excess (normally >100:1) to dilute the chamber sterilant gas before passing across the catalyst bed. Thus the "stack" gas moisture content may be assumed to be the same as that of the ambient air. The wet/dry bulb method may be used for determination of the ambient moisture content.

For hydrolytic scrubber units, the outlet gas may be assumed to be saturated with moisture (i.e., the temperature of the outlet stream must be obtained for the calculation).

At the discretion of the Source Test Protocol reviewer the moisture content of the exhaust gas may be measured using ARB Method 4 during the evacuation and wash stages of at least one cycle (out of the three).

#### **Stack Gas Flow Rate**

If volumetric flow measurements are required, measure the volumetric flow rate of the control device exhaust continuously during the evacuation and wash cycles using the procedures found in ARB test methods 2, 2A or EPA Method 2C or 2D, as appropriate. Following are the recommended procedures for flow rate measurements for hydrolytic scrubber and catalytic oxidation type control devices.

Hydrolytic scrubber type control units: ARB Method 2A is required for measuring flow rates from hydrolytic scrubber type control units. It may be necessary to have multiple meters available in order to cover the expected range of flow rates. To calculate the molecular weight of the gas, assume that the composition of the sterilant gas is delivered unchanged from the chamber to the control unit and that the balance of the control unit emission gas is sterilant balance gas (if any) plus the moisture content. If there is any dilution of the sterilant gas though, the diluent gas concentration will have to be measured along with the concentration of EtO in the gas streams for volumetric flow to be calculated correctly. Record the flow rate at 1 minute intervals throughout the test cycle, taking the first reading within 15 seconds after time zero. Time zero is defined as the moment when the pressure in the sterilizer is released. (The purpose here is to measure flow rates concurrently with the bag samples or on-site GC). Correct the flow to standard conditions (68°F and 1 atm) and determine flow rate in units of standard cubic feet per minute for the run as outlined in the test methods listed in this paragraph.

Catalytic oxidation type control units: Volumetric flow measurements may not be necessary for compliance testing of catalytic oxidation control units. In those systems that meet the following criteria the destruction efficiency calculation can be based solely on the EtO concentration measurements (not applicable where the inlet estimation technique is used).

1. no dilution between inlet and outlet sampling locations,
2. identical flow at inlet and outlet sampling locations, and
3. constant flow throughout the duration of the compliance test.

However, volumetric flow measurements may be required by the Districts in order to determine yearly mass emissions for inventory or facility risk assessment purposes. In those cases the following procedures shall be followed. Note that flow measurements need only be obtained at one of the sampling locations, either inlet or outlet, if the above conditions are met.

CARB Method 2 (type S pitot tube) should be used to determine stack gas velocity and volumetric flow rate of stacks greater than 12 inches in diameter. Testing stacks/ducts having cross-sectional diameters less than 12 inches and equal to or greater than four inches, must be conducted according to United States Environmental Protection Agency (USEPA) Stationary Source Sampling Methods 1A and 2C. The differential pressure gauge used to measure velocity head ( $\Delta P$ ) must meet the requirements of ARB Method 2, Section 2.2 (also USEPA Method 2, Section 2.2). Pitot tube dimensions and specifications must be demonstrated to meet the requirements of ARB Method 2, Sections 2.7 and 4.2 (also USEPA Method 2, Sections 2.7 and 4.2). The source test reports must (1) include reasonably accurate as-installed drawings of the stack from the sterilizer to the point of emission, and (2) identify sampling locations, including dimensions, for each facility. Volumetric flow measurements will be conducted in the following manner: 1. A complete velocity traverse of the exhaust duct will be conducted in a manner consistent with applicable ARB or USEPA reference methods for flow determinations. 2. An

average velocity pressure will be calculated from the individual pressure measurements made at each velocity traverse point as specified in the ARB/EPA reference method. 3. A traverse point, where the measured velocity pressure corresponds to the calculated average pressure, will be used to make single point pressure measurements during direct sampling and analysis of EtO emission. 4. Velocity pressure measurements will be made concurrently with each direct sample drawn out of the exhaust duct for analysis. The emissions flow rate will be determined from the set of pressure measurements made at the single traverse point and compared to the flow rate calculated from the initial, "complete" flow rate measurement procedure. The two flow rates must compare within 10% for the test run to be valid.

Typical cat-ox units operate at 50 and 100 scfm. The exhaust ducting of a typical control unit is 4 to 6 inches and occasionally up to 10 inches in diameter. The larger size ducting gives very low linear gas velocities (e.g., less than 10 ft/sec.) which are difficult to measure using standard pitot tube/manometer techniques. A practical solution is to reduce the diameter of the oversize stack to a temporary 4 inch stack during the test. Also, because low flow/low velocity pressure conditions are anticipated for the exhaust duct emissions from some control units, use of a pressure transducer whose sensitivity is applicable for low magnitude pressure measurements and whose performance is traceable to a National Institute of Standards and Technology (NIST) reference standard is acceptable. Calibrations of the pressure transducer must be routinely conducted and calibration curves maintained in the company's file.

### **Determination of Ethylene Oxide Concentration at the Inlet of Control Units**

Actual monitoring at the inlet of control devices, where concentrations of EtO are extremely high and may even be in the explosive range, may pose a significant safety hazard. There have been explosions at several commercial EtO sterilization facilities. These explosions may have been associated with catalytic oxidation control devices. Due to these concerns it is recommended that the estimation calculations (Appendix B) be used instead of actual monitoring measurements to determine the mass of EtO delivered to the inlet of the control unit.

Two options are provided, as outlined below, for determination of the mass of ethylene oxide delivered to the control unit inlet.

Option 1, Inlet Estimation: (sterilization cycle only, cannot be used for aeration tests) The mass of ethylene oxide emitted from the sterilization chamber and delivered to the control unit inlet, during a sterilization cycle, may be calculated using the estimation technique detailed in Appendix B. The procedures shall be performed, on an empty sterilizer, for the duration of the post-evacuation/wash stages under normal operating conditions. A short "soak" (exposure) stage, e.g., manually aborted after no more than ten minutes, should be used to minimize leak and chamber losses. For those sterilization systems where sterilant gas is also added as "make-up" during the exposure stage, the cycle shall be aborted and the chamber exhausted before such "make-up". These estimation procedures may be used with sterilization systems using recirculating water ring seal pumps for evacuation of the chamber if the "correction" procedures outlined in Appendix B are followed. All test conditions must be characterized and reported with the final test results.

Option 2, Inlet Measurement: (must be used for aeration tests)

The mass of ethylene oxide emitted from the sterilization or aeration chamber and delivered to the control unit inlet may be determined by monitoring the chamber exhaust volumetric flow rate and EtO concentration (as described in the Measurement Methods section below) at the control unit inlet. If using this inlet measurement procedure, only the "entire duration of the first evacuation", as defined by the ATCM, must be tested for compliance purposes. The inlet and outlet of the control unit must be tested simultaneously. If the chamber load is to be used for compliance testing of an aeration run, the "soak" (or exposure) stage may not be shortened, e.g., manually aborted. This inlet measurement procedure must be used for compliance testing of aeration cycles. All test conditions must be characterized and reported with the final test results.

## **Measurement Methods**

The mass of ethylene oxide delivered to the control unit inlet during an aeration cycle and the mass of ethylene oxide emitted from the control unit outlet during a sterilization or aeration cycle must be determined by using one of the following sampling/analysis procedures and the calculations found in Appendix F. For catalytic oxidation control units, if the mass of EtO at the inlet is measured rather than estimated, testers must report documented evidence that the inlet probe is placed such that the sampled gases are completely mixed (i.e., chamber exhaust and ambient make-up). This documentation may be obtained by following the steps outlined in Appendix D.

Tedlar bag sampling/analysis procedure: The Tedlar bag sampling procedure specified in Appendix I may be used to collect samples of sterilizer/aerator and control unit exhaust gas for subsequent analysis by GC/FID. The sampling quality assurance procedures detailed in Appendix I must be followed. In addition, the following procedures must be followed.

If Option 1, Inlet Estimation, is used then the entire 1st evacuation and wash period must be monitored for EtO emissions at the outlet of a control system. Sampling will be initiated for the first evacuation when the pressure in the sterilizer is released.

If Option 2, Inlet Measurement, is performed then the inlet and outlet monitoring will be conducted simultaneously. Sampling will be initiated for the first evacuation when the pressure in the sterilizer is released.

ARB staff recommends that one of the test personnel monitor the sterilizer chamber pressure during the run and communicate, with walkie-talkies, the sampling start and stop times to the sampling test crew.

Excess EtO shall be bubbled through a sulfuric acid (1 N solution) impinger before discharge, or alternatively can be routed back into the control unit inlet gas stream. Ensure that the excess sample gas which has passed through the acid filled impinger is discharged to a safe location and will not imperil test personnel.



The Tedlar bag samples must be analyzed within 8 hours (of the sample stop time) by the procedures listed herein. The mass of EtO associated with each bag sampling interval is calculated as outlined in Appendix F.

Repeat the procedures three times (three cycles). The arithmetic average percent efficiency (see Appendix F: Calculations) of the three runs shall determine the overall efficiency of the control device.

Direct Interface Sampling Analysis: As an alternative to the Tedlar bag sampling procedure described above, a gas chromatograph (with FID or PID) interfaced directly to the emission source may be used to continuously monitor ethylene oxide concentration at the outlet (and inlet) of the control device. This procedure shall only be used if the GC sampling frequency provides at least 10 analysis points over the duration of the primary chamber evacuation. In addition, the following procedures must be followed.

If Option 1, Inlet Estimation, is used then the entire 1st evacuation and wash period must be monitored for EtO emissions at the outlet of a control system. Sampling will be initiated for the first evacuation when the pressure in the sterilizer is released.

If Option 2, Inlet Measurement, is performed then the inlet and outlet monitoring will be conducted simultaneously. Direct GC sampling will be conducted for at least the duration of the entire 1st evacuation. Sampling will be initiated for the first evacuation when the pressure in the sterilizer is released.

ARB staff recommends that one of the test personnel monitor the sterilizer chamber pressure during the run and communicate, with walkie-talkies, the sampling start and stop times to the sampling test crew.

When testing 3M sterilizer systems, or other systems with pulsed chamber exhaust, if the inlet mass is measured using the direct-GC approach, testers must use a one liter Greenburg-Smith impinger (empty) in the GC sampling train. The impinger shall be placed between the catalyst bed control unit and the on-site GC. This impinger will be connected by a Teflon line (less than 2 feet) to the catalyst bed's inlet sample port and by a Teflon line (less than 1 foot) to the heated sample line to the GC analyzer. The insertion of this impinger into the sample train will function as a mixing chamber for the sampled sterilizer exhaust gas prior to introduction into the GC analyzer. Sterilizers with pulsed exhaust will be continuously sampled through the modified sample train. The impinger geometry will mix the sampled gas and "smooth out" the variable concentrations associated with the pulsed exhaust gas flow. The impinger must be included in the system leak check, field blank and field spike.

The sample train is leak checked by plugging the sample line at the stack end and running the sample pump. Flow indicated by the rotameter should fall to zero. If it does not, seek and correct loose connections and other potential sources of leakage, then repeat the leak check.

Maintain a constant flow rate of approximately 2 liters per minute through the sample probe and transfer lines. If the sample transfer line is more than 10 feet long it should be heated to approximately 150 °F.

Excess EtO shall be bubbled through a sulfuric acid (1 N solution) impinger before discharge, or alternatively, route the excess gas back into the control unit inlet gas stream. Do not route the sulfuric acid scrubber exhaust back to the control unit as damage may occur to the catalytic bed. Ensure that the excess sample gas which has passed through the acid filled impinger is discharged to a safe location and will not imperil test personnel.

Repeat the procedures three times (three cycles). The arithmetic average percent efficiency (see Appendix F: Calculations) of the three runs shall determine the overall efficiency of the control device.

## APPENDIX B

### PROCEDURES FOR ESTIMATING MASS OF EtO AT THE INLET

The amount of ethylene oxide, in pounds, loaded into the sterilizer shall be determined by one of the following three procedures. These estimation procedures are valid only if there are no significant leaks or loss of EtO before the control unit. These estimation procedures shall be performed using an empty sterilization chamber. A short exposure stage, e.g., manually aborted, should be used to minimize leak and chamber losses. For those sterilization systems where sterilant gas is also added as "make-up" during the exposure stage, the cycle shall be aborted and the chamber exhausted before such "make-up". These estimation procedures may be used with sterilization systems using recirculating water ring seal pumps for evacuation of the chamber if the "correction" procedures outlined in section 4 below are followed.

1. For small sterilizer operations using disposable sterilant cartridges, weigh the cartridge to the nearest .5 gram before and after use. Multiply the total mass of gas charged by the weight percent ethylene oxide present in the sterilant mixture. Alternatively, if the cartridge supplier has certified the weight of EtO contained in the cartridge then this weight may be used for the estimation calculation. Or,
2. Weighing the ethylene oxide gas cylinder(s) used to charge the sterilizer before and after charging. Record these weights to the nearest 0.1 lb. Multiply the total mass of gas charged by the weight percent ethylene oxide present in the gas. Or,
3. Calculating the mass based on the conditions of the chamber immediately after it has been charged and using the following equation. A calibrated differential pressure gauge shall be used to monitor the chamber pressure.

$$W_c = \frac{MW \times M \times P \times V}{R \times T}$$

where:

$W_c$  = weight of ethylene oxide charged to the chamber, in pounds (grams)

MW = Molecular weight of ethylene oxide, 44.05 lb/lb mol (gr/gr-mole)

M = mole fraction of ethylene oxide

P = chamber pressure, psia (atm)

V = chamber volume, ft<sup>3</sup> (L)

R = gas constant, 10.73 ft<sup>3</sup> psia mole<sup>-1</sup> °R<sup>-1</sup>  
(.08205 L atm mole<sup>-1</sup> °K<sup>-1</sup>)

T = temperature, °R (°K)

S = standard conditions are 68°F (°R or °K) and 1 atm.

4. For sterilization systems using a recirculating water ring seal pump to evacuate the chamber after the exposure stage (primary evacuation) a correction must be applied to the estimated inlet EtO mass. The amount of EtO retained in the pump water reservoir must be subtracted from the amount calculated by the above techniques. Follow the procedures specified in Appendix L to collect 2 aliquot water samples from the reservoir immediately before and after the sterilizer exhaust compliance test (i.e., water sampling times must directly correspond to start and stop times of the exhaust test). The pump reservoir may need to be fitted with a sampling port for this purpose. Determine the volume of water in the reservoir both before and after the exhaust test. Analyze the samples as per Appendix L and calculate the mass of EtO retained in the water, and the corrected inlet EtO mass, using the calculations shown below.

$$W_{cc} = W_c - W_w$$

where:

$W_{cc}$  = weight of ethylene oxide charged to the chamber and delivered to the control unit, corrected for EtO loss to the water, in pounds (grams)

$W_w$  = weight of ethylene oxide retained in the pump reservoir water, in pounds (grams)

where:

$$W_w = (EtO_{after})(Vol_{after}) - (EtO_{before})(Vol_{before})$$

where:

$EtO_{after}$  = concentration of EtO in the pump reservoir water after the exhaust test, in  $\mu\text{g/ml}$ .

$EtO_{before}$  = concentration of EtO in the pump reservoir water before the exhaust test, in  $\mu\text{g/ml}$ .

$Vol_{after}$  = volume of water in the reservoir after the exhaust test, in ml.

$Vol_{before}$  = volume of water in the reservoir before the exhaust test, in ml.

## APPENDIX C

### TESTING PROCEDURES FOR AERATION ROOMS

The following procedures shall be used to determine the efficiency of a control device used to control ethylene oxide emissions from an aeration room. An aeration room is defined as any facility used for the dissipation of ethylene oxide residue from equipment previously sterilized in a sterilizer. The procedures are identical to those used to test sterilization chamber/control units (Appendix A) with the exception of the following.

The test shall be performed by placing a normal load of previously-sterilized equipment into the aeration room. The exposure stage cannot be shortened or aborted.

The measurement procedures in Appendix A shall be used to determine the volumetric flow rate and EtO concentration at the inlet and outlet of the control device. (The inlet estimation technique cannot be used.)

If using the direct GC sampling and analysis procedure, sample and analyze a slipstream of the outlet concentration of EtO once every 3 minutes continuously for 1 hour.

The emissions test shall be conducted in the hour immediately following the loading of the aeration room. The test shall consist of one aeration cycle run. The test engineer and/or test administrator shall insure that the aeration room is being tested under normal operating conditions and equipment load. These conditions shall be documented and reported with the final test results.

## APPENDIX D

### DOCUMENTATION OF INLET PROBE POSITION FOR CATALYTIC OXIDATION UNITS

For catalytic oxidation control units, if the mass of EtO at the inlet is measured rather than estimated, testers must report documented evidence that the inlet probe is placed such that the sampled gases are completely mixed (i.e., chamber exhaust and ambient make-up). This documentation may be obtained by the following steps:

1. Install the sampling probe in the control unit inlet.
2. During a sterilizer chamber evacuation monitor the volumetric flow rate of the control unit exhaust. Also monitor the concentration of ethylene oxide, using the procedures outlined below, at the control unit inlet (e.g., after dilution in the control unit). Monitor both the flow rate and EtO concentration for the duration of the sterilization chamber exhaust (first evacuation and following washes).
3. Calculate the total amount of EtO delivered to the control unit. These calculations are outlined in Appendix F.
4. Calculate the estimated amount of EtO delivered to the control unit by following the procedures in Appendix B.
5. Perform the above operations 3 times.
6. The concentration of EtO measured at the control unit inlet must be within 10 % of the estimated amount for the probe to be documented as correctly positioned.

The above test must be performed every time the probe is replaced or moved. The documentation showing correct positioning of the inlet probe must be included in the test report.

## APPENDIX E

### CALIBRATION AND QUALITY CONTROL PROCEDURES FOR ANALYSIS

#### 1 INTRODUCTION

Each laboratory that uses this procedure is required to operate a formal quality control program. The minimum quality control requirements of this program consists of an initial demonstration of laboratory capability and an ongoing program of routine calibration and analysis of performance check samples to evaluate and document data quality. Two options are provided for routine calibration; calculation by linear regression or average response factor. The laboratory must maintain records of all performance checks to document the quality of generated data.

#### 2 APPARATUS

- 2.1 Flowmeter, 100 sccm.
- 2.2 Tedlar bags, 10 L.

#### 3 REAGENTS

- 3.1 Calibration standards can be obtained commercially in specially treated compressed gas cylinders. Concentrations of the minor components in each mixture must be traceable to the National Institute of Standards & Technology (NIST) or to a national measurement system approved by the Executive Officer of the Air Resources Board. NIST traceability may be accomplished by the specialty gas vendor via several methods:
  - (1) By analyzing the gas mixture directly against a NIST Standard Reference Material (SRM). This alternative can be utilized when an SRM with the proper component is available and the concentration is within a factor of two (2) from the gas mixture concentration.
  - (2) If SRMs are not available, analyzing the gas mixture against well characterized Gas Manufacturer Primary Standards (GMPS). These GMPS mixtures are analyzed against internal laboratory standards, gravimetric or volumetric, traceable to NIST.

#### 4 INITIAL PERFORMANCE DEMONSTRATION

The following steps must be followed before the analytical method may be used. The performance evaluation must be repeated at least every six months. NOTE: Two options are provided for daily calibration (see Section 5). If response factor method (5.2) is used, both

Option 1 and 2 (4.1.2 and 4.1.4) must be conducted during initial performance evaluation. Peak area integration, and not peak heights, must be used for the determination of instrument response.

#### 4.1 Multipoint Calibration

4.1.1 Standards are analyzed at least three times at four different concentrations. The concentration levels should be five times the limit of detection on the low end, approximately midway in the linear response range of the method, and near the high concentration end of the linear response limit. Results of the multipoint analyses must be documented and shall include data on intercept, slope, correlation of fit, relative standard deviations, range of concentrations tested, response factor and limit of detection calculations.

4.1.2 Option 1, Least Squares Fit. The least squares analysis of the data should produce a correlation coefficient of at least 0.99. Blank values shall not be subtracted from the raw data and the origin (0.0, 0.0) will not be used in the calculations. If the intercept deviates significantly from zero, the analysis must be reviewed for possible system contamination or other problems.

4.1.3 Standard deviation of the GC responses (area counts) are calculated at each level of the multipoint and must be included in the analytical report.

4.1.4 Option 2, Response Factor. For each calibration target compound, calculate the pooled mean response factor (RF) from the set of four multipoint levels. Calculate the standard deviation and the percent relative standard deviation. The laboratory must demonstrate that RF values over the working range for the target compounds are constant. The percent relative standard deviations of the mean RF's must not exceed 15%. The equation for calculating the pooled mean response factor is listed below.

$$Rf_{\text{pooled}} = (RF_{1a} + RF_{1b} + RF_{1c} + RF_{2a} + \dots + RF_{4b} + RF_{4c}) / 12$$

where 1a through 4c represent the individual response factors calculated from the 12 multipoint runs.

4.1.5 Analytical Limits of Detection (LOD) must be calculated. The LOD for each method must be calculated by the following equation:

$$\text{LOD} = |A| + 3S$$

where:

A is the least squares x-intercept, in units of ppmV, calculated from the multipoint data (section 4.1.1).



S is the standard deviation of replicate determinations of the lowest standard, in units of ppmV, calculated from the multipoint data by the following equation:

$$S = (Y - b) / m$$

where:

Y = the standard deviation of the GC response, in area counts, of replicate determinations of the lowest standard.

b = the least squares Y intercept

m = the least squares slope

At least 3 replicates are required. The lowest standard must be run at 1 to 5 times the estimated detection limit. If data is not available in the concentration range near the detection limit, S may be estimated by:

$$S = \text{RSD} \times A$$

where RSD is the relative deviation of the lowest standard analyzed.

4.1.6 The Limit of Quantitation (LOQ) must be calculated by the following equation:

$$\text{LOQ} = 3.3 \times \text{LOD}$$

No analysis results will be reported below the LOQ.

## 5 ROUTINE CALIBRATION PROCEDURE

Routine users of the method will use one of the following options for calibrations and result calculations. Compound concentrations used in the calibration curves must bracket levels found in stationary source emission samples. Peak area integration, and not peak height, must be used for determination of instrument response.

### 5.1 Option 1, Least Squares Fit

A least squares fit, i.e. as determined with the initial multipoint calibration, must be used for sample quantitative calculations. A calibration check must be performed every ten hours, or every ten sample analyses, whichever is more frequent. Use the midpoint calibration as a check. The GC response must be within 10% of the mean values established in the multipoint calibration or a new calibration curve must be prepared. The GC responses are recorded and inspected to check for trends which indicate the degradation of standards or instrument performance.

## 5.2 Option 2, Response Factor

The average response factors, i.e. as determined with the multipoint calibration, must be used for sample quantitative calculations. A calibration check must be performed every ten hours, or every ten sample analyses, whichever is more frequent. Use the midpoint calibration (see section 4.1) as a check. The measured RFs must be within 10% of the mean values established in the multipoint calibration or a new calibration curve must be prepared. The response factors are recorded and inspected to check for trends which indicate the degradation of standards or instrument performance.

For non-routine users of the method, ie. 1 test per month or less, calibration involves generation of at least a 3 point curve during each analysis day and a midpoint calibration check after every 10 samples. Either linear regression or mean response factor calculations can be used. The initial performance evaluation is still required.

## 6 ROUTINE QUALITY CONTROL

### 6.1 Laboratory Blanks

A laboratory method blank is a volume of ultra high purity gas carried through the entire analytical scheme. The gas used for blank runs should be certified by the gas supplier or laboratory to contain less than the analytical limit of detection (LOD) of the analytes of interest. The laboratory blank volume must be equal to the sample volumes being processed. Laboratory blanks are analyzed each shift before the analysis of samples may proceed. A blank is also analyzed after the analysis of a sample containing components with concentrations greater than the most concentrated standard used. The laboratory blank results will be reported along with raw sample data in final reports. Sample results should not be corrected for blank contribution. Note that a field blank analysis may be used in place of the laboratory blank. However, if the results of the field blank are greater than LOQ, a laboratory blank will be run to isolate the source of contamination.

### 6.2 Laboratory Replicate Samples

Replicates serve to measure the precision of an analysis. Ten percent of all samples, or at least one sample per batch, will be analyzed in duplicate to indicate reproducibility of the analysis and to monitor such conditions as instrument drift. The precision  $(|Ave. - X_i|/Ave.) \times 100$  of duplicate analyses must fall within predetermined limits, i.e.,  $3 \times RSD$  as established during the initial performance evaluation.

### 6.3 Calibration Check Sample

The midpoint standard used in multipoint calibrations must be analyzed every eight hours, or every ten samples, whichever is more frequent, to check instrument performance. The GC response of all analytes must be within 10 % of the mean values established in the

multipoint calibration or a new calibration curve must be generated. The GC responses are recorded and inspected to check for trends which indicate the degradation of standards or instrument performance.

#### 6.4 Performance Evaluation Samples

To demonstrate data quality, performance evaluation samples may be analyzed periodically. At the discretion of the Executive Officer, periodic analysis of performance evaluation samples may be required. If analysis of performance evaluation samples is required by the Executive Officer, the analyses shall be conducted in the following manner. The performance evaluation material shall be used to evaluate both sampling and analytical systems. Performance evaluation samples shall be analyzed at a frequency dependent on how often the method is used. If the method is used on a daily basis, the performance evaluation sample must be analyzed twice a month. If the method is used less frequently, the performance evaluation sample must be analyzed once a month or whenever the method is used (whichever is less). A value of  $\pm 10\%$  of the stated concentration of the performance evaluation sample must be recovered for the analyte of interest. The results of these analyses must also be recorded and placed on permanent file for at least three years and shall be made available to the Executive Officer upon request. All performance evaluation samples will be labeled with an expiration date and may be re-certified by the vendor if they contain sufficient volume (i.e. greater than 60% residual).

#### 6.5 Qualitative Analysis Criteria

The retention time of the target compound must be within 0.06 RRT units of the standard RRT.

#### 6.6 Quantitation Criteria

The column resolution criteria of 20% valley (as measured from the baseline to valley minimum) between a target compound and an interfering compound must be achieved before any quantitation can be allowed. When a compound interferes with the target compound and the degree of the interferences exceeds the column resolution criteria the compound can still be quantified if the following criteria is met. Set the reporting limit for the lowest amount that can be quantified high enough such that the interfering compound accounts for less than 10% of the area of the target compound.

### **7 ANALYTICAL REPORTING REQUIREMENTS**

Each report of analyses shall be in the following format and will include the following information. Refer to Appendix F for result calculations format.

#### 7.1 Complete identification of the samples analyzed (sample numbers and source). Pertinent

information should be submitted to the analytical laboratory via a chain of custody record.

- 7.2 Date of submittal of the sample, date and time of GC analysis. The latter should appear on each chromatogram included with the report.
- 7.3 The raw and calculated data which are reported for the actual samples will also be reported for the duplicate analyses, laboratory and field blank analyses, the field spike sample analyses, and any other QA or performance evaluation samples analyzed in conjunction with the actual sample set(s).
- 7.4 The calibration data, including average response factors calculated from the calibration procedure described in Section 5. Include the relative standard deviation, and data showing that the midpoint response factors have been verified at least once during each 10-hour period of operation or with each separate set of samples analyzed.
- 7.5 All relevant data used to define the reporting limit will be reported. This will include parameters such as sampling volumes, sample injection volume, chromatographic interferences, and Tedlar bag contamination levels. In no case will results be reported below the established reporting limit. Test reports should include a table summarizing reporting limits (per sample) including a description of causes of variation.

## **8 DIRECT SAMPLING CALIBRATION AND QUALITY CONTROL PROCEDURES**

Due to the nature of direct sampling, routine calibration procedures are somewhat different. The sequence of in-field calibration, quality control, and sample runs listed below is recommended when performing on-site analyses.

1. Run a 3 point calibration (triplicate runs at three levels) bracketing the expected sample concentration before each compliance test. The calibration curve prepared from the averages shall be used for quantitation of the cycle samples as well as determination of the limit of quantitation.
2. Run a field blank, through the entire sampling train, using zero air (ambient air normally can be used for this purpose for ethylene oxide sampling).
3. Run a field spike, through the entire sampling train, using the calibration standard closest to the sample concentrations. The spike gas introduced at the transfer line inlet should be at ambient pressure.
4. Analyze the field samples.
5. Run standard checks after sample analyses are complete for each cycle test. Standard check results must be within 10% of the pretest average values.

## APPENDIX F

### CALCULATIONS

For all of the monitoring options listed below the procedures and calculations will be repeated three times. The arithmetic average percent efficiency of the three runs shall determine the overall efficiency of the control device.

For Tedlar Bag Sampling: Calculate the mass of EtO emitted from the control unit during each bag sampling period by using the following equation. Throughout the calculations, sufficient significant figures will be carried to round off to the required destruction efficiency. For example, if the rule requires 99.9% destruction efficiency, the calculations will be carried to 4 significant figures with the result rounded to 3 significant figures.

$$W_b = C \times V \times 44.05 \text{ lb/mol} \times \text{mol}/385.32 \text{ scf} \times 1/10^6$$

where:

- $W_b$  = the mass of EtO emitted corresponding to each bag
- $C$  = concentration of EtO in ppm
- $V$  = volume of gas exiting the control device corresponding to each bag sample,  $\text{ft}^3$ . The volume is determined by integration of the area under the curve of volumetric flow rate (corrected) versus time for the period each bag was sampled.

Add the mass corresponding to each bag,  $W_b$ , (i.e., mass emitted during the 1st evacuation plus the mass emitted during washes) used during the evacuation for the total mass ( $W_o$ ).

$$W_o = (\text{Sum})W_b$$

Determine sterilizer control device efficiency (% Eff.) using the following equation:

$$\% \text{ Eff.} = (W_i - W_o) / W_i \times 100$$

where:

- $W_i$  = the total mass of EtO delivered to the control unit; this value can either be estimated using the procedures in Appendix B or measured using the procedures in Appendix A along with the calculations listed above (for  $W_b$ ). Note that where appropriate, as described in Appendix A, the mass values in the control efficiency equation may be replaced with the corresponding EtO concentration averages.

For Direct GC Sampling: If the direct GC approach is used, instead of Tedlar bag sampling, plot a concentration versus time curve. Calculate the mass flow at each sampling interval ( $\leq 2$  minutes for catalytic oxidation units,  $\leq 1$  minute for hydrolytic scrubbers) by selecting the concentration, C, and volumetric flow rate,  $F_v$ , at each interval. (Concentration and flow measurements must be synchronized.) Use the following equation to determine the mass flow rate  $W_t$  of EtO exiting the control device.

$$W_t = C \times F_v \times 44.05 \text{ lb/mol} \times \text{mol}/385.32 \text{ scf} \times 1/10^6$$

where:

C	=	EtO conc (ppm)
$F_v$	=	flow (scfm)
44.05	=	molecular weight of EtO lb/lb-mole (g/g-mole)
385.32	=	359 scf/mole ideal gas law constant corrected to 68° F and 1 atm. (24.04 l/mole at 68° F).

Plot a curve of mass flow rate versus time and integrate for total mass of EtO for the control device outlet ( $W_o$ ) (or inlet  $W_i$ ). Use the equation listed above for sterilizer control device efficiency calculation.

## APPENDIX G

### REPORTING REQUIREMENTS

The following outline of reporting requirements is meant to be used as a general guide for EtO source test report reviewing purposes.

Sterilizer: manufacturer and model number, volume of the chamber, the type of sterilant gas used, the type of materials sterilized, a cycle process diagram, e.g., a plot of chamber pressure vs. time including footnotes regarding start and stop points of cycle stages and including a detailed explanation of the evacuation flow discharge path (water and vapor) during all stages of the cycle. If pressure/volume calculations are used to determine the weight of EtO charged to the chamber then chamber pressure sensor calibration data shall be included in the report.

Control Unit: type of chamber evacuation pumps used, type of control unit, manufacturer and model number, the size or capacity of the control unit, the operating temperature, a diagram of the control unit and sampling locations. If monitoring is conducted at the inlet of a catalytic oxidation unit then the test report shall include documentation of the correct positioning of the inlet sampling probe.

Test Data: plots of volumetric flow rate versus time (the reviewer should determine whether integrated sampling is appropriate), results of moisture determinations, a plot of the multipoint calibrations used for quantitative calculations, calculations for limit of detection and reporting limits, tables of raw data, final results, and all chromatograms (refer to Appendix E, section 7 of this document for more detailed "Analytical Reporting Requirements"). If the direct GC approach is used then plots of EtO concentration vs. time should be included in the report along with the integrated total mass emission result.

Quality Control: the test report shall include complete identification of the samples analyzed (sample numbers and source), date of submittal of the sample, date and time of GC analysis. The raw and calculated data which are reported for the actual samples will also be reported for the duplicate analyses, laboratory and field blank analyses, the field spike sample analyses, and any other QA or performance evaluation samples analyzed in conjunction with the actual sample set(s).

## APPENDIX H

### METHOD LIMITATIONS

Alternative sampling and analytical methodologies that are demonstrated to be substantially equivalent may be used if approved by the Executive Officer. The term Executive Officer as used in this document shall mean the Executive Officer of the Air Resources Board or his or her authorized representative. The Executive Officer may require the submission of test data or other information showing that the alternate method is equivalent to Method 431. Any modifications to the sampling and analytical procedures described must also be approved in writing by the Executive Officer.

#### Tedlar Bag Sampling

Tedlar bag samples must be analyzed within 8 hours of end of the sampling period.

Tedlar bags with fittings other than those listed may not be suitable for EtO sampling. The appropriate recovery and stability tests should be conducted before using other fitting types (especially for bags with stainless steel fittings).

CARB staff have not conducted bag stability studies for EtO in dilute-acid hydrolytic scrubber emissions.

The integrated Tedlar bag sampling procedure is not applicable for testing of sources where both the emission gas volumetric flow rate and target compound concentration are variable. The test engineer and/or the reviewing agency will determine whether integrated sampling is appropriate.

Ethylene oxide may decay if exposed to sunlight. Thus, Tedlar bag samples and standards should be protected from sunlight exposure.

#### On-Site GC

At many hospitals, the control unit is not accessible from parking areas (i.e., with 150 foot heated lines to a parked GC-van). Thus, the GC, gas cylinders and associated support equipment must be physically moved to a location near the control unit, which may prove inconvenient. Also, adequate power may be difficult to get at some facilities. In addition to the equipment required, performance of on-site GC requires that an experienced chemist be involved in the field operations.

#### Inlet Estimation

The inlet estimation procedure assumes that there is no loss of EtO to the chamber, chamber contents, transfer plumbing or pumps and that there are no leaks before the control unit.



Use of the inlet estimation technique assumes that the composition of the sterilant gas is accurately defined and consistent in individual cylinders/cartridges. Thus, at the discretion of the District, a sample from the gas cylinder(s) used during the test may be analyzed to verify the exact sterilant gas composition for the inlet estimation.

Accurate estimates rely on accurate volume measurements and calibrated pressure gauges. Thus, manufacturer's chamber volume specifications should always be double checked and system pressure monitoring devices should be evaluated for accuracy.

Some sterilization systems add sterilant gas as needed to the chamber during the exposure stage because the chamber pressure may decrease slightly after initial pressurization. This addition of make-up gas would, if significant, invalidate the inlet estimation calculation since with existing systems it would be quite difficult to estimate the amount of make-up gas added. To minimize this source of error, when using the inlet estimation technique, the test should be conducted with an empty chamber and the exposure stage should be aborted after no more than 10 minutes.

Since the estimation technique can only be used for empty chamber tests, an exposed chamber load will not be available if subsequent aeration tests are to be performed. There must be an exposed load in the aerator for a valid test. Thus, an additional sterilization cycle with unaborted exposure stage would have to be run to provide the materials to be aerated. Furthermore, the inlet EtO concentrations must be physically measured with Tedlar bags or direct GC for aeration tests since estimation is not possible. Thus, where aeration tests must be conducted in addition to sterilizer tests, inlet estimation may not provide any time or cost benefit.

### Acid Scrubber

The stability of ethylene oxide in hydrolytic scrubber unit emission matrix, in Tedlar bags, has not yet been demonstrated (by ARB staff). Stability studies for ethylene oxide in this matrix should be conducted and results included in the test report.

This method allows the option to measure inlet concentrations (e.g., with bag sampling or by direct GC) instead of using the estimation technique outlined in Appendix B. However, the concentration of EtO at the inlet of hydrolytic scrubber units will be approximately 27% and 100% by volume for systems using 12/88 and 100% EtO sterilant gases, respectively. Due to the safety concerns associated with the high inlet EtO concentrations, it is recommended to use the calculation procedure in Appendix B. Anyone conducting tests at the inlet of a hydrolytic scrubber should use extreme caution to avoid exposure to personnel and explosions.

The direct interface option may only be used to test hydrolytic scrubber units (inlet or outlet) if sample frequencies are 1 minute or less.

Quantitation of the diluent gas may be necessary at facilities using a sterilant mixture in order to calculate corrected volumetric flow rate.

## Catalytic Oxidation

If the control unit inlet total mass is measured rather than estimated, testers must have documented evidence that the inlet probe is placed such that the sampled gases are completely mixed, i.e., chamber exhaust and make-up air (refer to Appendix D). This documentation shall be reported along with the test final results.

When testing 3M sterilizer systems, or other systems with pulsed chamber exhaust, if the inlet mass is measured using the direct-GC approach, testers must use a one liter Greenburg-Smith impinger (empty) in the GC sampling train. The insertion of this impinger into the sample train will function as a mixing chamber for the sampled sterilizer exhaust gas prior to introduction into the GC analyzer.

The direct interface option shall only be used to test catalytic oxidation units (inlet or outlet) if sample frequencies are 2 minutes or less.

Many sterilization systems use water ring seal pumps to evacuate the chamber. Some EtO will be retained in the water as the sterilant gas passes through the pump. Depending on system design, water ring seal pumps can cause a shift in EtO emission from the initial chamber purge to the air washes and even into the aeration cycle. Because of this emission shift, the inlet estimation technique may only be used with systems using water ring seal pumps if the “correction” outlined in Appendix B is applied.

Testers have speculated that EtO concentrations may, in some cases, be stratified in the exhaust duct flow from catalytic oxidation control units. Further investigation is necessary to define this problem. However, if stratification does occur, some sort of sample averaging probe would be required to obtain valid test results.

## APPENDIX I

# STANDARD OPERATING PROCEDURE FOR THE SAMPLING OF ETHYLENE OXIDE EMISSIONS FROM STATIONARY SOURCES INTO TEDLAR BAGS

## INTRODUCTION

This method should not be attempted by persons unfamiliar with source sampling, as there are many details that are beyond the scope of this presentation. Care must be exercised to prevent exposure of sampling personnel to hazardous emissions.

### 1 APPLICABILITY

This sampling method uses a Tedlar bag to collect ethylene oxide (EtO) samples from applicable source emissions.

### 2 LIMITATIONS

2.1 Refer to Appendix H.

### 3 EQUIVALENCY

Alternative sampling methodologies that are demonstrated to be substantially equivalent may be used if approved by the Executive Officer or his or her authorized representative. The Executive Officer may require the submission of test data or other information showing the alternate method is equivalent to Method 431.

### 4 APPARATUS

Apparatus required for sampling is described below. It is recommended that all equipment which comes in contact with sampled gas be made of Teflon or Tedlar unless these materials are found unsatisfactory and other materials demonstrated suitable in specific situations.

- 4.1 Sample line. Teflon tubing, 6.4 mm (1/4 inch) outside diameter, of minimum length sufficient to connect the probe to bag and not longer than 10 feet. If the sample line must be longer than 10 feet, then the sample line shall be heated and insulated and capable of operation at above 100 °C (212° F).
- 4.2 Teflon valves or fittings shall be used to connect sample train components. Mininert Teflon valves are recommended.
- 4.3 Sample bags. Bags shall be made of Tedlar film, at least 0.002 in. thick.
  - 4.3.1 Mininert Teflon valves are recommended.

- 4.3.2 Refer to Section 7 for this Appendix for apparatus used in Tedlar bag manufacture, cleaning, and contamination testing.
- 4.4 Rigid container(s) for filling sample bags by application of vacuum.
  - 4.4.1 The container shall be airtight when sealed.
  - 4.4.2 The container shall be opaque except that a small window to check the condition of the bag within is permissible.
  - 4.4.3 The container shall be fitted with couplings to mate with sample bags, sample line and vacuum line and a flow control valve capable of shutting off flow to the bag.
  - 4.4.4 Sample bags may be fabricated with rigid containers as an integral unit.
  - 4.4.5 An appropriate vacuum relief valve is suggested to protect bags and rigid container.
- 4.5 Pump, leak free, with capacity of at least 2 liters per minute.
- 4.6 Flow meter, rotameter type or equivalent, with measurement range of 0.05 to 1.0 liters per minute for observing sampling rate.
- 4.7 Shipping containers to protect bags in transport shall be opaque to protect bags from ultraviolet light. Containers shall have no staples, sharp edges or metal closures which might damage bags. The rigid container for filling bags may be used for bag transport; any window in the container shall be covered with opaque material during such transport.
- 4.8 Expendable Materials
  - 4.8.1 Standard gas mixture for field spikes. Appropriate cylinder gases containing the pollutant(s) of interest in known concentration.
  - 4.8.2 99.999% N<sub>2</sub> or zero air

## **5 PROCEDURE**

The following describes the procedure for collecting samples from stacks. A field blank and a field spike must be obtained for each source test (Refer to section 6 for discussion).

- 5.1 (Optional) Determine stack moisture content by ARB Method 4; if moisture content is above the 60° F saturation level, then dilution of the sample bag may be required. If moisture content of stack gas is not determined, then Tedlar bag shall be monitored for condensation during sampling (see Section 5.7).

- 5.1.1 Procedure for Sample Bag Dilution. Bags should be pre-filled with 99.999% nitrogen or zero air to approximately one-third the final sample volume. The exact volume of dilution gas must be recorded to allow for correction of data. If condensation still occurs, increase dilution as necessary.
- 5.2 Assemble the sampling train at the sampling site as shown in Figure 1.
- 5.3 Leak check the sample train. To start the leak check, connect the sample line to the bag, making sure the valve on the bag is closed. Place the bag in the rigid container and close as if for sampling. Turn on the vacuum pump until a reading of 15 inches H<sub>2</sub>O is maintained. Make sure that the probe line is **not** plugged and that the ON/OFF valve is open. If a leak greater than 5% of the sampling flow rate is found, then the problem must be located and fixed before the leak check continues. Turn the pump off, break the vacuum on the rigid container and open the mininert valve on the Tedlar bag. Place the bag back in the container and close as if for sampling. Plug (leak tight) the end of the probe. Turn on the vacuum pump and adjust until a reading of 15 inches H<sub>2</sub>O is maintained. If a leak greater than 5% of the sampling flow rate is found, then the problem must be located and fixed before sampling continues.
- 5.4 Break the vacuum on the rigid container. Unplug the end of the probe and place the end of the probe in the stack away from the walls. Care should be taken to avoid dilution of the stack gas sample with ambient air by sealing the open port area around the probe, especially in stacks with negative static pressure.
- 5.5 Make sure the sampling train is configured correctly, the valve on the sample bag is open and the ON/OFF valve is closed. Turn the vacuum pump on and adjust until a reading of 15 inches H<sub>2</sub>O is maintained. Begin sampling by opening the ON/OFF valve. Record the sample start time on the field data sheet.
- 5.6 Monitor the container vacuum and sample flow rate and adjust as necessary. After sampling for the planned interval, close the ON/OFF valve noting the time on the field data sheet. Bags should be filled no more than half full. If condensation occurs, discard sample and resample as per 5.1.1.
- 5.7 After sample purge is complete, close the ON/OFF valve, turn the pump off, break the vacuum on the rigid container and close the mininert valve on the bag.
- 5.8 Attach a label to each Tedlar bag sample (and impinger if used) containing the following information:

Job #  
Date  
Time  
Sample/Run #  
Plant Name

Sample Location  
Log #  
Initials of Sampler Operator

- 5.9 Promptly place the sealed bag in a shipping container; close the container to prevent possible degradation of the sample by ultraviolet light. Several bags may be placed in the same shipping container.
- 5.10 Fill out the Chain of Custody-Sample Record, Log Book Data sheets, and Field Data sheets. Copies of these forms are attached as Figures 2, 3 and 4.
- 5.11 Sample Bag Transport Procedure
- 5.11.1 Transport sample bags in opaque shipping containers.
- 5.11.2 Airborne transport could potentially result in rupturing of bags containing toxic samples. Surface shipment is advised. If airborne transport is unavoidable then bags should not be filled more than half way to avoid bag rupture.
- 5.11.3 Deliver bags to laboratory for analysis promptly. The maximum hold time is 8 hours.

## 6 QUALITY CONTROL

### 6.1 Sampling Runs, Time and Volume

- 6.1.1 Sampling runs. The number of sampling runs must be sufficient to provide minimal statistical data and in no case shall be less than three (3) runs per source test.
- 6.1.2 Sample time. Integrated bag sampling. The sampling must be of sufficient duration to provide coverage of the average operating condition of the source as specified by the ATCM or as directed by the District.

### 6.2 Routine Sampling Quality Control. This section outlines the minimum quality control operations necessary to assure accuracy of data generated from samples collected in Tedlar bags. These QC operations are as follows:

- \* Field blank samples
- \* Field spike samples
- \* Collocated samples (optional)
- \* Tedlar bag contamination checks

- 6.2.1 Field blank samples. At least one field blank sample will be taken per source test. At the discretion of the tester, more blank samples may be taken. Air or nitrogen from a compressed gas cylinder (ambient air may also be used) is collected in the bag in the manner described in section 5 of this method. This blank sample is transported and

- analyzed along with the stack gas samples. If field blank values are greater than 20 % of the stack gas values, then the data will be flagged. Field blank values will be reported along with the stack gas results.
- 6.2.2 Field spike samples. At least one field spike sample will be taken per source test. At the discretion of the field engineer, more spike samples may be taken. Pure air or nitrogen containing known concentration(s) of EtO is drawn from one bag to another through the sampling apparatus. The spiked sample is transported and analyzed along with the stack gas samples. Spike sample recoveries will be reported along with the source test results.
- 6.2.3 Collocated samples. Collocated sampling will be performed at the discretion of the tester. Samples are collected through two identical sampling systems simultaneously from the same stack sampling port. The analysis results of collocated samples are used to estimate method precision.
- 6.2.4 Tedlar bag contamination checks. Tedlar bags will be tested for contamination as outlined in Section 10 of this Appendix.

FIGURE 1  
TEDLAR BAG SAMPLING TRAIN

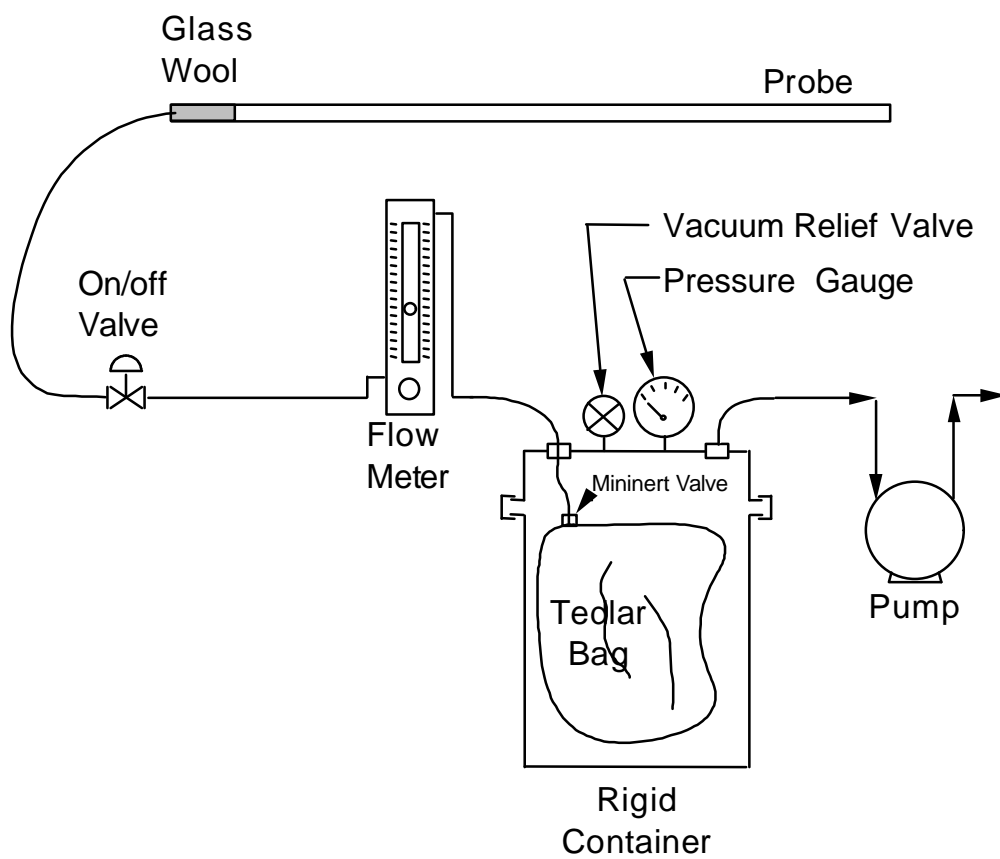




FIGURE 2

CHAIN OF CUSTODY

SAMPLE RECORD

Job \_\_\_\_\_ Date: \_\_\_\_\_ Time: \_\_\_\_\_

Sample/Run# \_\_\_\_\_

Sample Location \_\_\_\_\_

Type of Sample \_\_\_\_\_

Log # \_\_\_\_\_ Fitting # \_\_\_\_\_ Initials \_\_\_\_\_

Action Taken	Start Date	Time	Given By	Taken By

Related I.D. #s	Description

FIGURE 3

CHAIN OF CUSTODY  
LOG BOOK

PROJECT NO. \_\_\_\_\_

Log No.	Sample I.D.	Date	Time	Comment	Valve I.D. Bag Sample	Given By	Taken By

FIGURE 4  
FIELD DATA SHEET

Project Name \_\_\_\_\_

Date \_\_\_\_\_ Sample ID: \_\_\_\_\_

LOG ID: \_\_\_\_\_

Sample Type: \_\_\_\_\_

**BAG QUALITY ASSURANCE**

Bag ID No. \_\_\_\_\_ Initial Bag Leak Check \_\_\_\_\_

Bag Check Analysis (List Results of Bag check Analysis)

**FLOWMETERS**

Flowmeter ID \_\_\_\_\_

Date of Flow Meter Calibration Check \_\_\_\_\_

Sampler ID \_\_\_\_\_ Sampler Leak check \_\_\_\_\_

**SAMPLE TIME**

Time	Total time

Flowrate	Average Flow

COMMENTS \_\_\_\_\_

## 7 PRODUCTION OF TEDLAR BAGS

New bags are recommended for each sample. Previously-used bags may be used again if cleaned and checked for leaks and contamination as specified below. Tedlar bags may also be purchased already assembled, but must be certified to specified contamination levels before use.

### 7.1 Materials and Equipment

7.1.1 Tedlar, 0.002 inch thickness.

7.1.2 Fittings for connection to sample line. Mininert Teflon valves are recommended. Quick-disconnect Swagelock fittings are commonly used, but are suspected of possible interferences at low ppb concentrations. Fittings should be composed of inert materials, teflon and stainless steel are recommended.

7.1.3 Septum fitting for injection of surrogates or removal of sample by syringe.

7.1.4 Cork borers for installation of fittings.

7.1.5 Lay-out Table to measure and cut Tedlar to size.

7.1.6 Heat-Seal Apparatus for making seams in Tedlar. Vertrod Thermal Impulse Heat Sealing Machinery or similar device. May require compressed air cylinder.

7.1.7 Pump for evacuation of bags during purging operations, together with fittings or manifold system to connect pump to bags.

7.1.8 Ultrasonic bath for cleaning fittings.

7.1.9 Oven for drying fittings

7.1.10 99.999% Nitrogen for purging bags.

7.1.11 Distilled water.

### 7.2 Clean Fittings

Use of organic solvents is not recommended due to possible contamination of bags.

7.2.1 Clean fittings by placing them in soapy water in ultrasonic bath for about one hour. Rinse fittings thoroughly with clean water, followed by a rinse with distilled water.

7.2.2 Bake fittings in a 100 °F oven for at least 8 hours.

### 7.3 Manufacture of Tedlar Bag

Tedlar bags should be constructed in a clean area, with care taken to avoid contamination such as exposure to chemical fumes, solvent vapors or motor exhaust.

7.3.1 Cut one piece of Tedlar film from roll on lay-out table using a razor blade. A sheet of Tedlar measuring about 54" by 30" will make about a 30 Liter capacity bag (15 L at half-full).

7.3.2 Fold the Tedlar sheet in half and make two seams using heat-seal apparatus. Seams should be at least ½ inch from edge.

7.3.3 Place piece of cardboard inside bag. Use cork borer to make appropriate size hole for fittings, using cardboard to protect other side of bag. Tedlar film should fit snugly around base of fitting.

7.3.4 Attach previously cleaned sample line fitting. Use Teflon washers on inside and outside of bag to secure fitting.

7.3.5 Attach septum fitting if necessary. (Mininert valves have septum and sample line connections all on one fitting).

7.3.6 Seal remaining seam using heat-seal apparatus.

## 8 LEAK TEST

Check all sample bags for leaks by inflating with 99.999% nitrogen to a pressure of 2 to 4 inches of water. Good bags should hold constant pressure as indicated by a manometer for 10 minutes or (alternative test) should remain taut and inflated overnight. A small weight (e.g. Kimwipe box) may be placed on top of bag for the overnight leak check. Report bag acceptability on field data sheet (figure 4); destroy or repair and retest defective bags.

## 9 BAG CLEANING

Purge the bag with 99.999% nitrogen repeatedly until acceptable contamination values are attained. ARB staff experience has shown that 3 to 8 purges are needed to meet the target contamination levels of <1 ppb for most VOCs of interest.

## **10 BAG CONTAMINATION CHECK**

- 10.1 Check bags for contamination by filling them halfway (so that check volume approximates actual sample volume) with 99.999% nitrogen, allow to equilibrate for 24 hours, then analyze for EtO.
- 10.2 Acceptable contamination levels may vary depending on the expected sample concentration. However, bags which contain contaminants at levels greater than the LOD will be rejected.
- 10.3 Label bags and record contamination levels. Also record contamination levels on field data sheets.

## APPENDIX J

### DEFINITIONS AND ABBREVIATIONS

#### Response Factor

The response of the gas chromatograph detector to a known amount of standard.

#### Performance Evaluation Sample

A sample prepared by EPA, ARB or other laboratories containing known concentrations of method analytes that has been analyzed by multiple laboratories to determine statistically the accuracy and precision that can be expected when a method is performed by a competent analyst. Analyte concentrations are usually known to the analyst.

#### Calibration Check Sample

A standard, normally the midpoint of multipoint calibrations (see section 422.199.4.1), which is analyzed each shift (or cycle) to monitor detector drift. The values of all analytes must be within 10% of the mean values established in the multipoint calibration or a new calibration curve must be prepared.

#### Analytical Limit of Detection (LOD)

The lowest level at which detector response can be distinguished from noise. Refer to Appendix E for more detail.

#### Analytical Limit of Quantitation (LOQ)

The lowest level at which a compound can be accurately quantified. This value is 3.3 times the Limit of Detection.

#### Reporting Limit (RL)

The reporting limit (RL) is the lowest level that can be reliably quantitated within specified limits of precision and accuracy during routine analyses of source samples. Reporting limits will be based on parameters such as sampling volumes, dilutions, sample injection volume and chromatographic interferences.

#### Field Blank

A field blank is taken in the same way as a sample is taken except that pure air or nitrogen is used as a sample. The field blank is used to determine background levels in the sampling system. The

gas used for blank runs should be certified by the gas supplier or laboratory to contain concentrations less than the limit of detection for the analytes of interest.

### Field Spike

A standard gas containing ethylene oxide at known and certified concentration is introduced at the sampling probe inlet and transferred through the entire sampling train to be analyzed exactly as a normal stack emission sample. The standard gas used for the field spike should be the calibration standard closest to the actual sample concentrations. The spike gas introduced at the probe inlet should be at ambient pressure. The use of a Tedlar bag provides a simple procedure for introduction of the spike gas into the sample probe. The spike/standard gas can be transferred from a compressed gas cylinder into the Tedlar bag and the bag then attached (leak-tight) to the probe inlet. Spike gas can then be pulled through the sample train as under normal conditions.

### Laboratory Replicate Samples

Replicates serve to measure the precision of an analysis. Ten percent of all samples are analyzed in duplicate to indicate reproducibility of the analysis and to monitor such conditions as instrument drift.



## APPENDIX K

### TESTING PROCEDURES FOR STERILIZERS WITH JOSLYN RECOVERY TYPE CONTROL UNITS

Identified points of EtO emission from Joslyn system include:

1. Recovery compressor “burps” which are routed to an acid scrubber. These burps are short-duration (e.g., 3 seconds) recovery compressor pressure relief emissions which occur on an irregular basis (infrequent according to manufacturer). Recovery compressor “burps” are routed to an acid scrubber. These burps would only occur while the recovery compressor is in operation during sterilizer exhaust stage (i.e., the recovery compressor is not in operation during the detoxification-B and preconditioning stages). For the purpose of occupational safety, the composition of the emission from these burps should be assumed to be the same as the sterilant mixture and appropriate precautions taken.
2. An oil-sealed pump is used to evacuate the sterilization chamber during the primary exhaust and detox-A stages. The oil is held in an oil/water separator where oil and water intermingle. Moisture from the chamber collects in the separator and is normally discharged from the pump once per cycle at the beginning of the chamber evacuation. Volume of the discharge would normally be approximately 2 liters and normally has EtO concentrations in excess of 5000 mg/liter. The Joslyn system was modified to attempt to abate this waterborne EtO emission. The EtO-contaminated water collected during the exhaust and detox-A stages is transferred to a “heater” for hydrolysis followed by transfer to the heated sterilizer chamber water jacket, which is discharged to the floor drain.
3. A water ring seal pump is used to evacuate the chamber during the preconditioning and the detox-B stages. The pump working fluid (water) is discharged to the floor drain and vapors are discharged to a floor drain vent. The aeration stage (the manufacturer calls this stage “detoxification-B”) discharges of EtO must be controlled/compliance tested at those facilities permitted for use over 600 pounds of EtO per year (as per the statewide ATCM) or as dictated by the District Rule.

The following general test procedures are recommended:

#### Sterilization Exhaust

1. Use the inlet estimation technique, as described in Appendix B, to calculate the mass of EtO delivered to the inlet of the recovery/control system. The sterilizer/control system must have been used on each of the 2 days just preceding the compliance test-day. This practice is to insure that the emissions from the heated chamber water jacket are representative of “in-use” conditions. Documentation of sterilizer/control system use on the preceding 2 days must be included in the report.

2. Capture the total exhaust from the acid scrubber with a small volume Tedlar bag. Do not manually induce a compressor emission. This testing must be conducted in such a manner that no back pressure and/or leaks are produced in the acid scrubber. If the system does not off-gas during testing then the district may ask the facility to provide an engineering estimate (worst plausible case calculations) of mass of EtO emitted from the acid scrubber. This emission estimate could be used in calculating the system control efficiency.
3. Follow the Tedlar bag sampling and analytical quality control procedures described in Appendix I. In particular, follow the Initial Performance Demonstration, Routine Calibration Procedures and Routine Quality Control Procedures.
4. Repeat the above procedures and calculations (Appendix F) three times. The arithmetic average percent efficiency of the three runs shall determine the overall efficiency of the control device.
5. Collect and analyze water samples for the first cycle tested from the outlet of the heated sterilization chamber water jacket. Collect the entire discharge of the heated chamber jacket in separate ½ hour samples for a 2 hour period starting 5 minutes before the end of the exposure stage. The ½ hour samples should be collected in glass container and the total volume included in the report. Follow the procedure specified in Appendix L to immediately collect 2 aliquot water samples from each of the ½ hour samples. Analyze the samples as per Appendix L and report the average EtO concentration for each of the four ½ hour samples. Collect field quality assurance samples as specified by Appendix L.

#### Aeration Exhaust

1. Use the measurement methods described in Appendix A to determine the air concentration of EtO in the drain vent associated with the water ring seal pump used during the aeration (detoxification) stage. Monitor the vent emissions for 1 hour following the start of aeration. Do not abort or shorten the exposure stage. Report the average or integrated concentration of EtO.
2. If required by the District, use the volumetric flow measurement procedure appropriate for the facility's stack diameter, configuration and flow characteristics.
3. Collect and analyze the water discharge associated with the water ring seal pump used during the detoxification (aeration) stage. The pump is on, evacuating the chamber, for 5 minutes every 20 minutes. Collect the entire discharge of the water ring seal pump during the first 5 minute evacuation of the aeration stage. The water sample collection must be coordinated with the 5 minute "pump-on" times. The 5 minute samples should be collected in a glass container and the total volume included in the report. Follow the procedures specified in Appendix L to immediately collect 2 aliquot water samples from each of the 5 minute samples. Analyze the samples as per Appendix L and report the average EtO concentration for the 5 minute samples. Collect field quality assurance samples as specified by Appendix L.
4. Run one cycle (exposure stage may not be aborted early) with a normal load in the aeration chamber.

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**APPENDIX L**


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**PROPERTIES:** gas at room temp

M.W.: 44.05 B.P.: 10.7 °C; V.P.: 146 kPa (20 °C), water sol.: completely miscible  
vapor density: 0.98 (air = 1); explosive range: 3% to 80+% v/v in air

SAMPLING	MEASUREMENT
Section 6010B, Standard Methods for the Examination of Water and Wastewater, APHA, latest edition	<b>TECHNIQUE:</b> Gas Chromatograph, Flame Ionization detector
	<b>ANALYTE:</b> Ethylene Oxide (EtO)
	<b>INJECTION:</b> 2 $\mu$ L
	<b>TEMPERATURE</b> - INJECTION: 250 °C - DETECTOR: 250 °C - COLUMN: 50 °C for 2 minutes, 10 °C/min to 250 °C, hold for 1 minute
	<b>CARRIER GAS:</b> Helium, 30 cc/min
	<b>COLUMNS:</b> 30m DB - WAX megabore, 0.53 mm i.d., 1.0 $\mu$ m film thickness with 2-3 ft. deactivated fused silica guard column
	<b>CALIBRATION:</b> EtO standards in water at 500 or 1000 $\mu$ g/mL
	<b>ANALYTICAL RANGE:</b> approx. 1.0 ppm to 100 ppm, sample dilution will extend the range

**PRINCIPLE:** The mass of ethylene oxide contained in water associated with ethylene oxide control units is determined using the sampling analysis procedures described herein.

**APPLICABILITY:** This method is applicable to the measurement of ethylene oxide in water samples from sterilization chamber water jacket, water discharge associated with water ring seal pumps and other similar locations where possibility of EtO transfer to water exists.

**LIMITATIONS:** A minimum sample volume of 15 mL is required to avoid EtO losses during sample clean-up. No headspace should be present in field samples.

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**INTERFERENCES:** Sample clean-up is required for samples contaminated with process oils.

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**REFERENCED METHODS:**

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**REAGENTS:**

5. EtO and stock standards in solvent
2. Methanol, HPLC grade
3. Distilled water
4. Crushed ice

**EQUIPMENT:**

1. GC/FID with split/splitless injector, detector, integrator and columns
2. Reverse-phase cartridges - Baker Analyzed, Bakerbond, octadecylsilane bonded to silica gel (C-18), 40  $\mu$ M APD160A, P/N 7020-03 with gas syringes adaptor
3. 15 mL test tubes with teflon-lined screw caps
4. Liquid and gas syringes

**\*\* SPECIAL PRECAUTIONS:** Ethylene Oxide is a potential carcinogen. Work should be performed in a well ventilated fume hood. For specific regulatory requirements refer to the California Labor Code, Part 10, Section 9020; Title 8, California Code of Regulations, Section 5220.

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**CALIBRATION AND QUALITY CONTROL:**

Refer to Appendix E for multipoint and daily calibration and quality control procedures.

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**STANDARD PREPARATION:**

1. Aliquot 12 mL of d. water into a 15 mL vial or test tube with a teflon lined screw cap and place it into a container with crushed ice to chill.
2. Prepare a 10 ppm (w/w) standard by adding 120  $\mu\text{L}$  of a 1000  $\mu\text{g}/\text{mL}$  (1  $\mu\text{g}/\mu\text{L}$ ) ethylene oxide standard to the 12 mL of chilled water, cap, and shake vigorously for 1 minute. Return the vial to the ice and allow enough time for solvent in the standard to partition. If the standard solvent is miscible with water then gentle mixing is sufficient. With a disposable-pipet transfer from the bottom of the vial (to minimize the immiscible solvent pick-up) some the standard to an auto-sampler (a/s) vial and store on ice or in a refrigerator until ready to analyze.
3. Prepare a 5 ppm standard by adding 500  $\mu\text{L}$  of water in an autosampler vial, chill, and from the bottom of the vial add 500  $\mu\text{L}$  of the 10 ppm standard. Chill.
4. Prepare a 1 ppm standard by adding 1 mL of water to an a/s vial, remove 100  $\mu\text{L}$ , chill, add 100  $\mu\text{L}$  of the 10 ppm standard.
5. Prepare a blank by adding d.water to an a/s vial.

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**SAMPLE CLEAN - UP**

1. Using the gas syringe and the adaptor, activate the C-18 cartridge by flushing with 3 to 4 mL of methanol. Immediately wash out the methanol with repeated flushing of distilled water to minimize the methanol peak when the sample is analyzed. Ten flushings of 3 to 4 mL are sufficient.
2. Add water to the cartridge but do not immediately flush through the column. The C-18 must be kept wet prior to sample application.
3. Pass the sample through the cartridge into a clean vial. Use at least 15 mL or more than 3 times the cartridge volume. Discard the first 5-8 ml to waste and collect the remainder. Use slight air pressure from the syringe to increase the processing speed.