



Project Summary

Sampling/Analytical Method Evaluation for Ethylene Oxide Emission and Control Unit Efficiency Determinations

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The U.S. Environmental Protection Agency (EPA) is currently considering the development of regulations to control ethylene oxide (EO) emissions from commercial sterilization facilities. Therefore, a reliable sampling and analysis method for measuring EO emissions must be established. The method must be capable of measuring total EO emissions and must be applicable to determining the efficiency of EO control devices.

Measurement of EO emissions from commercial sterilization facilities is not a straightforward process. The EO is emitted from the chamber or control unit intermittently, and the emissions vary in intensity and EO content. This report describes the results of a field evaluation of a semi-continuous direct sampling procedure applicable to commercial sterilization facilities.

The facility chosen for the test used a mixture of 12/88 (w/w) EO/dichlorodifluoromethane (CFC-12) as the sterilizing gas. Ethylene oxide emissions to the atmosphere were controlled using a commercially available aqueous absorption-hydrolysis system.

Samples of the exhausted gas were continually removed from sample ports located before and after the EO control unit. Ethylene oxide and CFC-12 concentrations were analyzed at regular intervals using an on-line gas chromatograph

equipped with dual gas sampling valves, columns, and flame ionization detectors. In addition, the oxygen content of the gas exiting the control device was measured at selected intervals.

The volumetric flow rate from the control device was determined from differential pressure measurements across two restricted orifice plates installed in parallel on the control unit stack.

The method was evaluated for repeatability, precision, and usefulness in determining the efficiency of an aqueous absorption-hydrolysis control system.

This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

A method for sampling and analyzing ethylene oxide (EO) in the vent stream from a sterilization chamber and a dilute acid scrubber was field evaluated and the method's usefulness for measuring control unit efficiency was determined. The U.S. Environmental Protection Agency listed EO as a possible hazardous air pollutant, creating a need for standardized sampling and analytical method to consistently determine control

equipment efficiency. The evaluated procedure used semi-continuous direct sampling with on-line gas chromatographic analysis.

Using measured EO mass flow rates into and out of the scrubber, scrubber efficiencies were calculated. A throughput efficiency was calculated using the EO mass flow rates measured at the inlet and outlet of the control unit and a recovery that was equated to the control unit efficiency was calculated from the weight of EO charged into the chamber and the measured EO emission at the outlet of the control unit.

Facility Description

The field evaluation was conducted at a commercial medical supply sterilization facility that has three 28 cubic meter chambers that use 12/88 sterilant gas. The initial EO charge to the chamber was calculated using the weight of the supply cylinders before and after charging the chamber.

The sterilizer exhaust is controlled by a Chemrox DEOXX™ system, a dilute acid scrubber that hydrolyzes the EO to ethylene glycol. During the tests the scrubber contained a mixture of dilute phosphoric and sulfuric acid.

Each chamber is equipped with a total recirculating pump with a gas/liquid separator that emits the gas to the DEOXX system and recirculates the liquid to the pump inlet. All of the tests were conducted using chambers equipped with oil-sealed pumps.

The sterilization cycle is automatically controlled by a programmable micro-processor system that has the capability to control and record the chamber temperature, chamber pressure, and elapsed time from the start of the cycle. The tested sterilization cycles were scheduled so that only one sterilizer vented at a time.

Before the start of nine of the tests, the chamber was evacuated to 2 pounds per square inch absolute (psia) and then pressurized to 3.1 psia with steam. Next, the chamber was charged to 23.9 psia with 12/88 gas. During each evacuation and air in-bleed cycle, the chamber was evacuated to 2 psia and pressurized with air to 13.9 psia. For one test the chamber was initially evacuated to 7 psia, pressurized to 32.9 psia with 12/88 gas, and cycled between 7 and 13.9 psia during each evacuation and air in-bleed.

Sampling Locations

Samples were acquired before and after the control unit. The scrubber inlet sampling location, used to obtain a

continuous sample of sterilizer chamber exhaust, was midway between the sterilizer outlet and the scrubber inlet. The exhaust was transferred from the chamber outlet to the scrubber inlet via a 6-in. diameter polyvinyl chloride (PVC) duct. Sample was acquired with 3/16-in. Teflon probe. No direct flow measurements were made at this location.

A continuous sample of scrubber exhaust was obtained and volumetric flow measurements were made at the scrubber outlet. Exhaust exited the scrubber vertically through a 6-in. diameter PVC ductwork that exhausted 1.5 m above roof level. To measure volumetric flow, the stack was modified by installing 6-in. diameter PVC ductwork and two butterfly valves to divert the scrubber exhaust through one of the parallel ducts, a 48-mm sampling probe, two orifice plates in parallel, 1.9 m [12.7 duct diameters] downstream of their respective butterfly valves, and 40 cm [2.7 duct diameters] upstream of their respective 90° bends, and wet and dry bulb temperature probes.

Procedures

Sampling Procedures

Samples were taken simultaneously from both sampling locations.

Ethylene Oxide Sampling

Sample was withdrawn into heated, 64-mm I.D., Teflon lines using Teflon-lined diaphragm pumps. A 15-m line was used on the inlet port and a 30-m line was used on the outlet port. Stainless steel, 64-mm tees were used prior to the pumps to remove slipstreams from the main sampling lines. The slipstreams were routed through heated, 6-port, gas sampling valves that were used to introduce the samples onto the GC columns. Prior to the 6-port valves were pumps with Teflon-lined diaphragms and stainless steel, 64-mm I.D., toggle operated shut-off valves. Stainless steel fine metering valves and rotameters were used after the 6-port valves to control the flow rates of the slipstreams. Before exhausting to the atmosphere, the slipstreams and main sample streams were routed through dilute acid scrubbers to remove the EO.

Testing began when the DEOXX scrubber started to exhaust in preparation for the initial chamber evacuation. Each test consisted of seven evacuations, the initial chamber evacuation, and pump down and six air in-bleeds and subsequent evacuations.

Testing stopped at the start of the seventh air in-bleed. The start time and end time of the evacuations were identified by flow or lack of flow across the orifice plates.

The sampling lines were continually flushed with sample throughout the test day. Flow rates through the slipstreams that flushed the gas sampling loops were maintained at 100 ml/min. Samples were isolated in the 6-port valves by closing the shut-off valves simultaneously. When the rotameters indicated no flow, the sample loops were at atmospheric pressure, and the samples were injected into the GC.

After the first sample, samples were acquired at three or four minute intervals until the end of the first evacuation. For the second through the seventh evacuations the first sample was acquired at either one, two or three minutes after the start of the evacuation. Again, samples were acquired at three to four intervals.

Volumetric Flow Rate Measurement

Volumetric flow rate measurements of scrubber exhaust were performed at the scrubber outlet location using two standard, squared-edged orifice plates with standard pipe taps mounted in parallel ducts. The orifice diameters used were 1.763-in. (4.48-cm) and 2.591-in. (6.58-cm). Temperatures were measured using a thermocouple and a pyrometer.

Moisture Determination

The percent moisture of the stack gas was determined by the wet bulb/dry bulb method. Wet and dry bulb temperature measurements were recorded at least once during each exhaust episode.

Molecular Weight Determination

Nitrogen, oxygen, water, EO, and CFC-12 were considered the main components of the sterilizer exhaust gas. The emissions of EO and CFC-12 were continuously monitored by GC/FID. Oxygen emissions were measured with Fyrite oxygen indicator. The nitrogen concentration was determined by difference.

Percent levels of oxygen were usually measured once during each evacuation. For several of the runs oxygen was determined at 1- or 2-min intervals to determine the dead volume of the

scrubber system. Sample was removed from the stack upstream of the orifice plates using an aspirator bulb to pull the sample from the stack.

Analytical Procedures

The analytical method used for the measurement of the EO and CFC-12 was gas chromatography with flame ionization detection (GC/FID). The dual FID Varian 3400 GC was equipped with a Nutech heated valve box containing two 6-port valves. An 0.25 ml loop was used on the inlet sample line and a loop of 2 ml was used on the outlet sample line. The analytical columns were 10 ft (3 m) x 1/8 in. (3 mm) O.D. stainless steel columns containing 5% Fluorcol on 60/80 Carboxpack B. The FID electrometers were connected to Shimadzu CR1-A integrators.

The GC column oven was operated isothermally at 100°C, the injector oven at 175°C, and the detector oven at 200°C. Nitrogen carrier gas flow rates were 30 ml/min on the outlet channel and 60 ml/min on the inlet channel. Detector support gas flow rates of 30 ml/min for hydrogen and 300 ml/min for air were used.

The same FID electrometer range was used for the EO and CFC-12 on the inlet channel but the range used varied from 10⁻⁹ to 10⁻¹¹ depending on the inlet sample concentration. The FID electrometer range was programmed on the outlet channel. A range of 10⁻¹⁰ to 10⁻¹² was used for the EO and 10⁻⁸ to 10⁻¹⁰ was used for the CFC-12. The electrometer range was programmed to switch at 1.1 min during the first evacuations and at 1.55 min during the second through seventh evacuations for optimum quantitation of both EO and CFC-12.

Both channels of the chromatograph were calibrated for EO and CFC-12 at the beginning and end of the day. At least one standard was also analyzed between tests. Standards were purchased from Scott Specialty Gases, Scientific Gas Products, and MG Industries and ranged in EO concentration of less than 1 ppmv to 20% vol and in CFC-12 concentration from 1200 ppmv to 62.5% vol. Calibration curves consisted of a minimum of three standards.

Calculations

The data were reduced using LOTUS® 1-2-3 software. Rounding was

performed at the completion of the calculations.

Ethylene oxide and CFC-12 calibration curves were prepared by taking the logarithm of the peak area and plotting that logarithm versus the logarithm of the concentration. The EO and CFC-12 concentrations were interpolated at 10-sec intervals for the first evacuations. Usually, the concentrations were assumed to increase linearly, plateauing at a maximum determined by an average of the data points after the concentration versus time curve leveled off. In some cases the concentration was assumed to decrease linearly after reaching a maximum and in other cases the concentration was assumed to be constant throughout the evacuation.

For the second evacuations the concentrations were assumed to decrease linearly where enough data were present to validate that assumption. In most cases an average concentration was used. In all cases for the third through seventh evacuations average concentrations were used.

The molecular weight of the vent stream was the sum of the molecular weight of each component multiplied by the mole fraction of that component in the vent stream. For the first evacuations the oxygen was assumed to decrease exponentially from 20% to 0% vol. In several cases for the second evacuations the oxygen was assumed to increase linearly; however, in most cases either the average of all measurements was used or a value of 19% vol was assumed. For the third through seventh evacuations the measured value was used or, if no measurements were taken, a value of 20% vol was assumed.

The EO mass flow rate into the control unit was calculated based on the number of moles of gas exiting the chamber during each 2-min interval. Using the chamber pressure and jacket temperature, the moles of gas leaving the chamber were calculated from the ideal gas law, assuming that the chamber gas did not significantly deviate from ideal behavior at the chamber conditions tested.

The weight of EO entering the control unit during each time interval was given by multiplying the moles of gas leaving the chamber during each time interval by the molecular weight of EO and the mole fraction of EO in the gas. Summation of the weights of EO entering the control unit during each time interval

provided the total weight of EO entering the control unit during the test period.

The EO emission out of the control unit was calculated based on the pounds of gas exiting the control unit during each 10-sec interval. The weight of EO leaving the control unit during each time interval was given by multiplying the time interval by the mass flow rate of EO leaving the scrubber during that time interval. The total weight of EO leaving the control unit during the test was provided by adding the weights of EO leaving the scrubber during each time interval.

The total mass flow rate of gas was calculated from the pressure drop across standard orifices using equations taken from the American Society of Mechanical Engineers Research Committee on Fluid Meters Report "Fluid Meters--Their Theory and Application," 6th ed. 1971. Values for the specific heat ratio were obtained from Perry's Chemical Engineers' Handbook.

A Houston Instrument Digitizer was used to convert the stripchart lines representing continuous pressure readings across the orifice plates into numerical values.

The mass rate of EO flow out of the control unit was then given by:

$$m = 60 \times w \times (P_{EO} \times MW_{EO}) / MW_{av} \quad (1)$$

where:

m = mass flow rate of EO, lb/min,

w = total gas flow rate, lb/s,

P_{EO} = EO concentration, percent by volume = ppmv/10⁶,

MW_{av} = molecular weight of the vent gas, and

MW_{EO} = molecular weight of EO

A throughput efficiency was calculated using the emissions into and out of the control unit. The throughput efficiency (E_T) is given by:

$$E_T = 100 \times (W_{in} - W_{out}) / W_{in} \quad (2)$$

A recovery efficiency was calculated using the weight of the original EO charge and the measured EO emissions at the outlet of the control unit. The weight of EO originally charged to the chamber was obtained by multiplying the weight of 12/88 gas by 0.12. No analysis was performed on the sterilant gas to verify the EO concentration. A correction was made for the EO remaining in the chamber (W_R) which was determined using the ideal gas law. The mole fraction of EO left in the chamber was obtained from samples taken after Evacuation 7

either before or after the chamber had been refilled. The recovery efficiency (E_R) is then given by:

$$E_R = 100 \times (W_c - W_R - W_{out}) / (W_c - W_R) \quad (3)$$

where W_c is the weight of EO originally charged to the chamber.

Results and Discussion

The sampling method was evaluated using a gas cylinder containing known concentrations of EO and CFC-12. The gas cylinder was first analyzed on the GC. Then the gas cylinder was treated as a sample by installing a tee between the cylinder and the sampling line. The flow rate of the gas out of the cylinder was adjusted so that there was always excess flow past the tee during sampling. Response of the cylinder sample through the sample line was compared to the response of the cylinder sample analyzed directly.

The inlet sampling bias was measured twice using a 2,508 ppmv EO and 6,022 ppmv CFC-12 standard. The total sampling and analytical bias in the EO measurement ranged from 0-7% with an average of 3.5 percent. The sampling bias in the EO measurement ranged from 0.2 to 11.9% with an average of 6 percent. In both cases the sampling was biased positively for EO indicating that the method would tend to overestimate EO emissions. The total sampling and analytical bias in the CFC-12 measurement ranged from 4.3 to 12.5% with an average of 8.4 percent. The sampling bias in the CFC-12 measurement ranged from 0 to 15.2% with an average of 7.6 percent.

The outlet sampling bias was measured three times using a 502.4 ppmv EO and 1,200 ppmv CFC-12 standard. The total sampling and analytical bias in EO measurement ranged from 1.9 to 12.9% with an average of 7.4 percent. The sampling bias in the EO measurement ranged from -7.5 to 7.1% with an average of +1.3 percent. The total sampling and analytical bias in the CFC-12 measurement ranged from -9.5 to 4.8% with an average of -2.4 percent. The sampling bias in the CFC-12 measurement averaged 11 percent.

The analytical method was evaluated using a gas cylinder containing known concentrations of EO and CFC-12. The gas cylinder was analyzed on the GC using the same procedure as for the standard cylinders. Using the response of the cylinder sample and the prepared

calibration curve, a measured concentration of the cylinder sample was calculated. The measured concentration was compared to the expected or known concentration of the gas cylinder.

The inlet analysis bias was measured twice using a 2508 ppmv EO and 6022 ppmv CFC-12 standard. The analytical bias in the EO measurement ranged from -0.2 to -4.4% with an average of -2.3 percent. In both cases the analytical bias was negative. The analytical bias in the CFC-12 measurement ranged from -2.4% to 4.3% with an average of 1 percent.

The outlet analysis bias was measured three times using a 502.4 ppmv EO and 1200 ppmv CFC-12 standard. The analytical bias in the EO measurement ranged from 0.3 to 10.1% with an average of 6.2 percent. In all cases the analytical bias in the EO measurement was positive. The analytical bias in the CFC-12 measurement ranged from -5.6 to -18.5% with an average of -12 percent. In all cases the analytical bias in the CFC-12 measurement was negative, indicating that the column may be overloaded by the combination of the 2-ml sample size and the high CFC-12 concentration.

The utility of the method in determining emissions was evaluated by comparing the measured EO emissions for the six empty chamber tests on the assumption that the control device efficiency did not change with time.

The expected quantity of EO entering the control unit during the six empty chamber tests ranged from 41 to 44 lb and averaged 42 lb, based on 12% of the total weight of the 12/88 charge. The measured quantity of EO entering the control unit during these same six tests ranged from 24 to 62 lb and averaged 47 lb. In the one test where the measured weight of EO entering the scrubber was 24 lb, the inlet sampling pump leaked during the first 10 minutes of the evacuation and the FID flame was extinguished during portions of the third and fourth evacuations. The two tests where the measured weight of EO entering the scrubber was above 60 lb were performed on a day when the EO standard calibration curve for inlet samples was lower than on other test days.

The absolute difference between measured emissions and expected emissions was >40% for three tests and was <10% for only one test. In five of the six tests the measured emissions were larger than the expected emissions.

The measured quantity of EO emitted to the atmosphere from the control unit during the six empty chamber tests ranged from 0.011 to 0.043 lb and averaged 0.022 lb. The relative standard deviation (rsd) in these six measurements was twice the rsd for the inlet measurements indicating that more variation is associated with the scrubbing process than with the sterilization chamber.

Most of the error in EO emission measurement probably resulted from errors in the interpolation of the flow rate/concentration profile. Ethylene oxide emissions were measured with greater precision at the scrubber inlet than at the scrubber outlet as was expected because of the higher concentrations at the inlet. Part of this loss of precision in EO emission measurement may be due to difficulty in identifying the EO peak in the chromatogram because of EO retention times that shifted as the EO concentration decreased.

The utility of the method in determining control unit efficiency was evaluated by comparing the measured throughput efficiencies obtained from the six empty chamber tests on the assumption that the control unit efficiency did not change with time. All of the empty chamber tests were performed on the same chamber. The measured efficiency using the throughput method with the data from the six empty chamber tests ranged from 99.82 to 99.98% and averaged 94 percent. The median efficiency was 99.96 percent. Efficiency values were above 99.95% in five of the six tests. The one test in which the efficiency was below 99.9% was where sampling and analytical problems were encountered as described earlier.

Comparisons of the throughput and recovery efficiencies were done by a one-way analysis of variance (ANOVA) with sampling-calculational procedures as a fixed factor. The interaction term between the calculational procedures was tested to determine if there was a significant effect on efficiency results based on the calculational procedure used. A probability (P) that the calculational method used has no effect was calculated. If $P \leq 0.05$, then the effect is taken to be significant. A one-way ANOVA resulted in a P of 0.86 for the tests using chambers which did not contain product and 0.32 for the tests using chambers which did contain product; therefore, the procedure used to calculate the efficiency does not significantly affect the efficiency determined.

The efficiency results from the tests where product was present in the chamber were compared with the efficiency results from the tests where product was not present in the chamber using a fixed factor ANOVA. A probability that the independent variable does not effect the efficiency was calculated. If $P \leq 0.05$, then the effect was taken to be significant. The ANOVA calculation resulted in a P of 0.59 for the interaction between the calculational procedures; a P of 0.37 for the interaction between the chamber conditions; and a P of 0.79 for the combined interaction of the calculational procedure and chamber condition.

Since none of the dependent variables tested had a $P \leq 0.05$, there was significant effect on the efficiency measurement due to the presence of product in the chamber. Furthermore, there was no interaction between the calculational method used and the presence or absence of product in the chamber. Thus, the efficiency results were within random error of the overall mean efficiency.

Several outlet EO emissions were calculated using the chamber pressure and temperature data used to calculate inlet flow rates. No correction was made for the change in the gas composition that occurred while the gas was the scrubber. The largest change in gas composition occurs during the first evacuation when the gas composition changes from 30/70 % vol EO/CFC-12 entering the scrubber to $<1/>99$ % vol EO/CFC-12 exiting the scrubber. This meant that during the first evacuation approximately 30% of the moles of gas entering the control unit did not exit the control unit. Thus, the actual flow rate coming out of the control unit was probably less than the flow rate calculated by this method. This method should over-estimate EO emissions, resulting in an under-estimation of the control unit efficiency.

Statistical comparison of data based on estimated flows with data base on orifice plate measurements using a one-way ANOVA with flow calculational procedures as a fixed factor showed that the EO emissions from the scrubber calculated using orifice plate data were not significantly different from the EO emissions estimated using chamber temperatures and pressures. The probability that there was no difference in the calculated EO emissions was 0.35; in the calculated throughput efficiencies

0.59; and in the calculated recovery efficiencies, 0.25. A probability of 0.05 indicated a significant difference. The calculated efficiencies were not significantly different due to the high efficiency of the EO control unit. Therefore, in tests performed on units that are closed systems; therefore, flow estimation may be a possible alternative to orifice plate installation.

Conclusions and Recommendations

Six conclusions were based on the field test results. First, the sampling/analytical method adequately determined the EO mass flow rate into the control unit. Most of the error resulted from error in the interpolation of the flow rate/concentration profile.

Second, the sampling/analytical method adequately determined EO emissions at the outlet of the dilute acid scrubber, but identification of the EO peak in the chromatogram was complicated by EO retention times that shifted as the EO concentration decreased. The EO retention time shift was magnified due to the large range of EO concentrations. The bias in the sampling/analytical method averaged 7.4% for EO and -2.4% for CFC-12.

Third, the sampling/analytical method adequately determined the efficiency of the dilute acid scrubber. Measured efficiency calculated by the throughput method for empty chamber tests ranged from 99.82 to 99.98% and averaged 99.94 percent.

Fourth, the recovery method of determining control unit efficiency was comparable to the throughput method at this site. Efficiencies calculated empty chamber tests by the throughput method ranged from 99.82 to 99.98% and averaged 99.94 percent. Efficiencies calculated for empty chamber tests by the recovery method ranged from 99.90 to 99.97% and averaged 99.95 percent. A one-way analysis of variance (ANOVA) performed on the data for the empty chamber tests showed that the methods were not different. The sterilizer chamber/control unit tested was a closed system (i.e. leak-free) so this conclusion may not be valid at an older facility where more EO may be lost from the system as fugitive emissions.

Fifth, the presence of product in the chamber did not affect the scrubber efficiency measurement. The efficiencies calculated for empty chamber tests by the throughput method ranged from 99.82 to 99.98% and averaged 99.94

percent. The efficiencies calculated for full chamber tests by the throughput method ranged from 99.92 to 99.98% and averaged 99.96 percent.

Sixth, EO emissions and control unit efficiencies calculated using flow rates based on orifice plate data did not differ significantly for EO emissions and control unit efficiencies calculated using estimates based on chamber temperatures and pressures. Ethylene oxide emissions for empty chamber tests based on orifice plate data ranged from 0.011 to 0.043 lb and averaged 0.024 lb. Estimated EO emissions for the same tests ranged from 0.006 to 0.036 lb and averaged 0.017 lb. Throughput efficiencies based on orifice plate data ranged from 99.82 to 99.98% and averaged 99.93 percent. Throughput efficiencies based on estimated flows for the same tests ranged from 99.85 to 99.99% and averaged 99.95 percent. Again, the sterilizer chamber/control unit tested was a closed system so this conclusion may not be valid at an older facility where more EO may be lost from the system as fugitive emissions.

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John H. Margeson is the EPA Project Officer (see below).

The complete report, entitled "Sampling/Analytical Method Evaluation for Ethylene Oxide Emission and Control Unit Efficiency Determinations," (Order No. PB 88-204 235/AS; Cost: \$19.95, subject to change) will be available only from:

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