



Project Summary

Analytical Method Evaluation for Measuring Ethylene Oxide Emissions from Commercial Dilute-Acid Hydrolytic Control Units

Joette Steger

The Source Branch of the U.S. Environmental Protection Agency's (EPA) Environmental Monitoring Systems Laboratory (EMSL) at Research Triangle Park, North Carolina, has a program to develop stationary source test methods of known precision and accuracy for determining compliance with EPA standards. While participating in this program, Radian Corporation performed a field evaluation of a method for sampling and analyzing ethylene oxide (EO) in the vent stream from a dilute acid scrubber of a commercial sterilizer. The purposes of the test were to evaluate the ability of the analytical method for quantitating EO in the scrubber emissions, to determine EO stability in sample containers, and to measure the EO concentration profile and EO-to-oxygen and EO-to-dichlorodifluoromethane (CFC-12) ratios during the initial sterilizer evacuation.

The test method acquired three-second grab samples that were analyzed by gas chromatography with flame ionization detection (GC/FID). Samples were acquired at one-, three-, four- or six-minute intervals. All samples were analyzed in the field and a portion of the samples were reanalyzed in the laboratory.

The analytical method was evaluated on three 1/8-inch (32 millimeters) OD stainless steel columns packed with a liquid phase coated on 60/80 mesh Carbopack B. The 5% Fluorcol column was 10 feet (3 meters) long; the 3% SP-1000 column was 8 feet long (2.4 m); and the 1% SP-1000 column was 6 feet (1.8 m) long. Evaluations were based on column efficiency, resolution, linearity, retention time stability, and limits of detection and quantitation. Sample stability was evaluated in one-liter Tedlar bags, 5-mL gas-tight syringes, and Vacu-Samplers. The EO concentration profile was measured by taking samples at one-minute intervals during Test 1 Evacuation 1. This test used 12 wt% EO and 88 wt% CFC-12 as the sterilizing gas.

The full report contains conclusions and recommendations based on the field test results, a description of the field test site, the grab sampling and analytical method used, results of the field evaluation, test data, and references used to prepare the report.

This Project Summary was developed by EPA's Atmospheric Research and Exposure Assessment 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

Because EPA has listed EO as a possible hazardous air pollutant, a standardized analytical method is needed to measure EO levels in a vent stream and for determining control equipment performance. The method tested acquired three-second grab samples that were analyzed by GC/FID. The purposes of the field evaluation were to evaluate the analytical method using samples from an operating commercial sterilizer with a dilute acid scrubber, to determine EO stability in sample containers as a function of storage time, and to measure the EO concentration profile and the EO-to-oxygen and EO-to-CFC-12 ratios during the initial sterilizer evacuation.

Procedures

Facility Description

The field evaluation was conducted at Burron Medical, a medical supply sterilization facility, located in Allentown, Pennsylvania. The facility has three 1000-ft³ (28-m³) sterilizers, one uses a 12/88 (wt%/wt%) EO and CFC-12 gas mixture and two use 100% EO.

The exhaust from the sterilizers is controlled by a DEOXX™ system. The DEOXX system is a dilute acid scrubber manufactured by Chemrox, that hydrolyzes the EO to ethylene glycol. At the time of the test the scrubber contained dilute sulfuric acid and approximately 10 wt% of ethylene glycol.

Each chamber is equipped with a total recirculating oil-sealed pump. The pumps are equipped with gas/liquid separators that emit the gas to the DEOXX system and recirculate the liquid to the pump inlet.

The two different sterilization programs used for testing are shown in Figures 1 and 2. Three tests were performed, one with product in the chamber using 100% EO and two without product using 12/88 gas. Data from all of these tests were reduced and used to prepare this report.

Sampling Location

Samples were acquired after the scrubber, at a point as close to the end of the plant's stack as was feasible. The stack was modified by installing

additional pipe to remove exhaust gases from the sampling areas and orifice plates to provide a small amount of back pressure to facilitate sampling and eliminate the possibility of diluting the sample with ambient air.

Sampling Procedures

Grab sampling was used for determining EO, CFC-12, and oxygen concentrations. For EO and CFC-12 measurements, sample was withdrawn into a heated, 1/4-inch (64-mm), Teflon® line using a Teflon-lined diaphragm pump. A stainless steel, 1/4-inch (64-mm) tee was used after the pump to provide a continuous purge of the vent gas through the sampling system. After the tee, on one branch, the sample stream was routed through Tygon tubing and exhausted downwind from the sampling area. There was a pinch clamp on the Tygon tubing to block the exhaust line during sample collection. On the other branch of the tee, a stainless steel, 1/4-inch (64-mm), toggle-operated shut-off valve was placed prior to the sample container.

The EO and CFC-12 sampling line was continually flushed with sample throughout the test. Prior to attaching the sample container, the line was flushed with sample by closing the pinch clamp on the Tygon exhaust line and opening the toggle valve on the sample line. The same procedure was used to fill the sample container.

BACHARACH Fyrite oxygen indicator was used to determine percent levels of oxygen in the sterilizer exhaust at the sampling location. The oxygen was chemically absorbed from the sample by chromous chloride. Accuracy of analysis was ± 0.5 percent. Percent levels of oxygen were measured every time a bag sample was taken to indicate the dead volume of the scrubber system and to determine EO-to-oxygen ratios. An aspirator bulb removed sample from the stack downstream of the EO sampling port.

Exit gas temperatures were measured using a bimetallic temperature probe and a pyrometer. Stack temperatures were digitized by a calibrated pyrometer and recorded every time a bag sample was taken.

Analytical Procedures

The analytical method used for measuring EO and CFC-12 was gas chromatography with flame ionization detection (GC/FID). A dual FID Varian 3400 GC was equipped with a 10-ft (3-m) by 1/8-inch (32-mm) OD stainless

steel column containing 5% Fluorcol C 60/80 Carbowax B and a 6-ft (1.8-m) by 1/8-inch (32-mm) OD stainless steel column containing 1% SP-1000 C 60/80 mesh Carbowax B. On July 9, the 1% SP-1000 column was replaced with an 8-ft (2.4-m) by 1/8-inch (32-mm) OD stainless steel column containing 3% SP-1000 on 60/80 mesh Carbowax B. The FID electrometers were connected to Shimadzu CRI-A integrators.

The GC column oven was operated isothermally at 45°, 55° and 65°C on June 21, 22 and 23, respectively. Laboratory reanalyses were performed with an isothermal column temperature of 65°C except on July 9 when the 3% SP-1000 column was used at 55°C. The injector oven was heated to 175°C, and the detector oven to 200°C. Nitrogen carrier gas flow rates were 30 mL/min. The FID support gas flow rate recommended by the GC manufacturer were used. During Test 1 Evacuation, when both EO and CFC-12 were quantitated, the FID electrometers were programmed so that the range would shift from 10⁻¹⁰ or 10⁻¹¹ amperes to 10⁻⁹ amperes. One-milliliter sample were injected using a 5-mL gas-tight syringe with an on/off valve.

Gas Chromatograph Calibration

Both channels of the chromatograph were calibrated for EO at the beginning and end of the day. On the first test day the GC/FID was also calibrated for CFC-12 to determine the EO-to-CFC-12 ratios. At least one standard was also analyzed after every twentieth sample. Calibration curves consisted of a minimum of three standards that bracketed the sample concentrations.

Test Results and Conclusions

Linearity

Based on a one mL injection volume the FID response using these three columns was linear between 31.25 and 100 vol% for CFC-12. Below 31.25 vol% CFC-12 linearity was not evaluated. Using a one-milliliter injection volume, the FID response when using the 3% SP-1000 column had the largest linear range (0.5 to 100 vol% and 2.28 to 1,254 ppmv) for EO at the percent level and at the part-per-million (ppm) level. At the part-per-thousand (ppt) level, the FID response using the 1% SP-1000 column had the largest linear range (22.81 to 5,016 ppmv) for EO. Therefore, the FID response using the 1% SP-1000 column provides the best linear range for determining the

*Mention of trade names or commercial products does not constitute endorsement or recommendation for use

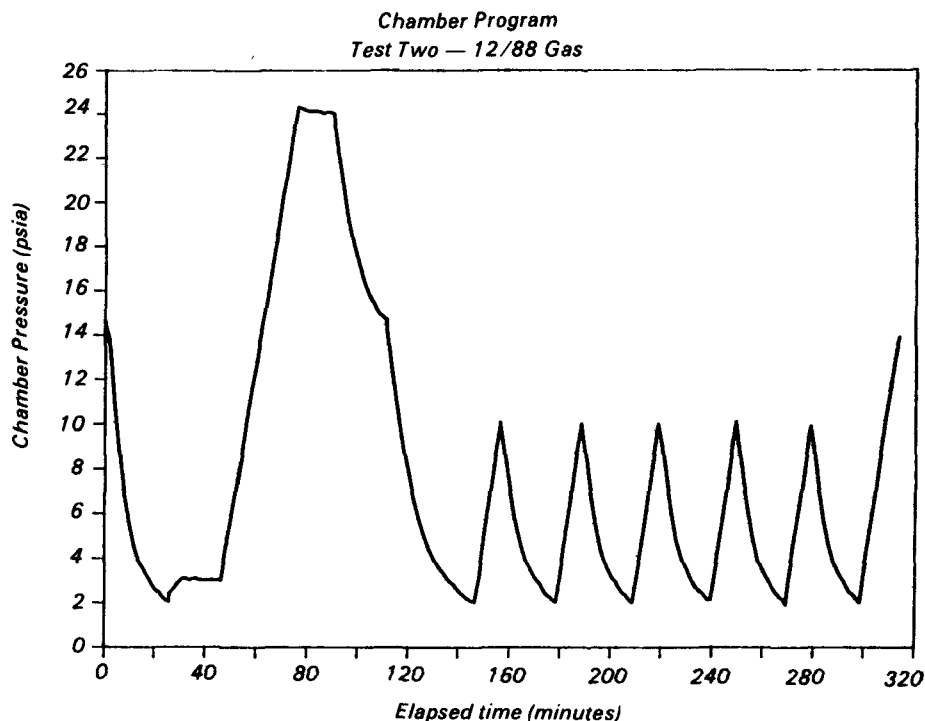


Figure 1. Chamber pressure during Test 2 using 12/88.

maximum EO concentration emitted from a dilute-acid hydrolytic control unit.

Efficiency

Of the three columns evaluated, the 5% Fluorcol column operated at 65°C provided the best efficiency for analyzing percent levels of EO. For ppm levels of EO the two columns were comparable. The 3% SP-1000 column was clearly the least efficient column at all tested temperatures and concentrations. Therefore, the Fluorcol column provides the best efficiency for percent level EO analyses and the 1% SP-1000 column provides the best efficiency for ppm level EO analyses.

Resolution

The 1% SP-1000 and the 5% Fluorcol columns provided comparable resolution of the EO from the CFC-12 at the percent and ppt levels. At column temperatures of 45° and 55°C baseline resolution of EO from CFC-12 was obtained on both columns. Both of these columns provided significantly better resolution of the two compounds than did the 3% SP-1000 column. Therefore, the 3% SP-1000 column is not

recommended for analyzing samples of 12/88 gas. Resolution was not evaluated at the ppm level.

Retention Time Stability

The EO retention times were most stable on the 1% SP-1000 column where they varied from 1.38 to 1.46 minutes ($\pm 6\%$) at 55°C and were least stable on the 5 Fluorcol column where they varied from 2.21 to 5.43 minutes ($\pm 150\%$) at 55°C. In general the EO retention times varied least at column temperatures of 65°C. The CFC-12 retention times were most stable on the 3% SP-1000 column where they varied from 1.46 to 1.56 minutes ($\pm 7\%$) at 65°C and were least stable on the 5% Fluorcol column where they varied from 4.72 to 5.57 minutes ($\pm 18\%$) at 45°C. Therefore, the Fluorcol column where they varied from 4.72 to 5.57 minutes ($\pm 18\%$) at 45°C. Therefore, the Fluorcol column should only be used to analyze for EO at the percent levels in situations where the concentration is not expected to change by more than two orders of magnitude.

Limits of Detection and Quantitation

The 3% SP-1000 column provided the lowest detection and quantitation limits; therefore, it would be the best column for low-level and trace analyses. The limits of detection and quantitation were comparable for the 1% SP-1000 and 5% Fluorcol columns; therefore, these two columns may not be distinguished by these criteria.

Ethylene Oxide Stability

Evaluations were made of the stability of EO in samples collected in 1-L Tedlar bags, 5-mL gas-tight syringes, and Vacu-Samplers. After 4 days in an unpunctured Vacu-Sampler four out of seven duplicate samples or 57% were within $\pm 8\%$ of the EO concentration in the original samples. The seven duplicate samples in the unpunctured Vacu-Samplers lost an average of 15% of the EO. Therefore, EO samples in unpunctured Vacu-Samplers remained stable for up to 4 days, with stability defined as over 50% of the samples being within $\pm 10\%$ of the original concentrations and the average of all EO

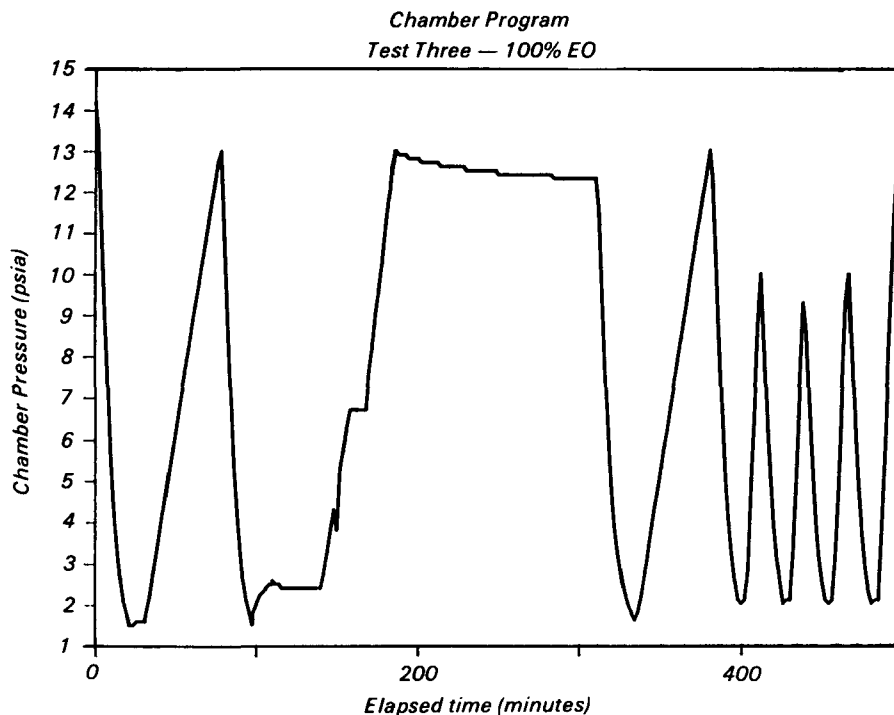


Figure 2. Chamber pressure during Test 3 using 100% EO.

concentration changes being within ± 15 percent.

After 4 or 5 days in gas-tight syringes, only 2 out of 12 duplicate samples or 17% were within $\pm 9\%$ of the EO concentration in the original samples. The samples in the syringes lost an average of 20% of the EO. Therefore, samples are not stable in syringes for 4 or 5 days.

Stability results are listed in Tables 1 and 2 for bag samples containing exhausts from 12/88 and 100% EO tests, respectively. In leak-free bags the EO in 12/88 exhaust at EO concentrations above 1,000 ppmv varied by an averaged relative difference of $+ 9\%$ after 48 hours. After 5 to 6 days the bags with concentrations of EO greater than 1,000 ppmv showed an average EO loss of 22 percent. In the same time period, bags with concentrations of EO less than 500 ppmv showed an average EO loss of 36 percent. After 17 to 18 days the bags with EO concentrations greater than 1,000 ppmv showed an average EO loss of 41 percent. Therefore, samples of 12/88 exhaust containing EO at concentrations above 1,000 ppmv are stable in Tedlar bags for up to 48 hours.

Leak-free bags containing 100% EO exhaust at EO concentrations above 1,000 ppmv varied by an averaged relative difference of $+ 3\%$ after four days. After 8 days these bags averaged a 20% loss and after 12 days an average of 33% of the EO was lost. In leak-free bags of 100% EO exhaust at concentrations below 500 ppmv an average of approximately 20% of the EO was lost after 4 days. No additional loss was observed in these bags between Day 4 and 12. Therefore, samples of 100% EO exhaust containing EO at concentrations above 1,000 ppmv are stable for at least 4 days.

Since the EO loss in the bags is concentration dependent and more EO is lost at lower concentrations, the EO loss is expected to be caused by adsorption of the EO onto the bag walls. Initially, an equilibrium probably occurs between the bag surface and the gas within the bag accounting for the 2- to 4-day period of stability observed. As the gas remains in the bag longer, the EO may be penetrating further into the bag wall, accounting for the additional EO loss. The sample stability was decreased by

the high surface-to-volume ratio in the 1-L bags.

Ethylene Oxide Concentration Profile

During the first evacuation of the first test using 12/88 gas, the EO concentration ranged from 400 ppmv to 1,500 ppmv and reached a maximum plateau between 13 and 20 minutes. Concentrations of EO during 12/88 exhausts were approximately 1,200 ppmv during the second exhaust, 600 ppmv during the third exhaust, 300 ppmv during the fourth exhaust, 100 ppmv during the fifth exhaust, and 80 ppmv during the sixth exhaust. During the first evacuation of the third test using 100% EO, the EO concentration ranged from 500 ppmv to 3,000 ppmv. Concentrations of EO during 100% EO exhausts were approximately 600 ppmv during the second exhaust, and 300 ppmv during the third exhaust. Therefore, to measure the maximum EO concentration emitted, samples should be acquired between 1 and 20 minutes after the start of the first chamber evacuation when 12/88 is used.

Ratios of the EO-to-CFC-1 concentration were calculated in 12/88

exhaust and a plot of the ratios versus time was similar to a plot of EO concentration versus time due to the high and relatively constant CFC-12 concentration. Oxygen concentrations in the 12/88 exhaust were monitored using Fyrite and indicated that after five minutes the exhaust contained minimal air. Therefore, EO-to-CFC-12 ratios could be established for determining the maximum EO concentration emitted from chambers using 12/88. The EO-to-CFC-12 ratios would only be useful during the first evacuation when the expected CFC-12 concentration is 99.9 percent.

Recommendations

Based on the test results, Radian makes the following 7 recommendations:

1. A 5% Fluorcol column at 65°C is recommended for measuring percent level EO and CFC-12 concentrations, levels expected at the scrubber inlet or in the exhaust of uncontrolled sterilizers. The FID response when using a 5% Fluorcol column is linear, as indicated by an F-test for linearity from 0.5 to 50 vol% EO. The 5% Fluorcol column is the most efficient column tested for percent levels of EO, and provides baseline resolution of the CFC-12 and EO at column temperatures of 45 and 55°C and near baseline resolution at 65°C. Also, the retention time instability on the Fluorcol is less pronounced at percent concentrations.
2. A 1% SP-1000 column at 45°C is recommended for measuring ppm levels of EO, levels expected at the scrubber outlet. The FID response when using a 1% SP-1000 column is linear from 22.81 to 5,016 ppmv EO. The 1% SP-1000 column is the most efficient column tested for ppm levels of EO, and provides baseline resolution of the CFC-12 and EO at 45°C.
3. It is recommended that a 3% SP-1000 column at 45°C be investigated for quantitating sub-ppm levels of EO, levels expected in ambient air at sterilization facilities. The 3% SP-1000 column provided limits of detection and quantitation almost three times lower than the other two tested columns.
4. It is recommended that grab samples collected in gas-tight syringes be analyzed within several hours of collection, samples collected in bags within 48 hours of collection and samples collected in

Vacu-Samplers within 4 days of collection. Syringe samples lost an average of 20% of the EO after 4 days. In leak-free bags, EO remained stable for at least 48 hours and may be stable for up to 4 days. After 5 or 6 days, bag samples lost an average of one-third of the EO. In unpunctured Vacu-Samplers, 57% of the samples were within $\pm 8\%$ of the expected concentration after 4 days and the average EO loss for all samples was 15 percent.

5. Sampling at least three times between 13 and 20 minutes after the first indication of flow through the stack is recommended for determining maximum EO concentration emitted during the first evacuation. The EO concentration in the exhaust increased linearly between 5 and 13 minutes, plateaued between 13 and 20 minutes, and dropped off after 20 minutes. This time frame corresponds to chamber pressures between 16 and 10 pounds per square inch actual and may need to be adjusted when using a different sterilization program.
6. If the second and following evacuations are monitored, sampling between 5 and 10 minutes during these evacuations is recommended. During the first 5 minutes, the gas coming out of the stack is a mixture of gas from the chamber and residual gas from the scrubber so samples taken during this time may be biased high or low.
7. To determine EO-to-CFC-12 ratios during the first evacuation, a 0.1-mL sample volume is recommended for CFC-12 quantitation. A 1-mL sample of percent levels of CFC-12 overloads the analytical column, decreasing the column performance.

The full report was submitted in partial fulfillment of EPA Contract No. 68-02-4119 by Radian Corporation under the sponsorship of the U.S. Environmental Protection Agency. The report covers the period from March to August of 1988.

Table 1. *Ethylene Oxide Stability in Tedlar Bags Containing 12/88 Exhaust Concentration (ppmv)*

<i>Sample Bag No.</i>	<i>June 21</i>	<i>June 22</i>	<i>June 23</i>	<i>June 27</i>	<i>July 1</i>	<i>July 5</i>	<i>July 9^a</i>
13	1230	1370	1320	995	824	716	733
20	1340	NA	NA	1010	830	1420	985
22	1200	1360	1320	956	828	790	760
25	NA	976	NA	734	562	962	536
30	NA	374	NA	NA	NA	166	NA
32	NA	133	96.5	34.2	34.4	NA	NA
36	NA	28.5	NA	NA	61.8	48.8	65.6
37	NA	36.7	NA	NA	NA	124	NA
39	NA	29.8	27.2	1.08	11.9	NA	NA
41	NA	1170	NA	NA	636	546	538
44	NA	NA	NA	1120	954	803	810
45	NA	1240	1380	958	865	690	683
48	NA	NA	NA	462	370	556	NA
50	NA	305	340	214	195	173	NA
55	NA	NA	80.6	57.4	75.2	71.0	NA
56	NA	NA	101	53.6	70.5	70.6	NA
57	NA	NA	83.5	51.8	65.8	48.4	NA

^a Samples analyzed on a 3% SP-1000 column
NA = Not available

Table 2. Ethylene Oxide Stability in Tedlar Bags Containing 100% EO Exhaust
Concentration (ppmv)

Sample Bag No.	June 23	June 27	July 1	July 5	July 9 ^a
58	343	NA	270	248	212.8
60	2,840	2,410	2,030	1,660	1,408.0
63	544	470	426	430	364.8
64 ^b	342	170	13.7	NA	NA
65	344	238	258	242	220.8
66	334	230	268	244	225.6
67	430	370	322	303	284.0
68	426	352	307	516	NA
69	387	282	270	226	NA
70	1,530	1,760	1,400	1,200	NA
71	1,440	1,490	1,080	902	NA
72	1,200	1,270	974	756	NA

^a Samples analyzed on a 3% SP-1000 column

^b Bag leaked

NA = Not available

Joette Steger is with Radian Corporation, Research Triangle Park, NC 27709

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

The complete report, entitled "Analytical Method Evaluation for Measuring Ethylene Oxide Emissions from Commercial Dilute-Acid Hydrolytic Control Units," (Order No. PB 89-155 253/AS; Cost: \$21.95, subject to change) will be available only from:

National Technical Information Service

5285 Port Royal Road

Springfield, VA 22161

Telephone: 703-487-4650

The EPA Project Officer can be contacted at:

Atmospheric Research and Exposure Assessment Laboratory,

U.S. Environmental Protection Agency

Research Triangle Park, NC 27711

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