Application note

Ethylene oxide continuous emissions monitoring by OE-FTIR

Background

Ethylene oxide (EtO) is a carcinogenic and mutagenic compound commonly used in the chemical industry, particularly as a sterilant for medical products and as a reaction intermediate in the production of ethylene glycol. Due to its toxicity, federal, state, and local regulators have expressed an interest in monitoring for very low levels of EtO in and around commercial sterilizers.

Measurement challenges

Low-level detection of ethylene oxide has been challenging for quadrupole mass spectrometry due to the presence of interfering species with identical molecular weights, including CO_2, propane, and acetaldehyde, which may appear in the sample matrix. EtO is also highly reactive, particularly with acids, making it difficult to collect a stable sample for subsequent analysis at a laboratory. Scrubber systems at sterilization facilities may utilize aqueous acids to convert ethylene oxide to ethylene glycol, and if any residual acid mists are present in the sample, some of it may be lost. EtO is also difficult to trap and concentrate due to its low boiling point. An analytical technology optimized for real-time, direct measurement of EtO is necessary to address these challenges.

Solution

The Thermo Scientific™ MAX-iR™ FTIR Gas Analyzer can meet these challenges with novel Thermo Scientific™ StarBoost™ Technology. This optical enhancement solution dramatically increases the signal-to-noise ratio (SNR) of the MAX-iR Analyzer, providing minimum detection limits (MDLs) that are 50x lower than other commercially available Fourier-transform infrared (FTIR) gas analyzers, without the need for extremely long pathlength gas cells. Optically enhanced FTIR (OE-FTIR) technology allows for the detection of <1 part-per-billion (ppb) EtO in real-time.

This MAX-iR Analyzer is the basis of the fully-automated Thermo Scientific™ EMS-10™ Continuous Emissions Monitoring System (CEMS), which includes flexible Thermo Scientific™ MAX-Acquisition™ Control Software and complies with United States Environmental Protection Agency (US EPA) CEMS standards.

In this application note, a combination of laboratory performance studies and field trials demonstrate how the EMS-10 System meets the application requirements for an EtO CEMS. Field trials were conducted at a commercial sterilization facility in North America, where the EMS-10 System was used to continuously measure EtO emissions from a common stack. (US EPA ALT-142 approves the use of OE-FTIR in lieu of gas chromatography (GC) for EtO emission testing at commercial sterilizers, which are regulated under 40 CFR Part 63, Subpart O.)

All data was collected using the EMS-10 System configured with a MAX-iR Analyzer and StarBoost Technology. FTIR configuration details are described in Table 1.

Detector	InAs
Laser type	VCSEL diode laser
Optical path length	9.86 m
Gas cell volume	0.4621 L
Pressure sensor	1 atm
Gas cell windows	CaF_2
Gas cell O-rings	Viton
Gas cell mirror material	Nickel-plated aluminum with gold coating
StarBoost optical enhancement filter	Long pass filter
Spectral range	2,900–3,400 cm^{-1}

Table 1. MAX-iR Analyzer configuration details.

Cylinder ID	Expiration date	Gas	Certified concentration	Analytical uncertainty
CC736527	30 September, 2023	Ethylene oxide	1,223 ppb	±10%
		Ethane	100.20 ppm	±10%
CC512410	25 May, 2030	Ethylene	97.78 ppm	±1%

Table 2. Reference gas cylinder information.

Laboratory performance study

Materials

Table 2 describes the certified EtO standard used in the test protocol (referred to as the "reference gas"), which also contained ethane as a tracer for dynamic spike recovery studies. Ethylene was used as a calibration transfer standard (CTS) for routine pre-test QA/QC. Compositions are verified by the gas manufacturer using direct comparison to National Institute of Standards and Technology (NIST) traceable calibration standards and/or NIST gas-mixture reference materials.

Ultra-high purity (UHP) nitrogen was used for dilution of the reference gas mixture and for zeroing the MAX-iR Analyzer. Prior to the study, routine MAX-iR instrumental diagnostics and direct calibration checks were performed to ensure the analyzer was functioning properly.

Limit of detection

A limit of detection (LOD) test demonstrates the minimum amount of EtO that can be detected above the background in a representative gas matrix. The EMS-10 System was set to sample ambient laboratory air at its target sample flow rate. The EtO response was measured for 7–11 consecutive 1-min scans, and the LOD was defined as 3 times the standard deviation of these measurements. Results are shown in Table 3.

	Average	Standard deviation (σ)	LOD (3σ)
Ethylene oxide (ppb)	-0.3	0.2	0.6

Table 3. Ethylene oxide LOD results.

Accuracy and linearity

Accuracy and linearity of the EtO measurements were determined near the emission standard concentration (this can also be performed for your specific actionable level). An EtO reference gas was introduced into the MAX-iR Analyzer for a direct measurement. The reference gas was then diluted in nitrogen to three target concentrations: a low (26.6 ppb), mid (51.9 ppb), and high (99 ppb) level. Each was measured in triplicate for a total of nine measurements, ensuring that the same gas concentration was not introduced twice in succession. For each level, the percent error was calculated as the difference between the expected reference concentration and the average measured concentration, divided by the span value (99 ppb). To determine linearity, the expected versus average measured concentration was plotted to calculate R2. For accuracy results, see Table 4. Linearity results are shown in Figure 1.

Level	Replicate	EtO concentration (ppb)		Error (% of span)
		Target	Measured	
Zero	1	0.0	-1.1	~MDL
Low	1	26.6	24.6	-1.95%
Mid	1	51.9	50.5	-1.38%
High	1	99.0	98.1	-0.93%
Zero	2	0.0	-1.1	~MDL
High	2	99.0	98.2	-0.76%
Mid	2	51.9	50.7	-1.12%
Low	2	26.6	24.8	-1.72%
Zero	3	0.0	-0.6	~MDL
High	3	99.0	99.4	0.35%
Low	3	26.6	25.2	-1.40%
Mid	3	51.9	51.0	-0.86%

Table 4. Ethylene oxide accuracy results.

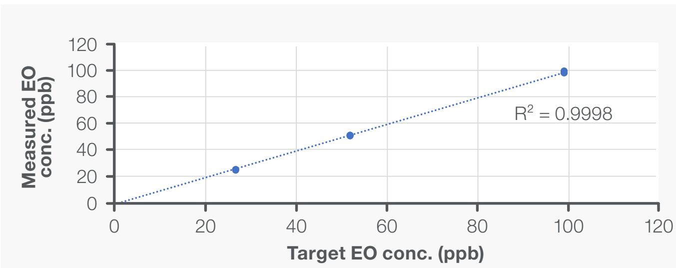

Figure 1. Ethylene oxide linearity results.

Response time

This test determines the time it takes the EMS-10 System to respond to a change in EtO concentration (operating normally at its target sample flow rate). The "zero" gas was introduced into the EMS-10 System at a flow rate that exceeds the sample pump flow. EtO reference gas was then introduced at the high level (99 ppb), and once the EtO response stabilized (i.e., didn't vary by more than 1%), the time required to reach 95% of full scale ("rise time") was measured (12 seconds). Zero gas was reintroduced, and once the EtO response stabilized, the time required to reach <5% of full scale ("fall time") was measured (11 seconds) (Figure 2).

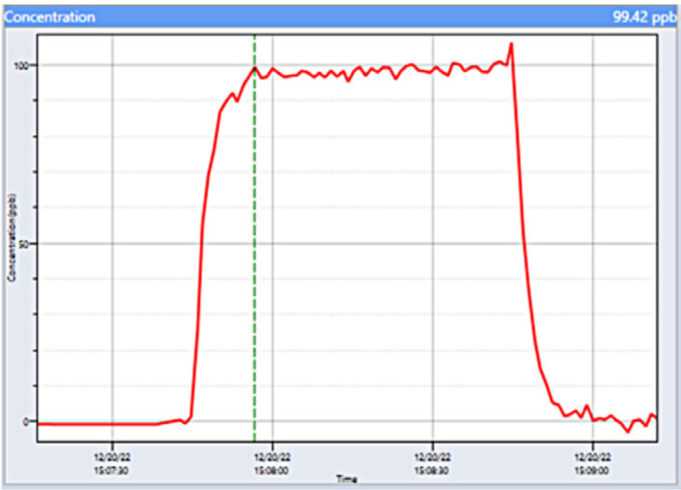

Figure 2. Ethylene oxide response time.

Field study

Field trials were conducted at a commercial sterilization facility, where the EMS-10 System was continuously measuring EtO emissions from a common stack, following US EPA ALT-142. A stainless-steel probe was inserted into the stack and attached to a 100-ft sample line that was heated to 120°C. This sample line was connected to the EMS-10 System, which contained a 120°C heated particulate filter and diaphragm pump. An unheated exhaust line was connected to the outlet of the EMS-10 System to remove the sample from the test location.

Following routine pre-test diagnostics and direct calibration checks, analyte spiking was performed to demonstrate the precision and bias of the instrument, according to US EPA Method 301. This also demonstrates effected transport of EtO through the EMS-10 System when the entire sampling train was challenged. EtO reference gas was spiked into the native stack emissions at 154 ppb (Tables 5 and 6).

Test run	Tracer (ppmv)		Dilution factor	Ethylene oxide (ppmv)		Calculated spike level (ppmv)	Percent recovery
	Spiked	Native		Spiked	Native		
1	29.188	0.013	0.061	0.136	0.028	0.146	92.7%
2	29.306	0.059	0.061	0.138	0.036	0.151	91.1%
3	29.273	0.041	0.061	0.140	0.034	0.148	94.1%
4	29.386	0.056	0.061	0.138	0.041	0.155	88.6%
5	29.365	0.047	0.061	0.142	0.038	0.153	92.8%
6	29.404	0.087	0.061	0.143	0.030	0.146	98.1%
7	29.392	0.048	0.061	0.144	0.042	0.157	91.7%
8	29.439	0.068	0.061	0.143	0.043	0.157	90.8%
9	29.373	0.048	0.061	0.146	0.044	0.158	92.5%
10	29.416	0.076	0.061	0.147	0.042	0.156	94.2%
11	29.422	0.051	0.061	0.142	0.045	0.159	89.3%
12	29.425	0.099	0.061	0.148	0.045	0.159	93.1%
Mean	29.366	0.058	0.061	0.142	0.039	0.154	92.4%

Table 5. Analyte spike data for US EPA Method 301 Section 12.

Bias analysis	Value	Criteria	Validation
Relative bias, BR	7.63%	< 10%	PASS
Relative standard deviation, RSD	2.82%	< 20%	PASS

Table 6. Statistical analysis for US EPA Method 301 Section 12.

Results and conclusions

The EMS-10 System, configured with StarBoost Technology, creates an ideal solution for monitoring low-level EtO emissions from commercial sterilization and chemical manufacturing facilities. With an LOD less than 1 ppb and responsivities of less than 15 seconds, the EMS-10 OE-FTIR System showed superior performance compared to standard GC systems, which typically have an LOD of 50 ppb and an analysis time of ≥10 minutes.

Using a technology with lower detection limits prevents the over-reporting of emissions when stack concentrations are routinely below 50 ppb.

Not only does the performance of the EMS-10 OE-FTIR System exceed today's US EPA standards for EtO, but the system's flexibility and sensitivity make it easier to adapt to shifting regulations, such as changes to the National Emissions Standards for Hazardous Air Pollutants (NESHAP) and Ethylene Oxide Emission Standards for Sterilization Facilities (40 CFR Part 63, Subpart O).

Test	Measurement	Result
Limit of detection	3σ	0.6 ppb
Accuracy	Avg. error (% of span)	-1.08%
Linearity	R^2	0.9998
Response time	Rise time	12 seconds
	Fall time	11 seconds
Spike recovery	Avg. % recovery	92.37%
US EPA Method 301	Relative bias	7.63%
	Precision (RSD)	2.82%

Table 7. Summary of results.

Learn more at **thermofisher.com/ems-10**