Monitoring ethylene oxide with OE-FTIR for workplace safety

Introduction

Ethylene oxide (EtO) is a hazardous air pollutant (HAP) with a unique molecular structure that promotes chemical and reactive properties indispensable for a variety of markets.

It is predominantly used as a sterilant in industrial environments such as medical device manufacturing and packaging. It can also be found in the agricultural realm as a synthetic pesticide and in the spice industry for eliminating food-borne pathogens. In addition to these applications, EtO is also prevalent in chemical manufacturing as a reaction intermediate for the production of ethylene glycol, which is a component in a wide variety of consumer products such as antifreeze and plastics.

In medical equipment production, EtO is essential for sterilizing single-use products such as surgical kits and bandages, and also sensitive medical devices that would be damaged by other techniques like steam treatment. EtO's ability to diffuse through most materials makes it highly efficient for fumigating pallets of finished product prior to shipment. Untreated products are loaded into sealed chambers where they are inundated with EtO gas. The gas penetrates the materials, destroying pathogens without damaging the product.

The same chemical properties that render EtO a superior sterilant gas also pose health risks. EtO is carcinogenic and mutagenic. It is also flammable, corrosive, and acutely toxic, making exposure prevention critical at sterilizer facilities. When treated products are removed from the sterilization chambers for storage or off-gassing, trace emissions of EtO can be released into the indoor air and threaten the safety of site personnel.

To enforce the mitigation of acute and long-term EtO exposure, in early 2023, the United States Environmental Protection Agency (EPA) published the Proposed Interim Decision (PID) and Draft Risk Assessment (DRA) Addendum for EtO in accordance with the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA). The PID presents a framework for reducing the inhalation risks of EtO emissions for workers and community members near sterilization facilities. The proposal requires real-time monitoring, with a 10 parts-per-billion (ppb) action limit: if the indoor EtO concentration exceeds 10 ppb at commercial sterilizers, the employees are required to wear respirators or vacate the premises.

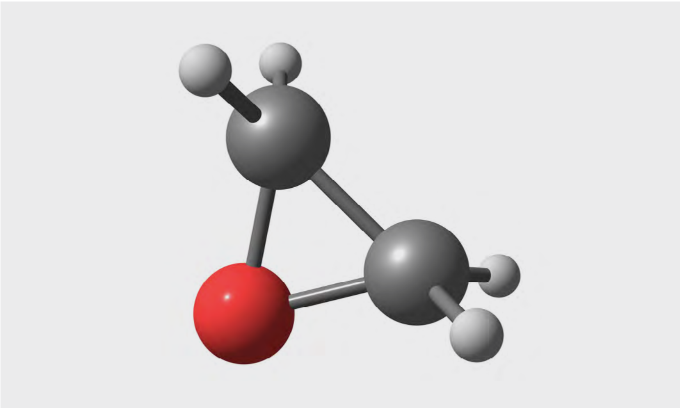

Figure 1: Ethylene oxide (C_2H_4O) molecule.

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Measurement challenges

Measuring ethylene oxide at 10 ppb and lower can present challenges for different analysis techniques. It is a highly reactive gas so it can be difficult to obtain stable results, especially using offline lab methods. Monitoring technologies on the market today such as mass spectrometry, gas chromatography, and cavity ring-down spectroscopy are highly susceptible to interferences from other chemicals present in ambient air samples. Carbon dioxide, acetaldehyde, isopropyl alcohol, and hydrocarbon fumes around a plant introduce challenges to monitoring EtO with these techniques, causing invalid data or false alarms. An analytical technology optimized for real-time measurement of EtO without interference from other compounds is necessary to address these challenges.

Solution

The Thermo Scientific™ MAX-iR™ FTIR Gas Analyzer meets these challenges with the novel Thermo Scientific™ StarBoost™ technology. The MAX-iR Analyzer is at the heart of the fully-automated Thermo Scientific™ MAX-iAQ™ Ambient Air Monitoring System. This cutting-edge solution is designed to revolutionize the way air quality is monitored and managed within a facility. The unique spectroscopic properties of optically enhanced FTIR (OE-FTIR) technology allow for the detection of <1 ppb EtO in real time. The "optically enhanced" descriptor arises from the heightened sensitivity introduced by an InAs detector paired with an optical filter. The analyzer is extremely sensitive in one specific region of the mid-infrared spectrum where EtO can be easily quantified. With these optimizations, the MAX-iR Analyzer with StarBoost technology can measure EtO concentrations from parts-per-trillion (ppt) to % levels.

The MAX-iAQ System is equipped with a 20-channel sample multiplexer and pump module. This enables sequential monitoring of up to 20 different locations in a 10-minute cycle and provides comprehensive coverage across a site. There are two system configurations available for covering different environmental health and safety needs: the standard (indoor) enclosure, or the advanced (outdoor) enclosure, which includes X-Purge and HVAC capabilities.

The entire system is powered by the Thermo Scientific™ MAX-Acquisition™ Control Software, which offers customizable alarm capabilities, reporting options, and sampling methods. This allows the user to tailor the system to fit their specific requirements. Reports can be generated on an hourly, daily, weekly or monthly basis, and rolling averages can be calculated to provide a comprehensive overview of air quality trends over time.

To ensure the accuracy and reliability of the collected data, the MAX-iAQ incorporates an automated Quality Assurance and Quality Control (QA/QC) system. This system conducts regular checks to validate the integrity of the measurements, eliminating the need for manual intervention and reducing the risk of human error.

The MAX-iAQ is designed for seamless integration into existing systems. It can easily integrate with other monitoring devices and systems using protocols such as Modbus TCP. This allows for efficient data exchange and centralized control. The MAX-iAQ also features analog and digital I/O capabilities for incorporating external devices like audible alarms and flow sensors. The goal of the MAX-iAQ is to make the jobs of operators easier and alleviate the burden of monitoring workplace safety 24/7/365.

Performance study

The following technical data supports the feasibility of StarBoost technology for real-time monitoring of EtO in ambient air at 10 ppb and lower. All assessments described in the following sections were performed using the MAX-iR FTIR Gas Analyzer (Model 101-0440) and MAX-iAQ Ambient Air Monitoring System (Model 101-0480).

Figure 2: MAX-iAQ System with the standard enclosure.

Limit of detection study

The purpose of this assessment was to estimate the lowest-detectable concentration of ethylene oxide above detector noise in a blank sample. For adequate precision at the actionable limit of 10 ppb, the detection limit of the analyzer must be one tenth of the actionable limit, or less than 1 ppb. To determine the limit of detection (LOD) on the MAX-iR Analyzer, the EtO response was measured for 12 consecutive 60-second scans of nitrogen (N_2). The LOD was defined as three times the standard deviation of these measurements. The results are shown in Table 1.

Measurement error and linearity study

Most analytical instrumentation requires continual calibration to provide accurate quantitative results. Optical technologies, such as FTIR and OE-FTIR, are supplied with a quantitative spectral library that is valid for the lifetime of the instrument, meaning the end user does not need to recalibrate the analyzer. The same EtO calibration curve in the spectral library is transferrable between OE-FTIR units.

For quality assurance, the accuracy of each unit should be validated periodically by challenging the system with a certified reference gas.

To assess the measurement error (accuracy) and linearity of the EtO measurement, EtO reference gas was first introduced undiluted into the MAX-iR Analyzer, using a mass flow controller. This direct measurement was used to assess the accuracy of the factory EtO calibration, with no span factor applied.

At approximately 1 ppm (the current OSHA exposure limit as an 8-hour time weighted average), the OE-FTIR was reading within 0.5% of the certified cylinder concentration, which is well within the standard tolerance of ±5%. This demonstrates the accuracy and transferability of the MAX-iR library calibration curve.

The direct measurement was used to calculate the expected dilution levels of the reference gas at three concentrations: a low-level (50–60% of span), a mid-level (70–80% of span), and a high-level (90–100% of span). For this study, the span value was defined as 10 ppb, the actionable level for ambient EtO monitoring as specified in the PID.

Spectrum	Time	EtO (ppb)
LOD 1-Min Scans_0000012.LAB	9/21/2023 15:44	-0.2
LOD 1-Min Scans_0000013.LAB	9/21/2023 15:45	-0.1
LOD 1-Min Scans_0000014.LAB	9/21/2023 15:46	-0.2
LOD 1-Min Scans_0000015.LAB	9/21/2023 15:47	-0.2
LOD 1-Min Scans_0000016.LAB	9/21/2023 15:48	-0.3
LOD 1-Min Scans_0000017.LAB	9/21/2023 15:49	-0.3
LOD 1-Min Scans_0000018.LAB	9/21/2023 15:50	-0.2
LOD 1-Min Scans_0000019.LAB	9/21/2023 15:51	-0.3
LOD 1-Min Scans_0000020.LAB	9/21/2023 15:52	-0.4
LOD 1-Min Scans_0000021.LAB	9/21/2023 15:53	-0.5
LOD 1-Min Scans_0000022.LAB	9/21/2023 15:54	0.1
LOD 1-Min Scans_0000023.LAB	9/21/2023 15:55	-0.3
Average (ppb)	**Std dev (σ) (ppb)**	**LOD (3σ) (ppb)**
-0.2	0.1	0.4

Table 1: Statistical detection limit test raw data.

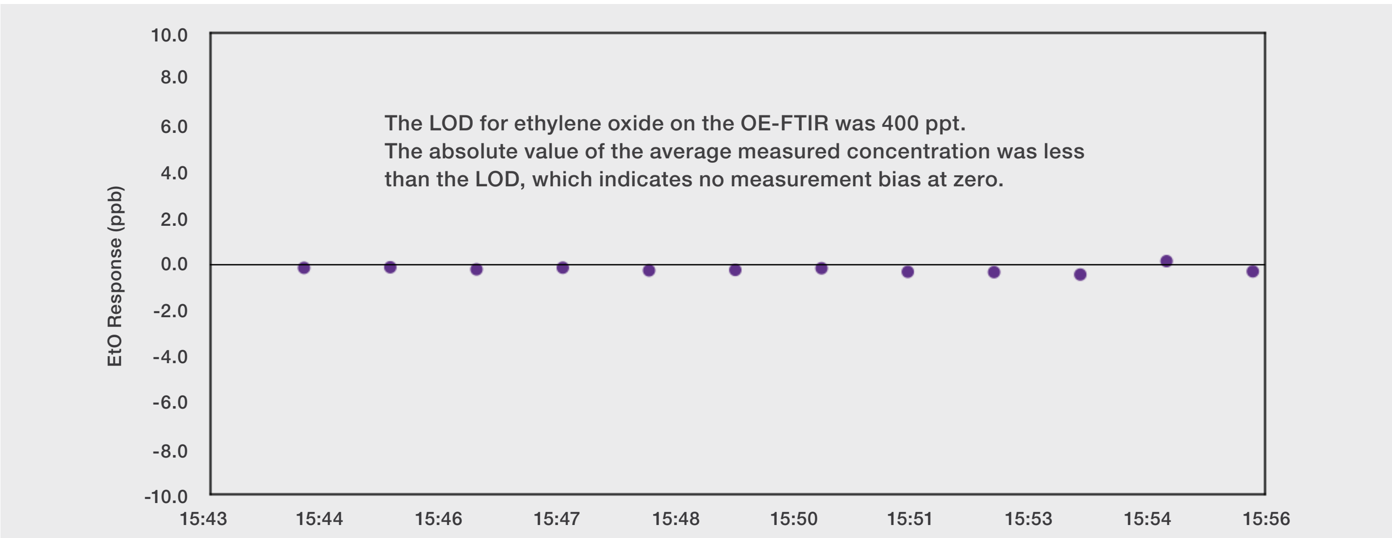


Figure 3: EtO concentration plot during a zero (blank) sample of UHP N_2.

Cylinder ID	Expiration date	Gas	Certified concentration	Analytical uncertainty	Direct measurement	% error
160-402821609-1	8/29/2024	EtO	1020 ppb	±2%	1025 ppb	0.49%

Table 2: Statistical detection limit test raw data.

Dilution information	Units	Zero	Low	Mid	High
Target Concentration	% of span	0%	50–60%	70–80%	90–100%
Ref Gas MFC Setpoint	mL/min	0	50	75	100
Zero Gas MFC Setpoint	L/min	10.00	10.00	10.00	10.00
Dilution Factor	N/A	0.000	0.005	0.007	0.010
Expected EtO Concentration	ppb	0.0	5.2	7.7	10.3

Table 3: Reference gas dilution information.

Each level was measured in triplicate for a total of nine measurements, and 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 (10 ppb).

For each replicate spanning the concentration range of 5–10 ppb, the measured EtO response on the MAX-iR Analyzer was within 5% of the expected concentration. To determine linearity, the expected versus average measured reference gas concentrations were plotted to calculate R_2. The R_2 was 0.9996 for the concentration range of 0–10 ppb.

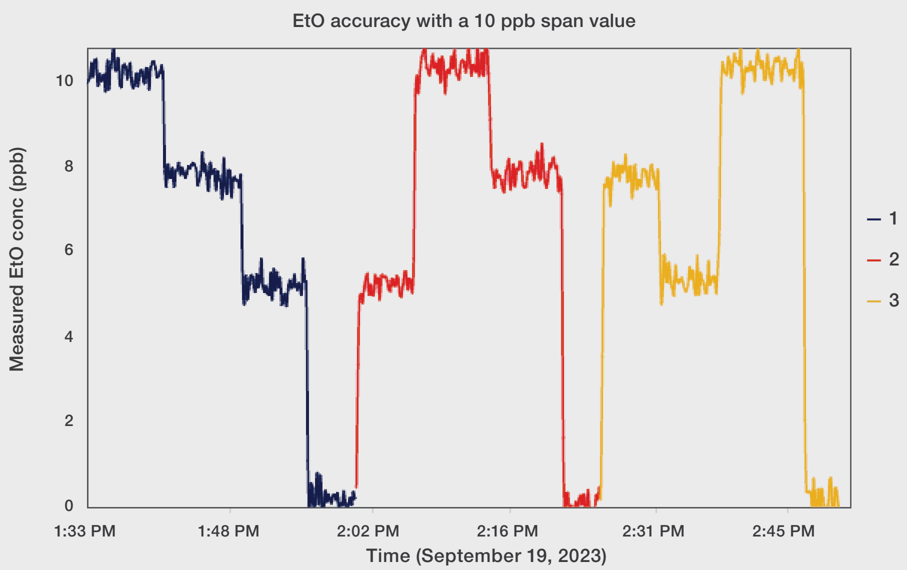


Figure 4: EtO concentration plot during measurement error and linearity study.

		EtO concentration (ppb)		
Level	Replicate	Target	Measured	Error (% of span)
High	1	10.3	10.5	1.88%
Mid	1	7.7	7.7	0.01%
Low	1	5.2	5.4	4.47%
Zero	1	0.0	0.1	~MDL
Low	2	5.2	5.4	4.47%
Mid	2	7.7	7.9	2.73%
High	2	10.3	10.7	4.31%
Zero	2	0.0	0.0	~MDL
Mid	3	7.7	7.9	1.82%
Low	3	5.2	5.4	5.05%
High	3	10.3	10.5	2.46%
Zero	3	0.0	0.1	~MDL

Table 4: Ethylene oxide accuracy at 5–10 ppb.

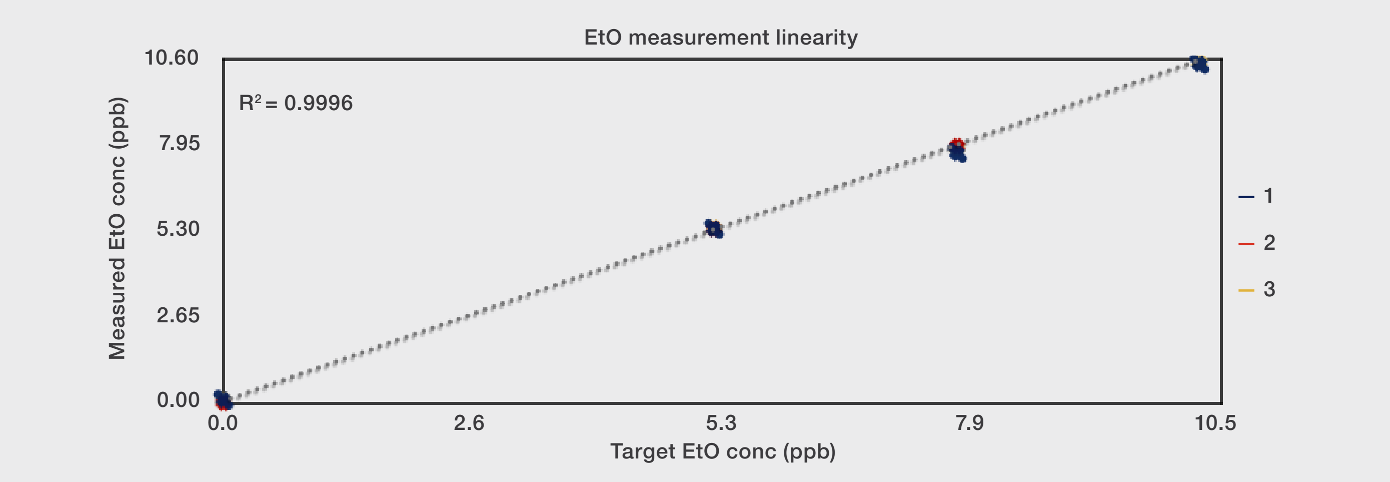


Figure 5: Ethylene oxide linearity over the concentration range of 0–10 ppb.

Repeatability study

A repeatability study was performed to demonstrate the precision of the ethylene oxide measurement near the actionable limit. One ppb of EtO reference gas was injected into a N_2 stream and sampled by the MAX-iR Analyzer at a 10-second scan rate. A total of nine, 1 ppb spikes were performed.

The average EtO concentration of each injection (excluding necessary equilibration time) and the relative standard deviation (RSD) of the measured EtO spike concentrations were calculated.

When measuring 1 ppb of EtO, the MAX-iR Analyzer had a relative standard deviation of 4.8%, demonstrating high precision and consistency at the trace levels required for monitoring workplace safety.

Replicate number	EtO concentration (ppb)
1	1.0
2	1.0
3	1.0
4	0.9
5	0.9
6	1.0
7	1.0
8	1.0
9	1.0
Relative standard deviation	4.8%

Table 5: Ethylene oxide repeatability results.

Spiking validation study

It's important to understand how an air monitoring system performs when challenged with a complex yet realistic sample matrix. To further confirm the precision of the MAX-iR Analyzer when measuring trace-level EtO, a spiking validation test was performed. Ethylene oxide reference gas was injected into a simulated ambient air matrix with approximately 2% moisture and 1 ppm methane.

The span level was identified as 5 ppb, and the EtO stream varied from the high (90–100% of span), medium (50–60% of span), and low (20–30% of span) levels at 5, 3, and 1 ppb, respectively. This process was replicated three times. The concentration results are displayed in the chart here.

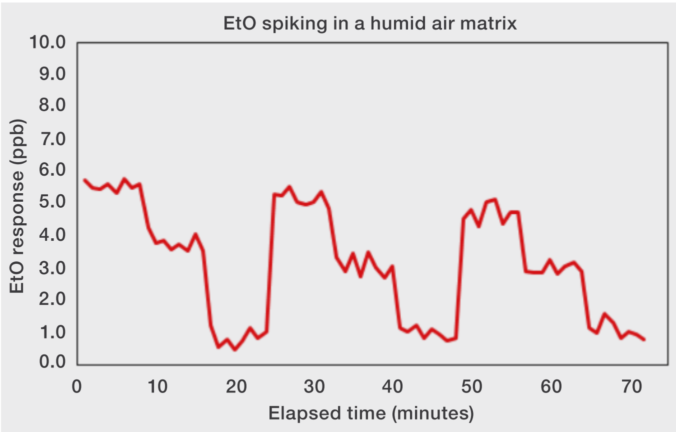
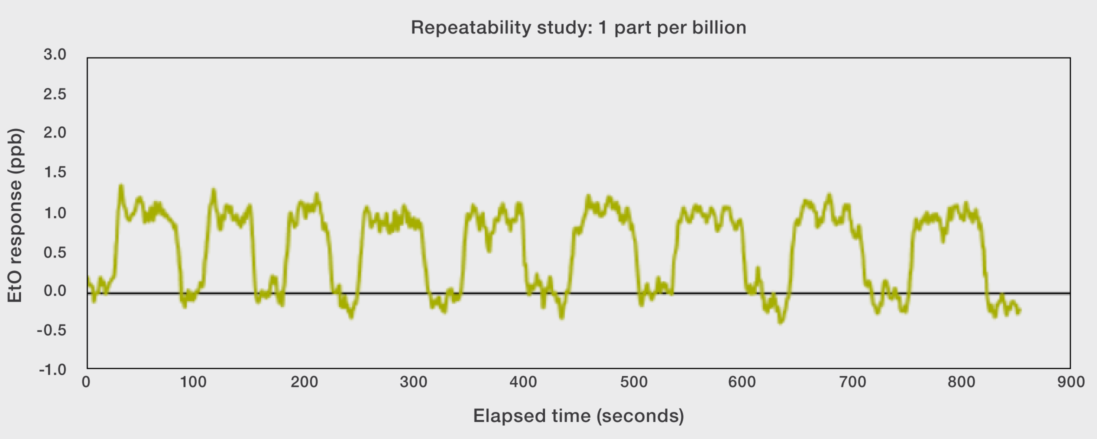


Figure 7: Spiking 5, 3, and 1 ppb of EtO Diluted in N_2 into 2% moisture and 1 ppm methane.

Figure 6: One ppb of EtO in spiked into UHP N_2 repeatability study



The error (% of span), average, and standard deviation of the moisture, methane, and ethylene oxide measurements at each level were calculated. See Table 6 below for a summary of the results.

The MAX-iR Analyzer demonstrates high precision, accuracy, and repeatability when measuring EtO in ambient air at concentrations as low as 1 ppb. Hydrocarbons and ambient humidity do not interfere with the MAX-iAQ's ability to quantify ethylene oxide.

The dynamic range of the MAX-iR Analyzer enables EtO to be measured in varying environmental conditions. The MAX-iR Analyzer provides the end user with a robust, reliable analytical option that instills confidence in data quality when faced with a challenging sample matrix.

Interference study

An interference study was performed to determine the effect of cross-interferences in the sample matrix on the EtO measurement. The primary spectral interferences for OE-FTIR technology are methane and water vapor. While other atmospheric gases, such as carbon dioxide or acetaldehyde, may be present in the sample matrix, they do not have IR absorbance features within the OE-FTIR spectral range.

This interference test was performed following the procedure in US EPA PS-19 Section 11.1. The table below provides a summary of the interferents analyzed in this study.

Interferent gas	Interference concentration
CO_2	1 ± 0.2%
CH_4	20 ± 5 ppm
H_2O	5 ± 1%

Table 7: Interference gases.

1 ppm of EtO reference gas was diluted to 50 ppb in zero gas. This measurement was recorded as the EtO concentration without interferences added. Next, the interference gases were added into the sample stream while maintaining a constant ethylene oxide concentration and total sample flow rate. The EtO was measured with and without interference gas in three replicates.

For each interference gas, the percent interference and total interference response was calculated according to US EPA PS-19 Section 12.2. The results of the interference test are provided in Table 8.

Replicate	Target ethylene oxide	Calculation	H2O (ppmv)	CH4 (ppmv wet)	Measured ethylene oxide (ppbv wet)	Error (% of Span)
1	5.1	Average	19316.1	0.9	5.7	10.8%
		Std Dev	26.6	0.0	0.3	
		3x Std Dev	79.7	0.0	0.9	
	3.1	Average	19288.0	1.0	3.5	12.0%
		Std Dev	50.5	0.0	0.4	
		3x Std Dev	151.5	0.0	1.2	
	1.0	Average	19190.6	1.0	1.0	2.7%
		Std Dev	48.9	0.0	0.3	
		3x Std Dev	146.8	0.0	1.0	
2	5.1	Average	17513.3	0.9	5.2	1.7%
		Std Dev	20.2	0.0	0.2	
		3x Std Dev	60.6	0.0	0.7	
	3.1	Average	17324.1	0.9	3.2	4.4%
		Std Dev	30.2	0.0	0.4	
		3x Std Dev	90.6	0.0	1.1	
	1.0	Average	16615.3	0.9	1.1	11.0%
		Std Dev	16.9	0.0	0.3	
		3x Std Dev	50.8	0.0	0.9	
3	5.1	Average	16416.8	0.9	4.7	-8.7%
		Std Dev	33.0	0.0	0.3	
		3x Std Dev	99.1	0.0	1.0	
	3.1	Average	16323.6	0.9	3.0	-4.9%
		Std Dev	15.4	0.0	0.1	
		3x Std Dev	46.1	0.0	0.4	
	1.0	Average	16293.1	0.9	1.1	11.9%
		Std Dev	21.3	0.0	0.2	
		3x Std Dev	63.9	0.0	0.7	

Table 6: Spiking validation study summary of results.

US EPA PS-19 Section 11.1 interference test results				
Interference gas	EtO concentration (ppbv)	EtO concentration with intf added (ppbv)	Absolute difference ppbv)	Average absolute Difference amc avg (ppbv)
20± 5ppm Methane 5 ±% Water	49.9 49.6 50.0	49.1 49.8 50.2	0.8 0.3 0.1	0.4
Sum of interference responses (ppb)			0.39	PASS

Table 8: Interference study results.

At 50 ppb of EtO, these levels of CO_2, CH_4, and H_2O bias the measurement by approximately 0.4 ppb. Please note that the concentrations of interference gases required by PS-19 are much higher than what would be expected in an ambient air sample. The normal, ambient concentrations of these interferences would have a lower total response than 0.4 ppb.

Results and Conclusions

The MAX-iAQ Ambient Air Monitoring System, configured with StarBoost technology, creates an ideal solution for monitoring low-level EtO emissions from commercial sterilization and chemical manufacturing facilities. With a limit of detection below 1 ppb and proven resilience against background interferences, the MAX-iAQ stands out as the optimal solution for monitoring EtO to ensure workplace safety.

Table 9 provides a summary of the performance criteria and manufacturer recommendations used to evaluate the OE-FTIR for the measurement of ethylene oxide at low parts-per-billion levels in ambient air. The data presented in this application note demonstrate the ability of the technology to meet and exceed the 10 ppb actionable limit described in the US EPA Proposed Interim Decision for ethylene oxide.

Test	Measurement	Result
Limit of detection	3σ	0.4 ppb
Accuracy	Ave error (% of Span)	3.0%
Linearity	R^2	0.9996
Repeatability	RSD	4.8%
Sum of interference responses	$\Sigma\Delta MC_{avg}$	0.4 ppb

Table 9: Summary results

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