CONTINUOUS FENCELINE MONITORING OF ETHYLENE OXIDE WITH FTIR SPECTROSCOPY UNDER THE HON MACT AMENDMENTS

Fabiano de Melas
AVL Analytical Technologies GmbH
Process & Environment
Neuss – Germany

Bertold Arlitt
AVL Analytical Technologies GmbH
Process & Environment
Gaggenau – Germany

(Corresponding E-Mail: fabiano.demelas@avl.com)

KEYWORDS

Fourier Transform Infrared Spectroscopy; FTIR CEMS; Ethylene Oxide; EtO; Fenceline Monitoring; NESHAP; HON MACT; EPA Method 327; PS-19; Multi-component Analysis.

ABSTRACT

The U.S. Environmental Protection Agency (EPA) has proposed significant amendments to the National Emission Standards for Hazardous Air Pollutants (NESHAP) for the Chemical Manufacturing Industry, introducing stringent requirements for continuous fenceline monitoring of hazardous air pollutants (HAPs), including ethylene oxide (EtO). Among the most promising technologies for real-time, decision-useful monitoring are optical based technologies such as Fourier Transform Infrared (FTIR) spectroscopy and Cavity Ring-Down Spectroscopy (CRDS). This abstract summarizes recent demonstrations and performance benchmarks from the literature and industry, compares achievable limits of detection (LOD) and data quality parameters for EtO, and embeds representative laboratory results from the AVL PA-FTIR C50 platform.

Extractive FTIR provides broadband, multi-component quantification governed by the Beer–Lambert law, with sensitivity boosted by long effective pathlength gas cells, low-noise MCT detection, and careful selection of spectral windows to minimize interferents (e.g., 3350–2850 cm^{-1} for EtO). Optically enhanced FTIR (OE-FTIR) implements an interferometer with an InAs (Indium Arsenide) detector and proprietary optical filtering to increase signal-to-noise, enabling single-digit-ppb EtO detection and short cycle times in multi-channel CEMS configurations. Field and laboratory published FTIR vendor data (1) report statistical LODs below 1 ppb with excellent linearity, and stable baselines suitable for EPA Performance Specification 19 (Performance Specifications and Test Procedures for Ethylene Oxide Continuous Emission Monitoring Systems) style validation.

For comparison, EtO-tuned CRDS analyzers achieve sub-ppb LODs with fast response and very low drift, making CRDS attractive for stationary fenceline, multi-point, and mobile monitoring. Published vendor data and field deployments report LODs near 0.25 ppb with very fast response and months-long calibration intervals.

This paper extends the original abstract by: (i) detailing FTIR principles and recent demonstrations for EtO on the AVL FTIR spectrometer PA-FTIR C50, (ii) summarizing CRDS fenceline performance, and (iii) presenting a concise comparison across LOD, linearity, multi-component coverage, and multi-stream sampling.

AVL's laboratory results are imbedded, including ~1 ppb EtO LOD in a 5 m hot cell at 150 °C and multi-stream sequencing representative of perimeter deployments.

1. INTRODUCTION

Hazardous Air Pollutants (HAPs) such as ethylene oxide (EtO) pose significant health risks and have become a central focus of evolving air-quality policy and community expectations. EtO's high reactivity, lack of odor, and carcinogenicity make real-time monitoring essential at facility perimeters to detect fugitive releases and to enable timely mitigation. Fenceline monitoring complements stack compliance programs by offering perimeter-level evidence of off-site impacts and by enabling rapid root-cause analysis of intermittent emission events.

Recent U.S. regulatory developments—specifically the 2024 revisions to the Hazardous Organic NESHAP (HON) rule—introduce fenceline monitoring expectations for EtO and other HAPs at organic chemicals and polymer manufacturing sites. While EPA Method 327 (Fugitive and Area Source Measurement of Selected Volatile Organic Hazardous Air Pollutants Using Specially Prepared Canisters) prescribes time-integrated, 24-hour canister sampling at eight perimeter points every five days, the regulation highlights the value of real-time instrumentation to resolve temporal variability and identify sources more effectively.

Among available real-time technologies, Fourier Transform Infrared (FTIR) spectroscopy and Cavity Ring Down Laser Spectroscopy (CRDS) and are well suited to fenceline applications.

2. REGULATORY CONTEXT AND PERFORMANCE TARGETS

Under the HON amendments, facilities must implement fenceline programs that include EtO. Method 327 stipulates 24-hour, every-five-day sampling at eight evenly spaced perimeter points using SUMMA canisters; action levels include (i) an annual rolling average of 0.2 μg m^{-3} and (ii) an 8-hour TWA of 100 ppb. While this approach establishes baseline compliance, it cannot characterize short-lived events or provide immediate diagnostics, motivating complementary real-time monitoring.

Instrumental systems deployed for compliance or supplemental monitoring are aligned with EPA Performance Specification 19 (PS-19), emphasizing calibration, linearity, bias/precision, drift, and response time over the intended concentration range. Properly configured FTIR platforms can meet these criteria while providing multicomponent coverage and second-to-minute reporting intervals.

3. PRINCIPLE OF FTIR MEASUREMENTS FOR EtO

FTIR (2) measures broadband infrared absorption; quantitative analysis follows the Beer–Lambert law:

$$A = a\,b\,c \tag{1}$$

Where A = absorbance; a = molar absorptivity; b = optical path length; c = gas concentration.

For EtO, characteristic molecular absorption peaks occur in the mid-IR; sensitivity is enhanced by long effective path lengths via multi-reflection gas cells, low-noise MCT detectors, and optimized spectral windows with minimal interferents. Hot/wet operation mitigates condensation and stabilizes spectral baselines for water-containing streams typical of industrial fencelines.

4. INSTRUMENTATION AND METHODS

Both FTIR and CRDS represent viable on-line optical analytical technologies and are suitable for industrial use as summarized in **TABLE 1.**

FTIR has been recently shown (3) to potentially achieve single-digit-ppb EtO detection with rapid cycle times and 1- or 4-channel multiplexing for EtO analysis. Reported laboratory detection limits at room temperature are ranging between 2 and 3 ppb (3) and in some circumstances where even shown to reach LOD <1 ppbv in nitrogen and $\lesssim$1 ppbv in simulated stack matrices, with EtO linearity characterized by $R^2 \approx 0.9998$ across relevant ranges (4). These advanced FTIR configurations are beeing exercised

in field trials at commercial sterilization facilities and positioned as an alternative to GC-based methods for EtO CEMS.

Modern EtO-specific CRDS analyzers used for stationary fenceline, mobile surveys, and multi-point monitoring report limits of detection near 0.25 ppb (5) with response times of a few seconds. High linearity over a wide dynamic range is key and it is very often associated with very low drift enabling infrequent calibration, and turnkey operation suitable for multi-point systems (6).

TABLE 1. Comparison: Extractive hot FTIR (AVL PA-FTIR C50), and CRDS for EtO measurements.

Parameter	**Extractive hot FTIR**	**CRDS/EtO-tuned (5)**
Achieved LOD (EtO)	~1 ppb (lab, 5 m hot cell, 150 °C; 90 s cycle)	~0.25 ppb to 1 ppb
Measurement temperature	150°C - Hot/wet operation minimizes memory effects; stable baselines	80°C
Multi-component capability	Yes: broadband FTIR quantifies multiple HAPs simultaneously	Typically single/limited analytes per laser
Multi-stream capability	Yes supported via external multi-point samplers (sequential) streams	Yes: supported via external multi-point samplers

FTIR measures multiple compounds simultaneously, supports multi-stream sampling, and can meet U.S. performance specifications for instrumental methods (PS-19) when properly validated. AVL FTIR platforms can address both stationary and mobile deployments: a stationary wall-mounted FTIR C50 platform is suitable for outdoor/sheltered installation with capability to work with a multi-stream sequential sampling, while a compact portable variant (PA-FTIR C50) can be deployed for spot checks, mobile surveys or small foot-print sheltered installation. Both provide

multi-compound capability and are designed to satisfy PS-19 performance expectations when validated, reducing operational complexity by consolidating target HAPs into a single optical analyzer.

The compact FTIR version has been the preferred choice by AVL to obtain the presented results. More specifically an advanced PA-FTIR C50 setup (5 Hz acquisition) with a 5.0 m hot multi-reflection gas cell at 150 °C, a thermo-electrically cooled high-D* MCT detector, and a spectral window of 3350–2850 cm^{-1} has been used for the present measurement campaign of this paper.

A high-D* MCT detector is a very sensitive infrared detector designed to pick up very weak signals (**FIGURE 1**). D* ("detectivity") indicates how well the detector can distinguish real absorption from noise: the higher the D*, the lower the noise floor and the better the sensitivity. A thermo-electrically cooled MCT detector reduces thermal noise, which further increases D* and improves signal-to-noise ratio.

For EtO measurement, this matters because the absorption features used for analysis—located in the 3350–2850 cm^{-1} range—are relatively weak. A high-D* detector makes these small features stand out clearly, enabling ppb-level detection and stable quantification even in the presence of water vapor or other interfering gases. In short: higher D* means cleaner spectra and expected lower detection limits.

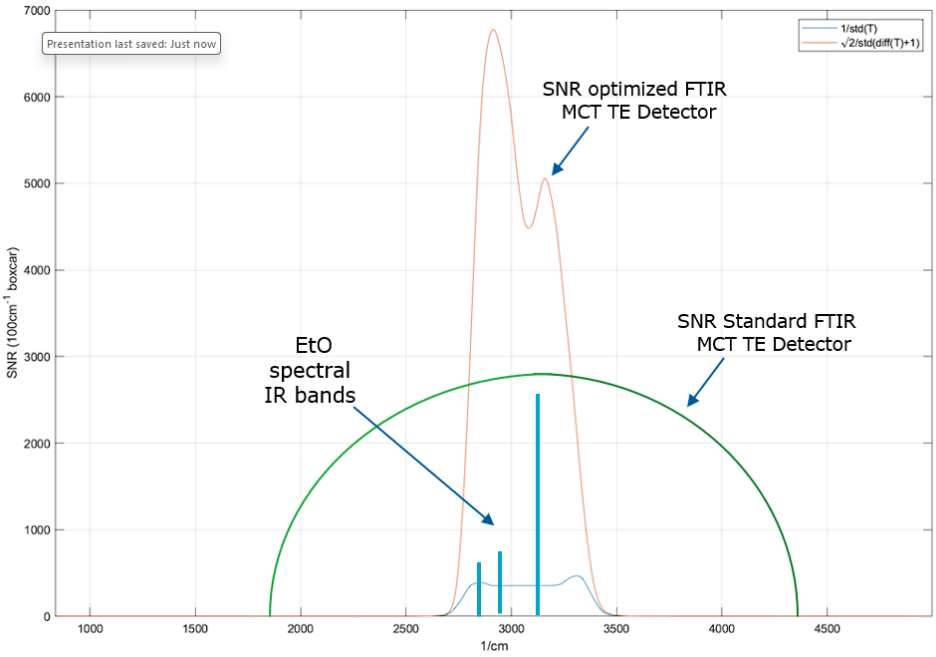

FIGURE 1. Spectral range of a thermo electrically cooled (TEC) high D*- MCT detector used on the AVL PA-FTIR C50.

A system as the one shown in **FIGURE 2** has been deployed for several laboratory tests at AVL Analytical Technologies. A 9.78 ppm EtO reference mixture was serially diluted (**FIGURE 3**) in nitrogen to ppb-level test points.

The optical setup of the used FTIR is based on a Michelson Interferometer coupled with a heated multi-reflection cell (**FIGURE 4**). Multi-component spectra were recorded continuously at 5 Hz to assess response, stability, and achievable LOD. The deployed FTIR is embedded in a compact enclosure suitable for both laboratory and harsh outdoor environment (**FIGURE 5**). The parameters used on the FTIR during the whole experimental work are summarized in **TABLE 2.**

TABLE 2. DEPLOYED FTIR C50 PERFORMANCE SUMMARY

Parameter	Value/Setting	Notes
Optical path length	5.0 m	Multi-reflection hot cell
Cell temperature	150 °C	Hot/wet operation
Acquisition rate	5 Hz	PA-FTIR mode
Spectral window	3350–2850 cm^{-1}	EtO features, low interference
Detector	MCT (TE-cooled), high-D*	Low noise regime
LOD on EtO	~ 1 ppb	3σ criterion in zero gas
Response behavior	~1 averaging interval	Step changes resolved at 5 Hz

Spectra were processed using least-squares fitting against EtO reference features within the selected window; the LOD was obtained from the standard deviation of the baseline in zero gas and the calibration slope at the operating temperature, adopting a 3σ criterion. Temperature influence online strength and baseline noise was assessed through controlled steps and hold periods.

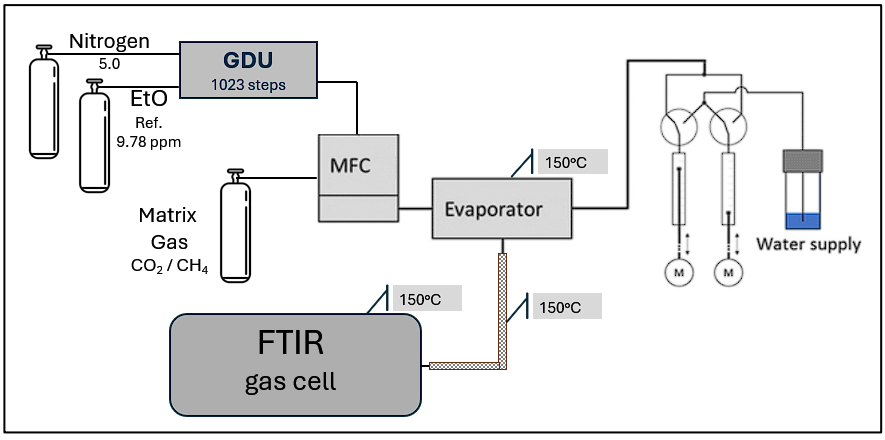

FIGURE 2. Experimental Analytical Setup.

FIGURE 3. Gas Dividing Unit AVL (GDU) deployed for EtO dilutions.

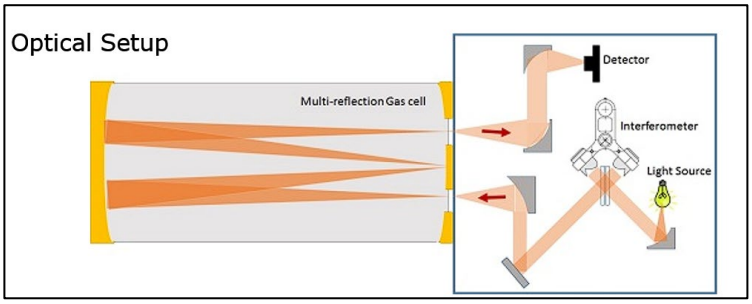

FIGURE 4. Optical Setup.

FIGURE 5. AVL Advanced PA-FTIR C50 (left side) used in the experimental setup

5. RESULTS

The PA-FTIR C50 achieved ppb-level sensitivity to EtO, with detection limits near 1 ppb in controlled laboratory conditions. The combination of a 5.0 m hot cell, high-D* MCT detection, and optimized windows was decisive for reaching this LOD.

An Air Liquide Ethylene oxide 9,78 Mol-ppm with an uncertainty of ± 5% rel. was used to generate a sample set of EtO reference standard with a gas divider (AVL GDU SL 1023), as an example **FIGURE 6** shows the IR adsorption features of the molecule for a 1.23 ppm concentration standard.

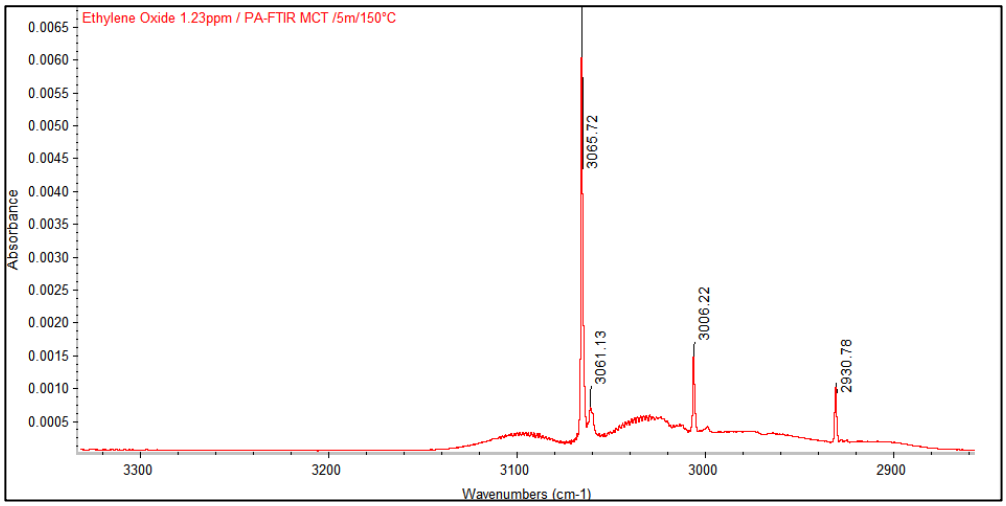

FIGURE 6. Spectrum IR band of EtO between 2850 to 3350 cm-1

All relevant EtO absorption bands, labeled by their wavenumbers, are evaluated using multivariate spectral analysis via the multi-reference standard AVL iQT quantification software. This approach leverages the full spectral fingerprint of ethylene oxide for robust quantification across the target application. The software's advanced fitting algorithm ensures precise deconvolution of overlapping features, enhancing measurement accuracy and selectivity.

FIGURE 7 shows the Allan deviation of repeated zero-gas measurements, showing how the instrument's noise changes when the signal is averaged for different lengths of time. When the averaging time is short, the noise gets smaller as we average longer—this is because the noise is mostly *white noise* (random noise). After a certain point, the noise starts to rise again, which means the instrument begins to drift. In a system dominated by white noise (the ideal state for averaging), the standard deviation of the measurements decreases with the square root of the number of samples (N) or the integration time (τ). The formula for the Allan Variance, $\sigma^2_y(\tau)$, is:

$$\sigma_y^2(\tau) = \frac{1}{2(M-1)} \sum_{i=1}^{M-1} (\bar{y}_{i+1} - \bar{y}_i)^2$$

Where: τ is the averaging time, $\tilde{y}_i$ is the average concentration of the i-th block of data, and M is the number of data blocks.

The lowest noise level for EtO appears at an averaging time of 90 seconds. At this point, the detection limit is 0.6 ppb. This tells us that 90 seconds is the best averaging time and shows the lowest EtO concentration the instrument can reliably measure.

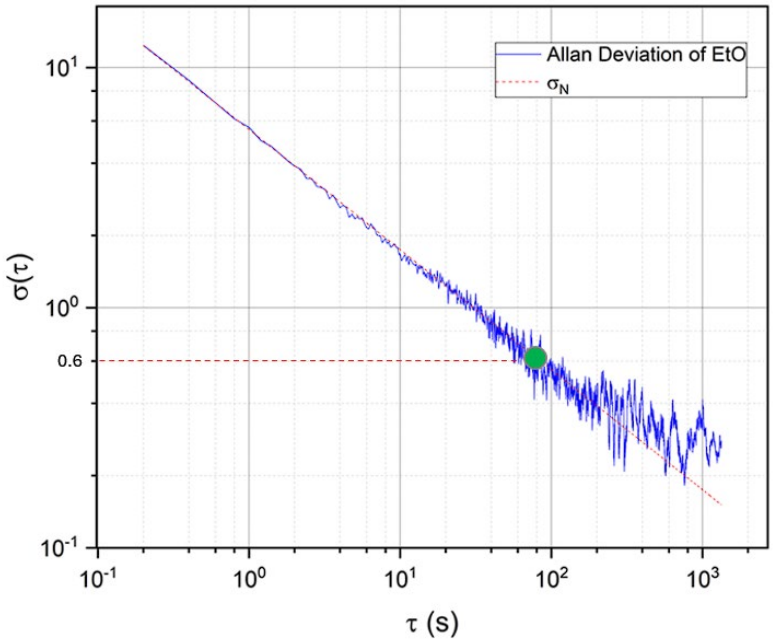

FIGURE 7. Allan Deviation Plot of EtO in (ppb)

A dedicated calibration strategy employing humidity-enriched gas standards was implemented (**FIGURE 8**) to correct for spectral interference and matrix effects induced by water vapor in this spectroscopically demanding application. The calibration spans the full humidity range relevant to the target measurements, allowing the water-vapor contribution to the absorption spectrum to be isolated and parameterized. Incorporation of this parameterization into the retrieval algorithm enables robust compensation for humidity effects, thereby reducing humidity-induced bias and drift and improving the effective detection limit under realistic, high-humidity sampling conditions.

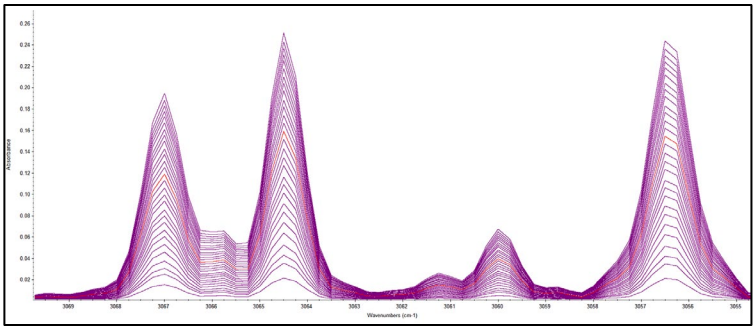

FIGURE 8. Calibration sample set of H2O refence standards

The 5 Hz acquisition enabled second-scale trend visibility. Step changes in concentration as shown in **FIGURE 9** were resolved within one averaging interval, supporting rapid leak detection and event attribution in fenceline scenarios. Operation at 150 °C minimized adsorption/desorption effects and condensation, improving baseline stability and reducing memory effects during low-ppb transitions. Eight different steps have been carried out and summarized in **TABLE 3.**

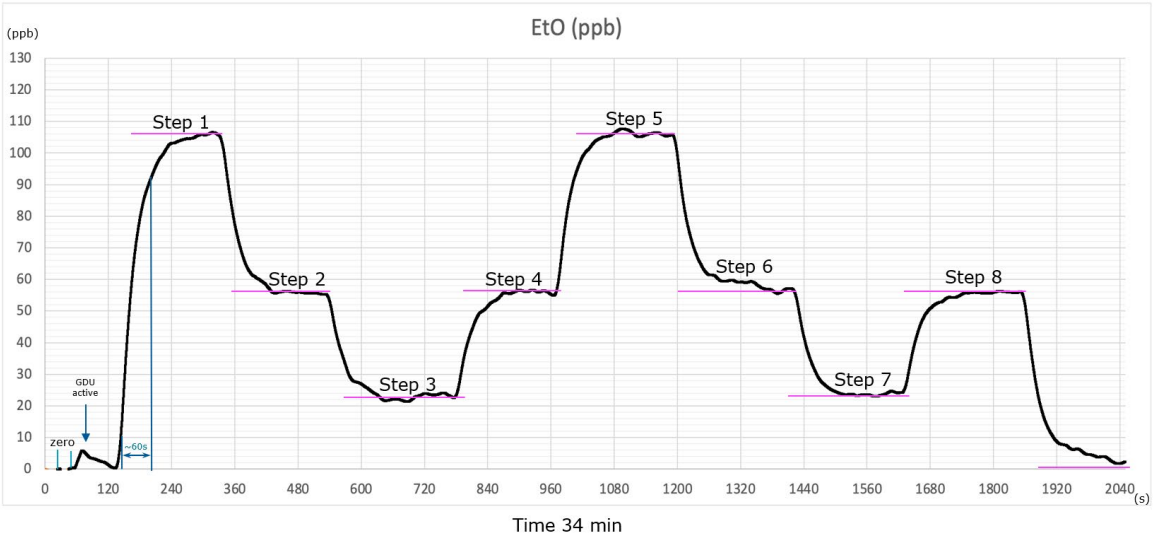

FIGURE 9. Laboratory Test results showing measurement steps.

TABLE 3. CONCENTRATIONS STEPS.

STEP	Value (ppb)
1	103
2	56
3	23
4	56
5	103
6	56
7	23
8	56

6. DISCUSSION

Real-time FTIR addresses key limitations of time-integrated canister methods by providing continuous temporal coverage for intermittent emissions, enabling multistream spatial coverage without field redeployment, and delivering near-instantaneous data to support maintenance actions and community communication. These capabilities align with the HON rule's emphasis on more protective monitoring and strengthen compliance programs that still incorporate Method 327 for recordkeeping.

To be decision-useful at the fenceline, EtO LODs should be significantly below action levels so that short events or low-level background enhancements are detectable with confidence. The demonstrated ~1 ppb LOD provides ample margin relative to the 100 ppb 8-hour TWA action level and supports early warning and root-cause analysis.

A single FTIR platform can track EtO alongside co-emitted HAPs, enabling correlation analyses that point to process units or operating states. Consolidating targets reduces consumables and maintenance compared with multiple single-species analyzers, while PS-19-style QA/QC ensures traceable performance.

7. CONCLUSIONS

FTIR spectroscopy provides a robust, real-time, multicomponent approach to fenceline monitoring of EtO, complementing Method 327 and aligning with PS-19 performance expectations.

Laboratory characterization with a 5.0 m, 150 °C hot cell and high-D* MCT detection on an AVL PA-FTIR C50 analyzer demonstrated EtO LODs near 1 ppb, suitable for early leak detection and for maintaining margin relative to EPA action levels.

Temperature control is critical to accuracy and response time by stabilizing baselines and minimizing surface interactions in hot/wet operation, thereby improving low-ppb quantitation.

Combining stationary multi-stream FTIR with portable screening supports continuous perimeter visibility, rapid incident response, and proactive environmental stewardship under evolving regulatory expectations.

ACKNOWLEDGMENTS

The authors acknowledge the AVL Analytical Technologies team for laboratory testing and the internal reviewers for manuscript feedback in accordance with ATC best-practice guidelines.

REFERENCES

1. O. Madamba (2023), A&WMA Air Quality Measurement Conference - Applying OE-FTIR for Compliance with Ethylene Oxide Emissions Test Methods
2. Griffiths, P. R., & de Haseth, J. A. (1986). Fourier Transform Infrared Spectrometry. John Wiley & Sons - ISBN: 0-471-09902-3
3. F. de Melas, B. Arlitt, A. Heiden (2025), IMM Conference - HAPs Real-Time Fenceline Monitoring with FTIR Spectroscopy
4. Thermo Fisher Application Note (2025): Ethylene oxide continuous emissions monitoring by OE-FTIR
5. Picarro: Service/Support page for EtO monitoring and CRDS specifications.
6. Sonoma Technology (2025): Considerations for Ethylene Oxide Instrument Selection