White Paper

# Carus and Picarro: Proving Remarkable Catalyst EtO Removal with Cutting-Edge Measurement Technology

*Figure 1. Picarro's EtO CEMS system and Carus's CARULITE® 500 granules. Picarro's Cavity Ring-Down Spectrometer systems were used to evaluate the remarkable destruction efficiency of CARULITE® 500 in this important white paper.*

## Summary

Carus LLC[I] produces a wide array of industry-leading catalyst products for industrial abatement systems. Its CARULITE® 500 product is used extensively in catalytic oxidizer systems to abate a variety of hazardous air pollutant and volatile organic compounds at the stack, and it is of particular importance in catalytic oxidizer abatement systems for ethylene oxide (EtO, EO). While CARULITE® 500 is an industry-leading product, 2024 revisions to the EPA's EtO NESHAP (40 CFR Pt. 63 Subpart O for EtO)[II] and the new accompanying Performance Specification 19 ("PS-19")[III] have set significantly more aggressive stack emissions requirements for commercial sterilizers using EtO. To date, regulators in the US have proposed and passed levels that would limit stack emissions to as low as 0.015 lb/hr on a rolling 30-day basis, to be verified either by a continuous maximum 10 ppb stack EtO concentration, or a demonstrated 99.99% abatement system destruction efficiency (South Coast AQMD, Proposed Amended Rule 1405)[IV]. This white paper describes destruction efficiency testing run by Carus and Picarro, Inc.[V] on Carus's CARULITE® 500 catalyst media using Picarro's Ethylene Oxide Cavity Ring-Down Spectrometer (CRDS)[VI] technology. Picarro's technology provides industry-leading sensitive, accurate, and virtually drift-free measurements at levels reaching below a part per billion, making it an excellent choice for studies where high levels of destruction efficiency need to be characterized and confirmed.  Measurements were run in a lab setting using an EtO standard blended to between 100 and 1000 ppm—concentrations typically seen by Catalytic Oxidizer systems during active batch sterilization. We describe a tracer method using $CH_4$, $H_2O$, and $CO_2$ to confirm flow of the process gas to the analyzer, and we show that CARULITE® 500 handily outperforms even the strictest regulatory standards in both destruction efficiency and effluent concentrations, with average observed destruction efficiency of 99.99988% and average outlet concentrations of 0.2 ppb across inlet concentrations.

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## Introduction

Ethylene Oxide ("EtO", "EO") is an essential sterilant gas and chemical precursor/intermediate used widely across industries like refining[VII], food processing[VIII], and medical device sterilization[IX]. Because of its ability to non-destructively and rapidly penetrate through many materials to kill microbes, it functions as an indispensable sterilization method for medical devices like pacemakers and spinal cord stimulators which cannot tolerate sterilization by irradiation, steam, or other alternatives. In fact, EtO is so effective that it is used to sterilize more than half of all medical devices sold in the United States each year—over 20 billion[X]—securing its spot as the technological backbone behind the safe sterilization of life-saving medical equipment.

In recent years, concerns about EtO's carcinogenicity have led to heightened scrutiny from community groups, industry workers, and regulators. This in turn has led to a series of new regulatory measures aimed at minimizing EtO emissions and occupational exposure. These measures, which will be enacted and enforced variously between 2024 and 2026, come chiefly from the United States Environmental Protection Agency (US EPA), and include: a) the revised EtO NESHAP (40 CFR Pt 63 Subpart O)[II], b) Performance Specification 19 (PS-19)[III] for source emissions monitoring, and c) the FIFRA Proposed Interim Decision for workplace and lifetime exposure[XI]. They also include distinct measures by local, statewide, regional, and other international authorities[IV], though many of these bodies follow the US EPA guidelines. These rules and measures necessitate a reevaluation of emissions containment and abatement strategies across the United States and the world. Companies employing EtO are directed to implement emissions management systems with the highest quality modern abatement materials, designed with regulatory compliance in mind. Proactive upgrades to these systems and materials, combined with intelligent monitoring, are crucial for industries to align with EPA and other international requirements before the 2024-2026 deadlines.

CARULITE® 500 efficiently converts EtO to carbon dioxide and water at 150°C with no toxic byproducts, to meet stringent regulatory discharge limits.

## Methods and Materials

### *Carus CARULITE® 500*

Carus has been providing innovative chemical products out of Starved Rock County, IL for over a century. Its CARULITE® 500 catalyst (see Figure 1) is used worldwide in abatement systems for the destruction of ethylene oxide. The catalyst effectively converts EtO to carbon dioxide and water at 150°C in a properly designed system, to meet stringent regulatory discharge limits.

Picarro's systems are provided as leased managed service agreements, providing facility managers with confidence that they will always have a well-maintained, up to date, and regulatorily-compliant system managed by Picarro's Environmental Systems team experts.

### *Picarro EtO Systems and Solutions*

Because very few ethylene oxide instruments have the lower detection limits to establish four nines of destruction efficiency (99.99%) for concentrations of EtO between 100 and 1000 ppm, Carus partnered with Picarro Inc, an industry-leader in analytical instrumentation, whose Cavity Ring-Down Spectrometers and spectrometer systems are used across the world to measure hazardous air pollutants and greenhouse gases at trace levels. Picarro offers a suite of ethylene oxide systems seen at www.picarro.com/eto that allow industry to monitor within the workplace at up to 25 points, at the stack for continuous emissions monitoring, at the fenceline, and around the facility to assess regulatory and health risks. Picarro's systems are provided as leased managed service agreements, providing facility managers with confidence that they will always have a well-maintained, up to date, and regulatorily-compliant system managed by Picarro's Environmental Systems team experts.

***Figure 3.*** *Picarro EtO Systems, all of which feature Cavity Ring-Down Spectrometers for fast, sensitive EtO reporting to help industry achieve and maintain regulatory compliance.*

## *Picarro Cavity Ring-Down Spectrometer*

Picarro's stack EtO instrument has a guaranteed lower detection limit of 0.25 ppb, and has industry-leading stability and selectivity for EtO, as well as fast response and a one-second measurement interval. It also reports highly precise concentrations of $CH_4$, $CO_2$, and $H_2O$, which allow for validation of destruction efficiencies through passive and stoichiometric-ratio tracer methods. Picarro instruments are carefully calibrated to handle complex gas matrices expected at the stack, in workplaces, and in ambient air, providing a powerful tool for industry to assess facility health and risk, and prove regulatory compliance.

***Figure 4.*** *Picarro Cavity Ring-Down Spectrometer EtO Instrument, present at the heart of all Picarro EtO systems and solutions.*

## *Testing Apparatus*

Carus's reactor column testing apparatus (see Figure 5) simulates the design of commercially available catalytic oxidizers. It features a 150°C air preheater necessary to preheat the catalyst bed before it encounters the EtO. Air then flows downward through the packed bed (102 g/120 ml of CARULITE® 500, held in place by refractory material), also at 150°C. Temperature control of the two components was handled through setpoint rheostat and temperature controller systems, respectively, and temperature was monitored during the testing to ensure the apparatus stayed at 150° ± 20°C, with deviations allowed only for short periods of time as the apparatus warmed due to exothermic destruction of EtO.

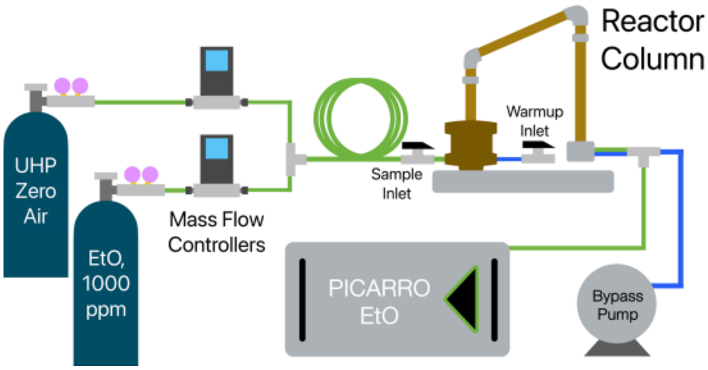

***Figure 5.*** *Experimental test apparatus design, using Carus test reactor column, and Picarro EtO Analyzer measuring the column effluent to verify the destruction efficiency of the CARULITE® 500 catalyst, showing variously the* ***warmup*** *and* ***sample*** *pathways.*

The test was run with flows of 15 l/min. **Sample air** was provided to two Alicat$^{XII}$ mass flow controllers with 0-20 l/min dynamic ranges, blending from an ultra-high purity zero air tank and a nominal 1000 ppm EtO tank (certified: 980.4 ppm ± 2% in air) to achieve levels of roughly 100, 200, 500, and 1000 ppm EtO at the reactor inlet. The Picarro instrument sampled downstream of the reactor, pulling a flow of 230 ml/min, while the excess flow was wasted to a fume hood.

During warmup of the reactor, **conditioning flow** air was pulled through the rig at a rate of 15 l/min to ensure even heating of the reactor. To save zero gas, this was performed by a bypass pump pulling ambient room air through a **second reactor inlet valve, and out a three-way valve at the reactor exhaust.** Once the temperature set point was reached, the **inlet was switched to zero air, and the outlet to the Picarro**, and after the water concentration at the Picarro dropped below 0.15%, the test was initiated using a program to control the two mass flow controllers and achieve the desired concentration set points.

Each step of the 2.5-hour test was run for 15 minutes, with both an ascending and descending leg to ensure memory effects didn't impart a consistent negative or positive bias on the system during rise or fall steps. The initial concentration of the zero air was taken as the "zero EtO" state and subtracted from all further steps to normalize the results of the experiment.

In order to prove that the outlet signal was truly representative of the effluent sample gas—not a leak or other gas stream—Picarro chose to add a conserved tracer, $CH_4$, to the tank at a nominal 10 ppm value (certified: 9.5 ppm ± 2%). Picarro knows from prior testing that trace-level $CH_4$ is stable below 200°C in catalyst beds.

> The experiment ran EtO through the reactor and to the the Picarro analyzer at levels between 100 and 1000 ppm for 2.5 hours, first ascending and then descending to avoid any memory effect bias on the results.

> All reactor outlet EtO values fall beneath 0.3 ppb, a truly remarkable finding considering the inlet concentration peaked at nearly 1,000,000 ppb.

## Results and Dicussion

### *Destruction Efficiency*

The **inlet concentration** is shown in Figure 6 below, in units of parts per million (ppm). Its values are inferred based on the measured mass flow controller blending ratios and the known concentration of the tank. On the second Y axis, we plot the **observed outlet EtO concentrations** in units of ppb showing a running 5-minute average value. *Nearly no difference can be seen to the eye because so little EtO is passing through the reactor column.*

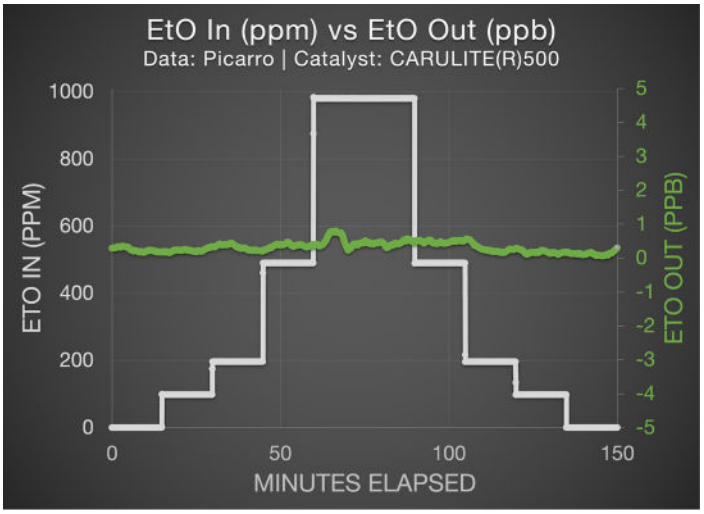

***Figure 6.*** *EtO In (ppm) and EtO out (ppb) of the test reactor column, showing that virtually no EtO makes it to the Picarro analyzer despite very high inlet concentrations up to ~1000 ppm.*

The ascending and descending legs for a given concentration were averaged to determine the average at a particular inlet concentration, and those average values are plotted below in **green** in Figure 7. *All reactor outlet EtO values fall beneath 0.3 ppb, a truly remarkable finding considering the inlet concentration peaked at nearly 1,000,000 ppb.* We show also the guaranteed **lower detection limit of the instrument**, 0.25 ppb, as an orange dashed line, showing that two of the observed concentrations fall beneath this guaranteed level.

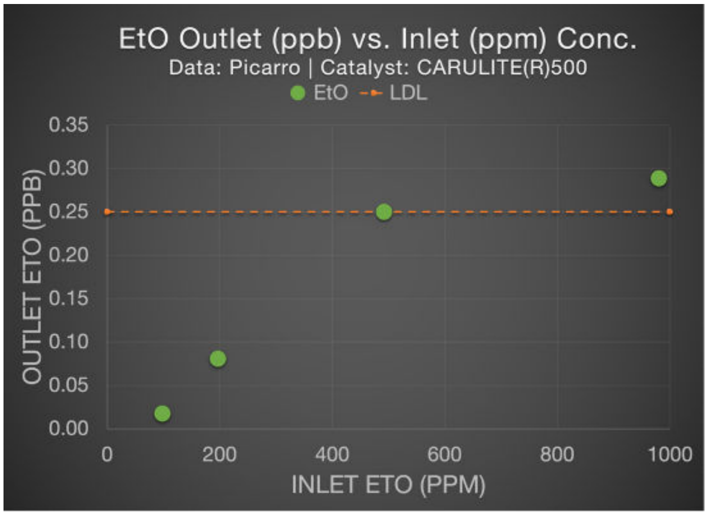

***Figure 7.*** *Average outlet EtO concentration in ppb as a function of inlet EtO concentration in ppm. Two outlet concentrations are so low as to drop below the guaranteed lower detection limit of the Picarro instrument.*

Destruction efficiency for these four concentrations was then assessed, as the observed corrected outlet EtO value divided by the inlet concentration, subtracted from 1, and multiplied by 100. These values all fell well above 99.999%. We plot these values in Figure 8 as both the **observed destruction efficiency** and the **destruction efficiency as limited by LDL** when the observed values fell below this level.

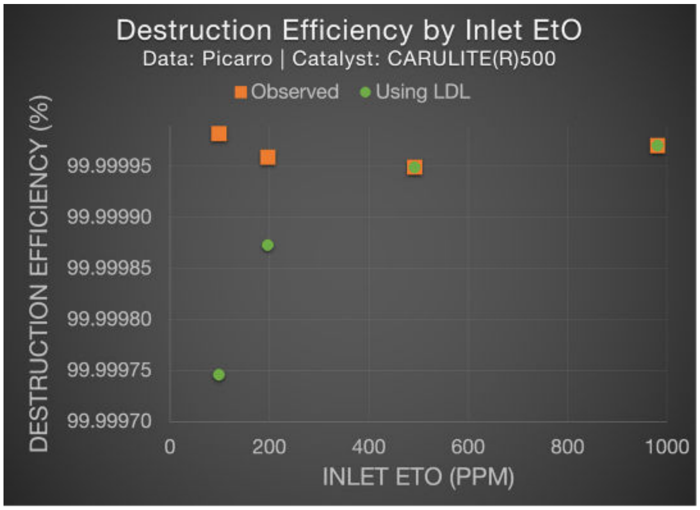

***Figure 8.*** *Destruction Efficiency at 100, 200, 500,1000 ppm inlet EtO concentrations. Constraining the observed efficiency by the official detection limit of the instrument slightly reduces the DE, as seen in the two green dots on the left, but still suggests incredible destruction efficiency above 5-nines.*

> The destruction efficiency of the CARULITE® 500 is significantly more than "five nines", averaging a remarkable 99.99988%.

The inlet, outlet, and destruction efficiencies are summarized in Table 1.

| | Inlet EtO (ppm) | Outlet EtO (ppb) | DE Obs (%) | DE (%) 0.25 ppb LDL |
|---|---|---|---|---|
| **Step 1** | 0* | 0** | n/a | n/a |
| **Step 2** | 98.4* | 0.02 | 99.99998 | 99.99975 |
| **Step 3** | 196.8* | 0.08 | 99.99996 | 99.99987 |
| **Step 4** | 492* | 0.25 | 99.99995 | 99.99995 |
| **Step 5** | 980.4* | 0.29 | 99.99997 | 99.99997 |
| **Avg. DE** | -- | -- | 99.999965 | 99.99988 |

***Table 1****: Inlet (ppm) and outlet (ppb) concentrations for the testing apparatus, with both the observed/implied destruction efficiency, and the destruction efficiency using the lower detection limit of the Picarro analyzer.*

**Inferred from MFC blending and known tank value*
***By Definition, as this is used to characterize the zero*

The average destruction observed is a remarkable **99.999965%,** and the destruction efficiency using the detection limit of the analyzer is a still-remarkable **99.99988%, more than "five-nines" destruction efficiency, almost six.**

## *Tracer Method and Stoichiometry*

The results above are so remarkable that is important to prove their validity independently. We do so with two methods.

### Methane Tracer Proof

First, the ~1000 ppm EtO tank has a roughly 10 ppm methane tracer gas (certified: 9.5 ppm ± 2%), which is known to be conserved below 200°C in reactor columns by prior Picarro work. The observed value of this gas at the outlet provides confirmation that the EtO from the cylinder is in fact passing through the reactor rig, not leaking out or otherwise being diverted. The **predicted $CH_4$ concentration is shown as a thin purple line** in Figure 9. Plotted on top of it is the observed **$CH_4$ tracer, shown as purple dots.** The choice of a line for the predicted and dots for the observed is made to distinguish two lines that are otherwise indistinguishable due to their similarity, because the methane is preserved with near-perfect recovery.

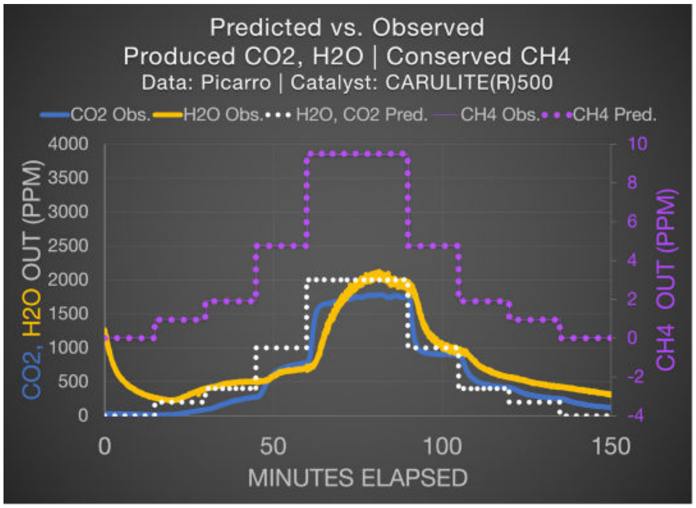

***Figure 9.*** *Expected vs Observed $CO_2$, $H_2O$, $CH_4$, showing $H_2O$ and $CO_2$ latency effects.*

### Stoichiometric Proof

Secondly, we plot the **$H_2O$** and **$CO_2$** data alongside the $CH_4$ data. **$H_2O$** and $CO_2$ are expected to be produced at double (white dotted line) the concentration of the inlet EtO, following the equation:

$$1\,C_2H_4O + {}^{5}\!/_{2}\,O_2 \rightarrow 2\,CO_2 + 2\,H_2O$$

The produced **$H_2O$** and **$CO_2$** track the expected value consistently near to the expected stoichiometry, but slightly shifted backward in time because of water and carbon dioxide's tendency to adsorb and desorb from the large surface area of the catalyst media.

The combination of the $CH_4$ tracer method, and the **$H_2O$** and **$CO_2$** stoichiometry lend undeniable credence to the validity of the ethylene oxide destruction efficiency by the Carus catalyst media.

## Picarro EtO Technology and PS-19: Demonstrating Excellence in Compliance

Instrumented systems used for EtO CEMS monitoring must undergo initial testing in a laboratory setting to establish that the system meets Interference, Measurement Error, and Level of Detection requirements of PS-19. Here we provide evidence of these tests to demonstrate the suitability of Picarro equipment in assessing the destruction efficiency of Carus catalyst media. We note that the testing conditions shown below include concentrations of $H_2O$, $CO_2$, and $CH_4$ far beyond what was shown in the above test, capturing "worst-case" scenarios measured under the most conservative conditions, which explains why the results have a slightly higher uncertainty response than that implied in the Carus catalyst testing work.

### *Interference Response, PS-19 Section 11.1*

The interference test must be run with each of the interferent species present, but can be run either one by one (easier to pass) or all together (typically much harder to pass). The results of this evaluation are shown below (Figure 10) for the Picarro CEMS system EtO instrument for **EtO (ppb)**, tested with all three interferent gases present alternating back and forth between real world ambient and the highest elevated conditions specified for PS-19 CEMS: **$CO_2$ at 1.2% (12,000 ppm)**, **$CH_4$ at 20 ppm**, and **$H_2O$ at 4.5%**. The mean difference between the ambient and elevated EtO is **1.44 ppb** (much less than the 30 ppb required in PS-19 Section 13.5.1), a remarkable value considering the simultaneous introduction of the interferents at maximum concentration, and a statistic not often provided by manufacturers of other technologies, such as FTIR, because of the performance challenges associated with simultaneous cross-talk correction algorithms, thermal oxidation modules, and optical filters.

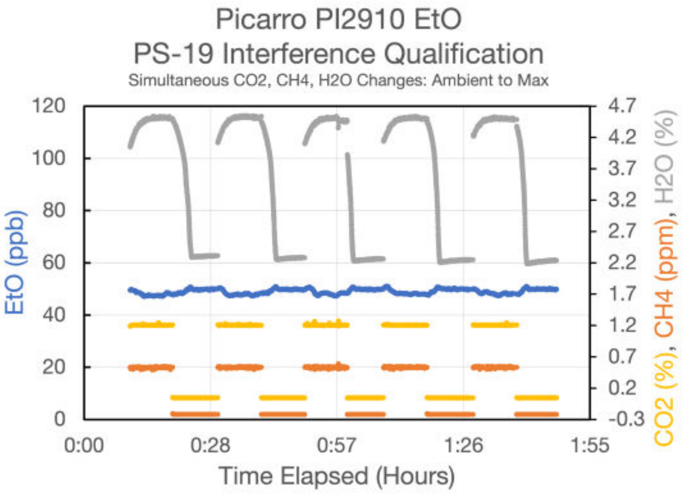

***Figure 10.*** *Picarro Interference Response Test, showing very minor changes to EtO when all specified interferent gases are sent to the analyzer simultaneously.*

### *Level of Detection, PS-19 Section 11.2*

Picarro also ran the “Level of Detection” (a.k.a. “Limit of Detection”) test required in PS-19 Section 11.2, varying the EtO between 0 and 6 ppb (a rough estimated 10x LOD), repeating the test seven times in an ambient matrix with maximum interferent concentrations (Figure 11). The LOD is defined as three times the standard deviation of the mean of the seven zero steps. While the exact nature of the LOD in PS-19 is slightly unclear based on the proscribed allowed emissions limit, the Picarro would handily meet a LOD of 20 ppb if the limit were to be stated as 100 ppb (20% * 100 ppb = 20 ppb). We determine the tested limit to be **0.239 ppb, more than 80x better than the likely requirement.**

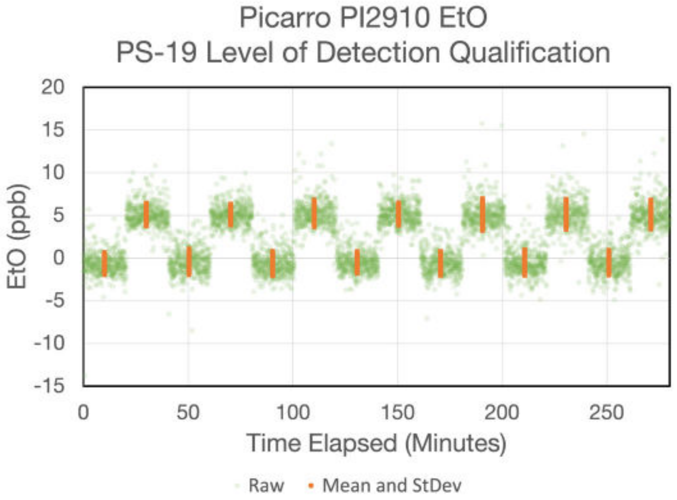

***Figure 11.*** *Picarro Level of Detection (LOD) test showing strongly reproducible and differentiable mean/StDev (orange dot with error bar) values for both zero and 10x LOD steps*

### *Measurement Error, PS-19 Section 11.4*

The Picarro CEMS also handily passed the Measurement Error test, which requires less than a 5% error on a span (undefined, but likely 100 ppb, so 5 ppb error allowed) or 10 ppb when comparing **measured** vs. **target** gas concentration, averaging just **0.154%** (much less than 5%, PS-19 Section 13.3), as seen in Figure 12.

The Picarro EtO CEMS system passes all three PS-19 lab qualification tests handily--even when run with the hardest criteria--beating the requirement by a factor of 20-80x.

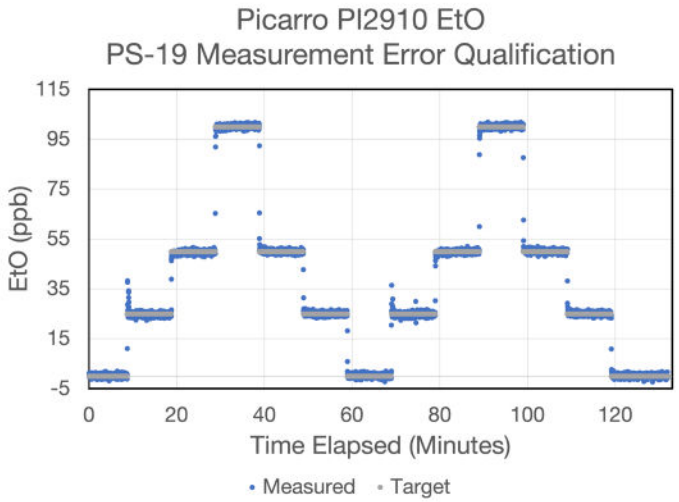

***Figure 12.*** *Picarro Measurement Error Test, showing measured (blue) and target (gray) concentrations, showing the power and linearity of Cavity Ring-Down Spectroscopy.*

## Conclusions

Carus and Picarro worked together to evaluate thedestruction efficiency of CARULITE® 500—a catalyst material at the core of many of the world’s best catalytic abatement systems—in lab settings using EtO concentrations typical of a commercial sterilizer or chemical plant CatOx. The results show a remarkable destruction efficiency of **99.99988%** over inlet concentrations of 100-1000 ppm **more than “five-nines” destruction efficiency, almost six.** Additional $CH_4$, $CO_2$, and $H_2O$ concentrations were used to verify the accuracy and integrity of this test, confirming that a tracer gas, $CH_4$, flowed through the test rig without loss, as expected at the temperature, while the ethylene oxide was destroyed with amazing efficiency into $CO_2$ and $H_2O$ at a 1:2 ratio as predicted by stoichiometry. In the modern regulatory environment of the new EtO NESHAP[II], and the Amended Rule 1405 in SCAQMD[IV], abatement systems must prove 99.94%, and 99.99% destruction efficiency, respectively. These results show that Carus’s catalyst products give abatement system manufacturers an incredibly solid core around which to build their abatement systems. Please reach out to your Carus representative if you’d like to discuss using Carus catalysts in your products, and please reach out to Picarro if you’re ready to evaluate your facility, and then use CRDS technology to ensure that your facility meets and exceeds the tighter regulatory standards beginning in 2024.

## Glossary

| | |
|---|---|
| **CatOx:** | Catalytic Oxidizer |
| **CEMS:** | Continuous Emission Monitoring System |
| **CRDS:** | Cavity Ring-Down Spectroscopy |
| **EPA:** | Environmental Protection Agency |
| **EtO, EO:** | Ethylene Oxide |
| **LDL:** | Lower Detection Limit |
| **LOD:** | Level of Detection or Limit of Detection |
| **ME:** | Measurement Error |
| **NESHAP:** | National Emission Standard for Hazardous Air Pollutants |
| **PPB:** | Parts per billion |
| **PPM:** | Parts per million |
| **PS-19:** | EPA Performance Specification 19 |
| **SCAQMD:** | South Coast Air Quality Mgmt District |

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**The authors wish to thank Karsten Baumann (Picarro) for his contribution to this work.**

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[I] Carus: https://www.carusllc.com/

[II] EtO NESHAP 40 CFR Pt. 63 Subpart O: https://www.epa.gov/system/files/documents/2024-03/7055_etosterilizers_final_20240301_admin_disc.pdf

[III] EPA PS-19: https://www.regulations.gov/document/ EPA-HQ-OAR-2019-0178-0490

[IV] South Coast Air Quality Management District Amended Rule 1405: https://www.aqmd.gov/docs/default-source/rule-book/reg-xiv/rule-1405.pdf

[V] Picarro and Carus's partnership Press Release: https://www.picarro.com/eto/company/press-releases/2023/carus_llc_selects_picarro_as_technology_partner_for_ethylene_oxide

[VI] Picarro Inc. Ethylene Oxide Solutions: https://www.picarro.com/eto

[VII] EtO use for manufacture of mono-ethylene glycol: https://en.wikipedia.org/wiki/OMEGA_process

[VIII] Choline Chloride Production with EtO and TMA: https://patents.google.com/patent/US3373201A/en

[IX] CDC Summary of use of EtO in Medical Device Sterilization: https://www.cdc.gov/infectioncontrol/guidelines/disinfection/sterilization/ethylene-oxide.html

[X] Gamma Industry Processing Alliance White Paper: file:///Users/jbent/Desktop/CleanUp/Comparison_Sterilization_Technologies_GIPA-WP-GIPA-iia-Sterilization-Modalities-FINAL-Version-2017-October-308772.pdf

[XI] FIFRA PID: https://www.federalregister.gov/documents/2023/04/13/2023-07727/pesticide-registration-review-proposed-interim-decision-and-draft-risk-assessment-addendum-for

[XII] Alicat Flow Instrumentation Equipment: https://www.alicat.com/

**LIT CODE:** V1.1-240904