White Paper

LESNI Catalytic Abatement Plants are Ready for the New Ethylene Oxide Regulations, and Picarro Monitoring Systems Prove It

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Figure 1. *LESNI EO CAP, which Picarro technology shows abates EtO emissions well below the new NESHAP requirements proposed by the US EPA.*

Summary

Ethylene Oxide (EtO, EO), a sterilant gas and important chemical feedstock, is undergoing significant regulatory oversight revision to require industrial facilities to limit fugitive emissions and worker exposure. Critical to the success of this effort are abatement technologies that can achieve regulatory destruction efficiency requirements, and monitoring technologies that can prove this at the stack.
This white paper outlines testing performed by Picarro Inc.—a leading manufacturer of continuous emissions monitoring systems powered by Cavity Ring-Down Spectroscopy (CRDS) and provider of end-to-end monitoring services—on a LESNI EO Catalytic Abatement Plant, considered by many to be the premier abatement solution for EtO.
This testing was performed at a medical device manufacturer and sterilizer facility in the United States during an active sterlization process. EtO concentrations were measured in real time upstream of the Catalytic Oxidizer (CatOx), and downstream, at the stack, to assess the destruction efficiency of the CatOx itself. Picarro's CRDS monitoring systems capably and repeatably measured single- and double-digit ppb values of EtO at the stack, triple digit ppm on the inlet, providing fast, sensitive data to demonstrate the superior destruction efficiency of the LESNI CatOx. The LESNI Ethylene Oxide Cataytic Abatement Plant (EO CAP) kept concentrations at the stack below 100 ppb on an hourly-averaged basis, with a 24-hour average of just 12 ppb, and with an incredible average destruction efficiency of 99.991%[I], well above the 99.94% required for large facilities by the new US EPA National Emission Standards for Hazardous Air Pollutants (NESHAP)[VI].

Introduction

Ethylene Oxide (EtO, EO) is an essential sterilant gas and chemical precursor/intermediate used widely across industries like refining[II], food processing[III], and medical device sterilization[IV]. 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 altern-atives. 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[V]—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 scrutiny 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) [VI], b) Performance Specification 19[VII] (PS-19) for source emissions monitoring, and c) the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) Proposed Interim Decision for workplace and lifetime exposure[VIII]. They also include distinct measures by local, statewide, regional, and other international authorities[IX], 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 urged to implement emissions management systems designed with regulatory compliance in mind. Proactive upgrades to these systems, combined with intelligent monitoring, are crucial for industries to align with EPA and other international requirements before the 2024-2026 deadlines.

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LESNI is an industry leader in engineering and implementing emission abatement systems for the most challenging industrial sectors, offering a portfolio of solutions including chemical scrubbers and solvent recovery systems, as well as catalytic, recuperative, and regenerative thermal oxidizers. They are recognized for effectively mitigating EtO emissions from sterilization processes well beyond the historical 99% destruction efficiency (DE) level and are committed to delivering solutions that meet the exacting needs of industry in stringent regulatory environments. Though LESNI systems have long been able to abate EtO well beyond 99.9%, few monitoring technologies have had the sensitivity to prove this, with the likely impact that facilities' true emissions—often estimated using a DE emission factor—are being significantly overstated. Legacy analytical techniques also struggle to demonstrate the destruction efficiencies required by updated regulations, putting abatement system manufacturers in a challenging position.

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Next-generation EtO systems from Picarro Inc.[X], an industry leader in analytical instrumentation and solutions, have overcome this issue, with PS-19-compliant continuous emissions monitoring systems (CEMS) capable of measuring down to as little as 0.25 ppb, making abatement performance validation and compliance readily achievable. In this white paper we investigate how Picarro CEMS were able to demonstrate superior destruction efficiency in a LESNI EO Catalytic Abatement Plant, providing the subject facility with verifiable excellent EtO abatement.

> LESNI's EtO Catalytic Abatement Plant achieved an incredible 99.991% average destruction efficiency, as determined by Picarro monitoring systems.

Methods and Materials

LESNI EO Catalytic Abatement Plant

The LESNI EO Catalytic Abatement Plant (CAP) used during this study was located at a facility that manufactures and sterilizes medical devices in the United States. This facility will soon be subject to the updated NESHAP[VI] and the newly-promulgated PS-19 CEM standard[VII], as well as local emissions standards that may be equally, if not more, restrictive than those at the federal level.

The facility runs on a 24-hour basis with three working shifts, operating one 12-pallet sterilization chamber and two LESNI accelerated degassing cells, which are connected, along with other sources of fugitive emissions, to the abatement system (see Figure 2). The facility operates LESNI's EO CAP which pairs a balancer with a catalytic oxidizer immediately before the stack. The balancer—a unique preconditioning step—absorbs high levels of EtO from the sterilizer vessels into water, and then slowly desorbs this gas over longer time periods using push gas from aeration cells where EtO concentrations are known to be much lower. The intelligent functionality of the system allows operators to run their sterilization cycles freely without down time. The LESNI EO CAP requires no chemicals and produces no waste product.

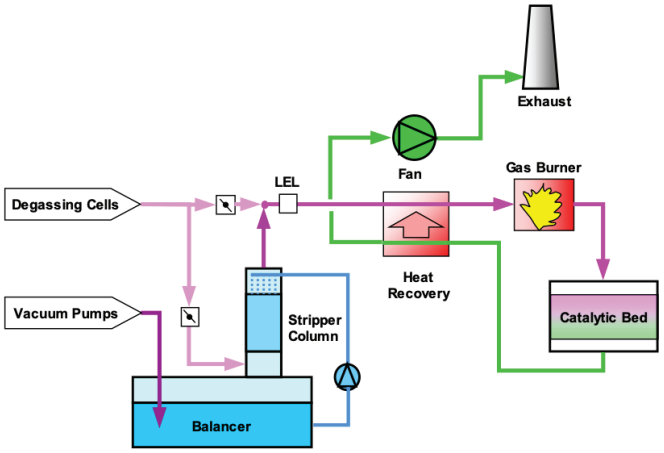

Figure 2. *LESNI EO CAP. The Balancer uses water and aeration cell air to modulate EtO concentrations at the CatOx, ensuring safe and efficient destruction efficiency. The CatOx recaptures the heat produced by EtO destruction to minimize the gas needed to maintain the CatOx bed temperature.*

The catalytic oxidizer itself is designed with efficiency in mind, using the intrinsic exothermic reaction of the stripped EtO at the catalyst with heat recovery technology to reduce the cost of maintaining the CatOx bed temperature at its set point (see Figure 2). This well-proven two-step system ensures that all process gas and fugitive emissions can be effectively captured and routed to the CatOx at safe low levels, ensuring that the CatOx itself sees concentrations of EtO well below the LEL (lower explosive limit)[XI].

Picarro CEMS: A CRDS Monitoring Solution

Because very few monitoring systems have the lower detection limits required to establish 99.9+% destruction efficiency for concentrations of EtO below 1000 ppm, LESNI partnered with Picarro Inc.[X], an industry-leader in analytical instrumentation and systems, whose CRDS systems are used across the world to measure hazardous air pollutants and greenhouse gases in a variety of industrial applications. Picarro's EtO CEMS has a guaranteed lower detection limit of 0.25 ppb and has industry-leading stability and selectivity for EtO, as well as an instantaneous response and 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 CEMS are not only sensitive, fast, and selective, but a total solution--a managed service agreement in which Picarro staff perform critical maintenance, and ensure a facility stays compliant with all relevant regulations.

Figure 3. *The Picarro EtO CEMS. State-of-the-art Picarro CRDS technology sits within a NEMA-12 (or better) industrial enclosure, with an umbilical connecting the system to the stack, where industry-leading flow monitoring and sample probes feed back essential parameters, and sample and calibration gases to enable real-time monitoring of both concentrations and mass emissions.*

Results

Data is shown below for a Picarro system measuring the CatOx inlet and stack effluent at the subject facility. Shown in Figure 4 are inlet EtO concentrations in parts per million (ppm) during three sterilization cycles lasting 33 hours.

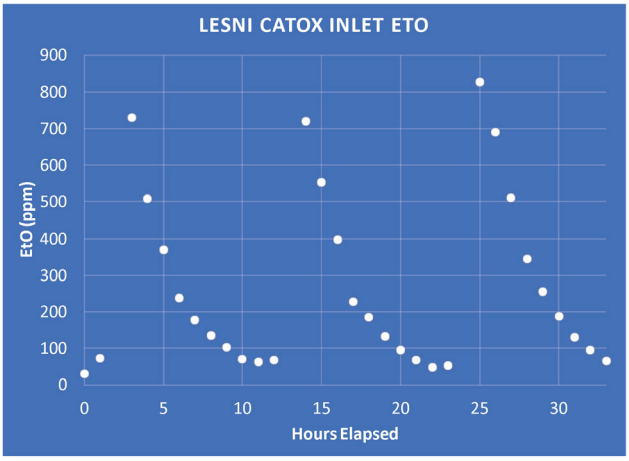

Figure 4. *CatOx Inlet EtO (ppm) showing repeatable balancer-modulated EtO well below lower explosive levels*

The balancer slows the introduction of otherwise high EtO peaks (double-digit %) coming from the sterilizer chambers to the CatOx to keep it well below the EtO LEL. One second data from the Picarro system are aggregated into one-hour averages to allow for easier viewing, for the calculation of destruction efficiency, and to show stack concentrations at the temporal resolution required by PS-19. The data show that the CatOx sees hour-average concentrations as high as 820 ppm coming from the balancer, as expected, with EtO levels dropping below 100 ppm before the subsequent sterilization cycle begins.

The LESNI Catalytic Abatement Plant achieves four orders of magnitude reduction in the EtO at the stack with no chemicals or waste product, and with a recuperative heat exchanger method that saves facilities significantly on their operating costs.

The stack data (CatOx outlet) are shown in Figure 5, this time in ***parts per billion*** (ppb), closely mimicking the Inlet values in shape, but roughly four orders of magnitude lower due to the abatement achieved by the catalytic oxidizer. The stack sees values between 3 and 60 ppb, with an average of 12 ppb.

While the exact average emissions level required by the NESHAP and PS-19 is not clear until the rule is finalized, it is likely to be around 100 ppb. The LESNI stack also keeps concentrations well below "above-span" levels (likely to be 2-3x the span value as seen on two consecutive hourly averages), but if for any reason it exceeded this value, the Picarro CEMS would trigger an above-span calibration check automatically to maintain compliance with Procedure 7 Section 4.1.5[XII], a feature not found in traditional CEMS solutions.

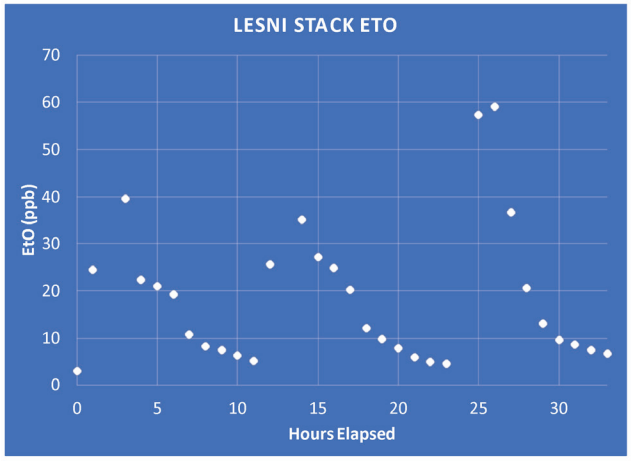

Figure 5. *Stack EtO (ppb), showing roughly a four order of magnitude reduction in EtO due to the efficiency of the CatOx*

Using the inlet and outlet concentrations, we produce hour-averaged destruction efficiencies shown below in Figure 6. Above 100 ppm, the data show a rolling average of 99.994% Below this, but above 2.5 ppm (the level at which 99.99% efficiency can no longer be effectively characterized by the sensitivity of the CEM), the efficiency is 99.989%. **The destruction efficiency of the system for all inlet values above 2.5 ppm is an incredible 99.991%.**

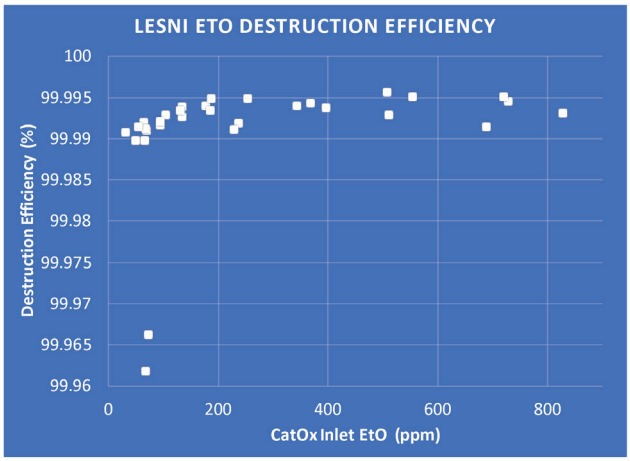

Figure 6. *CatOx destruction efficiency as a function of inlet EtO*

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 LESNI Catalytic Abatement Plants.

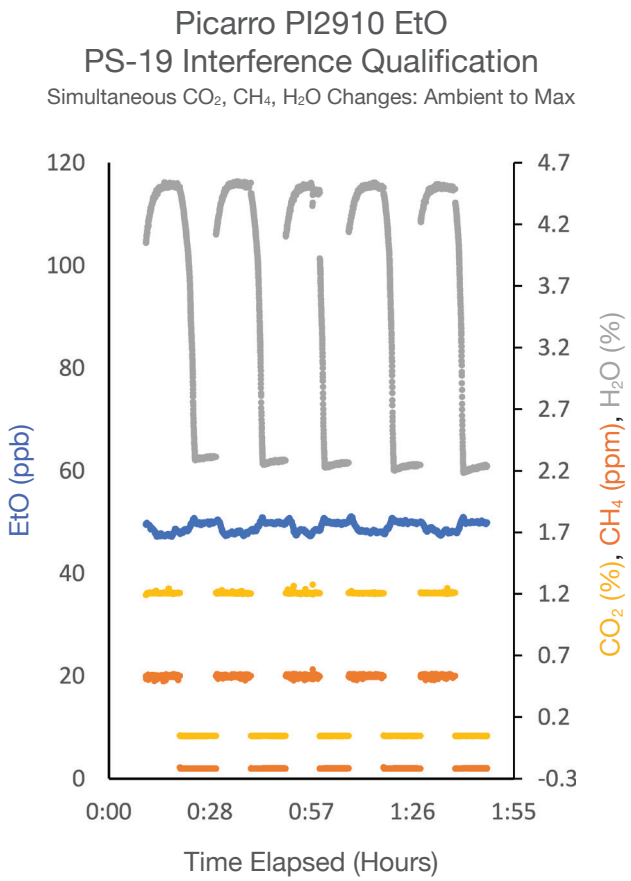

Figure 7. *Picarro Interference Response Test, showing very minor changes to EtO when all specified interferent gases are sent to the analyzer simultaneously.*

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 above (Figure 7) for the Picarro CEMS 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 (<<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.

The Picarro CEMS EtO instrument passed all PS-19 tests with flying colors even when subjected to the hardest challenge scenario options.

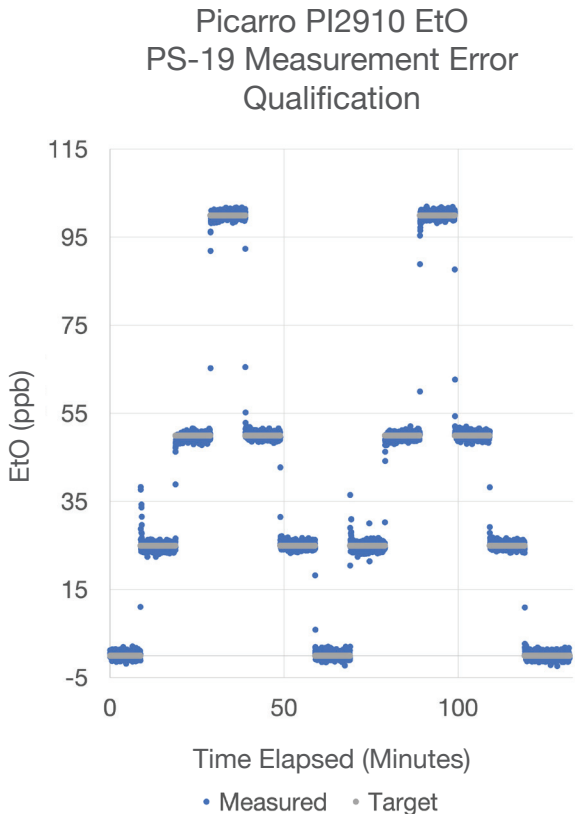

Figure 8. *Picarro Measurement Error Test, showing measured (blue) and target (gray) concentrations, showing the power and linearity of cavity ringdown spectroscopy.*

The Picarro CEMS also handily passed the Measurement Error test with an average ME of **0.154%, 0.154 ppb, <<5% or 10 ppb allowed in PS-19 Section 13.3**, when comparing **measured** vs. **target** gas concentration, as seen in Figure 8.

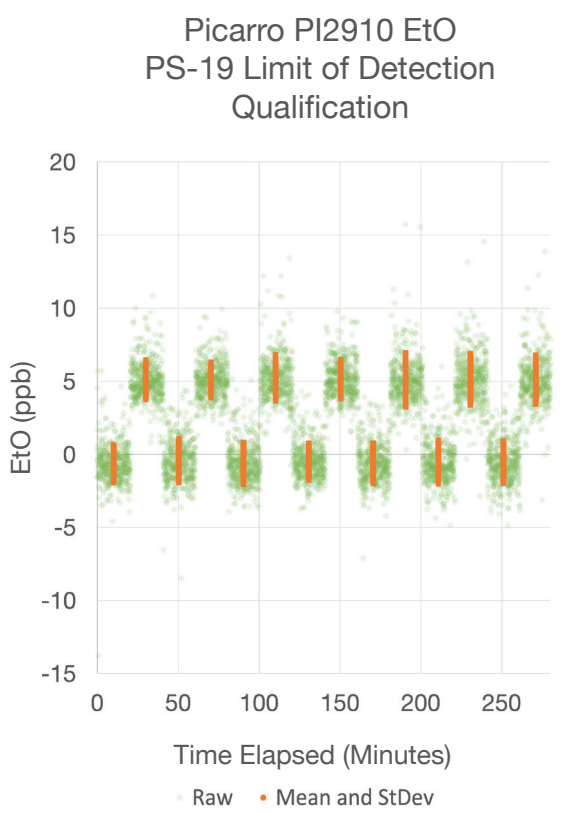

Figure 9. *Picarro Level of Detection (LOD) test showing strongly reproducible and differentiable mean/StDev (orange dot with error bar) values for both zero and 10x LOD steps.*

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 9). 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.**

Conclusions

The results of this evaluation show that LESNI's Ethylene Oxide Catalytic Abatement Plant provides a remarkable 99.991%[I] destruction efficiency under real-world conditions, averaging just 12 ppb EtO at the stack during three consecutive back-to-back sterilization cycles, well below a likely 100-ppb rolling average limit, and also well below 2-hour averaged "above-span" value limits expected in US EPA Performance Specification 19[VII]. These results show that LESNI's EO CAP systems are more than ready for the 99.94% destruction efficiency requirements of EPA's revised NESHAP. Picarro's Continuous Emission Monitoring Systems provide the industry-leading sensitivity to finally prove and continuously monitor this performance. Please reach out to your LESNI and Picarro representatives if you'd like to discuss how we can assist your facility in meeting the latest emissions requirements!

Glossary

CAP: Catalytic Abatement Plant

CatOx: Catalytic Oxidizer

CEMS: Continuous Emission Monitoring System

CRDS: Cavity Ringdown Spectroscopy

EPA: Environmental Protection Agency

EtO, EO: Ethylene Oxide

LEL: Lower Explosivity 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

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[I] Values where the Inlet concentration was above 2.5 ppm, the concentration below which a 99.99% efficiency cannot be measured by the CEM's detection limit of 0.25 ppb.
[II] EtO use for manufacture of mono-ethylene glycol: https://en.wikipedia.org/wiki/OMEGA_process
[III] Choline Chloride Production with EtO and TMA: https://patents.google.com/patent/US3373201A/en
[IV] CDC Summary of use of EtO in Medical Device Sterilization: https://www.cdc.gov/infectioncontrol/guidelines/disinfection/sterilization/ethylene-oxide.html
[V] 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
[vi] EtO NESHAP 40 CFR Pt. 63 Subpart O: https://www.ecfr.gov/current/title-40/chapter-I/subchapter-C/part-63/subpart-O
[VII] EPA PS-19: https://www.regulations.gov/document/EPA-HQ-OAR-2019-0178-0490
[VIII] FIFRA PID: https://www.federalregister.gov/documents/2023/04/13/2023-07727/pesticide-registration-review-proposed-interim-decision-and-draft-risk-assessment-addendum-for
[IX] E.g.: South Coast Air Quality Management District Amended Rule 1405: https://www.aqmd.gov/docs/default-source/rule-book/reg-xiv/rule-1405.pdf
[X] Picarro Inc. Ethylene Oxide Solutions: https://www.picarro.com/eto
[XI] EtO MSDS: https://www.osha.gov/chemicaldata/575
[XII] Procedure 7: https://www.regulations.gov/document/EPA-HQ-OAR-2019-0178-0492

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