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ETHYLENE OXIDE

PS-19 and Expanded EPA Regulations

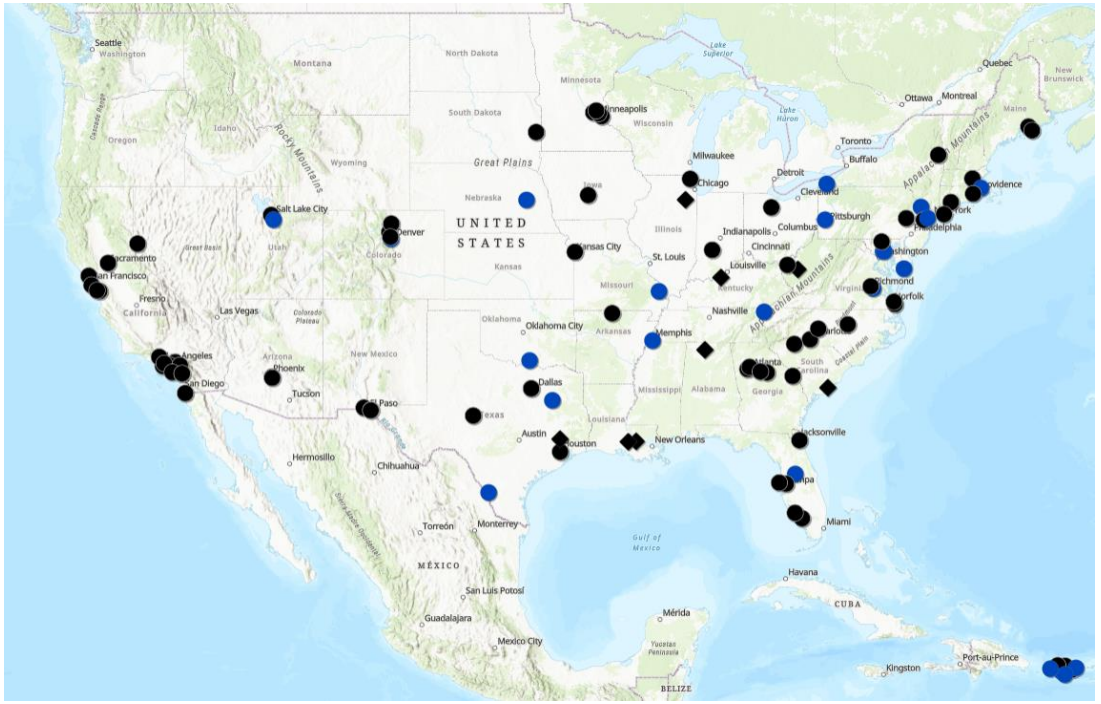
EtO – Environmental and Exposure

Environmental

- Release to air is primary pathway
- Water exposure is not expected
- Not readily absorbed by sediment or soil
- Limited information at hazardous waste sites

Exposure

- Primary route is inhalation
- Unlikely to remain in/on food for ingestion
- Workers have highest exposure risks;
- Workers at facilities without direct contact and those who live near production facilities may also be exposed
- OSHA permissible exposure limits (PEL)
  - 1 ppm (8 hr TWA)
  - 5 ppm (short term excursion limit, any 15 min period)



- Commercial Sterilizer
- Commercial sterilizer with EPA-identified elevated cancer risks
- Miscellaneous Organic Chemical Manufacturing (MON) facilities

Cancer Risk

Workers who are exposed during the course of their entire career
- 1 in 17 in medical devices commercial sterilization facilities
- 1 in 25 in healthcare sterilization facilities
- 1 in 36 workers in commercial sterilization facilities (spices)

Indirect exposure and public
- 19.4 million people live within 10 km of 97 facilities that have been assessed
- 100 in one million exposed at current levels
  - Spend entire career in commercial sterilization facilities (no direct handling)
  - Work entire career near commercial sterilizations facilities
  - Residents living and spending entire life near commercial sterilization facilities
  - Risks much lower near hospital sterilization – significantly less EtO used

No indication of risk:
- Consuming spices that have been sterilized
- Patients/healthcare staff using sterilized products or devices

Goal – Reduce these risk numbers by >80%

EPA EtO REGULATIONS

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Proposed EPA Actions to Reduce EtO-Related Risk

The air toxics rule for Miscellaneous Organic Chemical Manufacturing (MON): 40 CFR Part 63 Subpart FFFF

- In 2020, EPA finalized requirements to reduce emissions of hazardous air pollutants from the source category by 107 tons per year, which included reductions in ethylene oxide emission of approximately 0.76 tons per year.
- https://www.epa.gov/stationary-sources-air-pollution/miscellaneous-organic-chemical-manufacturing-national-emission

The air toxics rule for Ethylene Oxide Commercial Sterilizers: 40 CFR Part 63 Subpart O

- On April 11, 2023, EPA proposed new requirements for 86 commercial sterilizers across the country. These requirements, if implemented, will reduce the amount of EtO that comes out of commercial sterilizers by 80% and will reduce risk in nearby communities.
- https://www.epa.gov/hazardous-air-pollutants-ethylene-oxide/proposal-reduce-ethylene-oxide-emissions-commercial

The air toxics rule for Hazardous Organic NESHAP (HON): 40 CFR Part 60 and Part 63

- On April 6, 2023, EPA announced a proposal to significantly reduce emissions of toxic and other harmful air pollution from chemical plants, including the highly toxic chemicals ethylene oxide (EtO).
- https://www.epa.gov/hazardous-air-pollutants-ethylene-oxide/proposal-strengthen-standards-synthetic-organic-chemical

The Proposed Interim Decision on EtO use as a pesticide: Pesticide Registration Review

- On April 11, 2023, EPA proposed a broad set of new protections under the Federal Insecticide, Fungicide, and Rodenticide Act that will reduce risk for all workers who use EtO to sterilize things and for others who work, live, or go to school near sterilization facilities.
- https://www.epa.gov/ingredients-used-pesticide-products/regulation-ethylene-oxide-eto-under-federal-insecticide

Proposed Standards for Commercial Sterilizers

Existing and New Facilities emission reduction (12 month rolling average)	Sterilization Chamber Vent (SCV)	Aeration Room Vent (ARV)
EtO use at least 30 tpy	99.99%	99.9%
EtO use at least 10 but < 30 tpy	99.9%	99.6% (existing)
EtO use at least 10 tpy	99.9%	99.6% (existing) 99.9% (new)
EtO use at least 1 but <10 tpy	99.8%	99%
EtO use at <1 tpy	99%	99%

Chamber Exhaust Vent (CEV)	EtO Use	Reduction
At Major Source Facilities	N/A	99.94%
At Area Source Facilities	At least 400 tpy	99.9%
	At least 60 but less than 400 tpy	99.9%
	Less than 60 tpy	99%

* If combining sources, the most stringent reduction requirement must be met

Group 1 and 2 Air Room Emissions

Air Room Emission Source	EtO Use	Group 1
Major Sources (Existing and New)	N/A	97%
Area Sources (Existing and New)	>40 tpy	98%
	<40 tpy	80%

Group 1 – Indoor storage, dispensing, vacuum pump operations, and pre-aeration handling of sterilized material
Group 2 – Post-aeration handling of sterilized material

Air Room Emission Source	EtO Use	Group 2
Major Sources (Existing and New)	N/A	86%
Area Sources (Existing)	At least 20 tpy	98%
	At least 4 but less than 20 tpy	80%
	Less than 4 tpy	Lower the EtO concentration within each sterilization chamber to 1 ppm before the chamber can be opened
Area Sources (Existing)	At least 20 tpy	98%
	At least 4 but less than 20 tpy	80%
	Less than 4 tpy	80%

Continuous Monitoring

Previous detection level set to 1 ppm using Performance Specification 8 (PS-8) (Removed)

- Not selective to EtO
- Must be able to complete a collection, transport, and analysis cycle at least once every 15 min

10 ppb detection level with analysis cycle every 15 min

- Currently FTIR and Cavity Ringdown spectroscopy are being used for EtO monitoring
- “Some EtO CEMS manufacturers claim instrument detection levels much lower than 10 ppbv. However, we believe at the current time, this is the lowest level that can be consistently demonstrated and replicated across a wide range of emission profiles”

Performance Specification 19 (PS-19)

- Performance specifications and test procedures for ethylene oxide (EtO) continuous monitoring systems
- Procedure 7 – Quality Assurance Requirements for EtO CEMS Used for Compliance Determination

PERFORMANCE SPECIFICATION 19 (PS-19)

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Performance Specification 19 (PS-19)

Performance Specifications and Test Procedures for Ethylene Oxide (EtO) Continuous Emission Monitoring Systems

- Applicable for measuring gaseous concentrations of EtO on a continuous basis
- Covers the procedures that each EtO CEMS must meet during the performance evaluation test, including:
  - Installation and measurement location specifications,
  - Data reduction procedures, and
  - Performance criteria
- Used to evaluate the acceptability of EtO CEMS at the time of installation or soon after and whenever specified in the regulations

CEMS – Equipment and Supplies

Sample Extraction System – Must deliver a representative sample for measurement (sample probe and heated line)

Sample Conditioning Module – Removes particulate matter and moisture from the gas stream (must stay above dew point)

EtO Analyzer – Detects, quantifies and generates an output proportional to the sample gas EtO concentration

System Controller – Controls analyzer (and associated components) for continuous operation

Data Recorder – Record of analyzer output and other data (flow rates, temp, pressure, etc.)

Reference Gas System – Gas handling system capable of introducing reference and other gases into the system

Moisture Measurement System – If correction of the measured EtO emissions for moisture is required, you must install, operate, maintain, and quality assure a continuous moisture monitoring system for measuring and recording the moisture content of the flue gases.

Auxiliary Monitoring Systems – Measure stack gas flow rate, CO_2, O_2, or moisture, as applicable

CEMS Installation

- Accessible location where the EtO measurements are representative
- CEMS must be located:
  - At least 2 equivalent diameters downstream from the nearest control device, point of generation, or points where changes in concentration and/or emission rates may occur
  - At least a 0.5 equivalent diameter upstream from the effluent exhaust or control device
  - If time-sharing, the distance between the CEMS and each point should be similar
  - Not required to be installed in the same location as the RATA location

TESTING REQUIREMENTS

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PS-19 Testing Overview

Interference Testing (Manufacturer and upon install)

- Perform using an EtO reference gas concentration of approx. 10x the LOD or at 50 ppb
- Performed in triplicate documenting gas volume/rate, temperature, and pressure used
- Total interference response must not exceed 10x the LOD or 30 ppbv.

Potential interferent gas	Approximate Concentration
CO_2	1% ± 0.2%
CH_4	20 ± 5 ppm
H_2O	5% ± 1%
N_2	Balance

Level of Detection (LOD) Testing (Manufacturer and upon install)

- Lowest level of EtO that the CEMS can detect in the presence of interferent gases with 99% confidence
- EtO reference gas concentration must be <10x estimated instrument LOD
- Measurement data collected for 15 mins and averaged (7+ total runs required)
  - Ambient air purging between each run
- Calculate the standard deviation of the measured values and define the **LOD as three times the standard deviation** of these measurements

PS-19 Testing Overview

Response Time (RT) Testing

- The time it takes, under normal operating conditions to respond to a step change in concentration
  - Zero (low)-level to a high-level or high-level to a zero (low)-level concentration (greater value is the RT)
  - 95 percent of the change to the stable instrument response
- If time-sharing, determine the RT, sampling time, and cycle time at each measurement point.
  - The sampling time shall be at least 3x as long as the RT
  - The maximum number of measurement points shall not exceed 15 min total

Measurement Error (ME) Testing

- The mean difference between the measured concentration and the known concentration of a ref gas standard, divided by the span
- Challenge using a zero gas and 3 upscale EtO concentrations (high, mid, and low) in triplicate
- ME-RT
  - Introduce the calibration gas with sufficient flow rate to replace the entire source gas sample
  - Continue the flow until the response is stable (within 1.0% of span or 5 ppb)

PS-19 Testing Overview

Relative Accuracy (RA) Testing

- Absolute mean difference between the gas concentration (or emission rate) and the value determined by the RM of 9 test runs, divided by the average of the RM
  - EPA Method 320 – Vapor Phase Organic and Inorganic Emissions by Extractive FTIR
- RM tests results must representative of the emissions from the source that can be compared to the CEMS data
  - Collect samples that are at stack conditions (hot and wet) and you must traverse the stack
  - Conduct diluent, moisture, and pollutant measurements simultaneously as applicable

Seven Day Calibration Drift (CD) Test

- Absolute value of the difference between CEMS output response and an upscale reference gas
  - Challenged after a period of operation with no unscheduled adjustments
- Prior to starting RA testing, a 7-day CD test MUST be performed to verify the ability of the CEMS to maintain calibration
- Conduct test on each day at ~24hr intervals for 7 consecutive operating days
  - The zero-level and high-level CD for each day must be <5.0% of the span or an absolute difference of 10 ppb

Procedure 7 – Quality Assurance Requirements

- Evaluate the effectiveness QAQC procedures and to evaluate the quality of data produced CEMS used on a continuous basis
- Daily CD (zero and upscale measurements)
- Quarterly Audits
  - Relative Accuracy Test Audit (RATA)
  - Relative Accuracy Audit (RAA) (option to RATA in 3/4 quarters)
  - Cylinder Gas Audit
  - Dynamic Spiking Audit
- Out of Control Criteria
- Reporting Requirements

INSTRUMENTATION

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Continuous Monitoring System by Spectrum

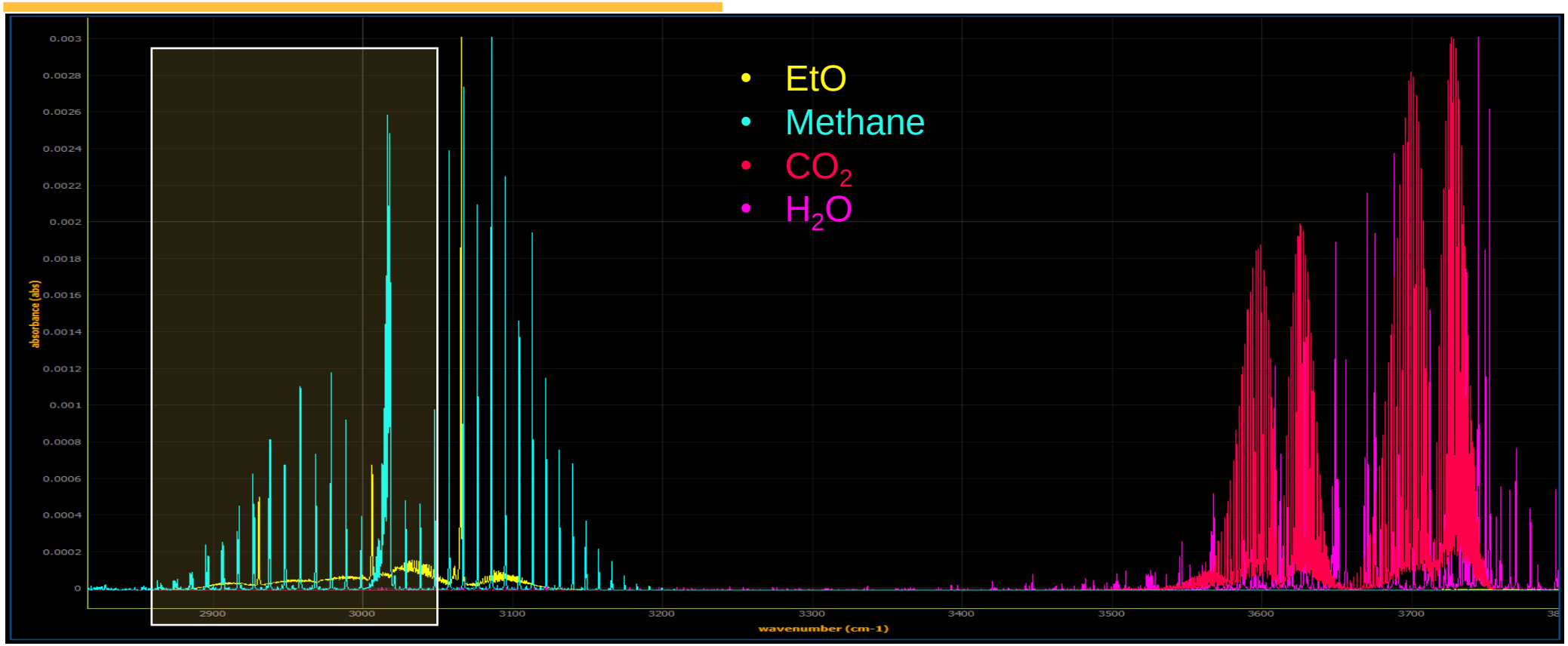
WaveRunIR™-EXT – Extractive FTIR Monitoring System

- Multi-gas analyzer capable of ppb level monitoring
- Variety of applications possible:
  - Continuous emissions monitoring (CEM)
  - Process monitoring
  - Ambient air analysis
  - Industrial hygiene monitoring
  - Source testing
  - Monitoring of various combustion sources

Differentiated by cell geometry and interchangeable detectors (“optically enhanced”)

- This unique feature enables substantially lower detection limits for EtO
- Additional compounds can be measured concurrently
  - Utilizes entire spectrum, including fingerprint region

Analytics – Reference Spectra



- Quantification Region: 2857.5 cm^{-1} – 3068.5 cm^{-1}
- No spectral overlap with CO_2 or H_2O – No analytical influence expected
- Convolved to 0.125 cm^{-1} resolution (1/8 cm^{-1})
- Source: PNNL

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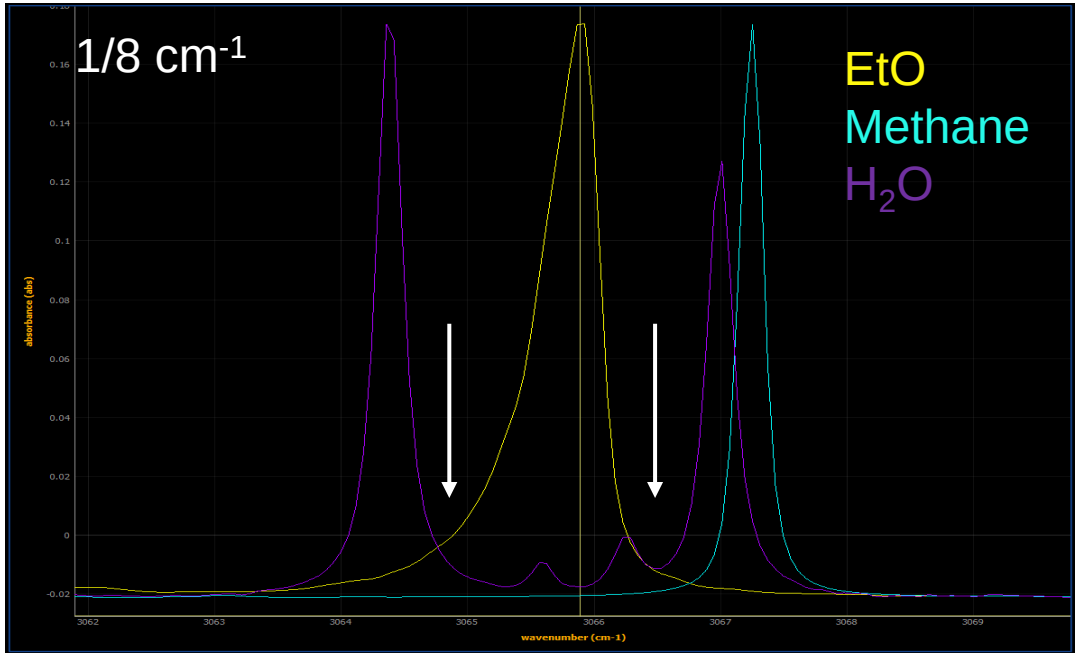
Analytics – High Resolution

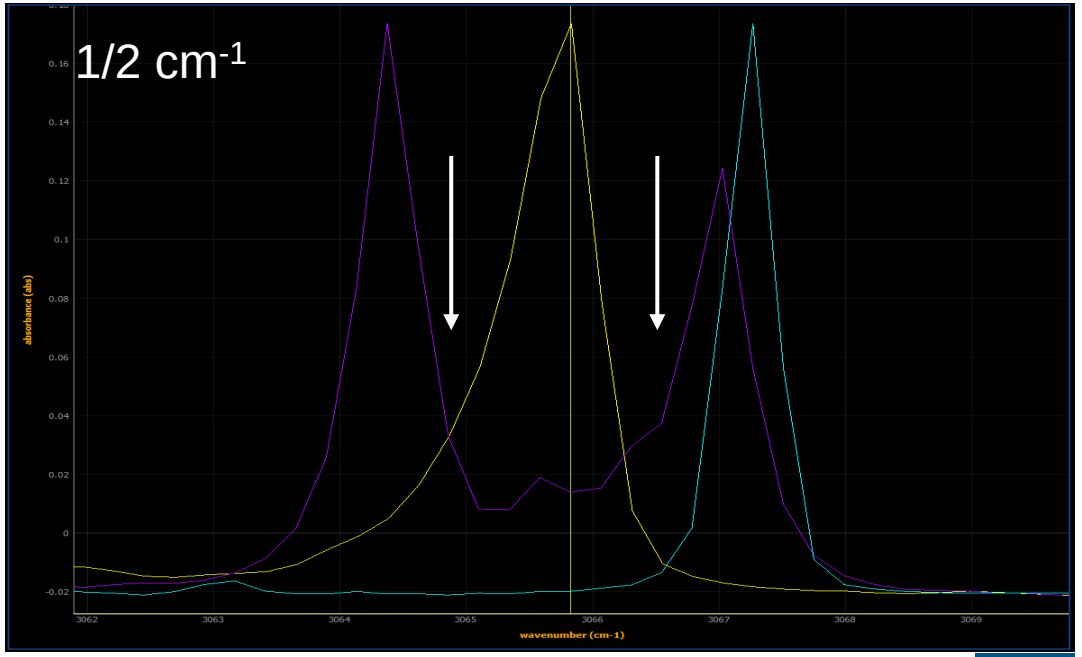
Problem: Interference could limited DLs

- At ~42m pathlength, possible absorbance from other interfering compounds
  - Mitigated by high resolution (1/8 cm^{-1})
  - Fully resolved H_2O lines at 3065.617 and 3066.271 cm^{-1}
  - Dominant EtO absorbance (3066 cm^{-1}) is now between the significant H_2O lines
- ~2.8 Greater peak height at 1/8 cm^{-1} compared to 1/2 cm^{-1}

Level of Detection Determination Test

- 15 min EtO spike with interferents
- **EtO LOD: <1 ppb**
- All spike recoveries pass EPA M320 requirement (± 30%)

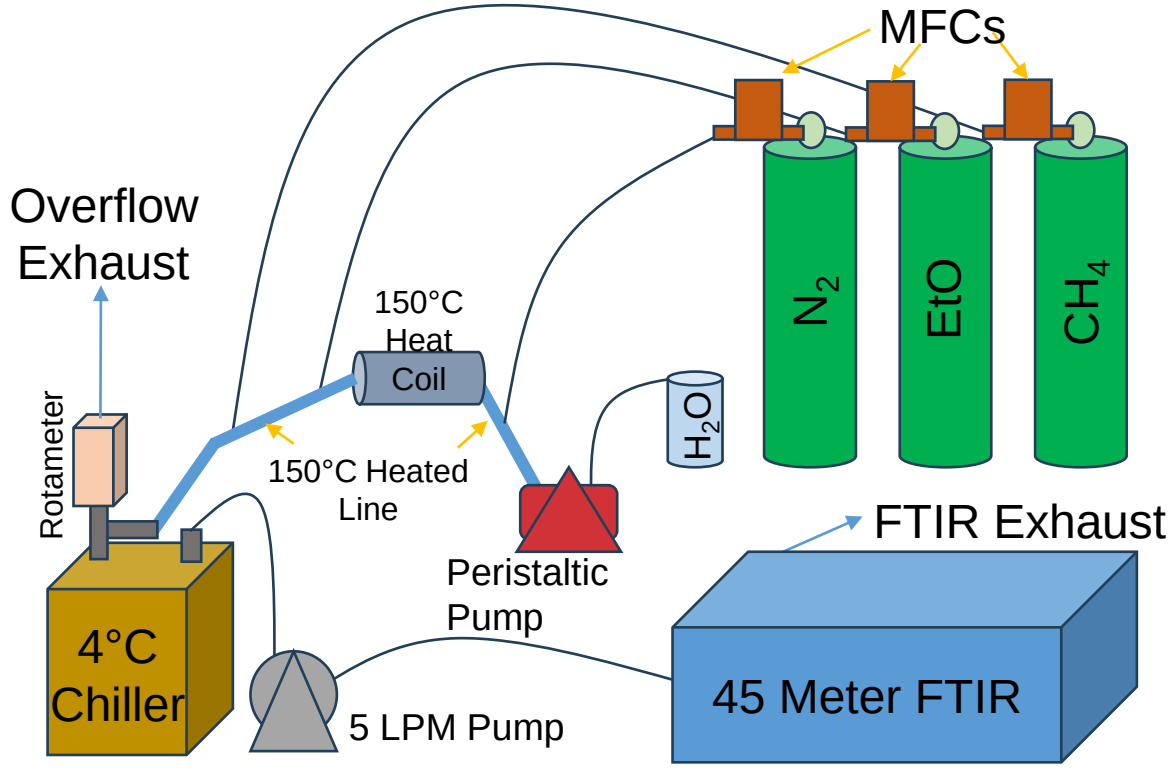




Interference Test - Sampling System

Perform measurements using an “optically enhanced FTIR is capable of measuring in-stack EtO concentration to approximately 10 ppbv”

- Liquid H_2O Introduced via peristaltic pump at constant flow rate
- H_2O picked up by diluent N_2, passed through 150°C heated coil to ensure vaporization
- EtO and CH_4 Introduced after the heat coil via Calibrated MFCs
- Excess N_2, EtO, CH_4, and water vapor flow monitored via rotameter
- 5 LPM sample pulled through 4°C dual active chiller via attached pump
- Sample pushed into 45m cell, temperature 50°C; TEC MCT detector; other optical enhancements



Limit of Detection Test per PS-19

Experiment
- 15 min EtO spike w/ Interferents
- Purge with air
- Repeat 7 times

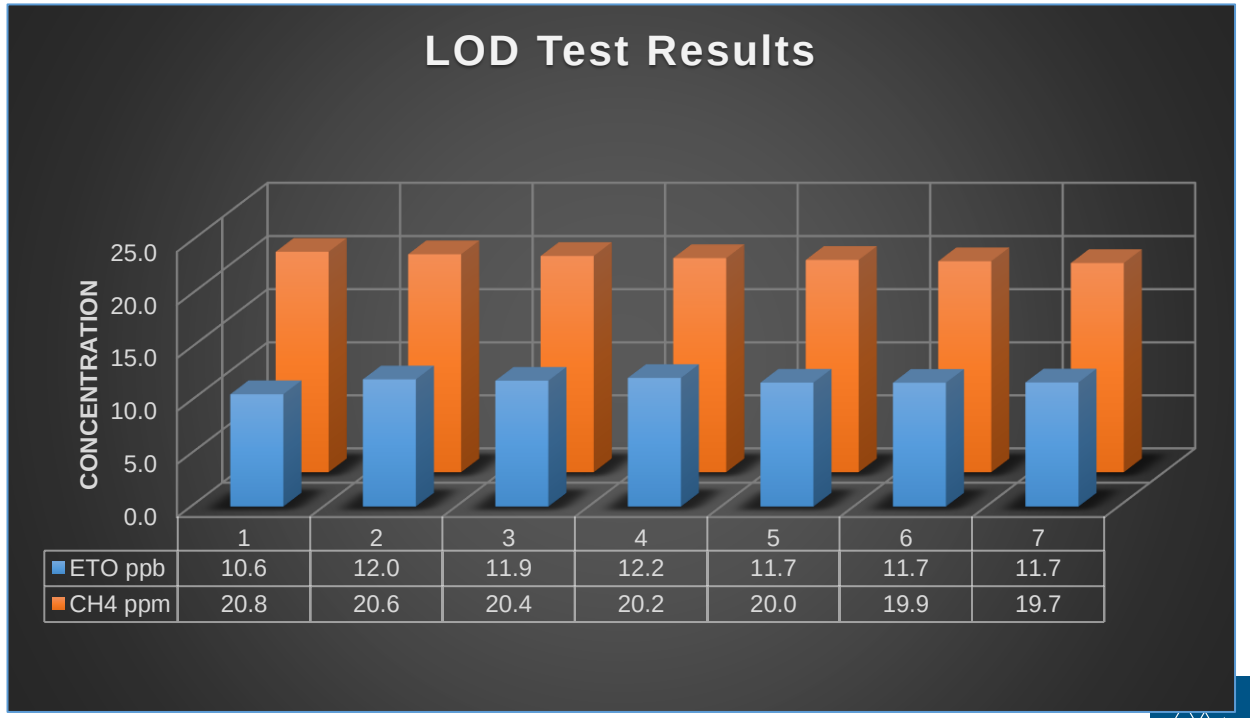
Metric
- Average result of each 15 min spike run
- LOD = 3*Standard Deviation

Setup
- 0.15 mL/min liquid H_2O
- 3.5 SLPM N_2 diluent
- 8 SCCM 1% CH_4
- 200 SCCM 186 ppb EtO

Expected Concentrations
- EtO: 9.51 ppb wet → 9.97 ppb after chiller
- CH_4: 20.45 ppm Wet → 21.44 ppm after chiller
- H_2O: 5.19% → 5800 ppm after chiller

Results
- EtO LOD: **1.51 ppb** (3*Standard Deviation)
- All Spike Recoveries Pass M320 ± 30%

% Recovery	LOD 1	LOD 2	LOD 3	LOD 4	LOD 5	LOD 6	LOD 7	Total
EtO	106 %	121 %	119 %	122 %	117 %	117 %	118 %	**117%**
CH_4	97 %	96 %	95 %	94 %	93 %	93%	92 %	**94%**



*Method 320 - Vapor Phase Organic and Inorganic Emissions by Extractive FTIR

Complete Solution by Spectrum

EtO Monitoring technology must provide a distinct response and address any appropriate interference corrections

- It must accurately measure ethylene oxide in a representative sample (path or point sampling) of stack effluent

WaveRunIR™-EXT monitor can measure low ppb levels

- Multiple sample points per instrument

NuWave™

- In-house developed, state-of-the art, custom software
- Unequaled flexibility to disseminate data for ethylene oxide (and hundreds of other compounds) from industrial sources and ambient air

Tsunami™ Data Management & Analytics Platform

- Handles all phases of dataflow, from acquisition to visualization
- Swiftly extract crucial insights and take proactive measures to stay ahead of emerging problems
- Data visualization

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THANK YOU

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