Status of Ethylene Oxide Source Measurements

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Agenda

- Background for source measurements
- Analytical techniques and instruments
- Gas standards, stability, and traceability
- Lessons learned/sample lines/ regulators/dilution systems

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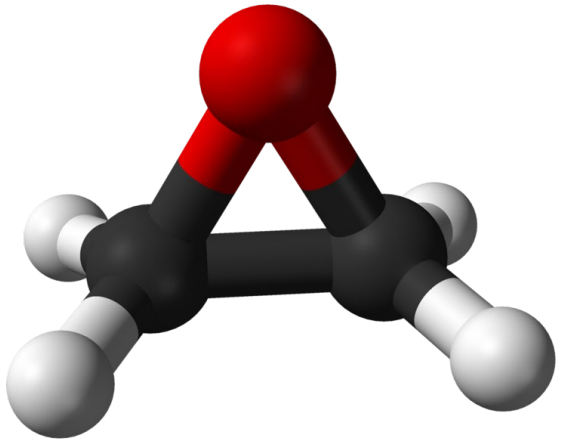
Source Measurements

- Potential Sources/Facility Types
- EtO Uses/Chemical Production + Sterilizers
- Stack Testing/Near Source/Fence-line Monitoring



Ethylene Oxide (EtO) Background

- Ethylene oxide (C_2H_4O, EtO) is:
  - a colorless, flammable, and reactive gas
  - one of 188 listed HAPs regulated under CAA
  - used for sterilization (by medical industry, food industry, etc.) and to produce a range of chemicals (by chemical manufacturing industry)
- EPA finalized EtO IRIS assessment in 2016
  - Characterized as carcinogenic to humans
  - Based on lifetime inhalation unit risk estimate (URE), 100-in-a-million cancer risk ➡ ~11 pptv
- EtO is a pollutant of emerging concern – ORD research is supporting stakeholders by studying potential sources and developing measurement approaches

Analytical Techniques: Integrated Sampling Issues

- Unable to time resolve when EtO events are occuring
- Typical laboratory analysis turn-around time can add weeks for results due to instrument availability or standard laboratory analysis lead times
- For source sampling, TO-15A canister samplers would need possible dilution to control water levels but would also increase detection levels
- Brominated carbon traps (OSHA Method 1010) would need additional testing to determine applicability for source sampling

Analytical Techniques and Instrumentation

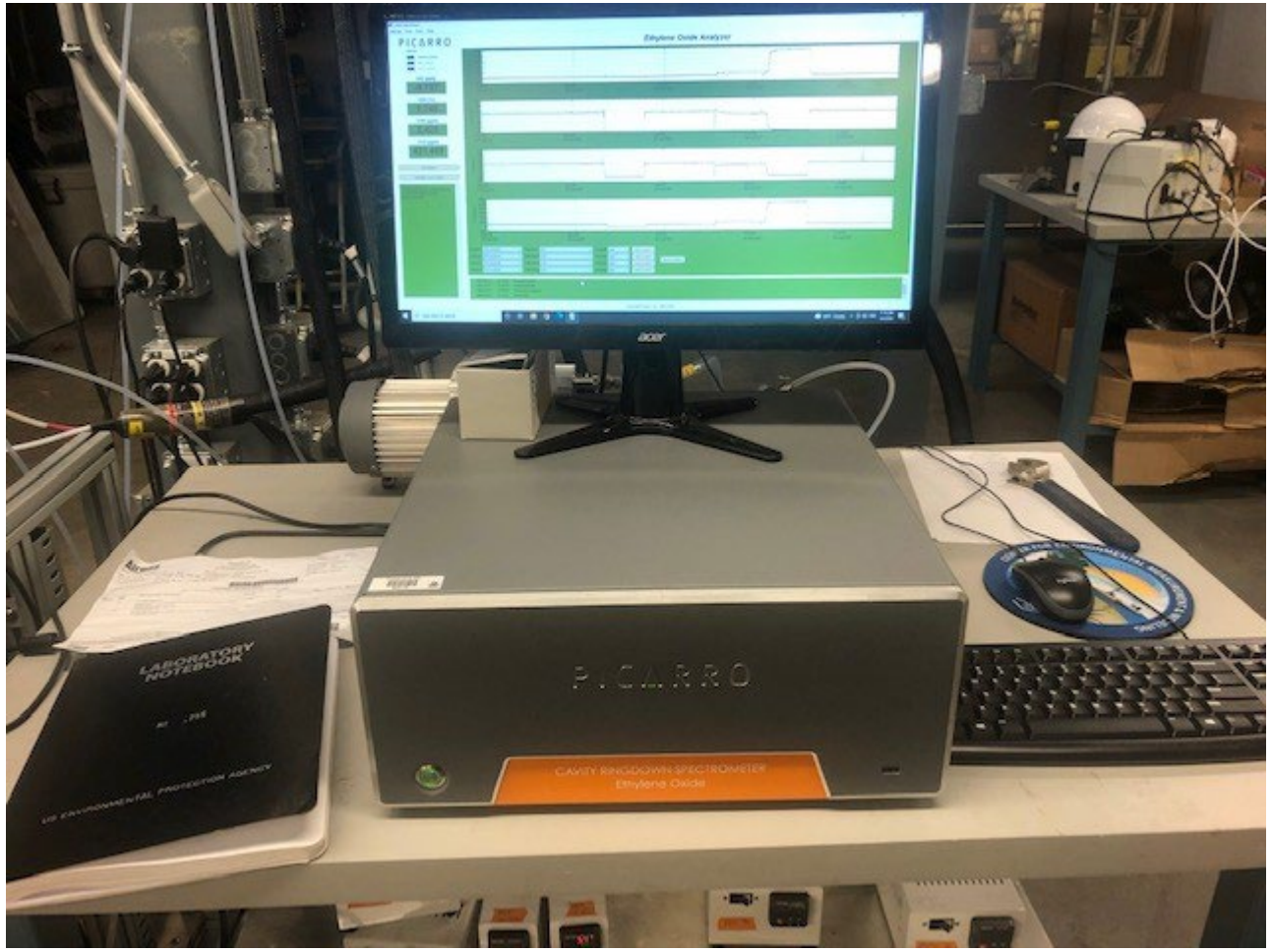
- EPA Method TO-15A (canisters)
  - Sample analysis by VOC Preconcentration/Gas Chromatography (GC)/Mass Spectrometry (MS)
  - Method Detection Level (MDL) ~ 15 pptv
- Modified OSHA Method 1010 (sorbent tubes)
  - Front and back of tube extracted separately, sample analysis by GC/Electron Capture Detector (ECD)
  - MDL ~ 1 ppbv

Instrument Model	Operating Principle	Measurement Rate	MDL (5 minute)
Aeris Ultra & Pico	Mid-Infrared Laser Absorption Spectroscopy	1 sec	2 ppb
Aerodyne	Quantum Cascade – Tunable Infrared Laser Differential Absorption Spectroscopy (QC-TILDA)	1 sec	0.1 ppb
AromaVOC	Preconcentration/CRDS	5 min. sampling / 30 min cycle	10 ppt
Picarro G2920 &G2910	Cavity Ringdown Spectroscopy (CRDS)	1 sec	0.1 ppb / 0.2 ppb
MAX Analytical Starboost	Fourier Transform Infrared Spectroscopy	1 min	5 ppb



Real-Time Measurements: Picarro/CRDS

- Cavity ring-down spectroscopy
- Long path length 5 km
- 1 Hz measurements
- Measures other gases (water, methane, and CO_2) which allows for dynamic spiking tracer testing when gases are blended with EtO
- Measurement range of 250 ppt to 60 ppm, very linear
- Sample cell is heated to 80 °C to control condensation and improve spectroscopy line width



Real-Time Measurements: Max Analytical Starboost/FTIR

- Uses a standard MKS 2030 FTIR system with optimized detector and band-pass filter to improve detection of EtO
- Capable of making 1 Hz measurements or can average spectra for reduced noise (1-minute)
- Best suited for source sampling due to a heated chemically inert sample cell
- Sample cell is heated to 150 °C to control condensation and acid gas

Max Analytical/ACS-10 + Zero Reference Module

- Automated Sample Controller is integrated with the MAX Starboost for source sampling
- Silco treated and heated internal plumbing
- Heated filter and pump to minimize
- System can perform zero and span checks as programmed
- Zero reference module (automated zero reference gas generator) can be used to check the source gas and provide measurements with the interferants present in the stack gas while only removing EtO from the gas stream

EtO Gas Cylinder Standards/Stability

Gas Cylinder Standards

- NIST currently unable to support development of EtO certified reference materials (CRMs), which are needed to enable “protocol” gases
- EtO “protocol” gas standards or equivalent are necessary to allow for regulatory monitoring
- Working with commercial gas vendors to produce alternative options in lieu of NIST CRMs
- EtO Gas Cylinder Stability Study
  - 42 cylinders analyzed from Oct 2019 to present, 5 gas manufacturers
  - Currently working closely with Airgas and Apel Riemer on the ability to produce Gas Manufacturer Alternative Certified Standards (GMACS), an alternative to NIST Certified Reference Material (CRMs) or NIST Traceable Reference Material (NTRMs)

Gas Cylinder Standards

Approach to Analysis:

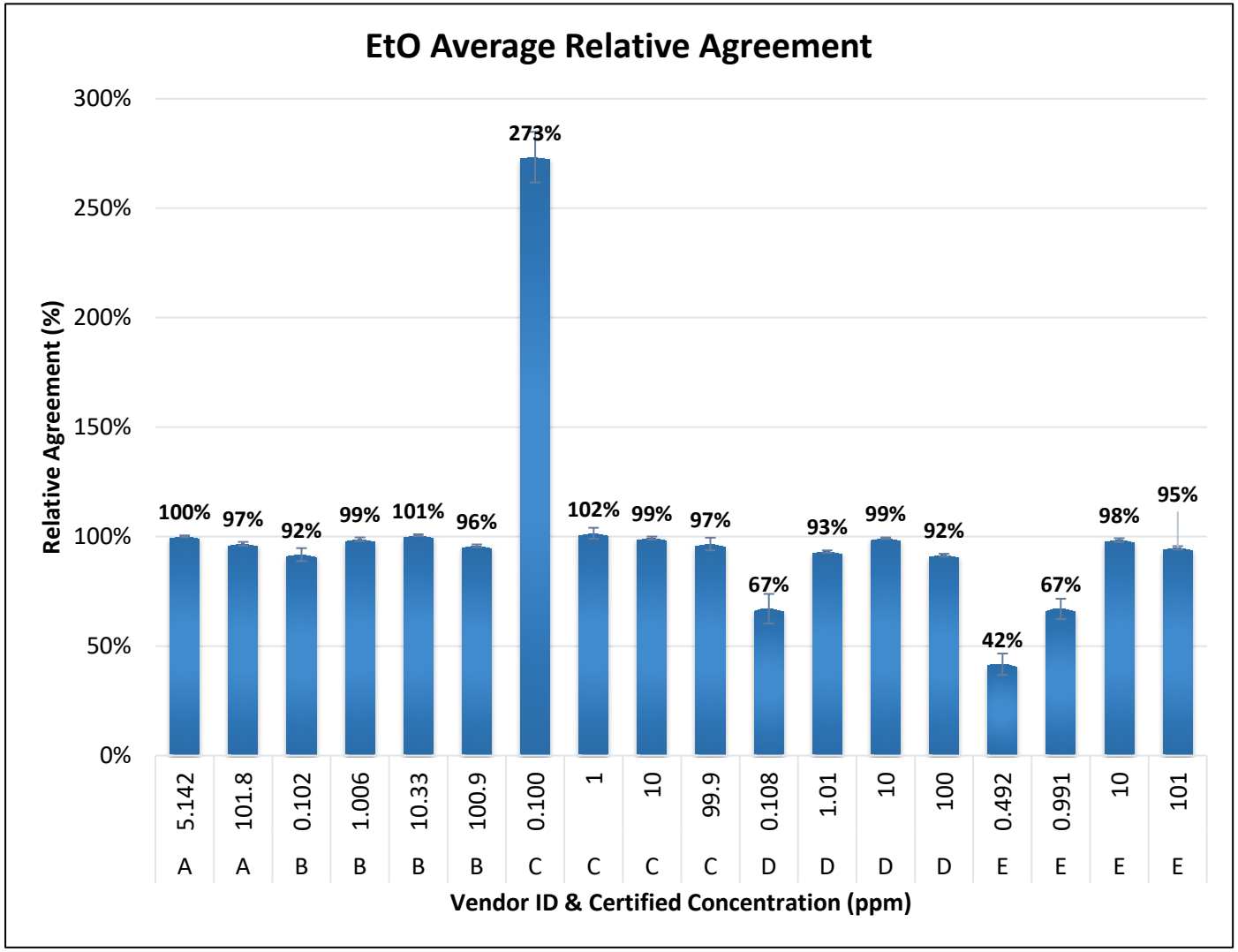
- Obtain EtO certified calibration gases from multiple commercial specialty gas providers:
  - Gas providers include (but are not limited to) Linde, Airgas, SpecGas, Custom Gas Solutions and Apel Riemer
  - This is not an exhaustive list of all available vendors
- Evaluate them as a function of concentration (0.1 ppm, 1 ppm, 10 ppm, 100 ppm):
  - Relative agreement with “certified” value
  - Stability over time
- Max Analytical Technology FTIR used as comparison measurement between cylinders

Instrumentation:

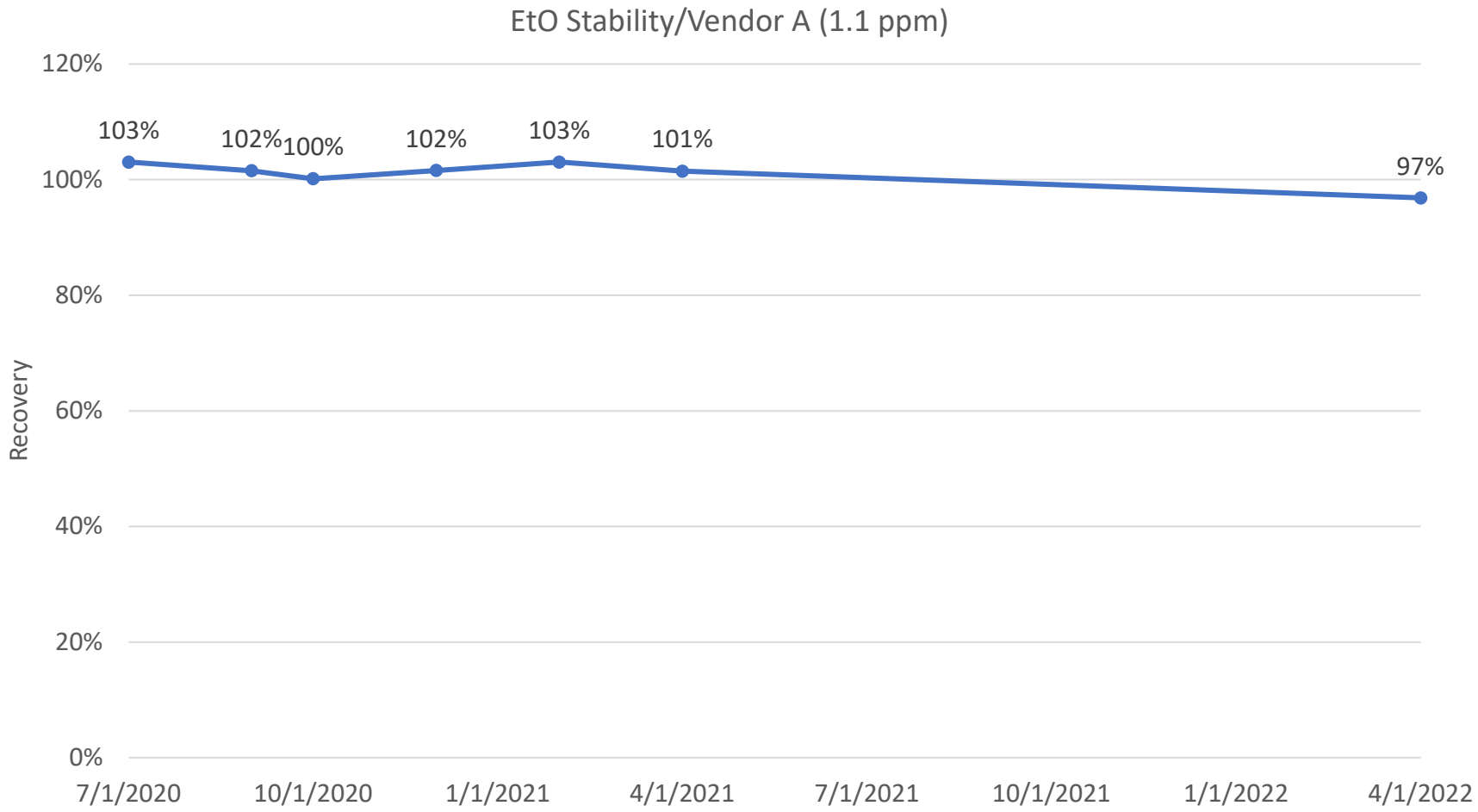
- Max Analytical Technology FTIR
  - Chosen because it was the first available real-time technology to the EPA capable at measuring EtO at 1 ppb
  - New enhanced FTIR that focuses on a narrow spectral range in the EtO region. This instrument uses a band pass filter to reduce noise from interferences and uses an analysis algorithm to enhance EtO detection
  - System has the data processing software capable of producing one minute data (configurable) and spectral validation
- MKS 2030 FTIR
  - Used for making comparative SF_6 and EtO measurements
    - SF6 is a stable gas, that FTIR is known to characterize well, and was used ONLY for comparison of measurement technique, but is not expected as a co-emitted compound

Gas Cylinder Standards

Vendor ID	Certified EtO Concentration (ppm)	Average Relative Agreement	Std Dev
A	5.142	100%	0%
	101.8	97%	1%
B	0.102	92%	3%
	1.006	99%	1%
	10.33	101%	0%
	100.9	96%	1%
C	0.100	273%	12%
	1	102%	2%
	10	99%	1%
	99.9	97%	3%
D	0.108	67%	7%
	1.01	93%	1%
	10	99%	0%
	100	92%	1%
E	0.492	42%	5%
	0.991	67%	5%
	10	98%	1%
	101	95%	1%

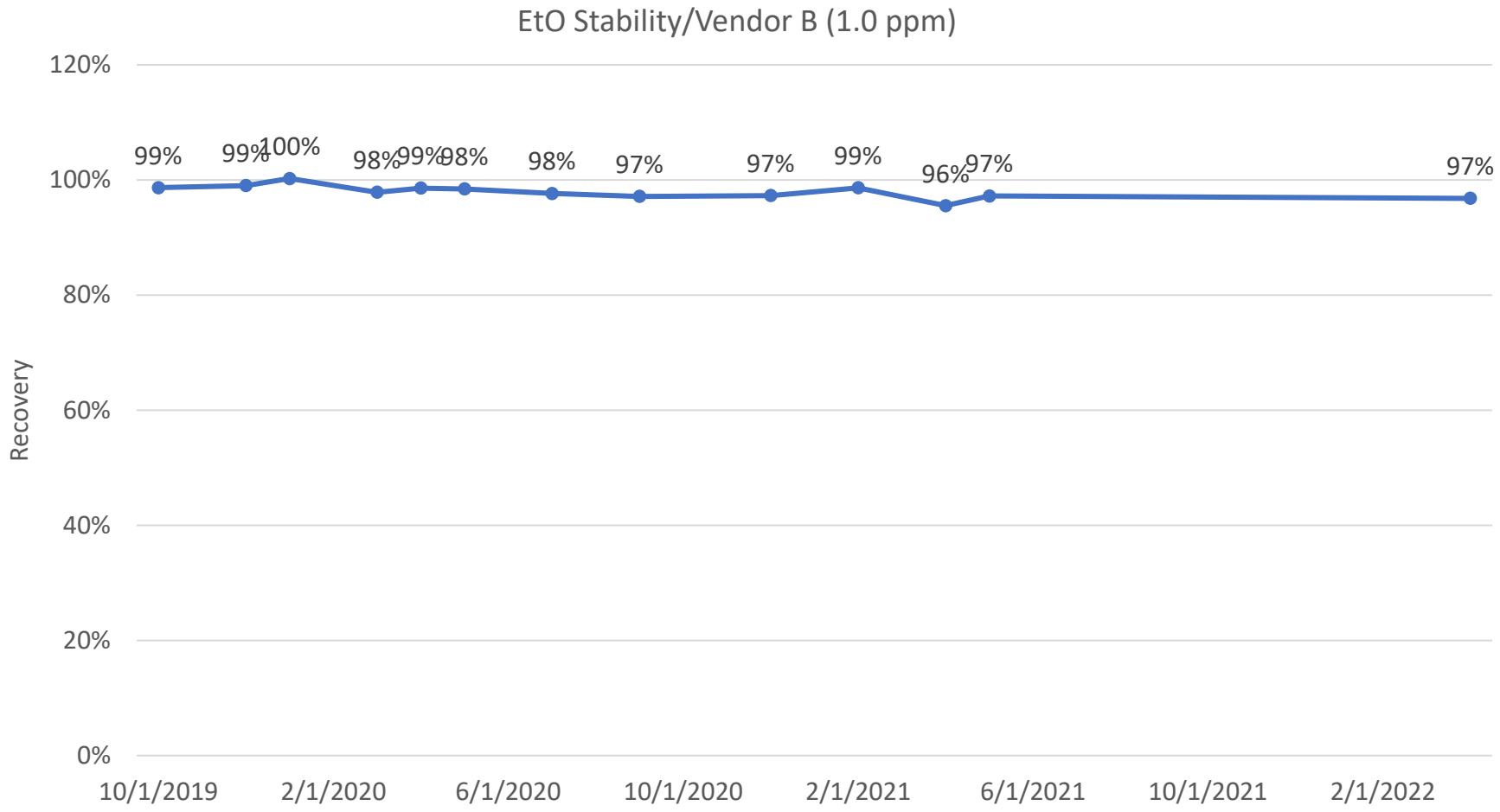


Gas Cylinder Stability



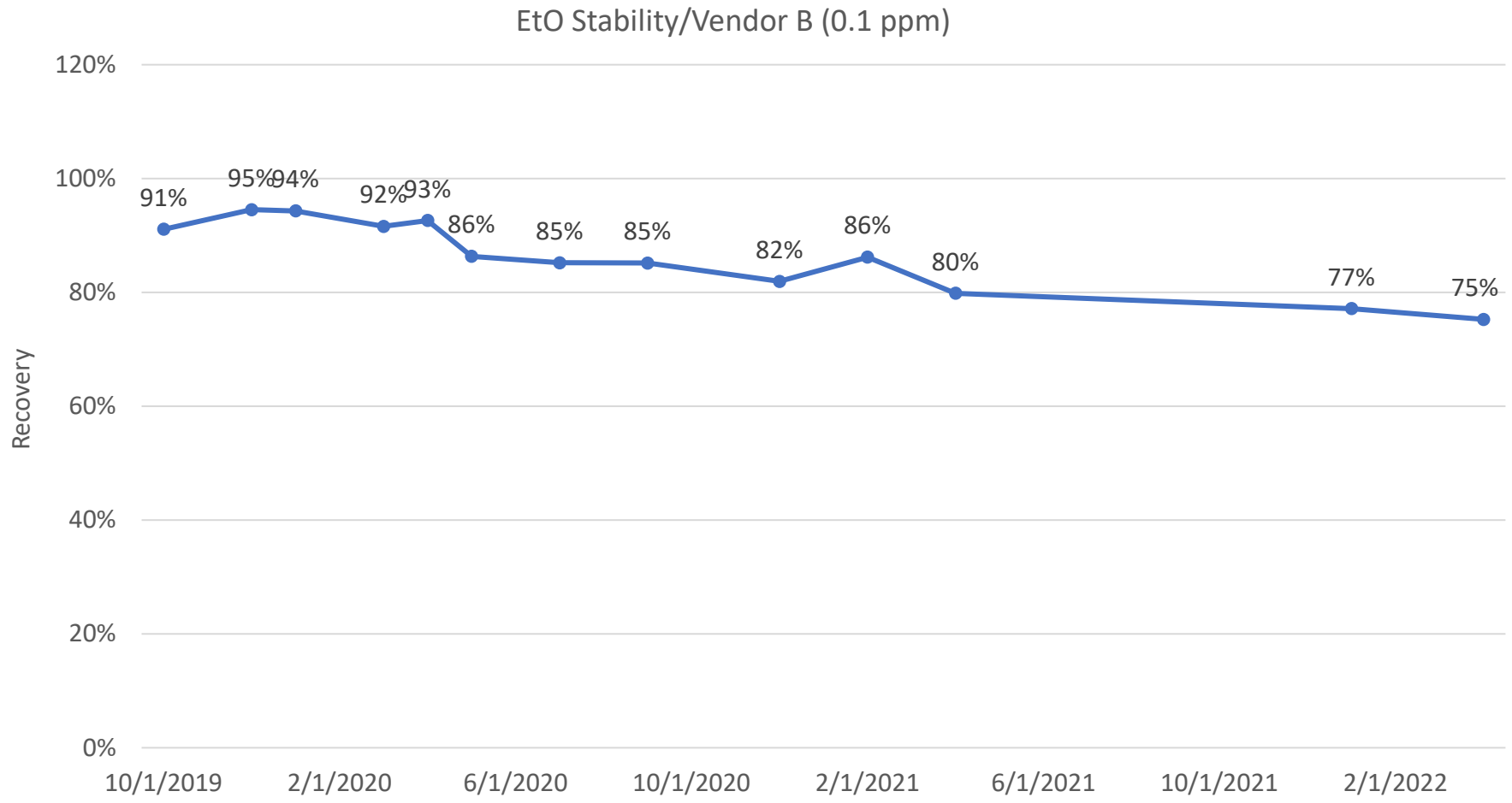
- Good stability at 1.1 ppm

Gas Cylinder Stability



- Good stability at 1.0 ppm

Gas Cylinder Stability



- Lower recovery and stability at 0.1 ppm

Source Sampling and Laboratory Equipment

Gas Standards Dilution Approach

- Since stable gas standards under 1 ppm are still in development, gas dilution systems can be used to make volumetric dilutions down to 1 ppb
- Environics systems have been tested with EtO standards to determine if losses are occuring
- Internal materials in the gas dilution systems should be made of electropolished stainless steel or silco steel.
- Be careful using reactive gases such as SO_2, as mass flow controller (MFC) seals were found to be reactive and caused EtO degradation

Gas Regulator Study

- Laboratory testing using various regulators after brand new regulators were only allowing 80% recovery of EtO
- New silco-treated low-volume regulator performed perfectly with no recovery loss
- Old (15+ years) brass regulators also performed with no recovery loss
- Plan to perform additional testing of new regulators of various construction materials (brass and silco steel) to test performance

Sampling Equipment

Heated probe and filter for stack sampling

Heated head pump for sample transport

Sampling Line Loss Study

- Six 100 ft. sampling lines used to test a broad range of materials and temperatures for heated sampling on sources such as scrubbers
- Materials include silco treated stainless steel, 316 stainless steel, polytetrafluoroethylene (PTFE), perfluoroalkoxy (PFA), high density polyethylene (HDPE), and FEP
- Data currently being analyzed/lines tested at various temperatures (ambient to 180 °C depending on line material type)
- Worst performer was the untreated 316 SS at temperatures over 120 °C

Heated line test rack

Lessons Learned

- Real time EtO measurements can be made on hot wet sources such as scrubbers
- EtO instrument linearity allows blending of higher concentration gases to determine limits of detection (LOD)
- EtO blending with a tracer can be used as a secondary validation tool using Method 205 to verify blended concentration
- Gas standards are available for calibrations and quality assurance checks
- Be aware of sampling/transport component materials, verify sample integrity, perform matrix spiking by Method 320

EtO Railcars

Thank You
Questions?

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