Trace Measurements of Ethylene Oxide using Cavity-enhanced Absorption Spectrometry near 3066 cm^{-1}

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Abstract

Ethylene oxide (EtO) is a key carcinogen that is widely used in chemical manufacturing and biotechnology industries. Recent work has suggested that permissible exposure limits for EtO be reduced from 1 – 5 ppm to sub-ppb levels. Such new standards will require new methodologies that are capable of measuring EtO with the requisite precision. In this paper, we demonstrate a new analyzer based on cavity-enhanced absorption spectrometry that utilizes a broad EtO absorption feature near 3066 cm^{-1}. A fit function is developed that includes water, methane, and EtO absorbances and accounts for absorption both inside and outside the cavity. A methane standard is used to determine the cavity gain factor, and the EtO absorbance spectrum is empirically determined. The final system shows excellent linearity from 0 – 909 ppb EtO ($R^2 \sim 0.9999$) with a measurement precision of better than ±1 ppb (1σ, 60 seconds) that improved to ±0.5 ppb (1σ, 15 minutes). Deliberate ambient EtO releases demonstrate the instrument's utility in rapidly detecting hazardous conditions. Further work will include improving the measurement precision and directly comparing the system to EPA Method TO-15.

Keywords: Ethylene Oxide, Cavity Ringdown, ICOS, EtO

1. Introduction

In 2018, 2.92M metric tons of ethylene oxide (EtO) was produced in the United States[1]. Most of this EtO was used as an intermediate chemical to produce glycols, ethoxylates, and ethanolamines. Additionally, it was also used in medical sterilization and the food industry. It has long been known that EtO is a carcinogen[2,3], and the Occupational Safety and Health Administration (OSHA) has set permissible 8-hour and 15-minute exposure limits of 1 ppm and 5 ppm respectively[4]. After an extensive review of the available data, the US Environmental Protection Agency (EPA) Integrated Risk Information System (IRIA) program concluded[5] that the "…confidence in the hazard characterization of EtO as 'carcinogenic to humans' is high." Using this data, the EPA has assigned a total cancer unit risk (inhalation unit risk) estimate[6] for EtO of 3.3×10^{-3} μg/m^3 (~12 ppt), though recent studies[7,8] suggests that this unit risk estimate may be too low and a value of ~2 ppb may be more appropriate.

These new standards will require new measurement technologies. Currently, EtO is measured via EPA Methods[9,10] TO-15 and TO-15A. Briefly, a discrete air sample is captured in a Summa canister[11] and shipped to a laboratory for analysis. The canister contents are directed through a solid adsorbent which preconcentrates the volatile organic compounds (e.g. EtO) as well as some common air constituents (e.g. CO_2). Cryogenic cooling is then used to remove most of the CO_2 prior to compound separation via a gas chromatography column. Finally, the EtO concentration is measured via selective ion or scanning mass spectrometry.

Though this method is extensively used, it has several limitations that make it difficult to address emerging EPA need to measure low ppt-levels of EtO. Foremost, EtO is typically characterized by

45 major m/z peaks at 44 and 29, which are confounded by CO_2 and co-eluting species (e.g. trans-2-
46 butene, acetaldehyde, and potentially others) respectively. This limitation can be partially
47 overcome by minimizing leaks, using a longer column, and exploiting other m/z peaks at 15, 41 –
48 43 and 56; however, this reduces the sensitivity of the analysis, making it unable to quantify low
49 levels of EtO. An extensive study[12] of ethylene oxide monitoring using EPA Method TO-15A
50 showed that Summa canister samples filled with dry nitrogen are stable for up to 15 days and can
51 provide EtO detections limits of 0.25 ppb, which is approximately 10 – 20 times higher than the
52 EPA targets noted above. Moreover, EtO production was observed in blank canisters filled with
53 humid air at 50% relative humidity[13]. Though mitigated by an extensive cleaning procedure, this
54 production mechanism produced 0.5 – 1 ppb of EtO in a standard canister in 1 – 2 weeks of storage.
55 In addition to sensitivity, cross-interference, and storage issues, EPA Method TO-15 requires the
56 acquisition and transport of discrete air samples. Thus, the measurement is not real-time or
57 continuous and may not be representative of actual, average EtO concentrations. Finally, as
58 described above, accurate and sensitive EtO analysis requires extensive infrastructure and
59 expertise, making it more complex and expensive.
60
61 There are several alternatives to EPA Method TO-15 that provide real-time EtO measurements,
62 including EPA Methods TO-18, 320, and 25A that use online gas chromatography, Fourier
63 Transform Infrared (FTIR), and flame ionization detection respectively. However, all these
64 methods suffer from limited sensitivity and cross-interference[14]. Recently, near-infrared cavity
65 ringdown spectroscopy has been used to quantify EtO at the ppb-level[15], and this method may
66 prove to useful for source monitoring.
67

In this paper, we present an ethylene oxide analyzer based on cavity-enhanced absorption spectrometry near 3066 cm^{-1} that is capable of making real-time measurements with sub-ppb precision. Previously, high-resolution FTIR spectra of ethylene oxide[16,17] show strong absorption features near 3060 cm^{-1} and 1270 cm^{-1}; however, tunable diode laser absorption spectrometry has only been used[18] near 5907 cm^{-1}. This latter work showed a precision of 17 ppm (1σ) using a 63.5 cm cell and extrapolated to a measurement precision of 30 ppb assuming a much longer pathlength (100 meters) and 10x reduction in noise using wavelength modulation spectroscopy. In this work we achieve a measurement precision of better than ±1 ppb (1σ, 60 seconds) by using a substantially stronger absorption feature and a high-finesse cavity to provide a very long effective pathlength.

2. Methods

2.1 Experimental Setup

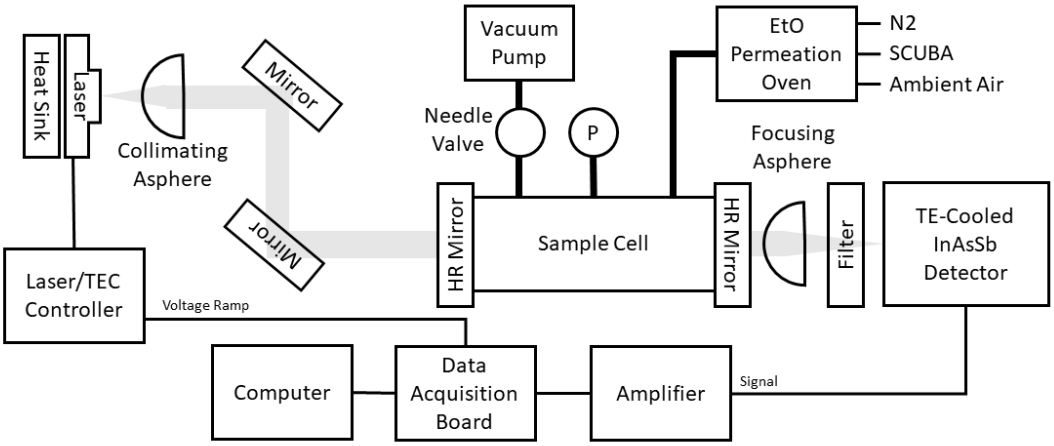

Figure 1: Schematic overview of experimental setup.

The experimental setup is shown schematically in Figure 1. A 25 mW distributed feedback DFB diode laser with incorporated TEC operating near 3066 cm^{-1} (3262 nm) with a linewidth of ~3 MHz (0.0001 cm^{-1}) at 6 °C (Nanoplus GmbH) is mounted onto a heatsink and collimated using an AR-coated asphere (NA = 0.56) mounted on an x/y/z stage. The collimated beam is directed into a high-finesse optical cavity comprised of two highly-reflective, 1-inch diameter mirrors (R > 99.8% at 3066 cm^{-1}, LayerTec GmbH). In order to minimize coherent interferences within the cavity, the cavity is intentionally misaligned, and the laser beam is slightly defocused akin to Integrated Cavity Output Spectroscopy (ICOS)[19] and off-axis ICOS[20]. The mid-infrared DFB diode laser was repeatedly tuned over 4 cm^{-1} by varying its injection current from 0 – 150 mA at a rate of 8 kHz. 8000 transmission spectra were averaged prior to analysis, yielding an analyzer data reporting rate of 1 Hz.

Light transmitted through the cavity is focused by an AR-coated, f/1 silicon asphere, passed through an optical filter, and directed onto a thermo-electrically cooled InAsSb detector (Thorlabs). The detector is AC-coupled and provides a gain of 10000 V/A, a responsivity of ~1.2 A/W at 3263 nm, and a bandwidth of 100 kHz. Note that, due to the low bandwidth of the system, the effective optical pathlength of the cavity cannot be determined by cavity ringdown measurements[21]. Instead, fits to a known absorption are used to determine the cavity gain factor as described below.

In an ideal incoherent cavity enhanced absorption spectrometry system, approximately I_0*T/2 milliwatts of light transmit through the cavity, where I_0 = 25 mW is the incident laser power and T ~ 0.1% is the mirror transmission (T ~ 1 – R). Thus, in an ideal situation, ~12 μW of laser light

would be focused onto the detector, resulting in a peak signal of ~140 mV. However, due to large losses in the mirror coatings (e.g. absorption and scatter coatings), the measured detector signal is only a few mV. To avoid limiting the system performance by bit-noise in the data acquisition system, the detector signal is passed through a 10 kΩ terminator and into an inverting amplifier with a gain of 200. The amplifier output is digitized by a custom data acquisition board at 4 MS/s and collected by a computer. The data acquisition board also provides a voltage ramp with a 90% duty cycle that is connected to a laser driver (Thorlabs) that controls the laser current and temperature.

The gas samples are generated by a programmable permeation oven (VICI Metronics) containing an ethylene oxide permeation tube that provides a permeation rate of 1799 ng/min at 45 °C. Different gases can be flowed through the permeation oven, including nitrogen, SCUBA air, ambient air (pushed by a small diaphragm pump), and 80 ppm CH_4/N_2. The pressure in the cavity is measured by a Baratron pressure gauge (MKS). In order to control the pressure in the cavity and maintain it at ~500 Torr, the upstream permeation oven flow rate is set, and gas is pulled through the cavity using a 3-head diaphragm vacuum pump (KNF) whose flow rate is manually controlled by a needle valve.

2.2 Data Analysis

Simulated spectra of probe region are shown in Figure 2 for a gas sample containing 1% water vapor, 4 ppm methane, and 1 ppm ethylene oxide. The former was simulated using HITRAN parameters[22], whereas the latter two species used data tabulated by Pacific Northwest National Laboratory (PNNL)[23]. Note that the entire PNNL and HITRAN databases were surveyed, and no

other compounds were found to have absorptions exceeding 0.0002 for 1 ppm compound in a 1-meter pathlength (1/100th the optical depth of ethylene oxide). Thus, we anticipate that the data analysis routine only needs to include water vapor, methane, and ethylene oxide.

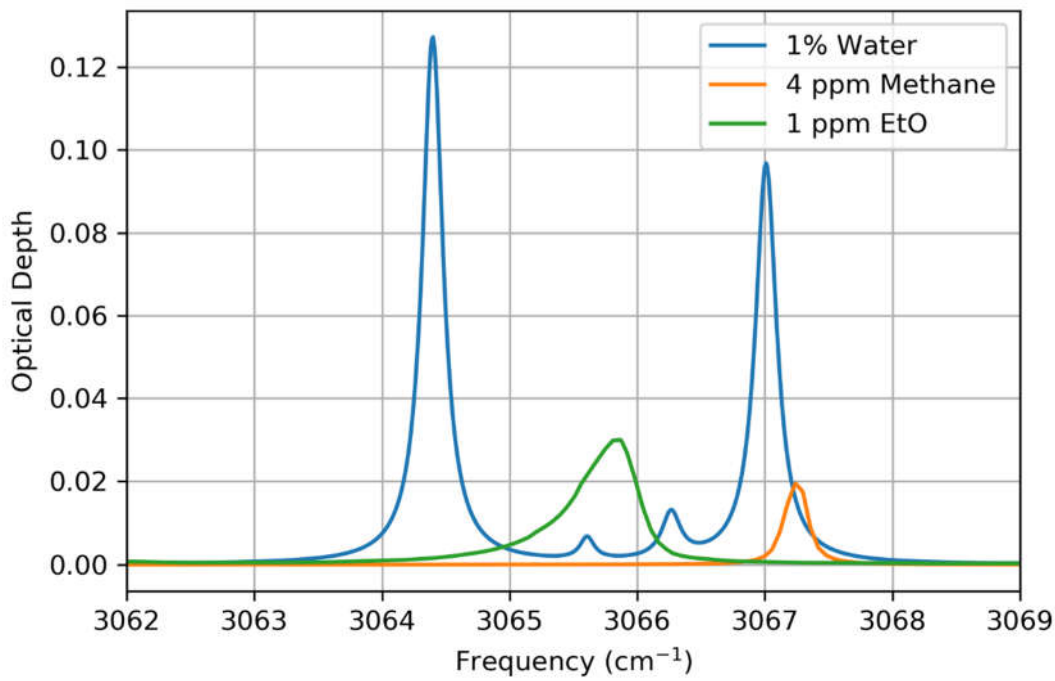

Figure 2: Simulated absorption spectra of water vapor (blue), methane (orange), and ethylene oxide (green) in the spectral probe region. Note that no other compounds in the PNNL database were found to absorb in this region.

A sample measured cavity-enhanced transmission spectrum of ambient air containing ~1.5 % water vapor and ~2 ppm methane is shown in Figure 3. Each data point represents 0.25 μs, commiserate with the sampling rate. Note that, as expected, the cavity-enhanced transmission spectrum is dominated by water vapor optical absorption.

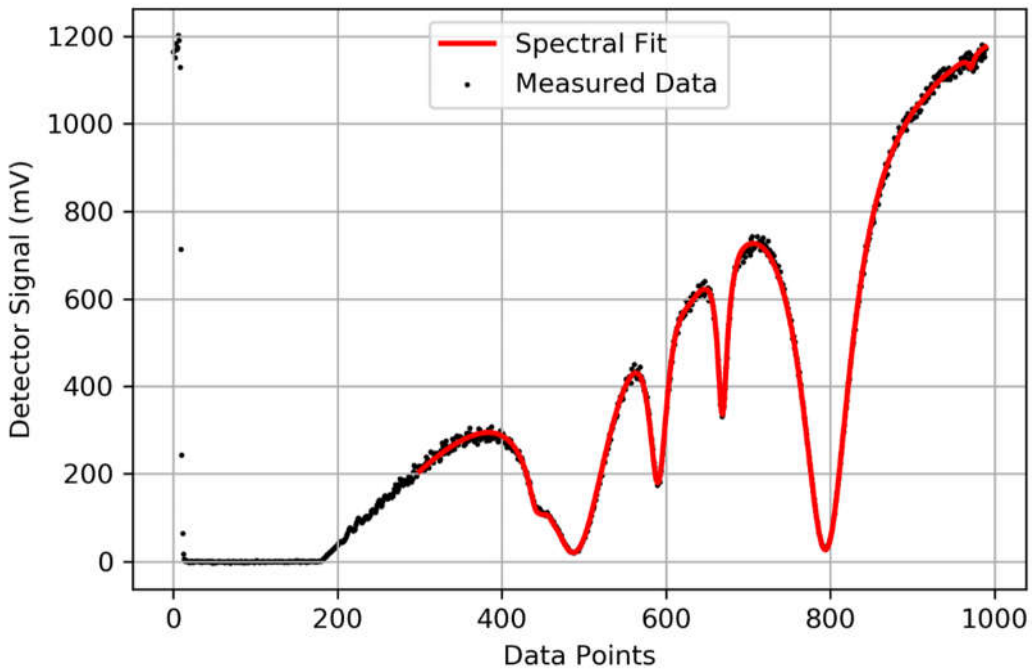

Figure 3: **Raw measured detector signal (black) with 500 Torr of ambient air in the cavity corrected for an offset value and fit to the function (red) described in the text. The sampling rate is 4 MHz (0.25 μs/datapoint) and 8000 spectra were averaged over 1 second.**

After subtracting the detector offset, the transmitted intensity, *I*, is fit to:

$$I(x, P_{H2O}, P_{CH4}, P_{EtO}) = \frac{I_0(x) * e^{-OD_{outside}}}{(1 + G * OD_{inside})} \quad (1)$$

where x is the datapoint (equivalent to the time axis), P is the partial pressure of the indicates species, $I_0(x)$ is the transmitted intensity in the absence of all absorption (approximated by a 3rd order polynomial), G is the cavity gain factor, $OD_{outside}$ is the optical depth due to ambient air absorption of water and methane outside the cavity, and OD_{inside} is the optical depth due to sample absorption inside the cavity. Equation 1 is a combination of the Beer-Lambert-Bouguer Law and

the absorption equation for cavity-enhanced absorption spectrometry[20]. For water vapor and methane, the optical depth as a function of frequency, *f*, is expressed using the standard HITRAN[22] formulation. For example, for methane, OD(f) is given as:

$$OD_{CH4}(f) = P_{CH4} * N * L * \sum_i S_i * V(f, LW, DW) \quad (2)$$

where N is a function of temperature, T, and is 2.479e19*296/T, L is the relevant pathlength, S_i is the linestrength of the ith tablulted line, LW is the Lorentz width of the feature, and DW is the Doppler width of the feature (function of total pressure and temperature). A similar expression is used for water vapor. All tabulated line parameters (line frequencies, line strengths, broadening coefficients…) are taken from the HITRAN database[22]. OD(f) for ethylene oxide is determined by measuring the basis set as described below. The total optical depth is then expressed as the sum of all components.

Since optical depth is expressed as a function of frequency and the measured intensity is a function of datapoint, the etalon function is approximated as:

$$f(x) = e_0 + e_1 x + e_2 x^2 \quad (3)$$

where e_n are coefficients determined from the fit. Note that, though the actual laser tuning curve is more complex, it can be well approximated by a 2nd-order polynomial over a small tuning range. A more accurate measure of f(x) can be obtained by measuring the laser transmission through a

germanium etalon of known length. This method may be employed in the future to further characterize the laser tuning curve.

Using this fit function, the gas temperature, gas pressure, and pathlength outside the cavity are fixed, whereas the species' partial pressures, baseline coefficients, and etalon coefficients are floated. The cavity gain factor is measured as described below and then fixed for all subsequent analyses.

In order to limit computational overhead, a subset of the HITRAN database is used to obtain the tabulated parameters. This subset spans from 3061 – 3071 cm^{-1} and only includes water and methane lines with linestrengths greater than 10^{-24} cm/molecule and 10^{-22} cm/molecule respectively.

2.3 Determination of the Cavity Gain Factor

The cavity gain factor, G, is typically determined from the mirror reflectivity, R:

$$G = \frac{R}{1-R} \tag{4}$$

This reflectivity is usually measured via cavity ringdown spectroscopy[21] on the empty (or nitrogen-filled) cell. However, due to the limited bandwidth of the detector (100 kHz), the cavity gain factor was determined by measuring dilutions of an 80 ppm CH_4/nitrogen standard from 0 – 7.3 ppm. The measured methane concentration (ppm) was then compared to the actual methane concentration and the gain factor was adjusted to yield a slope of ~1. Using this method, we

obtained highly linear results with a slope of 0.999 and an intercept of -0.011 by using a gain factor of 740 (Figure 4). This suggests mirror reflectivity R ~ 99.86%, consistent with the manufacturer's indication that R > 99.7 %.

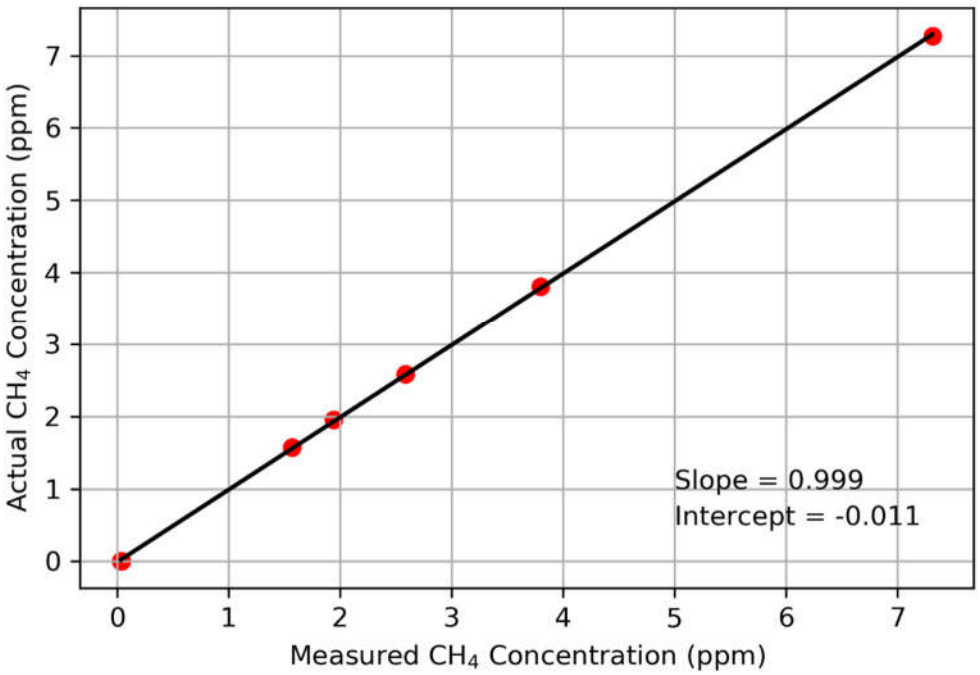

Figure 4: **By adjusting cavity gain factor to 740, the actual versus measured methane concentration yielded a slope of ~1 and an intercept of ~0.**

2.4 Measuring and Incorporating the Ethylene Oxide (EtO) Basis Set

Unlike water and methane, ethylene oxide absorption features are not in the HITRAN database. They have been measured and disseminated by Pacific Northwest National Laboratory (PNNL)[23]; however, the FTIR resolution of 0.125 cm^{-1} is insufficient for the high-resolution laser spectrometry presented here. Therefore, measurements of 500 Torr dry nitrogen and 500 Torr of 475 ppb EtO/N_2 were used to construct the EtO absorption basis set. The measured dry nitrogen

transmission spectrum was fit to equation 1 to determine $I_0(x)$. The cavity-enhanced EtO absorbance, A_E, was then determined as:

$$GA_E = I_0\left(\frac{1}{I_E} - \frac{1}{I_{N2}}\right) \tag{5}$$

where I_E and I_{N2} are the measured transmission spectra with and without EtO respectively. Finally, a spectrum of ambient air with no EtO was measured and fit to determine the etalon function, f(x). Combining these measurements and smoothing the resulting absorbance spectrum with a 3rd-order Savitzky-Golay filter (boxsize = 41 points) to minimize noise yielded the EtO basis set shown in Figure 5. Note that the data, which has been scaled to represent the absorption of 475 ppb EtO in a 1-meter pathlength, is in good agreement with the PNNL results, but slightly shifted in frequency.

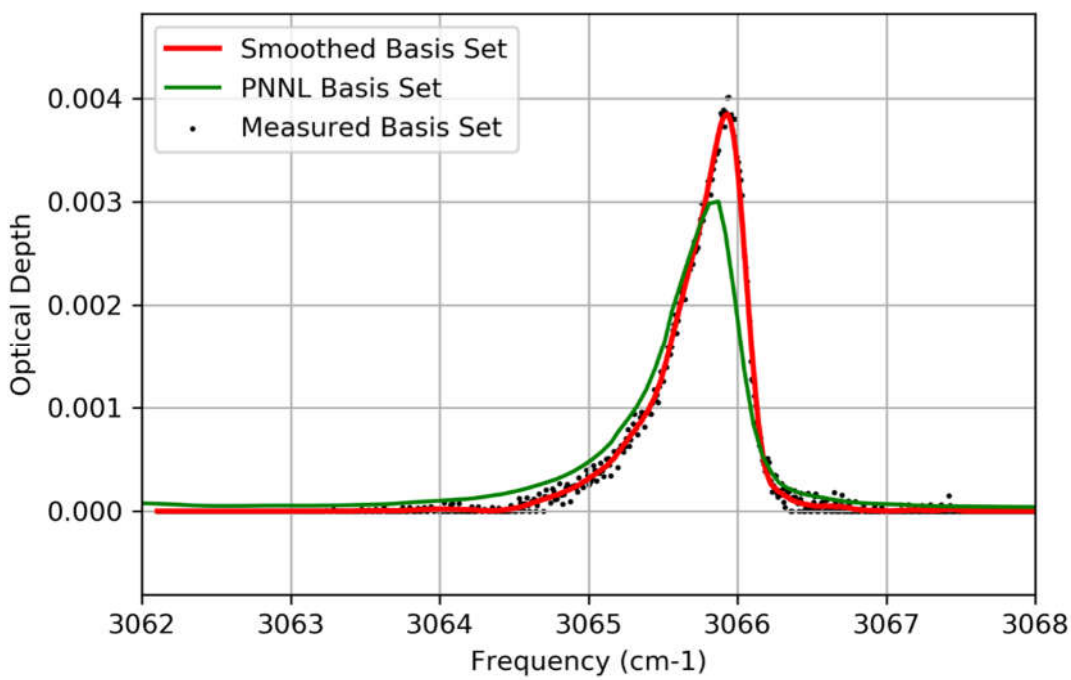

Figure 5: Measured (black dots) and smoothed (red) basis set for 475 ppb EtO in a 1-meter pathlength. The published PNNL FTIR spectrum is included in green.

This EtO basis set, $B_{EtO}(f)$, was incorporated into the fit by adding an EtO term to the optical depth:

$$OD_{EtO}(f) = C_{EtO} * B_{EtO}(f) \tag{2}$$

where C_{EtO} is a coefficient that is proportional to the EtO concentration, and the basis set was linearly interpolated at for all values of f. The relationship between C_{EtO} and the actual concentration of EtO was determined empirically as presented below.

3. Results and Discussion

3.1 Linearity and Relationship between C_{EtO} and EtO Concentration

In order to determine the relationship between C_{EtO} and the actual EtO concentration as well as gauge the linearity of the analyzer, the permeation oven dilution was adjusted to produce concentrations of EtO ranging from 0 – 909 ppb. The resulting data (Figure 6) was fit to line with zero intercept and yielded a slope of 2064.3 with a $R^2 \sim 0.9999$, suggesting that the analyzer provides a very linear response over this dynamic range. Note that the accuracy of the proportionality coefficient, C_{EtO}, is limited by the accuracy of the permeation tube to ±15 %.

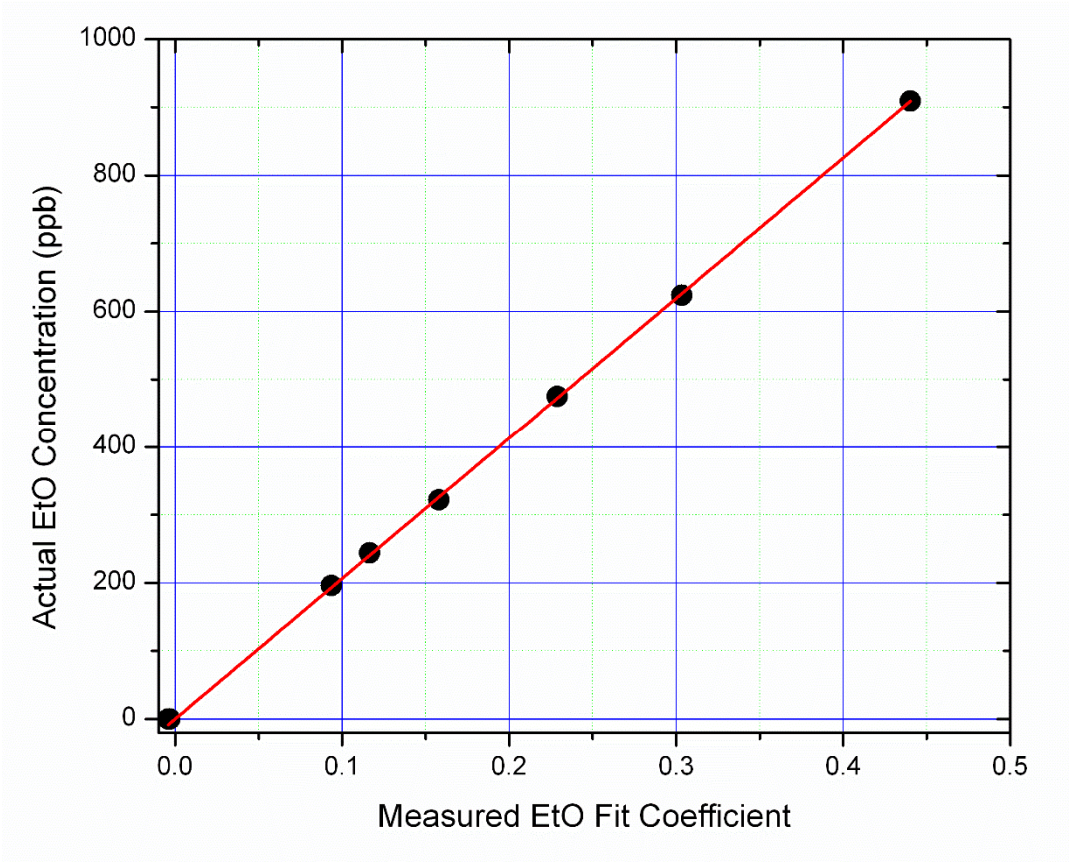

Figure 6: **Measured EtO coefficient versus actual EtO concentration from 0 – 909 ppb. Note that the analyzer provides a highly linear response (R^2 ~ 0.9999) and the slope yields a conversion factor of 2064 between the measured EtO coefficient and EtO concentration.**

3.2 Measurement Precision

The analyzer's measurement precision was determined by continuously measuring a sample of 60.5 ppb EtO/air for ~8 hours. The data and resulting Allan variance are shown in Figure 7. Note that the system provides a short-term precision of ±1.7 ppb (1σ, 10 s) that improves to better than ±0.5 ppb (1σ) with 15 minutes of averaging. As noted above, this is comparable to EPA Method TO-15, but provides real-time data with no user intervention.

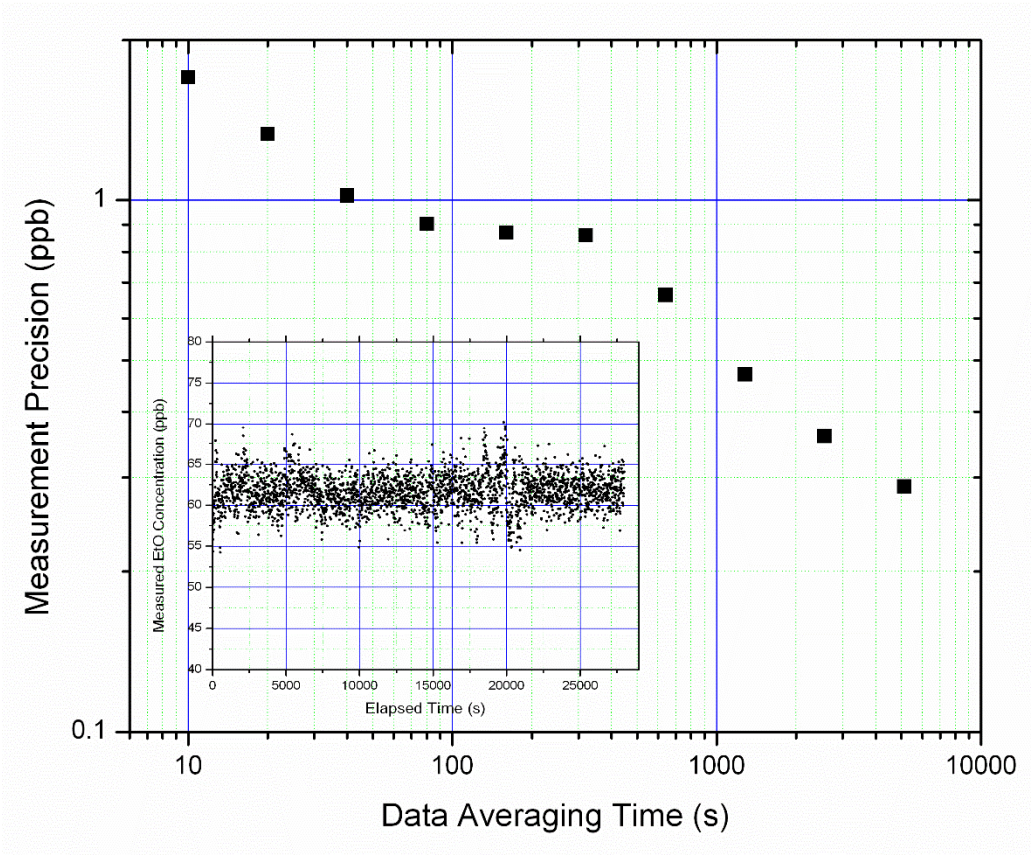

Figure 7: **Allan deviation plot showing the measurement precision as a function of data averaging time. The raw data is shown in the inset.**

3.3 Ambient Air Monitoring

Subsequent to the validation studies above, the analyzer was used to monitor ambient air in the laboratory during three deliberate ethylene oxide releases from the permeation oven. The cell inlet was disconnected from the permeation oven and sampled ambient air through a 0.1-micron Teflon membrane filter. The measured ethylene oxide values as a function of time are shown in Figure 8, and clearly demonstrate the ability of the system to detect ethylene oxide leaks and hazards at low levels.

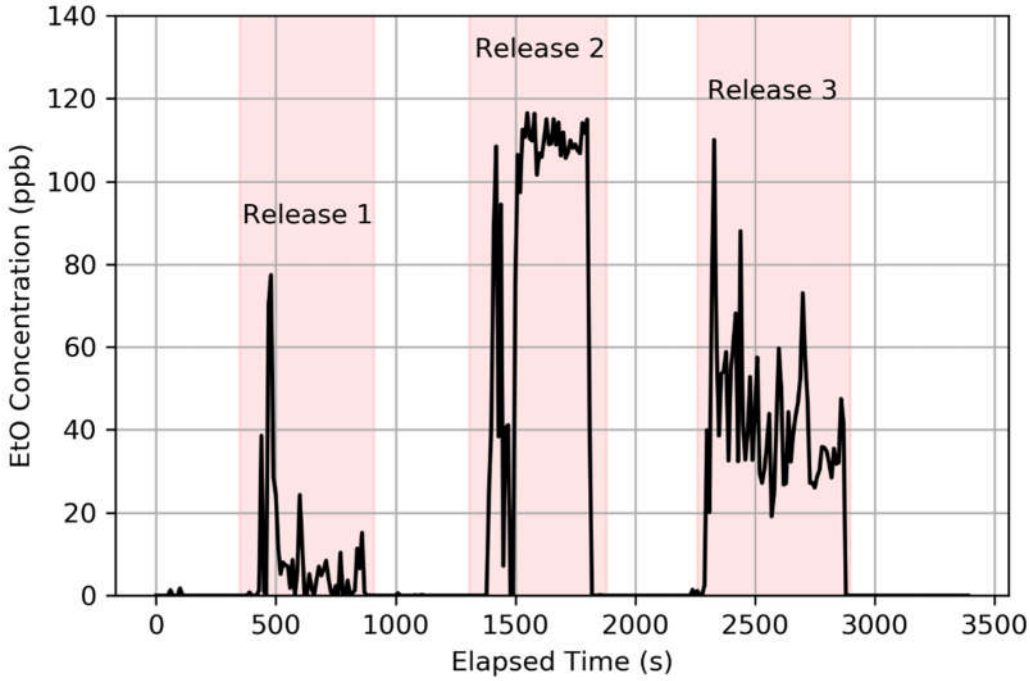

Figure 8: Measured EtO concentrations in ambient air during three deliberate EtO releases

4. Conclusion and Future Work

In this contribution, we have presented the test results of a mid-infrared, cavity-enhanced analyzer capable of providing real-time, rapid (1 Hz), ppb-level measurements of ethylene oxide. The technique will enable the accurate quantification of EtO source emissions, as well as enable fast alarm level measurements in facilities that generate or use large quantities of EtO.

In order to address next-generation EtO monitoring needs, the instrument precision needs to be improved by a factor of ~10 – 30. The methodology presented here can be improved in several ways to approach this goal. Foremost, the one-inch diameter mirrors can be replaced by two-inch diameter mirrors. Previous work[20] has shown that this decreases the noise of cavity-enhanced absorption spectrometry by a factor of ~10 by providing better incoherent coupling. Likewise,

since the system is limited by detector signal and thus requires an external amplifier, a higher power laser, reinjection[24], and mirror coatings with less absorption/scatter should also improve the SNR of the analyzer. Finally, a DC-coupled detector may help mitigate long-term changed in baseline curvature. Note that, since water since water is a strong optical absorber in the spectral region, using higher reflectivity mirrors is not expected to improve the analyzer performance.

In addition to improving the instrument precision, the system accuracy may be substantially increased by using gravimetric standards or intercomparisons to EPA Method TO-15, instead of permeation tubes. In order to account for changes in temperature and pressure, the EtO basis set can be further developed under different environmental conditions and appropriately interpolated. Finally, the analyzer should be deployed outside, under real-world conditions, and directly compared to EPA Method TO-15.

5. Acknowledgments

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