Intercomparison of commercial analyzers for atmospheric ethane and methane observations

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Abstract.

Methane ($\text{CH}_4$) is a strong greenhouse gas that has become the focus of climate mitigation policies in recent years. Ethane/methane ratios can be used to identify and partition the different sources of methane, especially in areas with natural gas mixed with biogenic methane emissions, such as cities. We assessed the precision, accuracy and selectivity of three commercially available laser-based analyzers that have been marketed as measuring instantaneous dry mole fractions of methane and ethane in ambient air. The Aerodyne SuperDUAL instrument performed best of the three instruments but it requires expertise to operate and space for the large footprint. The Aeris MIRA Ultra LDS analyzer also performed well for the price point and small footprint but required characterization of the water vapor dependence of reported concentrations and careful setup for use. The Picarro G2210-i precisely measured methane but it did not detect the 10 ppb increases in ambient ethane detected by the other two instruments when sampling a plume of incompletely combusted natural gas. For long-term tower deployments or those with large mobile laboratories, the Aerodyne SuperDUAL provides the best precision for methane and ethane. For smaller mobile platforms, the Aeris MIRA is a more compact analyzer, and with careful use, can quantify thermogenic methane sources to sufficient precision for short term deployments in urban or oil and gas areas. We weighed the advantages of each instrument, including size, power requirement, ease of use on mobile platforms, and expertise needed to operate the instrument, and we recommend the Aerodyne SuperDUAL or the Aeris MIRA Ultra LDS depending on the situation.
1 Introduction

The atmospheric concentrations of methane (CH$_4$), a strong greenhouse gas, have been rising at an unprecedented rate in recent years, with record breaking growth rates since 2020 (https://gml.noaa.gov/ccgg/trends_ch4/). Methane has an atmospheric lifetime of ~10 years compared to ~100 years for carbon dioxide (CO$_2$) and absorbs over 80 times more heat than CO$_2$ over 20 years (Szopa et al., 2021). Both of these characteristics make the reduction of methane emissions a priority target for short-term reductions in anthropogenic global warming. In recent years, methane has become the target of climate mitigation policies at many levels of government, including international (e.g. founding of the United Nations Environment Programme funded International Methane Emissions Observatory (IMEO) in 2022), national (e.g. Inflation Reduction Act, 2022, USA) and local (e.g. New York’s Climate Leadership and Community Protection Act, CLCPA, over 50 cities in the US banning natural gas new construction).

Methane sources are categorized as thermogenic (e.g. oil, natural gas, coal mining) or biogenic; which can be both natural (e.g. wetlands) or anthropogenic (e.g. agriculture, landfills, sewage) in origin (Saunois et al., 2020). Each of these methane sources co-emits different trace gas species, which we can use to identify the source of methane. Thermogenic sources of methane, such as natural gas, also contain ethane (C$_2$H$_6$) and other hydrocarbons. The incomplete combustion of natural gas can co-emit high concentrations of carbon monoxide (CO) and other Volatile Organic Compounds VOCs. Biogenic sources of methane do not co-emit ethane, but can emit carbon dioxide (CO$_2$) and more odorous trace gases such as hydrogen sulfide (H$_2$S). Therefore, ethane can be used to distinguish between thermogenic (methane/ethane co-emitted) and biogenic (no ethane emitted) sources of methane. Many studies have used methane/ethane ratios to identify natural gas leaks in the natural gas production and distribution networks (e.g. review of methods described in Ravikumar et al., 2019). Methane/ethane observations have also been used for mobile and stationary sampling in urban areas across many countries to identify natural gas leaks separately from biogenically produced methane (e.g. McKain et al., 2015; Lamb et al., 2016; Maazallahi et al., 2020; Defratyka et al., 2021).

Methane monitoring networks are being developed for city, state and national scales with the goal of evaluating the efficacy of methane reduction policies. Many of these networks will need to partition the contribution of methane between thermogenic and biogenic sources. In recent years, commercial analyzers have been developed to measure methane and ethane at ambient concentrations and many of these analyzers are marketed as allowing users to attribute the sources of methane.

Here, we evaluated three laser-based spectrometers that are marketed to measure ambient ethane and methane; (i) an enhanced infra-red (IR) absorption spectrometer (Aerodyne Research Inc SuperDual QCl/ICL), (ii) a mid-IR absorption spectrometer (Aeris Technologies Mira Ultra LDS) and (iii) a cavity ring down spectrometer (Picarro G2210-i CRDS). The precision and accuracy of each instrument was evaluated and compared to the advertised performance. We tested the water vapor response and assessed the long-term operation needs of each instrument.

Finally, we evaluated the performance of each instrument while sampling urban air at a rooftop site with large natural gas and biogenic emissions in the urban core of New York City in February 2022. We examine the requirements for long-term operation of each analyzer and make recommendations for operation.
2 Methods

2.1 Description of Analyzers

2.1.1 Aerodyne Research Inc SuperDual

Various configurations of Aerodyne laser spectrometers have been used to measure methane and ethane in stationary (McKain et al., 2015), ground-based mobile (Yacovitch et al., 2014) and airborne (Kostinek et al., 2019; Plant et al., 2019) platforms. These spectrometers use a continuous wave interband cascade laser (ICL) based spectrometer to measure methane, ethane and water vapor, often alongside a continuous wave quantum cascade laser (QCL) to measure dry mole fractions of carbon dioxide (CO$_2$), carbon monoxide (CO), and nitrous oxide (N$_2$O). Here, we use a SuperDUAL configuration of a two-laser system with a 2L astigmatic Herriott cell (path length 210m) at 50 Torr pressure. The instrument was manufactured in 2015 and refurbished with new lasers in 2020. We use the provided TDL Wintel software to fit the absorption spectra and quantify five target gases and water vapor. The ICL (Laser 1) sweeps from 2988.520 to 2990.625 cm$^{-1}$ to detect CH$_4$, C$_2$H$_6$ and H$_2$O. The edge of the ethane absorption feature (2990.081 cm$^{-1}$) includes a small methane peak (2989.98 cm$^{-1}$) that is fixed to the value determined from the main fit at 2989.003 cm$^{-1}$. The QCL (Laser 2) sweeps from 2227.550 to 2228.000 cm$^{-1}$ and includes absorption features for $^{13}$CO$_2$ (2227.605 cm$^{-1}$), CO (2227.639 cm$^{-1}$), N$_2$O (2227.843 cm$^{-1}$) and H$_2$O. We use the default water broadening value of 2 for all species except CO, which is 1.45. The analyzer has a large, heavy footprint (56 cm x 77 cm x 64 cm; 75kg) and requires an external pump and chiller (to maintain laser temperature stability) that require a stable power source. The instrument has been used extensively and successfully for long-term ground site observations and mobile lab deployments but it is not suitable for smaller/car based mobile sampling. As part of our regular ambient sampling, the Aerodyne SuperDUAL samples nitrogen gas each hour to account for instrument drift for lower concentration species such as ethane. A smooth spline is fitted to the reported zero for each gas species and subtracted from the 1Hz data.

2.1.2 Aeris Technologies MIRA Ultra LDS

The Aeris Technologies MIRA Ultra LDS (#100209; manufactured July 2021) uses a mid-IR ICL (~3000 cm$^{-1}$ range) with a multi-pass cell. There are few descriptions of the Aeris MIRA but (Travis et al., 2020) described the portable version of the instrument with an onboard battery (MIRA Pico, not evaluated here). The multi-pass cell (60 cm$^3$) has a path length of 13 m and an internal pump maintains the cell pressure at 180 Torr with a ~380 sccm flow rate. The small footprint of the rackmount configured analyzer (43 cm x 28 cm x 13 cm; 5 kg) makes it ideal for car-based mobile sampling. The current configuration using a small internal pump is not suitable for sampling below ambient pressure and care should be taken when configuring the system when sampling through long lines on towers.

2.1.3 Picarro G2210-i

The Picarro G2210-i (#3441-RFIDS2010, manufactured Aug 2019) is a Cavity Ring Down Spectrometer that measures CH$_4$, CO$_2$, C$_2$H$_6$, and $^{13}$C-CH$_4$. The instrument uses an external pump to reach a cell pressure of 148 Torr and flow rate of 24 sccm through a cavity of 35 cm$^3$ with a path length of up to 30 km (https://www.picarro.com/support/library/documents/g2210i_analyzer_datasheet). Methane data from the instrument has been used on mobile (O’Connell et al., 2019) and stationary (Lebel et al., 2020) platforms and is also mentioned...
in (Defratyka et al., 2021) but none of these studies have discussed or shown the observed ethane concentrations. The datasheet indicates that the instrument is designed to sample ambient air but may have interferences from elevated concentrations of gas species such as hydrogen sulfide (H$_2$S) or volatile organic compounds (VOCs).

### 2.2 Instrument Evaluation Set-up

#### 2.2.1 Humidity

The humidity of the sample line for the instruments was varied using a Perma Pure Nafion (TM) dryer. Nafion dryers have a semi-permeable membrane separating an internal sample gas stream from a counterflow purge gas stream contained within a stainless-steel outer shell. If the partial pressure of water vapor is higher in the purge gas stream, then water is added to the sample gas stream. A counter flow of air was drawn through the Nafion at ~2000 sccm using a vacuum pump and the inlet to the counter flow was alternatively sampling the top of a container of water that was at a temperature slightly warmer than the observatory or dry air-conditioned air in the observatory. To achieve the driest humidity, dry nitrogen was pushed through the Nafion. The flow rate through the Nafion was controlled using a ball valve and allowed for different rates of changes in the humidity. No liquid water was introduced to the sample lines for the instruments. A range of water vapor from 3% to 0.05% was used for all instruments except for the Aeris Mira Ultra LDS ethane data, which was cut off at 1.05% water vapor (for reasons discussed below).

#### 2.2.2 Calibrations against NOAA standards

Each of the instruments was calibrated against two ambient range cylinders calibrated by the Central Calibration Laboratory (CCL) at the National Oceanographic and Atmospheric Administration (NOAA) Global Monitoring Laboratory (GML) in Boulder, CO. CCL maintains the World Meteorological Organization (WMO) methane scale (WMO X2004A) and an internal CCL standard for ethane (C2H6-2012). A dry, compressed air cylinder was used to test multi-hour instrument stability.

#### 2.2.3 Instrument Stability

We evaluated the instrument stability by running a calibrated compressed air cylinder for a 4 hour period and calculating Allan-Werle variance and precision. During this time the regular zero for the Aerodyne SuperDUAL was not performed. The Aeris MIRA and Picarro G2210-i were humidified (1.7 - 1.9 % H$_2$O) to allow the Aeris MIRA to report ethane (see Section 3.1). The Aerodyne SuperDUAL was not humidified and reported less than 0.054 % H$_2$O for the same tests.

#### 2.2.4 Zero-air tests

During regular ambient operation, the Aerodyne SuperDUAL samples nitrogen gas each hour to account for instrument drift for lower concentration species such as ethane. We use the boil off from a large liquid nitrogen dewar, which can be refilled on site, and which contains a variable mole fraction of carbon monoxide (~250 ppb/nmol mol$^{-1}$). Regular zero sampling is not required for long-term either the Picarro G2210-i or the Aeris MIRA but we evaluated
each instrument’s performance when sampling the hourly zero air addition for dry air and for air humidified to >0.5% water vapor for the Aeris MIRA and Picarro G2210-i.

2.3 Site Description and Sampling of ambient urban air

The City University of New York (CUNY) Next Generation Environmental Sensor (NGENS) Observatory is on the rooftop of the 56m building in Hamilton Heights in Harlem. The sampling point is ~93m above sea level on a tower at the south end of the building. The Aerodyne SuperDUAL has been operated at the site over a number of years and was running from early January - June 2022. The site samples urban air that has been influenced by natural gas emissions (both pre and post combustion), wastewater treatment plants (North River to the north-west, Ward Island to the east) and sewer street emissions. During the long-term operation of the Aerodyne SuperDUAL, nitrogen (liquid nitrogen boil off, N₂) is added as a test of the zero drift in the instrument. For the experiments described here, N₂ was used hourly during ambient sampling and prior to and after the compressed air tank test runs. When the Aerodyne SuperDUAL is operated independently, air is drawn through ~10 m of ½” Synflex tubing at 20 L min⁻¹ using a diaphragm pump before being sub-sampled by the Aerodyne SuperDUAL (flow rate 1.7 L min⁻¹). The use of a separate pump to increase the total flow rate and reduce instrument response times is commonly used for ground operation with longer tubing (e.g. towers). However, the pump also reduces the pressure within the tubing to below ambient pressure, which was a problem when sampling with the smaller pump capacity of the Aeris MIRA. For the work described here, the external pump was removed and the response time through the tubing was reduced to 30s. Each instrument sampled from a Swagelok cross fitting using a ~1m ¼” Synflex tubing.

We sampled air from the roof in February, 2022 when ambient air temperatures ranged from below freezing (-9.3°C) to a warm spring day (19°C). The lowest temperatures were also associated with low humidity, which caused problems that were also detected during the humidity testing, so the sample line of the Picarro G2210-i and Aeris MIRA were humidified to >1% water vapor as a work around for these problems.

3 Results and Discussion

We characterized the laboratory performance of each analyzer with respect to humidity corrections, precision assessment, calibration to NOAA standards and long-term stability, before sampling ambient air in New York City. We used these tests to recommend the best instrument for use in different circumstances.

3.1 Characterization of Water Sensitivity

All three instruments showed a dependency on water vapor for methane that was statistically significant. Figure 1 shows the dependence of the retrieved methane and ethane with the water vapor reported by each instrument for a compressed air cylinder with variable humidity. A linear correction was calculated for methane and ethane for both the Aerodyne SuperDUAL and the Picarro G2210-i but a quadratic dependence was observed for the Aeris MIRA methane. The values of each water vapor correction are shown in Table 1. The Picarro G2210-i needed the smallest absolute correction for methane, and the Aerodyne SuperDUAL reported the smallest correction for ethane. The SuperDUAL was operated with the default water vapor broadening coefficient for methane and ethane of 2.0. This correction is likely too large for methane and moving closer to the value of 1.05 recommended by Kostinek et al., 2019 would reduce the water vapor correction. Here we have applied a linear correction with water vapor to the observed data that results in a 10 ppbv (parts-per-billion by volume; equivalent of nmol mol⁻¹) change in methane but a ~0.08 ppbv change in ethane for 0-2% water vapor.
Table 1: Summary of water vapor corrections derived for each instrument

<table>
<thead>
<tr>
<th>Instrument</th>
<th>CH$_4$ Correction ppb/% H$_2$O $y = m \times [H_2O]$</th>
<th>C$_2$H$_6$ ppb/% H$_2$O $y = m \times [H_2O]$</th>
<th>Notes: Using default water broadening coefficients for all instruments before calibration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerodyne SuperDUAL</td>
<td>-5.335 ppbv /% H$_2$O</td>
<td>0.042 ppbv /% H$_2$O</td>
<td></td>
</tr>
<tr>
<td>Aeris MIRA Ultra LDS</td>
<td>-25.53 (% H$_2$O)$^2$ - 59.22 % H$_2$O</td>
<td>0.23 ppbv / % H$_2$O</td>
<td>C$_2$H$_6$ only calculated for H$_2$O $&gt; 1.05 %$</td>
</tr>
<tr>
<td>Picarro G2210-i</td>
<td>-1.15 ppbv /% H$_2$O</td>
<td>-0.82 ppbv /% H$_2$O</td>
<td></td>
</tr>
</tbody>
</table>

Figure 1. Uncorrected (a) methane (ppbv) and (b) ethane (ppbv) vs water vapor (%) for the Aerodyne SuperDUAL (black), Picarro G2210-i (red) and Aeris MIRA Ultra LDS (blue)

We identified two separate, but related, situations with the Aeris MIRA that could prove to be a problem if not accounted for in operation in certain environments and configurations:

(i) The wavelength of the laser is tied to the water vapor absorption peak. When running a dry calibration tank, the instrument loses frequency lock and the laser wavelength can drift to the point that the ethane peak can no longer be resolved. The reported ethane concentrations vary between 200 ppbv and -100 ppbv during this dry air sampling, possibly driven by laser wavelength drift. When the water vapor increases again after a calibration, the ethane fit is not immediately recaptured. Noise in the reported ethane and methane concentrations increases significantly below 1.05% water vapor and below 0.5% the ethane fit is completely lost.

(ii) For most environments, water vapor in the atmosphere absorbs some of the mid-IR laser power and the laser power of the Aeris MIRA is optimized to achieve maximum sensitivity. However, New York City in February is cold and dry, with very low concentrations of ambient water vapor. Without enough water vapor to attenuate the laser power, the detector can be saturated, leading to no ethane detected and a noisy methane retrieval. This problem can be fixed by reducing the laser power slightly (using the procedure recommended by Aeris engineers) or by humidifying the sample line slightly. We opted for the latter fix for this study. At the other extreme, water vapor closer to 3% can also lead to increased noise in the fitted methane and ethane.
After losing the ethane peak during either of these circumstances, the Aeris MIRA analyzer will often fail to find the peak again until manually re-connected to the internet. We have not identified a cause for this behavior but it was more likely during (ii) and was not a problem after we humidified the sample flow. Using the GPS receiver provided by Aeris also seemed to mitigate the problem.

3.2 Instrument calibration

Each instrument was calibrated against two NOAA calibration standards after accounting for the water vapor correction described in Section 3.1. A linear fit (OLS, ordinary least squares) was calculated for each species and the span (slope) and zero correction (intercept) and 95% confidence intervals were calculated (Table 2). The span and offset were then applied to each species. As described above, the Aeris MIRA could not report ethane concentrations when sampling a dry tank so the sample line of both the Aeris MIRA and Picarro G2210-i were humidified to water vapor mole fractions between 1.7-1.9 % H₂O. For methane, all three instruments reported a span correction less than 3%, and zero corrections of between 3 and 14 ppbv. All three instruments report very similar methane mole fractions for a compressed air tank after all calibration steps were applied. For ethane, the Aeris MIRA and Aerodyne SuperDUAL reported a span less than 7% and offset of less than 2 ppbv. However, the slope and intercept for the Picarro G2210-i were not successfully resolved for the reported 1 Hz data and a two-point linear fit was calculated for the average values reported over the sampling period (Slope 0.427; intercept 4.275). The resulting correction successfully resolved the target gas mole fractions but with a large standard deviation in the 1 Hz data (Fig S5).

<table>
<thead>
<tr>
<th>Species (nmol mol⁻¹)</th>
<th>Slope</th>
<th>Intercept</th>
<th>Slope +/-</th>
<th>Intercept +/-</th>
<th>r²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aeris; CH₄ (ppbv)</td>
<td>0.977</td>
<td>-4.2</td>
<td>0</td>
<td>0.4</td>
<td>1</td>
</tr>
<tr>
<td>Aeris; C₂H₆ (ppbv)</td>
<td>0.992</td>
<td>-2.42</td>
<td>0.01</td>
<td>0.07</td>
<td>0.9806</td>
</tr>
<tr>
<td>Picarro; CH₄ (ppbv)</td>
<td>1.002</td>
<td>1.4</td>
<td>0</td>
<td>0.5</td>
<td>1</td>
</tr>
<tr>
<td>Picarro; C₂H₆ (ppbv)**</td>
<td>0.42</td>
<td>4.28</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aerodyne; CH₄ (ppbv)</td>
<td>0.969</td>
<td>-13.9</td>
<td>0.001</td>
<td>0.2</td>
<td>1</td>
</tr>
<tr>
<td>Aerodyne; C₂H₆ (ppbv)</td>
<td>1.069</td>
<td>0.064</td>
<td>0.001</td>
<td>0.004</td>
<td>0.9996</td>
</tr>
</tbody>
</table>

3.3 Instrument precision

The precision of each analyzer was evaluated by sampling a calibrated compressed air cylinder for four hours. We calculated an Allan-Werle variance (Fig 2) and the observed precision for methane and ethane for each instrument (Table 3).
Figure 2. Allan-Werle Variance for (a) methane and (b) ethane for all three instruments when sampling a compressed air cylinder on Feb 17th, 2022 11 am - 3 pm EDT. Each of the tanks was calibrated to NOAA cylinders after water vapor correction. The reported water vapor for the Aerodyne SuperDUAL (black) was below 0.054 %. The Aeris MIRA (blue) and Picarro G2210-i (red) were humidified to water vapor 1.7 – 1.9 %.

Table 3: Summary of various instrument performance metrics. *Aerodyne Superdual Quoted Precision from Kostinek et al., 2019

<table>
<thead>
<tr>
<th>Instrument Manufacturer</th>
<th>Flow Rate</th>
<th>CH₄ Quoted Precision nmol mol⁻¹</th>
<th>CH₄ Observed Precision (100 s) nmol mol⁻¹</th>
<th>C₂H₆ Quoted Precision nmol mol⁻¹</th>
<th>C₂H₆ Observed Precision (100 s) nmol mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerodyne SuperDUAL</td>
<td>1500 sccm</td>
<td>0.025 ppb* (100 s)</td>
<td>0.024 ppb</td>
<td>0.003 ppb* (100s)</td>
<td>0.003 ppb</td>
</tr>
<tr>
<td>Aeris MIRA Ultra LDS</td>
<td>380 sccm</td>
<td>0.5 ppb (1 sec)</td>
<td>0.14 ppb</td>
<td>1 ppb (1 sec)</td>
<td>0.02 ppb</td>
</tr>
<tr>
<td>Picarro G2210-i</td>
<td>24 sccm</td>
<td>&lt;0.1 ppb (5 min)</td>
<td>0.08 ppb</td>
<td>&lt;1 ppb (5 min)</td>
<td>0.48 ppb</td>
</tr>
</tbody>
</table>

For methane, the Aerodyne SuperDUAL had the best 1 Hz (0.227 ppbv) and 10s (0.072 ppbv) precision with a minimum of 0.021 ppbv at 3.2 mins but the variance increased slightly again (but still below 1 ppbv) after about 15 mins. There were no zeros performed for the SuperDUAL during the precision experiment so this increase in variance was not unexpected. The Aerodyne SuperDUAL matched the 100 s precision of (Kostinek et al., 2019) at 0.024 ppbv. At 100s, the Aeris LDS precision was 0.14 ppbv and the Picarro G2210-i precision was 0.08 ppbv, both of which exceeded their quoted precision of 0.5 ppbv (at 1 s) and 0.1 ppbv (at 5 min).

For ethane, the Aerodyne SuperDUAL had the best 1Hz (0.027 ppbv) and 10s (0.008 ppbv) precision with a minimum of 0.002 ppbv at 2.2 mins but the variance increased slightly again (but still below 0.03 ppbv) after about 15 mins. The Aerodyne SuperDUAL matched the 100s precision of (Kostinek et al., 2019) of 0.003 ppbv. At 100s, the Aeris MIRA precision was 0.02 ppbv and the Picarro G2210-i precision was 0.48 ppbv, both of which exceeded
their quoted precision of 1 ppb nmol mol⁻¹. The Picarro G2210-i ethane precision is similar to that observed with a Picarro G2201-i analyzer (0.8 ppbv at 1 minute; Defratyka et al., 2021).

3.4 Long-term instrument stability

We evaluated the stability of frequent additions of zero air (gas free of methane, ethane, CO₂, etc.) for all three analyzers. Fig 3 shows the instrument response when sampling dry and humidified nitrogen (methane and ethane free). The Aerodyne SuperDUAL was not humidified for the second period (Fig 3c-d) and the noise was not significantly different for the two periods (CH₄ < 0.01 ppbv; CH₃C₂H₇ < 0.95 ppbv; 1σ s.d.).

Figure 3: Instrument response when sampling (a-b) dry and (c-d) humidified methane (a, c) and ethane (b, d) in nitrogen. Picarro G2210-i (red) and Aeris MIRA (blue). Note the separate right y-axis for the Aeris (b) ethane and (c) methane. Also note that the Aerodyne SuperDUAL (black) did not sample humidified nitrogen in c-d.

The Picarro G2210-i instrument noise is reduced when sampling humidified nitrogen over dry nitrogen (Fig 3), especially for outliers in the reported methane (Fig 3a). However increased variability in methane is not evident in Fig 1(a) at low humidity so there may be another driver of this behavior. The reported ethane goes from -0.082 +/- 0.95 ppbv (1σ s.d.) when sampling dry nitrogen to -0.03 ± 1.73 ppbv (1σ s.d.) when the nitrogen is humidified to ~1%. The reported methane goes from 1.35 ± 6 ppbv (1σ s.d.) when dry to 0.007 ± 0.08 ppbv (1σ s.d.) when humidified.

The Aeris MIRA instrument response is statistically different when sampling dry or humidified nitrogen (Fig 3): The reported ethane goes from varying between -100 and 100 ppbv (with a mean of -3.92 ± 43.8 ppbv; 1σ s.d.) when sampling dry nitrogen to -0.05 ± 0.22 ppbv (1σ s.d.) when the nitrogen is humidified to ~1%. However, humidifying the nitrogen also affects the reported methane, which goes from 0.02 ± 0.5 ppbv (1σ s.d.) when dry to 2.5 ± 17.5 ppbv (1σ s.d.) when humidified. This is also shown as increased noise on the methane at low humidity in Fig S1.
3.5 Ambient sampling

In order to test the suitability of each analyzer to report accurate methane and ethane mole fractions in ambient air, we ran all instruments sampling ambient air from the CUNY Observatory in Harlem, NY. In general, air is cold and very dry in New York City in winter and we humidified the Aeris MIRA and Picarro G2210-i sample flows in response to the instrument characterization experiments described above. Figure 4 shows typical examples of the ambient methane and ethane mole fractions observed by all the analyzers when sampling ambient air in February 2022.

On February 18th a large-scale change in airmass resulted in a drop in ambient air temperature from 15°C to 7°C (during Fig 4a and b), residential heating increased and a plume of high methane and ethane was intercepted at the observatory for about 10 minutes. The Aerodyne SuperDUAL and Aeris MIRA both responded very similarly; reporting large coincident increases in methane (up to ~2800 ppbv) and ethane (~10 ppbv). The Aerodyne SuperDUAL also reported a large increase in carbon monoxide (CO) up to ~1500 ppbv for the same plume, possibly indicating an incomplete combustion source. The methane reported by the Picarro G2210-i also increased, but with a longer peak duration due to the much slower sampling flow rate (sampling time lags were corrected for previously). However, the ethane surprisingly decreased while sampling the plume.

On February 19th ambient air temperatures ranged from -3.7°C at night to -1.2°C in the early morning and wind speeds were low (2-4 m s⁻¹) leading to a build-up of methane and ethane in the nocturnal boundary layer (Fig 4c and d). The prolonged elevated methane (to ~3000 ppbv) and ethane (to ~11 ppbv) was easily observed by the Aerodyne SuperDUAL and the Aeris MIRA. The CO also increased (~700 ppbv) to about half of that seen on February 18th. The methane reported by the Picarro G2210-i also increased in line with the other reported methane but, again,
the Picarro G2210-i was not able to resolve the large increase in ethane, this time indicating an increase in ethane of 1-2 ppbv instead of the 7-8 ppbv seen by the other instruments.

The trace gases measured by the Aerodyne SuperDUAL indicate that Fig 4 (a and b) shows a post-meter plume of incompletely combusted natural gas, likely emitted close to the observatory. The nocturnal boundary build-up observed in Fig 4 c and d was coincident with a large increase in other combustion pollutants such as CO. As mentioned in the data sheet for this instrument, it is possible that the co-emitted species of natural gas combustion (such as CO or other volatile organic compounds, VOCs) are acting as an interferent for the Picarro G2210-i ethane retrieval. This result indicates that the Picarro G2210-i should not be used near flares, natural gas power plants or in urban areas that combust natural gas on a large scale. Indeed, care should be taken to ensure that thermogenic sources are not erroneously attributed to biogenic sources with the Picarro G2210-i.

4 Conclusions and Recommendations

We evaluated the performance of three commercially available laser-based ethane analyzers: Aerodyne Inc. SuperDUAL, Aeris Technologies MIRA LDS, Picarro Inc. G2210-i. We assessed the precision, accuracy and interferences of each analyzer. We measured ambient air in a cold urban environment with each analyzer and have made recommendations or analyzers based on performance, ease of use and reliability.

Across the month, the Aerodyne SuperDUAL reported with the highest precision of all three instruments but requires regular zero air/nitrogen to maintain accuracy. The large size of the instrument and external chiller and large pump mean that it is more suitable for tower/ground-based or large mobile laboratory operation and is not suitable for car-based sampling. There is a smaller footprint instrument from Aerodyne – the Aerodyne “mini” – which has the methane/ethane accuracy of the SuperDUAL but this also requires an external chiller and large pump. The Aerodyne SuperDUAL also requires expertise to operate and maintain but is the best performing analyzer if the space and expertise are available.

The Aeris MIRA was close to the Aerodyne SuperDUAL for precision for methane but was less precise for ethane. The Aeris MIRA pump is small so the analyzer cannot draw against pressures much below ambient pressures, such as those from long sampling lines. Methane required a large water vapor correction. Ethane could only be reported for humidified samples, which affects the calibration protocol most often used in long-term operation. The Aeris MIRA also had some software problems when not connected to the internet, so it requires regular attention. However, overall the Aeris MIRA performed well when sampling plumes of incompletely combusted natural gas and in large-scale ethane increases in a nocturnal urban boundary layer. The small size and internal pump also make the analyzer ideal for sampling from small mobile platforms such as cars and bikes (especially the Aeris MIRA LDS Pico, which is the battery-powered version of the analyzer tested here).

While the Picarro G2210-i reported precise methane mole fractions and the analyzer performed adequately in many of the test, it could not detect ambient ethane enhancements of over 5 ppbv observed by the other instruments. When sampling an incompletely combusted natural gas plume, it also reported a reduction in ethane when the other analyzers reported a plume of ~10 ppbv.

Overall, we recommend the Aerodyne SuperDUAL or the Aeris MIRA Ultra LDS depending on the situation. For long-term tower deployments or those with large mobile laboratories, the Aerodyne SuperDUAL provides the best precision for methane and ethane. The other reported trace gases in the Aerodyne SuperDUAL, including CO, carbon dioxide (CO2) and nitrous oxide (N2O) alongside ethane, also provide a way to more accurately attribute the methane sources. For smaller mobile platforms, the Aeris MIRA is a more compact analyzer, and with careful use,
can quantify thermogenic methane sources to sufficient precision for short term deployments in urban or oil and gas areas.

Data Availability. A permanent link will be added here once the permanent doi is available after the review process. Currently the data from this study is available at: https://atmoscomp.ldeo.columbia.edu/content/data-sharing

Author Contributions. RC, AHD and LM designed the study, RC and AHD operated the instruments, AHD conducted the tests, RC and AHD analyzed the data. RC prepared the manuscript with input from AHD and LM. The authors declare that they have no conflict of interest.

Acknowledgements

Funding for this study was provided through contracts to the New York State Energy Research and Development Authority (NYSERDA) grants #160536, #100413, #137484 and #183865, and National Oceanic and Atmospheric Administration (NOAA) grant #NA20OAR4310306. We thank Ricardo Toledo-Crow and the Next Generation Environmental Sciences Observatory of the Advanced Sciences Research Center, City University of New York for Observatory space while conducting the instrument evaluations.

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