FUGITIVE METHANE EMISSION IDENTIFICATION AND SOURCE ATTRIBUTION: ETHANE-TO-METHANE ANALYSIS USING A PORTABLE CAVITY RING-DOWN SPECTROSCOPY ANALYZER

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Introduction

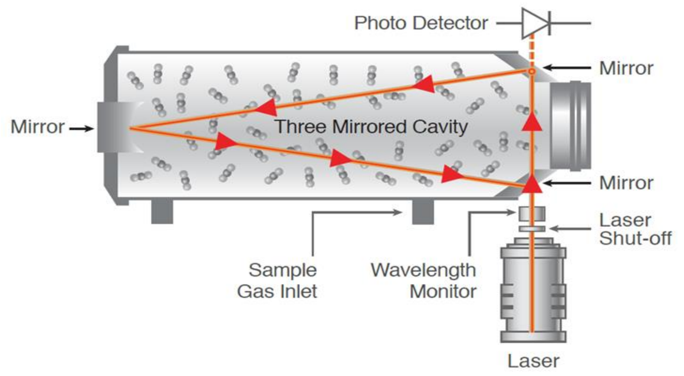
- Natural gas analysis and methane specifically have become increasingly important by virtue of methane's 28-36x greenhouse warming potential compared to CO2 and accounting for 10% of total greenhouse gas emissions in the US alone.
- Determining the specific fingerprint of methane sources by quantifying the ethane to methane (C2:C1) ratios provides us with means to understand processes yielding methane and allows for sources of methane to be mapped and classified through these processes; i.e. biogenic or thermogenic, oil vs. gas vs. coal gas-related. In the US, natural gas has a C2:C1 ranging from 2-5%.
- Here we present data obtained using a portable cavity ring-down spectrometry analyzer weighing less than 25 lbs and consuming less than 35W that simultaneously measures methane and ethane in real-time with a raw 1-σ precision of <30 ppb and <10 ppb, respectively at <1 Hz. These precisions allow for a C2:C1 ratio 1-σ measurement of <0.1% above 10 ppm in a single measurement. Furthermore, a high precision methane only mode is available for surveying and locating leakage with a 1-σ precision of <3 ppb. Source discrimination data of local leaks and methane sources using this analysis method are presented. Additionally, two-dimensional plume snapshots are constructed using an integrated onboard GPS in order to visualize horizontal plane gas propagation.

Instrumentation: CRDS Technology and GasScouter Analyzer

Cavity Ring-Down Spectroscopy (CRDS) Technology utilizes the unique infrared absorption spectrum of gas-phase molecules to quantify the concentration of (and sometimes isotopes of) H_2O, CO_2, CH_4, N_2O, CH_2O, NH_3.

CRDS Features:

- Small 3-mirrored cavity ~ 35 cc
- Long effective path-length (> 10 km)
- Time-based measurement
- Laser is switched on and off, and scanned across wavelengths



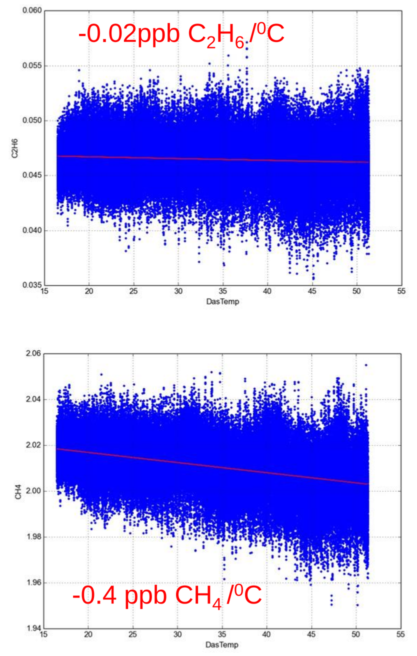
GasScouter, G4302:

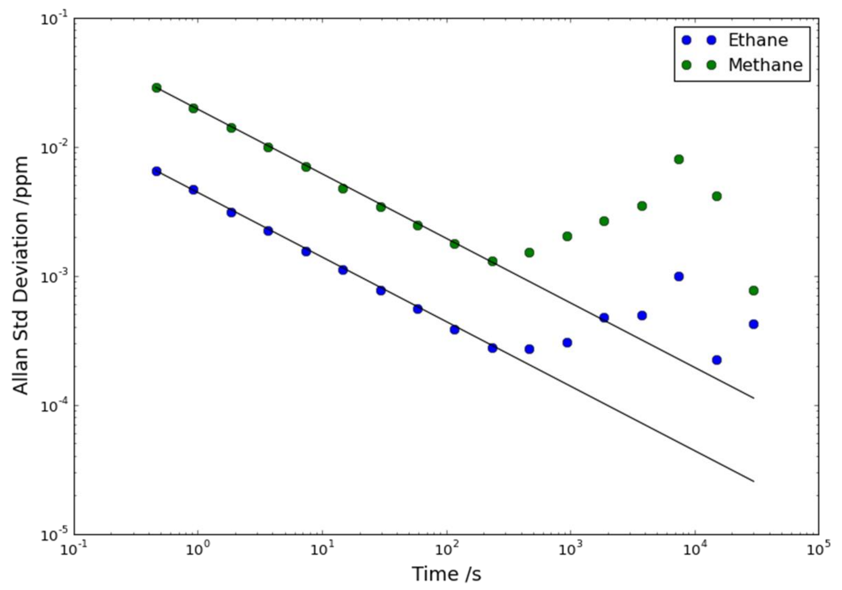
- Compact, mobile, and lightweight: 25 lbs
- Low power consumption: <35W
- Built-in Li-ion battery for 6-hr autonomy
- Hot-swappable battery for uninterrupted measurements
- WIFI connectivity to tablet or smartphone
- 2 modes:
  1) 3-ppb CH_4 only @ 5Hz
  2) 6-ppb C_2H_6 and 30 ppb CH4 @ 2 Hz

Methodology

1) Environmental Stability and Precision:

- Analyzer connected to a stable source of 2-ppm CH_4 and 50-ppb C_2H_6
- Analyzer placed in environment chamber subject to temperatures ranging from 10 to 50 degC
- All data reported have no temperature correction

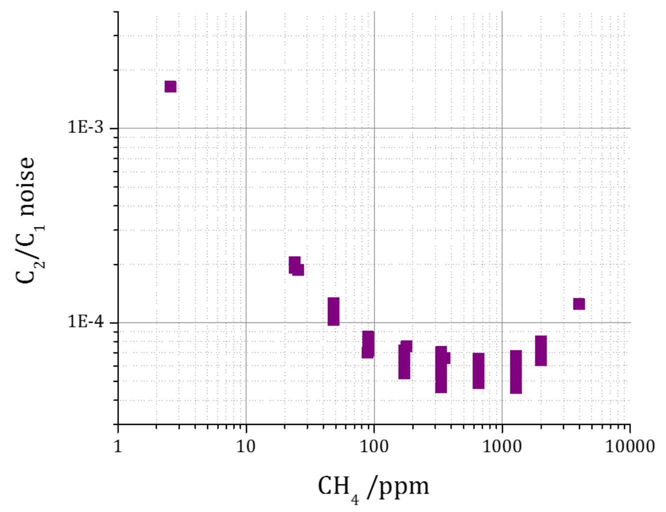




Stress test for Allan variance still shows strong stability and imperfections in temperature model from Hitran could account for noise and accuracy in temperature dependence.

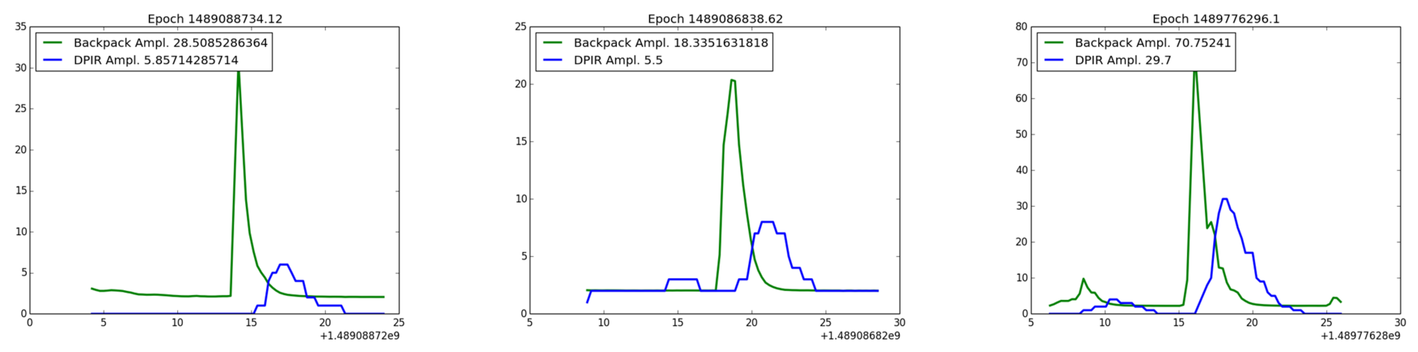
2) Increase in Precision

- Determination of C2:C1 ratio drops off as $[CH_4]^{-1}$ until noise is no longer shot noise limited, and reaches a minimum of 0.006% from 100-1000ppm and then noise is then increased above these concentrations
- Ability to determine gas composition within 0.1% in seconds at 20ppm
- C_2H_6 and CH_4 mode measurement range from 1-ppm to 10,0000-ppm CH_4



3) Improved Gas Response

- Measure at 450torr to give lower effective volume
- Gas flowrate 3 slm
- 1/e time <0.2 s

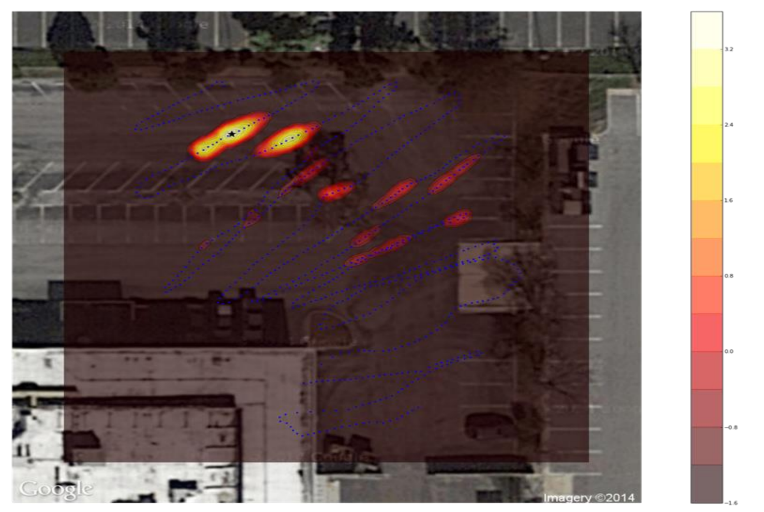


- Impulse response to plume measurements when compared to traditional DPIR sensor for methane pinpointing
- Faster flow enhances peak amplitude and peak width when compared to DPIR measuring from one inlet port

Field Application Results

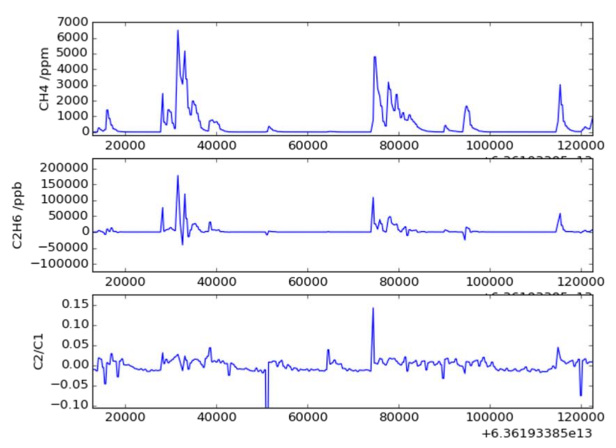
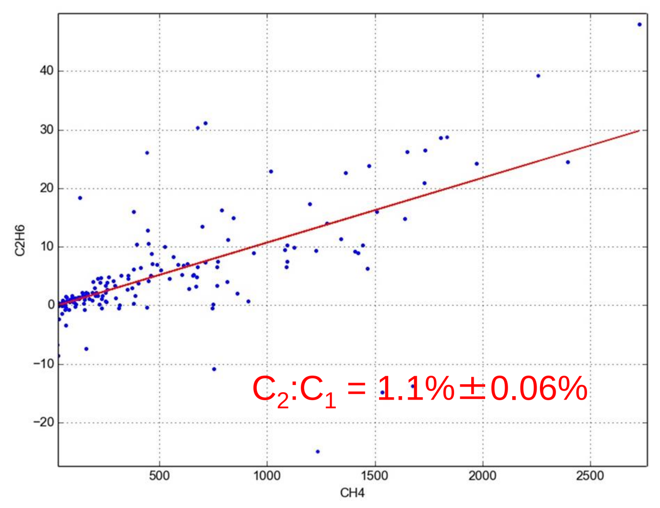
Controlled Release Plumes and Source Attribution:

- The figure below is a visualization of data collected using a 5Hz measurement of Methane and an integrated GPS
- Controlled release 100% CH_4 shows an average plume shape when path traverses perpendicular to the wind direction
- Scale is Log of CH_4 Concentration in order to see small background variations as well as enhancements close to and directly above leak




Controlled Release at 1000sccm 100% CH4

In practice, steady state concentrations only work when looking at stable samples, not actual leaks. Because the variations are so large in practice from localized leaks, you must look at correlations in the variations between C2H6 and CH4 over a period of time (~45sec), and not rely on instantaneous measurements. Additional error is added due to transients and variations in concentrations that happen at a much faster scale than the measurement rate of the instrument.

Conclusions

The stability of the cavity modes allows for a reliable measurement of CH_4 and C_2H_6. Stability is shown through minimal temperature sensitivities, pressure control within 50 mtorr, and precisions that are optimized through a wide range of concentrations. The combination of the sensitivity and fast (<0.5sec) response of the instrument allows the user to pinpoint methane leaks and quantify them quickly. All of this in a package that ways <12 kg and uses <35 W with a GPS.

Future Development will include understanding of noise variations throughout temperature range and improving data analysis through variation correlations.

Interested in learning more?

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- Visit www.picarro.com.