

# Calibration and Field Testing of Cavity Ring-Down Laser Spectrometers Measuring CH<sub>4</sub> Mole Fraction and the Isotopic Ratio of <sup>13</sup>CH<sub>4</sub> and Deployed on Towers in the Marcellus Shale Region

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## ABSTRACT

Four in-situ cavity ring-down (Picarro G2132-i) spectrometers measuring methane (CH<sub>4</sub>), carbon dioxide (CO<sub>2</sub>) and the isotopic ratio of methane (δ<sup>13</sup>CH<sub>4</sub>) were deployed at towers with heights between 46 and 61 m AGL. The study is focused on the Marcellus Shale natural gas extraction region of Pennsylvania. The leakage rate of CH<sub>4</sub> determines whether natural gas is useful as a bridge fuel, in terms of greenhouse effects, compared to coal. These tower data will be used in a top-down inversion to determine fluxes. Sources can be distinguished via the isotopic signature: heavy isotope ratios (e.g., -23.9‰) are characteristic of thermogenic (e.g., oil and gas) CH<sub>4</sub> sources and light isotope ratios (e.g., -66.5‰) are characteristic of biogenic (e.g., landfills, agriculture) sources. Here we describe the calibration of the instruments. Target compatibility (accuracy) is 2 ppb CH<sub>4</sub>, 0.2 ppm CO<sub>2</sub>, and 0.2‰ δ<sup>13</sup>CH<sub>4</sub>.

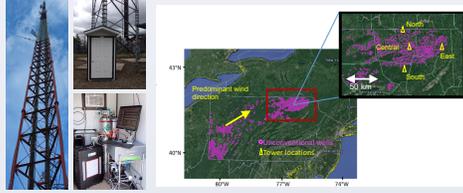


Figure 1. Map of Pennsylvania with permitted unconventional natural gas wells (magenta circles) and network of towers with methane and stable isotope analyzers (Picarro G2132-i). Towers East and South are also equipped with NOAA flask sampling systems. Two towers (East and Central) are predominantly downwind of the study region, whereas the South tower is predominantly upwind of the majority of the wells. The North tower is located in New York State, which does not allow horizontal fracturing of natural gas.

## CHALLENGES FOR CALIBRATION OF ISOTOPIC METHANE

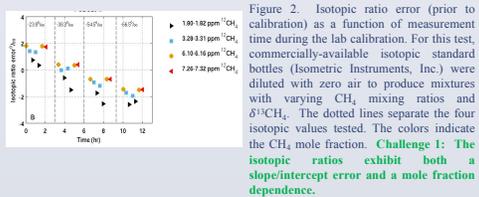


Figure 2. Isotopic ratio error (prior to calibration) as a function of measurement time during the lab calibration. For this test, commercially-available isotopic standard bottles (Isometric Instruments, Inc.) were diluted with zero air to produce mixtures with varying CH<sub>4</sub> mixing ratios and δ<sup>13</sup>CH<sub>4</sub>. The dotted lines separate the four isotopic values tested. The colors indicate the CH<sub>4</sub> mole fraction. **Challenge 1: The isotopic ratios exhibit both a slope/intercept error and a mole fraction dependence.**

| Gas Species                  | Typical maximum value or range             | Estimated error       |
|------------------------------|--|-----------------------|
| Carbon monoxide              | Range: 107.5-200.7 ppb                     | << 0.01%              |
| Water vapor                  | Range: 0.02 - 0.06%                        | < 0.02%               |
| Carbon dioxide               | Range: 375 - 475 ppm                       | < 0.03%               |
| Propane                      | Max: 3.6 ppb                               | < 0.01%               |
| Butane (i-Butane + n-Butane) | Max: 1788 ppt                              | < 0.01%               |
| Ammonia                      | Typical: 90 ppt                            | < 0.01%               |
| Hydrogen sulfide             | Typical: 30 ppt                            | < 0.01%               |
| Methyl mercaptan             | N/A  | N/A                   |
| Ethylene                     | 13.0 ppt                                   | < 0.01%               |
| Ethane                       | Max: 8.0 ppb (typical background: 1.3 ppb) | 0.23% (0.04% typical) |

Table 1. Maximum error estimate attributable to cross-interference for typical levels for this particular application. Typical maximum values determined by flask<sup>1</sup> level at which 99% of flask measurements at Towers South and East are below), by in-situ measurements at Marcellus towers<sup>2</sup>, or by typical values<sup>3</sup> (Warneck and Williams, 2012). <sup>1</sup>No known estimates (Barnes, 2015). **CHALLENGE 2: There are interferences with the isotopic ratio that have not been corrected for via manufacturer software. Fortunately, for our application, the errors are insignificant, except for ethane. Ethane is measured by the instrument, but it is not calibrated via manufacturer software.**

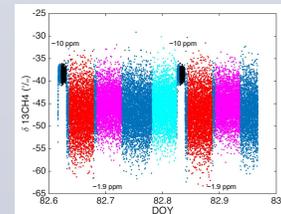
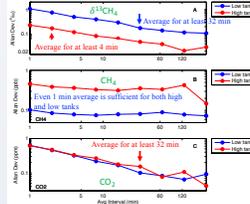


Figure 3. Example of laboratory data, cycling through various tanks for the round robin testing shown in Figure 5 (black: -10 ppm, -38.5‰; red: 1.9 ppm, -47.3‰; magenta: 1.9 ppm, -46.8‰; cyan: 1.9 ppm, -45.7‰). Time scale of the testing is 7 hours, data frequency is every ~2 seconds. **CHALLENGE 3: While the peak-to-peak noise in the typical atmospheric range of CH<sub>4</sub> is 2 ppb CH<sub>4</sub> (<the compatibility goal), the noise of δ<sup>13</sup>CH<sub>4</sub> is 20‰, 100 times the compatibility goal.**

## CHALLENGES FOR CALIBRATION OF ISOTOPIC METHANE

Figure 4. Allan deviation (for assessing the noise and drift response of the G2132-i analyzers) for (A) δ<sup>13</sup>CH<sub>4</sub>, (B) CH<sub>4</sub>, and (C) CO<sub>2</sub> for High (9.7 ppm CH<sub>4</sub>) and Low (1.9 ppm CH<sub>4</sub>) field calibration tanks. **CHALLENGE 4: Averaging times for CO<sub>2</sub> and δ<sup>13</sup>CH<sub>4</sub> at atmospheric mole fractions (for the desired compatibility levels) for the calibration cycles are longer than for the comparable mole fraction only instruments (Picarro G2301 and G2401): 32 minutes or longer.**



## CALIBRATION DETAILS

Prior to deployment, the instruments were calibrated for δ<sup>13</sup>CH<sub>4</sub> (both a slope/intercept calibration and a mole fraction correction) using four Isometric Instruments standards (-23.9/-38.3/-54.5/-66.5‰) diluted to varying degrees with zero air to obtain mole fractions ranging between 1.8 and 10 ppm.

Field calibration tanks at each tower location:

- High tank (-10 ppm, -38.9‰): filled by Scott-Marrin using Isometric Instruments standards to spike and calibrated at PSU
- Low tank (-2 ppm, -23.6‰): filled by Scott-Marrin using Isometric Instruments standards to spike and calibrated at PSU
- Target tank calibrated by NOAA/INSTAAR (-1900 ppb, -47‰)

Ethane was calibrated using the two Scott-Marrin tanks (containing no ethane) and the NOAA/INSTAAR tank (atmospheric levels of ethane) and a correction was then applied to the isotopic ratio data.

## OPTIMIZED CALIBRATION SCHEME

| Field calibration tanks (initial sampling scheme) | Field calibration tanks (improved sampling scheme) | Alternate field calibration tanks       | Reduced field calibration tanks (~0.5% accuracy)            |
|---|--|---|---|
| • HIGH (10 ppm, -38.3%, 26 min/day)               | • HIGH (10 ppm, -38.3%, 10 min/day)                | • HIGH (10 ppm, -38.3%, 4 min/day)*     | • HIGH (10 ppm, -38.3%, 8 min beg/end of day)               |
| • LOW (2 ppm, -23.9%, 54 min/day)                 | • LOW (2 ppm, -23.9%, 54 min/day)                  | • LOW/SECONDARY (54.5%, 4 min/day)*     | • LOW (2 ppm, -23.9%, 10 min beg/end of day)                |
| • TARGET (2 ppm, -47.2%, 6 min/day)               | • TARGET (2 ppm, -47.2%, 54 min/day)               | • TARGET (2 ppm, near -47%, 60 min/day) | • TARGET (2 ppm, -54.5%, 10 min beg/end of day) independent |

## Highlights:

- Performance was not improved via multiple calibration cycles within one day (i.e., insignificant drift during that time period).
- Can average multiple calibration cycles throughout the day, in order to not miss 60 continuous minutes of atmospheric data.
- Preferable to calibrate using tank within typically measured values.

## RESULTS – SIDE-BY-SIDE TESTING

Side-by-side testing of a G2301 analyzer and a G2132-i analyzer for June 2016 at the South tower resulted in mean hourly differences of 0.06±0.41 ppm CO<sub>2</sub> and 0.9±1.5 ppb CH<sub>4</sub>. **These side-by-side testing results indicate that the performance of the G2132-i is similar for CO<sub>2</sub> and CH<sub>4</sub> mole fractions, at least in terms of the long-term mean.**

## RESULTS – ROUND-ROBIN LABORATORY TESTING

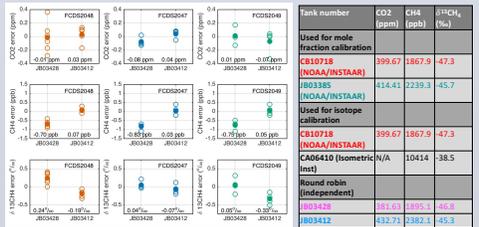


Figure 5. Errors compared to known values from a round-robin style lab test, using two tanks for each the mole fraction and isotope calibrations. Two tanks were treated as unknowns. Open circles are individual tests and filled circles are the means. **The magnitude of the mean errors for round-robin tank tests are within 0.1 ppm CO<sub>2</sub>, 0.8 ppb CH<sub>4</sub> and 0.3‰ δ<sup>13</sup>CH<sub>4</sub>.**

## RESULTS – INDEPENDENT TANK RESIDUALS

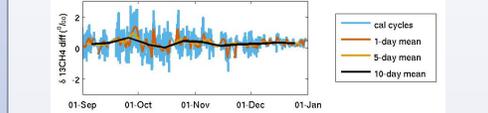


Figure 6. Independent ("low") tank methane isotopic ratio differences from known value, for the individual calibration cycles, and for 1-, 5-, and 10-day means, for the South tower for Sept - Dec 2016. The standard deviations of the low tank differences are a proxy for the noise in the calibrated ambient samples over those averaging intervals. The standard deviation of ~13 calibration cycles per day over the period September 1 - December 2 is 0.53‰. Using an averaging interval of one-day yields a standard deviation of 0.40‰. Therefore, for any one day during this period, differences between towers of less than 0.40‰ are likely not significant. For 5-day means, the standard deviation is 0.22‰, and for 10-day means, 0.03‰. **For the period after the calibration tank sampling scheme (primarily by sampling the target tank for 54 min/day instead of 6 min/day) was improved, December 3 - December 31, the standard deviation of the individual cycles is 0.25‰, of one-day means 0.18‰ and 5-day means 0.09‰.**

## RESULTS – FLASK TO IN-SITU COMPARISON

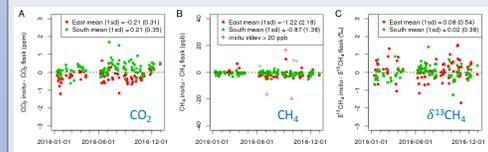
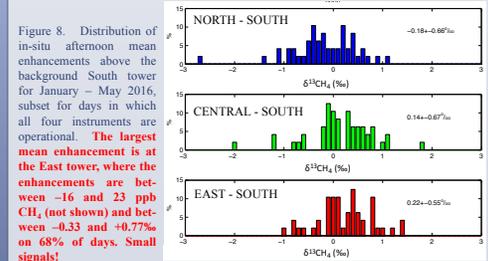


Figure 7. In-situ - flask differences for January - December 2016 for the East (red) and the South Towers (green) for (A) CO<sub>2</sub>, (B) CH<sub>4</sub>, and (C) δ<sup>13</sup>CH<sub>4</sub>. Means and standard deviation of the afternoon values are indicated for each site. **The magnitudes of the flask to in-situ differences are 0.2 ppm CO<sub>2</sub> and about 1 ppb CH<sub>4</sub> - within the WMO recommendation for those species. For δ<sup>13</sup>CH<sub>4</sub>, the differences are less than 0.1‰, the target compatibility level.**

## FIELD RESULTS – AFTERNOON ENHANCEMENT ABOVE BACKGROUND



## SUMMARY

We describe laboratory and field calibration of the analyzers for tower-based applications, and characterize their performance in the field for the period January - December 2016 as deployed on towers in the Marcellus Shale Gas region. Prior to deployment, each analyzer was calibrated using high mole fraction bottles with various isotopic ratios from biogenic to thermogenic source values, diluted in zero air. Furthermore, at each tower location, three field calibration tanks are employed, from ambient to high mole fractions, with various isotopic ratios. By testing various calibration schemes, we determine an optimized field calibration method.

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Miles, N.L., D.K. Martins, S.J. Richardson, T. Lauvaux, K.J. Davis, B.J. Haupt, and C. Rella, 2017 In-situ tower atmospheric methane mole fraction and isotopic ratio of methane data, Marcellus Shale Gas Region, Pennsylvania, USA, 2015-2016. Data set. Available on-line [http://datacommons.psu.edu] from The Pennsylvania State University Data Commons, University Park, Pennsylvania, USA. http://dx.doi.org/10.18113/D3SG6N.

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