# Calibration and Field Testing of Cavity Ring-Down Laser Spectrometers Measuring Methane Mole Fraction and Isotopic Ratio Deployed on Towers in the Marcellus Shale Region

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Four in-situ cavity ring-down spectrometers (Picarro, Inc.) measuring methane, carbon dioxide and the isotopic ratio of methane were deployed at towers with heights between 46 and 61 m AGL. The study was focused on the Marcellus Shale natural gas extraction region of Pennsylvania. The leakage rate of methane determines whether natural gas is useful as a bridge fuel, in terms of greenhouse effects compared to coal or oil. In addition to leakage from natural gas extraction, there are other unrelated sources of methane. The isotopic signature of the methane can be used to help distinguish these sources. Heavy isotope ratios are characteristic of thermogenic (e.g., oil and gas) methane sources and light isotope ratios are characteristic of biogenic (e.g., landfills, agriculture) sources.

The calibration of the continuous isotopic methane analyzers used in this study is challenging for several reasons, including the need for both a linear calibration and a mole fraction correction, and cross-interference from ethane. 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. Prior to deployment, each analyzer was calibrated using high methane mole fraction air bottles with various isotopic ratios, from biogenic to thermogenic source values, diluted in zero air. Furthermore, at each tower location, three field calibration tanks were employed, from ambient to high mole fractions, with various isotopic ratios. By testing various calibration schemes, we determined an optimized field calibration method. A method to correct for cross interference from ethane is also described. Using an independent field tank for evaluation, the standard deviation of 5-day means of the isotopic ratio of methane difference from the known value was found to be within our target compatibility of 0.2‰. Following improvements in the field calibration tank sampling scheme, the standard deviation of 1-day means was within the target compatibility. Round robin style testing using tanks with near ambient isotopic ratios indicated mean errors of –0.33 to 0.24‰ for the tests completed for each analyzer and round-robin tank. Flask to in-situ comparisons indicated mean differences over the year of 0.02 and 0.08‰, for the East and South towers, respectively, where the standard error was 0.06‰ and 0.04‰.