6.194 Isotopic Methane and Ethane-to-Methane Ratio Analysis Using a Cavity Ring-Down Spectrometer.

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Abstract:

Natural gas analysis and methane specifically have become increasingly important by virtue of methane's greenhouse warming potential compared. Large uncontrolled leaks, such as the recent one from southern California, originating from uncapped wells, storage facilities and coal mines have increased the total global contribution of methane missions even further. Determining the specific fingerprint of methane sources, by quantifying δ13C values and 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 this study we present a fully developed Cavity Ring-Down Spectrometer (CRDS) that precisely measures $^{12}CH_4$ concentration and its $^{13}C H_4$ isotope concentration, yielding δ ^{13}C measurements, C_2H_6 concentration, along with CO_2 and H_2O. This provides realtime continuous measurements without an upfront separation requirement or multiple analyses to derive the origin of the gas samples. The highly sensitive analyzer allows for measurements of scarce molecules down to sub-ppb 1-σ precision in 5 minutes of measurement; with CH_4 <0.1ppb, $\delta^{13}C$ <1‰, C_2H_6 <1ppb and CO_2 <1ppb. To complement this work, we provide the analysis of different methane sources providing a 2-dimensional mapping of methane sources as functions of $\delta^{13}C$ and C_2:C_1 ratios; which can be thought of as a modified Bernard Plot. This dual ratio mapping can be used to discriminate between naturally occurring biogenic methane sources, naturally occurring enriched thermogenic sources, and natural gas distribution sources.