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Currently, high-precision isotope ratios are determined using special-purpose isotope-ratio mass spectrometers (IRMS) that are fairly costly, require experts to operate and maintain, and are not portable – facts that have limited significantly the applicability of isotope ratio measurements in spite of the technological advances achieved with online sample introduction and combustion for compound-specific isotope analysis (CSIA). We present an alternative approach for making high-precision ¹³C/¹²C isotope ratio measurements of organic compounds, which is less expensive, does not require trained personnel, and is portable. The technique relies on the chromatographic separation of a mixture into individual organic compounds, the combustion of each organic compound into carbon dioxide, water, and other oxidation products, and the precise measurement of the ¹³C/¹²C isotope ratio in the carbon dioxide gas using the ultra sensitive absorption method of cavity ring-down spectroscopy. Short chain hydrocarbons are used as our test compounds owing to their mud logging diagnostic significance in exploratory and routine oil drilling and the suitability of our present instrumental setup for such a field measurement applications.

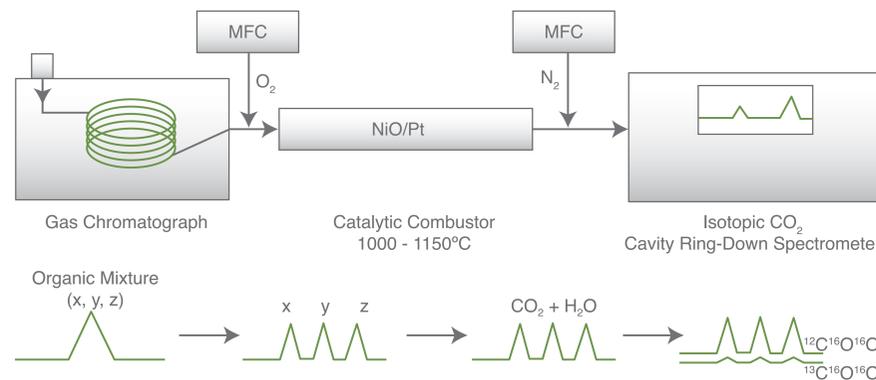


Fig 1. GC-CRDS scheme. The sample is separated with a gas chromatograph, combusted to produce carbon dioxide, and measured using cavity ring-down spectroscopy. Mass flow controllers are used to add oxygen before the catalytic combustor and nitrogen before the CRDS instrument

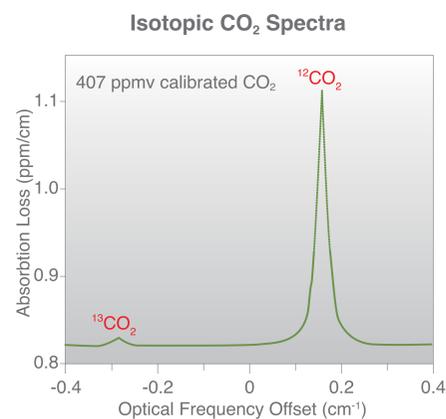
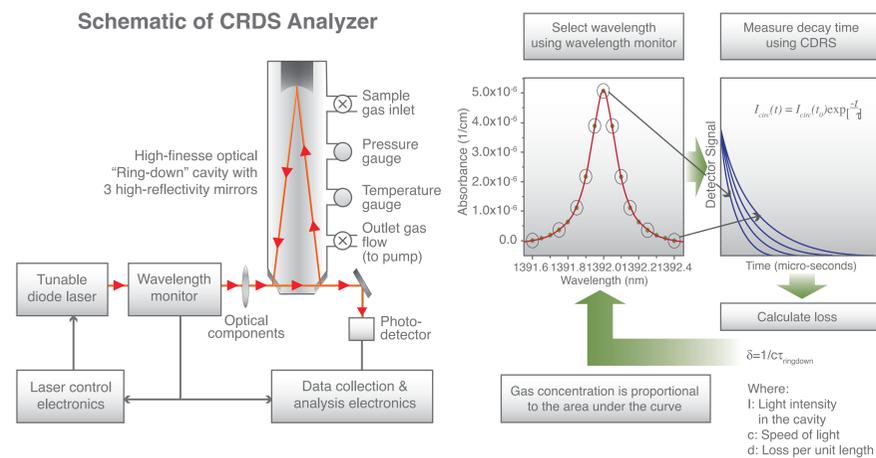


Fig 2. Cavity ring-down line shape profiles of the R(36) line of ¹²C¹⁶O¹⁶O and the R(12) line of ¹³C¹⁶O¹⁶O for the (3,0,1) – (0,0,0) combination band of carbon dioxide near 6251 cm⁻¹. The traces are for carbon dioxide in the atmosphere at 45 °C and a total pressure of 140 torr.

Cavity Ring Down Spectroscopy (CRDS) – How it Works

- Light from a tunable semiconductor diode laser is directed into a small (35 cc) optical resonator cavity containing the analyte gas
- When the build-up is complete, the laser is shut off
- Light circulates in the cavity ~100,000 times, traveling ~20 km or more. The high precision of CRDS comes from this incredibly long pathlength providing parts-per-trillion detection levels for some gases.
- There are three partially reflective mirrors on the cavity; a small amount of light leaks out from the third mirror with each pass. A photodetector is positioned behind this mirror, measuring the light intensity at each pass
- The energy decays from the cavity, through loss mechanisms, exponentially in time. This energy decay is measured, as a function of time, on the photodetector – and is known as a “ringdown”
- In an empty cavity, the only loss mechanisms are the mirrors and the ring-down time (the exponential decay time) is long
- When gas is present, the rotational vibrational modes provide additional loss mechanisms and the ring-down times get shorter, in proportion to gas concentration
- The ring down time measurement is continuously repeated (~100 times per second) at several different well-controlled points in wavelength as the laser is tuned across the molecular signature of the analyte gas
- The ring down profiles are transformed into an absorption curve with a well defined lineshape
- The gas concentrations or isotope ratios are determined by a multi-parameter fit to this lineshape (red curve) and are proportional to the area under the curve
- Picarro's patented Wavelength Monitor controls the laser position with incredible accuracy, ensuring the measurement is independent of potentially interfering gas species
- Importantly, CRDS is a measurement of time not of absorbance and so offers unmatched precision
- CRDS has complete immunity to laser noise since the laser is actually off during the measurement, thereby offering significantly better sensitivity than other laser techniques

Materials & Methods

A Hewlett Packard 5890 Series II gas chromatograph (Agilent, Santa Clara, California, USA) is connected to a prototype CRDS instrument through a homebuilt combustion chamber for this study. Injections of a mixture of methane, ethane, and propane (all 99.5% or higher grade purity) are separated on a GC capillary column (Agilent J&W, HP-PLOT Q, 30 m x 0.53 mm I.D., 40 μm film thickness). The helium carrier gas linear velocity (Ultra-High Purity 99.999%) through the column is 30 cm/s. For mixtures, the GC oven temperature program is as follows: 40°C for three minutes, then increased at a rate of 80°C/min to 80°C, and held there for 4 minutes. For individual samples of methane, ethane, and propane the temperature is held constant at 30°C, 40°C, and 80°C, respectively. The injector temperature was set to 80°C for all the analyses. The output of the column is connected with a stainless steel Tee-connector (Swagelok®, 1/8 inch) to a nonporous alumina tube (McMaster-Carr, 0.125" O.D. x 0.040" I.D. dual bore, 20" length) held in a resistively heated furnace with a feedback temperature control (Extech Instruments, Massachusetts, USA) operating between 1000°C and 1150°C. One platinum and three nickel wires (Elemental Microanalysis, 0.125 mm) are inserted into each bore of the combustion tube and the nickel wires were initially oxidized at an elevated temperature with oxygen passing over the wire. 10 Vespel ferrules (SGE, GV8-8) are used to seal the connections between the combustion tube and the connectors. The combustion tube is positioned so the ends of the tube are at least 5 cm from the furnace to reduce heating of the fittings on the end of the tube. A flow of one cubic centimeter per minute of oxygen (99.6% purity) is passed through the combustion tube, via the orthogonal port of the Tee-connector, during analysis runs to ensure the availability of excess oxygen supply for the complete oxidation of the sample and to regenerate the catalyst. All gases used were supplied by Praxair.

The combustion products from the oxidation reactor are fed directly into a prototype CRDS fast analyzer (Picarro, Sunnyvale, CA, USA) using a stainless steel Tee-connector (Swagelok®, 1/4 inch). A flow of 10 to 20 cm³/min of either nitrogen (99.95% purity) or approximately 500 ppm carbon dioxide in nitrogen is concurrently fed into the instrument to help control the flow rate of the sample passing through the CRDS cavity.

The chromatograms from the instrument are analyzed using third party software (WaveMetrics Igor or Microsoft Excel). Details of the peak integration algorithm are discussed in the results section.

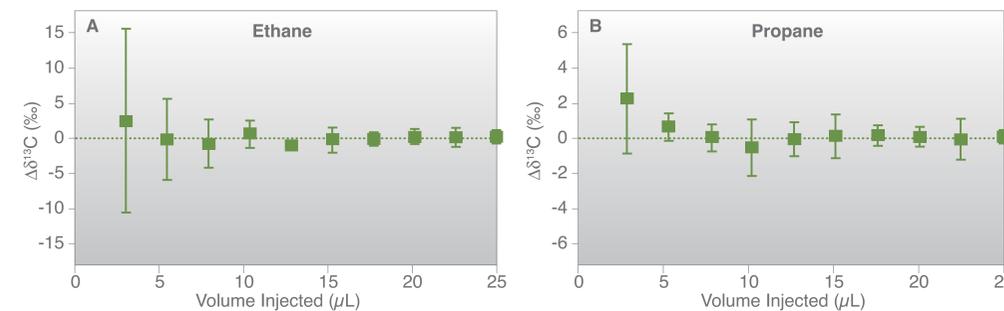


Fig 3. Measured $\delta^{13}\text{C}$ values for (A) ethane and (B) propane. The average of the measurements with volumes of 15 μL and greater is defined as zero. Error bars represent one standard deviation, which have been calculated for the five measurements whose average is the data point shown.

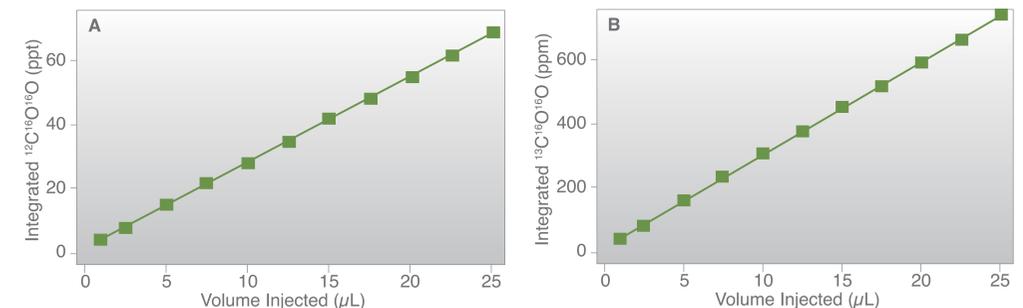


Fig 4. Plot of (A) the ¹²C¹⁶O¹⁶O signal and (B) the ¹³C¹⁶O¹⁶O signal produced from the combustion of ethane as a function of volume injected. Each data point represents the average of five measurements and the error bars (one standard deviation) are within the size of the marker.

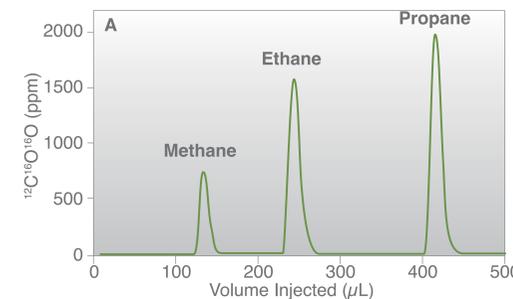
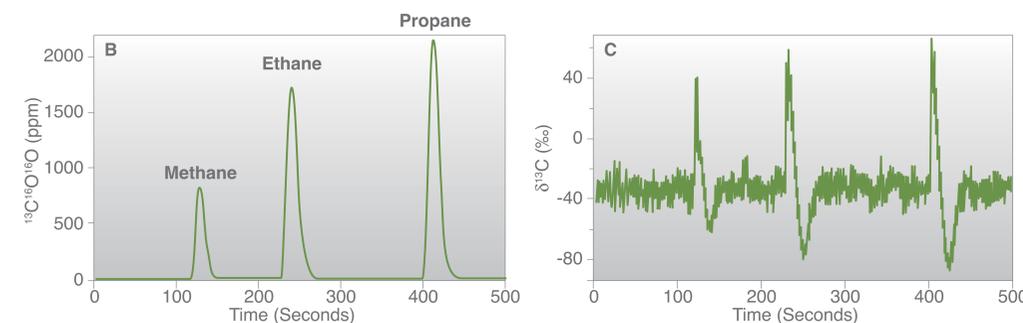


Fig 5. Chromatographic traces of (A) ¹²C¹⁶O¹⁶O and (B) ¹³C¹⁶O¹⁶O from a 25 μL mixture of methane, ethane, and propane from which the $\delta\text{V-PDB}^{13}\text{C}$ value is calculated for each component as shown in (C). The large amount of noise in the baseline of (C) arises from the low concentrations of CO₂. As the sample passes through the instrument, the higher concentrations of CO₂, especially ¹²C¹⁶O¹⁶O, allows for more precise measurements that results in the $\delta\text{V-PDB}^{13}\text{C}$ calculation to be made with a precision of less than 1 ‰.



Compound	GC-C-IRMS (‰) Individual Components	GC-C-CRDS (‰) Individual Components	GC-C-CRDS (‰) From Mixture
Methane	-44.07 ± 0.46	-47.16 ± 0.68	-44.76 ± 0.61
Ethane	-37.68 ± 0.41	-39.63 ± 0.89	-36.15 ± 0.89
Propane	-39.57 ± 0.20	-39.57 ± 0.82	-38.75 ± 1.04

Table 1. Comparison of $\delta^{13}\text{C}$ values for methane, ethane, and propane run individually on the GC-C-IRMS (2.5 μL injection; split ratio 1:30) and the GC-C-CRDS (25 μL , splitless). The GC-C-CRDS individual component amounts are scaled to have the same value for propane as for GC-C-IRMS. Also shown are the results from running a mixture of approximately 25 μL methane, 25 μL ethane, and 25 μL propane on the GC-C-CRDS, which have not been adjusted from the measurements obtained using GC-C-CRDS. Due to variations in the sample preparation process, differences in isotopic composition between samples run individually and as a mixture are expected.

Conclusion:

The GC-C-CRDS system proved to be linear over a three-fold injection volume dynamic range with an average precision of 0.95 ‰ and 0.67 ‰ for ethane and propane, respectively. The calibrated accuracy for methane, ethane, and propane is within 3 ‰ of the values determined using isotope ratio mass spectrometry (IRMS), which is the current method of choice for compound-specific isotope analysis. With anticipated improvements, the low cost, portable, and easy-to-use CRDS-based instrumental setup is poised to evolve into a credible challenge to the high-cost and complex IRMS-based technique.