STABLE CARBON ISOTOPE ANALYSIS OF AIRBORNE PARTICULATE MATTER USING A CARBON AEROSOL ANALYZER AND A CAVITY RING-DOWN SPECTROMETER

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Abstract

Particulate matter affects more people than any other ambient air pollutant, leading to increased risk of cardiovascular and respiratory diseases. Levels of PM10 and PM2.5 in the developing world, especially southeast Asia and the Indian subcontinent, routinely exceed World Health Organization guidelines, often by a factor of 10 or more. Despite their importance to poor air quality in urban areas in the developing world, the mechanisms that lead to heavy particulate loading are not well understood. Consequently, there is great interest in developing new tools for understanding the pollution sources and mechanisms that drive the formation of harmful aerosols. Stable isotope analysis of the carbon contained in the aerosols promises to provide important information about the sources and processes that govern aerosol formation and transport. We have coupled a Sunset Laboratories organic and elemental carbon (OC/EC) analyzer to a cavity ringdown spectrometer (CRDS) to create a system that provides hourly measurements of the d^{13}C content of PM in the ambient air. The OC/EC system executes a sequence of temperature and oxygenation steps to create distinct CO_2 pulses of organic carbon, carbonate carbon, and elemental carbon, which are subsequently analyzed by the CRDS instrument for d^{13}C -CO_2. We present laboratory measurements with this system, including calibration, precision, and drift, demonstrating that a system of this design can deliver aerosol stable isotope analysis at sub-permil accuracy and precision. This system can be operated unattended, and is thus suitable for remote field deployment.

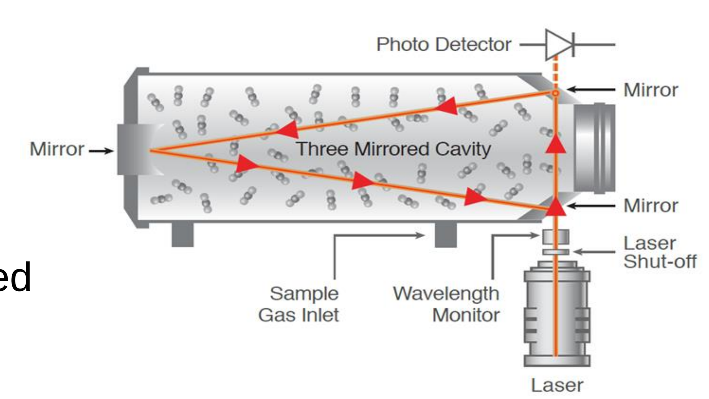
Instrumentations

CRDS Technology and Picarro G2131-*i* 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.

<u>CRDS Features:</u>

- 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



The Picarro G2131-*i* analyzer uses the CRDS technology to measure d^{13}C in CO_2 at <0.1‰. It also simultaneously analyze CO_2, CH_4, and H_2O concentrations.

<u>G2131-*i* Specifications:</u>

Precision, $\delta^{13}C$ in CO_2 (1-σ, 1 Hr window, 5 min)	<0.1‰ guaranteed precision at >380 ppm CO_2, <0.25‰ typical precision at 200 ppm CO_2, <0.05‰ typical precision at >1000 ppm CO_2
Max Drift at STP $\delta^{13}C$ in CO_2 (over 24 hrs, peak-to-peak, 1 hr interval average)	<0.5‰
Precision, CO_2 Concentration (30 sec, 1-σ)	200 ppb (^{12}C)/10 ppb (^{13}C)
Precision, CH_4 Concentration (30 sec, 1-σ)	50 ppb +0.05% of reading (^{12}C)
Precision, H_2O Concentration (30 sec, 1-σ)	100 ppm
CO_2 Dynamic Range	380–2000 ppm guaranteed specification range, 0.01–0.4% operational range Up to 100% pure CO_2 samples can be analyzed with the A0314 Small Sample Isotope Module 2 (SSIM2) peripheral, which includes dilution. Minimum sample volume per replicate with the SSIM2 is 10 µl of pure CO_2 (0.45 µmoles or 20 µg of CO_2) or the equivalent volume of CO_2 in air.

Sunset Organic Carbon – Elemental Carbon (OC-EC) Aerosol Analyzer

In the Lab OC-EC Aerosol Analyzer, samples are thermally desorbed from the filter medium under an inert argon atmosphere followed by an oxidizing atmosphere using carefully controlled heating ramps. A non-dispersive infrared sensor (NDIR) is used to monitor the analysis. The low dead volume carrier gas control system and proprietary quartz oven design provide high sensitivity with ultra low carbon background and no oxygen contamination.

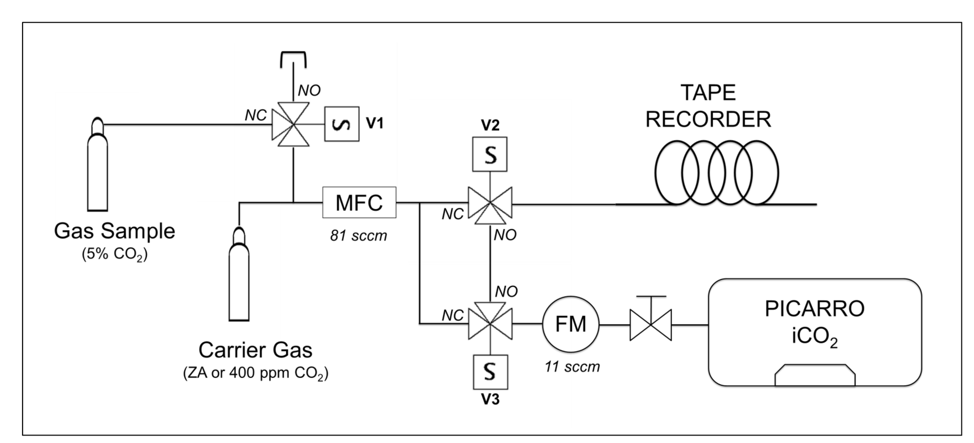
Method

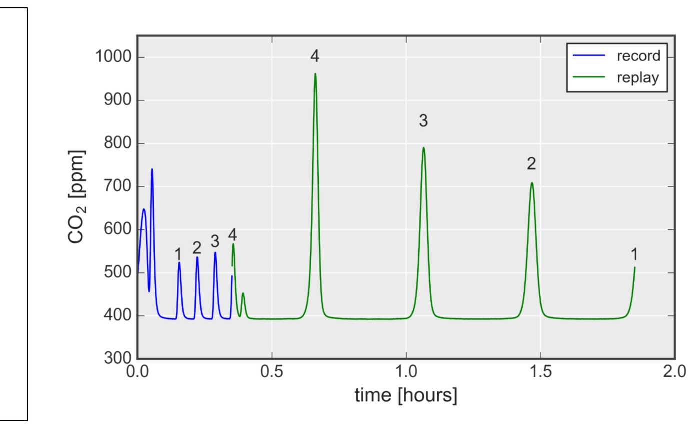
To analyze the isotopic composition (d^{13}C) of the effluent CO_2 gas coming from the Sunset analyzer, additional considerations need to be made for the CRDS analyzer.

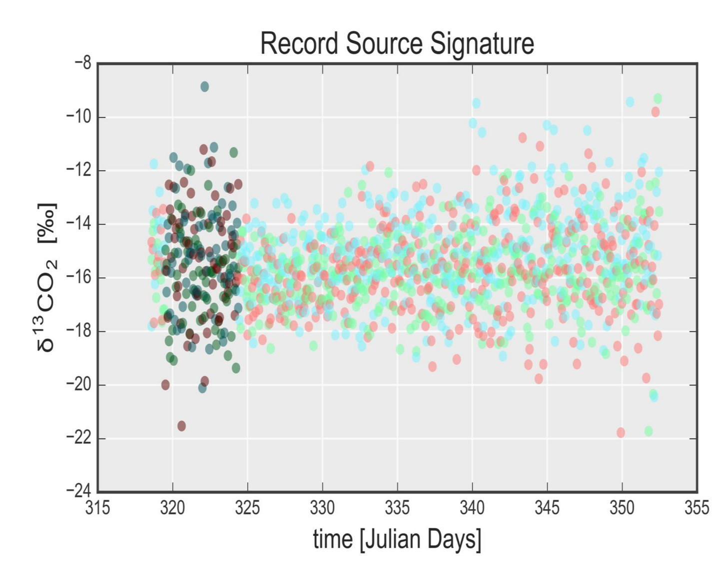
1) Carrier Gas

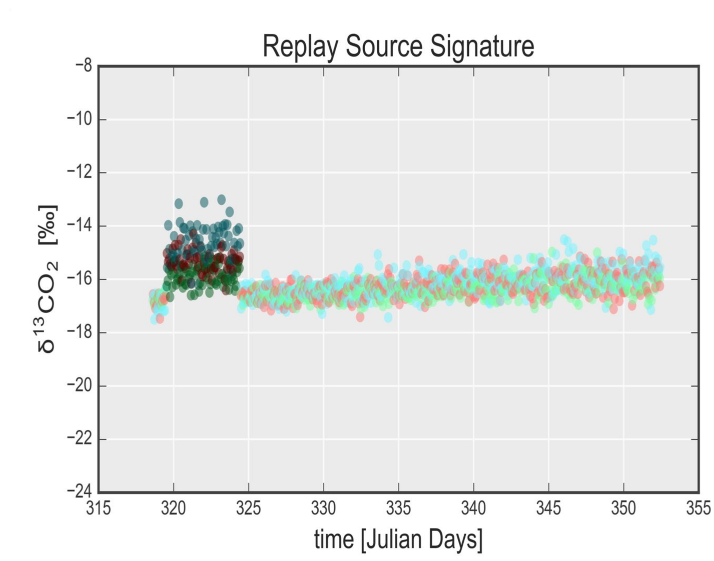
The Sunset analyzer accepts helium and argon as two carrier gas options. The argon has been chosen for the system, as the helium could degrade the pressure gauge used for cavity pressure monitoring due to its small atom size. Although the argon is a carrier gas that will broaden the CO_2 peaks differently than the air which the analyzer is designed for, the spectral fitter is kept the same. This is because the broadening effect caused by the argon does not differ much from the one caused by the air. The effect of the line shapes on the isotopic ratio measurement can be accounted for by calibrating the analyzer with samples of known isotopic composition in a background of argon.

2) Precision Optimization: Tape Recorder Technique



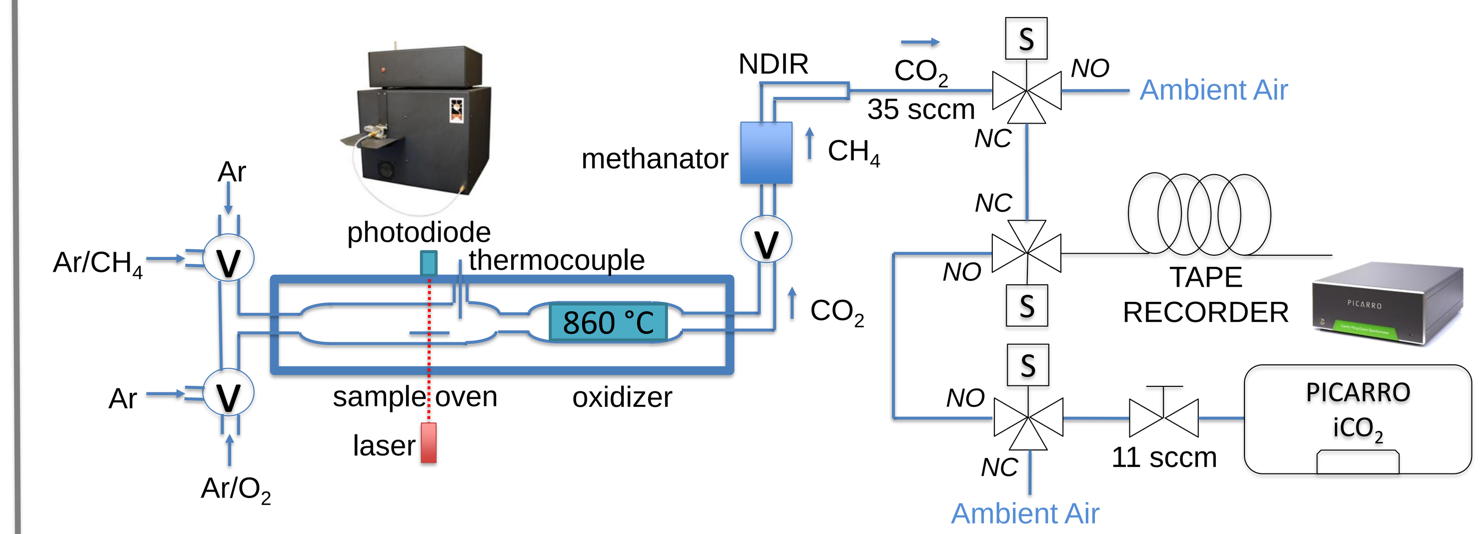






- Darker colors represent the measurement conducted with ZA as the carrier gas.
- Measurement precision is poorer for the directly measured 'record' phase than for the slower 'replay' measurement, for a couple of reasons: less time is spent measuring each pulse in the record phase (by a factor of 5-6), and the pulses are smaller. This is the main benefit of the tape recorder – improved precision.
- The per-pulse measurement noise on replay is about 0.4 permil for an average replay pulse peak height of 350 ppm and duration of about 2-3 minutes.

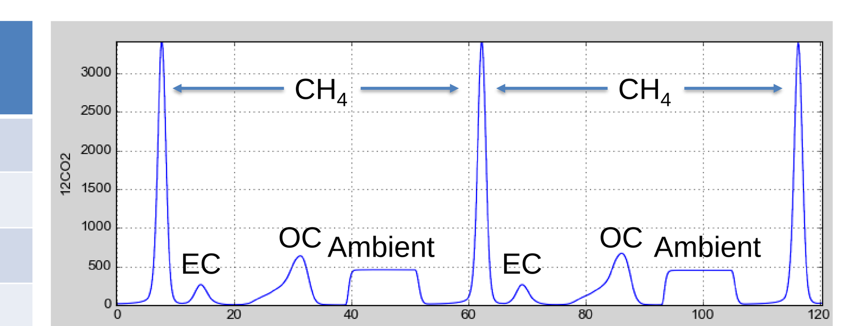
Experiment Setup

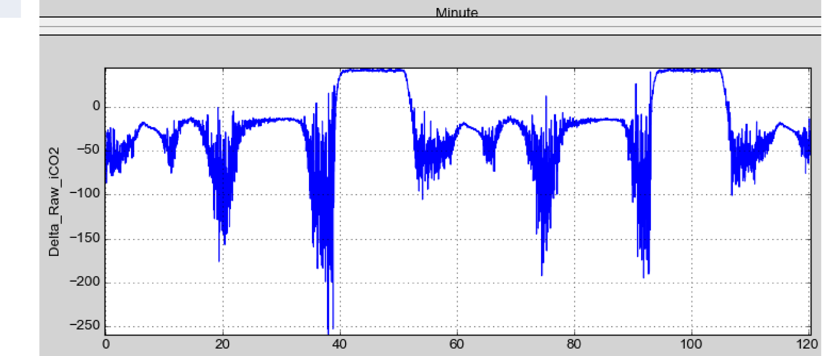


Phase	V1	V2	V3	Comments
Gas Storage / Aerosol Combustion	On	On	On	The collected aerosols get combustion in Sunset. The generated CO_2/Ar flows to the tape recorder. The sample gas flows to the tape recorder. The net gas flowrate going into the tape recorder is 35 sccm.
Isotope Analysis / Aerosol Collection	Off	Off	Off	The gas collected into the tape recorder is released to the Picarro analyzer at a lower flow (11 sccm). Thus, the dilation time is 3.2 greater than the pulse.

Results

	Mean	Standard Deviation
OC	617.9 ppm	23.2 ppm
OC Isotope	-27.8 ‰	0.2 ‰
EC	257.4 ppm	6.7 ppm
EC Isotope	-28.2 ‰	0.4 ‰





- The aerosol sample was collected near I-5 interstate highway.
- 10ug OC corresponds to a CO_2 pulse peaking at ~600ppm.
- The $^{12}CO_2$ and $^{13}CO_2$ pulses are integrated separately before the calculation of the isotope value.

The good precision reveals the potential of this method for practical use on in-situ monitoring stations. The fact that the precision gets higher as the amount of the aerosols increases suggests that more accurate isotopic information can be recorded during pollution episodes.

Future Work

The Picarro analyzer has been sent to Professor Zhang Yanlin's lab in Nanjing University of Information Science & Technology for the integration test with the field Sunset analyzer to complete the semi-continuous monitoring solution. Prof. Zhang will fine-tune the configuration of the system and deploy the system for field study.

Interested in learning more?

- Contact Zhiwei Lin (zlin@picarro.com)
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