An Executive Summary

The Delta Ray Road Trip

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Identifying the origin of CO_2 in various samples is a major challenge for environmental scientists, regulators and the industry. Different emission sources create CO_2 with different isotopic signatures. Analysis of this difference has traditionally required complex instrumentation in sophisticated laboratories, limiting the ability to monitor changes of isotope ratios of CO_2 in real time.

The Thermo Scientific™ Delta Ray™ Isotope Ratio Infrared Spectrometer (IRIS) is a user-friendly, field portable solution for CO_2 monitoring and analysis. A sealed, permanently aligned analysis chamber enables the system to tolerate a range of environmental conditions while providing continuous monitoring of CO_2 isotope ratios. The addition of a Universal Reference Interface (URI) provides easy calibration and internal controls for consistent results. The capabilities and robustness of the system are demonstrated by installing it in a recreational vehicle for a road trip across Canada, measuring CO_2 concentrations and isotope ratios while traveling from coast to coast.

The power of isotopes

CO_2 in nature is built of different stable isotopes of carbon (^{12}C and ^{13}C) and oxygen (^{16}O, ^{17}O, ^{18}O). Different reactions generating CO_2 tend to slightly favor different isotopologues. Graphing the isotope ratio of ^{12}C:^{13}C versus the ratio of ^{16}O:^{18}O in **Figure 1** reveals distinct clustering of samples from different sources, such as volcanic emissions, gasoline or methane combustion, plant or animal respiration, and atmospheric background.

Measuring isotope ratios

A molecule of CO_2 can rotate and vibrate at specific, quantized frequencies. Replacing one isotope with another e.g. a ^{12}C with a ^{13}C, changes the frequencies of these vibrational and rotational transitions, thereby changing the wavelengths of light the molecule absorbs **(Figure 2)**.

In the Delta Ray IRIS a laser beam passes through a gas sample and onto a detector, and measures the amount of light absorbed by the sample at a given wavelength. By shifting the color, or wavelength of the light, an absorption spectrum is generated, revealing the absorption features produced by the different isotopologues of CO_2.

The Delta Ray IRIS covers a range of wavelengths in the middle infrared, in the fundamental absorption bands of CO_2, where the absorption lines are about 8000 times stronger than in near-infrared and also minimizes interferences by other species. Other instruments operate in the near-infrared, yielding weaker and more ambiguous spectra.

The Delta Ray IRIS scans through wavelength range 500 times per second, averaging the results for one second before calculating isotope ratios by fitting the measured spectrum to a model built into the software.

Instrument

At the core of the Delta Ray IRIS is a difference frequency generation (DFG) laser operating near 4.3 µm. The laser beam is translated into a multi-pass cell, where it reflects between two mirrors for a total of thirteen passes before exiting to the detector.

During manufacturing the optical path is tuned for optimum performance and then the mirrors are permanently glued into place, producing a durable, monolithic structure. The mirrors have standard protected silver surfaces that make them relatively insensitive to contamination like dust particles.

Isotope ratio infrared spectrometers generally run in a flow-through mode.

To operate the Delta Ray IRIS, about 80mL of a gas sample is passed through the analysis cell per minute. This, combined with the once-per-second isotope ratio calculation, allows real-time measurement and analysis of CO_2 isotopes in the environment.

Figure 1: Isotope ratios of different CO_2 sources.

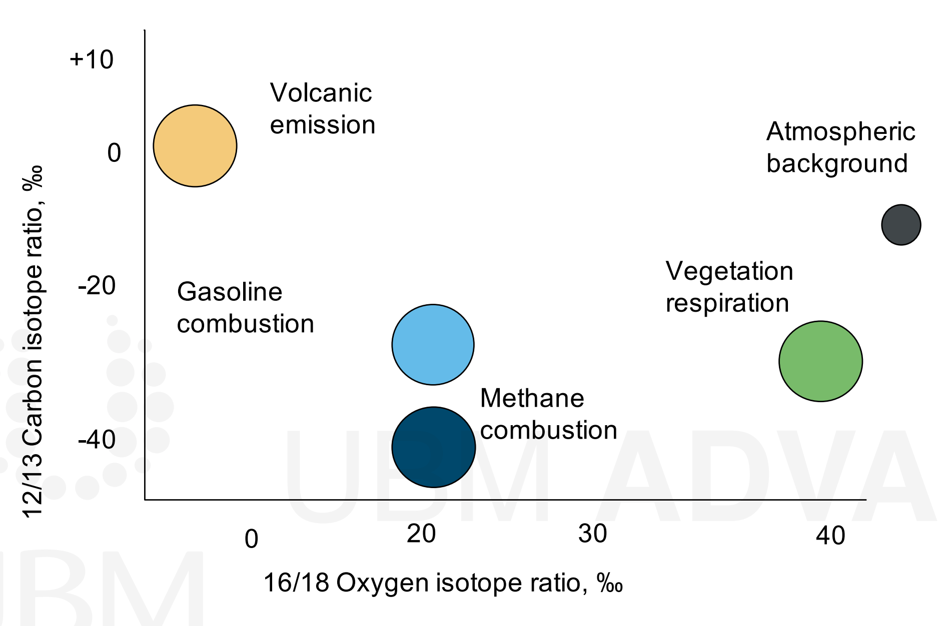
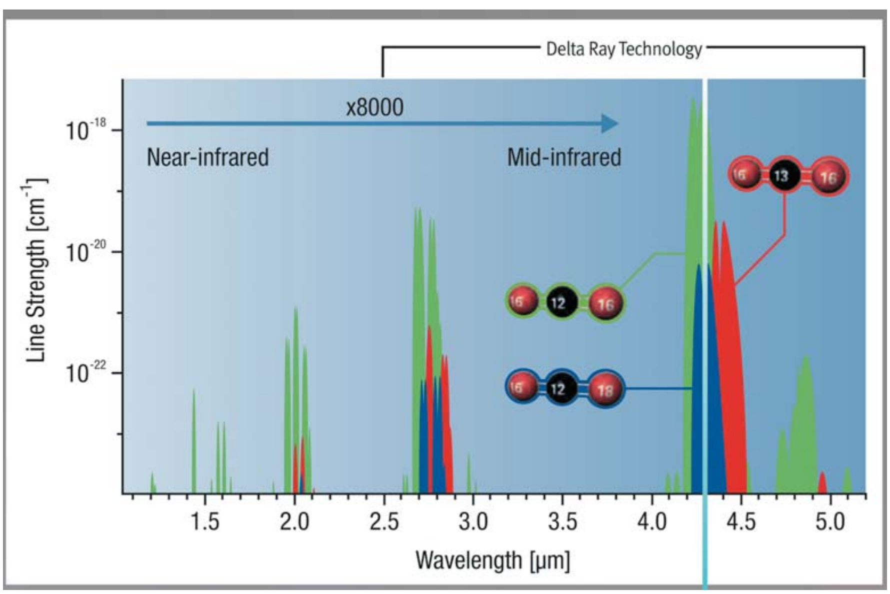


Figure 2: Isotope ratio infrared spectroscopy.



To provide meaningful results, a spectrometer requires calibration with a gas of known isotopic composition. The Universal Reference Interface (URI) provides the capability to perform such calibrations with the gas MIxing and swiTCHing device (MITCH) at its core. Specifically, the URI takes a pure CO_2 reference gas and dilutes it with synthetic air, which contains the gases normally found in air, but lacks CO_2. The URI adjusts this mixture to match the sample CO_2 concentration to eliminate the first-order nonlinearity that all gas analyzers have. This smart referencing system, in which the reference gas concentration automatically adjusts to match the sample concentration, corrects for instrument drift and first order nonlinearity. A second different reference gas is used for delta scale calibration.

The sample also passes through a dryer to remove water, for two reasons. First, naturally varying moisture levels cause a matrix effect that can lead to erroneous results. Second, CO_2 and water rapidly exchange oxygen isotopes when in contact, another cause for systematic errors. All similar systems on the market require users to add their own dryers, but the Delta Ray IRIS includes this important component.

Using the URI, the Delta Ray IRIS can be calibrated in the field by stepping the reference gas through several levels of CO_2 concentrations, determining the instrument's non-linearity which is then applied to automatically correct the samples by the software. The Delta Ray IRIS ships with two 1 liter flask of reference gas with different isotopic composition. Because the flasks are shippable, researchers can order replacements easily.

On the road

To demonstrate its capabilities and portability, the Delta Ray IRIS was installed in a recreational vehicle (RV) and was driven from coast to coast across southern Canada, stopping for demonstrations at 28 laboratories and a trade show along the way. The installation included an uninterruptable power supply (UPS) that could run the system for about fifteen minutes that allowed us to switch the Delta Ray IRIS to "shore power" when the RV was plugged in at a campground or other facility, or an inverter powered from the camper's batteries. This allowed keeping the Delta Ray IRIS running for 24 hours a day during the entire trip.

The Delta Ray IRIS itself was strapped into the bunk bed over the driver's seat. The built in Windows 7 PC, connected to a GPS receiver, completed the setup and allowed us to map the entire trip and all of the data. The inlet for sampling CO_2 was a capillary tube running through the seal of a skylight, which was not ideal but was the most feasible arrangement without modification of the RV.

We configured the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software to reference and calibrate the system every 30 minutes during the trip. However, in the parts of the trip where major changes in the altitude or the air temperature were expected referencing was set to be done every fifteen minutes. The one-liter flask of isotopically calibrated reference gas provided with the Delta Ray IRIS would allow such a system to run continuously for about three months with 30-minute reference intervals.

As documented on the Delta Ray Road Trip web site (http://www.thermoscientific.com/DeltaRayRoadTrip), the journey crossed the southern portion of Canada from Halifax to Vancouver, a total of 8,249 km (5,125 mi). While on the web site, visitors can click any segment of the trip to see a graph of the data from that segment. Buttons beneath the graph switch the view between CO_2 concentrations and isotope ratio data.

A graph of the entire data set reveals overall CO_2 levels **(Figure 4)** that varied between 400ppm and 1,500ppm, with several distinct peaks. There is also a short gap, which indicates the period after our arrival in Montreal for the Joint Assembly scientific conference, when we shut down the system to move it from the RV into the conference hall.

Figure 3: Optical core.

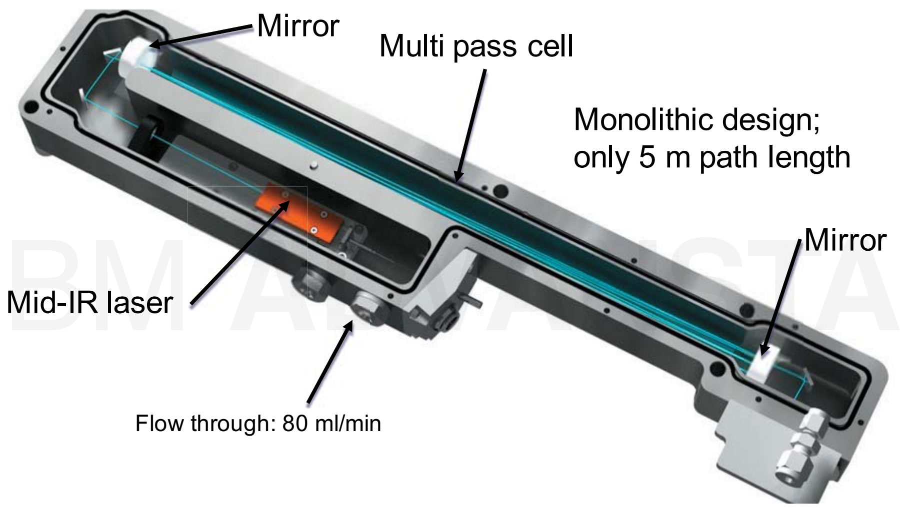
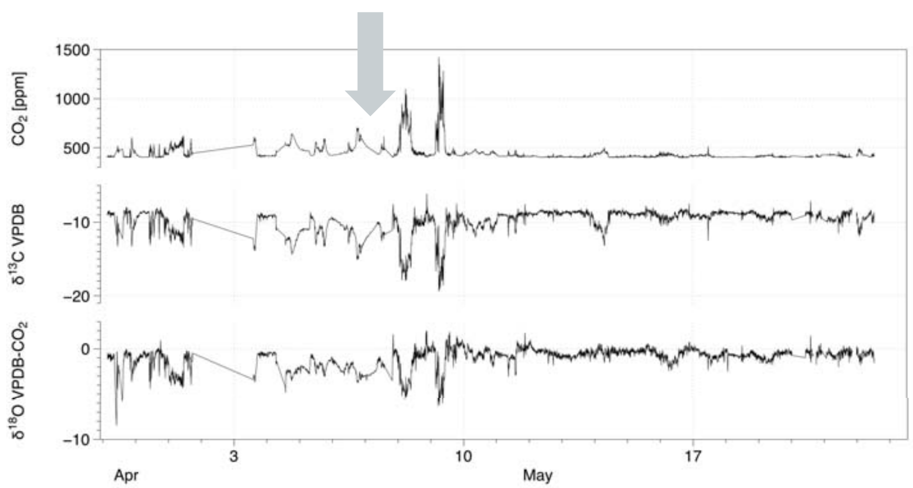


Figure 4: Overview of data.



Data analysis: The Conference hall

One of the major peaks was on the meeting in Montreal in which CO_2 levels sampled by the Delta Ray IRIS, rise from 400ppm to 700ppm. This took place while the system was set up in the Conference hall. Analysis of the time recorded data reveals a steady rise in CO_2 as people came into the exhibit hall just before lunch. After lunch there was a poster session in the hall, which correlated with a rise in CO_2. The levels trailed off as people left the meeting hall, but the decay was slow. Possibly the air conditioning system was turned off after the show ended for the day, resulting in less air exchange.

While the temporal correlation is suggestive, the Delta Ray IRIS allows us to drill much more deeply into the data to identify the source of the CO_2. To do that, we use a so called Keeling plot, which graphs the reciprocal of the CO_2 concentration on the X axis and the isotope ratio on the Y axis **(Figure 5)**. During the peak in the conference hall, the points all fall on a straight line, indicating a two-member mixing process: atmospheric CO_2 and some other source of CO_2. The Y-axis intercept of that line indicates the isotopic composition of the pure CO_2 from the second source. In this case, it points to human breath as the source, confirming our suspicions.

Interestingly, the rise in CO_2 concentration in the Conference hall stopped at 700ppm. This is probably due to system of the air condition that is monitoring the CO_2 level and it is set to increase the outside air flow to keep concentrations below that level.

Another large peak in CO_2 levels occurred while we were parked overnight and slept inside the vehicle. In this case, the time series shows CO_2 concentrations rising from 400 ppm to 1,000 ppm. The rise began shortly after we had returned from a late dinner, and continued until we awoke in the morning. The Keeling plot again shows a clear linear fit, consistent with atmospheric CO_2 mixing with a single additional source. Looking at the Y-axis intercept of the Keeling plot reveals an isotope ratio matching with human breath.

We examined the intake of the capillary tube and discovered that the opening in the skylight was not entirely airtight. Some air from inside the RV apparently leaked out of the opening and entered the sampling tube. As we slept inside the closed vehicle, the CO_2 concentration had steadily increased until we opened the doors in the morning. This prompted us to modify the inlet to be higher above the skylight, which prevented this artifact from affecting our data for the reminder of the trip.

Six days after the discovery of the impact of human breathing on rise CO_2, the data show another overnight CO_2 peak. This was a night when the vehicle was parked unoccupied next to a motel where we were sleeping. Over

Figure 5: What is the source of the CO_2: Keeling plot.

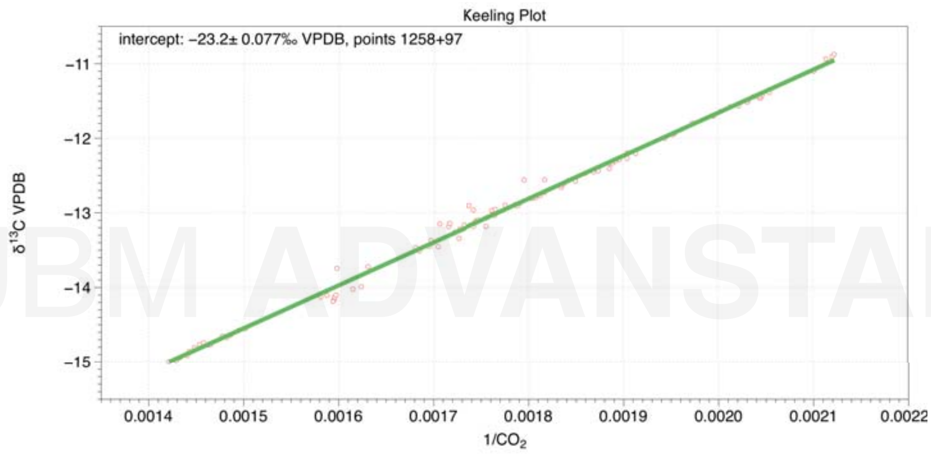
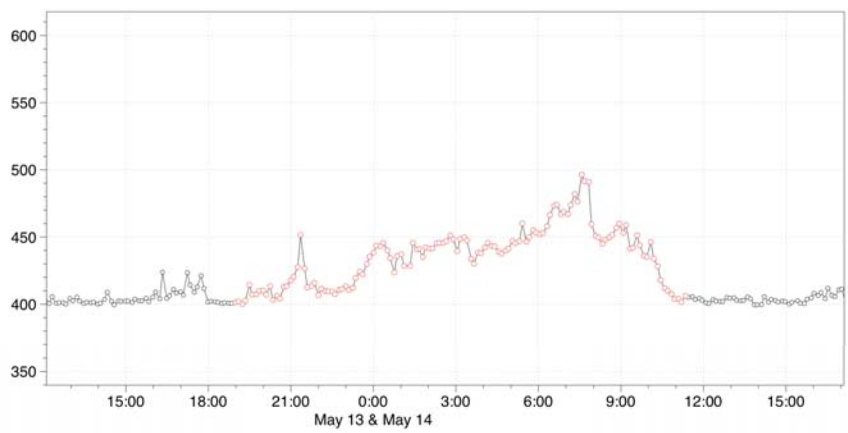


Figure 6: Sudbury.



the course of the night, CO_2 levels steadily increased, and after sunrise they began a steady decline. The Keeling plot showed another linear trend, but this time the Y-axis intercept points to the isotope ratio of a combustion source. The isotope ratio suggested that the CO_2 came mostly from gasoline combustion, but some portion of it also appeared to be from burning methane.

We believe the gasoline combustion signature came from the nearby road, while the methane was burned by the heating systems of the adjacent buildings. The gradual overnight increase and morning decline are consistent with an atmospheric boundary layer trapping the CO_2 during the calm night, until the advection of the morning breeze moved it away **(Figure 6)**.

For all of the peaks, the extremely high resolution of the data provides robust fits for the Keeling plots. Traditionally, obtaining this level of resolution would have required collecting many samples into flasks and shipping them to a laboratory for analysis, which would have been tremendously cumbersome and cost prohibitive. With the Delta Ray IRIS we can perform analyses on site every second, operating 24 hours a day.

Online resources and future plans

The Delta Ray road trip is documented online. Pictures are uploaded to Facebook, Instagram and Twitter under the #DeltaRayRoadTrip, and videos are available on YouTube.

Summary

The Thermo Scientific Delta Ray IRIS integrates several complementary technologies into a complete, durable, field portable system for measuring and analyzing CO_2 concentration and isotope ratios in the environment. The Delta Ray IRIS uses monolithic construction to ensure durability and reliability in a variety of settings. By measuring the absorption spectrum of CO_2 in the middle infrared range, the spectrometer reveals the most prevalent isotopologues present in a sample. Analyzing these isotope ratios it is possible to identify specific CO_2 sources even under changing atmospheric conditions.

The URI with a gas mixing interface, feeds a mixture of standard reference gases into the Delta Ray IRIS to match the concentration of the sample under study. Researchers can thus calibrate the system as frequently as they need to without disrupting their analyses. An included dryer eliminates interference from environmental moisture. Even while mounted in a moving vehicle on a trip of several thousand kilometers, across urban and rural landscapes, the Delta Ray IRIS provides continuous, reliable sampling and analysis around the clock.