Bulk Stable Isotope Analysis of Carbon from Solids and Liquids using a Total Organic Carbon Analyzer Coupled to a Wavelength-Scanned Cavity Ring-Down Spectrophotometer

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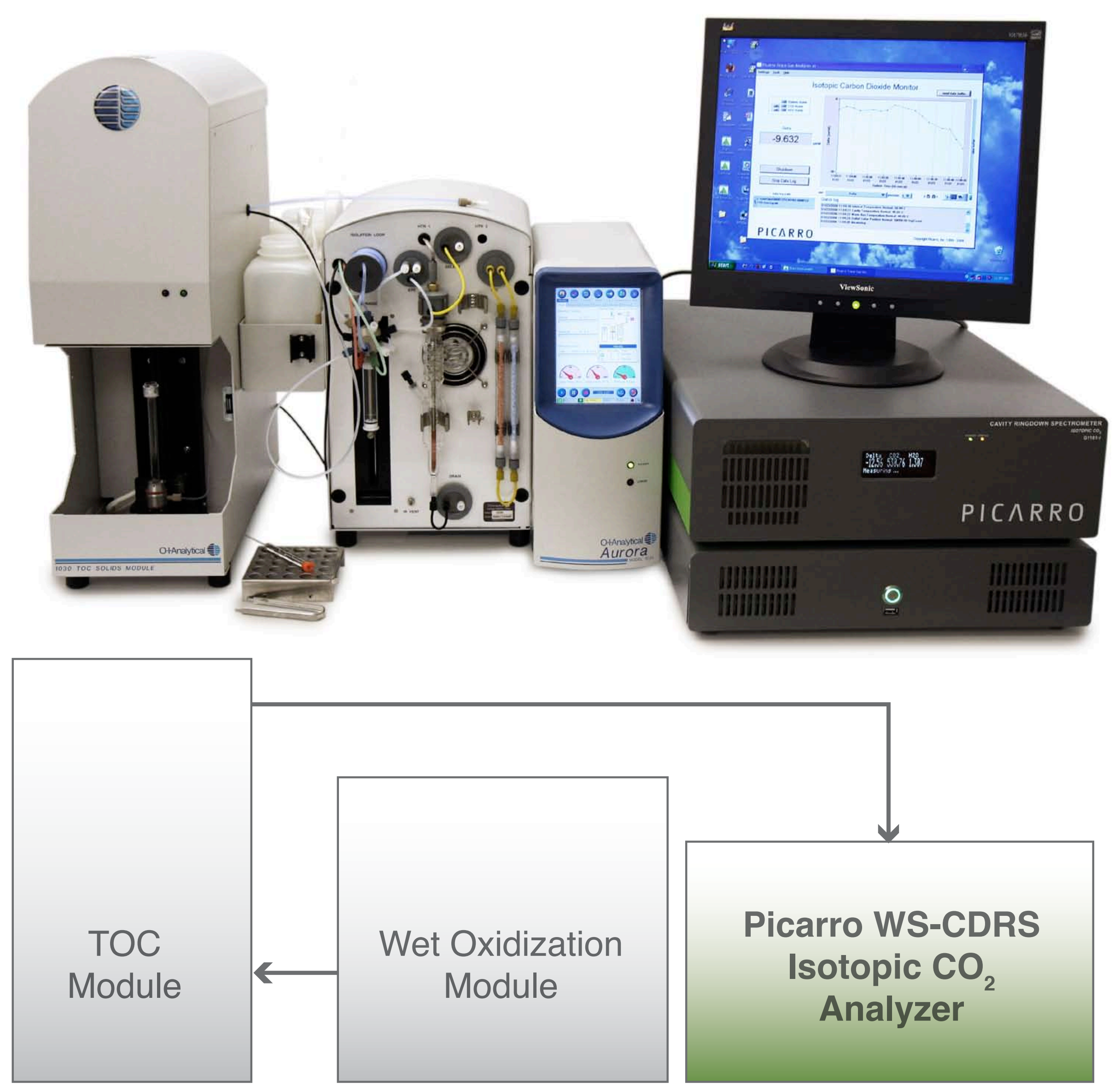
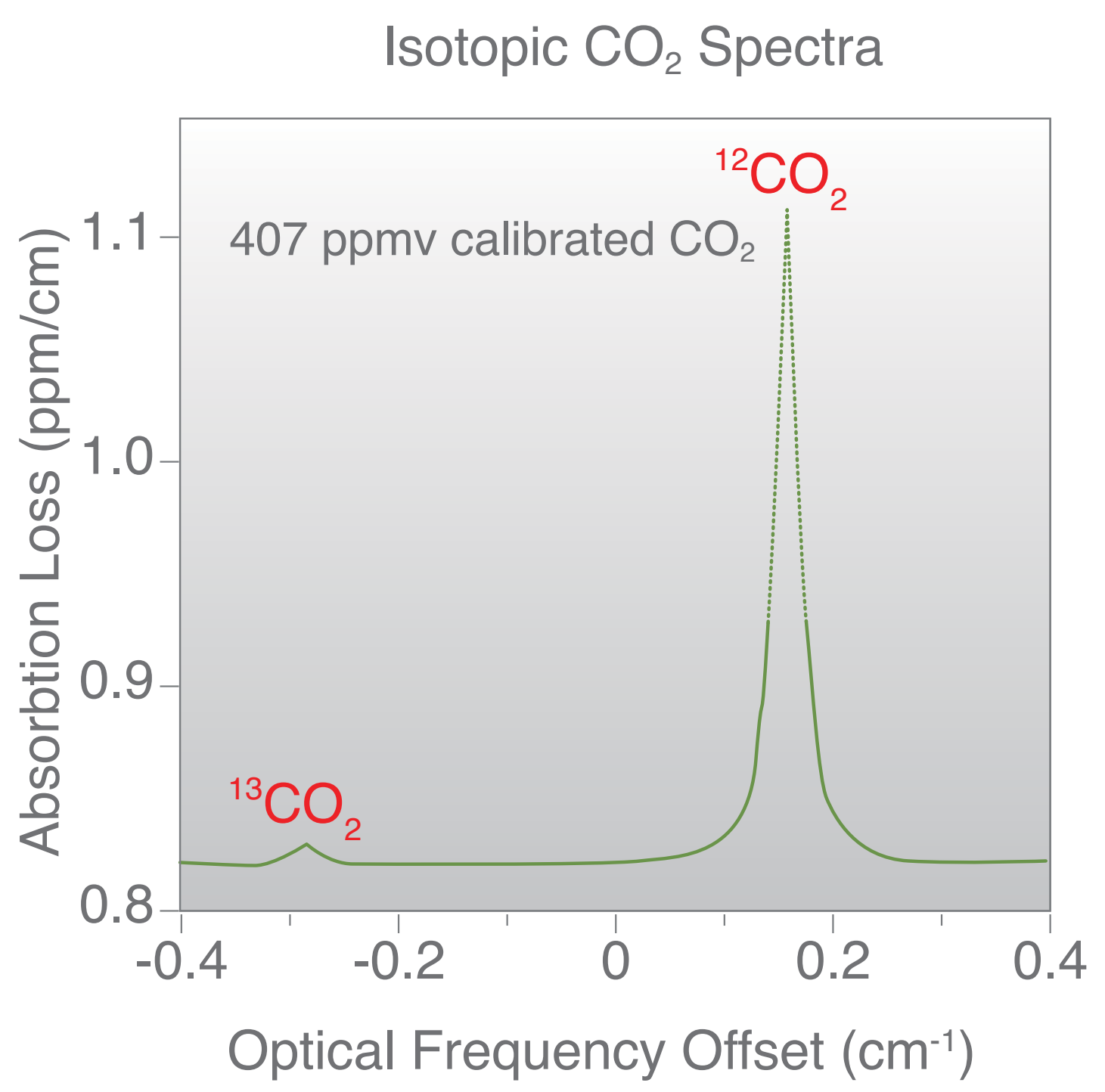
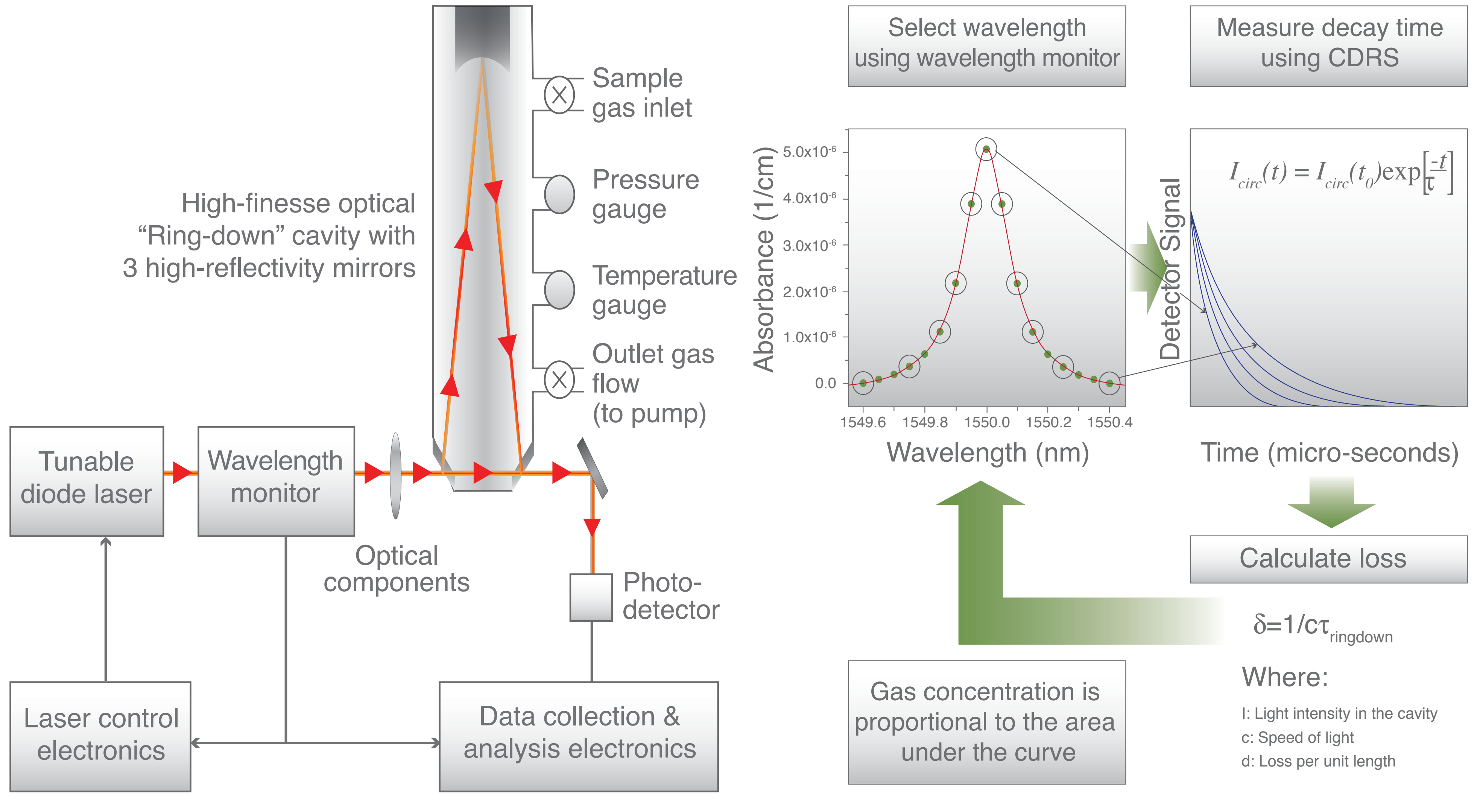
Among food authenticity technologies, stable isotope ratio monitoring instrumentation is essential for constructing databases, so-called "fingerprints", that enable regulatory agencies to compare, discriminate or classify samples; e.g. ^{13}C isotope discrimination is mainly attributed to the key phase of carbon assimilation in food sources. Since the isotope content/ratios in plants and animals depend on both biochemical and environmental factors, the designation of origin can be specified by referring to the previously constructed database. Application of isotope ratio monitoring to food authentication has been well established during the past two decades. To date, the tool of choice for conducting such measurements has been centered on Isotope Ratio Mass Spectrometry (IRMS) techniques, a magnetic sector-type instrument with multiple Faraday collectors. For instance, IRMS measurements of bulk samples are used to provide evidence for the addition of sugar to honey or fruit juices as well as for the blending of genuine vegetable oils due to economic interest. We report here our successful attempt to interface a novel, small-footprint Wavelength-Scanned Cavity Ring-Down Spectrometer (WS-CRDS) to a Total Organic Carbon (TOC) analyzer for the measurement of the bulk isotopic carbon signature in plants and food products. The novel *i*TOC-CRDS system is capable of measuring the bulk isotopic carbon value in addition to the total organic carbon concentration of the analyzed sample and provides an inexpensive alternative with unparalleled ease-of-use as compared to standard methods using the more complex analytical instrumentation of Isotope Ratio Mass Spectrometry (IRMS).



iTOC-CRDS photo and schematic. CO$_2$ from combustion in the TOC solids module or from a wet oxidation process is analyzed for total carbon and then analyzed for isotopic content by the WS-CRDS analyzer.



Shown here are the two spectral features used in the WS-CRDS analyzer to measure the isotopic ratio of carbon in CO$_2$.



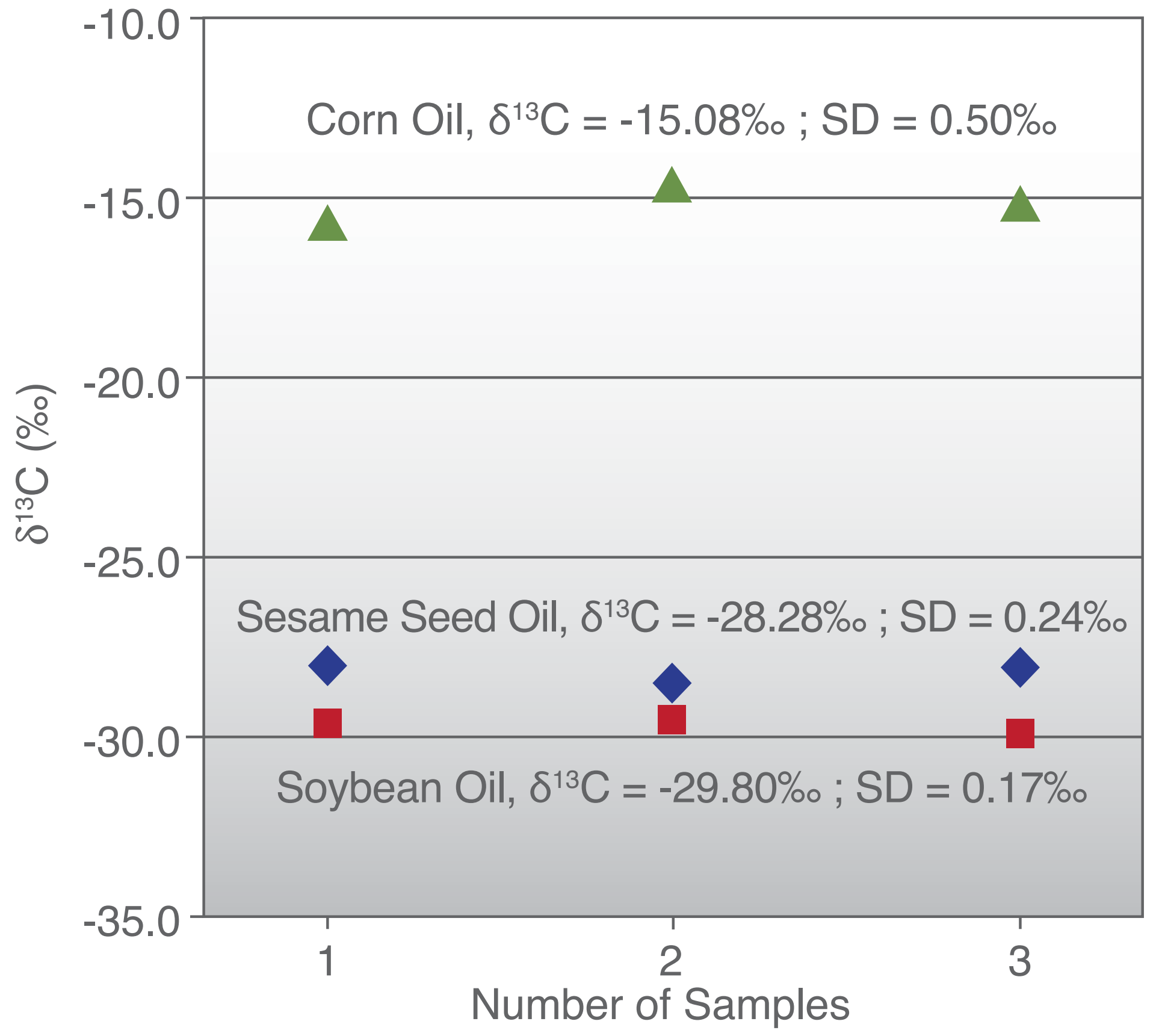
WS-CRDS analyzer schematic

Wavelength-Scanned Cavity Ring Down Spectroscopy (WS-CRDS) – Principle of operation

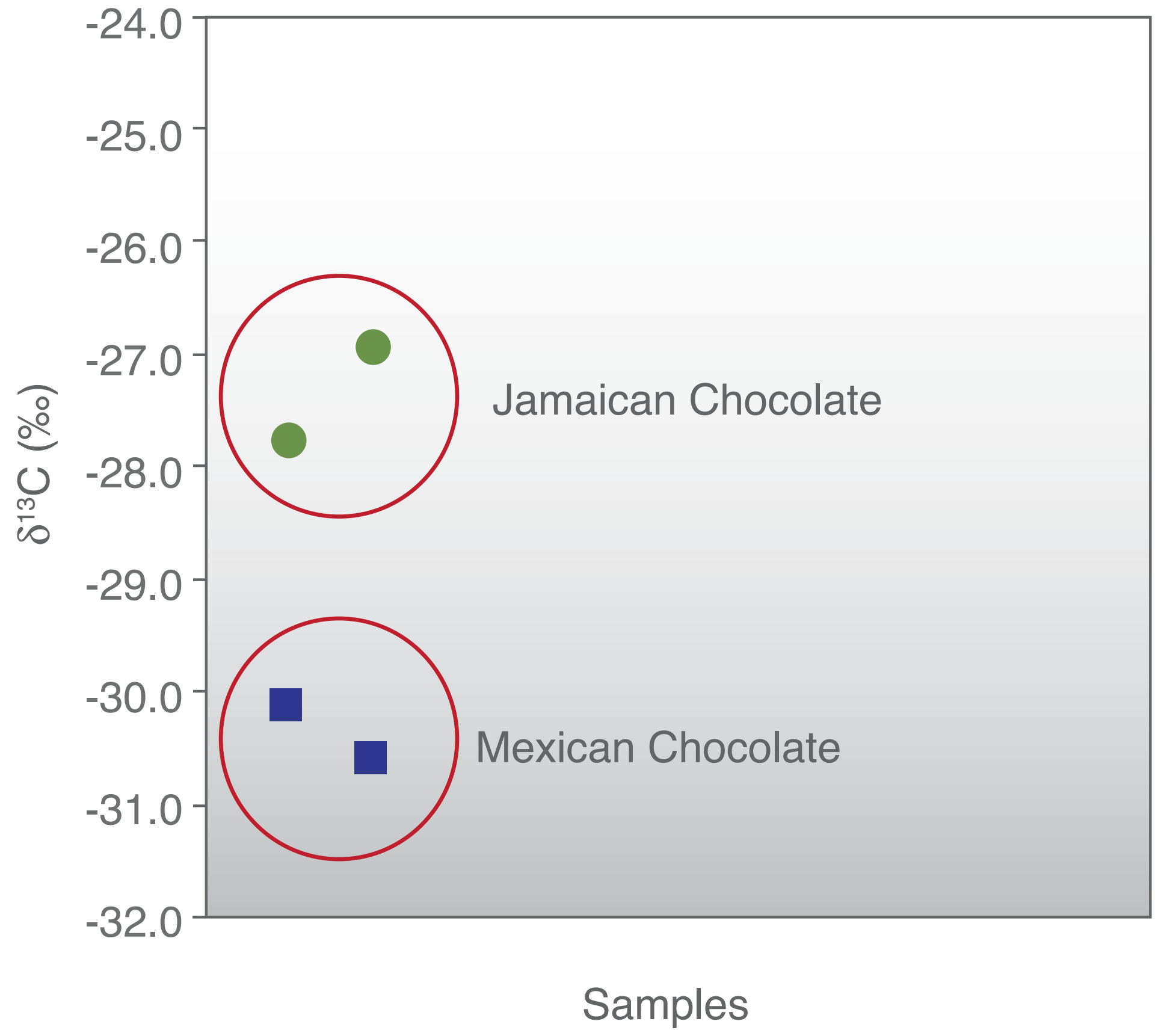
- The CO$_2$ gas generated from the combustion of bulk samples is first collected in a gas sampling bag. Then, the flow for the bag is diverted to the isotopic analyzer as a continuous gas stream.
- Light from a tunable NIR semiconductor diode laser is directed into an optical resonator cavity containing the analyte gas.
- When the optical frequency matches the resonance frequency of the cavity, energy builds up in the cavity.
- When the build-up is complete, the laser is shut off.
- The energy decays from the cavity exponentially in time, or "rings down," with a characteristic decay time. This energy decay is measured, as a function of time, on a photodiode.
- The ring down time measurement is continuously repeated at several different well-controlled points in wavelength as the laser is tuned across the molecular signature of the analyte gas and its isotopomer.
- WS-CRDS is a measurement of time not of absorbance. When the laser is at a wavelength where the gas in the cavity is strongly absorbing, the ring down time is short; when the wavelength is such that the gas does not absorb, the ring down time is long.
- The gas concentration or isotope ratio is determined by a multi-parameter fit to this lineshape (red curve) and is proportional to the area under the curve. The vertical axis is loss (or absorption, measured with cavity ring down); the horizontal axis is wavelength (measured with Picarro's patented Wavelength monitor)

Materials and Methods:

For total organic carbon analysis and isotopic carbon measurements, three types of edible vegetable oils (corn oil, soybean oil & sesame seed oil) were obtained from a grocery store. Using an SGE syringe, 2µl of each oil were independently aliquoted onto a crucible filled with quartz wool that soaks the oil sample. In the case of chocolate (solid material), samples from Jamaica and Mexico were obtained and a sample amount on the order of 1mg was weighed out then loaded onto the analysis crucible. The crucible has a 2mm hole in the center to allow oxygen to flow through once the TOC solids module (OI Instruments, College Station, Texas) carriage moves up into the combustion furnace and seals against its bottom fitting. The sample is then combusted for seven minutes with excess oxygen to ensure complete combustion of the sample material. A valve then diverts the combustion products into a gas sampling bag for homogeneous mixing. The CO$_2$ gas is then analyzed to determine its concentration with a Non-Dispersive Infrared (NDIR) detector before it gets diluted, in case necessary, and then diverted to the Picarro's isotopic WS-CRDS analyzer for carbon isotope analysis.



Isotopic analysis of three edible oil samples, each measurement repeated three times on the same sample.



Isotopic analysis of two chocolate samples, each measurement repeated twice on the same sample.

Conclusion:

The edible oil sample analysis with the *i*TOC-CRDS system yielded the high precision necessary to discriminate the sample photosynthetic pathway and origin. The *i*TOC-CRDS system provides excellent precision and accuracy (≤0.5‰) for δ^{13}C measurements from both solids and liquids, in minutes of measurement time. Edible oils derived from C-3 and C-4 plants as well as solid food items can be distinguished by their isotopic carbon signature using a fast, straightforward combustion process. Such precision can readily distinguish the isotopic carbon signatures of a variety of environmental and agricultural products from different origins, providing information about food authenticity and climate change effect on plant physiology.