LIAISON™: Fully-Automated Universal Interface for Bulk ^{13}C High-Precision Isotope Analysis using Cavity Ring-Down Spectroscopy

PICARRO

Nabil Saad and Bruce Richman – Picarro, Inc., 480 Oakmead Pkwy, Sunnyvale, CA 94085, USA, nsaad@picarro.com

Abstract

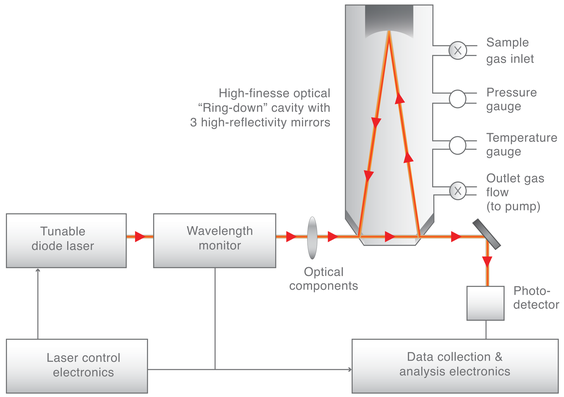
We have developed the world's first universal interface, named LIAISON, capable of coupling an isotopic CO_2 Cavity Ring-Down Spectrometer (CRDS) to almost any CO_2-generating sample preparation front-end ranging from an elemental analyzer to any dissolved carbon analysis module, which are of significant use in geochemical and biogeochemical studies. The LIAISON interface development has enabled an alternative approach for making high-precision bulk stable isotope analysis measurements of the $^{13}C/^{12}C$ isotope ratio of organic and inorganic bulk samples, which is less expensive, does not require trained personnel, and is portable. The technique relies on conversion of samples to CO_2 either through combustion of bulk material or the acidification of solid carbonate samples or aqueous aliquots, the automatic collection of the generated CO_2 in bellows for isotopic homogenization, and the precise measurement of the $^{13}C/^{12}C$ isotope ratio in the carbon dioxide gas from the simple and well established carbon dioxide infrared spectrum using the ultra sensitive absorption method of cavity ring-down spectroscopy.

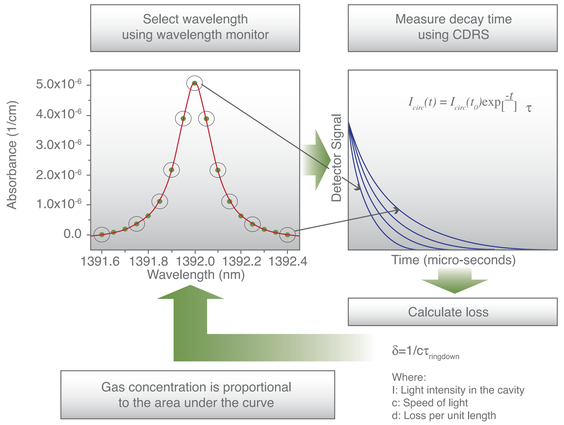
In this specific application, we have coupled LIAISON to a combustion module (CM) and to a cavity ring-down spectrometer (CRDS) for ^{13}C isotopic analysis of bulk samples. LIAISON is suited for a high-throughput sample analysis process by running three different gas handling operations in parallel: Admitting combustion gas from the CM into a first gas bag, analyzing the previous sample collected into a second gas bag with CRDS, and flushing and purging a third gas bag in preparation for the upcoming sample collection operation. The sample-to-sample analysis time is 10 minutes and the operation is completely automated for the duration of an auto-sampler tray capacity, requiring no operator intervention. The CRDS data is collected, tabulated and saved into an output text file. The memory effect between the L-Glutamic acid standard (USGS 40, $\delta^{13}C$ = -26.389 ‰) at natural abundance and the moderately enriched L-Glutamic acid standard (USGS 41, $\delta^{13}C$ = 37.626 ‰) is minimized by the selection of the adequate number and duration of flush and purge cycles of the gas sample bags. The system achieved a typical precision equivalent to 0.2 ‰ (1 sigma) or better, including the $\delta^{13}C$ -enriched samples

Conclusion

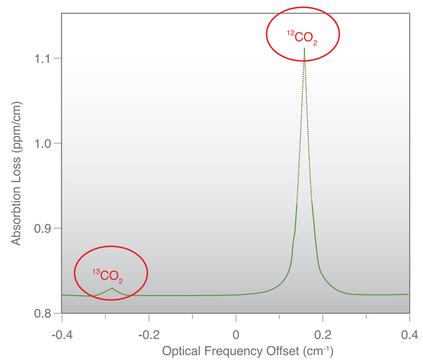
The CM-LIAISON-CRDS system presented here provides a fully automated solution for bulk $\delta^{13}C$ analysis with unprecedented ease-of-use, and possible field-portability with the current availability of a compact combustion module. In addition, LIAISON's universality enables CRDS to supplant IRMS in many continuous flow isotopic analysis applications, for $\delta^{13}C$ and possibly other stable isotopes, currently employing sample preparation modules in tandem with IRMS.

CRDS Analyzer Schematic





Isotopic CO_2 Spectra



Shown here are the two spectral features used in the CRDS analyzer to measure the isotopic ratio of carbon in CO_2.

Fig 1. LIAISON Universal Interface: N_2 carrier gas from front-end enters LIAISON from the front inlet and CO_2 gas from sample is collected in a gas sampling bag for isotopic homogenization. In parallel, the previous sample collected in a different gas bag is being isotopically analyzed by the CRDS. Simultaneously, a third gas bag is being purged with N_2 gas in preparation for the next sample collection.

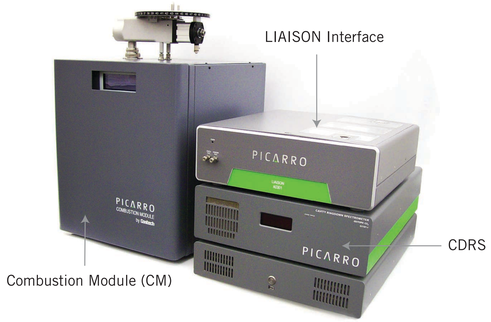


Fig 2. Combustion Module-CRDS system (CM-CRDS): Shown here is the Picarro CM with 50-sample tray autosampler connected to CRDS via the LIAISON interface.

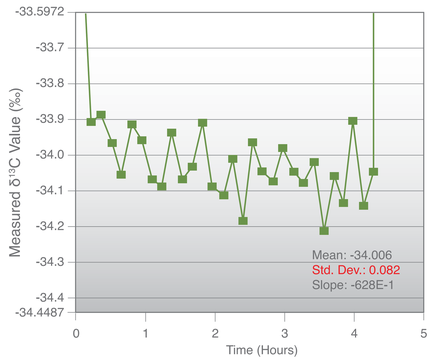


Fig3. $\delta^{13}C$ analysis of 29 acetanilide samples

Fig 3. Results of $\delta^{13}C$ analysis of 29 acetanilide samples over a period of 5hrs demonstrating excellent precision, with no use of CO_2 ref. gas.

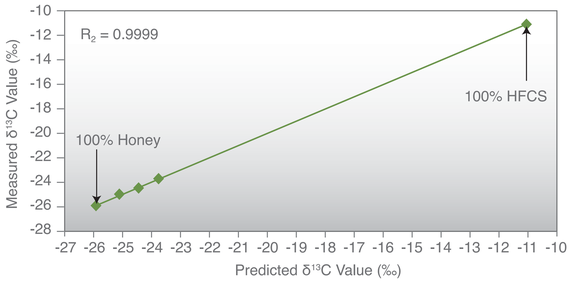


Fig4. HFCS Adulteration of Honey

Fig4. Analysis of deliberately adulterated honey samples with 5%, 10% & 15% High-Fructose Corn Syrup showing excellent correlation between predicted and measured $\delta^{13}C$ values.

Sample	CDRS $\delta^{13}C$ (‰)	S.D. (‰)	IRMS $\delta^{13}C$ (‰)	Δδ (‰)
Honey A	-22.22	0.165	-22.2	-0.02
Honey B	-21.85	0.120	-22.0	0.15
Honey C	-25.22	0.184	-25.6	0.38
Honey D	-25.08	0.047	-25.1	0.02
Honey E	-27.20	0.082	-26.8	-0.40
Honey F	-24.47	0.089	-24.4	-0.07
Honey G	-23.77	0.032	-23.9	0.13
Honey H	-23.65	0.065	-23.9	0.15
Honey I	-23.66	0.046	-23.8	0.14
Honey J	-23.74	0.107	-24.2	0.46

Table1. Honey Analysis: CM-CRDS vs. EA-IRMS

Table 1. Comparison of $\delta^{13}C$ values for honey samples run on CM-CRDS and EA-IRMS systems.

Sample	Honey (‰)	Protein (‰)	C4 Sugars (‰)
Sample1	-26.57	-27.35	0
Sample2	-26.79	-27.57	0
Sample3	-26.27	-27.45	5.0
Sample4	-26.21	-27.84	0
Sample5	-26.55	-26.19	2.1
Sample6	-27.80	-27.45	1.9

Table2. Honey & Protein Analyses with CM-CRDS

Table 2. Comparison of $\delta^{13}C$ values for six honey samples and their corresponding protein fractions with calculation of potential C4 sugars according to AOAC method 998.12. None of the analyzed honey samples are considered adulterated (C4 Sugars < 7%).