Continuous Flow–Cavity Ring-Down Spectroscopy: A Powerful Tool for Food Origin Analysis PICARD and Adulteration Detection

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Abstract

Continuous Flow – Cavity Ring-Down Spectroscopy (CF-CRDS) instruments now provide simple access to stable isotope ratios for the three life elements (C, H, O). Once the growing, harvesting and/or processing of natural products is complete, these ratios leave a permanent and characteristic signature that can be easily read and used to screen these products.

We present here data using CF-CRDS for the analysis of the water content in fresh apples collected from two different growing regions that were analyzed for their isotopic water content. A fast sample preparation technique was completed within five minutes and yielded liquid samples which were directly injected into an isotopic CRDS liquid water analyzer for ¹⁸O and D analysis. The high-precision results showed clear differences for the same apple varieties grown in different regions; furthermore, these differences were consistent with the isotopic composition of the region's precipitation.

In addition to the liquid water isotopic analyzer, we have developed the world's first universal interface, named LIAISON^m, capable of coupling an isotopic CO₂ Cavity Ring-Down Spectrometer (CRDS) to various CO_2 -generating sample preparation front-end ranging from an elemental analyzer to any dissolved carbon analysis module. The LIAISON interface development has enabled an alternative approach for making high-precision bulk stable isotope analysis measurements of the ¹³C/¹²C isotope ratio of total inorganic carbon. The technique relies on conversion of samples to CO_2 through acidification of aqueous aliquots, the automatic collection of the generated CO2 in bellows for isotopic homogenization, and the precise measurement of the ¹³C/¹²C 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 Dissolved Inorganic Carbon sample preparation device (AutoMate®) and to a cavity ring-down spectrometer (CRDS) for ¹³C isotopic analysis of aqueous samples. The operation of LIAISON has been described in a separate poster presentation.

Conclusion

The CF-CRDS systems presented here provides a fully automated solution for D & ¹⁸O in juice samples and δ^{13} C analysis of TIC with unprecedented ease-of-use, and possible field-portability. In addition, LIAISON's universality enables CRDS to supplant IRMS in many continuous flow isotopic analysis applications, for δ^{13} C and possibly other stable isotopes, currently employing sample preparation modules in tandem with IRMS.





Source of Carbonation in Sparkling Water: Natural or Industrial?

The Picarro water carbonation test relies on a well-documented detection method based on the analysis of the ¹³C/¹²C ratio in the dissolved inorganic carbon (DIC) of carbonated bottled water. Sparkling water that contains natural CO₂ has a ¹³C/¹²C ratio of -10 permil or greater. Sparkling water with carbonation from anthropogenic sources (primarily hydrocarbon combustion) has a lower ¹³C/¹²C ratio of -30 permil or lower. Picarro's Iso-CO₂ CRDS analyzer measures ${}^{13}C/{}^{12}C$ ratios with high-precision and high-accuracy.

Apple Juice Analysis

Picarro Analyzer Used: L1115-*i* equipped with an autosampler

Process: Two red delicious variety apples, one labeled as Watsonville California and the other as Washington State were obtained from a produce stand. Juice was extract from each fruit by putting the entire fruit into a Juiceman[™] fruit and vegetable juicer and capturing the resulting juice stream. A 8 ml aliquot of the juice was drawn into a syringe, forced through a graded glass and polypropylene filter (Whatman GDX 6878-202) to remove all particulates >0.2 microns, and used to fill two 2 ml sample vials which were sealed with a septum cap. These vials were added to the autosampler of the Picarro L1115-*i* and run using a series of six injections for each vial with an analysis time of ca. 9 minutes per injection. The first two values for each vial were then discarded to mitigate any memory effects.

Source	δ ¹⁸ Ο (‰)	δD
GNIP amount weight annual	-2 to -6 (Watsonville, CA)	-6 t
Precipitation map	-6 to -10 (Washington)	-38
USNIP station CA45	-7.1	not
USNIP station WA45	-12.5	not
Average Watsonville, CA	-0.69	-22
Average Washington	-5.05	-81

Table 2: Annual weighted average isotope ratios for the regions of origins of the apples, together with data from the closest USNIP station and measured values from apple samples.





CA Apples: $\delta^{18}O = -0.69 \pm 0.09\%$; $\delta D = -22.11 \pm 0.59\%$

Sparkling Water Origin	δ ¹³ C (‰)	S.D (‰)
U.S. 1 (artificial)	-37.96	0.13
U.S. 2 (natural)*	-38.77	0.08
E.U. (natural 1)	-6.56	0.27
E.U. (natural 2)	-6.75	0.07

*suspected use of artificial carbonation / mislabeling

Table 1: Analysis of 4 brands of sparkling water in bottles acquired off-the-shelf. U.S.2 brand analysis was repeated on a second batch acquired from a different supermarket to confirm δ^{13} C signature



Figure 2: Map of the western United States showing Watsonville denoted by the A, the major Washington state apple growing region is shown by the orange oval.