Detection of Coconut Water Adulteration with CM-CRDS

PICARRO

APPLICATION NOTE (AN037)
COMBUSTION MODULE CAVITY RING-DOWN SPECTROSCOPY SYSTEM

Summary

The production, sale, and distribution of coconut water is a multibillion-dollar global industry with beverage products from over 30 different companies. Given the increase in preference and consumption of pure 'organic' products, the coconut water industry is challenged to ensure product purity and maintain customer confidence. This requires controlling supply chain quality, certifying the grade of coconut water, and complying with customs regulations. Essential to this process are evaluations of authenticity (i.e., the absolute ability to distinguish between 'pure' products with no added sugars and 'adulterated' products that have added sugar). In this note, we present the application of the Picarro Combustion Module Cavity Ring-Down Spectroscopy (CM-CRDS) System as a low-cost, easy-to-use, accurate, and precise solution to identify the addition of C4 sugars (adulteration), based on the carbon isotopic ($\delta^{13}C$) composition of the coconut water. It is easier to use and a significantly lower capital and total-ownership cost alternative to Isotope Ratio Mass Spectrometry (IRMS), and it produces results that are indistinguishable. The CM-CRDS system is simple to install, easy to operate, and does not require sample pre-treatment. This application demonstrates that the Picarro CM-CRDS is a powerful analytical platform in the food and beverage adulteration market. It can easily distinguish down to ~5% adulteration of coconut water by the addition of C4 sugars, with excellent precision (about ±0.3 per mil) and accuracy.

Comparison of CRDS and IRMS Analysis for Coconut Water Authentication

The ability to determine the source of an organic substance stems from the relative isotopic abundance of elements which comprise the material. Measurement of isotopic ratios can be used to differentiate between samples which otherwise share identical chemical compounds. One application that has become prominent over the past decade is the authentication of organic food and beverage ingredients.

Isotope Ratio Mass Spectrometry (IRMS) is a specialization of mass spectrometry in which methods are used to measure the relative abundance of isotopes in a specific sample. Cavity Ring-Down Spectroscopy (CRDS) is a form of laser absorption spectroscopy. Numerous journal articles have validated that CRDS is as precise and accurate as IRMS for isotopic analyses in a range of natural science applications. This application note compares CRDS with IRMS for the specific purpose of organic beverage authentication, specifically, the detection of sugar adulteration in coconut water that is indicated to be pure.

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Elemental analyzer isotope ratio mass spectroscopy (EA-IRMS), where a sample undergoes combustion, has proven to be precise and accurate in detecting coconut water adulteration. However, combustion module cavity ring-down spectroscopy (CM-CRDS) provides measurement accuracy and precision comparable to EA-IRMS for the same application, and it has several advantages, including:

- Significantly lower capital cost for the system.
- Much simpler operation that does not require extensive, specialized training.
- Less frequent calibration and lower cost of maintenance.
- Lower cost of consumables required for operations.
- Greater automation and higher throughput.

Collectively, the features and capabilities of CM-CRDS can translate into annualized cost savings of up to 50%—including instrument depreciation, labor, and consumables—versus EA-IRMS.

Collectively, the features and capabilities of CM-CRDS can translate into annualized cost savings of 50% or greater, versus EA-IRMS.

The System and Method

The CM-CRDS system is composed of a Picarro cavity ring-down spectroscopy (CRDS) analyzer and a combustion module (CM). Each sample measurement requires 5 micro-liters of coconut water, does not involve any complex sample preparation steps, and takes only 16 minutes per sample. The system is automated, can process 50 to 147 samples in a single session, and requires only a pressurized supply of ultra-high purity (UHP) N_2 and O_2. The $\delta^{13}C$ composition of the CO_2 generated by sample combustion is reported by the Picarro CRDS analyzer.

COCONUT WATER SAMPLE TEST METHODOLOGY

- **The system is calibrated using primary and secondary isotopic combustion standards.**
- **5 micro-liters of coconut water are extracted using a pipette or syringe (not provided) and placed into a tin capsule (provided). No additional sample treatment is performed.**
- **The capsules are loaded into an auto-sampler attached to the combustion module. The default capacity of the auto-sampler is 50, with a potential upgrade to 147 sample holders.**
- **When a measurement is engaged, the sample automatically drops into the pre-packed reactor within the combustion module and is combusted. Pure oxygen is supplied to the module and regulated to drive complete combustion of the sample. CO_2 is released.**
- **The gas pulse travels from the reactor to the analyzer and passes through a water-filter and a GC-column.**
- **The Picarro CRDS is a continuous flow-through system and measures the arrival of the CO_2 pulse in real time.**
- **Once the complete pulse has been analyzed, the system calculates the $\delta^{13}C$ composition of the sample in per mil, relative to Vienna PeeDee Belemnite (VPDB).**
- **We recommend three replicates, averaged into a single value for statistically satisfactory standard and sample measurements.**

1 Liquid coconut water samples are placed into tin containers and loaded into the auto-sampler.

2 Samples are combusted one by one in a quartz reactor at 1000°C, turning each into CO_2.

3 The CO_2 arrives at the analyzer where Picarro software automatically reports a $\delta^{13}C$ value for each sample.

Fructose Adulteration Study

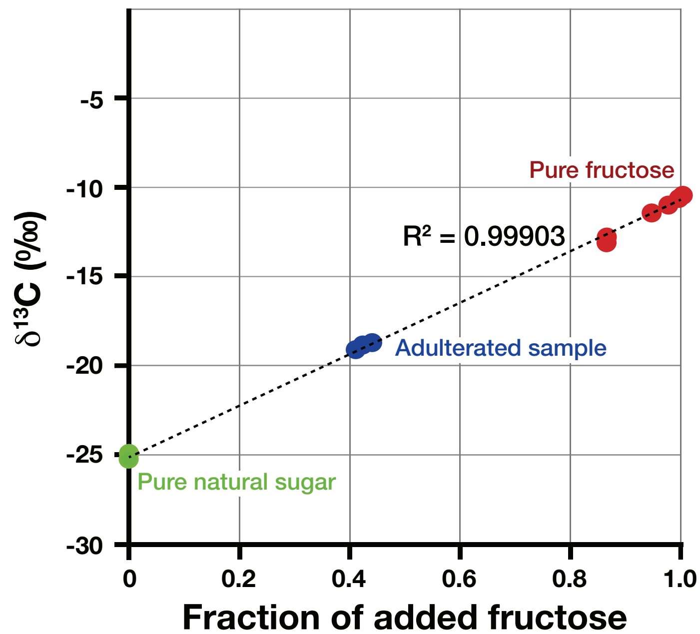
Coconut water samples provided by a commercial producer were analyzed to validate the linearity, reproducibility, and accuracy of the Picarro CM-CRDS. The system was calibrated using primary and secondary standards. Unadulterated coconut water and C4 sugar end-members ($\delta^{13}C$) were determined using respective reference material, and a linear mixing diagram was established (**FIGURE 1**). Over a range of 4 to 100% adulteration the R^2 value of the dataset was 0.999. Analyzing a second commercial sample of coconut water, known to be adulterated, confirms that ~40% of its total sugar content is added fructose. Measurements of the $\delta^{13}C$ composition of both coconut waters (pure and adulterated) using CRDS were compared to independent IRMS data provided by a coconut water producer, and they were found to be identical within ±0.1 per mil (**TABLE 1**). Precision for an individual measurement, obtained from three replicates, was ±0.3 per mil.

TABLE 1

Picarro CM-CRDS Coconut Water Adulteration Detection			
Pure Samples		Adulterated Samples	
Run No.	$\delta^{13}C$ (‰)	Run No.	$\delta^{13}C$ (‰)
1	-26.0	1	-18.8
2	-25.4	2	-18.7
3	-25.5	3	-19.1
4	-25.2	4	-20.3
5	-25.0	5	-18.7
Mean	-25.4	Mean	-19.1
IRMS Value	-25.3	IRMS Value	-19.1

Using the Picarro CM-CRDS and the mixing diagram, we were able to distinguish between coconut waters with and without added sugar and to pin-point the adulterated sample with high confidence.

FIGURE 1



Pure coconut water samples (green dots) mixed with high amounts of fructose (red dots) and measurements of a commercial brand of coconut water (blue dots) which is known to be adulterated. About 40% of the adulterated sample's total sugar content comes from fructose.

Conclusion

The study demonstrates that the Picarro CM-CRDS is a high-performance system that provides accurate isotopic measurements over a wide range of coconut water adulteration (4 to 100%). It maintains excellent precision, linearity, and minimal drift, with no need for any post correction to the final dataset. A comparison of samples provided by a commercial coconut water producer illustrates a clear difference in the $\delta^{13}C$ composition of the pure and the adulterated coconut water. It also illustrates the validity of the CM-CRDS data when compared to the more costly, difficult, and time-consuming IRMS analyses.

Our methodology does not involve complex steps for sample preparation. Several samples were prepared in a matter of minutes, and once ready, the automated system performed measurements continuously until completed with no additional supervision. A similar analytical approach can be applied in most natural beverage industries (e.g., apple, orange, and lemon), where dilution, addition of sugars, and mixing can erode consumer confidence, damage a brand, and harm a product's and company's financial performance.

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