PICARRO

The World's Highest Performing and Easiest to Use Analyzers

AN027

Measuring $\delta^{18}O$ and δD of Commercial Apples to Verify Region of Origin

A quick screening method of using stable isotopes to distinguish the true origin of fresh produce

Keywords:

Material: Apples, fruit, vegetables,
Process: Stable isotopes, $\delta^{18}O$ and δD, delta-^{18}O, delta-D

Summary and Relevance:

The agricultural, food and beverage industries can benefit from a technique to rapidly distinguish between the geographical provenance of similar raw and processed food products grown or produced in different regions. Stable isotopes can provide this fast screening capability. Every fruit, leaf or vegetable product has ^{13}C, D and ^{18}O stable isotope ratios unique to the plant type and local growing conditions (groundwater, temperature and amount of sunshine). These unique isotope ratios effectively affix a persistent atomic level geographical "bar code" to all plant matter and to many related animal products (e.g. honey, carries the signature of the primary feedstock of the bees that make it). Stable isotope ratios can in some cases be used to determine whether premium products such as honey and olive oil are 100% genuine or have been adulterated with cheaper ingredients[1]. (See Picarro Application Notes 23 and 28)

Despite government regulations mandating the verification and certification of the origin and authentic content of foodstuffs in the European Union and the United States, stable isotope ratios are still rarely used for this purpose. The high cost, complexity and time required to make these measurements using traditional scientific instrumentation, as well as the level of special expertise required, are significant barriers to widespread usage outside of university or laboratory. A new generation of simple-to-use, turnkey instruments which can in seconds or minutes provide stable isotopes for a wide range of samples at a fraction of the cost per sample of traditional instrumentation. These instruments are based on a proven technology called CRDS (Cavity Ring-Down Spectroscopy). In this application we demonstrate the simplicity, precision and discriminatory power of using CRDS to measure $\delta^{18}O$ and δD isotope values for apples grown in different U.S. states (California and Washington).

Picarro Analyzer Used:

L1115-*i* Isotopic Water Analyzer equipped with autosampler option

PICARRO

The World's Highest Performing and Easiest to Use Analyzers

Process:

Two Red Delicious variety apples, one labeled as originating from Watsonville California and the other as originating from Washington State, were purchased from a retail produce stand. Juice was extracted 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 2ml sample vials added to a 2 ml vial with an insert and 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.

Results:

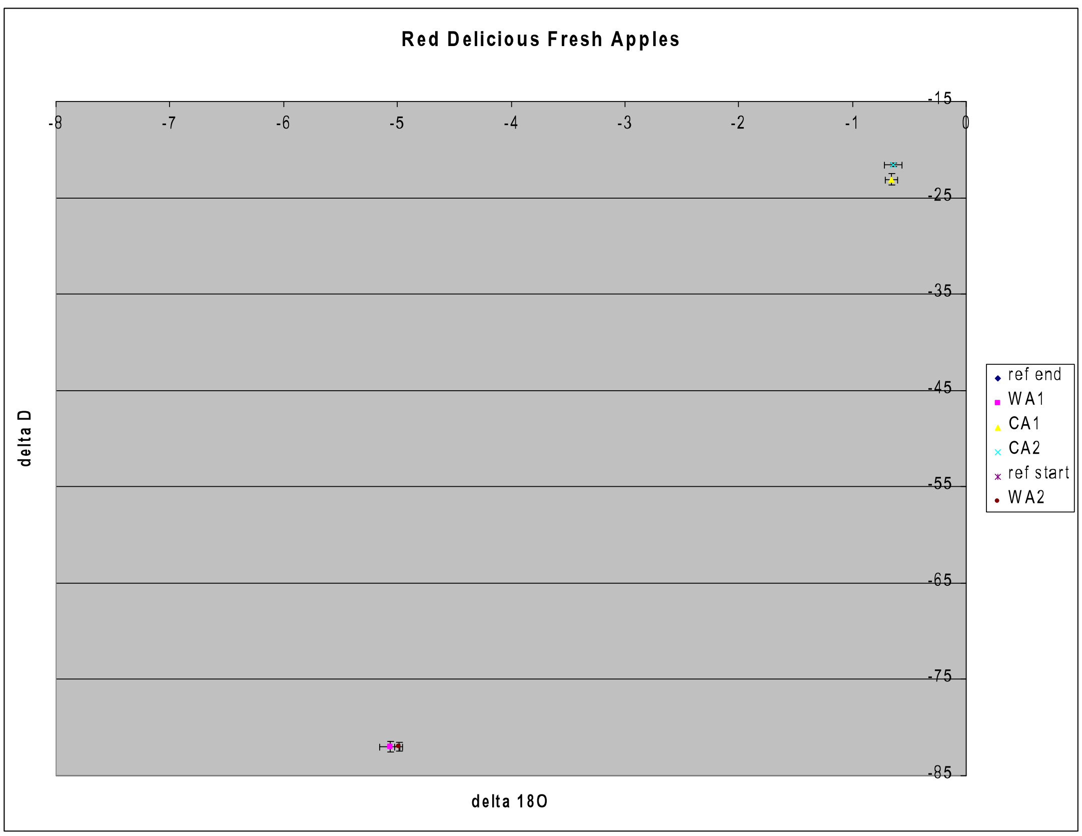

Figure 1: Data for Red Delicious apples. Each color represents the average of multiple injections from an individual sample. The error bars represent the standard deviation for that sample. Note the excellent precision and clear differentiation shown by the tight grouping.

PICARRO

The World's Highest Performing and Easiest to Use Analyzers

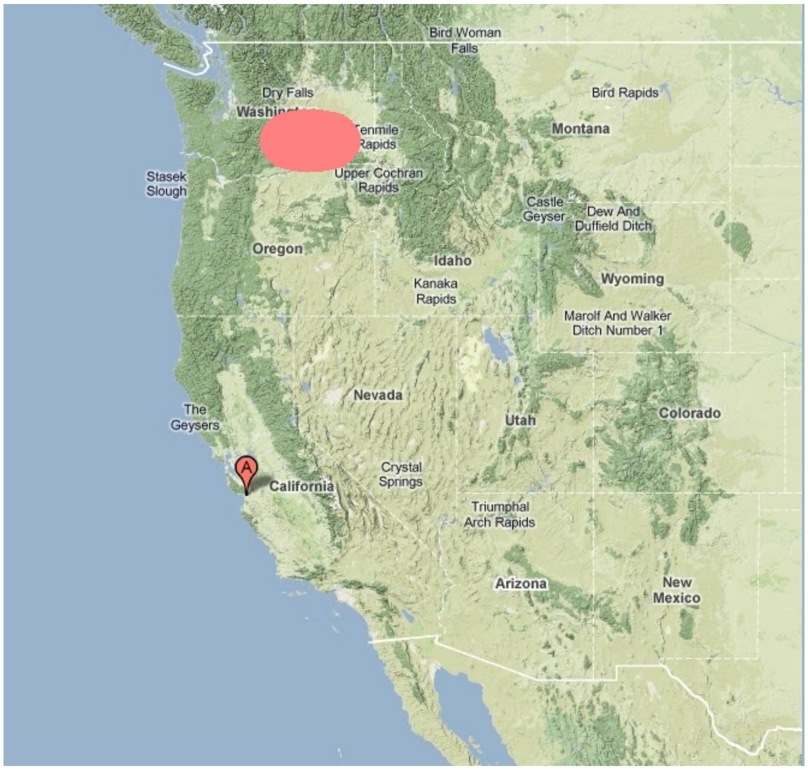

Figure 2: Map of the western United States showing Watsonville denoted by the A, the major Washington state apple growing region is shown by the orange oval.

Source	Delta ^{18}O	Delta D
GNIP amount weight annual precipitation map	-2 to -6 (Watsonville) -6 to -10 (Washington)	-6 to -38 (Watsonville) -38 to -70 (Washington)
USNIP station CA45	-7.1	Not published
USNIP station WA24	-12.5	Not published
Average Watsonville	-0.69	-22.11
Average Washington	-5.05	-81.74

Table 1: 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.

As shown in Figure 1 juice from fresh apples of the two apple growing regions exhibit clear isotope profile differences well in excess of the standard deviation of the measurement. This result is especially compelling in light of the simplicity of sample preparation, an operation that could be performed by any laboratory technician or assistant.

The apple growing region of Watsonville (Santa Cruz County) does not receive any irrigation water from outside of the county. (Irrigation water from outside the county could influence or alter the isotopic ratio of the apples grown in the county due to the uptake of this imported water during the growth process of the crop). Santa Cruz County is immediately adjacent to the Pacific Ocean and is bordered by a high mountain ridge to the East. Consequently, all water used within the county is well within the isotopic band ratio from the Global Networks of Isotopes in Precipitation (GNIP) map.

In contrast, the major apple growing regions of Washington State are located in the Columbia Basin and Yakima Valley. These regions are located east of the Cascade Mountains and have distinct isotopic band ratios on the GNIP map. Furthermore, these regions draw irrigation water from the Columbia River and related drainage basins further to the east. The drainage basins to the east have increased concentration of the lighter water isotopes due to their greater distance from the Pacific Ocean (isotope depletion increases further inland). These depleted isotope levels clearly impact the total isotope ratio of the tested apples from Washington.

In conclusion, the measured isotope ratios are fully consistent with the precipitation patterns and water sources available to the respective apple growers. Based on these findings, CRDS could be used for quick and inexpensive stable isotope measurements that can definitively authenticate provenance of food crops and some processed foods (depending on production location). Considering that this technique can be performed on raw produce, requires only a few minutes of preparation per piece of produce, and provides highly sensitive and repeatable results, the potential for widespread use to authenticate food provenance and track food origin is obvious.

PICARRO

The World's Highest Performing and Easiest to Use Analyzers

Comments:

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, e.g. to tell whether a wine is from South America or France, or to confirm whether orange juice is from Brazil or Florida, or to identify the sources of apple juice as Washington State or Northern California.