AN018

Automated Measurement of $\delta^{13}C$ for Identifying and Classifying Edible Oils

A fast screening method distinguishes between oils derived from different plant species and can be used to test for product adulteration. In addition, data from the same product (olive oil), harvested in different regions, is presented.

Keywords:

Material: Edible oils, vegetable oils, olive oil, corn, soybean, sesame
Process: Stable isotopes, $\delta^{13}C$, delta-13C

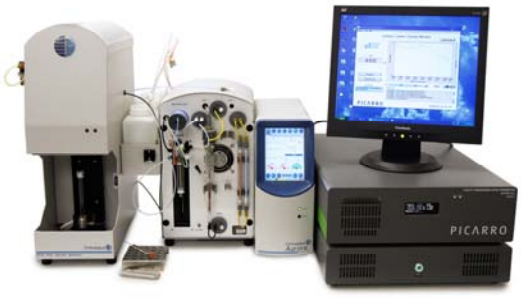
Summary and Relevance:

Edibles oils are derived from a wide variety of plant species including several types of nuts, seeds, and corn (maize). These vary significantly in cost and perceived value because of their taste and other quality parameters. Consequently, there is an economical incentive for unscrupulous adulteration of higher value and gourmet oils by dilution with lower cost (e.g. corn) alternatives, at several points along the supply chain. In addition to the fraud aspects, such un-recorded adulteration can have potentially negative consequences to consumers with strong allergic reactions to specific product types.

Stable isotope ratios have long been known to have enormous potential for food source screening, including the specific case of edible oils[1]. Although the stable carbon isotope value, $\delta^{13}C$, is very sensitive to plant type, this potential has remained largely unexploited because of the considerable difficulty, time and cost of obtaining this type of data with traditional IRMS instrumentation. In this application note we present isotopic carbon analysis data of samples from three different edible oils – sesame, soybean and corn. The data were obtained in minutes, using a totally new type of turnkey isotope analyzer, the *i*-TOC-CRDS, jointly developed by Picarro and OI Analytical. This device integrates a combustion chamber front-end from OI which converts solids, semi-solids and liquids into CO_2. This gas is then automatically injected into Picarro's wavelength scanned cavity ring down spectroscopy (WS-CRDS) detector for a high precision isotopic carbon measurement.

Analyzer Used:

i-TOC-CRDS



Process:

Three different premium brand oil samples were sourced from a local supermarket; sesame, soybean and corn. Each was labeled as 100% purity. Three samples of each oil were analyzed. For each data point, 2 microliters of oil was injected into the system's small removable quartz crucible using a standard chromatography syringe. The crucible was then inserted into the furnace stage and the oil combusted. The resultant CO_2, after an appropriate mixing time to ensure isotopic equilibration, was automatically passed into the WS-CRDS sampling chamber. The isotopic signature was then recorded during a 5 minute acquisition.

Results:

Photosynthetic carbon isotope fractionation is related to carbon dioxide uptake and enzymatic processes[2]. The so-called C3 plants, named due to the number of carbons in an intermediate molecule in the relevant biochemical pathway, discriminate more heavily against ^{13}C than the C4 plants and therefore have more negative $\delta^{13}C$ values. So, as expected, the data shows a dramatic difference between the oils from C3 plants (sesame, soybean) and that from corn, which is a C4 type plant. Second, even the two oils from C3 plants are clearly distinct and importantly, this new method produces absolute values that are in agreement with previously published data[3]. And finally, the data points are very consistent for each oil; the instrument's excellent precision is confirmed with standard deviations between 0.17 and 0.5‰.

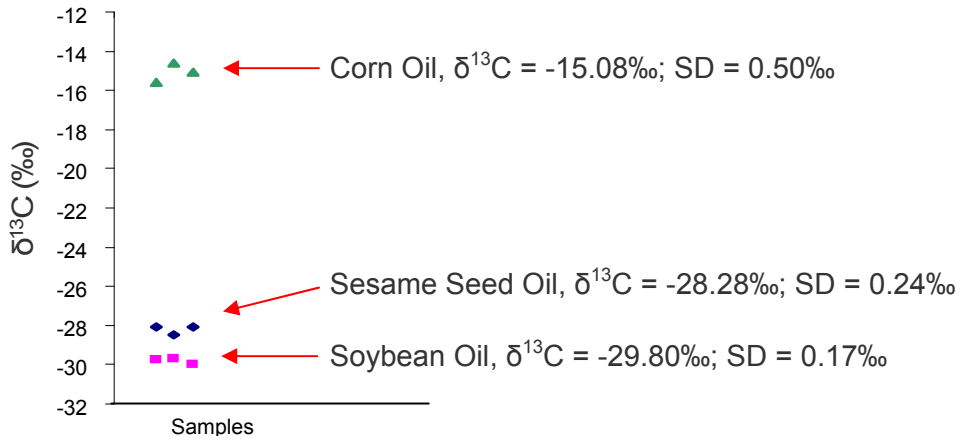


Table 1, below documents the comparison between the Picarro data and published IRMS results[3]. The correlation provides validation that this time-based optical technique is clearly capable of rivaling IRMS for these applications

2ul Inj. Vol.	PICARRO, $\delta^{13}C$ (‰)	IRMS, $\delta^{13}C$ (‰)
Corn oil	-15.08	-15.0
Sesame seed oil	-28.28	-27.9
Soybean oil	-29.80	-30.1

Table 1. Comparison of $\delta^{13}C$ values of selected edible oils. Data from Picarro WS-CRDS and IRMS, ref. 3

In a further development of this application, a series of olive oils were analyzed. The olive oils were sourced as premium branded products from Spain, Italy, Greece, Turkey, Lebanon and Australia. The data (see Table 2), was correlated with IRMS data.

2ul Inj. Vol.	PICARRO, $\delta^{13}C$ (‰)	S.D. (‰) (n=3)	IRMS, $\delta^{13}C$ (‰)
Spain	-28.95	0.18	-28.94
Italy	-28.98	0.05	-29.27
Greece	-29.29	0.02	-29.21
Turkey	-30.34	0.11	-30.32
Lebanon	-29.11	0.23	-28.87
Australia	-31.23	0.01	-31.19

Table 2. Comparison of $\delta^{13}C$ values of selected olive oils.

Once again, the excellent correlation and the superb precision of the results (see column 3) are indicative of the strengths of this instrument.

Comments:

A new generation of WS-CRDS-based analyzers enables simple and fast measurement of stable isotope ratios of carbon, oxygen and hydrogen. This study confirms that $\delta^{13}C$ values derived from the *i*TOC-CRDS system can be used as a fast screening tool for edible oil adulteration: to determine whether higher value oils have been diluted with corn-derived oil.

References:

1. Carbon Stable Isotopes and Olive Oil Adulteration with Pomace Oil, Angerosa et al, *J. Agric. Food Chem.*, 1997, 45 (8), pp 3044–3048
2. Carbon Isotope Discrimination and Photosynthesis, G D Farquhar et al, Annual Review of Plant Physiology and Plant Molecular Biolog, Vol. 40: 503-537 (1989)
3. Emerging Techniques in Vegetable Oil Analysis Using Stable Isotope Ratio Mass Spectrometry, Rhodes et al, *Grasas y Aceites*, 34 Vol. 53. Fasc. 1 (2002), 34-44