thermoscientific

Food and beverage fraud prevention using stable isotope fingerprints

Christopher Brodie, Oliver Kracht, Dieter Juchelka, Jens Radke, Jens Griep-Raming
Thermo Fisher Scientific, Bremen, Germany

ABSTRACT

The food and beverage industry suffers from fraudulent activities that include incorrect labeling of products and adulteration, which has a significant impact on food and beverage integrity, brand names and reputation and the market economy. Preventing food and beverage fraud is a key challenge that requires a reliable, cost-effective analytical process that can detect fraudulent changes in food and beverage products.

Stable isotope measurements can differentiate between food and beverage samples which otherwise share identical chemical composition: this is called the **isotope fingerprint**. Using **the isotope fingerprint of food and beverage products** is a reliable technique for fraud detection.

INTRODUCTION

Origin and authenticity can be routinely determined on food and beverage products using stable isotopes.[1-12] Measurement of stable isotopes can be used to differentiate between food and beverage samples which otherwise share identical chemical composition: this is the **isotope fingerprint of the food and beverage products**.

The food and beverage industry suffers from fraudulent activities that include incorrect labeling of products and adulteration, which has a significant impact on food and beverage integrity, brand names and reputation and the market economy. Preventing food and beverage fraud is a key challenge that requires a reliable, cost-effective analytical process that can detect whether the labeled product is authentic or if it has been changed after the final manufacturing process, or alternatively if it has been independently produced, using alternative ingredients, but labeled as an original product.

In this presentation, we provide examples of the use of isotope fingerprints in food and beverage fraud detection and provide an overview of the interpretation of these isotope fingerprints and the technology used.

ISOTOPES IN FOOD AND BEVERAGE ORIGIN AND AUTHENTICITY

Stable isotopes of **carbon, nitrogen, sulfur, oxygen and hydrogen** can be measured from food and beverage products, such as honey, cheese, olive oil, animal meat, milk powder, vegetables, wine, liquor, water and so forth, using isotope ratio mass spectrometry techniques.[1-12] These stable data can be interpreted to verify the origin, correct-labeling and trace adulteration of food and beverage products (Table 1).

Table 1. Isotope fingerprints in food and beverage samples.

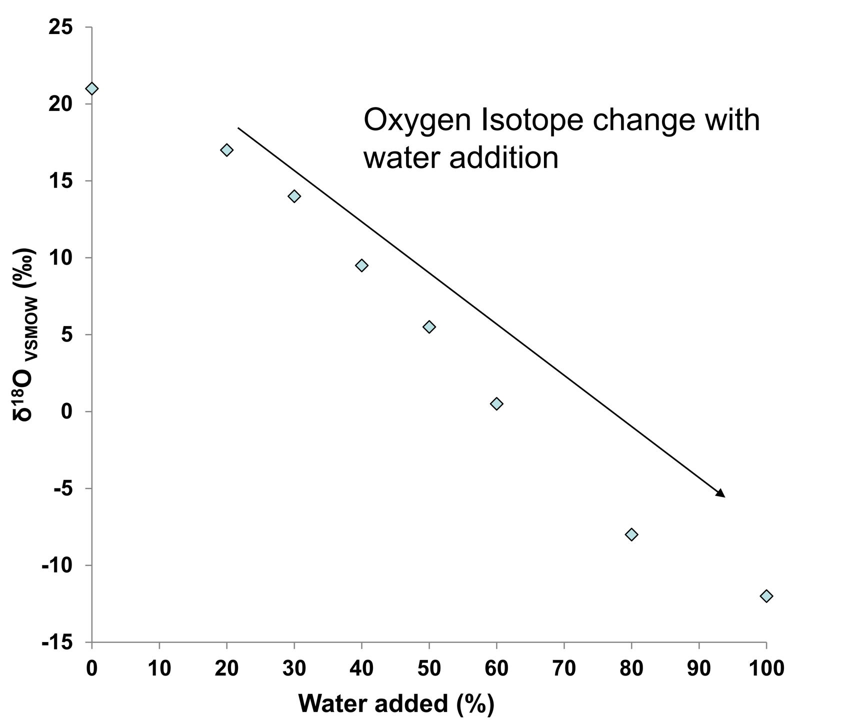
Stable Isotope	What is the biogeochemical interpretation?	What is an example of food fraud interpretation?	What products can be affected?
Carbon	Photosynthesis (C3, C4 and CAM pathways)	Adulteration (e.g. sweetening with cheap sugar)	Honey, liquor, wine, olive oil, butter
Nitrogen	Fertilizer assimilation by plants	Mislabeling (differentiate organic and non-organic)	Vegetables, animal meat
Sulfur	Local soil conditions, proximity to shoreline	Origin of product	Vegetables, animal meat, honey
Oxygen	Principally related to local-regional rainfall and hence geographical area	Watering of beverages, place of origin of product	Coffee, wine, liquor, water, sugar, animal meat
Hydrogen	Related to local-regional rainfall and hence geographical area	Watering of beverages, origin of product	Coffee, wine, liquor, water, sugar, animal meat

IS YOUR WINE WATERED DOWN?

The most common type of fraud for wine is adulteration, meaning the addition of cheaper products to the original wine, such as fruit juices, water and sweeteners, which are not related to the grapes or fermentation process from which the wine was originally produced.[7,8] Adulterated wine is then labeled as the original product, generally an expensive brand, and sold on the market as if the original product. It also relates to the re-labeling of wines, by adding the label of a more expensive wine to a bottle of a different, cheaper version and selling it on the market as an original product.

Wine adulteration by water addition is detected by oxygen isotopes (Figure 1) using a Thermo Scientific™ GasBench II System interfaced with a Thermo Scientific™ DELTA V™ Isotope Ratio Mass Spectrometer. A genuine red wine sample was measured initially to provide a baseline before the sample was sequentially adulterated by adding water. The watering technique is be used to reduce alcohol content and increase profits by producing more wine for sale, reducing tax and customs duty on exported products in certain countries.

Figure 1. Oxygen isotope fingerprints detect watering of wine.



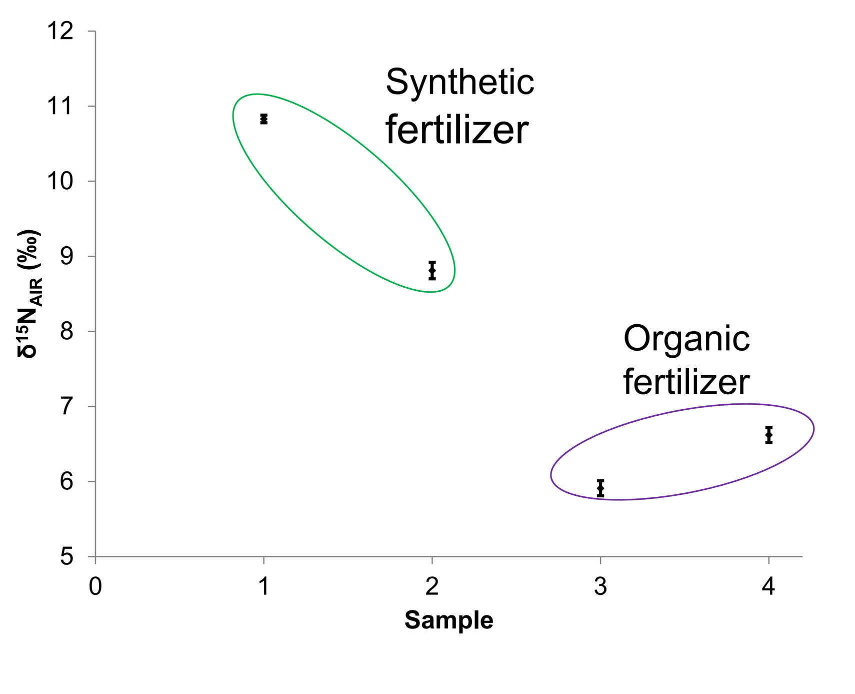
ARE YOUR VEGETABLES GROWN USING ORGANIC FARMING?

Supermarkets and market places stock vegetables that are labeled as "organic" because they are believed to be healthier and safer than their non-organic equivalents.[9,10] Vegetables grown using organic farming methods are sold on the market for higher prices, which relates to the higher costs of production and certification for products grown as organic.[1,2,9] This has led to mislabeled vegetables appearing for sale on the market, with those grown with synthetic fertilizers labeled as organic. The consumer question is: are my vegetables really organic grown?

Organic vegetables are grown using organic fertilizers, such as peat, sewage sludge and animal manure, and tend to have nitrogen isotope values between +10‰ to +20‰.[2,10] Vegetables that are not labeled organic are grown using synthetic fertilizers, such as potash and ammonia and tend to have nitrogen isotope values of +3‰ to +5‰.[2,10] This provides a framework within which to distinguish vegetables grown using organic or synthetic fertilizers thanks to an isotope discrimination due to ammonia volatilization, denitrification, nitrification and other N transformation.[2,7]

The nitrogen isotope fingerprint of the tomatoes, measured using an Elemental Analyzer Isotope Ratio Mass Spectrometer (EA-IRMS), such as the Thermo Scientific™ EA IsoLink™ IRMS System, show a clear difference between tomatoes grown using organic fertilizers and synthetic fertilizers (Figure 2).

Figure 2. Differentiating organic grown vegetables using nitrogen isotope fingerprints.



IS HONEY NATURALLY SWEET?

Honey consumption is high due to its natural properties, nutritional value and antioxidant qualities.[3,13] Consequently, market prices for honey vary providing opportunity for economically motivated adulteration. Sugars in honey are mainly glucose and fructose, produced by honeybees from flower nectar of C3 plants: the carbon isotope fingerprint of natural honey is -22‰ to -32‰.

Honey adulteration by adding high fructose corn syrup, glucose or saccharose syrup derived from beet or cane (C4 plant types) is known: the carbon isotope fingerprint of these sugars is -8‰ to -16‰, which differs from that of natural honey.[3,13]
Detection is by EA-IRMS, using the carbon isotope fingerprint of all sugar. Where this is not conclusive, Liquid Chromatography Isotope Ratio Mass Spectrometry, using the Thermo Scientific™ LC IsoLink™ IRMS System, measures carbon isotope fingerprint of fructose and glucose separately.

Table 2 summarizes EA- and LC-IRMS honey analysis and conclusively identifies 4 adulterated honey products (in bold), combining carbon isotope values, fru/glu ratios and C4 sugar amount.

Table 2. Honey adulteration using carbon isotopes.

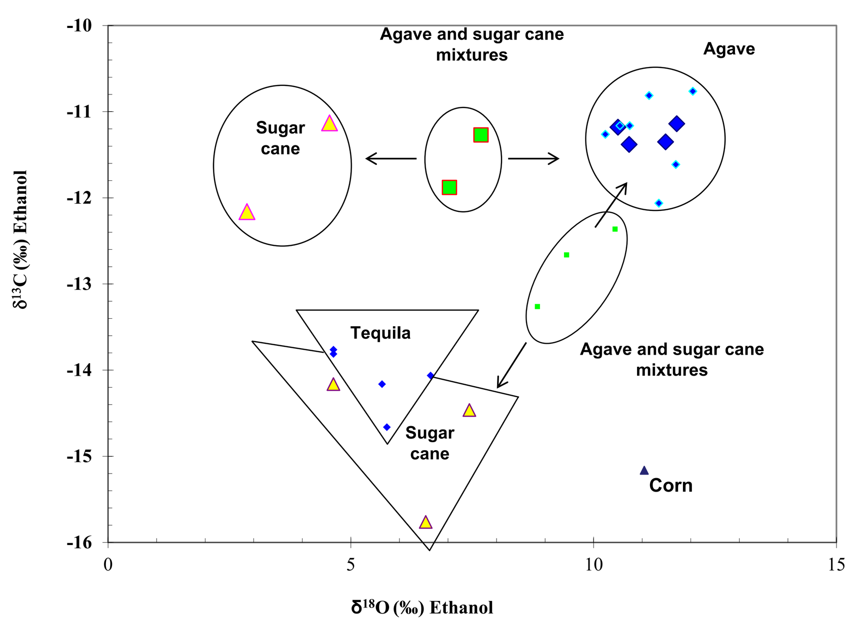
Honey	Glu-cose ($\delta^{13}C$, ‰)	Fruc-tose ($\delta^{13}C$, ‰)	All sugar ($\delta^{13}C$, ‰)	Fru/Glu ratio	C4 sugar %	Adulte-rated?
1	**-23.2**	**-22.9**	**-21.8**	1.07	**16.7**	**Yes**
2	**-11.2**	**-13.9**	**-11.9**	**0.65**	n.a	**Yes**
3	-24.9	-24.9	-24.8	1.42	0.0	No
4	-26.5	-26.4	-25.4	0.97	0.0	No
5	-26.1	-26.0	-25.8	**4.53**	1.9	**Yes**
6	-25.0	-25.3	-24.3	1.62	0.0	No
7	-25.2	-25.1	-24.2	1.16	3.4	No
8	**-25.1**	**-26.4**	-24.8	2.17	1.5	**Yes**

IS YOUR TEQUILA AUTHENTIC?

The *agave tequilana* plant is a native plant of the Jalisco region, Mexico and is an important economic product due to its use as a base ingredient in Tequila. The *A. tequilana* plant is used because of its high sugar (mainly fructose) content and is photosynthetically part of the C4 plant group, meaning it has a carbon isotope fingerprint of -8‰ to -14‰. During plant growth, the biosynthesis of organic molecules requires water that comes from rainfall (evaporation, sublimation, condensation and precipitation in the water cycle). Tequila is produced exclusively in 5 areas of Mexico: Jalisco, Nayarit, Michoacan, Guanajuato and Tamaulipas, meaning that the oxygen isotope fingerprint of the *A. tequilana* plant is given by water from rainfall in those regions and therefore provides a geographical origin tool.

In Figure 3, we show an example of carbon and oxygen isotope fingerprints of tequila, the *agave tequilana* plant and sugar measured using Gas Chromatography Isotope Ratio Mass Spectrometry, such as the Thermo Scientific™ GC IsoLink™ II IRMS System. The isotope fingerprint plot of carbon and oxygen data allows the differentiation of commercial tequila and tequila that may be adulterated due to sugar addition but labelled as a pure tequila.

Figure 3. Carbon and oxygen isotope fingerprints detect mislabeled and adulterated tequila.



ISOTOPE FINGERPRINTS IN FOOD AND BEVERAGE PRODUCTS

Food and beverage products have a unique chemical signature from the biogeochemical processes that occurred during the formation of their base ingredients. These biogeochemical processes can be detected by measuring stable isotopes : this is what we call the **isotope fingerprint of food and beverage products**.
These isotope fingerprints can provide conclusive information on the origin and the authenticity of a product.
By using isotope fingerprints, laboratories can:
- Trace unique answers on origin and authenticity.
- Extend their analytical capabilities.
- Work with an integrated analytical solution, driven by a single software for automated high sample throughput.

REFERENCES

1. Sturm, M., Kacjan-Marsic, N., Lojen, S. J. Sci. Food. Agric. 91. (2011), 262-267.
2. Ehleringer, J.R., Chesson, L.A., Valensuela, L.O. Elements. 11. (2015), 259-264.
3. Schellenberg, A., et al. Food Chemistry. 121. (2010), 770-777.
4. Camin, F., et al. Anal Bioanal Chem. 389. (2007), 309-320.
5. Bowen, G. J., Et al., Rap. Comm. Mass. Spec. 19. (2005), 3442-3450.
6. Greule, M., et al. Eur. Food. Res. Technol. 231. (2010), 933-941.
7. Calderone, G., Reniero, F., Guillou, C. Rap. Comm. Mass. Spec. 20. (2006), 937-940.
8. Cabanero, A.I., Recio, J.L., Ruperez, M. Rap. Comm. Mass. Spec. 22. (2008), 3111-3118.
9. Laursen, K.H., et al. Food Chem. 141. (2013), 2812-2820.
10. Schmidt, H.L., et al. Isotopes Environ. Health Stud. 3. (2005), 233-228.
11. Rhodes, C.N., Heaton, K., Goodall, I., Brereton, P.A. Food Chemistry. 114. (2009), 697-701.
12. Camin, F., et al. Food Chemistry. 118. (2010), 901-909.
13. Foldhazzi, G. Acta Alimentaria. 23. (1994), 299-311.

INVESTIGATE MORE

Visit http://www.thermofisher.com/IsotopeFingerprints and learn more about food fraud detection by isotope fingerprints by reading more application reports:

- **AB30477**: GC-IRMS Detecting purity and adulteration of tequila with isotope fingerprints
- **AB30399**: EA-IRMS Detecting organic grown vegetables
- **AB30427**: EA-IRMS Tracing the geographical origin of green coffee beans using isotope fingerprints
- **AN30147**: EA-IRMS Analysis of Ethanol in Wine.
- **AB30424**: EA-IRMS Testing sugar package label claims using carbon isotope fingerprints
- **AN30048**: GB-IRMS Isotope analysis in Water, Fruit Juice and Wine
- **AN300024**: LC-IRMS $\delta^{13}C$ of Carbohydrates in Honey
- **AN30276**: EA-IRMS Detection of squalane from animal and vegetable sources

TRADEMARKS

PO30397

ThermoFisher SCIENTIFIC