Food and Beverage Fraud Prevention Using Stable Isotope Fingerprints

Christopher Brodie, Oliver Kracht, Dieter Juchelka, Jens Radke, Andreas Hilkert, Thermo Fisher Scientific, Hanna-Kunath Str. 11, Bremen, 28199, 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 safety, 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 food and beverage fraud.

Detecting food and beverage fraud can be achieved using stable isotope measurements because stable isotopes 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 and unique technique in food and beverage fraud prevention and food safety.

We show data demonstrating how stable isotope fingerprints offer conclusive answers on questions associated with origin, adulteration and correct labeling of food and beverage products.

INTRODUCTION

The origin, meaning where a product comes from, and authenticity, meaning whether a product has not undergone change and if the product is correctly labeled, can be routinely determined on food and beverage products using stable isotopes.[1-6] 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 safety, 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.

Using **the isotope fingerprint of food and beverage products** is a reliable technique in food and beverage fraud prevention and safety.[1-12] 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 isotope data can subsequently be interpreted to determine the origin, correct-labeling and trace adulteration of food and beverage products, as summarized in Table 1.

Table 1. Stable isotopes and their interpretation in food and beverage origin and authenticity.

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; Oliver 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

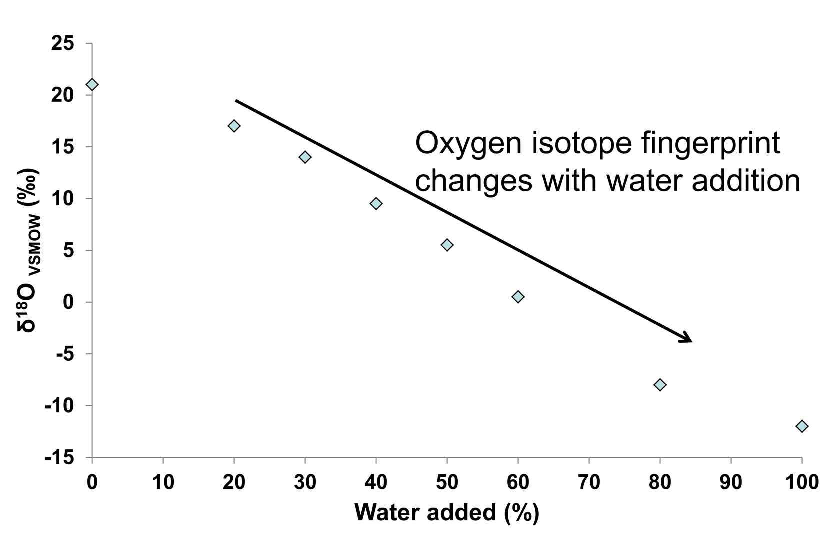
This poster demonstrates how stable isotope fingerprints of carbon, nitrogen, sulfur, oxygen and hydrogen are used to detect the origin and authenticity of food and beverage products conclusively.

IS YOUR WINE WATERED DOWN?

The most common type of fraud that relates to 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.

In Figure 1, we show an example of wine adulteration by the addition of water detected by oxygen isotopes 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 may be used to reduce alcohol content and increase profits by producing more bottles for sale and thus reduce tax and customs duty on exported products in certain countries.

Figure 1. Oxygen isotope fingerprints detect watering of wine.



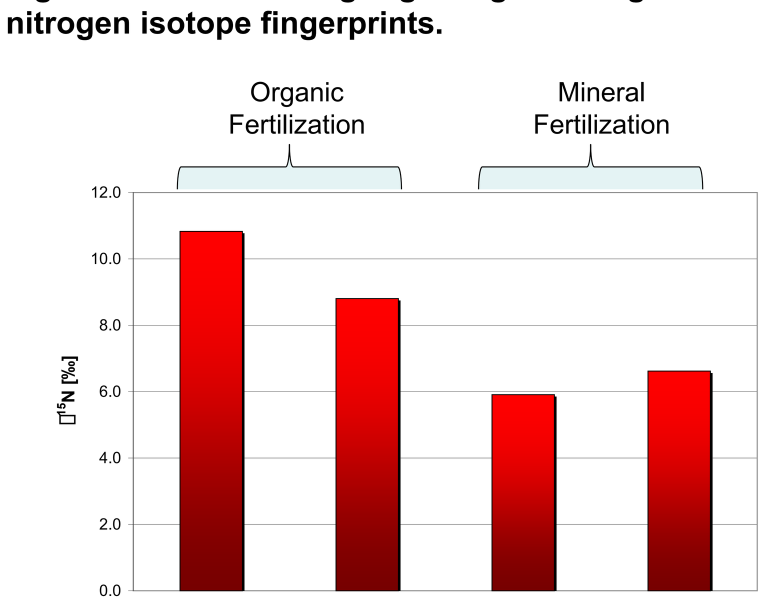
ARE YOUR VEGETABLES GROWN USING ORGANIC FARMING?

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 of the product as organic grown.[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 processes prior to plant uptake.[2,7]

In Figure 2, we show an example of tomatoes that have been grown using organic and inorganic fertilizers. 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. Differentiating organic grown vegetables using nitrogen isotope fingerprints.



IS HONEY NATURALLY SWEET?

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

Adulteration of natural honey 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 such sugars is -8% to -16%, which differs from that of natural honey. Adding C4 sugar to natural honey increases the detectable amount.[3,13]

Honey adulteration is detected by EA-IRMS, using the carbon isotope fingerprint of all sugar. However, where this is not conclusive, Liquid Chromatography Isotope Ratio Mass Spectrometry, using the Thermo Scientific™ LC IsoLink™ Interface for LC-IRMS, measures the carbon isotope fingerprint of fructose and glucose separately.

Table 2 summarizes the analysis of honey using EA- and LC-IRMS, identifying the 4 adulterated honey products from 8 honey samples (in bold). The combination of more negative carbon isotope values, fru/glu ratios and C4 sugar amount conclusively identify adulterated honey.

Table 2. Carbon isotope fingerprints detect honey adulteration.

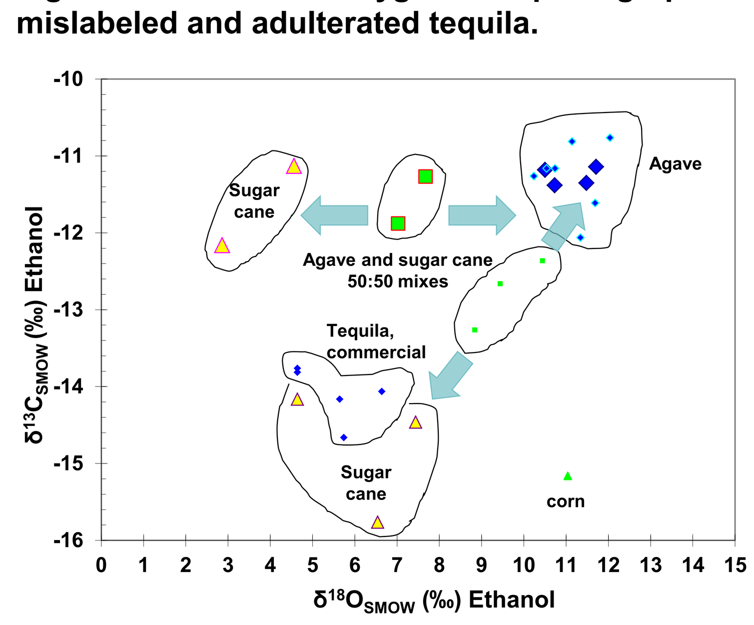
Honey	Glucose ($\delta^{13}C$, ‰)	Fructose ($\delta^{13}C$, ‰)	All sugar ($\delta^{13}C$, ‰)	Fru/Glu ratio	C4 sugar %	Adulterated?
1	**-23.2**	**-22.9**	**-21.8**	1.07	**16.7**	**Yes**
2	**-11.2**	**-13.9**	**-11.9**	**0.65**	n.a	**Yes**
3	-24.9	-24.9	-24.8	1.42	0.0	No
4	-26.5	-26.4	-25.4	0.97	0.0	No
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 native plant of the Jalisco region in Mexico and forms an important economic product due to its use as a base ingredient in the popular alcoholic beverage Tequila. The *agave 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 well defined carbon isotope fingerprint of -8% to -14%. During plant growth, the biosynthesis of organic molecules in plants requires water that comes principally 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 hydrogen and oxygen isotope fingerprint of *the agave tequilana* plant is primarily given by the water from rainfall in those regions and therefore provides a geographical tool for origin.

In Figure 3, we show an example of carbon and oxygen isotope measurements on tequila, measured using Gas Chromatography Isotope Ratio Mass Spectrometry, such as the Thermo Scientific™ GC IsoLink II™ Interface for GC-IRMS.

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



The data in Figure 3 shows pure tequila, tequila adulterated by the addition of sugar addition for a secondary source other than the *agave tequilana* plant and water from a source other than that of the 5 local regions in Mexico. The two dimensional isotope fingerprint of ethanol based on carbon and oxygen data allows the differentiation of authentic and commercial Tequila.

SUMMARY: ISOTOPE FINGERPRINTS IN FOOD AND BEVERAGE PRODUCTS

Food and beverage products carry a unique chemical signature that relates to the biogeochemical processes that happened during the formation process of the materials that are present in the final product. These biogeochemical processes leave a chemical fingerprint that can be routinely detected in food and beverage products by measuring the stable isotope values of the products: this is what we call the **isotope fingerprint of food and beverage products**.

These stable isotope values can be interpreted to provide conclusive information on the origin of a product, meaning you can identify where in the world or within a country a product has come from, and the authenticity of a product, which means understanding if a product has been changed from its raw composition to something else.

By using isotope fingerprints to detect food and beverage fraud, laboratories can:

- trace unique answers about 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), 3442-2450.
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.

LEARN MORE

Visit www.thermofisher.com and learn more about food fraud detection by isotope fingerprinting by reading our application reports:

- AN30177: EA-IRMS Detection of Honey Adulteration.
- AN30147: EA-IRMS Analysis of Ethanol in Wine.
- AN30048: GB-IRMS Isotope analysis in Water, Fruit Juice and Wine
- AN30052: GC-IRMS Food labeling and FAME analysis
- AN30024: LC-IRMS $\delta^{13}C$ of Carbohydrates in Honey
- AN30276: EA-IRMS Labelling of cosmetic products

TRADEMARKS

PO30397 - Presented at the Food Integrity 2017 Conference, Parma, IT. 10-11th May 2017