Tracing the geographical origin of green and roasted coffee with isotope fingerprints

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ABSTRACT
Coffee is one of the most popular beverages worldwide, sourced from different geographical regions and exported through a commercial chain that usually involves several intermediaries. To ensure that coffee beans come from labelled locations, laboratories need an analytical solution, enabling to discriminate geographical origin, with a special emphasis on the country of origin.

Roasted and green coffee beans have a fingerprint, a unique chemical signature that allows them to be identified: isotope fingerprints of carbon, nitrogen, sulfur, hydrogen and oxygen have been reliably used for origin, authenticity and product label claim verification.

In this poster, we report isotope measurements from green and roasted coffee beans measured using the Thermo Scientific™ EA IsoLink™ IRMS System. These data illustrate how isotope fingerprints can determine the origin of coffee beans. Consequently, it is evident that isotope fingerprints can support legislation on food integrity and labeling (EC Reg. No. 1169/2011) and protect consumers and brands.

INTRODUCTION
Complexities in the supply chain from the production site through to the consumer have presented significant, and at times relatively easy, opportunity for economically motivated fraudulent activities to occur but be undetected. This includes product mislabeling, in terms of country of origin declarations and also product adulteration, meaning replacing a higher quality, original ingredient with one of lesser quality or extending product by adding an adulterant.

Consequently, there is an increase in retailer and consumer demand to see proof that food products are what they are claimed to be, including origin and ingredient verification. Investigating food origin and authenticity in laboratories is one of the key ways of monitoring and enforcing legislation for food integrity and labeling (EC Council Regulation No 1169/2011) and protecting consumers and brands.

Coffee is one of the most popular beverages worldwide. Coffee beans from different geographical regions are imported through a commercial chain that usually involves several intermediaries. To ensure that coffee beans come from their labelled locations, laboratories need an analytical tool for geographical origin discrimination with a special emphasis on the country of origin. Coffee beans have a unique fingerprint, a unique chemical signature that allows them to be identified: isotope fingerprints have been reliably used for origin, authenticity and product label claim verification.

ISOTOPE CONFIGURATION
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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, cereals, vegetables, wine, liquor and water, and so forth, using isotope ratio mass spectrometry techniques. These stable isotope data can subsequently be interpreted to determine the origin, correct labelling 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.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Origin</th>
<th>Authenticity</th>
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<tbody>
<tr>
<td>Carbon</td>
<td>Phytoplankton, (C3, C4 and CAM pathways)</td>
<td>Adulteration (e.g. sweetening with sugar)</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>Fertilizer assimilation by plants</td>
<td>Mislabelling (differentiation organic and non-organic)</td>
</tr>
<tr>
<td>Sulfur</td>
<td>Local soil conditions, proximity to animal activity</td>
<td>Origin of product</td>
</tr>
<tr>
<td>Oxygen</td>
<td>Local-regional rainfall and geographical area</td>
<td>Watering of beverages, place of origin of product</td>
</tr>
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<td>Hydrogen</td>
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HYDROGEN AND OXYGEN ISOTOPE FINGERPRINTS IN COFFEE
The hydrogen and oxygen isotope fingerprints in coffee beans can be used to differentiate their geographical origin (Figure 2). The CO2 in the atmosphere, from which coffee beans are cultivated, carry a local-regional fingerprint primarily derived from the hydrological cycle (Figure 3), which is associated with local-regional rainfall[1]. This can be influenced by cultivation practices and produce local geographical characteristics of the local area, altitude and proximity to the shoreline[6].

The hydrogen and oxygen isotope fingerprints change in rainwater as you move further inland from the shoreline and with increasing altitude because the heavier isotopes are the first to be released from the clouds[47]. This effect can be tracked in the oxygen and hydrogen isotope fingerprints of plants and their fruits (e.g. green coffee beans)[18]. For example, relatively high 8° and 17° values of green coffee beans from Africa are likely the result of strong evaporation and condensation processes.

Figure 3. Changes in hydrogen and oxygen isotopes within the water cycle.

IMPROVING FOOD 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, cereals, vegetables, wine, liquor and water, and so forth, using isotope ratio mass spectrometry techniques. These stable isotope data can subsequently be interpreted to determine the origin, correct labelling and trace adulteration of food and beverage products, as summarized in Table 1.

Stable isotopes | From the atmosphere | Authenticity |
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ANALYTICAL CONFIGURATION
For hydrogen and oxygen analysis, around 800 μg of dried, cryo-milled green coffee beans were weighed into the silver cups and introduced into the pyrolysis reactor of the EA IsoLink™ IRMS System from the Thermo Scientific™ MAT Plus AutoSampler (Figure 1).

The reactor is held at 1450 °C and consists of an outer reactor with a cavity where the silver cups are placed. The temperature is controlled by the cavity pressure. The produced H2 and CO gases were separated using a 1 x 5A molecular sieve packed GC column held isothermally at 40 °C. After separation, the gases were transferred to a Thermo Scientific™ Delta V Plus Isotope Ratio MS via the Thermo Scientific™ ConFi VeN™ Universal Interface. For our samples, the sample weights correspond to 51-177 μg of H and 201-535 μg of O across all samples analyzed. Hydrogen and oxygen isotope ratios were calibrated against SLAP and VSMOW. Analysis time is less than 5 minutes, using 1 liter of helium per sample.

Figure 1. EA IsoLink IRMS System configuration.

WHERE DOES MY COFFEE COME FROM?

Nineteen unique green coffee beans and twenty unique roasted coffee beans from 12 countries, including Asia, Africa and Central and South America, were analysed to determine their geographical origin.

Figure 4 shows hydrogen and oxygen isotope fingerprints of green coffee beans and shows that they can be clearly differentiated from one another (Figure 5). In addition, Figure 5 shows hydrogen and oxygen isotope fingerprints of roasted coffee beans and illustrates how they can be differentiated at the continent scale.

Figure 4. Hydrogen and oxygen isotope fingerprints of green coffee beans from Africa (blue), Asia (brown) and central and South America (purple).

Figure 5. Hydrogen and oxygen isotope fingerprints of roasted coffee beans from Africa (blue), Asia (brown) and central and South America (purple).

CONCLUSIONS
Hydrogen and oxygen isotope fingerprints are powerful tools to determine the country of origin of coffee beans and therefore assessing product label claims. Verifying the correct labelling of food products is important for consumer confidence, brand reputation and producer revenue alongside reducing fraudulent activities. To achieve this, laboratories require a robust, automated analytical technique that provides unique and conclusive answers that enable to verify the authenticity, origin and correct labeling of food products. This can be achieved analyzing the oxygen and hydrogen isotope fingerprints with the EA IsoLink IRMS System.

By using the EA IsoLink IRMS System, laboratories gain:
- The ability to detect origin of food and beverages products (e.g. coffee beans) using isotope fingerprints;
- High throughput and low cost sample analysis;
- Complete automation, reducing user intensity;
- Automation capability to meet changing analytical requirements.

REFERENCES

INVESTIGATE MORE
Visit http://www.thermoscientific.com/tracing/fingerprints and learn more about food fraud detection by isotope fingerprints by reading more application reports:
- AB101047: GC-IRMS Detecting purity and adulteration of hulquas with isotope fingerprints
- AB103399: EA-IRMS Detecting organic vegetables
- AB103418: EA-IRMS Tracing the geographical origin of isotope fingerprints
- AB103427: EA-IRMS Tracing the geographical origin of green coffee beans using isotope fingerprints
- AB102177: EA-IRMS Detection of Honey Adulteration
- AB101474: EA-IRMS Analysis of Ethanol in Wine
- AB101424: EA-IRMS Testing sugar package label claims using carbon isotope fingerprints
- AB100406: GB-IRMS isotope analysis in Water, Fruit Juice and Wine
- AB105191: GC-IRMS Food labeling and PAME analysis
- AB100234: LC-IRMS 51C of Carbohydrates in Honey
- AB100054: GC-IRMS Detection of squelance from animal and vegetable sources

TRADEMARKS
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