EA-IRMS: Tracing geographical origin of Argan oil using carbon and oxygen isotope fingerprints

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Abstract

Here we demonstrate how the geographical origin of Argan oil can be traced using carbon and oxygen isotope fingerprints.

47 Argan oil samples were analyzed for authenticity control in collaboration with CNESTEN.

Introduction

The increasing demand for Argan oil world-wide is a result of its beneficial properties for use in the pharmaceutical, food and cosmetics industries, making this oil one of the key ingredients in cosmetic oils, shampoos, soaps, moisturizers and many other products.

Argan oil is extracted from Argan tree fruit seeds in a labor-intensive hand-made process. Argan tree (Argania spinosa) is an endemic species from south-western Morocco. Because of this, Argan oil has received a protected geographical indication status (PGI-MA-906), which assures that both local producers and consumers are protected. Such high quality and highly consumed products are also the target of economically motivated fraud. This means replacing a higher quality, original ingredient with one of lesser quality, extending a product by adding an adulterant and product mislabeling, including misrepresenting product origin and ingredients. Argan oil production has tremendous environmental, social and economic importance for Morocco, and it is necessary to verify authenticity and provenance of this valuable product to ensure its reputation protected and promoted.

To ensure authenticity of Argan oil and derived products, laboratories need an analytical tool for geographical origin discrimination with a special emphasis on the country of origin. Argan oil has an inherent isotopic fingerprint, a unique chemical signature that allows it to be identified.

Stable isotopes of carbon, nitrogen, sulfur, oxygen and hydrogen can be measured from food and beverage products, such as oil, honey, cheese, animal meat, milk powder, vegetables, wine, liquor, water and so forth, using isotope ratio mass spectrometry techniques. This stable isotope data can be interpreted to verify the origin, correct labelling and 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

Carbon and oxygen isotope fingerprints of Argan oil established by Elemental Analysis Isotope Ratio Mass Spectrometry (EA-IRMS) can be used to identify product's origin.[1]

Carbon and oxygen isotope fingerprints of Argan oil

The carbon and oxygen isotope fingerprints ($\delta^{13}C$ and $\delta^{18}O$) in Argan oil can be used to differentiate its geographical origin. Argan tree, and plants in general, carry a local-regional fingerprint primarily derived from the hydrological cycle, which is associated with local-regional rainfall, but can also be influenced by cultivation practices, soil processes and geological characteristics of the local area, altitude and proximity to the shoreline.[1]

The carbon isotope fingerprints of plants differ primarily because different plant species use two main alternate photosynthetic pathways for CO_2 assimilation. Also, environmental factors such as relative humidity, temperature, and amount of precipitation have an influence on plants' $\delta^{13}C$ and $\delta^{18}O$ values.[2]

The oxygen (and hydrogen) isotope fingerprints change in rainfall as it moves further inland from the shoreline and with increasing altitude because the heavier isotopes are preferentially released from the clouds as precipitation.[3] These effects can be additionally influenced by temperature and amount of rainfall, and biosynthetic pathways including the isotopic exchange between organic molecules and plant water in plant organs.[2]

Material and methods

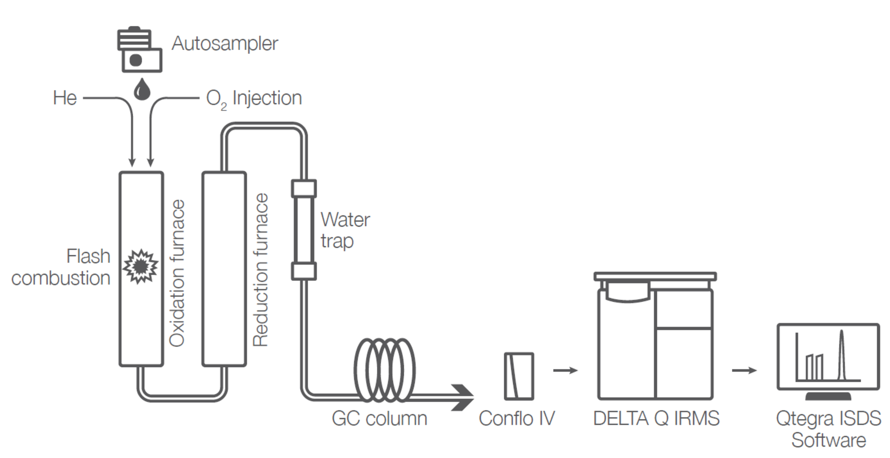
Analytical configuration

Samples were analyzed using the Thermo Scientific™ EA IsoLink™ IRMS System (Figure 1).

Figure 1. Thermo Scientific EA IsoLink IRMS System

The EA IsoLink IRMS System is designed to take an entire sample and convert it to simple gases that are separated on a column and measured in IRMS for their isotopic composition (Figure 2). This concept allows for burning the sample in oxygen to allow the detection of carbon, nitrogen and sulfur isotope fingerprints or breaking the sample down by thermal conversion at very high temperature to allow the detection of oxygen and hydrogen isotope fingerprints.

Figure 2. EA IsoLink IRMS System workflow



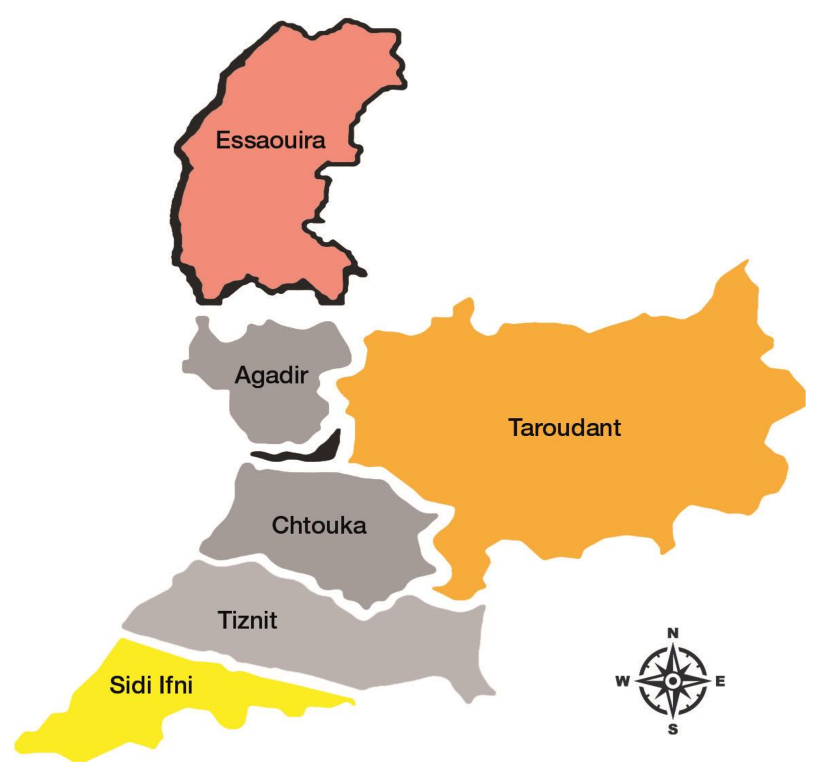
For carbon analysis, 0.3 mg of Argan oil was weighed into tin capsules and introduced into the combustion reactor from the Thermo Scientific™ MAS Plus Autosampler The CO_2 gas produced was then analyzed by Isotope Ratio Mass Spectrometry. Analysis can be achieved in 400 seconds.

For oxygen analysis, 0.6 uL of Argan oil was weighed into the silver capsules and introduced into the pyrolysis reactor of the EA IsoLink IRMS System from the MAS Plus Autosampler. The reactor was maintained at 1450 ˚C and consists of an outer ceramic tube and an inner glassy carbon reactor. After separation, the CO gas produced was analyzed for its oxygen isotope composition by Isotope Ratio Mass Spectrometry. Analysis can be achieved in 530 seconds.

Results

In this study, 47 Argan oil samples from different regions of Morocco (Figure 3) were analyzed for their bulk carbon and oxygen isotope fingerprints. Based on geographical area, different factors are influencing the resultant $\delta^{13}C$ and $\delta^{18}O$ values

Figure 3. Moroccan regions where Argan seed samples were obtained

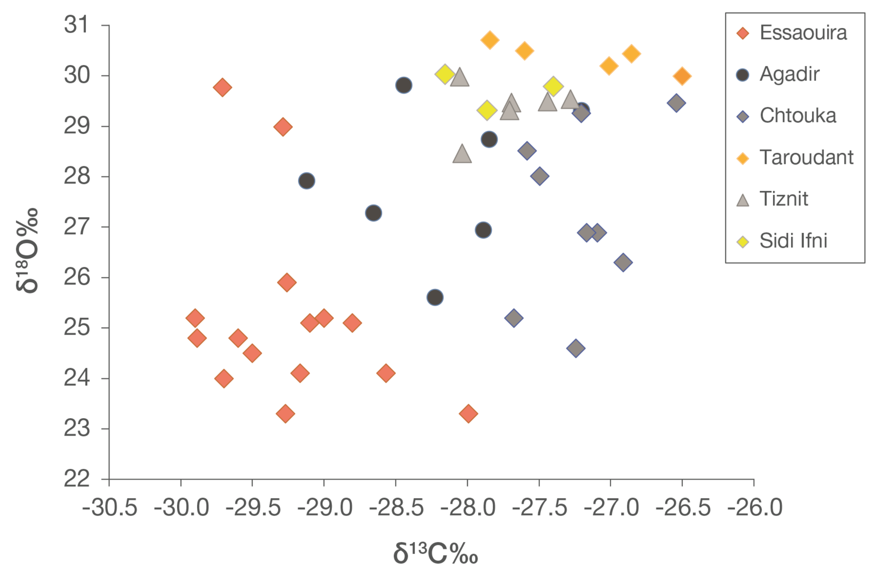


Lower values of mean $\delta^{18}O$ are observed for the Essaouira and Chtouka regions, whereas higher values of mean $\delta^{18}O$ were obtained for Argan oil produced at higher altitude. A very distinct geographical aspect of south-western Morocco is the High Atlas, creating a geographical barrier and specific climatic conditions that are reflected in distinct isotopic values of Argan oil originating from the northern or southern side relative to the High Atlas mountains.

Carbon isotope values are influenced by the relative air humidity, which is influenced by the proximity of a certain region to the shoreline and latitude. Argan oil coming from Essaouira and Agadir region, which are more humid, has more negative $\delta^{13}C$ values. The Taroundant region is characterized by a dry climate and this is reflected in higher enrichment of heavier isotopes.

By combining $\delta^{13}C$ and $\delta^{18}O$ values in a multi-isotope approach (Figure 4), it is possible to better distinguish the origin of Argan oil from different regions of Morocco. The data clustering is showing dependency on shore proximity, temperature, humidity, altitude and latitude.

Figure 4. Combined carbon and oxygen isotope fingerprints of Argan oil samples



Summary

Argan oil production economically supports millions of people in Morocco. In order to protect both producers of this valuable product and consumers, it is important to use analytical techniques providing control of its origin and the authenticity of primary ingredients. Analyzing oxygen and carbon isotope fingerprints of Argan oil allows the differentiation of samples from different regions and creates a framework for using isotopes as a tool for verifying Argan oil provenance. This helps protect producer reputation and consumer confidence by detecting fraudulent activity.

References

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