FOOD ORIGINS, ADULTERATION, AUTHENTICITY

Technology for stable isotope ratio measurement.

PRESENTED BY

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thermo scientific

Topics

- Introduction of IRMS techniques
- Tracking wine adulteration
- Detecting organic grown vegetables
- Tracing the geographical origin of coffee
- Testing sugar package label claims
- Tracing the origin of beef based on diet
- Detection of honey adulteration







Introduction to IRMS technology

Isotope-ratio mass spectrometry (IRMS) is a specialization of mass spectrometry, in which mass spectrometric methods are used to measure the relative abundance of isotopes in each sample.[1]

The isotope-ratio mass spectrometer (IRMS) allows the precise measurement of mixtures of stable isotopes.[2] The analysis of 'stable isotopes' is normally concerned with measuring isotopic variations arising from mass-dependent isotopic fractionation in natural systems.

Element	Minor Isotope	Natural Abundance [%]
Hydrogen	^{2}H (D)	0.01557
Carbon	^{13}C	1.11140
Nitrogen	^{15}N	0.36630
Oxygen	^{18}O	0.20004
Sulfur	^{34}S	4.21500

That‘s where the information is.

Major Isotope

Stable isotopes are chemical isotopes that may or may not be radioactive, but if radioactive, have half lives too long to be measured.

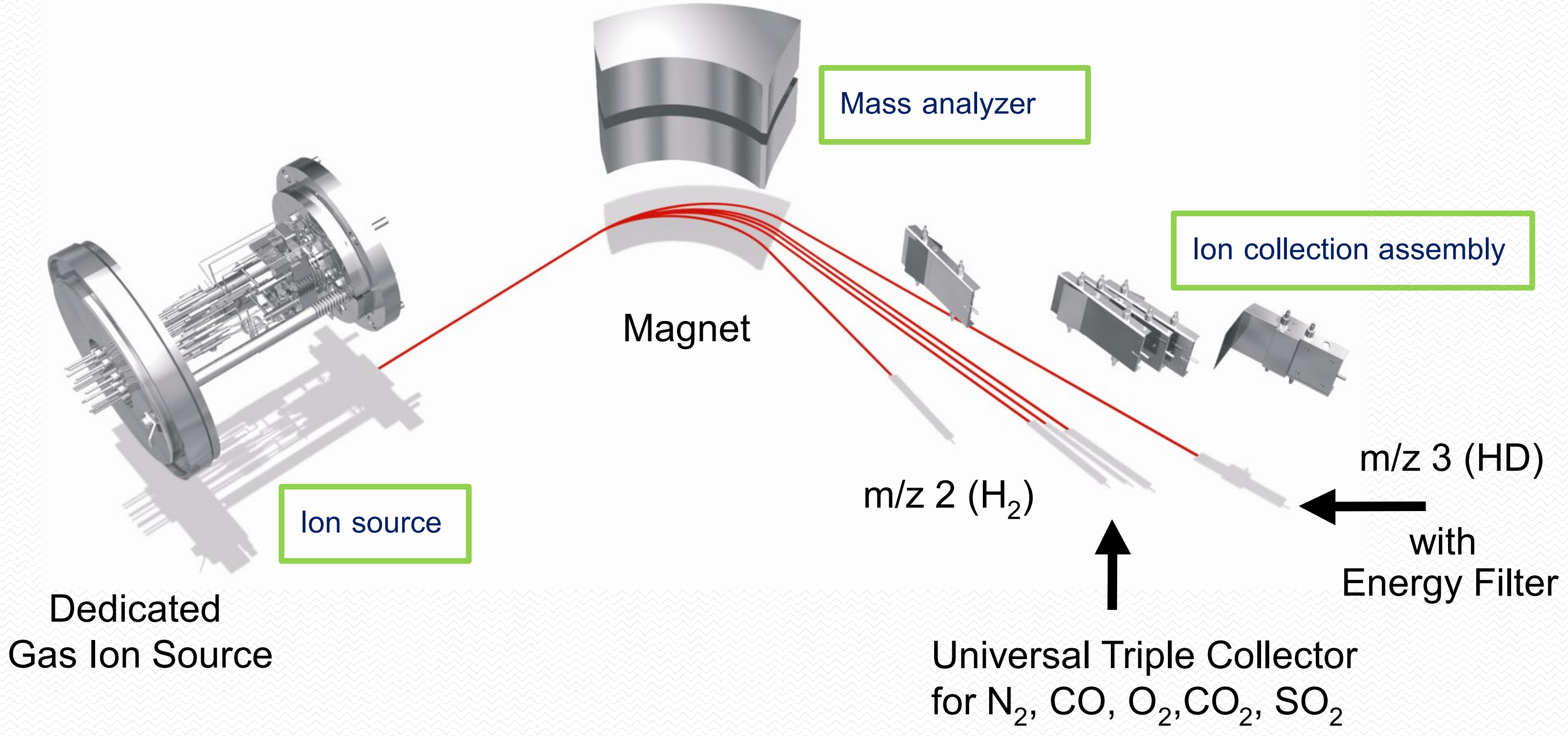
[1] Paul D, Skrzypek G, Fórizs I (2007). "Normalization of measured stable isotopic compositions to isotope reference scales - a review". Rapid Commun. Mass Spectrom. 21 (18): 3006–14.

[2] Townsend, A. (ed) (1995). Encyclopaedia of Analytical Science Encyclopaedia of Analytical Science. London: Academic Press Limited.

Isotope ratio mass spectrometer (IRMS)

The mass spectrometers used for isotopic analysis generally comprise three basic sections; an ion source, a mass analyzer and an ion collection assembly.

DELTA V Analyzer – ^{13}C, ^{15}N, ^{18}O, ^{34}S, ^{2}H



The Isotope Fingerprints and What They Tell Us for Food & Beverage
History can't hide from the Isotope Hunter. Geography, geology and growth conditions of foods, fibers, liquids or stone are embedded in their unique isotope fingerprints. Trace your sample history with the Thermo Scientific™ Isotope Ratio Mass Spectrometry portfolio.
13 Carbon
Interprets: Botanical origin C3, C4 and CAM photosynthesis
Identifies: Adulteration (e.g. sweetening with cheap sugar)
Foods Affected: Honey, liquor, wine, olive oil, butter and flavors
18 Oxygen
Interprets: Local-regional rainfall geographical area
Identifies: Dilution of beverages, and place of product origin
Foods Affected: Coffee, wine, liquor, water, sugar, animal meat and flavors
15 Nitrogen
Interprets: Soil processes, plant fertilizer processes
Identifies: Mislabeling (organic vs. non-organic)
Foods Affected: Fruits, vegetables and animal meat
34 Sulfur
Interprets: Local soil conditions, proximity to shoreline
Identifies: Product origin
Foods Affected: Fruits, vegetables, animal meat and honey
2 Hydrogen
Interprets: Local-regional rainfall geographical area
Identifies: Dilution of beverages, product origin
Foods Affected: Coffee, wine, liquor, water, sugar, animal meat and flavors
Official methods for food and beverage product origin, authenticity and label claims

Reporting Isotope Measurements

The isotopic composition measured relative to that of a standard material whose isotopic composition has been assigned

General element
$$R = \frac{Heavier\ isotope}{Lighter\ isotope}$$
$$\delta Heavier = \frac{R_{sample} - R_{standard}}{R_{standard}} \times 1000$$
units are ‰ or per mil or parts per thousand

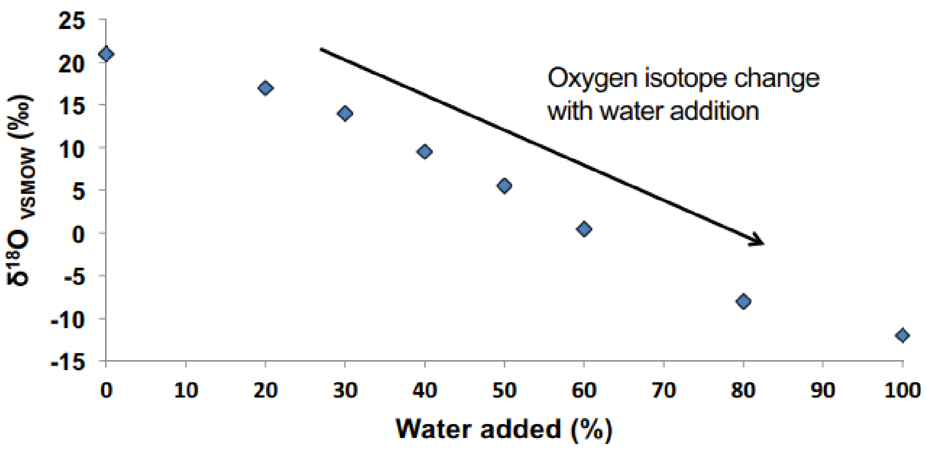
$$\delta^{13}C = \left(\frac{(^{13}C/^{12}C)_{sample}}{(^{13}C/^{12}C)_{standard}} - 1 \right) \times 1000$$

Name	Material	δ^2H	Standard deviation	Reference
VSMOW2	H_2O	0‰	0.3‰	VSMOW
SLAP2	H_2O	-427.5‰	0.3‰	VSMOW
GISP	H_2O	-189.5‰	1.2‰	VSMOW
NBS 22	Oil	-120‰	1‰	VSMOW

Name	Material	$\delta^{13}C$	Standard deviation	Reference
IAEA-603	$CaCO_3$	2.46‰	0.01‰	VPDB
NBS-18	$CaCO_3$	-5.014‰	0.035‰	VPDB
NBS-19	$CaCO_3$	1.95‰	-	VPDB
LSVEC	Li_2CO_3	-46.6‰	0.2‰	VPDB
IAEA-CO-1	Carrara marble	+2.492‰	0.030‰	VPDB
IAEA-CO-8	$CaCO_3$	-5.764‰	0.032‰	VPDB
IAEA-CO-9	$BaCO_3$	-47.321‰	0.057‰	VPDB
NBS 22	Oil	-30.031‰	0.043‰	VPDB

Tracking wine adulteration using isotope fingerprints

The most common type of wine adulteration is 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 that the wine was originally produced from.

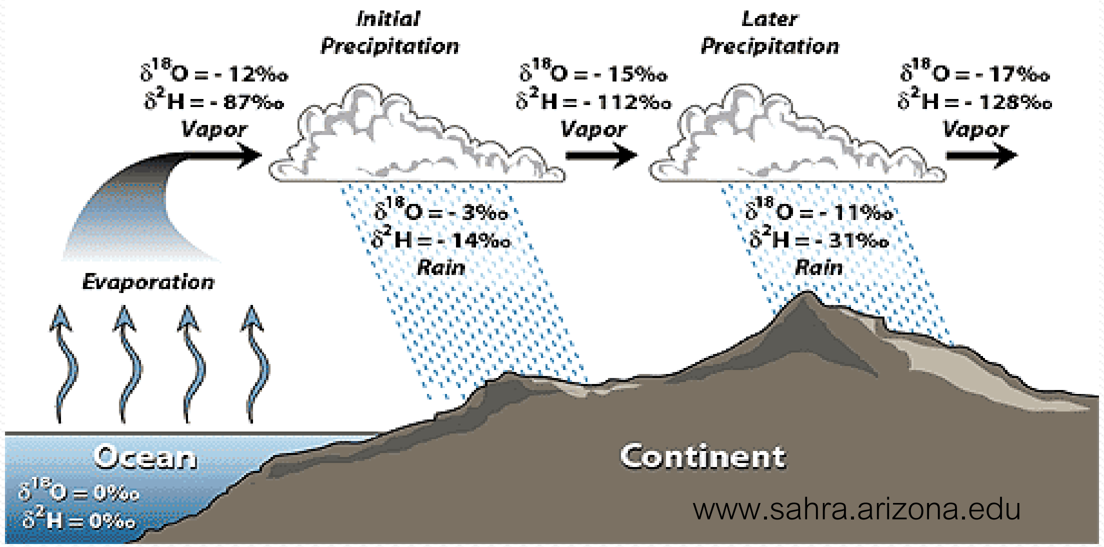


Oxygen isotope fingerprints detect watering of wine.

Oxygen and hydrogen isotope fingerprints can be used to identify the geographical origin of wine. The grapes, from which wine is produced, carry a fingerprint derived from local-regional rainfall.

Tracking wine adulteration using isotope fingerprints

Isotopes in Nature – ^{18}O and ^{2}H in the Water Cycle



The isotopic composition of water samples can be affected by several environmental parameters :

- Seasonality
- Amount of precipitation
- Altitude
- Continentally
- Temperature

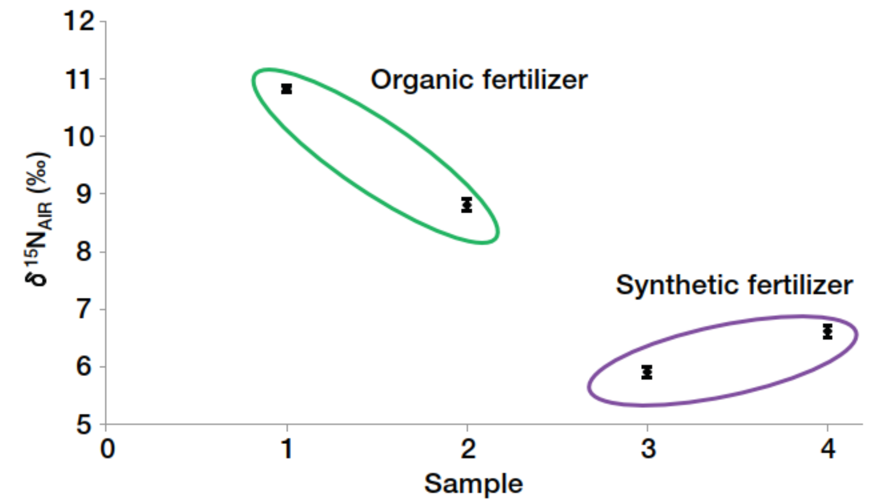
All these parameters can be characterizing the source region of a water sample.

IAEA water standard	$\delta^{18}O$	$\delta^{2}H$
SLAP2 (Standard Light Antarctic Precipitation 2)	-55.50 ‰	-427.5 ‰
GISP (Greenland Ice Sheet Precipitation)	-24.76 ‰	-189.5 ‰
VSMOW2 (Vienna Standard Mean Ocean Water 2)	0 ‰	0 ‰

https://nucleus.iaea.org/rpst/ReferenceProducts/ReferenceMaterials/Stable_Isotopes/2H18O-water-samples/index.htm

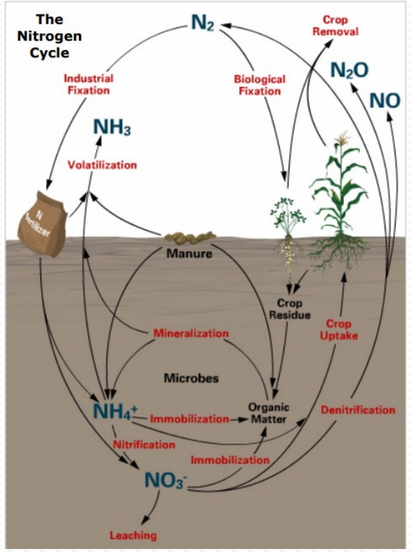
Detecting organic grown vegetables

As organic fruit and vegetables attract a higher price on the market, this can lead to economically motivated fraud through mislabeling produce as "organic" when they have been grown using synthetic fertilizer.



Nitrogen isotope fingerprints detect organic grown tomatoes.

The nitrogen isotope fingerprints of vegetables are used to differentiate whether the fertilizer used for plant growth was organic or synthetic. Vegetables grown using organic fertilizers, such as peat, sewage sludge and animal manure, tend to have nitrogen isotope values between +8‰ to +20‰.Vegetables grown using synthetic fertilizers, such as potash and ammonia, tend to have nitrogen isotope values of +3‰ to +6‰.



Tracing the geographical origin of coffee using isotope fingerprints

Green coffee beans have a 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.

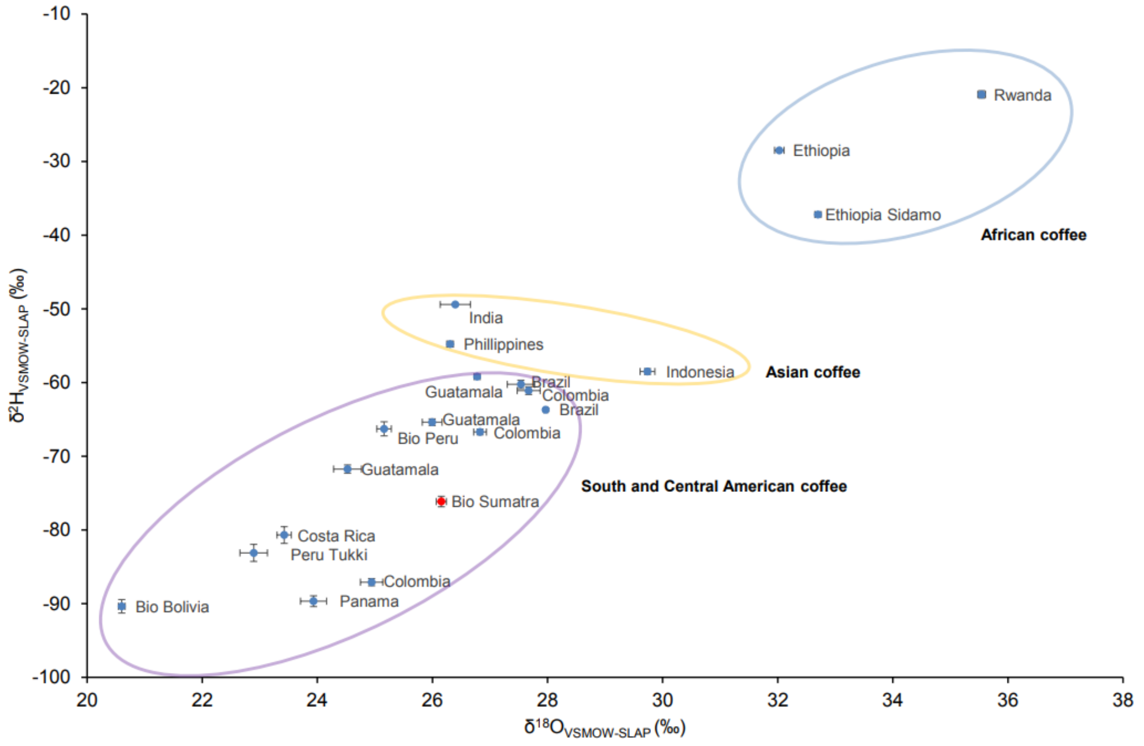


Figure 1. Hydrogen and oxygen isotope fingerprints of roasted coffee beans from Africa (blue), Asia (brown) and central and South America (purple).

The graph shows hydrogen and oxygen isotope fingerprints of coffee beans indicating they can be clearly differentiated at the continent scale.

Additionally, the Bio Sumatra coffee measured is grouped with coffee from South and Central America rather than from Asia (red marker), illustrating that mislabelling can be identified.

Testing sugar package label claims using carbon isotope fingerprints

The refining process for beet is simpler and faster than for cane. Furthermore, beet can grow in a variety of climates beyond tropical.

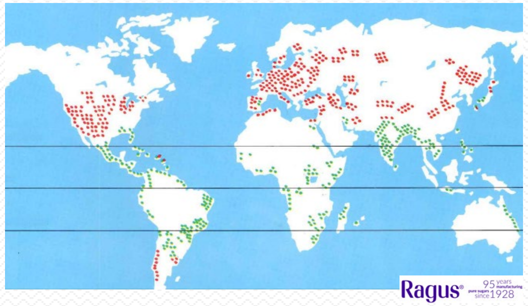
Consequently, beet sugar is cheaper to manufacture and source.

Sugar has a fingerprint, a unique chemical signature that allows it to be identified. The carbon isotope fingerprint ($\delta^{13}C$) of plants are different because of photosynthetic processes and broadly grouped as C3 and C4 plant types.

C3 plants like Beta vulgaris, cultivated as the source of beet sugar, utilize the Calvin photosynthetic pathway to fix CO_2 and incorporate less ^{13}C than other plants.

C4 plants, like Saccharum spp., cultivated as the source of cane sugar, utilize the Hatch-Slack photosynthetic pathway which does not fractionate atmospheric carbon dioxide to the same extent as the Calvin pathway.

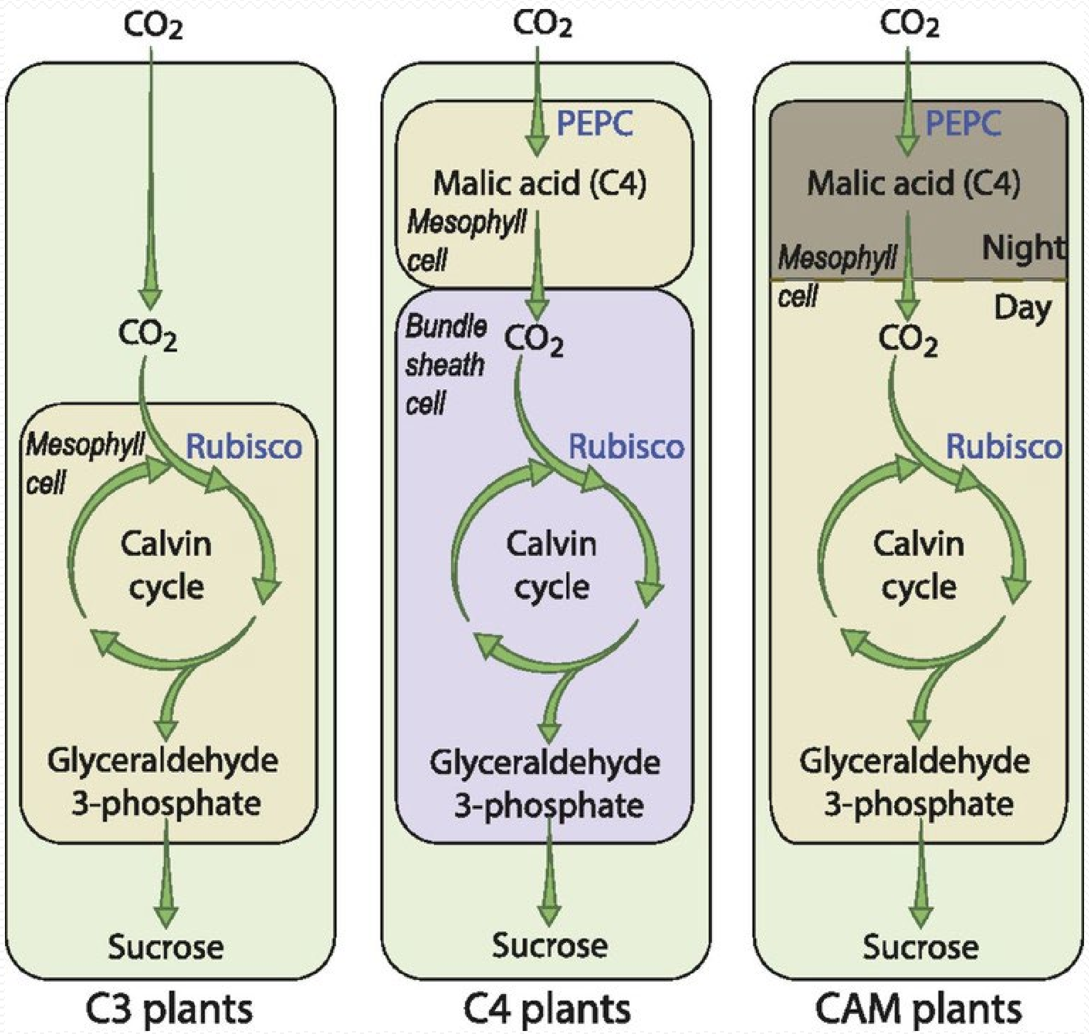
Therefore, C3 plants have a carbon isotope fingerprint between -33‰ to -22‰ and C4 plants have a carbon isotope fingerprint between -16‰ to -8‰.



Carbon isotope fingerprint of sugar.

Sample name	$\delta^{13}C_{VPDB}$ ± 1SD [‰, n=3]	Label claim	Identified by $\delta^{13}C$ as
Australia	-12.59±0.15	Not Stated	Cane sugar
Brazil	-12.21±0.17	Not Stated	Cane sugar
China (Shanghai)	-12.49±0.17	Not Stated	Cane sugar
China (Nan Jing)	-12.63±0.11	Not Stated	Cane sugar
Cuba	-12.46±0.06	Not Stated	Cane sugar
Denmark	-26.69±0.05	**Beet sugar**	**Beet sugar**
Egypt	-13.11±0.02	Not Stated	Cane sugar
Estonia	-13.19±0.08	Not Stated	Cane sugar
France	-12.14±0.12	**Cane sugar**	**Cane sugar**
France	-12.02±0.35	**Cane sugar**	**Cane sugar**
Germany	-26.69±0.08	**Beet sugar**	**Beet sugar**
Italy	-12.22±0.05	**Cane sugar**	**Cane sugar**
Ivory Coast	-12.24±0.19	**Cane sugar**	**Cane sugar**
Lebanon	-27.08±0.02	Not Stated	Beet sugar
Malaysia	-12.21±0.12	Not Stated	Cane sugar
Morocco	-12.58±0.03	Not Stated	Cane sugar
New Zealand	-12.33±0.10	**Cane sugar**	**Cane sugar**
Philippines	-12.95±0.09	**Cane sugar**	**Cane sugar**
Portugal	-12.51±0.04	Not Stated	Cane sugar
Romania	-12.47±0.04	Not Stated	Cane sugar
Senegal	-12.42±0.25	**Cane sugar**	**Cane sugar**
Taiwan	-13.08±0.01	Not Stated	Cane sugar
Thailand	-12.24±0.02	Not Stated	Cane sugar
Turkey	-13.29±0.12	Not Stated	Cane sugar
UAE	-25.02±0.02	Not Stated	Beet sugar
United Kingdom	-12.75±0.04	**Cane sugar**	**Cane sugar**
USA (Hawaii)	-12.41±0.13	**Cane sugar**	**Cane sugar**
USA (San Francisco)	-12.89±0.04	**Cane sugar**	**Cane sugar**

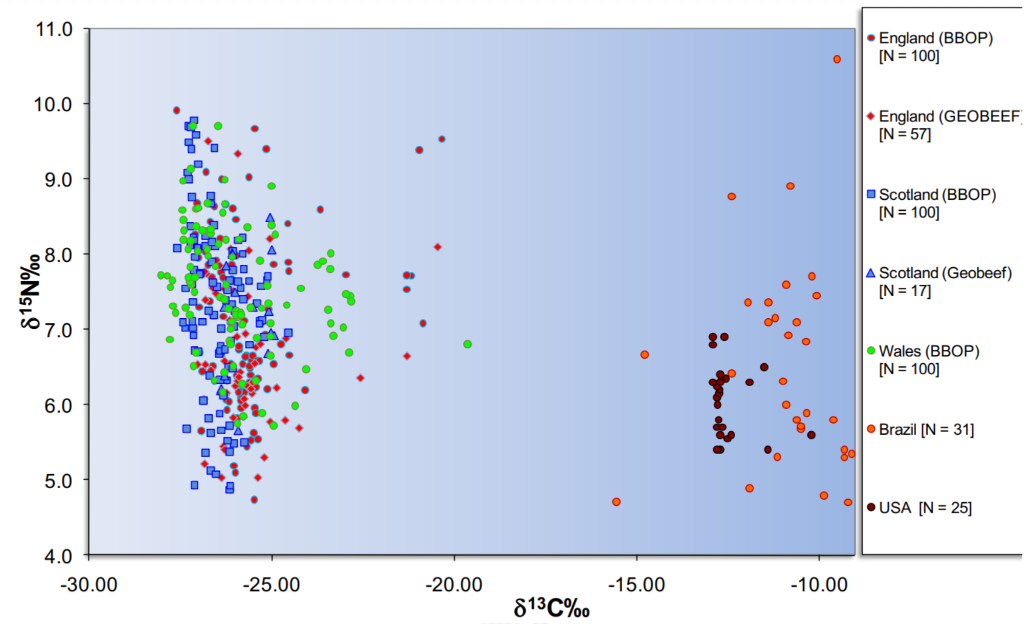
C3, C4, and CAM plants



ลักษณะ	พืช C_3	พืช C_4	พืช CAM
ช่วงเวลาที่เกิดกระบวนการสังเคราะห์ด้วยแสง	กลางวัน	กลางวัน	กลางวัน
จำนวนครั้งในการตรึง CO_2	1 ครั้ง	2 ครั้ง	2 ครั้ง
การตรึง CO_2 จากอากาศ			
- เอนไซม์ที่ใช้	Rubisco	PEP carboxylase	PEP carboxylase
- สารตั้งต้นที่ใช้	RuBP	PEP	PEP
- ผลิตภัณฑ์ที่เกิด	PGA (C_3)	OAA (C_4)	OAA (C_4)
- ช่วงเวลาที่เกิด	กลางวัน	กลางวัน	กลางคืน
เซลล์ที่เกิด Calvin cycle	Mesophyll	Bundle sheath	Mesophyll
อัตราการเกิด Photorespiration	สูง	ต่ำ	ต่ำ

กระบวนการตรึงคาร์บอกไดออกไซด์ของพืช c3 c4 cam | PPT (slideshare.net)

Tracing the origin of beef based on diet using carbon isotope fingerprints



Carbon and nitrogen isotope fingerprints of beef muscle.

The origin of beef can be tracked using the carbon isotope fingerprint which is related to the photosynthetic signature of the plants consumed by the animals during their grazing. To identify beef of UK origin relative to beef of Brazilian origin, this can be readily differentiated using carbon isotope fingerprints.

Table 1: Features of C3 and C4 grasses

NSW Department of Primary Industries	C3	C4
Initial molecule formed during photosynthesis	3 carbon	4 carbon
Growth period	Cool season or yearlong	Warm season
Light requirements	Lower	Higher
Temperature requirements	Lower	Higher
Moisture requirements	Higher	Lower
Frost tolerance	Higher	Lower
Feed quality	Higher	Lower
Production	Lower	Higher
Examples	weeping grass and common wheatgrass	kangaroo grass, red grass and wire grass

Detection of honey adulteration

AOAC Official Method 998.12 C-4 Plant Sugars in Honey Internal Standard Stable Carbon Isotope Ratio

Honey is subject to fraud by adulteration with low price sugar syrups. Saccharides in syrups derived from cane, corn or beet sugar are difficult to distinguish from those in pure honeys. Sugar cane and corn syrups, the most widely used adulterants, have distinctive ^{13}C isotope fingerprints because both sugar cane and corn plants use the C4 photosynthetic pathway in contrast to most honey which is derived from plants that use the C3 photosynthetic pathway. These differences in ^{13}C isotopic composition allow detection of > 7% addition of such sugars.

LC-IRMS and EA_IRMS analysis of eight honey samples.

Honey	Sucrose ‰	Glucose ‰	Fructose ‰	Fru/Glu ratio of areas	EA Honey (4) ‰	EA Prot. (4) ‰	Adult. (4) ‰
1	-23.3	**-23.2**	**-22.9**	1.07	**-21.8**	-24.2	**16.7**
2	-11.3	**-11.2**	**-13.9**	**0.65**	**-11.9**	n.a.	n.a.
3	-25.3	-24.9	-24.9	1.42	-24.8	-24.8	0.0
4	-26.4	-26.5	-26.4	0.97	-25.4	-21.6	0.0
5	n.d.	-26.1	-26.0	**4.53**	-25.8	-26.1	1.9
6	-26.1	-25.0	-25.3	1.62	-24.3	-24.3	0.0
7	-25.0	-25.2	-25.1	1.16	-24.2	-24.7	3.4
8	n.d.	**-25.1**	**-26.4**	2.17	-24.8	-25.1	1.5

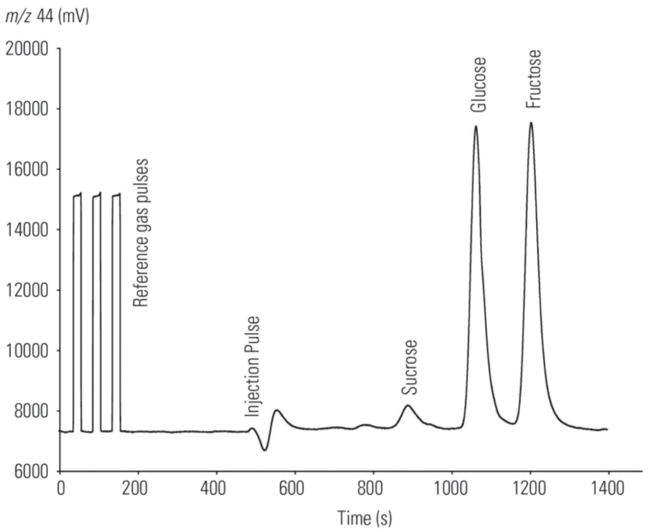
Carbon isotope fingerprints of three honeys and their extracted proteins.

	Honey-1	Protein-1	Honey-2	Protein-2	Honey-3	Protein-3
	-23.60	-24.08	-23.83	-24.01	-24.17	-24.49
	-23.68	-24.09	-23.81	-23.95	-24.06	-24.44
	-23.57	-24.09		-23.91	-24.07	-24.17
	-23.48	-24.09		-23.87	-24.11	-24.00
	-23.53	-24.01		-23.84		-24.29
	-23.60	-24.01				
	-23.61	-23.98				
	-23.60					
Average (‰)	-23.58	-24.05	-23.82	-23.91	-24.10	-24.28
1 sd (‰)	0.06	0.05	0.05	0.07	0.05	0.20

Calculate apparent C-4 sugar content as follows:

$$\text{C-4 sugars, \%} = \frac{\delta^{13}C_P - \delta^{13}C_H}{\delta^{13}C_P - (-9.7)} \times 100$$

where $\delta^{13}C_P$ and $\delta^{13}C_H$ are $\delta^{13}C$ values, ‰, for protein and honey, respectively, and −9.7 is the average $\delta^{13}C$ value for corn syrup, ‰. Report negative values from this calculation as 0%. Product is considered to contain significant C-4 sugars (primarily corn or cane) only at or above a value of 7%.



Chromatographic separation of honey carbohydrates by LC-IRMS.

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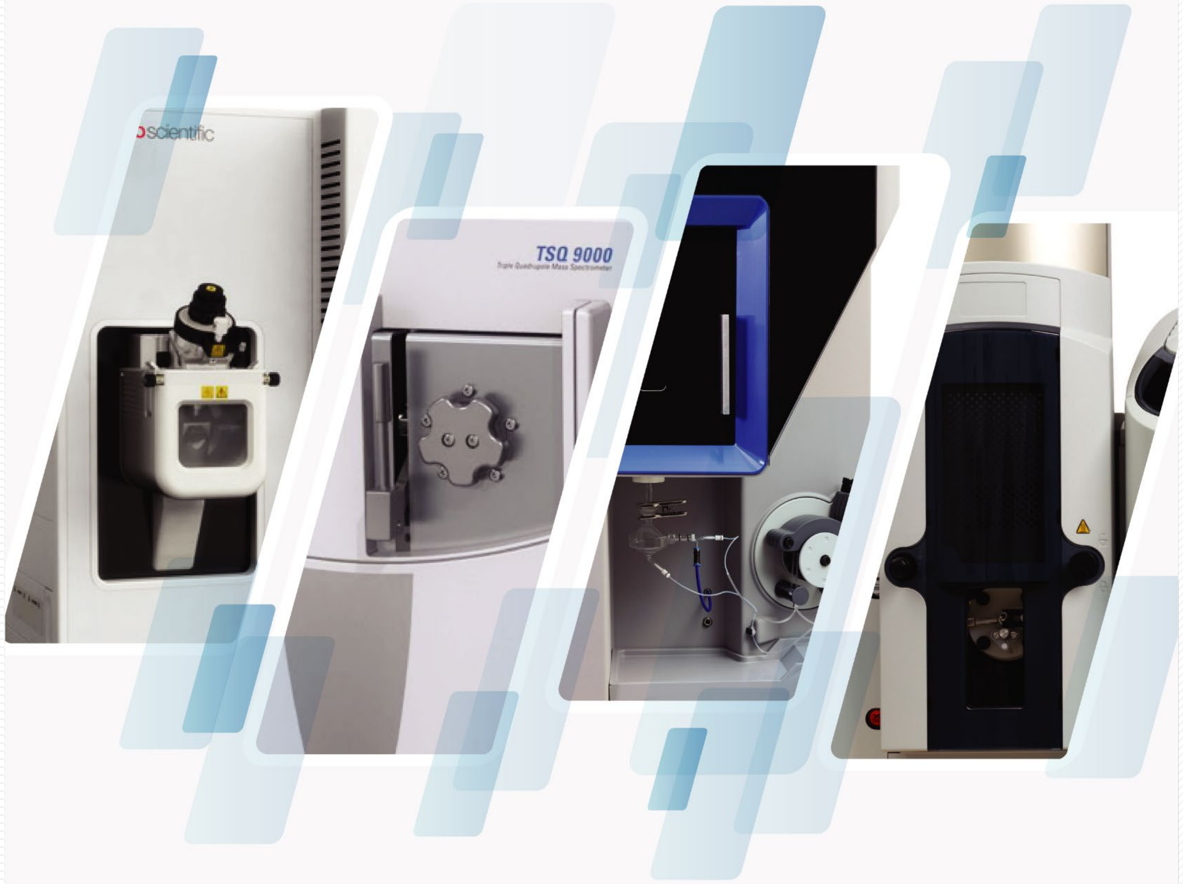

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