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EA-IRMS: Tracking wine adulteration using isotope fingerprints

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Keywords

Authenticity, EA-IRMS, EA IsoLink IRMS System, IRMS, Isotope Fingerprint, Origin

Goal

Demonstrate the use of the EA-IRMS for automated multi-element isotope fingerprint analysis of ethanol to support wine adulteration studies.

Introduction

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. One example is the addition of exogenous sugar to wines during the fermentation process to artificially increase the alcohol grade, a process known as “chaptalisation”. 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 the European Union, for example, European Commission Regulation (EC) No 607/2009 regulates the origin and labelling of wine, with bilateral agreements in place with Australian, Mexico, Chile, USA, Croatia, Switzerland, amongst others.

In this application brief, we report carbon, oxygen and hydrogen isotope fingerprints of ethanol from wine and illustrate how the addition of exogenous sugars can be successfully tracked and identified. This enables the evaluation of wine labels in terms of alcohol content and origin. In addition, analysts can refer to the official wine databank (EU-wineDB), which contains isotopic analysis of authentic and representative wine samples, to compare their data.

Analytical configuration

For $\delta^{13}C$ determination, 1 µL of purified ethanol was injected with a 1.2 µL syringe into a small tin container for liquids and introduced to the combustion reactor using a Thermo Scientific™ MAS 200R Autosampler. The CO_2 gas produced was then analyzed by the Thermo Scientific™ DELTA V™ Isotope Ratio Mass Spectrometer. For and $\delta^{2}H$ and $\delta^{18}O$ determination, 0.1 µL of

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pure ethanol was injected with a 0.5 µL syringe from a Thermo Scientific™ AS 3000 Autosampler directly into the pyrolysis reactor held at 1450 ˚C. The produced H_2 and CO gases were separated using a 5Å molecular sieve packed GC column held isothermally at 70 ˚C. The data were corrected against VSMOW and rescaled using the GISP standard. Analytical parameters are described in Table 1.

Table 1. Analytical settings used for EA-IRMS analysis.

	$\delta^{13}C$ analysis	$\delta^{2}H$ and $\delta^{18}O$ analysis
Reactor Temperature (°C)	1020	1400
GC Temperature (°C)	45	90
He Carrier Flow (mL/min)	90	100
O_2 Flow Rate (mL/min)	250	—
O_2 Injection Time (secs)	1	—
Autosampler Delay (secs)	23	—
Autosampler Type	MAS 200R	AS 3000
Syringe Size (µL)	—	0.5

The analysis of ethanol extracted for wine can be readily undertaken on the latest Thermo Scientific™ EA-IRMS system, the EA IsoLink™ IRMS System.

The isotope fingerprint 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, but that can also be influenced by cultivation practices, soil processes and geological characteristics of the local area, altitude and proximity to the shoreline.[1] Oxygen and hydrogen isotope fingerprints change in rainfall as you move further inland from the shoreline and with increasing altitude because heavier isotopes are released from the clouds first, meaning heavier isotopes are closer to the coast line compared to further inland.[1,2]

The carbon isotope fingerprint ($\delta^{13}C$) of plants are different because of photosynthetic processes and broadly grouped as C3, C4 and CAM plant types. C3 plants utilize the Calvin photosynthetic pathway to fix CO_2. C4 plants utilize the Hatch-Slack photosynthetic pathway and CAM by Crassulacean Acid Metabolism. Therefore, C3 plants have a carbon isotope fingerprint between -33‰ to -22‰, C4 plants a carbon isotope fingerprint between-16‰ to -8‰. And CAM plants between -20‰ to -10‰.[3]

Results

$\delta^{13}C$ values of ethanol show a precision (1σ) of ≤0.1% and simultaneously measured $\delta^{2}H$ and $\delta^{18}O$ values show precisions of 0.12% and 0.08%, respectively (Table 2). The sample “Ethanol Pineapple” has the expected isotope fingerprint, given it is a CAM plant.

Table 2. $\delta^{13}C$, $\delta^{2}H$ and $\delta^{18}O$ for ethanol and international standards (mean ± 1σ).

Sample identifier	*n*	$\delta^{13}C$ (‰)	$\delta^{2}H$ (‰)	$\delta^{18}O$ (‰)
Ethanol Standard	10	-26.93 ± 0.07	-234.80 ± 0.12	-24.18 ± 0.08
Ethanol Sweet Wine	6	-19.14 ± 0.09	Not measured	Not measured
Ethanol Pineapple	6	-14.32 ± 0.07	Not measured	Not measured
V-SMOW	10	—	0.00 ± 0.34	0.00 ± 0.08
GISP	10	—	-189.50 ± 0.40	-24.80 ± 0.05

Summary

The correct labeling of wine affects producer and consumer value and food safety. Laboratories require an analytical technique providing conclusive answers on origin and authenticity of primary ingredients. The carbon, oxygen and hydrogen isotope fingerprint of wine allows the identification of water addition in commercial wine, i.e. adulteration. This helps protect producer reputation and consumer confidence by detecting fraudulent activity and supports EC No 606/2009.

References

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For more details please refer to AN30147.

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