

THE USE OF ISOTOPE RATIO INFRARED SPECTROMETRY (IRIS) TO DETECT WINE FRAUD

OXYGEN ISOTOPES FOR WATER ADDITION AND CARBON ISOTOPE RATIOS TO AUTHENTICATE CARBON DIOXIDE (CO₂) IN SPARKLING WINE

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Overview

The determination of ¹⁸O/¹⁶O and ¹³C/¹²C isotope ratios of CO₂ for the detection of a water addition to wine on the one hand and carbon dioxide to sparkling wine on the other hand is carried out by an IRIS measurement system in combination with a gas bench.

Introduction

In vino veritas people say. The ancient Germanics drank wine in their council meetings because they knew nobody was able to lie effectively when they were drunk. But what if the wine was diluted with water? The people would not get drunk, were able to lie and the saying might have never been created. To prevent such and other practices, there are clearly defined standards and provisions in the oenological practice of wine making, an addition of water for example is generally forbidden. The oenological practices also include the addition of carbon dioxide to make sparkling wine. The CO₂ must originate from the (second) fermentation. An addition of industrial CO₂ made by the combustion of fossil fuels or the thermal treatment of carbonates is not permitted unless labelled in accordance with European legislation.

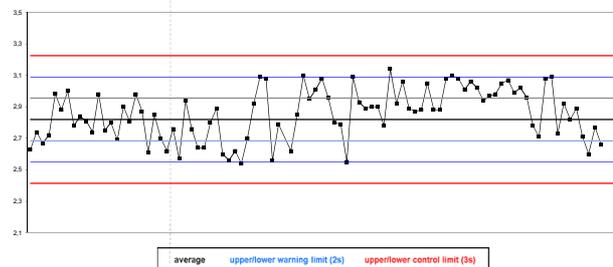
Results

¹⁸O/¹⁶O isotope ratios of water in different matrices

Tab. 1. Verification of the precision parameters according to "DIN V ENV 12141:1996 Bestimmung des Verhältnisses der stabilen Sauerstoff-Isotope (¹⁸O/¹⁶O) im Wasseranteil von Fruchtsäften using the Delta Ray

Statistical parameter	Specification*	Delta Ray results
repeatability (r)	r = 0,22‰	r = 0,21‰ ✓
reproduceability (R)	R = 0,58‰	interlaboratory trials (n=50) ✓
proficiency tests	z-score ≤ 1 (n=6) ✓	

Fig 2. Control chart for the analysis of ¹⁸O/¹⁶O isotope ratios of water in matrix.

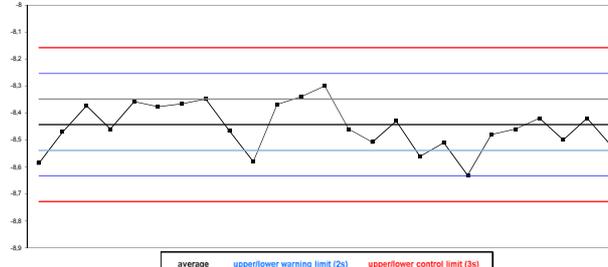


¹³C/¹²C isotope ratio of the CO₂ in different matrices

Tab. 2. Verification of the precision parameters according to "OIV-MA-AS314-03 Determination of the carbon isotope ratio ¹³C/¹²C of CO₂ in sparkling wines (Resolution Oeno 7/2005, Revised by OIV-OENO 512-2014) using the Delta Ray

Statistical parameter	Specification*	Delta Ray results
repeatability (r)	r = 0,56‰	r = 0,16‰ ✓
reproduceability (R)	R = 1,91‰	interlaboratory trials (n=9) ✓
proficiency tests	z-score ≤ 2 (n=1) ✓	

Fig 3. Control chart for the analysis of ¹³C/¹²C isotope ratios of carbon dioxide in matrix.



Conclusion

For the first time Isotope Ratio Infrared Spectrometry (IRIS) has been shown to deliver true and accurate results in a commercial routine food testing environment. Statistical evaluations of the performance characteristic are in line with respective requirements and make IRIS a useful tool to tackle fraud in wine and other commodities.

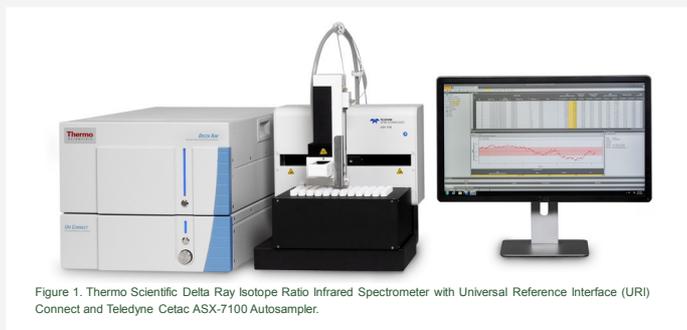


Figure 1. Thermo Scientific Delta Ray Isotope Ratio Infrared Spectrometer with Universal Reference Interface (URI) Connect and Teledyne Cetac ASX-7100 Autosampler.

Method

For the analysis of the ¹⁸O/¹⁶O isotope ratios of the wine (water) the indirect CO₂ equilibration technique is used. The method is based on the exchange of oxygen from the water molecules with the soluble carbonic acid. The sample vials are filled with 1% CO₂ in air and after the equilibration time, the ¹⁸O/¹⁶O isotope ratios of the CO₂ is determined against a certified reference gas by the IRIS measurement system (Delta Ray, Thermo scientific, s.Fig. 1). Using almost the same set-up the ¹³C/¹²C isotope ratios of the CO₂ of sparkling beverages can be analysed. The refrigerated samples are transferred to the gas-tight vials and after a short time of equilibration analysed by the system.



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In vino veritas people say. The ancient germanics drank wine in their council meetings because they knew nobody was able to lie effectively when they were drunk. But what if the wine was diluted with water? The people would not get drunk, were able to lie and the saying might have never been created. To prevent such and other practices, there are clearly defined standards and provisions in the oenological practice of wine making. An addition of water is generally forbidden, also in the course of chaptalization via the in water dissolved sugar. The oenological practices also include the addition of carbon dioxide to make sparkling wine. The CO₂ must originate from the (second) fermentation. An addition of industrial CO₂ made by the combustion of fossil fuels or the thermal treatment of carbonates is not permitted unless labelled in accordance with European legislation. The proof for an addition of foreign water to wine is made by the determination of the oxygen isotope ratios of the wine water. During ripening on the vine heavy ¹⁸O isotopes are enriched in the grape water (ca. $\delta^{18}\text{O}_{\text{V-SMOW}}=3\text{‰}$). This enables a differentiation towards regular tap water with $\delta^{18}\text{O}_{\text{V-SMOW}}$ values of ca. -7‰ . For the detection of an addition of CO₂ to sparkling wine the determination of its carbon isotope ratios is used. The CO₂ from fermentation has $\delta^{13}\text{C}_{\text{V-PDB}}$ values in the range of -26‰ to -17‰ and can be distinguished from industrial CO₂. Depending of the source of the added CO₂ sparkling wines with $\delta^{13}\text{C}_{\text{V-PDB}}$ values lower -29‰ and higher -10‰ can be considered falsified. We present a novel approach for the determination of the oxygen isotope ratios of water in matrices like wine and the determination of carbon isotope ratios of CO₂ in champagne or other sparkling products. The methods combine the classical CO₂ equilibration technique respectively a direct carbon isotope ratio determination of CO₂ via gasbench to an Isotope Ratio Infrared Spectrometer (IRIS). This setup brings various advantages such as precise, robust and cost-effective results as well as an easy to handle isotope ratio measurement system. For the validation, repeatability (r) and internal reproducibility (R) were determined. They fulfill the requirements of the Referencemethods OIV-MA-AS2-12 and OIV-MA-AS314-03 (International Organisation of Vine and Wine). Accuracy has been verified by CRM and successful PT participations.

Keywords: wine fraud, dilution, fake champagne, IRIS