IMPRINT ANALYTICS

AUTHENTICATION OF WINE, BEER AND SPIRITS
BY STABLE ISOTOPE ANALYSIS

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AUTHENTICITY OF WINE

Wine is technically defined as fermented grape juice. The adulteration of wine by substances that are not related to grapes in order to mislead equals to fraud. Usually, those with the intent to instigate a criminal activity (hereinafter 'fraudsters' for simplicity) use non-authorized additives (ingredients) to artificially mask non-quality and through this add value to an adulterated product. Processes that are allowed for wine production, as well as the use of technological aids and other permitted ingredients to be used during these processes are tightly controlled throughout the world. There is some harmonization of wine standards by organizations such as the International Organization of Vine and Wine (OIV), that facilitates international wine trade, but there are differences between what is permitted and what is not in different geographical regions of the world. Wine is also closely related to its geographical origin. Consumers not only want to know the origin of the wine but frequently they choose a wine based on this information. As so, wine fraud takes place by mislabeling the bottles either by using deceptive information of origin or by blending wines from different origin without correct designation. Note: Grape type is covered by a different test.

Addition of water to wine

One of the oldest forms of wine fraud is the dilution of wine with water. Although adding water to dilute wine was once considered common practice, today it is generally perceived as fraudulent. Depending on the economical aspect of the fraud, addition of water to wine or to grape must can serve in two ways: a. dilution can decrease high alcohol content below a threshold value, in order to avoid high duties and taxes in many countries. b. it is an inexpensive way to increase volume and gain profit from it.

The detection of added water in wine is achieved by oxygen stable isotope ratio analysis ($^{18}O/^{16}O$) in wine water, as recommended by OIV-MA-AS2-12. The principle is that the $^{18}O/^{16}O$ is higher in fruit (grape) water in comparison to the meteoric-(tap)-water used for dilution. Due to the geographical variation of the oxygen isotope composition of wine water, it is necessary to use an internal parameter for correlation, which is the $^{18}O/^{16}O$ of wine alcohol (ethanol)[1].

- ***DETECTION OF ADDED WATER IN WINE***

Addition of sugar and ethanol to wine

- ***DETECTION OF ADDED C3 ETHANOL/SUGAR IN WINE***
- ***DETECTION OF ADDED C4 ETHANOL/SUGAR IN WINE***

Adding sugar to unfermented grape must (chaptalization) is used in order to increase the alcohol content of the final product, when this is poor in sugar content, and by this increase the value of the wine. Wine is unstable without a certain content of alcohol, and the addition of sugar before fermentation may be vital for wine stability[2]. This procedure is legal only for specific wine-growing regions and vintages that suffer from a lack of sun hours during the grape-ripening period, leading to low grape sugar content. Chaptalization is, however, prohibited in most of the wine producing regions. A completely illegal practice is the addition of raw alcohol into wine for the same purpose (increasing the alcohol content). Sugar addition is used also occasionally to make the wine sweeter and upgrade the dry wines to sweet wines, since the production of sweet wines is expensive.

The detection of added sugar and ethanol in wine is achieved by carbon ($^{13}C/^{12}C$) and hydrogen ($(D/H)_I$, $(D/H)_{II}$) stable isotope ratio analysis in wine ethanol, as recommended by OIV-MA-AS312-06 and OIV-MA-AS311-05 respectively. The principle is that the carbon and hydrogen isotope ratios differ between different plant species due to their photosynthetic and metabolic properties. The combination of these parameters allows the detection of added sugars (cane sugar, beet sugar, corn syrup etc.) and ethanol (incl. synthetic ethanol).

Addition of glycerol to wine

- ***DETECTION OF ADDED GLYCEROL IN WINE***

In wine, glycerol is the most abundant compound after water and ethanol and is predominant amongst several polyols commonly found in wine. Glycerol contributes to the mouthfeel properties and smoothness of wine. It is also an important contributor to the sugar-free extract of wine, an index on which is based a quality scaling of wines in some European countries. Therefore, for such reasons, glycerol is sometimes fraudulently added to wine to disguise poor quality[3]. Glycerol is a colorless, odorless, viscous syrup that has little noticeable flavor except a slight sweetness.

The detection of added glycerol into wine is achieved by carbon ($^{13}C/^{12}C$) stable isotope ratio analysis in wine glycerol, as recommended by OIV-MA-AS312-07. The principle is that the carbon isotope ratio of wine glycerol differs significantly from synthetic glycerol which is a cheap option for this type of fraud. Detection of glycerol from other sources (e.g. plant source) can be done by using the carbon isotope composition of ethanol as internal parameter for comparison.

Addition of tartaric acid to wine

A sufficient level of acidity is needed in wine for correct ageing, stability and the organoleptic properties of the final product. L-tartaric acid is the main organic acid responsible for the acidity in wine. While generally abundant in less mature grapes, it is depleted in well-matured grapes which produce wine with low acidity and may need acidification. L-Tartaric acid is a natural by-product of the wine industry obtained from grapes through an extraction and crystallization process. Alternative sources of L-tartaric acid are obtained from the synthesis of fossil fuels and from the extraction of plants like tamarind. In the wine-making industry the use of tartaric acid is regulated in accordance with the International Wine Code[8]. Recently these rules have been amended in order to restrict the source of tartaric acid, authorized for wine and must acidification, to tartaric acid from exclusively grape origin which would ensure the integrity of wine products[9].

The determination of the source of tartaric acid used in wine is achieved by multi-isotope fingerprinting ($^{13}C/^{12}C$, $^{18}O/^{16}O$, $^{2}H/H$) of the tartaric acid present in wine. The principle is that the multi-isotope fingerprint of tartaric acid from grapes differs significantly from the synthetic tartaric acid as well as from tartaric acid from tamarind[10].

- ***AUTHENTICATION OF TARTARIC ACID IN WINE***

Addition of industrial CO_2 in sparkling wine

For several fermented products CO_2 must reflect the botanical origin of sugars from which the gas originated. Sparkling wines are among the most marketed foodstuff in the world. Carbon dioxide is an ingredient which gives drinks a sour and more pleasant taste. Sparkling and semi-sparkling wines are traditionally produced by a second fermentation that takes place directly in bottles or in tanks. An industrial gasification is possible, carbonation, by direct injection of ''food grade'' CO_2, but EU legislation[4] forbids the use of any exogenous carbonic anhydride in semi-sparkling and sparkling quality wines.

The detection of the carbon dioxide source in sparkling wine is achieved by carbon ($^{13}C/^{12}C$) stable isotope ratio analysis in CO_2, as recommended by OIV-MA-AS314-03. The principle is that the carbon isotope ratio of CO_2 in sparkling wine, which reflects the botanical origin of the fermented sugars, differs significantly from technical fossil CO_2 and CO_2 from other carbonate sources.

- ***CO_2 AUTHENTICITY TEST IN SPARLKING WINE***

Verification of geographical origin of wine

The rules concerning protected designations of origin (PDOs) and geographical indications are particularly important for wine as these are contributing factors to the cost of that wine. Fraudsters are keen to mislabel wines as for their geographical origin, since this can bring high profits by actually not adulterating the product with added substances. A recent report investigating 743 wine importers, distributors and retailers, as well as cafés, hotels and restaurants, found that in 2016 and 2017, 22% and 15% of the establishments misrepresented wine origin[5].

Geographical origin verification of wine is possible by different approaches, using simple or complex wine profiles. EU established a wine database for monitoring, among others, the geographical origin for certain countries. The method of choice[6] (stable isotope ratio analysis) is used today to create a multi-isotope fingerprint ($^{18}O/^{16}O$, $^{2}H/H$, $^{13}C/^{12}C$), indicative of the characteristics of the region of the wine production. The approach serves in different ways, for instance verifying the declaration of origin for specific regions or countries using reference datasets, batch comparison of sequential sublots of a specific initial charge, case specific verification of a certain local production etc.

- ***VERIFICATION OF GEOGRAPHIC ORIGIN OF WINE***
- ***BATCH COMPARISON OF WINE***

Authenticity testing of other alcoholic drinks

Counterfeit spirits cost the European economy €2.8 billion a year, according to the European Union Intellectual Property Office (EUIPO)[7]. In just one year, Interpol and Europol seized 26.4 million litres of counterfeit alcohol, worth an estimated €230 million. In February 2018, Mexican police seized 20,000 gallons of black-market tequila, with over 200 gallons containing dangerous levels of methanol, destined for resorts catering to North American tourists. Strict brewing standards, which render certain beers as unique in their characteristics, increase the production costs and drive fraudsters to use alternative raw materials and cheaper practices for beer production and gain profits. Beer is defined all over the world essentially as the fermentation product of musts prepared from malted barley, yeasts, water and hops as flavoring agent. Malted barley can be substituted with other cereals (wheat, rice or corn) at a variable percentage, depending on the specific national regulations. Other minor fermented beverages are cider and perry (or Perry pear cider) derived respectively from apple and pear juice, and hydromel which is obtained from fermentation of honey in water. National legislations can differ, however, European policies regarding quality products tend to protect geographical origin, traditional recipes and production methods of agricultural products (E.C. Regulations No. 2081/92 and 2082/92). In agreement with these principles, only those ciders, perries and hydromels not added with extraneous carbon dioxide or sugars

- ***ALCOHOL AUTHENTICITY TEST IN ALCOHOLIC BEVERAGES***
- ***CO_2 AUTHENTICITY TEST IN BEER***
- ***DETECTION OF ADDED C4 ETHANOL/SUGAR IN BEER***

(added to promote a second fermentation) can be considered as genuine, whereas carbonation is permitted in the USA for these types of products.
Stable isotope ratio analysis can be used to verify the authenticity of products' claims and to detect fraudulent practices in alcoholic drinks. The source material of alcohol, the natural carbonation, the provenance, are among the issues dealt with. Some applications are listed below:

Product	Compound	Detection
Beer	CO_2	Industrial CO_2, also for alcohol free beers
Beer	Ethanol	Source material of the alcohol
Ciders	Ethanol	Added sugar and CO_2
Tequila	Ethanol	Verify blue agave as botanical origin
Rum	Ethanol	Verify sugarcane as botanical origin
Vodka	Ethanol	Addition of alcohol from sugarcane or corn

ABOUT IMPRINT ANALYTICS

Imprint Analytics specializes in the analytical verification of the geographical origin and authenticity of products and raw materials. Using innovative methods, Imprint Analytics determines the authentic fingerprint of a product or material and can conclude where it comes from.
As an accredited laboratory, Imprint Analytics is the first point of contact for trade and industry, manufacturers and suppliers, as well as inspection authorities and consumer protection organizations in all matters relating to product authenticity and counterfeiting. Completely independent of documents, Imprint Analytics can determine the geographical origin and authenticity of food, additives, pharmaceuticals and other products for our clients.

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