beverages

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Review

Stable Isotope Analysis of Alcoholic Beverages: A Review

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Abstract: Alcoholic beverages represent a sector of significant economic and cultural importance but are also susceptible to fraud and adulteration, which can compromise their quality and authenticity. Isotopic analyses have become increasingly valuable tools for tracing the geographical origin and ensuring the quality control of products such as wine, beer, and distilled spirits. This literature review examines the main isotopic analysis techniques employed in this field, including Isotope Ratio Mass Spectrometry (IRMS) and Site-Specific Natural Isotope Fractionation by Nuclear Magnetic Resonance (SNIF-NMR), with a particular focus on the insights derived from the isotopic ratios of various elements, notably δ(^{2}H), δ(^{13}C), δ(^{18}O), δ(^{15}N) and δ(^{34}S).

Keywords: stable isotope ratio analysis; wine; beer; liqueurs; spirits

1. Introduction

The global alcoholic beverage market is valued worldwide at USD 2264.9 billion [1]. Forecasts indicate an annual increase of 6%, with the market expected to reach nearly USD 4 trillion by 2032. The American market is the fastest-growing one, yet Europe remains the region with the largest market share. This is closely tied to the strong tradition of alcohol consumption in these countries and the presence of major, long-established alcoholic beverage producers. Alcohol consumption in Europe is monitored by the European Commission, which regularly produces reports describing its impact on the population [2]. These documents assess the nutritional and health impact of alcohol consumption on the population, estimating approximately 200,000 deaths annually and the loss of healthy life years (Disability-Adjusted Life Years, DALYs) due to alcohol-related diseases and metabolic imbalances. The report also emphasizes that alcohol consumption can be managed in a way that minimizes health risks by keeping intake below 20 g per day, drinking with meals, and ideally incorporating alcohol-free days between drinking occasions to support overall well-being. Moreover, it highlights substantial variations in alcohol intake across European countries, with some populations consuming nearly twice as much as others, reaching levels as high as 60 g per day, which may contribute to nutritional imbalances and increased health risks. Finally, it consistently finds that women consume significantly less alcohol than men in every country.

Just like in the food industry, there is a steadily growing demand for high-quality, organic, and sustainable alcoholic beverages. Both the market and producers are well aware of this trend and have started to respond by increasing the production of such products. As a result, there is a growing presence of alcohol and food products bearing the organic label. Moreover, following the COVID-19 pandemic, the online market for alcoholic beverages has grown exponentially, further boosting the circulation of these products and making it

Academic Editors: Gabriela Cristea and Adriana Dehelean

Received: 21 February 2025
Revised: 30 April 2025
Accepted: 30 May 2025
Published: 10 June 2025

Citation: Roncone, A.; Bontempo, L. Stable Isotope Analysis of Alcoholic Beverages: A Review. *Beverages* **2025**, *11*, 89. https://doi.org/10.3390/beverages11030089

even more essential to carefully monitor production methods and the true origin of these products [1].

In this context, ensuring product authenticity and traceability has become increasingly important to protect consumers and maintain quality standards.

Stable isotope techniques have been applied in the field of food safety for many years and have proven to be powerful tools for verifying the traceability of various types of food products [3,4].

The isotopic signature of an alcoholic beverage depends on the ingredients used and the manufacturing process to which it has been subjected. We consider the five isotopes normally measured in isotopic studies for the purpose of product traceability and authentication:

- The carbon isotopic composition is a function of the type of metabolism of the plant from which the beverage is derived (C_3, C_4, and CAM) and is in turn influenced by certain climatic parameters. Carbon isotope signatures distinguish C3 (Calvin cycle), C4 (Hatch–Slack cycle), and CAM (Crassulacean acid metabolism) plants, as each pathway produces distinct $\delta^{13}C$ values: C3 plants (e.g., sugar beet) range from −22‰ to −33‰, C4 plants (e.g., maize, sugarcane, sorghum) have values ranging from −8‰ to −16‰, and CAM plants (e.g., pineapple, cactus, vanilla) show intermediate values between C3 and C4 (−10‰ to −16‰) [5].
- Hydrogen and oxygen are closely related to the water absorbed by the plant during its life and/or to the water used in the beverage manufacturing process.
- Nitrogen and sulfur depend on nutrient availability and are influenced by fertilization practices and soil characteristics.

In most countries, the addition of additives is strictly regulated. Many of these are added in amounts that do not alter the isotopic ratio of the beverage, with two exceptions: sugar and sulfites [6].

Sugar addition may or may not be allowed depending on the specific beverage, the production stage (e.g., pre-fermentation phase or after fermentation, as a sweetener or to promote secondary fermentation), and the specific regulations of the country. Since sugars can be produced from both C_3 and C_4 plants, they can alter the carbon isotopic profile of alcoholic beverages.

Regarding sulfur, since this element is naturally present in small quantities, the addition of sulfites makes them the main source of sulfur, negating the potential useful information that could be obtained from the isotopic analysis of this bioelement [6].

From a technical standpoint, despite the extensive arsenal of instruments available for measuring isotopic ratios, two techniques are used in most cases: Isotope Ratio Mass Spectrometry (IRMS) and Site-Specific Natural Isotope Fractionation Nuclear Magnetic Resonance (SNIF-NMR). These have entirely different operating mechanisms: the former allows us to measure the isotopic ratio of the five elements (C, N, S, O, and H) by separating isotopes based on their mass-to-charge ratio, while NMR is used to measure the distribution of the isotopic ratio (δ^2H or $\delta^{13}C$) at specific positions within a molecule based on the resonance of isotopic nuclei immersed in a magnetic field. According to the IUPAC (International Union of Pure and Applied Chemistry) guidelines, isotopic compositions are reported as delta (δ) values relative to international reference standards: V-PDB (Vienna-Pee Dee Belemnite) for $\delta^{13}C$, V-SMOW (Vienna-Standard Mean Ocean Water) for δ^2H and $\delta^{18}O$, and atmospheric N_2 (Air) for $\delta^{15}N$, as described in Equation (1):

$$\delta_{ref}\left({}^{i}E/{}^{j}E, sample\right) = \left[\frac{R({}^{i}E/{}^{j}E,\quad sample)}{R({}^{i}E/{}^{j}E,\quad ref)}\right] - 1 \tag{1}$$

Here, "standard" refers to the certified reference material, "sample" represents the measured material, and $^{i}E/^{j}E$ denotes the ratio of the heavy to light isotope. Delta values are scaled by a factor of 1000 and are typically expressed in "per mil" (‰) units, or, following SI nomenclature, as "milliurey" (mUr).

This review provides a comprehensive overview of the application of stable isotope ratio analysis in recent studies on alcoholic beverages, examining its role in authenticity verification, geographical origin determination, and quality control across various product categories, including beer, wine, and spirits. By exploring advancements in analytical techniques and their impact on detecting adulteration and fraud (substitution and mislabeling), this review underscores the continued relevance of stable isotope methods in the beverage industry.

2. Beer

Beer is an ancient beverage, with evidence of its existence dating back to 6000 BCE in Mesopotamia and Egypt when cereal cultivation was in full expansion [7]. It is defined as an alcoholic beverage brewed from germinated barley (malt), hops, yeast, and water.

The regulations drafted by the FAO—Codex Alimentarius identify legal limits for any additives that can be added to this type of beverage [8]. However, legal standards for beer production are not particularly stringent, resulting in lower scientific interest and fewer analytical approaches for verifying its authenticity.

From an isotopic perspective, the classic beer recipe does not include products derived from C_4 plants; therefore, $\delta^{13}C$ analysis could theoretically be a useful tool for identifying their use. These products, such as molasses or cane sugar, are generally cheaper, meaning that $\delta^{13}C$ analysis could indicate whether a beer was produced using only traditional raw materials (all derived from C_3 plants such as barley and wheat) or with more economical raw materials. However, since no legislation prohibits the use of C_4 materials, these practices cannot be considered fraudulent.

Brookes et al. [9] conducted a survey of 160 beer brands from around the world, assessing the isotopic composition of beers to quantify the use of C_4 sources as adjuncts and correlating this value with beer cost. Barley is a C_3 plant, and alcohol produced from its fermentation will have values consistent with its botanical origin. On the other hand, plants such as corn or sugarcane are C_4 plants, producing inexpensive sugars often used to accelerate fermentation and increase alcohol content. It has been demonstrated [10] that brewer's yeast ferments corn sugar more rapidly than more complex barley sugars. Thus, measuring the carbon isotopic ratio can be a useful tool for identifying the presence of adjuncts.

Within their dataset, the authors noted that almost all European beers had carbon values within the C_3 range, whereas American, Canadian, Mexican, and Brazilian beers contained, to varying degrees, some amount of C_4 materials. As observed in a similar study, large companies typically produce beers with a higher contribution of C_4 materials (the addition of maize syrup is legally permitted), while craft breweries have more depleted carbon values (around −25‰), indicating beers produced with pure malt. An interesting final aspect is that the authors noted a strong inverse correlation between beer price and the amount of C_4 materials present, consistent with the fact that products such as maize syrup or cane sugar (both C_4) are inexpensive [11].

Beer is not only an alcoholic beverage but also a carbonated one, with fizziness provided by CO_2, typically produced during malt sugar fermentation. If CO_2 is naturally produced during fermentation, its $\delta^{13}C$ isotopic value corresponds to the plant group from which the sugars were derived (e.g., in malt-based beers, the C_3 group, around −25‰).

If C_4-derived sugars or materials are added, the isotopic value may shift towards more positive values (around $-12‰$) [12].

Additionally, CO_2 may be added post fermentation (gasified). In this case, the isotopic values usually are $<-30‰$ or $>-10‰$. For example, atmospheric CO_2 has a $\delta^{13}C$ value of -7 to $-8‰$ [13], CO_2 from carbonates ranges between $-10‰$ and $0‰$, and technical CO_2 covers a wide range from $-50‰$ to $-30‰$ [14].

Calederone et al. [12] measured the $\delta^{13}C$ of headspace CO_2 in carbonated beverages using direct injections of headspace gas into a GC-C-IRMS system. The proposed technique avoids technical difficulties related to sample preparation and purification, thus reducing analysis time. The authors analyzed various types of carbonated beverages, including 17 beer samples, measuring the $\delta^{13}C$ values of both headspace CO_2 and ethanol content.

The analysis allowed for the division of the 17 samples into three main groups: The first group that appears to have a predominance of C_4 materials, with $\delta^{13}C$ (CO_2 and ethanol) $>-21‰$. The second group had a prevalence of C_3 ingredients, with $\delta^{13}C$ approximately $-27‰$ and very negative CO_2 values ($<-30‰$), which could indicate "classic" beers (thus with a predominance of C_3 materials) but with the addition of CO_2 of industrial origin (as later confirmed by one of the producers). The last group, with intermediate values ($27‰$ to $-21‰$), could indicate a mix of C_3 and C_4 ingredients. For example, this group includes beers from the Czech Republic, where the use of C_4 sugars (corn) is permitted for production. In conclusion, the authors state that, despite the extremely fragmented legislation on beer across different countries and the small number of samples analyzed, the results obtained in this study may still serve as a starting point for further research on the authenticity of this product.

Another important aspect concerns the water present in the beverage: for beer, the water is added by the producer during brewing, meaning isotopic analysis could only allow for the identification of the geographical origin of the water used. Given that, from an economic standpoint, it is more convenient to use local water rather than transport it to the production site, this analysis could be useful for identifying the geographical location of the brewery.

However, it is essential to keep in mind that, as demonstrated by Brettel et al. [15], every stage of the brewing process results in isotopic fractionation affecting $\delta^{18}O$ in beer water, with an increase of $+1.3‰$ between the beginning and end of the process (since the wort is boiled for 45 min to 2 h). This fact causes a slight deviation in the relationship between $\delta^{2}H/\delta^{18}O$ in beer water and the Global Meteoric Water Line (GMWL) curve. Moreover, the isotopic composition of the water can vary over time due to changes in the supply network. Nevertheless, as shown by Carter et al. [16], the $\delta^{2}H/\delta^{18}O$ values of the beers correlated strongly both with each other and with the longitude and latitude of the declared brewing locations.

In this study, researchers examined the isotopic composition of hydrogen and oxygen in beer, alongside the $\delta^{13}C$ signature of the dry residue and various cations and anions. The objective was to establish a reference database to identify beers that might be adulterated or counterfeit. By utilizing mapped isotopic datasets (alcoscapes), the team could evaluate whether a beer's isotopic profile was consistent with its reported brewing location.

Additionally, most of the 162 beers analyzed displayed $\delta^{13}C$ values in the solid residue indicative of C_3 crops like barley and wheat. However, beers from warmer climates exhibited varying degrees of $\delta^{13}C$ enrichment. A few samples showed $\delta^{13}C$ signatures, suggesting the possible substitution of cereals with cane or corn sugars during the brewing process.

Similarly, Chesson et al. [17] conducted a survey on three widely consumed beverages, including beer, to determine whether there was a correlation between the point of purchase and its isotopic composition, by correlating δ^2H and δ^{18}O values in the water of the beverages (bottled water, soda, and beer) with the GMWL.

The authors highlight three key factors that influence the isotopic ratios of water in a beverage:

1. The original source of the water used to produce the beverage.
2. The transport and fractionation of the water source before beverage production.
3. Seasonal variability affecting the water source before transport.
4. The fractionation during brewing as demonstrated by Brettel et al. [15].

Moreover, Chesson et al. [18] proposed another study introducing a method for analyzing the water content in beverages (including beer) using isotope ratio infrared spectroscopy (IRIS). This technique allows for isotopic analysis without the need to extract water from the sample, provided that the precautions outlined by the authors are followed, especially regarding the suppression of the instrument's memory effect. The water contained in a beverage is usually measured either by first extracting it using offline methods and subsequently injecting it into the IRMS as a pure compound to be measured in gaseous form (H_2 and CO_2) or by applying the equilibration method with a reference gas of known isotopic composition. These approaches are generally time-consuming; therefore, the main advantage of using infrared spectroscopy lies in its ability to significantly reduce analysis time.

Concerning the analysis of δ^{15}N as a potential means of distinguishing between organic and conventional beers, it is extremely difficult to find bibliographic references on this subject. Some studies have observed an effect of manuring on δ^{15}N values in barley amino acids [19], and more generally, several works investigate the possibility of distinguishing organic from conventional crops based on nitrogen isotopic ratios [20,21].

One of the few, if not the only, studies [22] considering δ^{15}N in beer is a Slovenian study that compared δ^{15}N in hops and freeze-dried beers (as well as a series of metabolites) to distinguish between organic and conventional hops and beers. The authors observed statistically higher δ^{15}N values in organic hop samples compared to conventional ones (as previously observed for other crops [23]). Regarding beer, although δ^{15}N values were also statistically higher in organic (3.4–7.4‰) than in conventional samples (2.9 to 4.9‰), the authors stated that distinguishing between them based solely on δ^{15}N values would be difficult due to their partial overlap in isotopic values. Rightly, the authors noted that hops represent only 1% of beer components, so the smaller difference between organic and conventional beers compared to hops was expected.

In another study [24], the authors estimated the natural variability of sulfur in beer. They investigated δ^{34}S in 26 beers using Multi-Collector Inductively Coupled Plasma Mass Spectrometry (MC-ICP-MS) to develop a method for the traceability and authentication of this product. The authors concluded that while distinguishing individual beers solely based on δ^{34}S values (range: −0.2‰ to +13.8‰) is not possible, the method can distinguish different brands and estimate the natural variability of sulfur in beers for future tracer experiments.

3. Wine

The International Organisation of Vine and Wine (OIV) defines wine as "the beverage resulting exclusively from the total or partial alcoholic fermentation of fresh grapes, whether crushed or not, or grape must. The finished alcohol content cannot be less than 8.5% vol." [25]. Like beer, wine legislation varies between countries, even within Europe, the world's leading wine producer. Regulation (EU) 2024/1143 of the European Parliament and of the Council establishes the general framework for the protection of geographical indications (GIs) for wines, spirit drinks, and agricultural products. Additionally, Commission Delegated Regulation (EU) 2019/33 supplements Regulation (EU) No. 1308/2013 by setting specific rules for the protection of protected designations of origin (PDOs), protected geographical indications (PGIs), and traditional terms in the wine sector. Furthermore, Commission Implementing Regulation (EU) 2019/34 lays down practical procedures for the implementation of registration, opposition, and amendment processes for PDOs, PGIs, and traditional terms for wine products. Regulation (EU) No. 251/2014, which concerns the definition, designation, presentation, labeling, and protection of geographical indications of aromatized wine products, has been amended by Regulation (EU) 2021/2117 and Delegated Regulation (EU) 2024/585.

The OIV establishes appropriate analytical methods to verify the authenticity and traceability of wine.

The application of isotopic techniques for wine traceability began between the 1970s and 1980s. Among the key contributors was G.J. Martin, who, in the early 1980s, recognized the potential of isotopic analysis for detecting fraud and ensuring wine traceability. He developed a method based on SNIF-NMR for identifying wine chaptalization [26–28]. In 1990, the European Commission adopted this method, making it the first official stable isotope-based method in Europe [29].

3.1. Deuterium

To increase the alcohol content of wine, one of the most common methods is to add sugar to grape must; this practice is considered fraudulent except for specific winegrowing regions and vintage areas, e.g., Brazil, Canada, Chile, China, France, Germany, Japan, New Zealand, Switzerland, the United Kingdom, and the United States [30]. Among the most commonly used sugars for wine adulteration is beet sugar, which is inexpensive and easily available on the market. However, its deuterium values differ from those of the sugars naturally present in grapes. If this sugar is added in significant quantities to the must and converted into ethanol by fermentation yeasts, it can alter the deuterium values of the alcohol, shifting them (downward) outside the reference ranges. Wine samples with deuterium values outside the established reference ranges may be deemed non-compliant by competent bodies designated by member states for ensuring compliance with the EU rules in the wine sector (Regulation EU 2018/273, 2018/274). The addition of sugar to grape must is allowed for an increase of no more than 3% vol, in the European Union only in specific production zones [31], which correspond to high-latitude regions where solar exposure is scarce, necessitating sugar addition to achieve alcohol levels consistent with current standards. In other zones with milder climates, sugars can be added to the must only if they are of grape origin (from concentrated must or rectified concentrated must). However, some wine producers choose to add non-grape sugar where it is not permitted or exceed legal limits where it is allowed. ^{2}H SNIF-NMR remains the only analytical technique capable of identifying this practice so far [31].

The technique OIV-MA-AS311-05: R2011 essentially consists of measuring the D/H ratio at the methyl $(D/H)_I$ and methylene $(D/H)_{II}$ sites of the ethanol molecule obtained from the distillation of wine or grape-derived products. The deuterium content at the methyl $(D/H)_I$ site is strongly related to the botanical origin of the sugars from which ethanol is derived, and its value is commonly used to identify the addition of beet sugar. On the other hand, the $(D/H)_{II}$ site is primarily influenced by the fermentation water; in fact, 78% of the hydrogen present at this site comes directly from the water in which the fermentation process takes place [32,33].

The isotopic deuterium values in ethanol from wines and related products have well-defined ranges that depend on both the geoclimatic characteristics of the area where the plant grows and the physiological characteristics of the vine itself. Since stable isotope ratio analysis (SIRA) is primarily a comparative technique, measuring the deuterium content of ethanol in a wine is not sufficient to determine its origin. Each measurement is made in relation to a reference database. Since the early 1990s, the European Union has established an isotopic database used to compare commercial wine samples with the specific reference values of a given production area. For example, Italy has a fairly extensive database with about 500 samples collected annually by the Italian ministry, analyzed, and used to determine whether a given sample falls within the typical variability ranges of the different production areas of Italy. Given Italy's great climatic and orographic diversity, there is variability in the deuterium content $(D/H)_I$, ranging from approximately 98 ppm to 105 ppm [34].

The deuterium content in a plant primarily originates from the water it absorbs during growth, undergoing fractionation processes within the plant. In particular, the deuterium content of water becomes concentrated through evapotranspiration. The extent of this concentration is influenced by the temperature and humidity of the growing environment and consequently varies annually due to climatic differences. As a result, plant water exhibits higher deuterium levels compared to local groundwater. This deuterium enrichment is integrated into the sugars produced during photosynthesis. While different plant species may alter the degree of enrichment, it has been demonstrated that various vine varieties do not produce differing levels of deuterium enrichment [35].

Although the deuterium isotopic ratio alone is never considered for authentication purposes, several studies specifically describe the isotopic variability of the δ^2H ratio: in different areas of France [36] and Slovenia [37,38], among different grape varieties and production years in Romania [39] and Spain [40], and among different production areas and grape varieties in China [41].

3.2. Carbon

3.2.1. Ethanol

Deuterium isotopic analysis alone is not sufficient to identify all different types of wine adulteration. Over the years, fraudsters have developed increasingly sophisticated systems to circumvent controls. They realized that identifying the addition of beet sugar had become "easy" thanks to the NMR method developed by Martin. They then began blending two different sugars: beet sugar and cane sugar. While the deuterium content of beet sugar is significantly more negative compared to that of must sugars, cane sugar exhibits a more positive deuterium signature. By using molasses derived from a combination of the two sugars in the right proportion, it is possible to achieve deuterium values for must sugars (and consequently for the ethanol derived from them) that fall within the typical values of grape-derived sugars [31]. The presence of cane sugar, however, poses another problem: cane is a C4 photosynthetic cycle plant and can therefore alter the carbon isotopic ratio in the resulting alcohol.

At this point, the development of a new analytical technique capable of measuring the carbon isotopic ratio in ethanol became crucial, the OIV-MA-AS312-06, which was adopted as an official method by the EU [42]. The method consists of measuring the δ^{13}C ratio in an ethanol molecule obtained from the fermentation of grape-derived products (must, concentrated must, and grape sugars). The interpretation of isotopic data is conducted in the same manner as for other isotopes, relying on a reference database. Following the selection of reference samples, authenticity thresholds are determined by computing key descriptive statistical parameters, including the arithmetic mean, median, and standard deviation. If the measured value of the sample falls beyond the established upper or lower limits, while also accounting for the sample's measurement uncertainty, it is deemed adulterated [43].

Ultimately, wine chaptalization is identified through the combination of these two techniques (SNIF-NMR and IRMS), the first to verify the addition of beet sugar and the second to detect cane sugar.

3.2.2. Glycerol

During the fermentation of must sugars, approximately 92% of sugars are converted into alcohol, with the remaining 8% converted into glycerol. Glycerol contributes to the smoothness of wine and is often considered an indicator of high-quality products; for this reason, it is sometimes fraudulently added to wine [44]. There is an official method to determine the possible addition of glycerol to wine (OIV-MA-AS312-07:R2010), which, through the measurement of the $\delta^{13}C$, can establish whether the glycerol's origin is grape-derived and thus legally permitted, or if it comes from vegetable oils, synthetic–industrial sources, or C_4 plants. This distinction is based on the fact that different sources of glycerol exhibit characteristic carbon isotopic ratios: grape-derived glycerol typically shows more negative $\delta^{13}C$ values, whereas glycerol from C4 plants, synthetic production, or certain vegetable oils displays comparatively more positive $\delta^{13}C$ signatures. Several papers explore the variability of isotopic values by measuring the isotopic ratio through both liquid and gas chromatography [44–47].

3.2.3. CO_2

Sparkling wines can be classified into three categories: those in which the second fermentation occurs in a bottle (the Champenoise method), those in which the second fermentation takes place in an autoclave (Charmat or Martinotti method), and carbonated wines, which are obtained by adding exogenous CO_2. The addition of exogenous CO_2 is allowed, provided it is declared on the label.

An official method, OIV-MA-AS314-03: R2015, allows the identification of the origin of added CO_2, based on the $\delta^{13}C$ ratio of the CO_2 present in the headspace. Historically, the first offline method was introduced in 1997, involving initial CO_2 extraction followed by analysis with EA-IRMS. Over the years, online methods such as GC-C-IRMS and Gas Bench have been developed, significantly reducing analysis time.

The carbon dioxide produced by the second fermentation of grape sugars (C_3 plant) typically has carbon isotopic values ranging from −26‰ to −17‰ If the CO_2 is produced from C_4 plants, it will have a value range between −10‰ and −7‰. Carbonated wines usually have values below −29‰ or above −10‰ depending on its origin [48].

Several studies in the literature explore the variability of the $\delta^{13}C$ ratio of CO_2 in different production regions. Martinelli et al. [13] observe that in Brazil and America, the $\delta^{13}C$ value of CO_2 and the wine itself tend to be more positive than in Europe, indicating the extensive use of C_4 sugars (both added to the must and for the second fermentation). It is worth noting that some of these wines exhibit extremely negative values, suggesting a post-fermentation addition of industrially sourced CO_2.

Conversely, Chilean and European wines are primarily consistent with C_3 sugar presence, with a $\delta^{13}C$ wine range of −26.9‰ to −23.4‰ and CO_2 between −22.4‰ and −20.5‰ [13]. It should be noted that this difference between the isotopic value of wine and CO_2 is often due to the fact that there are no laws preventing the second fermentation from being carried out using C_4 sugars, which consequently causes a shift towards less negative $\delta^{13}C$ values in CO_2.

Another study [49] also highlights the widespread use of C_4 sugars in Brazilian wines, and in more than 10% of cases, the addition of industrial CO_2 is suggested due to its highly negative values (<−25‰).

A different approach is proposed by Cabanero et al. [50], who used a Gas Bench for the analysis of headspace CO_2. The authors demonstrate how this method offers several advantages: no need for sample purification, a fast analysis time (less than 11 min per sample), and good repeatability (SD < 0.1%). A similar performance was also achieved by Calderone et al. [51], who employed GC-C-IRMS for headspace CO_2 analysis. In this case, as well, no extraction is required, the analysis time is approximately 10 min, and repeatability is below 0.1%.

3.2.4. Other Applications

Many analytical laboratories operating within official methods often attempt to develop new techniques, contributing to scientific advancements and the creation of new methodologies. For instance, in a recent article [30], Pianezze et al. propose an alternative method to the official OIV-MA-AS-312-06: R2009. This method is based on the $\delta^{13}C$ analysis of must sugars using liquid chromatography (LC-IRMS). The proposed method allows for the identification of potential cane sugar addition without the need for fermentation and subsequent distillation, thus saving a considerable amount of time. The construction of the official must and wine database requires the exclusive use of the OIV-MA-AS-312-06: R2009 method. However, the authors propose this innovative method as a faster and more cost-effective alternative to the official one.

An interesting application of isotopic analysis was presented in two studies [52,53] by Spangenberg et al., who correlated various isotopic parameters: the $\delta^{13}C$ of ethanol, whole wine, solid residue, and sugars with leaf water potential (Ψpd). They found that the carbon isotopic ratio in wine ethanol and must sugars is highly correlated (inversely) with leaf water potential. Specifically, the authors observed that for all vine varieties considered, as the plant experiences lower water availability, $\delta^{13}C$ values (especially for ethanol and sugars) become less negative. This information can, for example, be used to quickly reconstruct water availability in the vineyard and, consequently, the evolution of local climatic conditions.

Interest in isotopic variability and the chemical characteristics of specific compounds also emerges in two other studies [54,55], where the authors developed an analytical method to identify, quantify, and determine the isotopic and enantiomeric ratios of the main volatile compounds in yellow muscat wine. In these studies, the authors observed that the primary VOC in this type of wine is linalool in its (3S)-(+) form. Additionally, they provided an initial isotopic characterization of $\delta^{13}C$ and $\delta^{2}H$ values of the main volatile compounds, potentially useful as an isotopic database to enhance consumer protection and combat fraud in the wine sector.

3.3. Oxygen

The isotopic analysis of $\delta^{18}O$ in wine can provide two key pieces of information: geographical origin and watering. These details are essential for ensuring product authenticity, and for this reason, such analyses are often routinely conducted in accredited isotopic laboratories.

The variability of $\delta^{18}O$ in a plant or its derived products is closely linked to the isotopic value of the water absorbed by the plant during its growth.

The isotopic composition of vapor reaching continental margins is initially influenced by the isotopic makeup of water in the vapor-source regions. This composition is subsequently modified by temperature, which affects evaporation rates, and by humidity. As air masses travel across continental regions, they lose water through condensation and precipitation, processes that are strongly temperature-dependent. This “rainout” effect causes a gradual depletion of heavy isotopes in precipitation, leading to a general decline in the isotope ratio along the paths of atmospheric vapor transport and with increasing altitude. However, this effect can be mitigated or even counterbalanced by vapor derived from moisture recycling over the continents, which enters the air masses via the hydrological cycle. These interactions ultimately shape the isotopic composition of the water available to plants during growth. By analyzing the variation in isotopes such as δ^2H and $\delta^{18}O$ in a specific plant, influenced by processes like assimilation, evapotranspiration, and photosynthesis, it is possible to trace the plant's origin [56].

This aspect is extremely useful for identifying a specific type of fraud: the false declaration of geographical origin compared to what is stated on the label. Declaring a different geographical origin from the actual one is an old type of fraud that arises from the fact that some wine-producing regions are considered of higher prestige. Claiming an origin from these more renowned areas allows the product to be placed on the market at a higher price.

For this reason, the European wine database also includes $\delta^{18}O$ values, thereby allowing the comparison of wines suspected of having a false geographical origin with the actual isotopic values of the specific declared production area.

The analysis of $\delta^{18}O$ can also provide indications regarding the vintage of wine production, especially when considered in relation to meteorological archives. For example, particularly dry and hot years can result in significantly high $\delta^{18}O$ values, and vice versa [57,58].

The analysis of $\delta^{18}O$ can also be used to detect wine dilution. In fact, there is an official method, OIV-MA-AS2-12: R2009 [48], which allows the identification of added water (dilution) in wine. The principle is based on the fact that, due to natural evapotranspiration processes occurring within the plant, an enrichment of the heavier isotope occurs, leading to an increase in the oxygen isotopic values of the wine water. When tap water is added, the $\delta^{18}O$ value will decrease, potentially bringing it outside the reference values established by the EU database, thus determining its non-compliance.

From a technical perspective, the method relies on an equilibration process between a reference gas with a known isotopic value (CO_2) and the wine. During equilibration, an exchange occurs between the oxygen in the water present in the wine and the oxygen in the CO_2. After the equilibration period, the isotopic value of the oxygen in the CO_2 is measured. Then, using an equation, the oxygen value of the wine water is calculated and finally compared with the reference values in the EU database.

Many studies in the literature address the variability of $\delta^{18}O$ in wine water. For instance, Rossman et al. [59], in an extensive study on wines from the European database, investigated whether the differences in $\delta^{18}O$ values between must and wine were negligible, indicating almost no fractionation of water during fermentation. Additionally, the authors describe the relationships between oxygen values, vine variety, annual precipitation, and location.

The conclusion is that the interpretation of $\delta^{18}O$ values in a given sample must be conducted carefully, considering the vintage, region of origin, and harvest date (if available) and evaluating everything in light of a detailed understanding of the climatic parameters of the area during the harvest.

Perini et al. [60] proposed a method to further improve watering detection. This method is based on the principle that, as already observed for other matrices by Jamin et al. [61], there is a stable linear correlation ($R^2 = 1$) between $\delta^{18}O$ in water and $\delta^{18}O$ in ethanol. Adding water to wine disrupts this correlation, altering the R^2 values of the lines describing $\delta^{18}O$ values in water and ethanol. The reason is that $\delta^{18}O$ in ethanol does not change when water is added, but the $\delta^{18}O$ value of the wine water does, shifting the correlation beyond the threshold value and enabling the identification of water addition. To demonstrate that comparing δ^{18}O values in water and ethanol is more effective in detecting water addition in wine than analyzing only δ^{18}O in water, the authors added increasing amounts of water to wine and then compared the oxygen values. This method allowed the identification of a greater number of adulterated samples, increasing from 3 out of 69 when considering only the oxygen value in water to 10 out of 69 when comparing δ^{18}O in ethanol and water.

3.4. Nitrogen

There are few studies in the literature addressing the variability of the δ^{15}N ratio in wine. One such study, conducted by Paolini et al. [62], investigates the potential use of this isotopic ratio as a tracer to determine the geographical origin of wine. The study employed both bulk approaches (soil, leaves, grapes, and wine) and compound-specific analysis (δ^{15}N proline). Although the addition of adjuvants can alter nitrogen isotopic values in many components of the plant system, the study highlights that proline is not affected by these practices or the fermentation process, making it a potential and robust marker for geographical origin.

4. Liquors and Distillates

Liqueurs are spirit-based beverages in which the addition of sugars is allowed within certain limits. They are obtained using ethyl alcohol of agricultural origin, an agricultural distillate, one or more spirits, or a combination of these products and are flavored with one or more aromatic compounds [63].

Distillates are obtained by distilling a fermented mixture containing cereals, fruit, molasses, or starches of different origins. The addition of ethyl alcohol is not allowed, and the addition of sugars is only permitted to round out the final flavor. The use of flavorings is generally prohibited, except in some cases where caramel is allowed. Although the production of these beverages is regulated at the European level by Regulation (EU) 2019/787 [63], the imposed rules are not as strict as in the case of wine. On the one hand, this provides greater freedom to producers, while on the other, it reduces the pressure for the development of new analytical techniques. Nevertheless, there are still some limitations, and isotopic analysis is a useful tool to identify products that do not comply with regulations.

4.1. Whisky

In addition to European regulations, various national laws govern whisky production in different countries. Perhaps the most well known is the UK's Scotch Whisky Regulations of 2009, which set specific standards for Scotch whisky production. According to European regulations, the addition of flavorings is prohibited, except for caramel as a coloring agent. The addition of alcohol is also not allowed. The minimum alcohol content must be 40%, and the whisky must be aged for at least three years in wooden casks with a maximum capacity of 700 L.

Furthermore, for single malt scotch whisky, only malted barley may be used, and the maturation process must take place exclusively in Scottish distilleries using oak barrels.

The first method used to verify whisky authenticity involves identifying the profile of volatile organic compounds, as proposed by Simpkins [64]. Years later, Parker et al. [65] expanded on this approach by combining the identification of volatile congeners using a gas chromatography–flame ionization detector (GC-FID) with compound-specific stable isotope analysis (GC-C-IRMS). This provided an initial characterization of the isotopic profile of whisky congeners, potentially useful for distinguishing between brands that would otherwise be indistinguishable using a GC-FID alone.

A further advancement was made by Rhodes et al. [66], who proposed a method to detect the addition of neutral alcohol without the need to build a reference database. The system is based on the principle that there is a linear correlation between the $\delta^{13}C$ values of the main higher alcohols (particularly 1-propanol) and the ethanol present in whisky since they are biosynthetically related. The addition of exogenous ethanol with a different $\delta^{13}C$ value compared to the native ethanol disrupts this linear relationship: while the $\delta^{13}C$ of ethanol changes due to the external addition, the $\delta^{13}C$ of 1-propanol remains unaffected, thus breaking the original correlation. When the deviation exceeds a certain threshold, adulteration can be detected. It should be noted that the method loses effectiveness if the added alcohol has a $\delta^{13}C$ value identical to that of the ethanol naturally present in whisky.

One of the reasons whisky is aged in oak barrels is the release of vanillin (and other aromatic compounds) from the wood, which gives the beverage its characteristic aroma. Some producers, however, add exogenous vanillin to enhance the aroma or compensate for inadequate aging. Leeuwen et al. [67] developed a GC-C-IRMS method capable of distinguishing between natural and synthetic vanillin based on their carbon isotopic ratio. In their study, the authors first identified the typical $\delta^{13}C$ values of vanillin from different sources (natural, synthetic, and tannin-derived) and then analyzed 32 commercial spirit samples to verify the origin of the vanillin they contained.

In conclusion, isotopic analysis enables the detection of adulteration with cane sugar in C3-derived whiskies (e.g., Scotch), but not in C4-based whiskies (e.g., bourbon). Finally, compound-specific $\delta^{13}C$ analysis (CSIA) allows the identification of synthetic additives.

4.2. Vodka

Vodka is a spirit obtained from ethyl alcohol of agricultural origin, derived through fermentation with yeast from potatoes and/or cereals (wheat or rye) [63].

In an investigation conducted on various types of alcoholic beverages [68], $\delta^{13}C$ values were measured on bulk samples using flow injection IRMS (FIA-IRMS). As expected, most samples fell within the range of products derived from C_3 plants (−28.0‰ to −24.0‰). However, the particularly high $\delta^{13}C$ values of some samples indicated the presence of C_4-derived products used in alcohol synthesis. It is known that some types of vodka are made using molasses, an inexpensive byproduct obtained during cane sugar (C_4) production. As already observed in beer [9], the samples with the highest contribution from C_4 materials were those with a lower market price.

According to Polish law, true "Polish vodka" can only be made from rye, wheat, barley, oat, triticale, and potatoes grown within the territory of the Republic of Poland. Ciepielowski et al. [69] analyzed 30 samples of Polish spirits from both local and commercial producers using EA-IRMS and ^{2}H-NMR to determine which samples could be classified as true Polish vodka. In this study, some samples were identified as being made exclusively from C_4 plants, others as mixtures of C_3 and C_4, and others entirely from C_3 plants, thus confirming their authenticity.

4.3. Brandies, Spirits and Liqueurs

Brandies and spirits are obtained through the fermentation and subsequent distillation of cereals, wine, grape, pomace, fruits, or other sugary or starchy materials. Due to the wide variety of raw materials, they are highly complex matrices to interpret from an isotopic perspective.

There are few studies in the literature on this topic. One such study [70] attempts to differentiate various types of spirits based on both isotopic parameters ($\delta^{2}H$ and $\delta^{13}C$) and volatile profiles (GC/FID and GC/MSD). The authors conclude that while the volatile profile is more efficient for distinguishing different types of spirits, isotopic analysis is particularly useful for identifying adulterated samples (e.g., those suspected of containing alcohol from a different botanical source).

Similar approaches have been applied to tequila [71,72], where the $\delta^{18}O$ analysis of ethanol was also included, and sake [73,74].

Regarding liqueurs, the only requirement for alcohol origin is that it must be of agricultural origin rather than synthetic. Although from a commercial standpoint it is not cost-effective to use synthetic ethanol due to its higher cost, it has already been demonstrated [60,75] that isotopic analysis, particularly of D/H and ^{18}O, clearly allows for the distinction between ethanol of agricultural and synthetic origin.

Unlike in distillates, where alcohol must be derived from the fermentation of specific materials, in liqueurs it can come from both C_3 and C_4 plants, making $\delta^{13}C$ analysis less meaningful in determining origin.

Similarly, for flavorings, since the addition of aromatic substances is allowed, measuring their isotopic ratio often becomes ineffective in distinguishing whether they originate from the raw materials used or have been artificially added.

One application of stable isotopes in liqueurs is presented by Akamatsu et al. [76] in their study on Japanese apricot liqueur. In this case, to label the liqueur as traditional, the addition of exogenous citric acid (industrially produced from corn) is not permitted. The authors extracted citric acid from both authentic and commercial samples and then measured their δ^2H and $\delta^{13}C$ values to determine its origin.

In summary, in distilled beverages, where ethanol must originate solely from the fermented raw material (e.g., grape must, cereals, or fruits), carbon isotope analysis is a valuable tool for detecting the fraudulent addition of cane sugar, the only economically viable adulterant. Conversely, in liqueurs, where the ethanol can legally come from various sources, stable isotope analysis serves primarily to verify label compliance in cases governed by specific national regulations (as in the aforementioned case of Japanese apricot liqueur).

5. Conclusions

The applications of stable isotope analysis in alcoholic beverages have proven to be an extremely effective tool for verifying authenticity, identifying fraud, and ensuring traceability across various categories of alcoholic products. Carbon isotope ratios ($\delta^{13}C$) enable the detection of C4-derived additives such as cane sugar or corn syrup, and in carbonated drinks, they can distinguish between fermentation-derived and exogenous CO_2 sources. As previously noted, if the product label states the use of a specific type of plant material (C3, C4, or CAM), then isotopic analysis is justified. Conversely if current legislation allows the use of any type of source, the need to apply this analytical approach becomes less relevant. Hydrogen isotopes (δ^2H), closely linked to plant water uptake and physiology, provide insights into the botanical origin of raw materials (e.g., sugar beet vs. grape ethanol) and geographic provenance, especially when referenced against regional databases. Oxygen isotopes ($\delta^{18}O$) are widely used for geographical origin assessment and, in wine, for dilution detection. Nitrogen isotopes ($\delta^{15}N$) show potential for differentiating organic from conventional products, though research is still developing. Sulfur isotopes ($\delta^{34}S$), despite limited studies, may offer geographic discrimination due to their sensitivity to soil characteristics. As consumer demand for transparency and quality in their purchases continues to grow, it is crucial to keep developing new isotopic approaches both to keep pace with the new categories of products constantly entering the market and to combat emerging types of fraud. Cutting-edge instrumentation and the expansion of reference databases will further enhance the ability to distinguish between genuine and counterfeit products.

Author Contributions: Conceptualization, A.R. and L.B.; investigation, A.R.; writing—original draft preparation, A.R.; writing—review and editing, A.R. and L.B.; supervision, L.B. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Autonomous Province of Trento through the ADP project agreement.

Acknowledgments: We would like to give a heartfelt thank you to Martina Moretton for her unwavering support and encouragement throughout the writing of this text.

Conflicts of Interest: The authors declare no conflicts of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

Abbreviations

The following abbreviations are used in this manuscript:

DALYs	Disability-Adjusted Life Years
IRMS	Isotope Ratio Mass Spectrometry
SNIF-NMR	Site-Specific Natural Isotope Fractionation Nuclear Magnetic Resonance
CAM	Crassulacean acid metabolism
GC-C	Gas chromatography–combustion
GMWL	Global Meteoric Water Line
IRIS	Isotope Ratio Infrared Spectroscopy
MC-ICP-MS	Multi-Collector Inductively Coupled Plasma Mass Spectrometry
PDO	Protected designation of origin
PGI	Protected geographical indication
GI	Geographical indication
SIRA	Stable isotope ratio analysis
LC	Liquid chromatography
Ψpd	Leaf water potential
VOCs	Volatile organic compounds
GC-FID	Gas chromatography–flame ionization detector
FIA-IRMS	Flow Injection Analysis–Isotope Ratio Mass Spectrometry
EA-IRMS	Elemental Analysis–Isotope Ratio Mass Spectrometry
GC-MSD	Gas chromatography–mass selective detector

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