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Review

# A Review of Representative Methods Used in Wine Authentication

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**Abstract:** Authenticity and the methods for determining fraud are two of the most important issues in the field of quality control and food safety. In the winemaking field, the study of authenticity is all the more necessary, with wine being one of the most adulterated foods, as the monthly reports of the European Commission show. This results in a two-fold problem: consumer expectations are not met and there is a disloyal competition among wine producers in the field. Authenticity has been a priority research direction worldwide for centuries. Today, researchers are working on improving already existing methods of authenticity monitoring, but also on creating new ones. The intention is to have results that are as accurate, fast and inexpensive as possible for confirmation or rejection of the hypothesis. The bibliographic study of the literature undertaken for the development of this article aims to identify the classical methods of establishing authenticity, describe them and establish their degree of efficiency. Moreover, a review of the current research trends is presented in this work.

**Keywords:** authenticity; wine; isotopes; metals; phenolic compounds



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## 1. Introduction

Food is a commercial product, and its production is constantly evolving, with the food industry being one of the most powerful and profitable industries in the world. Besides the undeniable profits involved, the food industry is primarily about all the investments and costs of the manufacturer. So, clearly, all want to release products at the lowest cost. This is not a negative aspect as long as the reduction in cost does not lead to a reduction in the final quality of the products. However, in the pursuit of profit, some manufacturers resort to various methods of counterfeiting, either the final product or even the raw material, with these practices being used all over the world since ancient times [1].

Today's agri-food industry is based on meeting consumer demands for food quality, safety and security [2].

Food safety refers to possible hazards that may arise during the food production, so that food safety becomes the responsibility of producers, distributors or traders. Quality is closely related to the characteristics that can influence the value of a particular food as it is perceived by the consumer [3].

Achieving food security involves ensuring food availability (production, stocks), by redistributing food at national or international levels through agreements. There is effective access of the population to the purchase of food, by ensuring a balanced consumption vs. demand. Thus, the authenticity of wine does not refer to security, with the authenticity of wine being directly related to food quality and consumer safety [4].

However, according to the European Commission, food fraud expenditures raise between 8 and 12 billion euros every year. This causes customers to lose confidence in

what they are buying and also brings significant damage to honest businesses in the area. For these reasons, determining authenticity is one of the most important issues in the field of quality control and food safety. On the one hand, genuine products protect the consumer and on the other hand, they protect the honest producer from unfair competition in the market [5].

The importance of studying the authenticity of wine is also determined by the fact that wine is a product that can influence the health of the consumer through the numerous bioactive compounds it contains. Modern society tends to look for foods that could improve health and increase longevity. Several studies which highlighted the benefits that a moderate consumption of red wine (especially) can have on the health of the human body have been identified. Many of the components found in red wines are well known as powerful antioxidants, as they have anti-inflammatory, antimicrobial or even anticarcinogenic properties. These are the reasons why wine, along with other foods, can be considered a functional food. The concentration of these compounds is strictly dependent on the area, grape variety and wine-making technique, so, in general, on the authenticity of the final product [1,6].

In relation to wine, the study of its authenticity is even more important, as this beverage is a leading agricultural product of the European Union exported worldwide. Wine is one of the most easily counterfeited food products, unfortunately with a widespread practice [7]. According to the monthly reports of the European Commission, in the wine industry in the European Union, frauds of more than 1,000,000 L of wine and more than 1,200,000 euros were detected in the last 6 months of 2020.

Since the adulteration of wine is a current and common problem, it is important to study the chemical composition of wines to correlate any kind of fiddling with the product (either dilution of wine with water, addition of alcohol, use of substances to enhance color or flavors, chaptalization, deliberate misrepresentation of origin, misrepresentation of grape variety or age of wine, etc. [8]) that can lead to changes in the structure of the wine [9].

Worldwide, wine production and trade are regulated by the OIV (International Vine and Wine Organization). The International Vine and Wine Organization is an intergovernmental organization of a scientific and technical nature whose main purpose is to inform, monitor, assist and harmonize standards and legislation in the wine sector worldwide. The 47 states that are currently members of the OIV govern 85% of world wine production and 80% of consumption. The addition of water in the must in order to decrease the sugar concentration and consequently the alcoholic concentration of the future wine is a fraudulent practice, not accepted at the level of the OIV [10].

However, in addition to the states that have adhered to the OIV regulations, there are also states that by internal legislative norms accept the addition of water in wine in order to reduce the sugar concentration, but in their case, wine export is not possible, the wine being intended for domestic consumption only. In Chile (OIV Member State), for example, a decree was adopted in January 2020 by which the addition of water has become an authorized practice, under certain conditions, for reducing the sugar content of musts with Brix levels above 23.5. However, this practice is at present not allowed within OIV countries [11].

Also, the authentication of wines by establishing the origin is not only relevant in relation to the sustainability of production systems or in terms of wine quality [12]. Determining the origin of wines is also closely linked to the assessment of geographical indications. It is essential to safeguard terms such as: protected geographical status (PGS), protected designation of origin (PDO), protected geographical indication (PGI) or traditional specialty guaranteed (TSG), used to characterize wines from different regions or countries [13]. Consumers (especially the least informed in this field) tend to choose and appreciate wine depending on the designation of origin. Thus, they consider that the level of quality of a wine increases gradually from the geographical indication (IG), the most qualitative being the wines with the indication designation of controlled and guaranteed

geographical origin (DOCG) [14], which is consistent with the results of other studies. Of course, there are many consumers who analyze a wider range of factors in determining the quality of a wine, but among them is often the geographical indication [15]. That is why it is essential to prevent illegal practices in this context and to create common values in the wine sector.

## 2. Methods in Wine Authenticity

Research has led to the development of a variety of methods aimed at validating the authenticity of wines. There is no clear separation between the old and new methods for authenticating wines. While principles are the same, innovative methods are based on a combination of two or more types of older analysis that can confirm or disprove the origin of a wine, the variety from which it was obtained, the year of production, etc. [16].

The principles of classical methods of wine analysis, such as: determination of metals [17], determination of glycerol and ethanol by high-performance liquid chromatography (HPLC), determination of ethyl alcohol in wine using ebulliometric methods, determination of acids such as malic, tartaric, citric, etc., by titrimetric method, determination of volatile acidity by distillation, determination of polyphenols using the Folin-Ciocalteu method, etc. [16], are the basis of the innovative methods used today for wine authentication.

Nowadays, analytical techniques also involve the qualitative and quantitative determination of various compounds in wine, such as: polyphenols (using HPLC), volatile compounds (using GS-MS—Gas chromatography–mass spectrometry), minerals (using atomic absorption spectrometry: AAS—Atomic absorption spectroscopy or ICP-MS - Inductively coupled plasma—mass spectrometry) or combinations of these techniques. More recently, FTIR (Fourier Transform Infrared Spectroscopy) spectrometry and NMR (Nuclear Magnetic Resonance) spectroscopy have been introduced and are used to authenticate the origin of the wine and the grape variety [16,18].

In order to identify the variety from which a wine originated, DNA methods have been developed, which involve DNA extraction from must or wine using PCR (polymerase chain reaction) technology [19]. Also, some wines from Spain (Canary Islands) have been successfully characterized using the CZE technique (capillary zone electrophoresis) [20].

### 2.1. Mineral Analysis as a Method of Wine Authentication

One of the analyses often used to determine the geographical origin of wine is the one based on analysis of minerals. Of course, in most cases, this is associated with other methods to determine the authenticity of the wine [21,22]. Previous studies have highlighted some elements that are often cited in technical papers related to the ways of authenticating wines: K, Na, Fe, Ca, Cu, Co, Sb, Cs, Cr, Mn, Al, Ba, Mg and Sr [23].

According to the elemental analysis carried out for 60 Romanian wines from different regions, in comparison with the elemental analysis of the soils from which these wines originated, it was found that Mn, Sr, Ag, Co and Cr can be used as distinguishing features between the wines from two regions in Romania: Dobrogea and Moldova, and that the methodology proposed by Geană et al. can also be used for the classification of wines of unknown origin. The analyses were performed using ICP mass spectrometry (ICP MS) [24].

A 2020 study of 111 sparkling wines from four countries on two continents found that only three (K, B, Na) of the 12 quantified elements were sufficient to divide the analyzed samples by country of origin. Statistical tests showed an accuracy of the method of 94%. Elemental composition was evaluated using an ICP-OES (inductively coupled plasma optical emission spectrometer) [25].

A study carried out on 83 red wines from four of the Canary Islands has demonstrated the possibility of grouping these wines by island of origin using statistical analysis. The experiment involved the quantitative determination of some metals (K, Ca, Cu, Na, Mg, Fe, Zn, Mn, Rb and Li) using atomic absorption spectrometry (AAS) to quantify Cu, Zn, Fe, Na, Mn, Ca, Mg and K, and atomic emission spectrometry (AES) to quantify Rb and Li [26].

In 2008, a study of some commercial wines in Australia aimed to demonstrate the possibility of using visible spectrum (VIS) and near infrared spectroscopy (NIRS) as a possible method for the quantitative determination of elements. In this sense, the concentrations of Mg, K, Ca, P, S, Na, B, Fe and Mn were determined for the 126 wines using ICP-MS. The study was able to show that there are correlations between the NIR spectra and the concentrations of some elements in the wine, but the VIS and NIR calibrations used at this stage cannot be used for usual quantitative determinations in analytical laboratories. In this sense, it is necessary to develop databases that can be used for stable calibrations [27]. Also, in Australia, in 2012, a very comprehensive compositional analysis of over 1000 wines from different Australian states (51 regions) was published. The analyzed batch (a number of 1397 wines) consisted of varietal wines, produced from 39 grape varieties, from 19 different harvest years. ICP-AES technology was used to quantify the elements. The conclusions emphasized that the elemental composition of wines (with the most representative elements: Li, Na, Mg, Si, P, K, Ca, Mn, Fe, Ni, Zn, Rb, Sr, Cs and Ba) can be used to classify wines by country of origin or even by region. However, statistical tests have shown that the mini database obtained cannot be used to classify the same wines by year of production or variety [28].

A study conducted in Serbia in 2017 on 63 wines (white and red) using inductively coupled plasma with optical emission spectrometry (ICP-OES) demonstrated the possibility of classifying wines by color based on their elemental composition. In this sense, the most representative elements were: Be, Al, Rb, Mg, K, Cu, Mn and Na. The same author pointed out that the elements Cd, Pb, As, Sb, V, Na, K and Zn gave the best results in distinguishing the same wines by year of production. Of course, with the help of elemental analysis, it was possible to separate the wines by geographical origin, the most representative elements in this case being: Al, Mn, Be, Ba, Cr, Ni, Ca, Na and Mg [29].

So far, the analysis of wine elements towards proof of authenticity can only be used to classify/distinguish wines of a particular lot by geographical origin. However, in order to be able to say with certainty that a particular wine belongs to a specific country or region, it is necessary to create a sufficiently large database, with the help of which specific elemental profiles can be formed for each region or country.

Table 1 summarizes information on the determination of wine minerals, the method used, the country, the number of samples analyzed, the elements determined and the used bibliographic sources collected from the literature. All sources cited in the table used elemental analysis in their studies in order to authenticate wines by geographic origin.

**Table 1.** Studies and analytical techniques to confirm the authenticity of wines according to the quantification of mineral content.

Country	Sample Number	Elements	Methods	References
Italy	5	Na, K, Ca, Mg, Cl	Flame emission spectroscopy, AAS	[7]
France	-	K, Ca, Mg, Mn, Fe, Zn	FAAS	[30]
Spain	42	Li, Na, K, Rb, Ca, Fe, Mn	AAS, AES	[31]
Spain, UK	112	Li, Al, Cr, Mn, Fe, Cu, Zn, As, Cd, Pb	ICP-MS	[32]
Italy	68	Si, Mg, Ti, Mn, Mo	ICP-MS	[33]
Canary Islands	83	K, Na, Li, Rb, Ca, Mg, Sr, Fe, Cu, Zn, Mn	AAS	[26]
Romania	60	Ni, Ag, Cr, Sr, Zn, Cu, Rb, Zn, Pb, Co, V	ICP-MS	[24]
Germany	88	As, B, Be, Cs, Li, Mg, Pb, Si, Sn, Sr, Ti, W, Y	ICP-MS, ICP-OES	[34]
Germany	127	Li, Zn, Mn, B, Fe, Sr, Cs, Pb	SF-ICP-MS	[35]
South Africa	40	Al, Mn, Rb, Ba, W, Se, Cs, Tl, Sr	ICP-MS	[36]

Table 1. Cont.

Country	Sample Number	Elements	Methods	References
Spain, France	35	Zn, Sr, Pb, Na, Cu, Ni, As, P, Cd	ICP-AES AAS	[37]
Hungary, Romania, Czech Republic, South Africa	400	Na, Mg, Si, P, S, Cl, K, Y, U, Cr	ICP-MS	[38]
Spain	150	K, P, Sr, Al, Na, Mn, Mg, Fe	ICP-OES	[39,40]
Australia	126	Mg, K, Ca, P, S, Na, B, Fe, Mn	ICP-MS, VIS, NIRS	[27]
New Zealand	120	Sr, Ni, Pb, Rb, Co, Cd, Mn, Ga, Cs	ICP-MS	[41]
Italy	120	Ag, B, Ca, Cd, Eu, Fe, Ga, La, Lu, Mn, Nd, Pr, Sm, Th, Tm, V, Yb, Zr Al, Mg, Ti, Tl, Sc Zn, Ba, K, I, Rb	AAS, ICP-MS	[42]
Hungary, Czech Republic South Africa, Romania	1188	Ni, Mn, Cd, S, As, Pb, Zn, Cs, Rb, U, Na, K, Mg, Ca, Fe, Mn, Cu, V, Ba, Cl	ICP-MS	[43]
Spain	67	Li, Ho, Mn, Sm, Fe	ICP-OES	[44]
Argentina, Brasil, Chile Uruguai	28	Tl, U, Li, Rb, Mg	ICP-MS, ICP-OES	[45]
Serbia, Montenegro, Macedonia	41	Mg, Na, K, Fe, Ca, Cu, Zn, Mn, Pb	FAAS	[46]
Portugal	85	B, Ba, Fe, K, Mg, Mn, Ni, Sr, Al, Ca, Na	ICP-MS	[47]
Australia	1397	Li, Na, Mg, Si, P, K, Ca, Mn, Fe, Ni, Zn, Rb, Sr, Cs, Ba	ICP-AES	[28]
China	56	V, Cr, Sc, Se, Pd, Sr, Sn, Tl, Ga, U	ICP-MS	[48]
Spain	34	Sr, Ba	ICP-AES, ICP-MS	[49]
Turkey	111	Sr, Ni, Ca, Cu, Li, Pb, B, Al	ICP-AES, ICP-MS	[50]
Romania	22	Ba, Be, Cr, Cs, Li, Mg, Na, Ni, Sr, U, Zn	ICP-MS, FAAS	[51]
South Africa (23 estates)	120	B, Ba, Cs, Cu, Mg, Rb, Sr, Tl, Zn	ICP-MS	[52]
Argentina	57	Ba, As, Pb, Mo, Co	ICP-MS	[53]
France	29	Na, Mg, K, Ca, Li, B, Si, P, Ti, Mn, Fe, Cu, Zn, Rb, Sr, Ba, Pb C, H, O, N, Al	LIBS	[54]
France	3	Na, Mg, K, Ca, Li, B, Si, P, Ti, Mn, Fe, Cu, Zn, Rb, Sr, Ba and Pb	LIBS	[55]
Serbia	63	region: Al, Mn, Be, Ba, Cr, Ni, Ca, Na, Mg red/white: Be, Al, Rb, Mg, K, Cu, Mn, Na vintage: Cd, Pb, As, Sb, V, Na, K, Zn	ICP-OES	[29]
Italy	24	B, Ca, Mo, Sb, Sr.	ICP-MS	[56]
Brazil, Argentina, Spain, France	111	K, B, Na	ICP-OES	[25]

Legend: AAS—atomic absorption spectrometry; FAAS—flame atomic absorption spectrometry; ICP-AES—inductively coupled plasma atomic emission spectroscopy; ICP-MS—inductively coupled plasma mass spectrometry; ICP-OES—inductively coupled plasma optical emission spectroscopy; SF-ICP-MS—sector-field inductively coupled plasma mass spectrometry; VIS—visible spectrum; NIRS—near-infrared spectroscopy; LIBS—laser-induced breakdown spectroscopy.



## 2.2. Organic Profiles as a Method of Wine Authentication (Phenolic Compounds, Amino Acids and Volatiles)

Chromatography is a cascade separation process in which a mixture is separated into individual components, followed by their detection. In principle, chromatography requires two phases: one mobile and one stationary. In liquid chromatography, the mobile phase is liquid and the stationary one is most often bound to a solid, which fills a column. Traditional column chromatography (be it of any type—adsorption, ion exchange partition, etc.), in thin layer or on paper and modern liquid chromatography are all forms of chromatography for liquids analyses. Equipment characteristics, chromatographic material, working technique, etc., make the difference between these analysis modes. Liquid chromatography is used to identify and determine most organic compounds from must and wine. It is the most frequently used chromatographic technique, the application procedures being the most diverse [57].

### 2.2.1. Phenolic Compounds

Phenolic compounds are a group of compounds found in grapes as well as in must and wine. The positive functions that polyphenols have in plants (growth, fertility, reproduction) are also noticeable in must (antioxidant), and in relation to wine, they play a particularly important role in shaping the sensory profile (influences on color, aroma and flavor) [58]. The following classes of compounds have been frequently identified in grapes, must and wines: tannins, anthocyanins, flavonols, stilbenes and acids. However, the polyphenolic imprint varies from one wine to another, which is influenced by the following factors: the grape variety(s) used in the winemaking process, the climatic conditions and, to a large extent, the technology used. Over time, the following technologies have been applied to the phenolic imprint of wines: Nuclear Magnetic Resonance (NMR), spectrophotometric methods and multi-elemental analysis techniques. Currently, the most commonly used techniques in the identification and quantification of phenols in wine are still liquid chromatography (LC), but coupled with certain detectors such as: Diode array (DAD), UV/Vis (Ultraviolet, visible) or mass spectrometer (MS) [59].

An overview of studies on phenolic compounds in wines to determine their authenticity is presented in Table 2.

**Table 2.** Studies and analytical techniques to confirm the authenticity of wines characterized by the quantification of phenolic compounds.

High-Performance Liquid Chromatography (HPLC)					
Country	Sample Number	Data Analyzed	Methods	Classification	References
Spain	23	Anthocyanins	HPLC	V; G.O.	[60]
Chile	172	Polyphenols	HPLC-DAD	V.	[61]
Italy	91	Flavonols, Anthocyanins	HPLC-DAD-MS	V.	[62]
Uruguay	8	Anthocyanins	HPLC-UV/Vis	V.	[63]
China	9	Anthocyanins	HPLC-MS	V.	[64]
Greek	35	Acids, stilbenes	HPLC-UV/Vis	V, G.O.	[65]
Austria	22	Polyphenols	HPLC-MS	G.O., V., Vt.	[66]
Chile	248	Flavonols	HPLC	V.	[67]
Spain	90	Polyphenols	HPLC-MS	G.O., Vt	[68]
Czech Republic	43	Acids, stilbenes	HPLC	G.O.	[69]
Brazil, Chile	38	Anthocyanins	HPLC	G.O.	[70]
Romania	22	Phenols	HPLC-MS	G.O., V.	[51]

Table 2. Cont.

High-Performance Liquid Chromatography (HPLC)					
Country	Sample Number	Data Analyzed	Methods	Classification	References
Argentina		Anthocyanins	HPLC-MS	G.O., V.	[71]
Brazil, Argentina	32	Phenols	HPLC-UV/Vis	G.O.	[72]
Italy	72	Anthocyanins	HPLC	V.	[73]
Turkey	111	Phenols	HPLC	V, Vt.	[74]
Italy	22	Phenols	HPLC-DAD-MS	V	[75]
Romania, Bulgaria, Republic of Moldova	52	Anthocyanins	HPLC	G.O., Adt.	[76]
Italy	-	Phenols	HPLC	V	[77]
China	19	Phenols	HPLC-DAD	Vt.	[78]
Italy	73	Polyphenols	HPLC	G.O.	[79]
Brazil, Argentina, Uruguay, Chile	83	Phenols	HPLC-MS	G.O.	[80]
Canada	44	Phenols	UHPLC-QToF-MS	V.	[81]

Legend: DAD—photodiode array detector; DAD-MS—photodiode array detector-mass spectrometry; UV/Vis—ultraviolet-visible detector; MS—mass spectrometry; G.O.—Geographical origin; V—variety; Vt.—vintage; Adt.—Adulteration; UHPLC-QToF-MS—ultra-high-performance liquid chromatography electrospray ionization quadrupole-time-of-flight mass spectrometry.

Twenty-year-old studies have shown that anthocyanins are able to differentiate wines by variety or geographical origin. This is demonstrated in a 1999 study that aimed to classify 23 Spanish wines according to these two criteria. Using a HPLC technique, a number of anthocyanins were identified and quantified, and statistical analysis revealed that malvidin-3-acetyl-glucoside was the compound with the highest power to differentiate wines by variety. A clear separation of the same wines was achieved with p-coumaric acid ester of malvidin-3-glucoside [60].

The anthocyanin imprint was also used a few years later to distinguish some wines from Uruguay and China by variety. In the case of Uruguayan wines, delphinidin and petunidin were categorized as variety markers for Tannat, malvidin for Cabernet Sauvignon and peonidin for Merlot wines [63]. Anthocyanin composition was used to distinguish wines from China obtained from different hybrids from those of noble varieties such as Cabernet Sauvignon and Marselan [64].

Phenolic acids and stilbenes can be used, according to a Greek study conducted on 35 experimental wine samples, as markers for differentiating wines according to variety but also geographical origin. The phenolic compounds with good results in this regard were: benzoic acid, gallic acid, vanillic acid and syringic acid, but also astringin, piceid and resveratrol [65]. The same two classes of non-flavonoid phenolic compounds as in the previous study were analyzed in the case of 43 wines from five regions of the Czech Republic. Hydroxybenzoic acids, hydroxycinnamates and stilbenes were analyzed using the HPLC-MS method, and due to statistical analysis, it was possible to differentiate the wines according to geographical origin, based on the following: protocatechuic acid, p-hydroxybenzoic acid, caftaric acid, p-coutaric acid, trans and cis resveratrol. Thus, according to the two studies, it can be concluded that non-flavonoid phenolic compounds could be used as markers of geographical origin for wines [65,69].

Two studies carried out on Spanish and Austrian wines, in both cases using HPLC-MS for identification and quantification of polyphenols, showed that both Spanish and Austrian wines could be differentiated according to variety, and moreover, their phenolic profile also allowed a differentiation according to their geographical origin [66,68].



Another study conducted on 52 wines of different origins (Romania, Bulgaria and Moldova) demonstrated the possibility of using anthocyanin imprint, determined by liquid chromatography, to distinguish commercial table wines by variety. Among the analyzed anthocyanins, those on the basis of which the differentiation was made were: delphinidin-3-O-glucoside (De), petunidin-3-O-glucoside (Pt), peonidin-3-O-glucoside (Pe) and malvidin-3-O-glucoside (Mv) [76].

The phenolic composition of wines is significantly influenced by genetic and environmental factors, but the greatest contribution comes from technology. For this reason, authentication of wines using polyphenolic imprinting can sometimes be quite a challenging task [82]. This is the reason why the identification and quantification of phenolic compounds cannot sit by itself in answering authenticity issues. It can only be used as an additional or over-verification method.

### 2.2.2. Amino Acids

Free amino acids could help characterize wine by variety when studied in conjunction with other compounds that may act as variables in a multivariate analysis. The amino acid profile in wines depends on too many factors (climatic conditions, the maceration time, alcoholic fermentation, etc.) and therefore it is difficult for them to be independent markers [40].

However, sparkling wines have a richer profile of amino acids, mainly due to the second fermentation that takes place in the bottle. A study in France showed that it was possible to separate some Champagnes from other sparkling wines with a different geographical origin using the amino acid profile [83].

A 2003 study of Greek and European wines showed that the amino acid profiles of these wines provided sufficient information and, together with statistical analysis, it was possible to classify them according to geographical origin, year of production and grape variety. The main amino acids that helped to discriminate the wines were: arginine and  $\gamma$ -amino butyric acid, lysine, alanine, glycine and leucine [84].

Gas chromatography is a technique that appeared in 1952 and was later perfected and it involves the use of a mobile gaseous phase. This method allows the investigation of volatile molecules in wine with low chemical stability (such as esters, ketones, alcohols, amines, etc.). The principle of this method is to transport the organic compounds in the gas phase by a carrier gas (mobile phase) along a chromatographic column containing a solid phase with adsorbent properties. The mobile phase has both the role of moving the substances on the column to the detector and to participate in the gas-chromatographic separation [57].

### 2.2.3. Volatiles

Wine is a hydro-alcoholic solution that contains hundreds of compounds, some of them from grapes and others formed during alcoholic fermentation or during the maturation and aging of wine. The aromatic identity of a grape variety consists of combinations of flavor compounds with different concentrations. In the case of aromatic varieties, for example, terpenic compounds are more numerous and in higher concentrations than the neutral varieties, with norisoprenoids contributing the most, especially to the formation of the aroma. Most of these compounds give pleasant, floral or fruity aromas but have low perception thresholds. Wine flavor compounds (or volatile compounds) can act as a fingerprint when identifying the variety [16,85,86].

The oldest study cited in this paper, which refers to the profile of volatile compounds as a possible marker of authenticity, is from 1995. It was then possible to differentiate some Spanish wines according to geographical origin and variety based on the study of more than 100 identified volatile compounds [87].

Two other studies in Spain have shown the potential of 30 volatile compounds from different classes (alcohols, acids, esters, aldehydes) to create a varietal fingerprint, including:

3-isobutyl-2-methoxypyrazine, isoamyl acetate, isovaleric acid, ethyl isobutyrate, ethyl isovalerate, fusel alcohols, c-3-hexenol, methionol and eugenol [88,89].

Table 3 presents the results of studies from the last 25 years that aimed to analyze the aromatic profile of wine as a marker of authenticity.

**Table 3.** Studies and analytical techniques to confirm the authenticity of wines based on the quantification of aroma compounds.

Country	Sample Number	Data Analyzed	Methods	Classification	References
Spain	22	Alcohols, acids, esters, terpenes, aldehydes, acetones	GC (SPI)-MS	G.O., V.	[87]
Spain	-	Alcohols, acids, esters, aldehydes	Dynamic-headspace GC-MS	V.	[88]
Spain	52	Alcohols, acids, esters, aldehydes	GC-MS	V.	[89]
Portugal	19	Ketones, norisoprenoids	GC	G.O.	[90]
Italy	93	Terpenes, alcohols, Norisoprenoids	GC-MS	V.	[91]
China	-	Terpenes, norisoprenoids, alcohols, esters, fatty acids, volatile phenols, sulfur compounds	GC-MS	V., G.O.	[92]
China	3	Alcohols, esters, fatty acids, terpenes, aldehydes	GC-MS	G.O.	[93]
South Africa	334	Alcohols, esters, acids, aldehydes	GC-MS	G.O., V.,	[94]
Brazil	54	Alcohols, acids, aldehydes, esters, ketones, terpenes, pyrans, lactones, furans, sulfur compounds, norisoprenoids	HS-SPME combined with GCxGC/TOFMS	V.	[95]
Australia	30	Ketones, aldehydes, terpenes, esters	HS-SPME combined with GCxGC/TOFMS	G.O.	[96]
Slovakia	26	Terpenes, esters, alcohols	GC-MS	G.O., V., Vt.	[97]
France	38	Alcohols, ketones, aldehydes, esters	GC-MS	barrels vs. chips	[98]
Portugal	23	Furans, lactones, volatile phenols, acetals	HS-SPME combined with GCxGC/TOFMS	Age markers	[99]
Argentina	7	Alcohols, aldehydes, esters,	HS-SPME-GC-MS	V.	[100]
Chile, USA, France, Bulgaria, Moldova, Spain, Argentina, Australia, South Africa	120	Alcohols, acids, ketones, esters, terpenes	SPME-GC-MS	V., G.O.	[101]
Romania	3	Acids, esters, terpenes, terpenoids, norisoprenoids	GC-MS	V.	[102]
Germany	234	ketones	GC-MS	V.	[103]

Legend: GC (SPI)-MS—Gas chromatography (septum-equipped programmable injector)-mass spectrometry; GC-MS—gas chromatography-mass spectrometry; HS-SPME—headspace solid phase microextraction, GC × GC/TOFMS—two-dimensional gas chromatography with time-of-flight mass spectroscopy.

Two Chinese studies examined wines made from Cabernet Sauvignon, Cabernet Gernischet and Chardonnay from different parts of China. Both concluded that the chromatographic analysis of the volatile compounds together with the statistical analysis provided precise information regarding the origin of the wines [92,93].

A very well-conducted study on a sample of 38 French wines showed that the fingerprint of volatile compounds could also be used to differentiate wines according to the type of oak wood used to mature them (either in barrels or with wooden fragments). The method of determining the studied compounds was GC-MS combined with a multivariate statistical analysis. The classes of compounds that helped classify wines were alcohols, ketones, aldehydes and esters [98].

Noteworthy is a study of 23 Portuguese wines that identified 103 volatile compounds (furans, lactones, volatile phenols, acetals) and grouped them using statistical analysis, thus leading to their classification according to the year of production [99].

A very large study, conducted on 234 German wines, highlighted the usefulness of a single class of volatile compounds, namely ketones, to differentiate them according to the variety from which they were obtained [103].

Given that the variety of volatile compounds in wine definitely depends on the grape variety, a difficult issue is pinpointing that specific aroma compound. In this sense, a study was developed in Brazil (54 samples) establishing the two specific esters for Chardonnay (diethyl malonate and ethyl 9-decenoate) and the two specific furanones for Cabernet Sauvignon—tetrahydro-2 (2H)-pyranone and 3-methyl-2 (5H)-furanone [40].

Studies propose that red wines can be recognized by the type and concentration of specific flavor compounds [104].

For storage and stability purposes, or obtaining wines that are more commercial, semi-volatile additives can be introduced in wine. Methods have been proposed for the identification of compounds such as sorbic acid, benzoic acid and propylene glycol by GC-MS techniques [105].

### 2.3. Isotopic Ratios in Wine Authenticity

Isotopes are nuclear species with the same atomic number  $Z$ , but with a different mass number  $A$  (the same chemical properties but different physical properties). The ratio of stable isotopes of important bio-elements (H, C, O) is influenced by plant material, which in turn depends on the type of plant and the growth area. Therefore, climatic and geographical factors (e.g., humidity, temperature, precipitation, altitude, latitude, longitude) and factors concerning the photosynthesis cycle are those that actually influence the isotopic ratios, such as:  $D/H$ ,  $^{13}C/^{12}C$ ,  $^{18}O/^{16}O$  [106]. The analysis of the stable isotopic ratio has applications in the wine authentication: identification of exogenous addition of sugar in wine, identification of the addition of exogenous water but also the verification of the geographical origin of the wine. After determining one or more isotopic ratios for an analyzed given wine, it is necessary to compare them with the isotopic parameters of an authentic wine from the same region [107]. The unique fingerprint that these isotopic ratios create for each wine can be measured using mass spectrometry (isotopic ratio mass spectrometry (IRMS)) or magnetic resonance imaging (specific natural isotope fractionation—nuclear magnetic resonance (SNIF-NMR)) [108].

In addition to bio-elements, isotopic analysis has been extended and successfully applied to some heavy elements, such as Sr and Pb [109].

Table 4 presents the conclusions of some studies on the isotopic ratios used and the method of analysis in order to establish the authenticity of the wines.

**Table 4.** Studies using isotopic analysis to confirm the authenticity of wines.

Country	Sample Number	Isotopes/Ratio	Methods	Classification	References
Slovenia	102	D/H $^{13}\text{C}/^{12}\text{C}$ (ethanol); $^{18}\text{O}/^{16}\text{O}$ (water)	SNIF-NMR, IRMS	G.O.	[110]
Italy	5220	(D/H) <sub>1</sub> , (D/H) <sub>2</sub> , $^{13}\text{C}/^{12}\text{C}$ (ethanol); $^{18}\text{O}/^{16}\text{O}$ (water)	RMN IRMS	G.O.	[111]
Brazil	112	$^{13}\text{C}/^{12}\text{C}$ (ethanol); $^{18}\text{O}/^{16}\text{O}$ (water)	IRMS	G.O., Vt.	[112]
Germany	718	(D/H) <sub>1</sub> , (D/H) <sub>2</sub> , $^{13}\text{C}/^{12}\text{C}$ (ethanol); $^{18}\text{O}/^{16}\text{O}$ (water)	SNIF-NMR IRMS	G.O., Vt.	[113]
Romania	21	$^{87}\text{Sr}/^{86}\text{Sr}$	Q-ICP-MS	G.O.	[114]
Cyprus	96	D/H, $^{13}\text{C}/^{12}\text{C}$ (ethanol); $^{18}\text{O}/^{16}\text{O}$ (water)	SNIF-NMR IRMS	G.O.	[115]
Romania, Bulgaria, Republic of Moldova	52	$^{13}\text{C}/^{12}\text{C}$ (ethanol); $^{18}\text{O}/^{16}\text{O}$ (water) D/H	CF-IRMS SNIF-NMR	G.O.	[76]
Macedonia, Montenegro, Chile		D/H $^{13}\text{C}/^{12}\text{C}$ (ethanol); $^{18}\text{O}/^{16}\text{O}$ (water)	SNIF-NMR IRMS	Adt., G.O.	[116]
France	60	$^{87}\text{Sr}/^{86}\text{Sr}$	MC-ICP-MS	G.O.	[117]
France	60	$^{206}\text{Pb}/^{207}\text{Pb}$ , $^{208}\text{Pb}/^{206}\text{Pb}$ , $^{206}\text{Pb}/^{204}\text{Pb}$ , $^{208}\text{Pb}/^{204}\text{Pb}$	MC-ICP-MS	G.O.	[118]
Portugal	3	$^{87}\text{Sr}/^{86}\text{Sr}$	Q-ICP-MS	Wood aging	[119]
Russia	9	$^1\text{H}$ , $^2\text{H}$	qNMR	G.O., Adt.	[120]
France	29	$^1\text{H}$	qNMR	G.O.	[121]

Legend: The ratio between deuterium and hydrogen of the methyl group in alcohol is indicated with (D/H)<sub>1</sub>, the corresponding ratio in the alcohol methylene group with (D/H)<sub>2</sub>. SNIF-NMR—site-specific natural isotope fractionation—nuclear magnetic resonance; IRMS—isotopic ratio mass spectrometry; Q-ICP-MS—quadrupole inductively coupled plasma mass spectrometry; MC-ICP-MS—multi-collector ICP-MS; qNMR—quantitative NMR spectroscopy.

A study from 2013, aimed at differentiating experimental Brazilian wines by production area, concluded that the ratio of stable oxygen isotopes ( $^{18}\text{O}/^{16}\text{O}$ ) was more effective in differentiating Merlot wines by area of origin, while for Cabernet Sauvignon wines, the  $^{13}\text{C}/^{12}\text{C}$  ratio was more useful. At the same time, the authors pointed out that a multivariate statistical analysis of the two isotopic ratios ( $^{18}\text{O}/^{16}\text{O}$  and  $^{13}\text{C}/^{12}\text{C}$ ) showed large differences between the two harvests (which took place at 15-day time intervals) [112].

In 2017, a study was conducted on some Cypriot wines in which isotope variations in relation to the grape variety and some environmental factors were monitored. SNIF-NMR and IRMS were the two applied techniques and the conclusions confirmed the hypothesis from which the study started; moreover, a multivariate statistical analysis confirmed the possibility of discriminating wines according to production year by correlating the isotopic analysis with that of metals [115].

Two studies carried out in the last two years in France on 100% authentic Bordeaux wines compared to non-authentic wines concluded that both the isotopic ratios,  $^{87}\text{Sr}/^{86}\text{Sr}$  but also  $^{207}\text{Pb}/^{204}\text{Pb}$ ,  $^{208}\text{Pb}/^{206}\text{Pb}$  and  $^{206}\text{Pb}/^{204}\text{Pb}$ , can be used to authenticate the wines from this region [117,118]. In contrast, a recent study in Portugal on the impact that the maturation of wine in contact with oak wood may have on the isotopic ratio  $^{87}\text{Sr}/^{86}\text{Sr}$  concluded that this isotopic ratio cannot be influenced by this maturation process [119].

Two studies on wines from France and Russia have highlighted a new possible approach to the authenticity of wine, namely qNMR (quantitative nuclear magnetic resonance spectroscopy), which allows a quantitative identification of  $^1\text{H}$  and  $^2\text{H}$  isotopes in wine

water, thus obtaining information on the geographical origin of the wine or the possible addition of water to the wine [120,121]. Such an analysis could be a complementary analysis to the classical one for determining the D/H isotopic ratio, being a cheaper, faster analysis, which allows the measurement of several parameters on a very small volume of wine, without requiring any sample preparation [122].

Methods of stable isotope analysis for wine have been used since 1990 (when the SNIF-NMR method was officially adopted by the European Commission), when it was used to detect added sugars in wine [123]. As it can be observed, from that time until now, new methods for wine authentication based on stable isotope analysis have been developed, so a large amount of data could be collected in this direction [124]. Today, the stable isotope ratios of wine components not only allow the authentication of a wine but can also provide information about the viticultural conditions [125].

#### 2.4. DNA Analyses: Variety Authentication

To authenticate the variety from which a particular wine was made, an efficient and accurate method is that based on the identification, extraction and amplification of microsatellites of DNA. It can be used as a stand-alone method or in conjunction with methods for analyzing chemical profiles of wines. The high stability of DNA at high temperatures and low pH and its independence from environmental conditions are two of the main advantages of this method [77]. A microsatellite is a repetitive DNA segment in which certain DNA motifs are usually repeated 5 to 50 times. They have a higher mutation rate than other areas of DNA and are found at thousands of sites in an organism's genome. Microsatellites are often referred to by plant geneticists as simple sequence repeats (SSRs) [126]. Microsatellites can be amplified for identification by the polymerase chain reaction (PCR) process [127].

The main steps in DNA-based analytical methods are identifying the most efficient method for extracting DNA from wine and establishing optimal polymerase chain reaction (PCR) conditions for its sufficient amplification for detailed analysis and confirmation of the variety by comparison with a known DNA sequence [128]. However, there are some limitations with this method: DNA-degrading factors (clarifications of musts or wines, fermentation process, wine polyphenols, long-term storage of wine, etc.), and complex process of DNA separation, which, if not efficient, may lead to impossibility of amplification of DNA for its study [129,130].

Table 5 presents the results of several studies carried out in the last decade, that have materialized by identifying the varieties used in wine production after applying DNA extraction methods and analyzing them by one of the PCR or real-time PCR techniques.

**Table 5.** Studies using DNA extraction used to confirm the authenticity of wine.

DNA Based Methods			
Country	Varieties	Methods	References
Portugal	Tinta Roriz, Fernao Pires	Extraction + PCR	[131]
Italy	Merlot, Pinot noir, Zinfandel, Italian Riesling, Sauvignon blanc, Sangiovese, Alicante	Extraction + real-time PCR	[132]
Italy	Moscato bianco	Extraction + PCR	[133]
Romania	Tămâioasă românească, Galbenă de Odobești, Fetească neagră, Busuioacă de Bohotin	Extraction + PCR	[134]
Italy	Cabernet, Sauvignon, Merlot, Pinot Noir, Syrah, Chardonnay, Pinot Gris	Extraction + PCR	[135]
Italy	Sangiovese, Alicante, Cabernet sauvignon, Merlot	Extraction + PCR	[136]

In the literature, there are both examples of research (such as those reported in the table above) that have led to the successful identification of one or more varieties used

in the production of wines using DNA-based methods, but also research that did not face the same success [126]. A study from 2016 involving the extraction of DNA from vine leaves, grape must and then wine, while comparing microsatellites, confirmed the authenticity of the varieties mentioned on the labels of some Portuguese commercial wines [131]. The usefulness of microsatellites in determining the genetic traceability of mono-varietal sparkling wines was demonstrated in a 2012 study which concluded that after multiplication and analysis, seven SSR markers specific to chloroplast sequences (cpSSR) resulted in a unique genetic profile for the variety Moscato bianco [133].

Unfortunately, there are also situations when due to the limitations of the method, either a sufficient amount of DNA could not be extracted from the wine to be analyzed, or it could not be amplified by PCR (due to the type of matrix and the interferences that take place between tannins, polysaccharides and polyphenols) [137]. These were also the impediments encountered in a 2016 study, whose conclusions showed that it was impossible to authenticate the Sangiovese variety from a Brunello di Montalcino wine with a method based on DNA characterization [138].

## 2.5. Others Techniques and Analytical Methods for Wine Authenticity

### 2.5.1. Capillary Electrophoresis

Capillary electrophoresis encompasses a number of electro-kinetic techniques that have the task of separating compounds based on either differences in electrophoretic mobility, phase partitioning, or molecular size, or a combination of these properties. To date, capillary electrophoresis has been used as a technique of food analysis in several ways: CZE (capillary zone electrophoresis), CIEF (capillary isoelectric focusing), CITP (capillary isotachopheresis), CGE (capillary gel electrophoresis) and CEC (capillary electrochromatography), all in order to analyze and characterize a wide range of simple inorganic ions, small organic molecules, nucleic acids, proteins, peptides, etc. [139].

Capillary electrophoresis has been successfully used in the identification and quantification of resveratrol in wine. Unlike HPLC techniques, the CE method is faster but with similar sensitivity and the possibility of differentiating between the cis and trans isomers of resveratrol. This method is shown to be promising for the determination of glycosides or aglycones in wine [140].

A 2004 study described a possible protocol to be used for the rapid identification of phenolic acids in wine (gentisic acid, ferulic acid, vanillic acid) and other foods using capillary-electrophoresis, in order to characterize them [141].

Capillary electrophoresis was also applied for the evaluation of proteins and shikimic acid in wines. HPCE (high-performance capillary electrophoresis) was the technique used in a 2008 study, which led to the characterization of the wines according to the variety used [142].

The results obtained by Moreno-Arribas et al. conclude that the analysis of must proteins by capillary electrophoresis is an easy-to-use technique and has been successfully implemented in identifying the grape varieties from which the analyzed musts came [143].

### 2.5.2. Sensorial Analysis (e-Tongue, e-Nose)

The electronic tongue (e-tongue) is an analytical tool that measures the intensity of tastes and compares them. It includes a set of non-selective chemical sensors with specificity for different components in a given solution and a recognition tool capable of identifying the qualitative and quantitative compositions of simple or complex solutions. The multi-electrode sensors of the electrical device detect organic and inorganic compounds, with each sensor having a different reaction spectrum than the other. The detection thresholds are similar to or better than those of human receptors. Combining the results from all sensors produces a unique fingerprint for each evaluated product [144]. Such a device was used in a 2019 study on Tokaji wines and helped separate those sweetened by adding concentrated must from those obtained naturally by botrytized grape berries during production [145].



Electronic noses are devices of various types and operating principles that are widely used as analytical tools in the beverage industry. An electronic nose consists of a series of sensors that collect chemical signals, which it then analyzes and interprets in a way that mimics the human nose. E-nose tools are constantly improving. From the first devices in this category, which were simple matrices of several sensors based on polymers and metal oxide semiconductors, modern devices based on gas chromatography have been used in recent years [146]. Electronic noses can provide many ways to authenticate wines, including distinguishing wines by variety, geographic origin and year of production [147].

The study by Antocea and Nămoleşanu concluded that the wine samples analyzed with an e-nose can be categorized by geographical origin and variety if the selection of the sensors (peaks) used in the statistical analysis is rigorous and correct [148].

### 3. Conclusions

Since not all chemical compounds and minerals are modified during the winemaking process, the selected ones can be considered good markers in wine authenticity.

The assessment of the stable isotope ratios offers adequate evaluation about the grape variety and the geographical origin of wine, while also being used for spotting adulteration (like water or sugar addition).

Analyses based on DNA are smart solutions for accurate and proficient variety identification of wines. These methods can be used as an alternative to or in combination with chemical profiling.

In general, volatile substances are used to label varieties, while minerals can influence geographical classification. Amino acids and phenolic compounds can stand in for both purposes.

To analyze different target components, to assess the geographical origin of the wine and to detect adulterations, different instrumental techniques are used. High-performance liquid chromatography (HPLC), mass spectrometry (MS), gas and liquid chromatography (GC, LC), atomic absorption spectroscopy (AAS), and inductively coupled plasma optical emission spectrometry (ICP-OES) or inductively coupled plasma mass spectrometry (ICP-MS) are most commonly found in the scientific literature.

In all the quoted articles, a huge role was played by the statistical interpretation of the results, using chemometrics and other various software that help to cluster the samples or compounds that play a role in authenticity.

The bibliographical study shares different perceptions on analysis methods used for wine authenticity, an issue that has been at the core of consumer trust for centuries. However, it must be taken into consideration that some fundamental requirements such as comprehensive databases and properly regulated traceability systems are a definite must for the success of the analysis.

The extensive bibliographical research that was carried out will stand as a theoretical base in a practical research study conducted on Romanian wines and their authenticity degree.

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