

Review

Advancements in Analytical Strategies for Authentication and Quality Control of Grappa and Wine Brandy with Geographical Indications

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Abstract: In recent years, food authentication has acquired significant importance due to the increase in the incidence of fraud and counterfeiting. Alcoholic beverages are among the food products most susceptible to these kinds of illicit practices due to their high commercial value. In the EU alone, there are 47 categories of spirit drinks and approximately 250 geographical indications (GIs). The production and labeling of GIs are strictly regulated, and developing analytical procedures that can ensure compliance with the legislation is essential to guarantee the typicality of these products. The aim of this review is to summarize the most relevant analytical techniques used for the authentication and quality control of two well-renowned GIs: “Grappa” and wine brandy. It considers the last decade of advancements for both conventional targeted chromatographic techniques and less common methods mainly based on spectrometry coupled with chemometrics for quick and non-destructive discrimination of samples. Novel approaches and future perspectives are also highlighted.

Keywords: geographical indication; rappa; wine brandy; analysis; authentication; quality control



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1. Introduction

The issue of food authentication has become particularly relevant in recent years due to the intensification of illegal practices such as fraud and counterfeiting. Alcoholic beverages are particularly subject to these practices because of their high demand and their significant impact on the economic sector of many countries [1]. In the EU alone, there are 47 categories of spirit drinks and approximately 250 geographical indications (GIs) from different countries [2]. The quality, sensory features and reputation of GIs are strictly linked to the country, locality or region of their geographical origin [3]. A recent study found that the sales value of a product with a protected name is, on average, double that of similar products without a certification [4]. Alcoholic beverages with GIs include, among others, “Grappa” (Gr) and “Brandy Italiano” from Italy and GI Brandy from other European countries, such as “Brandy de Jerez” from Spain, “Deutscher Weinbrand” from Germany and “Brandy Français” from France. These beverages must comply with the category standards set by the EU Commission regarding presentation, labeling, origin and production process [5] as well as with the peculiar GI product specifications. “Grappa”, for instance, can only be produced from grapes grown, vinified, distilled and fined in Italy [6], while “Brandy de Jerez” is obtained and aged in the Spanish province of Cádiz only in the three localities of Sanlucar de Barrameda, Jerez de la Frontera and El Puerto de Santa Maria [7] following specific production steps described in the product specification itself. It is evident that the ability to verify the origins and technological paths of these products is crucial for counteracting fraud. Different approaches have been developed to verify compliance with the above-mentioned regulations and authenticate Gr and wine brandy (WB) GIs. Many of these approaches use traditional analytical techniques such as chromatography, mainly coupled to mass spectrometry, with the aim of identifying marker compounds for discrimination [8]. These methodologies are very effective but

often time- and/or sample-consuming and expensive. Other approaches use different techniques mostly based on spectroscopic methods and, to a lesser extent, other methods such as those based on multisensory systems (electronic nose and tongue) coupled with chemometrics to obtain an overall profile of the many compounds constitutive of the product without identifying specific congeners. These untargeted methods are usually rapid, non-destructive and cost-effective. Both approaches can furnish accurate results in terms of discriminating power and have both advantages and disadvantages. The aim of this review is to provide an overview of studies on the techniques for the authentication and quality control of distillates with a specific target on Gr and WB GIs, covering the research carried out in the last decade. The subject has been divided into five main chapters concerning spectroscopic, chromatographic and hyphenated methods; sensor arrays; multi-platform techniques; and other methods. For each chapter, the pertinent chemometric methods are briefly described, directing the reader to basic references for more in-depth explanations. In the final chapters, an overview of chemometric tools applied in the authentication of Gr and WB GIs and technical challenges and future perspectives are highlighted.

2. Analytical Strategies for Authentication and Quality Control

2.1. Spectroscopic Methods

Spectroscopic methods are used to determine the authenticity of alcoholic beverages, commonly by adopting an untargeted approach [8]. The present chapter focuses on studies concerning infrared (IR), Raman and fluorescence spectroscopic techniques, which emerged as the most effective for Gr and WB GI authentication. Other spectroscopic methods, such as ultraviolet–visible (UV–VIS) and nuclear magnetic resonance (NMR), successfully applied for other categories of spirit drinks or other GIs [9–11], appear to be less considered in the recent literature for such a scope. An NMR application for Gr discrimination according to the aging technology is presented at the end of the chapter on multi-platform techniques.

2.1.1. Infrared Spectroscopy

IR showed good potential in food authentication as a fast, low-cost analytical technique with minimal sample preparation, demonstrating the capacity to identify different compounds or classes of compounds [12,13]. IR theory utilizes the concept that different functional groups display different absorption frequencies. In this way, it is possible to identify compound categories present in foodstuffs, such as proteins, carbohydrates, lipids, vitamins and minerals [14]. The IR region of the electromagnetic spectrum spans from 14,000 to 50 cm^{-1} and is divided into three areas: near-IR (14,000–4000 cm^{-1}), mid-IR (4000–400 cm^{-1}) and far-IR (400–50 cm^{-1}) spectroscopies [15]. In particular, near-IR (NIR) and mid-IR (MIR) spectroscopies have proven to be efficient and cost-effective compared to reference analysis methods. A study on the quality control of a group of 166 grape-derived spirits was carried out to predict some legally relevant parameters, namely the alcohol strength and contents of methanol, acetaldehyde and fusel alcohols, by applying Fourier transform infrared (FTIR) spectroscopy with attenuated total reflectance (ATR) in the MIR region and partial least square (PLS) chemometric regression models [16]. The comparison of the results with those obtained with official methods based on gas chromatography coupled with flame ionization detection (GC-FID) and densimetry [17,18] showed satisfactory correlation coefficients for methanol ($r^2 = 99.4\%$), alcoholic strength ($r^2 = 97.2\%$), acetaldehyde ($r^2 = 98.2\%$) and fusel alcohols (r^2 from 97.4% to 94.1%). The same dataset allowed the determination of the ratio of performance to deviation of the method, obtaining values of 12.8 (methanol), 6.0 (alcoholic strength), 7.5 (acetaldehyde) and 6.2–4.1 (fusel alcohols); a value of 2.5 is the minimum threshold for a reliable calibration [19]. These results demonstrated the good accuracy of the proposed method for quick and easy sample screening. Another study showed the potential of NIR spectroscopy to predict the aging time of brandies. [20]. The authors applied NIR spectroscopy combined with principal component analysis (PCA), PLS and linear discriminant analysis (LDA) to discriminate the samples. Ethanol, esters, acids, methanol and higher alcohols were also determined

(with official methods) to obtain reference values to correlate with NIR spectra. The study showed that the most significant regions of the NIR spectra (linked to phenolic and aromatic compounds) were in the ranges from 904 nm to 935 nm and from 1400 nm to 1699 nm.

The same authors found that the PCA based on the phenolic composition and on alcohols with a higher molecular weight allowed the best discrimination between brandies of different ages. Furthermore, the same authors developed some PLS calibration models for each parameter evaluated, i.e., total phenolic content, total higher alcohol content and total phenolic plus higher alcohol content, and an LDA classification model based on individual phenols with a classification rate of 100%. Other authors [21] studied the capacity of NIR to discriminate between wine spirits aged in wooden barrels or in stainless-steel tanks with wooden staves made from different types of wood (Limousin oak and Portuguese chestnut). They determined the alcoholic strength and the main volatile compounds in wine spirits aged for 6, 12 and 18 months by electronic densimetry and by GC-FID. The same samples were analyzed by NIR spectroscopy coupled to PCA. The results showed that the aging technology had more influence than the type of wood on the features of the samples and that the most significant spectral regions for differentiating the samples were around 6859 cm^{-1} and from 5200 cm^{-1} to 4200 cm^{-1} . Another study [22] applied MIR and NIR spectroscopies combined with four different chemometric methods to discriminate between Gr and other spirits and between authentic and adulterated Gr. In the discriminating part of the study, 59 samples of pure Gr and 17 fruit and cereal distillates were analyzed. The NIR and MIR spectra were processed, separately, by PLS-DA [23,24] and simultaneously by three different data fusion tools, namely multi-block partial least squares (MB-PLS-LDA) [25,26], sequential and orthogonalized covariance selection (SO-CovSel-LDA) [27] and sequential and orthogonalized partial least squares (SO-PLS-LDA) [28]. The best strategy was the data fusion carried out with SO-PLS-LDA and SO-CovSel-LDA, which provided the best results with classification rates around 77% for Gr and 60% for the other spirits. In the second part of the work, a group of 36 different Gr spirits, intentionally adulterated with vodka, was analyzed by NIR and MIR spectroscopies. The resulting NIR and MIR spectra were processed individually by PLS-DA and simultaneously by multi-block analysis. All the obtained models showed very good prediction capabilities (up to 100% classification rate).

2.1.2. Raman Spectroscopy

Raman spectroscopy is an optical measurement technique that provides information on molecular composition based on the inelastic scattered light from a sample when excited by a laser beam. The photons of a laser beam interact with the molecules of the matrix: a part of the radiation diffuses elastically in all directions without loss of energy, that is, at the same frequency as the incident radiation (elastic or Rayleigh scattering), while a smaller part is diffused inelastically yielding (Raman scattering Stokes) or gaining (anti-Stokes Raman scattering) energy [29]. It is possible to obtain information about the vibrational modes of molecules from the energy shift obtained. Raman spectroscopy is widely used to identify molecules and detect functional groups. [29]. Its main advantages are the high analytic selectivity and the possibility of carrying out rapid “in situ” analysis through plastic or transparent glass containers, thus limiting contact with the sample. Recently [30], Raman spectroscopy (performed at an excitation wavelength of 532 nm) combined with chemometric algorithms and machine learning was applied to classify 42 brandy and cognac samples with various geographical origins and aging times. To compute the chemometric models, the range of Raman shifts between 800 cm^{-1} and 300 cm^{-1} was selected because it was considered the most informative. The chemometric classification models were processed by an extreme gradient boosting (EGB) algorithm [31], reaching an accuracy of 100% for both geographical origin and aging period. With the aim of differentiating wine spirits based on aging time, wood species and aging technology, other authors [32] applied the FT-Raman methodology to 60 samples of differently aged wine spirits. The Raman spectra processed by PCA confirmed the good capabilities of FT Raman to discriminate the differently aged samples. The most relevant regions to observe differences were in the range from 3000 to

2600 cm^{-1} and from 1570 to 790 cm^{-1} . Despite the rather limited number of applications in the field of distillates, Raman spectroscopy combined with multivariate analysis or machine learning techniques appears to be a promising technique for the authentication of brandy spirits especially because it allows, in many cases, obtaining very specific chemical information without sample manipulation.

2.1.3. Fluorescence Spectroscopy

Fluorescence spectroscopy is a technique that is gaining importance in the analysis of beverages due to its sensitivity and selectivity. Fluorescence spectra of beverages generally consist of broad, overlapping fluorescent bands containing chemical and physical information about different components of the sample. WB GIs contain several fluorophores, but there are relatively few recent works about the use of fluorescence on these matrices, most of which use a fluorescence excitation spectrum recorded at one emission wavelength [33,34]. A technique that provides more detailed information on fluorescent species is excitation-emission matrix (EEM) fluorescence spectroscopy. Using this technique, all fluorophores within the sample are excited simultaneously over the explored wavelength range, allowing the collection of all excitation and emission spectra and obtaining the total fluorescence spectrum of the sample. This analytical approach, with front-face and right-angled arrangements, combined with specific chemometric calibration tools, namely parallel factor analysis PARAFAC multiple linear regression (MLR) and PARAFAC-PLS, was applied to quantify mixed wine spirits in some adulterated brandy blends [35]. The most promising results were obtained using right-angled geometry and PARAFAC-PLS. This approach allowed the determination of the presence of wine spirit mixed in the adulterated brandy with a coefficient of determination of 0.995% at a level below 1.9% (*v/v*). The same approach was used in another work [36] to quantify the amount of water and ethyl and methyl alcohols in adulterated brandy mixtures, obtaining root mean square prediction errors < 0.24% and coefficients of determination in prediction > 0.993. Another technique frequently applied to analyze spirit drinks is synchronous fluorescence spectroscopy (SFS). It is based on the simultaneous scanning of excitation and emission signals with a fixed wavelength range with the aim of obtaining more resolved spectra than those coming from conventional fluorescence spectroscopy [37]. Some authors compared SFS spectra with emission spectra (both processed by PCA) and with EEM spectra (processed by unfold PCA and PARAFAC) to authenticate 44 brandy samples based on their geographical origin [38]. The SFS method performed at two wavelength ranges (20 and 60 nm) on diluted samples showed the best performance with 95.5% correct classification. Innovative techniques such as SFS, which appear to have a high potential for brandy authentication, highlight the importance of accurate data analysis in order to have good discriminating power.

In Table 1, an overview of the main features of the cited studies on spectroscopic techniques for the authentication of Gr and WB is reported.

Table 1. Overview of spectroscopic techniques for the authentication of Grappa and wine brandy GIs.

Samples	Discriminating Parameters	Method of Analysis	Data Analysis	Results	References
Grape marc spirits, wine spirits and brandies (166 samples in total)	Screening analysis for alcoholic strength and content of methanol, acetaldehyde and fusel alcohols	FTIR-ATR spectroscopy in the MIR region (4000–400 cm ⁻¹)	PLS	Accuracy values: methanol ($r^2 = 99.4\%$; RPD = 12.8); alcoholic strength ($r^2 = 97.2\%$; RPD = 6.0); acetaldehyde ($r^2 = 98.2\%$; RPD = 7.5); and fusel alcohols (r^2 from 97.4 to 94.1%; RPD from 6.2 to 4.1).	[16]
Wine spirits (5 not aged, 2 aged briefly and 6 aged for a long time) + 3 commercial brandies	Aging duration	NIR spectroscopy (904–935 nm and 1400–1699 nm).	PCA, PLS, LDA	Accuracy values: total phenolic content ($R^2 > 0.95$; RPD > 4.0); total fusel alcohol content ($R^2 > 0.90$; RPD > 3.0).	[20]
40 wine spirits aged for 8, 180, 365 and 540 days with different aging technologies (wooden barrels and micro-oxygenation and staves) and wood species (Chestnut and Limousin oak)	Aging technology and duration	NIR spectroscopy (12,500–4000 cm ⁻¹) and GC-FID for major volatile compounds	PCA	Discrimination between wine spirits based on the wood species used, as well as the aging technologies, with an accuracy of up to 90% (for a specific aging time).	[21]
59 pure Grappa samples + 8 pear distillates + 4 cereal distillates + 3 apple distillates + 2 distillates of berries and 36 mixtures Grappa–Vodka	Spirit drink categories	MIR (400–4000 cm ⁻¹) and NIR (10,000–4000 cm ⁻¹) spectroscopies	PLS-DA (on NIR and MIR spectra separately), MB-PLS, SO-PLS, SO-CovSel PLS-DA (on NIR and MIR spectra simultaneously)	Best classification rate for discrimination between Grappa and other distillates (% on test set): 79.6 with SO-PLS-LDA and SO-CovSel-LDA (data fusion). Best classification rate for discrimination between pure and adulterated Grappa (% on test set): 100 with PLS-DA on MIR, and 100 with SO-PLS-LDA and SO-CovSel-LDA (data fusion).	[22]
60 wine spirits aged with Limousin oak, Portuguese chestnut and Limousin oak + Portuguese chestnut for 8, 30, 180 and 360 days in barrels and stainless-steel tanks with staves of the same types of wood	Aging period, type of wood and aging technology.	Raman spectroscopy (excitation wavelength: 1064 nm; range of Raman shifts: from 70 to 3500 cm ⁻¹)	ANOVA, PCA	Ratio of calibrated to validated residual variance of 0.5; ratio of validated to calibrated residual variance of 0.75; and residual variance increase limit of 6%. Most relevant spectral regions: from 3000 to 2600 cm ⁻¹ and from 1570 to 790 cm ⁻¹ .	[32]

Table 1. Cont.

Samples	Discriminating Parameters	Method of Analysis	Data Analysis	Results	References
16 brandies (4 brands \times 4 batches from each brand) from 3 different producers + 60 mixed wine spirits (15 brands \times 4 batch from each brand) from 5 different producers + 62 brandies adulterated with mixed wine spirits	Pure brandies from adulterated brandies with mixed wine spirit	EEM fluorescence spectroscopy (emission wavelength range 485 \div 580 nm. Excitation wavelength range 363 \div 475 nm)	PARAFAC-PLS, PARAFAC-MLR	Determination of mixed wine spirit in adulterated brandy at levels down to 1.9% (<i>v/v</i>). Coefficient of determination (R^2) between the reference content and the predicted values of 0.995.	[35]
44 brandies produced in different countries	Geographical origin	SFS ($\Delta\lambda = \lambda_{\text{emission}} - \lambda_{\text{excitation}}$) and EEM fluorescence spectroscopies	PCA-LDA, UPCA-LDA, PARAFAC-LDA	Highest total correct classification: 95.5% (SFS recorded at $\Delta\lambda = 20$ and $\Delta\lambda = 60$ nm on diluted samples).	[38]

2.2. Chromatographic and Hyphenated Techniques

One of the most important parameters for evaluating the quality, safety and authenticity of alcoholic beverages is the content of volatile compounds, named congeners. These molecules are formed together with ethanol in the processes of fermentation, distillation and maturation. Chromatographic techniques, most commonly GC-FID and GC coupled to mass spectrometry (GC-MS), are the techniques traditionally used for the determination of these compounds. The European Commission Regulation n. 2870/2000 [18], which establishes community reference methods for the analysis of spirit drinks, provides a GC-FID method for the determination of acetaldehyde, higher alcohols, ethyl acetate and methanol, which are parameters that must be checked for compliance with the legal limits prescribed for the category of spirit drink by the European Regulation n. 2019/787 [5]. In accordance with the official method mentioned above, some authors [39] proposed a faster method with good accuracy and precision parameters to quantify 16 main volatile compounds, including acetaldehyde, ethyl acetate, methanol and propan-1-ol, by using Fast GC. Fast GC includes fast, direct heating/cooling technology that reduces post-run cooling and steep temperature gradients in combination with a high-pressure operating column. According to the authors [39], this combination allowed them to achieve a total analysis time of 8 min instead of the 40 min of conventional GC-FID while improving analytical performance and achieving lower LOQ and LOD values. The Fast GC method was tested on eight different spirits (including brandy) and wines supplied by proficiency-testing providers or taken from the market. Another proposal to improve the official GC-FID method by using the ethanol already present in the sample as an internal standard instead of 4-methylpentan-2-ol (as indicated in the reference method) is reported in a more recent study [40]. The method, developed to quantify the 10 main volatile compounds subjected to regulatory limits, was tested on 25 samples of spirits (including Gr and WB) and, after validation, was compared with the official method with regard to parameters of precision. A comparison of the results obtained through the two methods displayed non-significant differences from -1.3 to 0.9% at $p \leq 0.05$. The advantages of using pre-existing ethanol as an internal standard are many. The European regulation, in fact, requires congeners concentrations to be expressed as mass of congener (in g) per 100 L of ethanol in the sample. This implies determining the density and the ethanol content for each sample by distillation and densimetry, respectively. These sample preparation steps, combined with the addition of the internal standard, increase the measurement uncertainty as well as the time required for the analysis. With the proposed method the concentrations of the congeners are directly expressed in grams per 100 L of ethanol without any other analytical step, eliminating further sources of uncertainty and significantly shortening the analysis times. Another study [41] demonstrated the potential of GC-FID combined with LDA and PCA to verify the authenticity of Gr samples. The authors analyzed the content of the 10 main volatile substances mentioned above and the alcoholic strength of 123 spirit drinks belonging to different categories, including Gr, wine spirit, grain spirit and fruit spirit. The data were processed by LDA to develop a classification model in which to project two samples considered not compliant for flavor. The model, previously validated, provided a percentage of correct classifications higher than 97% in both cross-validation and external validation. To verify the assignment of the LDA model to the "wine spirit" category, the authors computed two one-class PCA models for the "Grappa" and "wine spirit" categories, finding that the suspect samples did not belong to any of the classes considered, as incorrectly predicted by the LDA model. This study highlighted the intrinsic problem inherent in LDA models: the algorithm assigns a projected sample to one of the categories used to develop the model even if the unknown sample belongs to a category not represented in the model itself as, in fact, occurred in the case reported in that study. Other authors [41] evaluated the effectiveness of headspace solid-phase microextraction gas chromatography-mass spectrometry (HS-SPME/GC-MS) coupled with two different chemometric tools, PLS-DA and Soft Independent Modelling by Class Analogies (SIMCA), as an analytical approach to discriminate 60 Gr samples with GI from 22 fruit and cereal

distillates produced in the same geographical area. SPME was performed using a 50/30 μm (divinylbenzene/carboxen/polydimethylsiloxane) DVB/CAR/PDMS fiber. The PLS-DA model provided the best results with the correct classification of all but one test sample. To identify the chemical markers that gave the greatest contribution in discriminating Gr from other categories of spirit drinks, the Variable Importance in Projection (VIP) indices were calculated [42,43]. Compounds with a VIP index > 1 are considered significant for discrimination. Several discriminating compounds were identified, including α -terpinene, α -terpineol, ethyl heptanoate, ethyl dodecanoate and furfural. Interestingly, the same discriminating compounds for Gr spirits were also identified by other authors [44]. These authors analyzed 34 samples of Gr and Gr liqueurs of different brands using an integrated approach based on SPME-GC-MS (to identify compounds of the volatile fraction) coupled with chemometrics, the matrix-assisted laser desorption ionization time of flight mass spectrometry (MALDI-TOF/MS) technique (to determine the fingerprint of the non-volatile fraction) and MALDI-TOF MS/MS (to identify the components of the non-volatile fraction). SPME was performed using a 50/30 μm DVB/CAR/PDMS fiber, as in the previous study. PCA analysis of SPME-GC/MS data of volatile compounds highlighted that Gr samples were discriminated by brand and that the most important marker compounds were ethanol and, to a lesser extent, ethyl esters of decanoic and octanoic acids, ethyl acetate and 1-pentanol. The MALDI-TOF MS technique allowed the simultaneous determination of many compounds of the non-volatile fraction, showing the differences at a qualitative and semi-quantitative level between the analyzed samples. This method proved to be an effective approach for reliable discrimination between the analyzed Gr samples. A more in-depth structural analysis of molecules within spectra performed by MALDI-TOF MS/MS allowed the identification of 12 non-volatile organic molecules. Furthermore, MS/MS spectra of some samples showed the presence of 5-methylfuran resulting from the degradation of carbohydrates during the aging period inside the barrels. Another technique used in the analysis of Gr volatile compounds is comprehensive bidimensional gas-chromatography (GCxGC or 2D-GC). It can provide more sensitivity and selectivity if compared with the more conventional GC-MS. In a work [45], HS-SPME/GCxGC-ToF/MS and HS-SPME/GC-MS were used to study the changes in the composition of volatile substances of an unaged Gr during the storage period and the relationship of those compounds with sensory attributes. After HS-SPME (performed using a DVB/CAR/PDMS 50/30 μm fiber), the separation of the volatile substances was carried out with a GC-MS and then with a 2D-GC system working with two columns with moderate difference in polarity. This study demonstrates how 2D-GC analysis could be effective in determining compounds with similar chromatographic features that would be unresolved in one-dimensional analysis, allowing a greater number of compounds to be determined and correlated to sensory analysis. Besides Gr from Italy, other popular grape marc distillates with GI are Orujo from Spain, Eau-de-Vie de Marc from France and Greek Tsipouro [46]. Outside Europe, Brazil produces a grape mark spirit named Grappa with a production technology similar to that of Italian Grappa. To authenticate the geographical origin, comparative studies have been carried out in the past years [47] and more recently [48] between some of these spirit drinks and Italian Gr. In the most recent study [48], 28 compounds were determined by GC-FID and GC-MS to discriminate 15 samples of Italian Gr from 6 samples of Brazilian Grappa. The results of chemometric analysis using PCA and hierarchical cluster analysis (HCA) demonstrated the method's capability to discriminate between the two groups of grape mark spirits. Furthermore, analysis of variance (ANOVA) highlighted that methanol, diethyl succinate, isoamyl alcohol and propanol were the main discriminating compounds between the two sample groups. Although traditionally, Gr is not aged in wooden barrels, in the last two decades, Gr producers have started to age Gr spirits to meet the demands of the world market. For this reason, studies comparing the composition of this distillate according to different aging techniques are of increasing interest. Some authors used the SPE-GC-MS technique to compare the profile of volatiles present in Gr aged in oak casks with that present in Gr aged in cherry casks [49]. In that study, the effects of grape variety

(Cabernet Sauvignon/Merlot blend and Prosecco) and ethanol content (55% and 68% *v/v*) on the overall volatile profile were also considered. The results showed that Gr aged in oak barrels was ten times richer in volatile substances than Gr aged in cherry barrels and that the compounds most affected were coniferaldehyde, syringaldehyde, vanillin, eugenol and guaiacol derivatives. Furthermore, both ethanol content and grape variety influenced the extraction of volatiles from wood, with higher contents found for the Prosecco variety with 55% *v/v* ethanol. There is no legal obligation for producers to declare the wood seasoning conditions on the label, although they sometimes choose to claim this feature to differentiate their products from similar ones. It is, therefore, important to develop useful methods for verifying the declared seasoning protocols. In this regard, very recently [50], ionic chromatography (for the determination of organic acids) and GC-FID (for the determination of volatile compounds) coupled with chemometric tools have been used to characterize Brandy de Jerez aged in sherry casks seasoned for 0, 3, 6, 12, 18 and 60 months with different sherry wines. The study showed that the factors that mostly influenced the composition of organic acids and volatile substances of the brandies under investigation were the characteristics of the sherry wines used for barrel seasoning and the duration of seasoning. Similarly, ionic chromatography for the determination of short-chain organic acids [51] and ultra-high-performance liquid chromatography coupled with a photodiode array detector (UHPLC-PDA) to quantify polyphenols and furfurals [52] were used by other authors [53] to differentiate brandies of Jerez according to seasoning and aging time.

Apart from the identification and quantification of marker compounds in spirit samples, other studies use the so-called “fingerprinting” approach, in which the overall analytical signal of the samples is acquired and analyzed with multivariate statistical techniques, which allow the different fingerprints to be clustered into distinct groups or categories. This approach, frequently used in food authentication [54], has been employed in two recent works to discriminate brandies according to different production processes. In the first study [55], the phenolic fingerprint determined by UHPLC-PDA and analyzed by chemometrics was used to differentiate brandies according to oak type, toasting degree and aging time. In the second work [56], the GC-FID technique was used to obtain the fingerprints of the main volatile fraction (corresponding to aldehydes, higher alcohols and major esters) of a series of brandies of Jerez aged 14 and 28 months. Unsupervised (hierarchical cluster analysis and PCA) and supervised (PLS-DA and support vector machine) pattern recognition tools were then used to examine the fingerprints. This untargeted approach is considered to provide greater discriminating power than the targeted one, as it can exploit the entire information included in the raw profile of samples.

Unlike spectroscopic techniques, which often allow analysis after minimal sample handling, for chromatographic methods, a very crucial part is the selection of appropriate sample-handling procedures. In many cases, in fact, the direct analysis of samples may be hindered by interfering substances, low analyte concentration or specific sample characteristics that require preparatory steps of cleaning, concentration and/or derivatization. Some authors compared the profile of volatiles and semi-volatiles contained in grape mark spirits by GC-TOF-MS analysis after previous extraction by dispersive liquid-liquid microextraction (DLLME) or SPME. The study highlighted that the DLLME extraction technique was able to provide higher responses than SPME for most substances. Two relevant aspects to consider in the application of DLLME, especially in routine analysis, are the use of chlorinated solvents and the difficulties in automating the procedure [57].

Table 2 presents an overview of the main features of the above-mentioned studies on chromatographic and hyphenated techniques for the authentication of Gr and WB.

Table 2. Overview of chromatographic and hyphenated techniques for the authentication of Grappa and wine brandy GIs.

Samples	Discriminating Parameters	Method of Analysis	Data Analysis	Results	References
8 spirit drinks (eau-de-vie de marc, armagnac, rhum, calvados, grape marc distillate, brandy, whisky and cognac) + 4 wines (fortified red wine, sparkling red wine, dry white wine and sweet Champagne) + 20 different grape marc spirits and 20 different red wines	Determination of 16 volatile congeners (acetaldehyde, ethyl formate, ethyl acetate, acetal, methanol, butan-2-ol, propan-1-ol, 2-methylpropan-1-ol, butan-1-ol, 2-methylbutan-1-ol, 3-methylbutan-1-ol, ethyl lactate, 1-hexanol, furfuraldehyde, benzyl alcohol and 2-phenylethanol) for quality control	Fast GC-FID: high-speed injection system, CP-Wax 57 CB column (25 m × 0.25 mm × 0.2 µm), rapid oven heating/cooling	Determination of calibration curves, LOD, LOQ, recovery, repeatability and reproducibility for each congener.	For all analytes: Correlation coefficient ≥ 0.95 ; LOQ (1.0 ÷ 1.5 µg/g); LOD (0.3 ÷ 0.5 µg/g); Recovery values $\geq 93\%$; Repeatability $\leq 10\%$; Reproducibility: 1.6 ÷ 13%.	[39]
25 spirit drinks (rum, whiskey, bourbon, brandy, calvados, Grappa, slivovice, tsikoudia, vodka, gin, grain spirit, liqueurs, vermouth, sake, nalewka, cocktail, glühwein and rectified spirit) purchased from local markets	Determination of 10 volatile congeners (acetaldehyde, acetal, ethyl acetate, methanol, propan-1-ol, 2 methylpropan-1-ol, butan-1-ol, butan-2-ol, 2-methylbutan-1-ol and 3-methylbutan-1-ol) for quality control	GC-FID with pre-existing ethanol as internal standard	Student's test, ANOVA	For all analytes, the relative differences between the results obtained with the proposed method and the official method are in the range of $-1.3 \div 0.9\%$ and statistically insignificant at the 0.05 significance level.	[40]
123 spirit drinks (43 Grappa samples, 35 wine spirits, 15 grain spirits, 15 apple spirits, 15 pear spirits) + 2 non-compliant samples	Spirit drink category	GC-FID (for the determination of volatiles) and distillation and electronic densimetry (for the determination of the actual alcoholic strength by volume)	LDA, one-class modeling PCA	LDA model: % of correct classifications > 97 both in cross-validation and external validation. Non-compliant samples classified as "wine spirit". One-class modeling PCA: non-compliant samples classified neither as "wine spirit" nor "Grappa".	[41]

Table 2. Cont.

Samples	Discriminating Parameters	Method of Analysis	Data Analysis	Results	References
82 spirit drinks (60 Grappa samples, 4 grain spirits and 18 fruit marc spirits)	Spirit drink category	HS-SPME/GC-MS SPME:50/30 μm DVB/CAR/PDMS	PLS-DA, VIP scores of PLS-DA, SIMCA	PLS-DA average correct classification rate: 94.3% (cross-validation) and 100% (external validation). SIMCA analysis: specificity and sensitivity of 92.9% and 87.5%, respectively, in cross-validation and 100% and 33.33%, respectively, in external validation.	[42]
34 spirit drinks (32 Grappa spirits and 2 Grappa-based liquors)	Characterization of the profile of volatile and non-volatile compounds in Grappa spirits for quality control	SPME-GC/MS (for the determination of the volatile fraction), MALDI-TOF/MS (for the fingerprint determination of the non-volatile fraction), MALDI-TOFMS/MS (for the identification of molecules of the non-volatile fraction)	PCA	PCA analysis: Grappa samples are grouped according to producer.	[45]
1 Grappa	Characterization of volatile profile for quality control	HS-SPME/GC-MS, HS-SPME-GC \times GC-ToF-MS. SPME fiber: DVB/CAR/PDMS, 50/30 μm		HS-SPME-GC \times GC-ToF-MS provides more and better resolved peaksthan HS-SPME/GC-MS.	[46]
21 grape mark spirits (15 Italian Grappa and 6 Brazilian Grappa)	Geographical origin	GC-FID (for the determination of higher alcohols and acetic acid). GC-MS (for the determination of esters, terpenes, lactones and ionones)	ANOVA, PCA, HCA	PCA, HCA analysis: discrimination of the two groups of grape marc spirits on the basis of chemical differences between their distillates.	[49]

Table 2. Cont.

Samples	Discriminating Parameters	Method of Analysis	Data Analysis	Results	References
32 Grappa spirits: 2 pomace varieties (Cabernet Sauvignon/Merlot blend and Prosecco) × 2 barrique types (oak wood and cherry wood) × 2 ethanol contents (55% and 68% <i>v/v</i>) × 4 aging times (1, 3, 6 and 12 months)	Aging conditions	SPE-GC/MS and sensory analysis SPE cartridge: C ₁₈	PCA, PLS-DA, VIP scores of PLS-DA	No significant changes in fruity ethyl esters and floral terpenols during aging in oak and cherry barrels. Significant changes in the volatile profiles of the final products depending on the type of barrel, ethanol content and variety of Grappa.	[50]
24 Brandies de Jerez aged in different types of casks (seasoned for 3, 6, 12, 18 and 60 months with Fino, Oloroso and Pedro Ximénez Sherry wines)	Aging technology	Ionic chromatography (for the determination of organic acids), GC-FID (for the determination of volatile compounds) and sensory analysis	ANOVA, Fisher's least significant difference test, HCA, factorial analysis	HCA and factorial analysis: grouping of brandies based on the duration and type of cask seasoning.	[51]
148 Brandies de Jerez aged for different times in casks seasoned with 3 types of wine (30 with Fino wine, 64 with Oloroso wine and 54 with Pedro Ximénez wine)	Aging technology	HPLC-conductivity detector (for the determination of short chain organic acids) and UHPLC-PDA (for the determination of phenolic and furfural compounds)	ANOVA, Fisher's least significant difference test, cluster analysis, PCA, MLR	ANOVA and Fisher's least significant difference test: significant differences in most variables depending on the type of casks seasoning. Cluster and PCA analysis: grouping of brandies depending on the type of cask seasoning. MLR: correlation coefficient = 0.909115.	[54]
72 brandies aged for 12 and 24 months in casks of 3 oak species (<i>Quercus Alba</i> , <i>Quercus Robur</i> and <i>Quercus Petraea</i>) and 2 levels of wood toasting (medium and light).	Oak species, levels of wood toasting and aging time	UHPLC-PDA (for the determination of phenolic fingerprint)	PCA, PLS-DA	PCA analysis: groupings based on toasting level, oak species and aging time. PLS-DA analysis: % of correct classifications ≥ 0.86 (cross-validation and external validation).	[56]

Table 2. Cont.

Samples	Discriminating Parameters	Method of Analysis	Data Analysis	Results	References
7 Brandies de Jerez made from wines with different total sulfur dioxide content (in the range 10 ÷ 73 mg/l), distilled using 4 different distillation methods and aged for 14 and 28 months in light and medium toasted oak casks (<i>Quercus alba</i> , <i>Quercus robur</i> and <i>Quercus petraea</i>).	Production and distillation conditions of base wines and aging time of wine spirits	GC-FID (for determination of the major volatile fraction)	PCA, HCA, PLS-DA, support vector machine	HCA and PCA analysis: clustering of the samples based on the fermentation and distillation conditions applied to the base wines and the aging time of the wine spirit. Support vector machine models are more reliable than PLS-DA models for classification based on the above-mentioned variables.	[57]
11 grape mark spirits with different ethanol content (40 ÷ 62 vol%) obtained by direct and steam distillation from 4 grape varieties (Mencía, Torrontés, Treixadura and Albariño) of 2 geographical origins (Galicia and Cantabria).	Characterization of the profile of volatile and semi-volatile compounds of grape mark distillates	GC-TOF-MS with DLLME	PCA	PCA analysis: clear separation between the four different Galician grape varieties and between the Cantabrian and Galician samples.	[58]

2.3. Sensor Arrays

Sensor arrays comprise a series of electronic sensors, such as electronic noses, capable of detecting certain categories of compounds [58]. The interaction between sensors and analytes occurs mostly through physical adsorption producing an electrical signal that enables molecular recognition through comparison with a pre-existing database [59]. They do not provide information on specific components but give quick general information on the sample [60]. There are many types of sensor arrays used in spirits assessment, including mass-sensitive quartz crystal microbalances [61], photonic crystals [62], UV-vis, fluorescence and cataluminescence [63–65]. Many devices, however, have a low chemical specificity, which makes it difficult to detect small differences between very similar compounds [66]. An effective discrimination between 14 spirits, including brandy, was achieved with a colorimetric sensor array made up of 36 different classes of indicators (pH, acid–base, redox and containing acid and amine nucleophiles specific for aldehydes and ketones) and solvatochromic dyes [66]. Color variations in the sensor before and after exposure to the vapors of the spirits enabled a color difference pattern to be obtained, allowing the 14 spirits to be correctly classified according to their alcohol percentage and brand with high accuracy (>99%). An optoelectronic tongue sensor array consisting of a negatively charged, positively charged and two neutral poly(para-aryleneethynylene)s (PAE) at different pH values (3, 7 and 13) was applied for the discrimination of 37 brandy-like alcoholic beverages, including the GI German Weinbrand, aged for different times and a number of “fake” brandies consisting of mixtures of various brandies with ethanol, caramel-colored clear spirits and blends of different brandies [67]. The discriminating power of the assay was compared to that obtained by measuring alcohol, density, extract and different volatile compounds by GC-MS, showing that the sensor was able to discriminate between different brandies with 99% accuracy and between identical brandies from heterogeneous batches with higher discriminating power than that obtained by GC-MS. Given the scarcity of studies, further research may be needed to improve the application of sensor arrays for the authentication of distillates.

2.4. Multi-Platform Techniques

Alcoholic beverages and food in general have a complex composition, and data from single analytical techniques may not be sufficient to fully characterize such complex products. Analytical characterization and authentication of foodstuffs can benefit from combining data from different instrumental sources. Multi-platform analysis, in fact, presents several advantages over single techniques, such as increased information, reduced impact of interferences and lower prediction errors [68]. A study based on a multi-platform approach for differentiating Gr from other distillates was carried out with a set of 75 representative samples of traditional Gr and other Italian fruit and cereal distillates produced in the Italian regions of Trentino Alto Adige and Veneto [69]. The spirits were analyzed with GC-MS, MIR and NIR techniques and classified with SO-PLS-LDA [28,70,71] and SO-CovSel-LDA [27] to combine multi-platform data into single classification models [72,73]. The SO-PLS-LDA approach provided the best results, with a total classification rate of 100%, compared to the SO-CovSel-LDA model with a total classification rate of 76.5%. The difference between the two results was attributed to the fact that the NIR data were excluded in the creation of the SO-CovSel-LDA model because the cross-validation procedure for this model indicated the NIR block as irrelevant. On the contrary, it probably provided relevant information to discriminate the two categories under consideration. Another multiple analytical approach was used to differentiate Gr distillates matured in different types of wood casks [74]. In this study, 15 Gr samples obtained from virgin Moscato pomace and aged using oak or poplar wood fragments of different sizes and toasting levels were analyzed by GC-MS, NIR, electronic nose (E-nose) and ¹H NMR. GC-MS analyses were performed to obtain an aromatic characterization of the distillates, while the other techniques were carried out for classification purposes. The E-nose employed was a portable commercial model with a sensor array consisting of 10 different metal oxide semiconductors. Each

sensor generated a specific response to volatiles, simulating the human nose. There are many advantages of ^1H NMR, such as its high reliability and reproducibility, which make it suitable for statistical studies on geographical origin and adulteration recognition, where minute variations of many components must be detected simultaneously [75]. Unlike the previous study, the multi-platform data were processed individually without combining them into a single classification model. The GC-MS data were statistically processed by ANOVA and PCA and the NIR, NMR and E-nose data by PCA. The spectral region between 11 and 5.5 ppm was selected for the NMR statistical analysis because it was linked to relevant aromatic compounds such as phenols, aldehydes and aromatic groups. Good separation was shown by ^1H NMR-PCA analysis according to the toasting level but with only partial separation among the groups with respect to the different wood formats. The spectral ranges $6900\text{--}6800\text{ cm}^{-1}$ and $5500\text{--}4000\text{ cm}^{-1}$ were selected for NIR characterization. The NIR statistical analysis highlighted discriminating power between the wood format groups, but further studies with larger datasets are needed to confirm its potential. The E-nose showed good capability to classify the samples, mainly according to the assortment of wood. This capability, combined with the ease of use and portability of the device, makes the technique particularly promising. The results of these studies highlight the effectiveness of multi-block strategies for authenticating and protecting the geographical indications under study also in relation to the aging technologies used.

2.5. Other Techniques

2.5.1. Elemental Analysis

The determination of trace elements, mainly by means of inductively coupled plasma (ICP)-MS, for the authentication of spirits according to their botanical origin and/or production processes has been described in the literature [76–79]. Unlike other beverages, such as wine, however, in Gr and WB, the influence of raw materials appears to be much less important [80], probably because distillation reduces the concentration of non-volatile elements. The metal content in distillates can depend on several factors, including raw materials, fermentation vessels, distillation apparatus, aging/storage containers, water dilution and bottling [81]; therefore, a study on the release of metals at different production stages could be useful to define elemental criteria for discriminating distilled products according to their origin and production technology. Elemental analysis was not so considered in the last ten years in Gr and WB GI authentication studies, although it has been used for other similar grape mark GIs. [82].

2.5.2. Isotopic Analysis

The elements carbon, hydrogen, oxygen and nitrogen are composed of several stable isotopes, and it has been observed that their ratios within a given molecule are linked to its origin [83]. Isotopic analysis is widely applied for the determination of origin of agri-food products. There are different hyphenated isotopic techniques, including elemental analyzer–isotope ratio mass spectrometry (EA-IRMS), GC–combustion–IRMS (GC-C-IRMS) and specific natural isotope fractionation–NMR of deuterium (SNIF- ^2H -NMR). These techniques have found various applications in verifying the authenticity of spirits, especially whisky [79,84,85]. In aged distillates, including Gr and WB, GC-C-IRMS has been successfully applied to differentiate wood-derived vanillin from synthetic and natural vanillin [86]. Vanillin is one of the degradation products of lignin that is released in distillates due to the toasting of wood [87]. The addition of synthetic or natural vanillin to distillates is prohibited by the European Regulation 2019/787 [5].

The recent research works on the use of isotopic analysis, sensor arrays and other techniques for the authentication of Gr and WB, described above, are summarized in Table 3.

Table 3. Summary of sensor array, multi-platform and other less commonly used techniques for the authentication of Gr and WB GIs.

Samples	Discriminating Parameters	Method of Analysis	Data Analysis	Results	References
14 spirit drinks (5 whiskeys, 7 whiskies, 1 brandy, 1 vodka)	Spirit drink category and adulteration for quality control	Colorimetric sensor array	HCA, PCA, support vector machine	Correct categorization with accuracy rate > 99%.	[67]
37 spirit drinks (2 Armagnacs, 9 brandies, 4 German Branntwein, 3 cognacs, 5 Spirituose, 5 German Weinbrände, 8“fake” brandies, 1 aged Grappa).	Spirit type, brand, batch, aging time and adulteration for quality control	Hypothesis-free sensor array (optoelectronic tongue)	PCA, LDA	Classification accuracy: 99% (cross-validation).	[68]
75 Italian distillates (58 Grappa, 17 spirits from fruits or cereals)	Grappa from other spirits	GC-MS, MIR and NIR spectroscopies	SO-PLS-LDA, SO-CovSel-LDA	SO-PLS-LDA: 100% correct classifications for the category “Grappa” (external validation). SO-CovSel-LDA: 75% correct classifications for the category “Grappa” (external validation).	[70]
15 Grappa (12 samples aged with oak and 2 with poplar wood chips of different sizes and toasting levels)	Aging technologies	SPE-GC-MS, NIR (11,500–4000 cm ⁻¹), ¹ D ¹ H-NMR, E-nose	ANOVA and PCA (for GC-MS data), PCA (for NIR, NMR and E-nose data)	PCA (NIR and E-nose): grouping based mainly on wood assortment. PCA (NMR): clustering based mainly on wood toasting level.	[75]
32 distillates (20 Scotch malt whiskies, 4 bourbons, 3 cognacs, 3 rums, 1 Grappa, 1 brandy)	Wood-derived vanillin from added vanillin	GC/C/IRMS	ANOVA	ANOVA analysis: the $\delta^{13}\text{C}$ values for synthetic vanillin, tannin-extracted vanillin and natural vanillin are significantly different ($p < 0.05$).	[86]

3. Overview of Chemometric Tools Applied in the Authentication of Gr and WB GIs

In the analytical strategies for the authentication of Gr and WB GIs, an important role is played by the chemometrics tools used to process the large datasets produced by the application of state-of-the-art analytical methods. Although there are no strict guidelines for the selection of the multivariate statistical technique, it is possible to define a rational scheme (Figure 1). Initially, it is essential to establish whether the collected data can effectively discriminate samples within the different target classes. To this aim, PCA is one of the most frequently applied tools as it can reduce the dimensionality of a large amount of data by projecting samples into a low-dimensional space, allowing the identification of sample groupings and patterns [88]. While PCA is commonly used for two-way data (such as those generated from conventional chromatographic methods, for example), PARAFAC may be the technique of choice for three-way data obtained, for instance, from EEM. PARAFAC can, in fact, decompose the information into several components that more specifically describe the variability of the entire dataset [89]. Another tool, frequently used for exploratory data analysis in Gr and WB authentication studies, is the HCA. It allows similar observations to be grouped into clusters based on the values of different variables for each object [88].

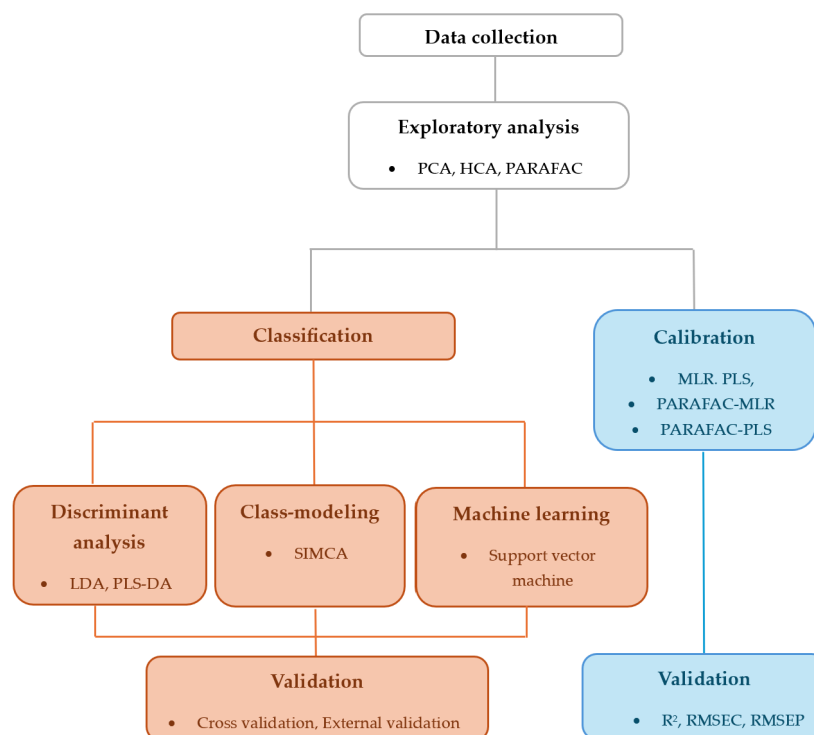


Figure 1. Visual overview of chemometric tools applied in the authentication of Gr and WB GIs.

Once explored, the data can be classified or calibrated. Both discriminating and class modeling approaches have been considered in classification studies of Gr and WB. Among discriminating tools, mainly LDA and PLS-DA have been applied. LDA calculates linear combinations of the original variables to maximize the separation between the different categories and minimize the variance within each category. PLS-DA applies regression to predict the category of a sample [89]. Indeed, SIMCA is a class modeling approach that determines significant principal components to predict the class of samples based on their distance from the model of each class [90]. The purpose of multivariate calibration methods, instead, is to determine correlations between the responses and the independent variables. MLR and PLS are often used for this purpose in Gr and WB GI authentication studies. In multi-platform authentication methods, SO-PLS-LDA and SO-CovSel-LDA were frequently carried out to obtain single classification models by the fusion of data extracted from

different analytical techniques. Furthermore, the last few years have seen rapid growth in the use of machine learning algorithms to build classification and prediction models.

After statistical modeling, the determination of model performance and evaluation of the existence of possible overfitting [90] is generally carried out. For this purpose, cross-validation and external validation have been the most applied in Gr and WB GIs. The former involves separating the dataset into calibration and validation sets, while the latter is performed when using independent test sets. Correct classification rates are the most frequently used parameters to assess the performance of authentication methods in the works presented in this review. In multivariate calibration models, the performance evaluation includes the coefficient of determination (R^2), which provides a measure of the good fitting of the model, and the root mean square calibration and prediction errors (RMSEC and RMSEP), which are applied to estimate the prediction capability of the models.

4. Technical Challenges and Future Perspectives

A main point for the authentication of GIs is the analytical traceability of raw materials. Since the chemical profile of raw materials is modified during the various production steps, including alcoholic fermentation and fractionation applied during the distillation and aging processes [49], future research on the fate of specific chemical markers and raw materials along the production process could be necessary. Further studies will also be necessary on untargeted and multi-platform methods considering the general trend towards these fast approaches that have only been partially explored on such matrices. Among the rapid methods, sensor arrays seem to be very promising, while, with regard to innovative technologies, digital image analysis [91], which has already been successfully employed to discriminate different brands of other alcoholic beverage categories [92,93], may also deserve to be considered. Finally, an aspect that should be better evaluated in the construction of chemometric models is the number of samples considered representative of a certain category. Many studies, to date, have been carried out on a relatively small number of samples, with the risk of obtaining wrong or partial results due to the heterogeneity and variability of such matrices. In this sense, the construction of shared databases containing data on different samples from various characterization studies would be useful. Further, in combination with techniques that collect a large amount of information, it will be necessary to develop specific chemometric tools and advanced processing algorithms to process this large volume of data.

5. Conclusions

This review represents an overview of the main studies for the authentication and quality control of Gr and WB GIs over the last 10 years. The evidence that emerged is that the scientific literature relating to the authentication of these matrices is scarce compared to that for other categories of distillates such as whisky [94]. The studies presented in this overview highlighted that targeted methods, mainly chromatographic and hyphenated, are the most frequently adopted for the classification and quality control of these products. These techniques, coupled with suitable chemometric tools, have proven effective in discriminating Gr from other categories of spirit drinks, enabling the identification of distinctive chemical markers. The same techniques also showed good potential in discriminating Gr samples according to brand, origin of raw materials and aging conditions. For WB GIs, the literature is mainly related to the authentication of the aging processes, which are essential for developing the distinctive organoleptic characteristics of this distillate [95]. In this respect, chromatographic techniques appear to be effective approaches for discriminating WB GIs according to aging time and characteristics of the wood used for aging, including its seasoning and toasting. However, some of the main disadvantages of these techniques are the high costs and long analysis times. Another approach is based on spectroscopic methods, in particular IR (MIR and NIR) Raman and fluorescence spectroscopies, combined with chemometrics. Despite relatively few research works on Gr and WB samples, these techniques appeared very promising for both discrimination and for

the detection of adulterations with low-quality spirits. These methods, generally, do not identify specific chemical markers but focus on particularly informative spectral regions and rely heavily on the use of chemometrics. Their main advantages are cost-effectiveness, reduced analysis time and ease of sample handling. Furthermore, a comparison of some of these methods with official analysis methods has shown comparable or even better results, although they have no legal value until they are approved as standard methods. A third analytical approach is a combination of the previous two. It involves the fusion of chromatographic and spectroscopic data into individual chemometric models. This multi-platform strategy, successfully carried out for discriminating Gr from other distillates, seems to produce better results and more information about the type of adulteration than single techniques, combining the advantages of chemical marker identification with the quickness of untargeted methods. Finally, among new technologies, sensor arrays have proven reliable for discriminating between WB samples according to alcohol content and brand name and for discriminating between adulterated and authentic WB GIs.

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