Chapter 38

Authentication of wine and other alcohol-based beverages—Future global scenario

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1 Introduction

Authentication as a practice has long been applied in some form throughout the history of mankind. In agriculture, it became a necessity as the identity of raw ingredients needed to be verified before consumption to ensure their edibility. As societies advanced, authentication remained necessary in the food and beverage industries where it was not only used for safety purposes but also the verification of various agricultural products' descriptive parameters, such as variety, origin, and manufacturer. In the beverage industry authentication mainly focused on adulteration problems and, especially in the case of wine, on origin verification since origin served as a brand name ultimately determining market prices. Wine origin (and variety) is of such high importance that many countries have set classification systems based on vineyard location, such as the AOC (Appellation d'Origine Contrôlée-controlled designation of origin) system of France and the subsequent protected designation of origin framework issued by the European Union (Jackson, 2008; Tosato, 2013). Nowadays new areas of interest regarding authenticity are in the spotlight as consumers prefer chemical-free, explicitly labeled products, made following sustainable practices and eco-friendly production protocols. It should be noted that wine is treated differently by the market because it is considered to be a natural product that due to its high antioxidant content can be beneficial to human health, as opposed to all other alcoholic beverages (Pabst et al., 2021). Moreover, wine is closely associated with the notion of terroir, i.e., the concept that the place of origin imparts different characteristics to the product, mainly due to its climate, soil characteristics, and winemaking tradition (Foroni et al., 2017). For these reasons, authentication efforts slightly differ between wine and other alcohol-based beverages.

Alcoholic beverages have a serious impact on national economies, with almost 10% of their recorded production entering international trade and the rest sold in the domestic market (Room and Jernigan, 2000). Production modes differ depending on each country's gross domestic product (GDP) and include low- and high-scale industrial production. Production of alcoholic beverages using high levels of technology is predominant in countries with strong economies, while home or small-scale production represents a higher percentage of the production in developing countries. Alcoholic beverages produced on home or small-scale facilities are difficult to tax and control and tend to have lower prices to compete with higher quality beverages (Room and Jernigan, 2000). The lack of quality control testing especially in homemade alcoholic beverages increases the risk for health issues and has been linked to several fatalities. In general, the higher the economic development of the country, the higher the consumption of alcohol; however, lower economic development equals higher alcohol-attributable mortality as well (OMS (Organización Mundial de la Salud), 2011).

The cost for instruments that would certify that a beverage is safe to consume is not affordable for small production facilities, and certainly not for at home use. For these reasons authentication efforts nowadays focus not only on the detection of key chemical compounds that will reveal consumption side effects but also on the development of methods and instruments that are cost-efficient, rapid, without the need for trained personnel. In this chapter future needs for authentication of alcoholic beverages will be discussed and methods of analysis will be presented based on their usage, success, and future possibilities.

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2 Wine authentication

Authentication in the wine industry is a well-established practice, used not only to certify that wine belongs to a certain appellation or protected geographical indication but also to verify the identity of wine especially in the case of collectible wines that can be considered an investment.

2.1 Types of authentication needs in the wine industry—Permanent needs and future trends

Authentication needs evolve according to consumer preferences; however, parameters such as safety remain constant verification needs throughout the years. New marketing practices, trends set by young consumers, and changing environmental conditions are the basis for future scenarios of authentication.

Safety

A wine is considered unsafe to consume either due to microbial contamination resulting from grape development, environmental factors, or poor winemaking practices or due to chemical contamination resulting from agricultural practices, product handling (packaging, storage, etc.), or winemaking processes (Ubeda et al., 2020). The first category includes mycotoxins and the second pesticide residuals, biogenic amines, ethyl carbamate, and fining material residuals among others. Microbial contamination can occur due to different species and strains of yeasts, lactic acid bacteria, and in many cases acetic acid bacteria (Cosme et al., 2018).

Wines today are routinely analyzed to ensure they are not contaminated so the risk of consuming an unsafe wine is low. Recently, however, a consumer advocacy group reported traces of glyphosate (the active ingredient of broad-spectrum systemic herbicides) in various alcoholic products including wine, and almost at the same time 1300 wines tested by an independent laboratory were found to contain very high levels of arsenic (Cook, 2019; Haelle, 2015). These finds had a substantial impact on the wine industry, with many winegrowers publicly disavowing the use of glyphosate products (Ségolène, 2020). Arsenic on the other hand is a compound that can contaminate wine through pesticides; however, it may be also found in grapes due to natural rock erosion (Monnot et al., 2016; Murphy et al., 2020). Its levels are usually low, even though its concentration is higher in berries that are kept longer on the vine (Huang et al., 2015). Wildfires happening more and more often may increase arsenic as well, as they may lead to changes in hydrology which in some cases can mobilize arsenic from underground water (Murphy et al., 2020). The higher frequency of wildfires, which is also a result of extreme weather conditions connected to climate change and hazard reduction burns can also be responsible for smoke tainted wines, which recent research found to be potentially harmful for consumption from sensitive members of the population; however, no regulations have been set regarding their safety as of yet (Bo et al., 2020; Krstic et al., 2015).

Adulteration

Wine adulteration includes mixing, substitution of original with others and in general non-conformation with official standards (Kamiloglu, 2019). The basis of these standards is the protection of the consumer and the guarantee of quality wine, but also the protection of the producer or the state/country, through the prohibition of added substances that although may be safe to consume may indirectly and unfairly increase profit or market price (Geana et al., 2016). Ethanol substitution with other alcohols is the most common and most harmful—in terms of human health—type of adulteration in alcoholic beverages in general, however, in wine the most damaging type is label counterfeiting (Grijalba et al., 2020). Selling an imitation wine can be financially detrimental for the buyer of the fraudulent wine—as old vintages of specific wines can be considerably expensive—but also damaging for the authentic wine in terms of reliability and loss of prestige (Basalekou et al., 2020). During the past 10 years wine has reached new markets, China being the fastest growing one (Wu et al., 2021). High demand in these new markets led to an increase in domestic wine production in cases where establishing a vineyard was feasible; however, it also increased the number of mislabeled wines, making the need for rapid and effective methods to inspect authenticity urgent and essential (Wu et al., 2021).

Adulteration aims to add value to the finished product. Typical cases of adulteration include the addition of sugar which increases alcoholic strength and the addition of water which increases volume. Given the cost of aging, another common type of adulteration is the usage of unauthorized methods of aging such as the use of wooden fragments or barrels made from unauthorized types of wood (Geana et al., 2016; Herrero-Latorre et al., 2019). Regarding unauthorized methods of aging, current trends show that consumers prefer less matured wines, so producers turn to alternative and cost-effective means of maturation such as the use of oak chips. Use of oak or other types of woods and method of aging (i.e., barrel aging or with alternative methods) may be subject to limitations especially if the wine bears a PDO label (Basalekou et al., 2017).

Origin and variety

Origin and variety authenticity are the basis of wine authentication, as they are inextricably linked to wine marketing. As mentioned earlier, many countries have set denominations of origin to facilitate the wine trade, making the place of origin a strong brand name through the years (Basalekou et al., 2020). Recent research showed that even country of origin has a strong impact on wine traders which in turn has important implications for marketing and export activities (Rodrigues et al., 2020a). Many successful efforts have been made in origin and variety authentication, however mostly in single varietal wines and not blends (Basalekou et al., 2016, 2017; de Lima et al., 2020; Kyraleou et al., 2020). In most cases, the focus of the research was wines made from the so-called noble varieties, which include Pinot noir, Chardonnay, Cabernet Sauvignon, and Sauvignon blanc (Fourcade, 2012). Today winemakers strive to produce unique and memorable wines using new or forgotten grape varieties, the number of commercially productive ones reaches 1368 (Robinson et al., 2013). Small denominations of origin with broad consumer appreciation face serious challenges with the origin and variety falsification, as not only the denomination of origin can be damaged by low-quality fraudulent wines, but also consumers will turn away from genuine wines which due to limited production dynamics are higher priced (Vlahos, 2020).

Winemaking practices

Authenticating winemaking procedures includes verification of whether a wine was produced following a specific winemaking protocol or practice, e.g., if it contains—or not—additives and which if it is made following biodynamic processes, or if it is organic, vegan, natural or GMO (genetically modified organism) free. Authentication can provide answers on whether there has been the use of certain additives that leave residues in the wine, such as gelatin or is in glass that could potentially be harmful to consumers with allergies or unappealing to vegan consumers. It can also verify that no pesticides or chemicals were used or if they were used within the limits set by legislation (Weber et al., 2010). Even though not all countries require that wineries prove they are free of animal byproducts or even disclose major allergens consumers today tend to prefer being informed about all aspects of winemaking (AFDL, 2006; FSANZ, 2014; Galati et al., 2019). Recently, there have been wines marketed under the term “clean” which according to their producers was used to signify that these wines were made with minimum intervention and without the addition of chemicals (O’Brien Coffey, 2020). To signify this claim, the wines were certified for numerous different parameters since their consumers tend to be the most interested in label information (Galati et al., 2019; O’Brien Coffey, 2020).

Typicity and identity

Wine is not only a matter of components such as grape variety and type of aging. As a product of terroir, wine sensory profile is susceptible to changes due to location and climate and as a product driven by consumer preference, its profile evolves through time. However, each variety possesses certain core characteristics irrespective of environmental or winemaking variability. These characteristics form a wine’s identity and are used by critics and sommeliers to assess the wine’s “typicity,” i.e., if the wine is a true representative of the variety it is made of. Given that grape geographical origin has a great impact on the final product, typicity is influenced by terroir. Thus, a typical Sauvignon blanc wine is expected to present vegetative, grassy, and green pepper nuances, which are better expressed in Bordeaux, its place of origin (Marais, 1994). Quality is another important issue, as it can be interrelated to typicity especially in Old World wine-producing countries where provenance criteria can be translated to quality indications by consumers (Souza Gonzaga et al., 2020). For new varieties cultivated nowadays and for internationalized local forgotten varieties, identity and typical sensory profile do not exist yet. They will be formed through the collection of a large number of wine samples made from various wineries in different locations which will be subsequently sensory evaluated and analyzed along with samples from various vintages since the concept of typicity includes information about a wine’s aging character as well. After their sensory profile establishment, authentication of these wines will be possible; however, it will be a long but essential process.

Future authentication needs

Authentication in wine can take many forms as already discussed, depending on the parameter that the consumer, the producer, the market or a regulatory authority deems as verifiable. For example, the producer needs variety authentication when a wine is produced from rare or forgotten varieties so that it can retain its comparative advantage. These needs are largely determined by the market, which nowadays has shifted toward cleaner and healthier products. New trends do not cancel the need for old authentication practices, which means that a sustainable wine will always need to be safe to consume. This way, however, certifications build in number and along with the belief that consumers require access to complete information about the ingredients of the products they consume, wine labeling is set to become a difficult task (Neufeld et al., 2020; Pabst et al., 2019). A future challenge will most likely be the need for simultaneous authentication of various parameters, such as variety and origin or type of aging and ingredients used, cost-effectively and rapidly. Regarding the matter of identity authentication research must first chemically define what constitutes “a wine representative of its quality” considering origin, winemaking and vintage influence, and then develop the methods that will help verify it.

2.2 Methods of analysis in wine authentication

Authentication methods can be divided into two types: the first type is based on the presence or absence of certain compounds that are called “chemical markers” and the second type authenticates wine based on its profile using various statistical analysis techniques. Both methods can provide accurate results; however, a combination of the two currently seems to be the most suitable option regarding all authentication needs. Due to its nature, wine is subject to another type of assessment to evaluate its quality and verify its aromatic typicity, and that is a sensory evaluation by a trained panel.

Methods based on chemical markers

Most authentication analyses are based on chemical markers. Safety, adulteration, and type of winemaking can all be authenticated through the identification of key chemical compounds. These marker compounds may be volatile or elemental and possess various discriminative powers. For this reason, frequently more than one is used. Their identification and quantification can be achieved through techniques such as high-performance liquid chromatography or gas chromatography but also with the use of more sophisticated techniques such as nuclear magnetic resonance spectroscopy or isotope ratio mass spectrometry and more (Basalekou et al., 2020). Chemical markers mostly used with chromatographic techniques are compounds from the group of polyphenols (liquid chromatography) or volatile constituents (gas chromatography) (De Simón et al., 2014; Nasi et al., 2008).

Polyphenols

Polyphenols are routinely determined during the standard analyses for quality control in wine. To be used for authentication purposes a large number of individual phenols need to be identified and quantified so a large dataset can be constructed, as each phenol has different classification powers. This dataset is subsequently (statistically) analyzed using unsupervised or supervised methods. Recently, concentrations of polyphenols including anthocyanins and condensed tannins, but also from single compounds belonging to the group of phenolic acids, hydroxycinnamates, and flavonoids were determined and statistically analyzed using classifiers like Bayesian networks, support vector machines and multi-layer perceptrons, showing great potential in blend verification, which seems to be one of the most difficult authentication cases in wine. The research concluded that selection of a suitable classification methodology can greatly reduce the number of chemical analyses; however, a large number of samples is still needed (Portinale et al., 2017).

Volatile compounds

Volatile compounds are critical for product acceptance by the consumer and are analyzed to assess a wine’s sensory profile. Numerous sophisticated techniques are developed for volatile compound identification and quantification with the ultimate goal of wine aroma interpretation and the prediction of sensory panel results. Their presence and analogy can be useful for many types of authentication including typicity. What is most important in the use of volatile compounds for authentication is their selection as wine aroma is influenced by many different factors and is extremely complex. Typicity and authenticity markers are documented in the literature; however volatile compound identification and aroma description are still being investigated (Nasi et al., 2008). Due to synergy effects, wine aroma is not analogous to volatile concentration, and for this reason, nowadays their analysis is more and more used to provide aroma profiles and volatile compound fingerprints (He et al., 2021). However, together with polyphenols, volatile compounds used as chemical markers can produce accurate results regarding typicality (Valentin et al., 2020).

Stable isotopes

Stable isotopes, called “origin markers,” have successfully been used in wine authentication for the last 30 years, especially in cases of adulterations such as exogenous sugar or water addition but also to authenticate geographic origin (Christoph et al., 2015). To give reliable answers, isotopic results need to be compared with authentic and representative samples from official wine databanks such as the one set by the European Commission (EC, 2008). Carbon and oxygen isotope ratios are mostly used, based on which recent research gave successful results in adulteration cases regarding exogenous sugar or water addition and alcoholic strength (Geana et al., 2016).

A relatively new approach to address the geographical origin of wine is by monitoring the natural variation of lead isotope ratios, as lead is continually emitted from both natural and anthropogenic sources into the atmosphere and is ultimately absorbed by plants, providing wines with a specific lead isotopic signature. Temporal changes in elemental and isotopic lead (Pb) content of Bordeaux wines assessed with the use of high-resolution multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) helped in the discrimination of origin and the detection of counterfeit wines (Epova et al., 2020).

Mineral compounds

Another set of compounds that can also be used for authenticity purposes in more than adulteration cases are mineral compounds. Inductively coupled plasma optical emission spectrometry (ICP-OES) analyzed 12 elements from 111 sparkling wines from different countries and provided a 94% accuracy in country-of-origin classification. Mineral elements can be used as chemical markers as they represent not only soil pH and geochemistry but also anthropogenic factors (Rodrigues et al., 2020b). A new methodology based on multi-elemental analysis has been developed recently, using inductively coupled plasma optical emission spectrometry combined with ultrasonic nebulization. Multivariate exploratory analysis was ultimately performed and samples were successfully classified according to their origin (de Andrade et al., 2020).

Profile analysis methods

Profile analysis methods are mostly based on spectroscopy techniques, rely heavily on the use of chemometrics, and are used to authenticate wine mostly based on variety and origin. Wine classification according to these parameters or according to age and quality is a complex task mainly because there is no single compound or even a specific group of compounds that is directly linked to each parameter. For this reason, techniques such as Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy, and NMR that produce a graphic depiction of each wine have advanced greatly during the last years. At the same time, there is also renewed interest in techniques that even though they cannot produce accurate compound identification such as UV-Vis spectroscopy can be used in scan mode and produce a type of spectral profile. The specificity of these methods is that by producing a unique spectrum for each wine, they produce each samples' profile, and by containing spectrum areas with specific information they can ultimately produce its fingerprint. The biggest advantage of these techniques is that they are fast and sensitive and can give answers not only regarding well-defined parameters such as variety or origin but also for more chemically vague ones such as quality. Recently, the term "spectralprint" has been introduced to describe this type of analyses that coupled with chemometrics provide answers regarding the authentication of complex systems highlighting their potential for broad use in the future (Reina et al., 2020).

FT-IR spectroscopy specifically, is gaining a lot of interest during the last years as it has been shown to produce accurate classification results for a broad range of wine authentication parameters such as origin, aging, variety, and type of production (Basalekou et al., 2017; Cozzolino et al., 2009; Cozzolino and Smyth, 2013). The infrared region mostly used is the mid-infrared, as various well-defined and sharp peaks are exhibited helping produce information related to molecular composition (Arslan et al., 2020). Very similar to FT-IR, Raman spectroscopy is starting to be used as well since it can allow the detection of structural molecules and reveal characteristic spectral patterns through the information it draws from fundamental chemical bonds of the sample's matrix (Arslan et al., 2020; Mandrile et al., 2016). Recent research examined the feasibility of merging vibrational spectroscopic data for wine origin classification; however, the use of surface-enhanced Raman spectroscopy alone was more successful in white wine origin and variety discrimination (Teixeira dos Santos et al., 2017; Zanuttin et al., 2019).

Another type of spectroscopy, front-face fluorescence spectroscopy was successfully used in wine origin authentication through a new approach combining absorption and luminescence information. Wines from different varieties were discriminated against based on their optical absorption and emission fingerprints, while data chromaticity coordinates were also efficiently utilized (Carbonaro et al., 2019). Spectral profiles, along with intelligent algorithms and fluorescent measurements were recently used to examine storage conditions and detect wine adulteration, highlighting the potential of developing similar analytical methods for quality control and fraud authentication (Cancilla et al., 2020).

Apart from spectroscopy, wine fingerprint can also be produced by the identification and quantification of specific compounds provided that the number of analyses is large and sophisticated statistical analysis techniques are used. Indeed, wines were successfully classified according to their origin based on analyses on antioxidant activity and polyphenols using support vector machines and neural networks. All analyses were based on colorimetry and chromatographic techniques (Costa et al., 2019). Another approach in varietal discrimination through the use of the liquid chromatography-quadrupole time of flight tandem mass spectrometry and chemometrics was the use of phytosterol content for metabolite profiling. In this experiment discrimination was complete; however, no individual compounds were quantified as pure standards were unavailable, so more study should be done to confirm the researches' results (Millán et al., 2016). Another interesting approach based on digital imaging and chemometrics authenticated aged high-quality wines quantifying as well the percentage of younger wines present in adulterated samples (Herrero-Latorre et al., 2019). Digital image was also successfully used for the classification of red wines according to their geographic origin, grape type and even winemaker, with a methodology based on color histograms and supervised pattern recognition techniques (de Lima et al., 2020).

Analysis of minerals and trace element patterns observed using various methods (e.g., atomic absorption spectrophotometry (AAS), inductively coupled plasma (ICP)-MS, and ICP-optical emission spectroscopy (OES)) can also be used to fingerprint wines and reflect the provenance or region of origin (Dutra et al., 2013; Potortí et al., 2017). Isotopes and rare earth elements were recently used to create the isotopic and elemental fingerprint of wines and with the help of chemometrics successfully discriminated them according to their origin and variety (Kamiloglu, 2019). Lately, the molecular fingerprint of a wine was also obtained, using excitation-emission matrices (EEM) provided by fluorescence spectroscopy. Extreme gradient boosting discriminant analysis (XGBDA) coupled with the EEM of each sample gave a 100% correct classification according to wine origin (Ranaweera et al., 2021).

Volatile profile analysis is mostly used for variety authentication, especially in cases of wines made from grape varieties with characteristic sensory profiles such as Cabernet Sauvignon or Sauvignon blanc. Volatile compounds were the basis for a recent varietal discrimination and classification study, using cyclic voltammetry. In this research, a voltammetric sensor array based on screen-printed electrodes, coupled with chemometrics, allowed the fingerprinting of different wines (Geană et al., 2020b). Voltammetric sensors based on screen-printed carbon electrodes modified with polypyrrole coupled with chemometrics were also used for the classification of wines according to their variety. The voltammograms illustrated the oxidation of the wine's phenolic compounds and showed the potential of cyclic voltammetry for the rapid fingerprinting of wine oxidizable compounds. The ability of this method to discriminate between young and old wines shows that this fingerprint is related to the aging process as well (Geană et al., 2020a).

Authentication through sensory evaluation

Typicity and identity of wine are notions difficult to define as they are difficult to accurately measure. Sensory authenticity refers to the verification of the aromatic profile according to what is expected in terms of variety or location. Wine is a product directly affected by the climatic conditions, grape origin, and winemaking procedure; however, a wine brand is expected to present organoleptic consistency regardless of vintage, so that the product itself can be distinctive but also recognizable by the consumers (Parrish and Downing, 2020). Sensory evaluation in wine is performed by trained tasters although recently the electronic nose (*E*-Nose) which simulates human olfaction system and quasi-electronic noses based on ultrafast chromatography have been commercialized for routine analyses and are used more and more often, each with its advantages and limitations (He et al., 2021). However, professional sensory evaluations are still considered unsurpassed and are mostly used for typicity and quality evaluation of wine samples. To avoid subjectivity and bias, a specific procedure is set (ISO 17025) so that objective results can be produced (Pasvanka et al., 2019). Regarding typicity, the experience of industry professionals has even led to methodologies of tasting that don't require training before evaluation (Ballester et al., 2005; Ballester et al., 2008). In recent years, new grape varieties have been rediscovered, and intraspecific hybrids have started to be used not only for variability reasons but also as a result of climate change highlighting the need for trained groups of tasters firstly to describe their sensory profile, and then to evaluate their quality (Manso-Martínez et al., 2020).

Sensory evaluation to assess conformation to typicity expectations according to location can be based on different factors depending on the country of origin, as different laws in each country can govern provenance. The concept of typicity deals with how much a wine expresses its regional individuality, by expressing sensory characteristics that are considered to be typical of its delimited area of origin. This statement contains a great deal of subjectivity in itself, however, this is the basis of the strategic building of regional brands which ultimately promote local wine styles (Souza Gonzaga et al., 2020). The influence of terroir complicates discrimination based on varietal typicity, as it has been observed that panelists may have difficulties classifying wines from different terroirs solely based on variety even though the opposite was feasible i.e. classifying wined based on variety and terroir (Foroni et al., 2017). Recently, a new methodology was developed to study the typicity of PDO wines and facilitate its objectification for communication purposes by highlighting descriptors involved in the sensory-perceptual typicity for each wine sample (Leriche et al., 2020). It should be noted that to define and describe a single variety explicitly, the tasting panel needs to assess a large number of samples. For example, to gather information about the regional profile of Australian Cabernet Sauvignon 2598 wine reviews—out of a total of 8454—were used for the creation of an accurate sensory lexicon of descriptor categories (Gonzaga et al., 2019).

Future needs on authentication methods

Today there is an urgent need for the development of rapid and user-friendly methods that would easily be performed even at home to provide the consumer with a tool to assess unregulated or homebrewed products. IR-based instruments fulfill these requirements, however, the development of a database representative of various types and categories of alcoholic products is essential. Communication and data exchange between researchers is imperative for this reason. The development of new products may require the selection of new chemical markers or new method setups, which will prolong the time needed to assess a sample. For this reason, profile analysis methods seem advantageous for use in the future.

3 Authentication of distilled alcoholic beverages

Authentication of distilled alcoholic beverages is mostly linked to their economic significance as without a doubt they are a great part of most countries' gross domestic product and can be a large part of its exports as well. In EU alone there are more than 40 categories of distilled alcoholic beverages or spirit drinks from different countries. These beverages follow the regulations set by the EU committee regarding labeling, origin, and production process, hence, these parameters need to be authenticated to prevent adulterations and fraud, and ultimately protect consumers. Trade agreements, which help promote alcoholic beverages in new large markets, targeting transparency in production, high-quality spirits and competitive prices, often lead to the development of new regulations to protect product reputation. Recently, for example, Irish whisky, among other alcoholic beverages, was registered as a geographical indication (GI) product in China and Japan according to the new agreements between those countries and EU. This agreement simultaneously creates the need for the development of authentication tools, which would help verify the products' provenance.

Regulations in alcoholic beverages are used in a similar way to wine regulations to certify the product according to its geographical origin (geographical indication, GI; Protected Designation of Origin, PDO; etc.), the type of raw material used and the production pathway (CRT, 2019; EU—COM 2014/015, 2014). The flavor and composition of distilled alcoholic beverages are associated greatly with the origin of raw material (Arnold et al., 2019; Biernacka and Wardencki, 2012; Cortés et al., 2011), the production method and the storage conditions of the final product. As it was aforementioned, the expression of these parameters and their association to the final product are underlined using the term of terroir, which only recently was related to alcoholic beverages (Arnold et al., 2019). Recent studies indicated the impact of the environmental and soil conditions to the cereal crop and the sensory profile of beer (Herb et al., 2017), to new make bourbon (Arnold et al., 2019) and Irish whisky (Kyraleou et al., 2021) revealing terroir's link to the alcoholic beverage authentication. However, similar to wine, the most important need for authentication is consumer safety and market stability, as non-authentic distilled alcoholic beverages may be dangerous for consumers' health, mislead the purchasers, cause alterations on the organoleptic characteristics but also have economic consequences for industries and indirect losses for countries, since counterfeit products are often untaxed.

3.1 Types of authentication needs in the distilled alcoholic beverages industry

The high demand of distilled alcoholic beverages and their significant impact on the economic sector of each country have caused an increase of adulterated products in the market. Adulterations in alcoholic beverages as part of the market chain can occur from different parties resulting in an enormous impact on the credibility of producers, on consumers' satisfaction, or even on their health.

Distilleries are applying specialized techniques to increase their products' flavor complexity, which ultimately leads to an increase in its market price as well. Aged distillates with a long maturation duration and especially whisky could become premium products on the market with high prices, provided they are single malted originating from traditional production areas (e.g., Scotland) (Roullier-Gall et al., 2020; Stupak et al., 2018). Authentication of the maturation process and geographical origin of the raw material is very important for the market, as these are the two most recognizable characteristics for the consumers. One of the challenges in aged-whiskies' authentication is the finishing practice that in some cases is applied before bottling. A secondary maturation into other wood barrels (e.g., Oloroso Sherry, Sauternes, Porto, Bourbon barrels) contributes to the final flavor and complexity of the whisky, although it is labeled on the bottle as a high-quality feature, it could mask the flavor of adulterated spirits and make more challenging the authentication of the original distillate. The flavor of aged distillates (rum and whisky) is influenced by the barrel history (Bourbon, Sherry) and their initial chemical composition before maturation (Kew et al., 2017; Roullier-Gall et al., 2018). It is also impacted by the brand (Belmonte-Sánchez et al., 2018; Cantarelli et al., 2015; Martins et al., 2017). Recently, in counterfeit whiskies the addition of red wine was detected, used in an attempt to imitate the aging process and improve the flavor of a low-quality spirit. False labeling is often used to minimize the production cost and it may concern the raw material (e.g., single malt or blended), the geographical origin labeled on the bottle (e.g., highly recognized regions from consumers), the production method (doubled or triple distillate), the maturation process (history of the oak barrels, addition of flavorings) and the years of aging.

Counterfeit whiskies first appeared in auctions 30 years ago and an increase started to be noted as more people invested in rare and premium products. To achieve high prices in the market or auctions, a trader could supply a fake label in a lower quality or a non-authentic product from a well-known brand, especially from the brand's rare vintages or special editions; rare whiskies. Authentication methodologies aim to prevent or minimize these incidents, before fraudulent products are released in the market. Fraud can be sometimes detected visually, from inconsistencies in the label, unexpected color of the liquid; even the bottle level can reveal that an auctions' vintage whisky is not genuine. However, the official verification procedure of a high-valued distilled alcoholic beverage can include glass dating determination, cork and capsule assessment, organoleptic evaluation of the liquid, analysis of heat-derived compounds and chemical analysis to determine if the whisky is a malt or a blend. It is widely accepted that the production process of a spirit can be the signature of a distillery (Cantarelli et al., 2015; Martins et al., 2017) because it is affected by personal preference and staff experience. According to the previous observations, the discrimination between authentic and counterfeit whiskies cannot depend on a single parameter but multiple variables are essential to define authenticity.

Adulterations of distilled alcoholic beverages can also be observed in bars and restaurants after dilution with water, addition of colorants and flavorings or the presentation of low quality spirits as the original ones in an attempt to cover the high demand of a product (Fernandez-Lozano et al., 2019). Counterfeit beverages which are imitating famous brands (e.g., vodka, rum, whisky) can be also purchased from online shops sometimes with prices from 6 to 15 times lower that the original ones (Kuballa et al., 2018). Authentication methodology is essential in these cases as the low quality of those products, which might involve the addition of flavors or unlabeled ingredients, could affect the brands' reputation and be harmful to the public health. Methanol is one of the ingredients that have being used as cheap substitutes of ethanol in adulterated spirits and is responsible for poisoning leading to blindness and even death (Necochea-Chamorro et al., 2019; Rostrup et al., 2016). Methanol outbreaks were observed in Libya (2013) and Kenya (2014) with a high number of deaths reported (Rostrup et al., 2016). Additionally, in 2015 and 2016 two methanol poisoning outbreaks were caused by counterfeit whisky bought via the internet resulting to the death of 13 people in the Siberian city of Krasnoyarsk (Kuballa et al., 2018). Because of that incident's relation to the online market of alcoholic beverages, hundreds of websites of that sector were disconnected by the Russian Consumer Protection Service "Rospotrebnadzor" (Kuballa et al., 2018).

3.2 Methods of analysis for distilled alcoholic beverages

Distilled alcoholic beverages' chemical composition is very complex and a high number of congener compounds (thousands) has being detected according to various techniques; however, most of these compounds are still unidentified (Roullier-Gall et al., 2018). The authentication of distilled alcoholic beverages could be based only on targeted analysis and the use of specific chemical markers. In the past years, non-targeted approaches (Belmonte-Sánchez et al., 2018) were used to give insights on the significance of the unidentified compounds and their utilization as potential chemical markers (Jeleń et al., 2019) but also to highlight the importance of the chemical profile of spirits (Cantarelli et al., 2015; Martins et al., 2017). The classification and authentication of alcoholic beverages is a combination of the analytical characterization of their profile, the detection of key compounds and the use of appropriate statistical approaches. In each study, the source of purchase or the production method, the number of samples and the storage length should be considered to achieve the best results.

Whiskey/whisky and other grain fermented distillates

Alcoholic beverages produced by the distillation of fermented sugars extracted from grain mash (e.g., corn, barley, rye, wheat, etc.) and matured in wooden barrels also belong in this category, whisky however is the most popular. There is a number of different denominations according to the type of whisky, its geographical origin, production process and maturation length. For example, Bourbon whisky must contain 51% of corn and be produced in America, Scotch whisky (Scotland) is peated or not and along with Irish whisky (Ireland) can be labeled as malt or blended.

Fourier-transformed infrared (FT-IR) spectrometry was recently successfully applied for the discrimination and authentication of whiskies according to their geographical origin (10 Scottish, 5 Irish, and 5 American) and years of aging (2, 3, 6 and 12 years old) (Sujka and Koczoń, 2018). Discriminant models were developed based on data acquired from different spectral ranges depending on the discrimination focus. Spectral data from the region of 3100–2800 cm^{-1} were used to discriminate American and Scottish whiskies, while those derived from the range of 2400–500 cm^{-1} were used to discriminate Irish whiskies with different aging duration (3 and 12 years old).

Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) was used to discriminate whiskies matured in barrels of different prior usage; Bourbon, Sherry or both (Kew et al., 2017; Roullier-Gall et al., 2018). Kew et al. (2017) conducted a non-targeted method on 87 commercial Scotch whiskies and PCA and Orthogonal Projections to Latent Structures Discriminant Analysis (OPLS-DA) tools were applied on the key compounds detected during the analysis. Scotch whiskies were discriminated based on the type of whisky and the type of wood barrel. Ellagic, gallic, and syringic acids were proposed as key compounds for the classification of malt whiskies or for those matured in Sherry barrels. However, the OPLS-DA models that were constructed based on other parameters such as region, peating level and age of whisky were weak (Kew et al., 2017). Roullier-Gall et al. (2018), observed the effect of wood barrel type on the phenolic composition by comparing the composition among new make spirits, spirits during maturation and wood extracts. They selected 11 phenolic compounds as barrel wood markers, including syringic acid, caffeic acid, catechin, and epigallocatechin. The identification of specific compounds was conducted with liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS), but still most of the detected compounds were unidentified.

The same technique (FT-ICR-MS) and chemometrics were applied for the discrimination of a high number of samples (106) of Scotch whisky based on the geographical origin (Highlands, Lowlands, Speyside, and Islay) and the maturation time (3–43 years) from 32 different distilleries (Roullier-Gall et al., 2020). The impact of the geographical origin appeared less significant compared to the maturation time according to the principal component analysis (PCA) classification of the non-volatile profiles of the samples (5979 different molecular formulas). However, a partial least square (PLS) regression analysis on the same data showed a grouping of Scotch whiskies according to their geographical origin, independently of the distillery or the maturation time.

In contrast, ^{1}H NMR method did not generate data able to discriminate 148 Scotch whiskies according to their geographical origin (different regions in Scotland) or the years of aging and also created weak models for their discrimination according to the barrel type and the alcoholic strength (Kew et al., 2019). Whiskey classification was achieved based on other parameters such as their blend status, peated character, alcohol strength as well as general authenticity. PCA model distinguished blended and malt whiskies however malt samples with more intense wood character (matured in both Sherry and Bourbon casks or finished in Port casks) were the outliers of the model, while premium blends (high percentage of malt) were grouped with malt whiskies. These problems were overcome by applying a OPLS-DA model. 3-Methylbutanol was determined as the key compound for the grouping of the samples, in accordance to previously reported results that 3-methylbutanol was more abundant in malt than blended whiskies. The OPLS-DA model for peated and not peated samples was based on the spectrum range from 6 to 10 ppm, which was not correlated to the major known peat-derived phenols and remains unidentified. 148 authentic Scotch whiskies sourced from distilleries and 32 counterfeit samples were significantly grouped with an OPLS-DA model based on the whole spectrum or on the spectrum range from 6 to 10 ppm. High levels of vanillin, glycerol, sugars or insufficient levels of 2-phenylethanol and furfural, which are not typically found in Scotch whiskies, were determined in adulterated spirit and they were used as key compounds (Kew et al., 2019).

UV-Vis spectroscopy methods combined with PCA, linear discriminant analysis (LDA), and PLS-DA models were built to discriminate whisky brands (Cantarelli et al., 2015; Martins et al., 2017) and years of aging (Cantarelli et al., 2015). This method is considered to be faster and of low cost since the identification of targeted compounds is not essential to provide results. Data were collected between 200 and 600 nm after sample dilution (Cantarelli et al., 2015) or between 190 and 1100 nm with no sample dilution (Martins et al., 2017). Cantarelli et al. (2015) analyzed 15 samples and the results showed that the whisky brand and the years of aging were correctly classified (>99%) by PCA, LDA and PLS-DA using the absorbance values from 200 to 400 nm. Martins et al. (2017) built a PLS-DA model based on seven whisky brands using the absorbance values from 200 to 500 nm. Additionally, the seven whisky brands were discriminated from 11 authentic whisky brands that were not included in the PLS-DA model and also from 73 counterfeit samples that did not belong to the brands that were included in the training set. Genuine and false samples had 98.6% and 93.1% correct classification rates, respectively. The identification of whisky brands based on their UV-spectrum profile makes essential the existence of a high number of reference samples to create an efficient model database before the analysis.

Han et al. (2017) proposed a rapid method, only with the addition of a small portion of whisky sample in a fluorescent-based tongue (fluorescent systems: poly(p-aryleneethynylene)s (PAEs) and chimeric green fluorescent proteins (GFPs)). Whiskies (33 samples) were successfully discriminated by applying LDA and PCA chemometric tools according to their country of origin (Ireland, America, or Scotland), brand, blend status (blended or single malt) and age. The best results, especially those concerning the blend status, were achieved with the combined PAE-GFP tongue. Additionally, the discrimination according to the peatiness of Scotch whiskies was not possible but they could be differentiated based on their taste (rich or light) (Han et al., 2017).

A fluorescent fingerprinting technique was used to study the impact of six external fluorophores' addition in whiskies and to determine potential markers for their geographical origin. Their emission spectra was measured by a (400–700 nm) and images of a 96-well plate containing mixtures of whiskies and a fluorophore were taken by a digital camera (254 and 366 nm UV light). The discrimination of 16 commercial spirits according to their origin (Scotland, Ireland, America, and other countries) was achieved using only one fluorophore, ($Ru(bpy)_3^{2+}$) and by applying PCA on the data obtained from the digital images or emissions spectra. Pre-treatment (e.g., contrasting, RGB splitting, normalization) of digital images and combination of data from the two wavelengths (254 and 366 nm) in an exposure time of 5 s resulted in a qualitative discrimination of the samples similar to that obtained using the emission spectra (400–700 nm, excitation at 366 nm) (Rukosueva et al., 2019).

Authentic and counterfeit blended Scottish whiskies were discriminated after the application of paper spray mass spectrometry (PS-MS), with negative ionization mode combined with chemometric classification models of PCA and PLS-DA (Teodoro et al., 2017). The entire analytical procedure was very fast (less than 1 min), required no sample preparation and very low solvent consumption. PLS-DA gave the best results and reached high reliability rates of 96.6% and 100% for the training (57 samples) and test (31 samples) sets. Characteristic ions for each category were determined, which can be used for the identification of the chemical marker compounds. The diagnostic anions for the authentic whiskies were of m/z 105, 143, 171, 301 and 486 and for the counterfeit whiskies were of m/z 124, 179, 195, 215, 347, 387, and 521 (Teodoro et al., 2017). The same method was applied in 19 adulterated blends of whiskies with cachaça (sugarcane spirit) and analysis took place in both positive (PS+) and negative ionization (PS−) mode. Competitive adaptive reweighted sampling partial least squares (CAR-PLS) (ti einai auto) model in PS (−) mode resulted in better discrimination accuracy of the samples compared to CAR-PLS in PS (+) mode data. Decreased and increased signals in the m/z 200–350 and in the $m/z > 350$ region respectively were correlated to the increased concentration of sugar from cachaça addition (Tosato et al., 2018).

The discrimination between malt whiskies of different maturation processes (matured only in Bourbon vs matured in Bourbon and wine barrels) was also achieved by gas chromatography coupled to tandem mass spectrometry (GC-Q-ToF) (Stupak et al., 2018). Two chemometric approaches—unsupervised PCA and supervised PLS-DA—were used for the evaluation of data obtained by GC-Q-ToF analysis after two extraction techniques; head space-solid phase micro extraction (HS-SPME) and liquid-liquid extraction (LLE) with ethyl acetate. PCA showed better discrimination based on the data obtained from the LLE extraction because of the higher number of compounds detected; however, the PLS-DA model was more accurate. In whiskies matured only in Bourbon barrels, the chemical markers *N*-(3-methylbutyl) acetamide, 5-oxooxolane-2-carboxylic acid and 4-(2-hydroxyethyl) phenol were not detectable and ethyl 5-oxoprolinate was in lower levels. They were also associated with the barrel wood type (Sherry, Port) used in the latter phase of maturation (finishing procedure). Additionally, the PLS-DA model showed significant discrimination between malt, "premium" blend (high percentage of malt whisky), and blended whiskies and the chemical markers responsible for the distinction were vanillin, β-damascenone, phenylmethanol, 2,4-ditert-butylphenol, ethyl vanillin and propivanillone. Interestingly, adulterated whisky samples showed high concentrations of 3-ethoxy-4-hydroxybenzaldehyde, 5-butyloxolan-2-one, ethyl heptanoate, 1,3-benzodioxole-5-carbaldehyde, 2,6-dimethoxyphenol, 1-phenylethyl acetate, 4-hydroxy-3-methoxybenzaldehyde, and benzaldehyde (Stupak et al., 2018).

The determination of the volatile profile using SPME-GC × GC-ToF MS analysis in combination with PCA followed by LDA on key compounds was used to distinguish peated single malts from mild single malts, blended and American whiskies in a group of 36 whiskies (Jeleń et al., 2019). In peated single malts 20 key odor compounds were identified and the most odorous, such as guaiacol, 4-ethylguaiacol, 4-methylphenol, 4-vinylguaiacol and 4-ethyl-2-methylphenol, were volatile phenols. Moreover, the discrimination of peated single malts from the other three categories was based on a LDA model of 10 compounds, the majority of which belonged to the ester group; ethyl undecanoate, ethyl-3-methylbutanoate, ethyl dodecanoate, 3-methylbutyl acetate, 2-methoxyphenol, 2-methylpropan-1-ol, *cis*-oak lactone, phenol, propan-2-ol, γ-decalactone. Additionally, the four investigated types of whiskies were successfully discriminated with a LDA model (explain 89.77% of variance of data matrix) based on their volatile profile of 61 compounds, independently of each volatile's odor contribution.

Wine and grape marc spirits

Grape-based spirits are produced after the distillation of the wine or the grape marc that remains after the separation from wine. In France, brandies are classified according to the production region and the most famous are Cognac (Regions: Charente-Maritime, Charente, Deux-Sévres, and Dordogne) and Armagnac (Regions: Gers, Landes, and Lot-et-Garonnethe) which are produced from the registered varieties of each defined region. Brandies are also classified based on the aging time of at least 2, 4, or 6 years as very special (V.S.), very superior old pale (V.S.O.P.), or extra old (X.O.), respectively (Špánik et al., 2015). Spirits from grape marc may have different denominations according to the production country such as Grappa from Italy, Tsipouro from Greece, Orujo from Spain, Pisco from Chile, etc. Most of them are bottled directly after the distillation and in some cases their dilution with water (unaged spirits), but recently barrel-aged spirits, which traditionally were consumed as unaged, appeared in the market.

Sádecká et al. (2019) used fluorescence spectrometry to discriminate 44 grape spirits according to their geographical origin (Bulgaria, Greece, Spain, France, Georgia, Slovakia, Moldova, Ukraine, Romania) by applying different types of spectra (emission, total luminescence and synchronous fluorescence) and sample dilution. EEM fluorescence spectra led to better results for non-diluted samples, but synchronous fluorescence spectroscopy (SFS) was more suitable for diluted samples and resulted in a higher value of correct classification (95%) at wavelength differences of 20 and 60 nm (Sádecká et al., 2019). Wine spirits produced in Slovakia were also classified according to their geographical origin in addition to their production method and maturation time (Špánik et al., 2015). A GC-MS method by direct injection was applied in 25 wine spirits (36%–40% ABV), combined with a PCA approach. The highest discrimination of the samples was observed in a specific range of retention times, which contains 6 peaks (phenol, butane-1,4-diol and 4 tentatively identified: 5-ethoxymethyl furfural, 5-butyl-4-methyldihydro-2(3*H*)-furanone, maltol, methyl-2-furoate).

Different aging processes of wine spirits were studied by the application of FT-Raman methodology (Anjos et al., 2020). Wine spirits were matured in three different types of wood barrels (chestnut, oak, and chestnut + oak) or in stainless steel tanks (with wood staves addition) for 4 different maturation periods (8, 30, 180, and 360 days) and a total of 60 samples was produced. PCA of FT-Raman data allowed the discrimination of wine spirits according to the wood species and the aging period within the first 12 months of the process based mainly on two spectral regions, from 3000 to 2600 cm^{-1} and from 1570 to 790 cm^{-1} (Anjos et al., 2020). Aged wine spirits are usually expensive due to the high cost of the maturation process but also due to the consumers' preference for their complex wood flavor. Among the characteristic sensory attributes of the aging process is vanilla aroma and the brown color originating from the barrel. However, the addition of vanillin as an aroma enhancer (not permitted) and the excessive addition of caramel as a color enhancer (permitted) are common practices in cheaper imitations to avoid extended periods of barrel aging. Canas et al. (2019) proposed to consider the ratios of furanic and phenolic aldehydes such as 5-hydroxymethylfurfural/furfural, vanillin/syringaldehyde, vanillin/coniferaldehyde, vanillin/sinapaldehyde, vanillin/syringaldehyde + coniferaldehyde + sinap-aldehyde as markers to indicate vanillin adulteration or increased contents of caramel in spirits. This was achieved by the application of a simple and rapid HPLC-UV-Vis method which analyzed 333 samples for the determination of furanic and phenolic aldehydes in combination with factor analysis and individuals control charts (Canas et al., 2019).

Three studies were conducted to discriminate Grappa (grape marc spirit) and other Italian spirits (grain or fruit marc spirits, other than grape) by applying different instrumental techniques (Giannetti et al., 2019b, 2020; Schiavone et al., 2020). HS-SPME-GCMS analysis has been applied on 82 spirits and PLS-DA showed a total classification rate of 95% between Grappa and other Italian spirits (Giannetti et al., 2019b). Mid-infrared (MIR) and near infrared (NIR) based spectroscopy has been used for the discrimination of Italian spirits originated from different raw material but also for the detection of possible adulteration of Grappa spirits (Schiavone et al., 2020). The group of authentic samples included 76 Italian spirits (59 Grappa and 17 other spirits) collected from their producers, while the adulterated group consisted of 36 samples where addition of a spirit of lower price took place. Classification of authentic and adulterated Grappa samples based on PLS-DA combined with multi-block partial least squares (MB-PLS) methodology gave the best results (100% of correct classification) compared to sequential and orthogonalized partial least squares (SO-PLS) or sequential and orthogonalized covariance selection (SO-CovSel) strategies. However, the discrimination between Grappa spirits and other Italian fruit spirits from apples, pears or berries based on MIR and NIR spectra was weak ($<$77%). Higher discrimination between Grappa spirits and other Italian spirits (spirits of fruits or cereals) was achieved with the combination of all the previous techniques, MIR and NIR spectroscopy and HS-SPME-GCMS, by collecting data from 75 spirit samples (Giannetti et al., 2020).

Additionally, NMR spectroscopy along with PCA and PLS-DA was applied to classify 57 Greek grape marc spirits (named tsipouro and tsikoudia) from different regions (North Greece and Crete Island) and five grape varieties (Romeiko, Malvasia, Xinomavro, Sangiovese, Nebbiolo). The results revealed the differences according to their geographical location based mainly on volatile compounds (amyl alcohols, methanol, ethyl acetate, acetaldehyde, 2-phenylehanol, etc.) (Fotakis and Zervou, 2016).

Fruit spirits

A wide range of fruit spirits are produced after the distillation of fermented juice or must, followed or not by an aging process according to the production regulations for each country. Czech, Hungarian, and Slovak plum spirits (Sádecká et al., 2016) were classified according to their geographical origin by applying SFS and NIR spectroscopy in combination with chemometric tools.

Appling PCA-LDA tools on SFS data obtained at a wavelength difference of 60 nm provided the best results especially for colorless spirits, compared to NIR data (5500–6000 cm^{-1}) where the total correct classifications were lower (Sádecká et al., 2016).

A NIR method targeting a similar spectral region from 5500 to 6050 cm^{-1} combined with PCA and LDA or general discriminant analysis (GDA) was employed to classify 67 commercial fruit spirits according to the raw material used for the fermentation (apple, apricot, pear, and plum). The above spectral region corresponds to either the CH stretch of the first overtones of CH_3 and CH_2 groups, or to compounds containing OH aromatic groups and was the one that gave the best results (Jakubíková et al., 2016).

Tequila

There is a range of agave-derived spirits, such as mezcal, raicilla, bacanora, tequila, most of them are domination of origin-protected spirits and they are produced in specific regions of Mexico representing the different terroirs of the country. The most known agave-derived spirit is tequila and it is produced from agave Tequilana Weber, blue variety, which is cultivated within a protected region of Mexico (geographical Denomination of Origin Tequila). The agave plants are harvested and then the agave hearts are cooked and milled to extract the juice. The juice is fermented, and double distillation is taking place. According to the aging time tequila is classified as "Silver or White" which is unaged, "Young or Gold" which is a blend of unaged and one of the following types of tequila, "Aged," "Extra Aged," and "Ultra Aged" which correspond to aging for at least 2 months, 1 year, and 3 years, respectively. According to the sugar, origin tequilas are distinguished in "tequila 100% agave" or "tequila"; the latter one contains maximum enrichment up to 49% of sugars from different origin and cannot be sugars coming from any other agave variety (CRT, 2019). All the brands that produce Tequila have to meet specific quality regulations and are mandatory to be registered in the Regulatory Council of Tequila (CRT). The cost of tequila has a high range (13–145 euros/bottle or more) according to the sugars origin, resting time, aging time in oak barrels and the blending process (De La Rosa Vázquez et al., 2015; Pérez-Caballero et al., 2017; Prado-Jaramillo et al., 2015).

The quality of many authentic tequilas has been diminished because of the introduction of low cost and low-quality components or even improper labeling such as the geographical origin or the years of aging (Pérez-Caballero et al., 2017). A big study of 170 commercial tequila samples of different aging period was conducted and data were collected from UV-Vis spectra (190–700 nm wavelength) by using a spectrophotometer (Andrade et al., 2017). PCA revealed that three groups of tequila were differentiated with slight overlaps. Additional classification methods employed showed that nonlinear models performed better than linear ones. Finally, genetic algorithm combined with partial least squares discriminant analysis (GA-PLS-DA) yielded the best classification of the samples, however it was proposed that PCA with quadratic discriminant analysis (QDA) was the most acceptable because of its simplicity and broad availability (Andrade et al., 2017). Additionally, a fluorescence method combined with the use of a spectrometer (homemade system) was applied to detect counterfeit tequilas. Genuine mixed, rested, and aged tequilas, especially 100% agave aged tequilas, showed high fluorescence intensities in the range from 400 to 750 nm compared to counterfeit and silver tequilas. Additionally, the wavelength of 255 nm could discriminate counterfeit tequilas from genuine ones (De La Rosa Vázquez et al., 2015).

Carreon-Alvarez et al. (2016) analyzed a number of physicochemical properties in 53 commercial tequila brands registered or not in the CRT. The companies that are registered in the CRT have to follow specific production regulations to ensure the quality of tequila. PCA and cluster analysis based on one-way ANOVA were applied on the data collected from the measurements of conductivity, density, pH, sound velocity, viscosity, and refractive index of the samples. All tequila samples from the registered brands appeared together in the PCA plot while in the cluster analysis the non-registered samples had similar characteristics such as higher conductivity and density and lower viscosity and refractive index values. A common adulteration in alcoholic beverages is the addition of methanol that could be also harmful for consumer's health. A simple method for the detection of methanol in adulterated tequila was based in the use of a fiber optic sensor coated with a thin film of zinc oxide nanorods and on transmission measurements using a laser diode with wavelength, $\lambda = 532$ nm (Necochea-Chamorro et al., 2019).

Rum and other spirits

Rum is a spirit produced from fermented sugar cane juice, syrup or molasses and follows the process of distillation and aging similar to whisky production (Belmonte-Sánchez et al., 2018; Roullier-Gall et al., 2018). FT-ICR-MS analysis revealed similarities based on polyphenolic compounds between rum and whisky, however rum was lower in concentrations of higher alcohols and fatty acids compared to whisky (Roullier-Gall et al., 2018).

Targeted and non-targeted HS-SPME-GCMS methodology was applied for the classification of 33 commercial rums of different origin (Cuba, Dominican Republic, Grenada, Trinidad & Tobago, Guatemala, Jamaica, Nicaragua, Republic of Mauritius, Spain, Venezuela), aging period, raw material and distillation method (Belmonte-Sánchez et al., 2018). Targeted analysis revealed that ethyl acetate and the sum of ethyl esters with 8–16 carbons (e.g., ethyl octanoate, ethyl decanoate, etc.) increased during aging but could not be used as chemical markers since their concentrations were highly impacted by the brand. A non-targeted method in combination with chemometrics resulted in better grouping of the samples. Hierarchical cluster analysis (HCA) distinguished traditional rums from those with flavoring addition. PCA revealed 40 ions as chemical descriptors, which are correlated to 13 volatiles (Table 1) and LDA resulted in the classification of traditional rums based on country of origin, raw material, distillation method and aging process.

Kuballa et al. (2018) analyzed authentic alcoholic beverages (rum, whisky, vodka) and potential counterfeit spirits from the same brands. The non-authentic spirits were purchased online and some of them had even 10–15 times lower prices (rum and whisky from online shops) in comparison with authentic ones. According to the results, ^{1}H NMR spectroscopy could detect counterfeit spirits; however, the sensory evaluation from a panel based on the results from a triangle test revealed that only a small group of tasters was able to detect the differences between counterfeit or authentic spirits (Kuballa et al., 2018).

3.3 Further discussion

In the last 6 years, the above studies have given insights in the transparency and authenticity of spirits' production and suggested potential methodologies that could detect adulterated alcoholic beverages and prevent fraudulent practices. Spirits can be classified according to the nature of raw material (fruit, grain), the geographical origin, the brand, the type of blend (single malt, blended), specific characteristics of the product (peated whisky), the maturation process/type of barrel and the years of aging. Adulterations may occur during the production, which concerns one or more of the above stages as well as the addition of flavorings or other chemicals during process. Although the exact type of adulteration is not always highlighted, authentic and counterfeit spirits are usually discriminated based on their chemical composition. For this reason, a wide range of methods has been developed for the determination of the chemical composition and authentication of spirits based on specialized equipment (FT-IR, GC-Q-ToF, GC-MS, HPLC-UV-Vis, NMR, etc.) in combination with chemometric approaches (PCA, PLS, OPLS-DA, LDA, etc.) applied in small or large groups of samples. These studies and methodologies revealed also a few drawbacks, without weakening their importance in the alcoholic beverage sector, that have to be noticed in an attempt to highlight the future needs on the development of alcoholic beverages authentication tools.

It is well known that the chemical composition of raw material during spirit production is altered during the alcoholic fermentation, the fractionation applied during distillation or the barrel aging process. Spirit's geographical origin can be classified based on chemical compounds, such as volatiles; however, their chemical path from the raw material to the final product is not always apparent or properly studied. For that reason, the identification of specific compounds as chemical marker should be correlated to the raw material through their chemical path. The detection of the alterations that occur by each process, to understand any effect of the production method to the final product, can determine the type of adulteration and the spirit's origin.

In the studies where non-targeted or profile methods are applied, the discrimination of spirits is based on chemometric models which are built on databases of known samples. Those models need to be built on a high number of samples, which is not always possible, but it is essential to improve the accuracy and preciseness of the results. It was also observed that in some cases, the analyzed samples were mainly purchased by the market, which does not confirm their authenticity or the type of adulteration and it does not take into account the effect of the production method and the brands as a parameter of the discrimination. A proper selection of samples can improve the effectiveness of an authentication tool.

Authentication includes more than one specification and it should be the result of multiple parameters. For example, a Scotch whiskey might be authentic based on its geographical origin because it is produced in Scotland. However, only this characteristic does not certify that its production method is safe (e.g., methanol above the permitted limits) for consumption or its label is not misleading (e.g., high addition of caramel/less maturation) to the consumers.

4 Authentication of other fermented beverages

Beer adulteration is not as extensive as what is observed in wine and spirit industry mainly due to the lower prices of beers and other fermented beverages in the market. However, in recent years there was an increase in consumers' preference in

TABLE 1 Discrimination approaches for various alcoholic beverages.

Product	Discrimination	Chemical markers	Number of samples	Analytical method	Chemo-metrics	References
Whiskey	Geographical origin (Scotland, Ireland, America) and maturation process (years of aging)	Spectral data from specific regions (e.g., 3100–2800 cm^{-1} discriminated American and Scottish and 2400–500 cm^{-1})		FT-IR	Mahalanobis distances	Sujka and Koczoń (2018)
	Maturation/barrel type (Sherry, Bourbon, finishing process)	Malted vs blended: Syringic acid, ellagic acid, gallic acid and four unidentified compounds Barrel type: Ellagic acid, glucono delta-lactone, gallic acid, syringic acid, decanoic acid, dodecanoic acid, hexadecanoic acid, hexadec-9-enoic acid, tetradecanoic acid	85	FT-ICR-MS	PLS-DA, OPLS-DA, and PCA	Kew et al. (2017)
	Brand, geographical origin (Scotland, United States but also France, Germany, Japan, Canada, and Austria), maturation process (1 day to 43 years aging), barrel type (Sherry Casks, Bourbon barrel, new make casks)	High number of unidentified compounds + phenolic compounds (caffeic acid, catechin, epigallocatechin, ethyl vanillate, ferulic acid, quercetin-glucuronide, isoquercetin, myricetin-glucoside, quercetin, syringaldehyde, syringic acid)	150	FT-ICR-MS and LC-MS/MS	PLS-DA	Roullier-Gall et al. (2018)
	Geographical origin (Scotland: Highlands, Lowlands, Speyside, and Islay)/maturation process	Volatiles and phenolic compounds (e.g., syringic acid, caftaric acid lyoniresinol, patuletin, digallic acid, stearyl acetate, syringaledehyde) + high number of unidentified compounds	106	FT-ICR-MS	PLS	Roullier-Gall et al. (2020)
	Blend status, use of peated malt, alcohol strength, barrel type, authentic vs counterfeit whiskies	3-Methylbutanol for blend status/ whole spectrum/spectrum range from 6 to 10 ppm	148 + 32 (counterfeit)	NMR	OPLS-DA and PCA	Kew et al. (2019)
	Whisky brand, authentic and counterfeit spirits	Spectra data between 200 and 500 nm	237	UV-Vis spectroscopy	PCA, LDA, and PLS-DA	Martins et al. (2017)
	Whisky brand, authentic, counterfeit spirits, years of aging	Spectra data between 200 and 400 nm	15	UV-Vis spectroscopy	PCA, LDA, and PLS-DA	Cantarelli et al. (2015)
	Geographical origin (Ireland, America, Scotland), brand, blend status (blended or single malt), maturation process (years of aging), and taste (rich or light)	Spectra data	33	Electronic tongue addition of fluorophores	LDA	Han et al. (2017)

	Geographical origin (Scotland, Ireland, America, and other countries)	Addition of flurophore Ru(bpy)$_3^{2+}$ and digital image at 254 and 366 nm UV light or emission spectra 400–700 nm	16	Spectrofluorimeter or digital camera/addition of flurophores	PCA	Rukosueva et al. (2019)
	Authentic vs counterfeit whisky	Diagnostic anions for authentic whiskies: *m/z* 105, 143, 171, 301, 486 and for counterfeit whiskies: *m/z* 124, 179, 195, 215, 347, 387, 521	88	PS-MS in negative ionization mode	PCA and PLS-DA	Teodoro et al. (2017)
	Adulteration with sugarcane spirit	*m/z* 200–350 region and *m/z* >350	19	PS-MS in both positive and negative ionization mode	CARS-PLS	Tosato et al. (2018)
	Maturation process/barrel history (Sherry, Bourbon, finishing process)	*N*-(3-Methylbutyl) acetamide, 5-oxooxolane-2-carboxylic acid, *y* (2-hydroxyethyl)phenol, ethyl 5-oxoprolinate	191	LLE GC-Q-ToF	PCA	Stupak et al. (2018)
	Blend status (malt, "premium" blended and blended)	β-Damascenone, phenylmethanol, 2,4-ditert-butylphenol, 4-hydroxy-3-methoxybenzaldehyde, ethyl 4-hydroxy-3-methoxybenzoate and 1-propanone-1-4-hydroxy-3-methoxyphenyl	191	HS-SPME/LLE GC-Q-ToF	PLS-DA	Stupak et al. (2018)
	Use of peated malt, mild single malts, blended and American whiskies	2-Methoxyphenol, 2-methylpropan-1-ol, 3-methylbutyl acetate, *cis*-oak lactone, ethyl undecanoate, ethyl-3-methylbutanoate, ethyl dodecanoate, phenol, propan-2-ol, γ-decalactone—volatile profile	36	SPME-GC × GC-ToF MS	PCA and LDA	Jeleń et al. (2019)
Grappa	Grappa vs Italian spirits from apples, pears, or berries. Authentic Grappa vs adulterated Grappa	MIR spectra: ester bond C—O (in the fingerprint region, between 1000 and 1100 cm^{-1}). NIR spectra: wavelengths range between 5500 and 6000 cm^{-1} (which identifies the first overtone of the C—H stretching), and around 7000 cm^{-1} (which is relative to the first overtone of the O—H stretching)	76	MIR and NIR spectroscopy	PLS-DA, MB-PLS, SO-PLS, SO-CovSel	Schiavone et al. (2020)
	Grappa vs Italian spirits from fruits or cereals	Volatile compounds, MIR and NIR spectra	75	HS-SPME-GCMS, MIR, and NIR spectroscopy	SO-PLS-LDA, SO-CovSel-LDA, PLS-LDA	Giannetti et al. (2020)

Continued

TABLE 1 Discrimination approaches for various alcoholic beverages—cont'd

Product	Discrimination	Chemical markers	Number of samples	Analytical method	Chemo-metrics	References
	Grappa vs Italian spirits from fruits or cereals	Volatile compounds (α-terpinene, p-cymene, α-terpineol, a-cubebene, β-bourbonene, isoledene, α-calacorene, ethyl heptanoate, ethyl octanoate, ethyl dodecanoate, diethyl succinate, furfural)	82	HS-SPME-GCMS	PLS-DA	Giannetti et al. (2019b)
Tsipouro	Geographical origin	Volatile compounds (amyl alcohols, methanol, ethyl acetate, acetaldehyde, 2-phenylehanol, etc.)	57	NMR	PCA, PLS-DA	Fotakis and Zervou (2016)
Grape distillates	Geographical origin (Bulgaria, Greece, Spain, France, Georgia, Slovakia, Moldova, Ukraine, Romania)	Wavelength differences of 20 and 60 nm	44	Fluorescence spectrometry	PCA-LDA, UPCA-LDA, and PARAFAC-LDA	Sádecká et al. (2019)
Wine distillates	Types of wood (chestnut, oak and chestnut + oak), type of maturation (in barrels or in stainless steel tanks with wood staves), four maturation periods (8, 30, 180, and 360 days)	Spectral regions, from 3000 to 2600 cm^{-1} and from 1570 to 790 cm^{-1}	60	FT-Raman	PCA	Anjos et al. (2020)
	Aging imitation (addition of vanillin and high amounts of caramel)	Furanic and phenolic aldehydes ratios (5-hydroxymethylfurfural/furfural, vanillin/syringaldehyde, vanillin/coniferaldehyde, vanillin/sinapaldehyde, vanillin/syringaldehyde + coniferaldehyde + sinapaldehyde)	333	HPLC	Factorial analysis	Canas et al. (2019)
	Geographical origin, production method and maturation process	Phenol, butane-1,4-diol and four tentatively identified: 5-ethoxymethyl furfural, 5-butyl-4-methyldihydro-2(3*H*)-furanone, maltol, methyl-2-furoate	25	Direct injection-GCMS	PCA	Špánik et al. (2015)
Plum spirits	Geographical origin (Czech Republic, Hungary, and Slovak Republic)	Wavelength at 60 nm	44	SFS	HCA, PCA, LDA	Sádecká et al. (2016)
	Geographical origin (Czech Republic, Hungary, and Slovak Republic)	Spectral regions 5500–6000 cm^{-1}	44	NIR	HCA, PCA, LDA	Sádecká et al. (2016)

Fruit spirits	Type of raw material (apple, apricot, pear, and plum)	Spectral regions 5500–6050 cm^{-2}	67	NIR	PCA-LDA, GDA	Jakubíková et al. (2016)
Tequila	Maturation process (aging type: white, ested, aged, and extra-aged)	Wavelength 190–700 nm	170	UV-Vis spectroscopy	GA-PLS-DA, PCA-QDA	Andrade et al. (2017)
	Authentic vs counterfeit tequila	Wavelength 400–750 and 255 nm	40	Fluorescence method combined with a spectrometer	–	De La Rosa Vázquez et al. (2015)
	Non-registered vs registered in CRT	Conductivity, density, viscosity, refractive index	53	Physicochemical measurements (conductivity, density, pH, sound velocity, viscosity, and refractive index)	PCA and one-way ANOVA	Carreon-Alvarez et al. (2016)
	Methanol adulteration	–	–	Fiber optic sensor coated with zinc oxide nanorods/ laser diode ($\lambda = 532$ nm)	–	Necochea-Chamorro et al. (2019)
Rum	Type of distillate (rum and whiskey)	Higher alcohols and fatty acids	8	FT-ICR-MS and LC-MS/MS	PLS-DA	Roullier-Gall et al. (2018)
	Geographical origin, raw material, distillation method, and maturation process	Ethyl hexadecanoate, ethyl octanoate, ethyl decanoate, ethyl acetate, ethyl tetradecanoate, ethyl-(*E*)-9-octadecenoate, 3-methylbutyl octanoate, ionene, ionene-derivative, tetrahydropyran-2-methanol, 1,1-diethoxy-3-methylbutane, 1.1-diethoxymethane and one unidentified compound)	33	HS-SPME GCMS	HCA, PCA, LDA	Belmonte-Sánchez et al. (2018)
Rum/ whiskey/ vodka	Authentic vs counterfeit beverages from the same brand			^{1}H NMR and sensory evaluation		Kuballa et al. (2018)
Beer	Craft vs industrial	2-Methylpropyl 2-methylpropanoate, 3-methylbutyl acetate, β-myrcene, 3-methylbutan-1-ol, ethyl hexanoate, hexan-1-ol, 1,1-dimethyl-4-methylenehexahydro-1*H*-cyclopenta[*c*]furan, ethyl octanoate, β-linalool, ethyl decanoate, 2-phenylethyl acetate, 2-phenylethanol and octanoic acid	79	HS-SPME GCMS	PCA and PLS-DA	Giannetti et al. (2019a)
	Craft vs industrial	Adenosine/inosine, trehalose, asparagine, trigonelline, lactate, acetate, and succinate	31	^{1}H NMR	PCA and PLS-DA	Palmioli et al. (2020)

Continued

TABLE 1 Discrimination approaches for various alcoholic beverages—cont'd

Product	Discrimination	Chemical markers	Number of samples	Analytical method	Chemo-metrics	References
Cider	Geographical origin (Madeira)	(*E*)-Rose oxide, 2-heptanol, (*Z*)-3-hexenol, octanol, acetic acid, limonene oxide, nonanol, propanoic acid, 2-methylpropanoic acid, bornyl acetate, linalyl acetate, butyl octanoate, α-terpineol, ethyl phenylacetate, and 2-phenylethyl acetate	7	HS-SPME GCMS	PLS-DA	Perestrelo et al. (2019)
	Geographical origin (Europe vs Australia)	Potassium, sulfur, phosphorus, calcium, magnesium, and sugars	21	IRMS, ICP-OES, ICP-MS, HPLC-RID	PCA and CDA	Carter et al. (2015)

HCA, hierarchical cluster analysis; *PCA*, principal component analysis; *LDA*, linear discriminant analysis; *PS-MS*, paper spray mass spectrometry; *CDA*, canonical discriminant analysis; *HPLC*, high performance liquid chromatography; *RID*, refractive index detector; *ICP-OES*, inductively coupled plasma–optical emission spectrometer; *MIR*, mid-infrared spectroscopy; *NIR*, near infrared spectroscopy; *MB-PLS*, multi-block partial least squares; *SO-PLS*, sequential and orthogonalized partial least squares; *SO-ConSel*, sequential and orthogonalized covariance selection; *HS-SPME*, head space solid phase microextraction; *GCMS*, gas chromatography mass spectrometry; *CARS-PLS*, competitive adaptive reweighted sampling partial least squares; *GDA*, general discriminant analysis; *QDA*, quadratic discriminant analysis; *GA-PLS-DA*, genetic algorithm combined with partial least squares discriminant analysis; *CRT*, Regulatory Council of Tequila.

craft beers, which are considered to be of higher quality and have more complex flavor because of their production in small and traditional breweries. For this reason, craft and industrial beers were discriminated based on NMR spectra data combined with PCA and PLS-DA approaches. Higher concentrations of adenosine/inosine and trehalose, were detected in industrial beers, while higher concentrations of asparagine, trigonelline, lactate, acetate and succinate were detected in craft beers (Palmioli et al., 2020).

An HS-SPME-GCMS method combined PLS-DA chemometric tools was also used to classify beer (Giannetti et al., 2019a) and cider (Perestrelo et al., 2019; Sousa et al., 2020). A total of 79 beers from different countries were discriminated according to their different process methods (craft vs industrial beers) based on 13 out of 111 volatile compounds using a PLS-DA model (Giannetti et al., 2019a). As chemical markers, β-myrcene, hexan-1-ol, 1,1-dimethyl-4-methylenehexahydro-1*H*-cyclopenta[*c*]furan, ethyl octanoate, β-linalool, and ethyl decanoate were specified with higher concentrations in craft beers and 2-methylpropyl 2-methylpropanoate, 3-methylbutyl acetate 2-phenylethyl acetate, 2-phenylethanol and octanoic acid with higher concentrations in industrial beers. Two studies were applied to discriminate (PCA and PLS-DA methods) cider samples from Madeira Island based on their geographical origin. Perestrelo et al. (2019) proposed 15 volatiles ((*E*)-rose oxide, 2-heptanol, (*Z*)-3-hexenol, octanol, acetic acid, limonene oxide, propanoic acid, 2-methylpropanoic acid, bornyl acetate, linalyl acetate, butyl octanoate, α-terpineol, ethyl phenylacetate and 2-phenylethyl acetate) as chemical markers for the characterization of geographical region of seven ciders (Perestrelo et al., 2019). Sousa et al. (2020), in a larger scale study conducted on 53 samples from two consecutive years (2018 and 2019) proposed nine volatile congeners as geographical markers, such as 1-hexanol, 1-octanol, methyl acetate, (*Z*)-3-hexen-1-ol acetate, ethyl hexanoate, ethyl nonanote, ethyl octanoate, isoamyl octanoate, and limonene.

Carter et al. (2015), applied isotopic (d^2H, $d^{18}O$, $d^{13}C$, and $d^{18}O$) and chemical (cations, anions, and sugars) analysis on 21 ciders from Europe and Australia in an attempt to distinguish the geographical origin of the products. The discrimination (PCA) of the ciders was based on the concentrations of potassium, sulfur, phosphorus, calcium, and magnesium (chemical data). In addition, by applying canonical discriminant analysis (CDA) on chemical or on the combined chemical and isotopic data the correct classifications in discriminating the country of production were 100%, in contrast to CDA analysis of the isotopic data, which was lower (Carter et al., 2015).

5 Future scenario

The future of authentication is closely related both to environmental conditions as they determine the quality of the raw materials but also to new marketing styles and trends as they set the foundations for new product development.

5.1 Wine

As already mentioned, authentication focus shifts from time to time however safety remains a permanent need for verification. With this view, improvement of current analytical methods and development of fast and accurate techniques for chemical residues is of high importance, and even more so is pesticide residue monitoring, which can be used as a tool to manage both their levels on grapes at harvest time and predict their presence in wines (Urkude et al., 2019). Regarding the recent consumer concern on arsenic in wines, a new method based in nanostructured paper-based electrodes has already been developed for arsenic determination, while progress is already noted in the detection of residual pesticides as well, using nanotechnology based colorimetric techniques (Núñez Bajo and Fernández Abedul, 2020; Singh et al., 2020).

Spectral techniques present many advantages besides cost effectiveness and robustness, with most appealable their ease of use and handling. Portability is another big advantage that can allow even in situ and real time analyses while the continuous advantages in hardware will soon lead to more user-friendly device interfaces hence faster results. However, not one from these techniques has been recognized as an official method. Instead, all authentication studies based on spectroscopy and chemometrics call for the construction of databases in the form of libraries or highlight the need for larger sample sets to improve classification. These needs should be met to improve calibration of predictive models (Reina et al., 2020). Given the complexity of wine matrix, as well as the vintage effect, origin and type of variety influence and the impact of maturation and aging in wine composition, wine samples that will be used to construct data libraries should be numerous and present high variability. Advances in chemometrics and the use of data fusion, which is presented as promising, will help overcome analytical challenges and improve authentication results. Between the different analysis methods, NMR fingerprinting and stable isotope analysis provide the most reliable, reproducible and accurate authentication analysis to date, and the possibility for in situ authentication at any step of the production chain would make their use essential, however their high cost makes their use appealable mostly to official control bodies (Christoph et al., 2015).

Chemical marker selection has advanced greatly over the past decade, to the point that a large number of marker compounds has been studied extensively and are now available for authentication purposes. Together with multivariate analysis and metabolomic analysis they are expected to provide important information (Dey and Montet, 2018).

Introduction of new wine regions as a result of climate change or changing demand in the wine market, and the potential reevaluation of preexisting geographical classifications—even though less probable due to historical reasons and political implications—will require authentication based on different criteria (Ferretti, 2020; Meloni and Swinnen, 2013). Emerging wine countries such as England, China and Japan are establishing PDO rules and are using both autochthonous and international varieties whose distinctiveness (for autochthonous) or conformation to the typical features (international) will have to be examined, recorded and authenticated (Chen and Kingsbury, 2019; Department for Environment Food and Rural Affairs, 2011). Extensive cultivation of noble varieties in various parts of the world may alter typicity expectations in terms of sensory profile and will heighten the need for a universal register of certification to protect against confusion and deception (Friedmann, 2020).

The multiplication of the place of origin for noble grape varieties and the alterations in a multifaceted notion such as typicity will lead to a reevaluation of the term by wine experts and will ultimately complicate wine tasting by trained panels. This will increase the need for an analytical approach to be used complementary to sensory evaluation. Electronic nose can provide a suitable tool for this task, as it is already used with success not only to detect wine spoilage and assess wine quality but also to differentiate wines according to their aging time and yeast format (de Lerma et al., 2013; Martínez-García et al., 2021; Rodriguez Gamboa et al., 2019). Taste and aroma active compound analysis and characterization has also been recently used to provide information on the connection between these compounds and a wines' sensory attributes and subsequently produce models which will predict aroma profile or even objectively measure wine quality (Tian et al., 2021). Prediction of wine sensory properties was achieved using mid-infrared spectra and chemometrics as well; however, accuracy needs to be improved as it is highly influenced by vintage variability (Niimi et al., 2020).

Climate change presents a major challenge to viticulture, therefore to wine production as well. First, viticulturists will have to adapt to changing climatic conditions including increasing temperatures, decreased rainfall, and potential extreme weather events such as hail and flooding. Even though temperature changes can be beneficial for some regions (e.g., England), many of the Old-World winemaking regions will face difficulties retaining a stable wine sensory profile. Adaptation strategies are needed to maintain typicity regardless of the changing climatic parameters and continue to produce wines of high quality. Warm regions will have to tackle high alcohol levels as a result of increased temperatures which trigger advanced phenology, but also modified fruit aroma and lower yields as a result of water stress (Van Leeuwen et al., 2019). Higher potential alcohol will increase adulteration cases and the production of counterfeit wines while adaptation techniques to maintain a certain aromatic profile will need to be authenticated in terms of typicity. To efficiently tackle global warming potential results, studies on the impact of higher temperatures on the aromatic profile of Bordeaux wines have already showed that freshness and their ruby color have a tendency to be reduced, hence to preserve their typicity winemaking processes should adapt to the changes in wine composition (Drappier et al., 2019).

Calculation of bioclimatic indexes for the next 30 years has already led to the delimitation of potential viticultural areas and the development of new maps for PDO areas in some countries (Sánchez et al., 2019). Mapping new viticultural areas to produce wines of consistent high quality is expected to increase grape origin authentication needs. Indeed, consumer preference is already strongly associated with set geographical indications, thus change of grape origin in a PDO wine will be most likely met with scepticalness and mistrust, which underlines the need for consumer education prior to radical adaptational changes (Rodrigues et al., 2020a). Another result of climate change is going to be the proliferation of mycotoxins and undesired microorganisms and is set to increase biogenic amines content in wines. These changes, along with the production of higher pH and lower acidity wines with higher alcohol levels will lead to an increase in wine treatments with certain ingredients to maintain a consistent quality (Ubeda et al., 2020). High sugar content will increase the use of alcohol tolerant yeast species and may create a higher need for genetically improved yeasts which due to society refusal is highly likely to require authentication analysis regarding their presence or absence from a wine (Pérez-Torrado et al., 2015).

Counterfeit wines are expected to increase, and fraud types will evolve as a result to increase demand for premium wines in new (and less educated regarding wine) markets such as India. For these types of analyses non-invasive methodologies will facilitate label authentication (Grijalba et al., 2020). Evolution in analysis that will allow detection of changes in wine composition during transportation will also be imperative.

Environmental pollution and increased anthropogenic contamination through tourism and increased transportation emissions already present a moderate ecological risk to certain ecosystems, however they are expected to deteriorate wine quality through grape contamination. This will lead to increased need for residual pesticide authentication analysis (Brtnický et al., 2020).

Interest in label information is increasing, and many wineries are already satisfying conscious customer needs either through more informative labels or QR code and wine apps (Higgins et al., 2014). The abundancy of information seems to attract curious customers and overwhelm less curious ones; however, it plays a significant role on the willingness to pay for consumers who are aware of their consumption choices' environmental impact. In the future, improved customer access to information along with increased business orientation to greener practices will increase the need for authentication especially because these parameters will be used by consumers to evaluate wine quality (Galati et al., 2019). Discrimination between different types of wines with similar features such as green, natural and organic would benefit from the creation of a common regulation, which in turn will call for authentication analyses.

5.2 Distilled alcoholic beverages

It is an indisputable fact that there is a need for alcoholic beverage authentication for the economical protection of their associated industries and their countries of origin, together with the need of food ingredients transparency that arrive on the consumers' plate or glass. It is preferable and essential for the consumer to know the ingredients, the origin or even the story that is behind of an alcoholic beverage or a brand. Future trends in alcoholic beverage industry are creating the need of tools to prevent adulterations and create new perspectives in authentication.

Authentication will be essential, as it will provide more transparency in the alcoholic beverages' sector by allowing their quality verification via the authentication of the ingredients used for their production. The number of people following specific diets (vegetarian, allergies) is growing, so ingredient verification could make safer the consumption of alcoholic beverages.

New techniques will be used to limit the time of production, to improve the flavor characteristics of the product and to enhance protection during their production pathway or storage (oxidation, bacterial infections, etc.). Moreover, new techniques may be applied to produce new types of beverages (e.g., spirits with lower alcoholic content) in an attempt to reach new audiences. These techniques will have to be evaluated to detect their effect in alcoholic beverage composition and thus their authentication.

Terroir in beverages is an idea that has become increasingly popular in recent years. As it is becoming more common with other alcoholic beverages, it will eventually create new geographical indications that will need verification. Certification of the production pathway based on the provenance of the raw material can increase the quality of the alcoholic beverages. Complexity that is originated from the raw material and less from the maturation process (barrel) increases the need for terroir establishment as well.

Due to the climate change high variation in climatic conditions was observed during the last few years (e.g., rainfalls, sunny days) which can affect the growth of a crop, its maturity and eventually the flavor of the alcoholic beverage. This may lead to the production of a spirit by vintage i.e. according to the year of harvest as it is applied to wines.

Regarding methods of analysis, although there is a trend moving from targeted to non-targeted methods, the combination of both techniques can give better results and more details for the type of adulteration. Discrimination based on chemical markers could correlated with rapid untargeted methods (e.g., FTIR) in order for them to be used from non-specialists (industry workers, consumers, or traders). Most of these methods already require the development of a database for each country which will include the flavor profile of a beverage, the production method, the origin of raw material.

Certification of the production method via the efficient application of authentication but also traceability from the raw material to the final product, will help develop a product's ID. However, this should not undermine the privacy as many of the alcoholic beverages are produced based on recipes kept "secret" and which ultimately make them unique. Authentication in alcoholic beverages is expected to be applied more often, so the need for certifications that visually verify the brand or country, such as special seals used in certificated wines and holograms will become necessary. However, since the package can be imitated, the development of authentication methods that do not require unpackaging will be essential as well.

6 Conclusion, opportunities and future challenges

Wines and other alcoholic beverages authentication future will depend on the advance of the techniques used for authentication implementation as well as the advance of the analytical techniques for the identification of adulterants. Combining information from various analytical techniques has already proven promising, while data interpretation through statistical analysis seems imperative for the improvement of classification and prediction analyses. The construction of databases containing different sample profiles is essential but even more so is the establishment of free data exchange formats, which will facilitate the circulation and targeted utilization of research results. Finally, any future developments in analytical techniques, specifically concerning techniques that collect large amount of information will need specially designed chemometric tools to handle such data as well as advanced processing algorithms and interpretational tools for rapid and accurate authentication results.

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