Authentication and Traceability of Wine

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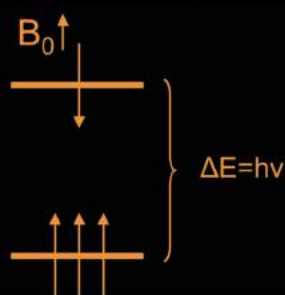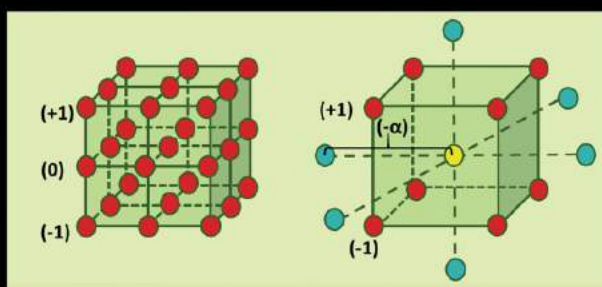Najran University
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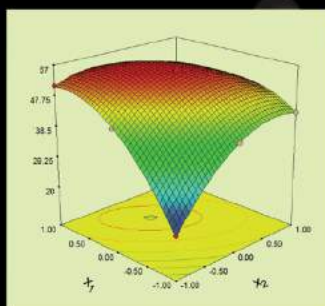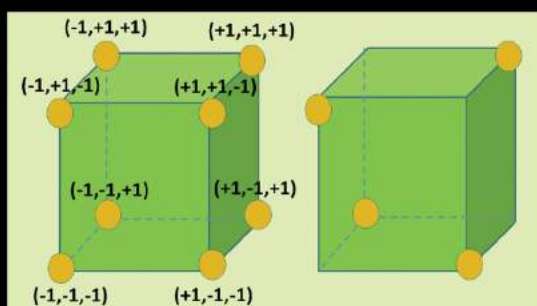
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Authentication and Traceability of Wine

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14.1 INTRODUCTION

Wine is a beverage whose value is influenced by many factors, amongst which the origin, vintage, grape variety, and growing conditions play major roles. Wine is characterized by a wide variety of sensory characteristics. The information provided on the wine label is connected to the consumer's expectations concerning the sensory and quality criteria. The label may therefore indicate significant and price determining characteristics such as brand, type, vintage, variety, and origin of the product, which represents the wine identity (Palade and Popa, 2014). Wine control is traditionally and strongly associated with the proof of authenticity. Generally, chemical falsifications that are to be dealt with are the addition of water, glycerol, alcohol, dyes, sweeteners, flavor substances, the non-authorized addition of sugars, preservatives, and acidity adjustments. However, wine authentication aims to confirm all the declarations on the label descriptions or to detect fraudulent statements by various analytical methods (Schlesier et al., 2009).

The adulteration of alcoholic beverages may not be conducted only to increase the alcoholic strength by using cheaper sources of sugar and starch besides grapes or fruit—sometimes combined with watering-down—but also to increase the presumed or apparent quality of the product such as in the case of the 1985 scandal in Austria, when diethylene glycol was added to wine to increase sweetness (Tagliabue, 1985). Another agent to sweeten wine that has been historically applied is lead acetate, which was documented in Greco-Roman times (Lessler, 1988), and chronic Pb poisoning outbreaks have been frequently recorded in history (Eisinger, 1982). The causality with wine adulteration was recognized early and the Pb addition was prohibited, for example, in 1427 in France and Spain and in 1478 in Germany (Lessler, 1988).

The analysis of wine is of great importance since wine components strongly determine its stability, organoleptic, or nutrition characteristics. In addition, wine analysis is also important to prevent fraud and to assess toxicological issues (Grindlay et al., 2011).

The great number of parameters affecting wine quality has initiated the development of different protocols for analysis. Wine constituents are strictly regulated by international organizations or government agencies to avoid fraud and health risks. Luque de Castro et al. (2005) have recently reviewed methods of analysis for the most commonly determined parameters in wine such as ethanol, sulfur dioxide, reducing sugars, polyphenols, organic acids, total and volatile acids, Fe, soluble solids, pH, and color (Grindlay et al., 2011). For the wine industry and market sector, it is particularly essential that the intended value traits created via genetics (variety), the origin of production (typicity), and the unique inputs or processing methods are preserved. In other words, it must be ensured that a product's label is accurate and not misleading, since consumers distinguish peculiar commodities from a mass of other similar ones with the belief that they bear a superior quality. However, wine is a product that can be easily adulterated, and for this reason wine authenticity is guaranteed by strict guidelines laid down by responsible

national authorities and includes sensory evaluation, chemical analyses, and examination of the records kept by wine producers (Makris et al., 2006).

The EC regulations dealing with geographical indications (GI) include traceability provisions. These are built into the provisions dealing with certification schemes and the various requirements concerning the overall control of the producers' operations. For example, Article 118p of EU Regulation 1234/20073 incorporated EU Regulation 479/2008 (dealing with wine) provides for annual verification of compliance with GI product specifications by relevant bodies (e.g., product certification bodies, public authorities, etc.). In all cases, producers will need to show inspectors how and where their products were produced using reliable traceability systems (Palade and Popa, 2014).

In the certification and control processes provided for GIs under the EU regulations, traceability is a core element. Only by recording the origin of the various components and by tracking the production chain is it possible for the certification and control bodies to verify, certify, and monitor whether the final product actually has the claimed link with its geographical origin and conforms to the relevant specifications and quality requirements (Sciarra and Gellman, 2012).

Wine authenticity is very important, especially in case of quality control and consumer information. Since wine quality is dependent on the consumer demands, compliance with traceability provisions satisfies the associated economic needs. It is necessary that a traceability information system exists in the wine supply chain in order to provide a better management of all the representative events that may arise on this chain, from grape production to wine selling. Traceability documents allow the detection of certain deviations from the usual processes, which may render the final product unsafe or of a lower quality than the one expected. Therefore, identifying the safety and quality issues during the process, by means of authentication and traceability, assures compliance within the framework of international regulations with the consumers' request for certification of quality attributes (Ashurst and Dennis, 1996). Table 14.1 presents different types of fraud commonly found in the wine industry.

TABLE 14.1   The Types of Wine Fraud (Holmberg, 2010)

Type	Description	Risk for Consumer
Mislabeling Regarding Origin, Classification, or Vintage	Most common type of wine fraud. Often facilitated by a "chain of bills" when wine is sold in a chain of retailers with a stepwise "quality enhancement".	Typically, no health risk because portable, cheap wine is misrepresented as a better quality product. Deception and fraud for the consumer.
Artificial Wine	Wine based solely on additives and water. Occurs very seldom now.	Health risk such as allergenic risk dependent on the (unlabeled) additives.
Wine Enhancement	Enhancement, most often accomplished by adding sugar, glycerol, diethylene glycol, or other sweeteners, and/or other flavor compounds to the wine, or through blending with sweeter, foreign wine.	Typically, no health risk except cases of addition of toxic compounds (e.g., methanol). Deception and fraud for the consumer.

14.2 TRACEABILITY OF WINE

Traceability is defined as the ability to follow a product batch and its history through the whole, or part, of a production chain from raw materials through transport, storage, processing, distribution, and sales (called chain traceability), or internally in one of the steps of the chain, for example, the production step (called internal traceability). Simply traceability of wine is defined as a method through which anybody in the wine supply chain will be able to verify the origin and composition of each batch of wine, its conditions of storage, and all the products that came in contact with the wine after the production. Traceability in the wine industry has an important role in the quality assurance management system. It ensures the registration of specific documents for all the manipulations of raw materials, ingredients, and final products. They are created specifically to allow a rapid identification of the product history. The wine supply chain requires traceability from grape production to processing and wine distribution. Traceability of products was introduced in the 1990s and is still under investigation by scientific and industrial bodies (Bevilacqua et al., 2009). A number of traceability systems, technologies, and standards have been developed to carry out supply chain traceability and internal traceability for different business objectives (Bechini et al., 2008; Bertolini et al., 2006). Nevertheless, only large enterprises, which are characterized by a tightly aligned supply chain and supported by a considerable use of information and communication technology, employ very efficient and fully automated traceability systems. On the contrary, small enterprises only rarely implement traceability and, when they do, they add the traceability management to their normal operation, thus decreasing the efficiency and increasing the costs. Thus, today, a considerable challenge is to develop agile and automated traceability platforms for communities of small-scale enterprises.

14.2.1 Grape Growers

Grape growers are responsible for the production, harvest, and delivery of grapes. Growers should record details about the locations, types of wines, annual production records, origins, chemical contents of water used for cleaning and irrigation, and annual treatments. For each treatment product, growers should record the supplier's details, a description of the product received, as well as the applicable batch numbers. The growers provide, with each delivery, the location numbers of the plots from which the grapes came and the date of picking, so that the receiving wine producers can link the related details to the wine made from these grapes.

14.2.2 Wine Producers

Wine producers are responsible for the production, manufacture, and/or blending of wine products. Wine producers should record where, in the winery, grapes or juice was stored. They must keep accurate records of the procedures and operations performed. The wine producer is responsible for identifying each production run with a batch number. For the receipt of additives, the producers should record the supplier's details, receiving date, a description of the product received, as well as applicable batch numbers.

14.2.3 Bulk Distributor

The bulk distributor is responsible for receipt, storage, dispatch, processing, sampling, and analysis of bulk wine. The bulk distributor checks the receiving documents, records all the information including the amount of received wine, and takes samples for tasting and analysis. If the wine is rejected, the wine returns to the source; otherwise two distinct processes are performed:

  i. Storage and dispatch of bulk wine without any blending or any other processing.
  ii. Storage, blending of different wines, and dispatch of the new bulk blend. Identification is handled by the bulk distributor and the bulk wine container. To ensure forward tracking, it is essential to record references of the delivery items and link these to the recipients.

14.2.4 Transit Cellar

A transit cellar is responsible for the receipt, storage, dispatch, processing, sampling, and analysis of bulk wine. The transit cellar receives bulk wine from bulk distributors in different kinds of containers. Each of these containers is identified with a proper code. The transit cellar sends batches of bulk wine to the fillers/packers. Each container sent is identified with a unique number and with the associated quantity of wine (liters). In order to maintain accurate traceability throughout the chain, it is necessary that the transit cellar records the items and batch numbers, as well as the identifier of each dispatched item. To ensure forward tracking, it is necessary to record the global identifiers of the shipped items and link these to the locations of the recipients.

14.2.5 Filler/Packer

The filler/packer is responsible for the receipt, storage, processing, sampling, analysis, filling, packing, and dispatch of finished goods. The filler/packer receives containers of bulk wine from the transit cellar, and also "dry goods" in contact with wine (bottles, caps, corks, etc.). Each of the containers of bulk wine and logistic units of dry goods is identified with a proper batch number. During this stage, the wine is poured into different kinds of containers such as bottles, bags, kegs or barrels, and a lot number is allocated to them. A link between these components (bulk wine, finished product) should be maintained. The next step is packaging into cartons and pallets and the dispatch of these cartons and pallets (identified with a lot number) to the finished goods distributor. The lot number must be linked to the batch(es) of bulk wine used to fill the bottles. To ensure forward tracking, it is necessary to record the global lot numbers of the shipped items and link these to the location numbers of the recipients.

14.2.6 Finished Goods

A finished goods distributor is responsible for the receipt, storage, inventory management, and dispatch of finished goods. The finished goods distributor receives pallets and cartons from the filler/packer and dispatches them to the retailer. These trade items are

identified with lot numbers. To ensure forward tracking, it is necessary to record the global lot numbers of the shipped items and link these to the location numbers of the recipients. The retailer receives pallets and cartons from the finished goods distributor and picks and dispatches goods to the retail stores. The container number of an incoming pallet is recorded and linked to the location numbers of the suppliers. The retailers keep a record of the container numbers and the lot numbers of the components of the pallets and cartons they receive. The retailers sell consumer items (bottles, cartons) to the final consumers. Each of these items is identified with a number allocated by the brand owner.

This brief description of a wine supply chain has highlighted that all the processes from the grape grower to the consumer can be traced by associating appropriate identifiers with the traceability entities managed by the single supply chain actors and by creating a record for each identifier with all the information required about the entity. Each actor of the supply chain is therefore responsible for recording traceability data corresponding to specific entities. Further, each actor has to create links between the identifiers which identify correlated entities.

14.3 AUTHENTICITY OF WINE

The authenticity of wine is guaranteed by strict guidelines laid down by the responsible national authorities that include official sensory evaluation, chemical analyses, and examination of the registers kept by the wine producers (Rapeanu et al., 2009). The authenticity of wine has been extensively investigated because wine is an easily adulterated product due to its chemical composition and its availability throughout the world (Ashurst and Dennis, 1996). Responsible and continuous controls are required to maintain the quality of wine.

Wine is a very easy product to adulterate because of its strong chemical basis (high alcoholic content, low pH) and its availability throughout the world; it is also probably one of the food products that is most often analyzed and for which legislation is the most complete. The imaginations of potential deceivers seem to be without bounds and the extent of such fraud remains unknown. Even if they are scarce, fraudulent products cause considerable damage to the wine trade and, in addition to a potential loss of prestige, the damage to the product image in terms of consumer confidence can be immense, especially in the current context of surplus where "new world" products are becoming increasingly competitive. Until recently, tasting by experts was the only way of verifying authenticity, but because experts are not readily available and because of the subjectivity of the technique, methods were developed that sometimes combined advanced mathematical tools and the latest analytical technologies to guarantee the authenticity of wine. Usually, volatile compounds are used to characterize varieties, whereas minerals are used for geographical differentiation. Amino acids as well as phenolic compounds are used for both. The development of advanced techniques for wine authentication is a challenge, which is currently being given a special attention (Ashurst and Dennis, 1996).

14.3.1 Authentication of Geographical Origin

Climatic, edaphic, and orographic factors influence the process of wine growth with direct influence on the compositional and sensory parameters of wines (Ballabio et al.,

2006). Since the area of production raises a visible mark on originality and quality characteristics of products, the determination of geographical origin is the main requirement for wine authenticity. The concept of "terroir" has been introduced in Europe, considering the specific characteristics of wine that are induced mainly by the geographical location and the characteristics of production in the concerned areas. The "denomination of origin" (DOC) regions are areas within the designated traditional wines, which have great quality features. Sensory evaluation done by specialists (tasters) was the only way to determine the geographical origin of wines. This method has a high degree of uncertainty; therefore, instrumental analysis is used to identify the compounds that are present in very small quantities (Rapeanu et al., 2009). The principal methods used for the authentication of geographical origins are discussed below.

14.3.1.1 Organic Compounds

14.3.1.1.1 Analysis of Volatile Compounds Profile   Based on the content of 1-hexanol and cyclohexanone, it was possible to differentiate between Pinot noir wines of French and American origins. Using data processing and laboratory methods that generate numerous relatively accurate data (e.g., high pressure liquid chromatography (HPLC), gas chromatography (GC), atomic absorption (AA)), a pilot database can be developed (Kwan and Kowalski, 1978). Further, it was possible to identify the geographical origins of French red wines and Spanish white wines by the use of more volatile compounds (ethyl esters, isoamyl esters, aldehydes, acetals) (Rapeanu et al., 2009). More recently, by the means of purge and trap followed by capillary gas chromatography and mass spectrometry (MS), Garcia-Jares et al. (1995) performed the differentiation of some white wines of Galicean origin (Rias Baixas) using 19 highly volatile compounds.

14.3.1.1.2 Analysis of Amino Acidic Profile   Amino acids are useful substances for differentiating wines. Production of wines, such as sparkling wines, where the second fermentation producing the overpressure of CO_2 is performed in the bottle leads to an increase in amino acids.

By investigating the amino acids like arginine, alanine, tyrosine, valine, and leucine that are responsible for the amino acidic profile of wines, it is possible to identify the geographical origins of wines (Flamini and De Rosso, 2006; Chambery et al., 2009).

Tusseau et al. (1994) used this technique to separate authentic Champagnes from sparkling wines; unfortunately, wines made from the Pinot Noir grape from the same place but with different vintages show wide variations that do not assist in characterization. However, Champagnes are richer than sparkling wines in all amino acids, except arginine, because of the second fermentation in the bottle and the long contact with the lees. Using a linear discriminant function and amino acid analysis on a total of 110 wines, 4% of the Champagnes and 15% of the sparkling wines were misclassified. This performance—certainly far better than any achieved by tasting—is not judged to be sufficient (Tusseau et al., 1992) and more parameters have to be introduced. Using linear discriminant analysis of 20 amino acids (Derde et al., 1983), it was possible to correctly separate wines from Bourgogne, Bordeaux, and Beaujolais.

14.3.1.2 Mineral Profile Analysis

The "fingerprinting" of the mineral profiles of wines is the most valuable method of assessing the geographical origins. Investigation of mineral elements in wine is the main procedure to authenticate the geographical origins of wines.

Minerals seem to be the primary candidates for obtaining a "fingerprint" as they are stable. The use of trace elements for the differentiation of wines closely followed the advances in analytical techniques. Strangely, 20 years ago neutron activation analysis (NAA) was capable of determining concentrations smaller than parts-per-billion (ppb), but it was costly and time-consuming. Atomic absorption, although adequate for parts-per-million (ppm) (flame) and ppb determinations (furnace), lack the ability to carry out simultaneous determinations that are mandatory in this kind of research; the ICP (inductively coupled plasma), although simultaneous, lacked adequate sensitivity. It was not until the appearance of ICP/MS that the analysis of most of the elements in wines was readily achievable (Ashurst and Dennis, 1996).

Since some of the macro and micronutrients undergo great changes during technological processes, such as Na, K, Ca, Fe, Cu, Zn, and others, attention has been focused on the elements which show very small changes during technological processes, although they are found in small quantities or as traces (Cr, Co, Sb, Cs, Sc, Eu, Hf, Ta, etc.). Li and Rb are most relevant for geographical origin authentication.

Li is found at a very low level in wine (1–200 ppb), but flame emission spectrometry using acetylene fuel is very sensitive and permits an accurate evaluation of this element. Rb is also easily determined in wines and has values in the range 0.5–5 ppm. Consistent work has been performed using these metals (Sudraud and Medina, 1993).

Investigation of rare earth elements (lanthanides) also provides valuable information in order to detect the growing areas of wines by using ICP/MS (Dutra et al., 2011).

14.3.1.2.1 Trace Elements   Siegmund and Bachmann (1977; 1978) used the powerful neutron activation method for trace element analysis; today, very few authors have been able to match the level achieved by that study for 15 trace and ultra-trace elements in wines. Their method was very cumbersome and required a nuclear reactor. The analysis itself, after irradiation for more than 2 days, took more than 3 months to perform. Nevertheless, 15 elements were correctly determined using this technique.

- Elements currently determined: K, Na, Fe, Zn, and Rb at ppm and sub-ppm levels
- Trace elements: Cr, Co, Sb, Ag, Cs, and Br at ppb levels
- Ultra-trace elements: Sc, Eu, Hf, and Ta at sub-ppb levels.

The authors realized that mono-dimensional statistics, simple ratios, or graphical representations were unable to perform a good identification and, therefore, they used taxonomic analysis (cluster analysis) with Euclidian distances to group wines. With the elements Na, K, Rb, Cs, Cr, Fe, Co, Zn, and Ag they showed that clusters were formed according to the area of production as well as the grape variety. They assumed that the transfer of elements from the soil to the plant had the greatest influence on their contents in the wine. When analyzing the soil, however, the only correlation found with the content in the wine was related to the alkaline metals (Na, K, Rb, Cs) and this was not true for all the sites. The year of production also introduced some variations in the levels of the 15 elements in the same wine (place and grape). One important conclusion they drew was that if a control wine exists, then the profile of the mineral content proves the similarity in wines for a given producer. This is obviously not the case with classical determinations, such as alcoholic content, total acidity, volatile acidity, sulfur dioxide, etc. Partly because of the fact that this technique was not convenient for the normal or advanced wine laboratory, no other determinations were conducted at this level for several years. Using ARTHUR

(K nearest neighbors, discrimination analysis, Informetrix Corporation, 1981), Kowalski and his team (1979) used only two mineral elements, Ca and Ba, to classify 14 French (Bourgogne) and 26 American Pinot Noirs (there was a single misclassified sample) correctly. They used a simultaneous emission technique (dichloropropane, DCP) and 17 elements for this study. Following this pioneering work, more extensive use of minerals was applied to French and other wines. Lacasta (1982) separated wines from the French regions of Medoc and Saint-Emilion, where 64 wines (85%) were classified correctly. Medina and Van Zeller (1984) determined 14 mineral elements by atomic absorption and emission spectrometry (with flame and furnace). A correct classification of a reduced set of wines from three French regions was obtained using Li, K, Ca, Cu, and Ni and linear discriminant analysis as well as other classification techniques (soft independent modelling of class analogy, SIMCA) (Informetrix Corporation, 1981). Gonzales-Larraina et al. (1987) found that Mn, Li, K, and Fe were the most important elements for classification of the three regions of Spanish Rioja. Classification reached 93% whichever method was used (e.g., multilinear regression, K nearest neighbors, SIMCA). Using the first two elements, Mn and Li, a good distribution was obtained, the distinction occurring even between two types of productions from big wineries and a family style operation (Rioja Industrial and Rioja Cosechero) could be detected. Maarse et al. (1987) used those elements together with Na and Fe to distinguish German wines from the Rhein-Pfalz and Mosel regions. The difference in mineral elements was shown as the basis of typicity for Spanish wines from Galicia (northern Spain) and the rest of Spain (Herrero-Latorre and Medina, 1992). At the regional level in Galicia, Latorre et al. (1994) showed that using only Rb and Li, a very good differentiation can be found for Rias Baixas as compared to other white wines from two other regions: Ribeiro and Valdeorras.

Using Ca, Na, K, and Fe in the same dataset, they pointed out that these elements can be influenced by the fertilization and wine-making process and are not relevant for classification as shown by the pattern recognition techniques (Fisher weights in ARTHUR, Infometrix, 1981).

It is important to know to what extent the mineral content must reflect that of the soil and also how much mineral content is transferred from the soil to the wine. However, it is not the total content of the minerals in the soil that is important but its availability, which in turn depends on several factors such as pH, humidity, porosity, clay, humic acid complex, etc. The composition of vegetation reflects some extent that of the soil. This fact has given rise to geobotany, a geological science devoted to the search of species that are characteristic of certain ores and deposits (Brooks, 1972). It has been proven (Kim and Thornton, 1992) that vegetation (e.g., lettuce and rice) growing on soils such as uraniferous black shales that are rich in elements such as Cd, Mo, and Se accumulate these elements up to levels that may be of concern for health. Grape varieties seem to take up certain elements selectively; it must be kept in mind that grape cultivation and harvest is by no means a sterile process and that pollution by dust and soil is unavoidable. This pollution varies from year to year (because of rain and wind) and must account for a significant part of the mineral content in wine. The bunching of grapes that facilitates the retention of dust is also a factor not found in larger fruits. It is also clear that the wine-making process can alter the mineral content of wine considerably. For example, the use of technological additives or processes, such as cold treatment, can lower the content of K. In the future, more advanced technology, such as reverse osmosis, will probably introduce more factors of variation. Wine-making equipment is also of great importance for metallic elements such as Fe, Cu, Zn, and Pb (Legrand et al., 1991). When using mathematical analysis, the important thing to consider is the selection of elements

that can vary in the same way in all the wines during the processing; it is not so much the absolute concentration of one element that is important but its relationship with the others. Taking all the previous arguments into consideration, the choice of the mineral elements based on experience can be summarized as follows: K, Ca, and Na are elements that can vary widely, both in the process and from wine to wine. K and Ca can combine with tartaric acid and form potassium bitartrate and calcium tartrate, respectively; these molecules can precipitate the K influenced by temperature. The deacidification of wine can be carried out with calcium carbonate or potassium bicarbonate, thus producing an increase in the content of these elements. Bentonite fining adds Na and Al to the wine (Etchats, 1986). Metallic elements that are likely to migrate into the wine from poor equipment are not the ideal choice because even though the trend toward stainless steel is making progress, traditional apparatus will be used for some time to come. That is why Fe, Cu, and Zn coming from bronze or brass are inappropriate for our purposes. High Pb content (above 150 μg/l) shows that the wine has been in contact with the material not suitable for food manufacture. This may also lead to other elements that are previously mentioned having an elevated value in the wine, sometimes going over the L'Organisation internationale de la Vigne et du Vin (OIV) recommendations: for Cu 1 mg/l; for Zn 5 mg/l; and for Pb 0.25 mg/l. Another problem arises with the oenological treatments, i.e., potassium ferrocyanide. This practice, authorized for wines by the EC regulation (JOCE, 1987) and performed only under the supervision of an oenologist, removes excess Fe and other metals, namely Zn, Mn, and Cu (Etchats, 1986). French legislation is more restrictive and this treatment is forbidden in red wines. As pointed out by Siegmund and Bachmann (1977), the only correlation found between soil and wine was shown for alkaline elements, even more so for Li, which together with Rb appears to play a key role in geographical classification. Both elements are, however, relatively easy to determine in wines using flame emission spectrometry (Lacasta, 1982). Li is found at a very low level in wine (1–200 ppb), but flame emission spectrometry using acetylene fuel is very sensitive and permits an accurate evaluation of this element. Rb is also easily determined in wines and has values in the range of 0.5–5 ppm. Consistent work has been performed using these metals.

Sudraud and Medina (1993) summarizes the elements (Table 14.2) selected for a correct classification by several authors, although it is not intended to be exhaustive. The elements most often cited by order of weight are: Rb, Li, Ba, Sr, Mg, Al, Mn. The last two elements have to be considered carefully as already indicated. These consistent results must be considered with caution because elements such as Ni, Cr, and Li are components of the glass bottle that can over time migrate into the wine (Medina and Sudraud, 1979; 1980).During aging, the relative proportion of these elements may change according to the glass composition, leading to inaccurate results in terms of geography. This fact is partially confirmed by a careful study by Siegmund and Bachmann (1977) where high Cr levels have also been found in wines (up to 2.5 ppm). Apart from these considerations, alkaline metals being easily mobilized in the soil and easily transported into the plant, are good indicators of geographical identity.

14.3.1.2.1.1 Ultra-trace Elements: The Lanthanides   Lanthanides or rare earth elements (REE) have a mass of 140–180 and their patterns give insight into the history of a particular rock or soil as pointed out by the abundant bibliography on the subject in the geological sciences. Extensive research on these elements has led to efficient determination techniques, even at the extremely low levels at which they are found in wine. ICP/MS is frequently the best technique for such determinations, largely because of the simple,

TABLE 14.2 Mineral Elements Used for Classification

Reference	Country or Region	Elements Used
Kwan et al., 1979	USA/France	Al, Ba, Ca, K, Mg, Sr
Medina and Van-Zeller, 1984	France	Ca, Cu, K, Li, Ni
Maarse et al., 1987	Germany	Fe, Na, Rb
Gonzales-Larraina et al., 1987	Spain (Rioja)	Li, Na, Rb
Etievant et al., 1988	France	Li, Ma, Rb
Herrero-Latorre and Medina, 1992	Spain	Ba, Li, Mn, Rb
Day, 1993	France	Al, Ba, Fe, K, Rb, Sr, Zn
Latorre et al., 1994	Spain (Galicia)	Li, Rb

easily interpreted spectra and the exceptionally low limits of detection possible even with standard ICP/MS instruments. This technique has evolved rapidly and the development of new instruments allows the accurate determination of ng/l or ppt in wines without preconcentration. The authors used this technique to investigate the case of REEs in relation to the geographical determination of the wine origin. In geology, it is a widely accepted practice to normalize REE concentrations using chondrite values (Masuda et al., 1973). The chondrites are meteorites whose values represent the natural pattern of REE levels, which were unaffected by geological/geochemical processes on earth (they act as a control for the state of matter when the solar system was formed). For rocks of volcanic origin, chondrite is normally used, whereas marine sedimentary rock REE patterns are usually corrected using values from reference marine shale.

Soils are the compositional reflections of the underlying rocks that gave birth to them. Plants growing on these soils take up trace elements according to the compositions of the soils as well as their chemical properties, which the REE composition also reflects (Brooks, 1972).

14.3.1.2.2 Stable Isotopes A very appealing and sophisticated technique using "stable" isotopes, such as mass spectrometry of isotope ratios (MSIR) and nuclear magnetic resonance (NMR), has been used for geographical determination of wines. However, the results are difficult to interpret in terms of variations in the year, climate, grape varieties, fermentation process, etc. and even the reference to a physical or biochemical process remains somewhat empirical. The use of Pb isotopes is related to atmospheric pollution and seems much more practical because this phenomenon is fairly well understood and is less dependent on small, local variations.

14.3.1.2.2.1 Carbon (^{13}C), Hydrogen (^{2}H), and Oxygen (^{18}O) Isotopes Several isotopes can be used: those from the water of the wine and those from the ethanol (main organic component). The sources of variations of these products can be summarized as follows. Water absorbed by the roots is combined with carbon dioxide from the atmosphere to produce sugars by photosynthesis. During this process, there is fractionation of the different isotopes. A well-known process is the isotopic fractionation of ^{13}C during photosynthesis, which divides plants into three main groups. The evapotranspiration of water in a plant has a concentrating effect on the heavy isotopes of oxygen and hydrogen. Rain during the ripening stage can also have an influence by dilution, especially just before the harvest because, at this time, it contains fewer "heavy" isotopes. The addition of concentrated must (rectified or not) will complicate the matter further. Climate, continent,

and topography can all have an influence on isotopic fractionation; even as little as a 150 m elevation is significant (Forstel, 1995). Owing to all these sources of variations and relativity of the measurements, a well-conceived database is absolutely essential for these methods to be useful and accurate.

14.3.1.2.2.2 Deuterium   Deuterium is specifically distributed in the ethanol molecule produced during fermentation and is related to the deuterium content of the water and the sugar molecules. The deuterium of the methyl group (D/H) I in ethanol comes from a non-exchangeable site of the sugars. On the methylene (D/H) II site it contains a contribution from the fermentation water; and the hydroxylic group is in equilibrium with the deuterium of the wine water (Martin et al., 1988). The site-specific isotope fingerprint has been used for detecting exogenous sugars in wines (Martin and Martin, 1983). The use of these parameters permits the differentiation of wines produced in countries with substantial climatic or latitudinal differences. Using the (D/H) I, (D/H) II, and (D/H) of the water from wine and must, Martin et al. (1988) accomplished a good separation even when the wine produced from different grapes varieties gave different values for the same region, and even when the maturation effect influenced the values (non-matured grapes lead to a 0.3–0.8 ppm increase). A good distinction is made among three different types of climates:

- Cold and humid
- Cold and dry or hot and humid
- Hot and dry

Even for the same country (France), the regions (Alsace, Anjou, Bordeaux) were correctly separated for the same year of wine production.

As it is so dependent on the climate and its variation, the use of these isotopes, although useful, cannot be extrapolated from the year of production. Without this information, the sample can be attributed to several regions of origin in France (Day, 1993). These variations will be more severe for the "Atlantic" climates than for the Mediterranean ones. As discussed later in this chapter, determining the year of production is not an easy task.

14.3.1.2.2.3 Lead   Pb is a wine contaminant with an average of 60 µg/l in wines (OIV, 1995). The current limit set by the OIV is 250 µg/l. This metal is a special case in the determination of authenticity. It is a very old toxicological problem known since the time of the Roman empire, whose decline was supposed to be caused partly by excess Pb intake from food, especially wine, because lead acetate was added as a sweetener. A famous theory says that the high level of Pb hampered the intellectual capacity of the ruling class at that time. Currently, wines with a Pb content under 100 µg/l are considered to be unpolluted by the material during the wine-making process or storage. This very old problem has recently found a new solution with the application of sophisticated analytical techniques, otherwise until now it was just confined to geological and environmental studies (Ashurst and Dennis, 1996).

14.3.1.2.2.4 Organo-lead   Using techniques developed in the Arctic circle ice field for the determination of organo-lead compounds from gasoline additives, these compounds were found in wines. The determinations were set up at Anvers University by Lobinski and coworkers (1994), who used the special hyphenated technique (gas chromatography/

microwave induced helium plasma/atomic emission spectrometry). The authors found ethyl lead and methyl lead, but the latter was predominant. The compounds were derived from tetraethyl and tetramethyl lead, respectively, which were added as antiknock agents in gasoline. Partially burned in the motor (40–80%), they are decomposed in the atmosphere under the action of ultraviolet light, ozone etc. Extremely low levels were found—in the range of 10–500 ng/l for trimethyl lead and 0–50 ng/l for triethyl lead. The maxima were found in wines produced from grapes from vineyards close to the junction of two major highways in France in the Rhone valley. This study compared levels in the "vertical" series of wines, covering over 40 years in the same area. The concentration of trimethyl lead is no higher than 25 ng/l in rural areas, but it increases with the proximity to highways and cities. With the increased use of unleaded fuel in the EU in the last 10 years, the level of these compounds in wine has diminished sharply. For the chronological series of wines between 1950–1991, there has been an increase in trimethyl lead after the introduction of the tetramethyl compound in 1960, a maximum *circa* 1978 and then a sharp decrease from 1980 to the present. Triethyl lead is present in 1960, but the levels decrease after 1980 (Lobinski and coworkers, 1994). Until recently, there was no European wine that did not contain alkyl lead compounds. In the USA and Australia, which have used unleaded fuel for a longer period of time, there is no organic Pb in wine at present; however, before 1987, levels similar to those of European wines were found. The use of this time shift and the relative proportion of methyl and ethyl lead allows one to plot concentration curves to give an evaluation of the age of the wine from the 1960s to the present. The use of these curves permits several deductions with reference to the year of production and the origin of the wine.

- No organo-lead: The wine originates from countries that have banned these compounds many years ago (USA and Australia) or is a very recent European wine.
- According to the vintage, the relative proportion of trimethyl and triethyl lead indicate the year of production (i.e., pre-1960 there was no methyl lead present).
- High levels of organo-lead imply proximity to a heavily used road or a city (trimethyl lead > 100 ng/l and triethyl lead > 15 ng/l).

14.3.1.2.2.5 Lead Isotopes   Pb has four isotopes, three of which come from the decay of U and Th. Consequently, Pb ores have different proportions of Pb isotopes according to their original content in these radioactive minerals. One major reason to use Pb isotope variation as an indicator lies in the fact that their variation is much greater than that of lighter elements such as carbon or oxygen, which are in the ppm range. The variation between two major Pb mines (Missouri, USA and Broken Hill, Australia) is close to 30%. Indeed, Pb isotope ratios have been used for 20 years to trace Pb pollutants (Chow et al., 1975). In addition, heavily polluted soil has been found in metropolitan areas and the level of Pb here is proportional to the proximity and the volume of traffic, ranging from 100–1000 ppm; these values should be compared with the level of Pb in the earth's crust, which is 16 ppm (Krauskopf, 1956).

Organo-lead is volatile and can be found in places that are as far away as the poles, but most of it is burned and remains in the same geographical area. The variation, therefore, reflects the origin of Pb that is used as an anti-knock additive: Missouri in the USA or Broken Hill in Australia. The situation in Europe is intermediate since Pb comes from different sources (Morocco, Australia, etc.). Even if the total amount of Pb emitted into the atmosphere is reduced, the current levels of pollution will remain unaffected for some time as will the Pb ratios (MacKay, 1994).

14.3.1.2.2.6 Age Using Lead Isotope Ratios   The increased use of unleaded gasoline in Europe also leads to variations in specific ratios. Wine is therefore strongly marked in its composition by the environment, and this provides valuable data. The concentration trend of Pb is moving from a situation of Pb pollution toward natural earth crust ratios. Indeed, this trend was found for aerosols in a study in San Diego, California, from 1964–1974 (Chow et al., 1975) and it was confirmed by Grousset et al. (1994) who worked on European aerosols. Another factor in favor of reduced pollution is the fact that very low levels of Pb are now found in wine, regardless of the source of the constituents. It is interesting to note that Pb concentrations in aerosols are also decreasing in a similar fashion (Grousset et al., 1994).

Differences existing between the wines from Australia and the USA are mainly because of the atmospheric pollution caused by Pb present in the exhaust of automobiles that burn leaded gasoline. Organic Pb can be found in extremely low levels (0.5 µg/l), thus testifying the influence of this phenomena. Further study shows that the extent of atmospheric pollution can be traced more extensively in wine. Only a small fraction of organic Pb introduced into the gasoline exhaust remains unaffected by combustion (1%–10%); in addition, natural reactions occur that decompose the remaining compounds (ultraviolet light, etc.). That is why only very sophisticated techniques (such as GC-atomic emission detector (AED)) are able to detect alkyl lead in wine. However, isotopic ratio determination of $^{206}Pb/^{204}Pb$ shows a definite variation according to the year of production, following the increased use of unleaded fuel throughout Europe (Ashurst and Dennis, 1996).

14.3.1.3 Organic and Mineral Features

It is appealing to construct a database where minerals and organic substances are mixed in the hope of encompassing several factors of variation such as grape variety, soil, climate, and so on all in one step. Several authors have used this approach, following the pioneering work of Kowalski and coworkers (Kwan and Kowalski, 1980a; 1980b). Using the database in their work and the partial least squares (PLS) method, Frank and Kowalski (1984) showed that elemental analysis performed much better than organic analysis while differentiating French, Californian, and Pacific Northwest wines. A combination of the two chemical blocks gave the best prediction.

Medina and Van Zeller (1984) used minerals and volatile, polyphenolic, and organic acids and classical determinations (62 variables) in a study on French red wines. Wines representative of their areas of production were selected. In this feasibility study, the principal component analysis (PCA) technique was able to distinguish among wines of the three examined regions. A search for the smallest number of substances that could successfully characterize groups led to the selection of Li, propanol, procyanidin B2, and decanoic acid. Each group of substances (e.g., phenols, minerals, etc.) could be used individually for an accurate separation using group classification methods (KNN, LDA in ARTHUR, Infometrix, 1981). Following this work and having examined the most useful elements, Manterola (1985) used three mineral elements (Li, Mn, and Rb) and one all-purpose HPLC technique for 13 neutral polyphenolic substances (Salagolty-Auguste and Bertrand, 1984).

Etievant et al. (1988) used minerals and amino acids to achieve 94% accuracy when classifying 68 French red wines provided by three agronomical stations and made from pure grape varieties typical of the Loire (Angers), Southern France (Narbonne), and Bordeaux regions. Fisher's test showed that only Rb, Li, and Mg could discriminate among the regions, although six amino acids showed potential. Stepped discriminant analysis selected Rb, ethanolamine, arginine, and Mg. It is well known, however, that the

amino acids are dependent on fertilization, climatic conditions, and the duration of skin contact in most cases; those indigenous to the grapes are metabolized by the yeast, and are excreted and released during the autolysis of the dead yeasts; more complex phenomena also exist. In contrast, the minerals selected do not vary even after the time needed to obtain the red wine—48 h of skin contact (Rizzon, 1985).

14.3.2 Authentication of Grape Variety

Biotic factor has a major contribution in the formation of the qualitative characteristics of wine, so the compositional and sensory parameters are largely dependent on the variety of wines.

14.3.2.1 Sensory Analysis or Tasting

The tasting was, until recently, the only way to classify wines according to vintage and origin; however, no extensive and objective research has been performed on the subject. Is tasting accurate enough for a correct classification of wine? An expert taster will answer positively and every year there is an amazing worldwide contest of "sommeliers" where even the name of the chateau is guessed. Sensory evaluation can be easily rationalized and the use of wine-tasting cards is now widespread. Frank and Kowalski (1984) showed that sensory data do not provide enough information to separate wines from France and the USA. A spin-off of this study demonstrates that elemental analysis contains more information relevant to the organoleptic characteristics than the organic composition analyzed at the time. In a very interesting study (Thurin, 1984), where the expert tasters were asked to guess the name of the pure variety (Cabernet Sauvignon, Merlot, Cabernet Franc) of grapes that the wine was made of, a surprisingly low percentage (20%) of correct answers was achieved; indeed, less than what was achieved from random guessing. However, when using all the 28 criteria of the wine-tasting card and the classification method SIMCA in ARTHUR, (Infometrix, 1981)—which performs a reduction of the variables—the classification reached 90% (using 110 tasting cards). The typicity of the grapes is characteristic enough to be inscribed in a wine score card, even when grown on different soils. The wine score cards are designed to use the tasters as sensitive machinery without a cognitive function that, in this case, interfere with the results.

Sensory evaluation is limited by the influence of several factors (ecological, agro, and technological) that modify the primary characteristics of the variety significantly. Although sensory analysis is still influenced by human subjectivity, statistical interpretation of results and the use of equipment such as "electronic nose" and "electronic tongue" improved the performance of sensory evaluation (Biernacka and Wardencki, 2012).

14.3.2.2 Mineral Profile Analysis

As the different wine varieties selectively accumulate various metals, their identification can be achieved from the content of certain elements in the wine like Li, Ni, Ca, Rb, etc. (Rapeanu et al., 2009; Dutra et al., 2011).

14.3.2.3 Amino Acid and Protein Profile Analysis

While soil, agrotechnical, and technological factors cause large variations, the content and nature of amino acids may contribute to the recognition of the wine variety. Recent research has shown that molecular weights of proteins recorded small variations in different wines depending on the variety. Proteins are stable in must and can be found in

wine and even those are subject to stabilization. Protein quantification is relatively simple and can be done by conventional methods (electrophoresis) or by modern methods (mass spectroscopy, etc.) (Rapeanu et al., 2009).

14.3.2.4 Analysis of Polyphenolic Profile

Their evaluation is useful to authenticate individual wines by botanical origin. Investigation of phenolic compounds by multidimensional NMR allows the differentiation of wines by variety and even the clones of the same variety. The most representative phenolic compounds of red wines are the anthocyanins. They are in the free form—anthocyanins/anthocyanidins (malvidol, delfinidol, cyanidol, peonidol, and petunidol)—as well as in acyl and coumaryl compound forms. Cabernet Sauvignon is characterized by a higher content of malvidol and coumaryl anthocyanins, while Merlot is highlighted by a higher content of peonidol and coumaryl anthocyanins (Gonzalez-Neves et al., 2004). Because during the grape processing and wine preservation acyl and coumaryl anthocyanins are more stable, it is proposed that anthocyanin fingerprinting of red wines should be used to express the number of acyl anthocyanins and coumaryl anthocyanins and the ratio of acyl anthocyanins-to-coumaryl anthocyanins (Von Baer et al., 2008).

Since the authentication of variety by using the fingerprint anthocyanins is operational only in case of red wines, white wines, and roses, even the reds are investigated by the content of shikimic acid (Mardones et al., 2005). Shikimic acid is found in small amounts in various fruits including grapes. In wine, it is found in the concentration of 10150 mg/L. The evaluation of shikimic acid content is especially recommended for white wine authentication and as an additional indicator in red wine authentication (Makris et al., 2006).

14.3.2.5 Analysis of Volatile Compounds Profile

Quantification of the odorant substances in wines, compounds that are usually found in extremely small quantities, is achieved by their extraction with various solvents and their determination is done with modern methods such as GC coupled to MS (GC-MS, LC/ESI-MS, MALDI-TOF-MS) (Nasi et al., 2008).

14.3.2.6 Residual DNA Analysis of Grapes

Since it has been found that wines contain small amounts of DNA from grapes, DNA analysis has been done in order to identify the variety of the wine (Baleiras-Couto and Eiras-Dias, 2006). The difficulties—like low content of DNA in wine, contamination (DNA from yeast, bacteria), changes during processing, and inhibitors for the PCR reaction—were solved by using appropriate methods of DNA extraction and by improving the performance analysis using microsatellite PCR amplification.

14.3.3 Authentication of Wine Age

With time, the wines undergo a number of beneficial changes such as physical-chemical and even biochemical changes. They cause the development of a refined sensorial quality, thus old wines are more valuable. Moreover, the crop year, which benefit from favorable weather conditions, also gives great features to the wines, therefore they are appreciated by the consumers. The analytical method that is frequently used is determination of the radioactivity of the ^{14}C isotope of the ethanol molecule in wine. The method is relatively simple and consists of determination of the ^{14}C isotope radioactivity of the

concentrated solution (minimum 95%) of alcohol obtained by the distillation of wine or other alcoholic beverages. For red wines, to increase certainty, the combination of these results with those obtained from the analysis of polyphenolic compounds and color indices is indicated. Determination of radioactivity by measuring the activities of wine sediment isotopes such as ^{210}Pb, ^{210}Po, ^{239}Pu, ^{240}Pu, ^{13}Cs, etc. is another way of knowing the wine age. The validity of the method was verified by appropriate dating of wine during 1850–1968 for every 6 years. Age rating wines and other alcoholic beverages by determining the radioactivity of isotopes has a high degree of reliability only for products of a considerable age (Dutra et al., 2011).

Carbon isotope ^{14}C: One of the oldest methods for determining the age of an alcohol takes advantage of nuclear fallout by determining the ^{14}C content of the ethanol (Martiniere et al., 1979). Cosmic rays colliding with nitrogen produce ^{14}C. The radioactivity of carbon in ^{14}C remained constant for two centuries (1752–1952) at a level of 13.6 dpm/g (disintegration per minute per gram). Atomic bombs and, especially the hydrogen bombs tested in the atmosphere, produced neutrons that reacted with nitrogen and produced radioactive carbon. This carbon is rapidly oxidized to form CO_2 and is incorporated in plants. Unlike deuterium (^{2}H) and ^{18}O, the diffusion of the radioactive $^{14}CO_2$ was worldwide and homogeneous. There is little variation (±5%) among plants or with latitude and longitude. The maximum value of 28 dpm was obtained in 1963 because most of the atmospheric nuclear testing stopped in 1964; a decrease has been observed since then but it currently remains above the natural level (Mongereau and Evin, 1993). This technique can also be applied to wines and spirits after a distillation process that must reach at least 95% by volume of ethanol (double distillation for the wines). Nevertheless, several factors can affect the results such as chaptalization, if it is carried out with sugar that is of a different age than the grape. Given the shape of the curve, it is not possible to distinguish between the age lying on each side of the curve along the same horizontal line. Given the curve's tendency to flatten out and the uncertainty associated with the technique, the method is not sufficiently accurate at present and no improvement is foreseeable. This technique is, however, useful in some circumstances such as for very old spirits or products of special vintages (±1 or 2 years). For red wines, this technique combined with the analysis of polyphenolic compounds (polymerization, tannin indicators (Glories, 1978)) or color indices (the tile color increasing with age) will narrow the margin. The addition of sugar to the wine complicates the process (because it is sugar of a different age) and widens the uncertainty to over 1 year (Mongereau and Evin, 1993).

14.3.4 Authentication Technology for Wine Production

There are a variety of techniques and processes of wine-making, authorized or used fraudulently, altering appreciably the compositional and sensorial wine parameters. This aspect of authenticity has a particular relevance to special wines like the sparkling wine, the oxidative wines, etc.

14.3.4.1 Authentication of Sparkling Wines

Sparkling wines are elite alcoholic beverages, much appreciated by consumers. There is a wide range, determined both by the diversity and quality of raw materials (wine-based) and also by developing technology. Besides the general aspects of wine authentication, sparkling wines represent a clear distinction between products which contain

endogenous origin CO_2 (sparkling wine) and which have totally or partially exogenous CO_2 (Martinelli et al., 2003). The most information is provided by the component amino acid analysis, the certainty being higher when it is associated with the study of other compounds like odorant substances, polyphenol content, carbohydrates, etc. Isotopic analysis generates the most rigorous investigation results by determining the amount of isotope ratio $^{13}C/^{12}C$. In this way, it is possible to determine precisely the origin of carbon dioxide in the product, whether it comes from plants with C3 metabolism (the wine) or C4 (sugar beet, etc.) or from other sources (industrial, synthesis, etc.) (Calderone et al., 2007).

14.3.4.2 Authentication of Oxidative Type Wines

Oxidative type wines, the main representatives being Port wine, Madeira, Jerez, etc., are characterized by sensorial properties, generated mainly by biochemical oxidative processes. Authentication aims to detect the original products of imitation. In addition to sensory evaluation, content analysis of metals (Rb, Li, Mn, Fe, and Al), phenolic compounds, carbohydrates (including the ratio of glucose to fructose), presence and content of amino acids, etc. generate information that is useful in identifying the original products (Camara et al., 2006).

14.3.4.3 Authentication of Rose Wines

Rose wines lie between white and red wines, having specific chemical compounds, so it is difficult to license their origin. Authentication of rose wines has two major objectives. The first step is to identify the source of raw material, i.e., whether it comes from red grapes or a blend of white and red grapes or from white and red wines. The second step is to assess the authenticity of color, i.e., to detect possible fraud color of white wines by oenocyanin addition. Analysis of compounds and parameters such as polyphenols, sugars, volatile acidity, extract, especially the color indices, etc. and comparison of the results with reference values provide a high degree of certainty. The recommended method for defining color is the spectrophotometric method that is the reference method, which monitors the three-color indices: brightness, chromaticity, and purity (Rapeanu et al., 2009).

14.3.4.4 Authentication of Blending Wine

The blending of wine is authorized in certain well-defined circumstances. It is a problem that needs to be evaluated as it is one of the primary frauds concerning wines. According to EU regulations, Champagne rose is the only authorized blend of wines of different colors. The blending of white and red table wine is permitted in Spain, but the products may not be sold elsewhere (JOCE, 1994). In France, a distinction exists even between the "rose" wines and the "clairet' category. Clairet wines, between red and rose wines, are quite easily ascribed to their category by the analysis of their color using tri-stimulus parameters L, a, and b (Garcia-Jares et al., 1992; 1993). However, a much more complex task is to distinguish a true "rose"—made from only red grapes and a light maceration— from one produced by the blending of red and white grapes, particularly when calculating the extent of blending. Garcia-Jares and Medina (1993b) assessed this difficult problem by associating a highly sophisticated mathematical construction model such as PLS with a simple determination such as the ultraviolet-visible spectrum. In the first stage, a model was built using the spectra of red and white wines mixed in different proportions (from 1% to 20% red wine) that simulate the visual characteristics of true roses. The robustness of the model was then tested against wines of known mixed compositions and the validity of the calculation of the proportion of red and white wine was estimated. A fairly good

agreement was obtained; thus, this method could be applied successfully to the detection of blending in the production of rose wines.

14.3.4.5 Authentication of Port Wine

Pessanha (1987) tackled the problem of the authenticity of Port wines in a way that mixes several components. A part of the scope of this study was to differentiate genuine Port wine, imitations (mainly from Spain but not sold under this label), and wines made with similar techniques, for example, Banyuls, a Yin Doux Naturel (VDN) from southern France. In all, 100 chemical determinations were made including:

- Classical determinations
- 14 metals
- Esters and fatty acids
- Superior alcohols and methanol
- Phenolic substances (acids and neutral)

Owing to the limited number of imitations available, all the groups of chemicals (grouped by techniques) were discriminated well. For the imitations, an unknown substance was present almost universally in the HPLC determinations of the phenolic substances. With classical determinations, because the imitations (unlike Port wines) are produced mainly with must fortified by alcohol with very little fermentation, the glucose-to-fructose ratio is above 0.9 for the imitations and below 0.8 for Port wines. The most useful metals used in discrimination were Rb, Li, Mn, Fe, and Al. Rb permits an accurate separation of the imitations (Port wines having a mean value of 1 mg/l). When halting fermentation in Port wines, wine alcohol (76%–78% vol) with very little rectification is used; the resulting product is consequently rich in higher alcohols. Isoamyl acetate and ethyl octanoate are the best indicators in the volatile series (Andrade Perez, 1961).

14.3.4.6 Authentication of Spirits

More recently, Cantagrel et al. (1993) proposed several methods, described in the following paragraphs, to distinguish the principal spirits. The distribution of common components or their ratios in spirits, for example, higher alcohols, caprylic acid, isopentanol (M3Bl/M2B1), syringaldehyde/vanillin, is the first useful step. Using only six components, it is possible to separate almost perfectly (with a 0.6% error) Cognacs, Armagnacs, and Brandies from different countries using Bayesian classification and PARVUS software (Forina et al., 1988). These components are meaningful in terms of wine-making, distillation process, and aging. Discriminant analysis using 23 variables correctly separates 120 spirits into their main classes: Brandies (French, Spanish, Italian), Cognacs, Armagnacs, Calvados, and Whiskies. Isotopic analysis of the site-specific deuterium has proven useful in the distinction of chaptalization in wines, but it requires the use of a data bank because the natural distribution of deuterium in the ethanol molecule is closely related to the geographical origin (Martin et al., 1983). Three isotopic variables, D/H1, D/H2, and R, i.e., the relative concentration of deuterium on the first carbon of ethanol ($CH_2D–CH_2–OH$), the relative concentration on the second ($CH_3–CHD–OH$), and the intramolar ratio, respectively, permit good discrimination of Cognacs from other spirits; even the Whiskies are distinguished from the pure malt (Cantagrel et al., 1993). However, if Brandies are made with wines of different geographical origins, then the distinctions are less obvious (e.g., for German Brandies produced with wines from the Cognac area).

14.3.4.7 Authentication of Botrytized Sweet Wines

Chauvet (1981) studied carefully the botrytized sweet wines of the Sauternes area. Using chemical determinations on wines and grapes, he developed an over-maturation index, which reflects the extent of growth of the so-called "noble rot"—an essential step in the wine-making process for those wines. Using his data, a PCA was performed on wines from botrytized grapes; it showed that the different stages during the development of the noble rot could be distinguished. The plots for most of the commercial wines are found between the second stage and the third when projected as supplementary parameters on this graph. While building the first axis, Mg and tartaric acids weighed the most. A two-dimensional plot of tartaric acid versus Mg gave a very useful representation of the three groups. The plane can be separated grossly into four quarters. It is well known that noble rot decomposes tartaric acid and, later, concentrates the grape. The decomposition is followed from group 1 (non-botrytized) to group 2 (fully botrytized). Concentration then occurs and the levels of Mg rise to stage 3 ("roasted" stage). The fourth quarter (upper right) would correspond to grapes concentrated by the sun (no tartaric decomposition).

14.4 CONCLUSION

The verification of wine authenticity might lie in the use of combined techniques such as those using isotopes and minerals. However, the difficult problem of chaptalization has been resolved by the use of a data bank, which may also be a possible solution to the problem of geographical origin. With the use of a database, however, problems such as represent activity, authenticity, rules of interpretation, and the transposition of results from one laboratory to another arise. Authenticity and rules of interpretation are the easiest to solve through official action. The inter-laboratory variances require the use of robust methods and, more importantly, the use of a reference material. Isotope determination requires cumbersome and expensive techniques (e.g., NMR, isotopic mass spectrometry). Isotope techniques, although enticing, require the same sophisticated mathematical tools as the easier and more affordable means, which often work equally well. Determination of the authenticity in wine calls for a pan-European effort since a database completed in one laboratory will always be limited to an informal level (pilot level or feasibility level). Nevertheless, it has been proven with consistency over many years that this problem can be solved using the mineral content of wines (stable components with time), and that the easiest cases can be solved with inexpensive determinations (e.g., Li, Rb, Mn, etc.). It has been solved for, what in our opinion is a much more difficult problem, chaptalization. The mineral profile of wine is so characteristic that it is unique to a specific wine and can be used as proof of authenticity where a control exists. It fares so much better than classical determinations. At any rate, it is possible to make accurate classifications of unknown wines and, even if for the moment, no rational explanation is completely satisfactory (e.g., transfer of the minerals from the soil to the grape), the empirical solution is sufficient for practical purposes.

The case of diethylene glycol in wine, which went undetected for some time because of it not being included in the list of tested compounds, is an excellent reminder of the limitation of targeted analysis, which is still predominant in private and governmental food-testing laboratories. These are only the first approaches into the use of nontargeted analysis, which may have the capability to detect novel or unusual compounds or may just provide a fingerprint of the beverage that can be compared against a database of authentic beverages. Various techniques may be suitable for such a nontargeted analysis,

including UV/VIS, IR spectroscopy, and specifically NMR spectroscopy for which several promising approaches were published (Lachenmeier et al., 2009). The wine screening using targeted and nontargeted NMR spectroscopy have become the first method in the field of alcoholic beverages that is applied in a routine fashion (Godelmann et al., 2013). To determine the origin of a completely unknown wine, a global strategy could be conducted in three stages.

- Lead isotope ratio determination to locate the origin of wine by continent.
- 18O or site-specific deuterium for the determination of latitude, north or south.
- Metal determination such as Li, Rb, or Mn for classification according to the sub-region.

An alternative global approach would be the use of more complex fingerprints and much more site-specific elements such as the lanthanides. Other approaches such as mixing minerals, amino acids, and volatiles have already been used as a legal basis for detecting falsified products. Polyphenolic content of wine is also a good mark of authenticity (for detecting variety and region) (Ashurst and Dennis, 1996).

From a standpoint of production technology, a tighter implementation of the hazard analysis critical control point (HACCP) system was suggested to avoid adulteration. Indeed, this may detect crude forms of adulteration (e.g., methanol addition) along the supply chain, if regular sampling and analysis are implemented. However, HACCP would probably not be able to prevent intentional fraud on the last steps of the supply chain, similar to what occurred in the Czech Republic (Kourtis and Arvanitoyannis, 2001). In future, DNA sequencing and PCR techniques will probably be used as ultimate proofs of authenticity (Time Magazine, 1995).

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