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REVIEW ARTICLE

POSSIBILITIES TO ASSES THE WINES AUTHENTICITY

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Abstract
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. Responsible and continuous controls are required to maintain the quality of wine. Usually volatile compounds are used to characterise varieties, whereas minerals are used for geographical differentiation. Amino acids as well as phenolic compounds evaluation are used for both. The development of advanced techniques for wines authentication is a challenge, which currently is given a special attention.

Key words: Wine, authenticity, geographical origin, DNA fingerprinting

Introduction

Wine is one of the most complex alcoholic beverages. Due to high economic value of the wine-product for some worldwide typical geographical areas and annexed socio-cultural reasons, the development of analytical methods for wines classification is extremely important, mainly for the assignment of a trade mark such as protected designation of origin (PDO), controlled denomination of origin (CDO), protected geographic indication (PGI) for quality wines. In this context, useful analytical methods serve to wines identification and, consequently, to protect the trade-marked quality wines and to prevent their illegal adulteration (Penza and Cassano, 2004).

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 register kept by the wine producer.

Commission Regulation (EC) [No 753/2002] lays down certain rules for applying Council Regulation (EC) No 1493/1999 regarding the description, designation, presentation, and protection of certain wine sector products. Regulation EC 753/2002 governing the designation, naming and protection of wines has been amended by regulation [No 316/2004] and by Commission Regulation (EC) [No 1429/2004].

In this paper the problems posed by the geographical origin of wines, grapes variety from which wines are made (botanical origin), year of wine production and wine production technology will be discussed.

1. Authentication of geographical origin (production area)

Climatic, edaphic and orographic factors influence the process of vine growth, and also the quantity and quality of grape harvests, with direct influence on the compositional and sensory parameters of wines (Ballabio et al., 2006).

Since the area of production raises the visible mark on originality and quality characteristics of products subsequently reflected on the final price, the determination of geographical origin is one of the primary requirements for certification of wines authenticity.

To highlight the importance of wine production areas within the Europe it has been introduced the concept of "*terroir*" which considers the specific characteristics of a wine that are induced mainly by geographical location and characteristics of production in the concerned areas.

Regions DOC (denomination of origin) are areas within designated wine, traditional, whose wines have great quality features, personality, that making them unique. To protect the controlled

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names and geographical indications, most countries have developed laws in Romania being Ord. 458/2003.

To authenticate geographical origin of wines is quite difficult because the sensory and analytical results of investigations should be linked to factors in the vineyard ecosystem that often recorded very large variations.

Recently, sensory evaluation done by specialists (tasters) was the only way to determine the geographical origin of wines (Stoian, 2001). Despite progress in recent years in the field, this method has a high degree of uncertainty and fails to identify the precise geographical area. Therefore instrumental analysis is used to separate and to identify the compounds which are in very small quantities or as trace (Garcia-Beneytez et al., 2002, Siret et al., 2002).

The principal methods used for authentication of geographic origin are:

1.1. Analysis of volatile compounds profile

Determination of volatile compounds profile allowed differentiation of wines by geographical origin. Thus, Kwan and Kawalski (1978) were able to distinguish among the Pinot noir wines of French origin from the U.S. ones, based on the content in 1-hexanol and cyclohexanone. Further, Medina and Sudraud (1980), and then Garcia-Jares and Medina (1993) were able to identify the geographic area of French red wines and Spanish white wines by using the content of a greater number of volatile compounds (ethyl esters, isoamyl esters, aldehydes, acetals etc.).

1.2. Analysis of amino acidic profile

Although the content and nature of amino acids in wines is dependent on many factors, their investigation, especially is useful for authentication of sparkling wines, providing valuable information and to locate areas of wine production (Ferreira et al., 2002)

Thus, by investigating the five amino acids (arginine, alanine, tyrosine, valine and leucine) that are responsible for the amino acidic profile of wines, is possible to identify geographical origin of wines from different regions of France (Bourgogne, Bordeaux and Beaujolais) or to establish authenticity of wines from Porto/Portugal (Flamini and De Rosso, 2006), white wines from Campania Region/Italy (Chambery et al., 2009).

1.3. Mineral profile analysis

Since some of the mineral elements have a high stability, the "fingerprinting" of mineral profile of wines is the most valuable method of assessing the geographical origin. Plant chemical composition largely reflects the composition of soil, even if it is depending on other factors. It is valuable in the case of grapes and musts and less in case of wine, because the mineral profile of wines undergo significant changes due to different sequences of technological processing of grapes into wine, conditioning and storage of wines.

However, investigation of mineral elements of wine is the main procedure to authenticate the geographical origin of wines.

Since some of the macro and micronutrients have great changes during technological process, such as Na, K, Ca, Fe, Cu, Zn and others, attention has been focused on those elements which recorded very small oscillations, although they are found in small quantities or only as trace (Cr, Co, Sb, Cs, Sc, Eu, Hf, Ta etc.). Some trace elements content of which is less affected by technological factors are alkaline earth metals, and lithium and rubidium are most relevant to geographical origin authentication.

Lithium and rubidium are in very small quantities, usually like traces, 1-200 ppm lithium and rubidium 0.5-5.0 ppm but may be relatively simple quantified by modern methods (in flame atomic emission spectrometry).

Investigation of rare earth elements (lanthanides) also provides valuable information in order to detect the growing areas of the vine. By using mass spectrometry with inductively coupled plasma (ICP-MS), various researchers successfully identified the geographical origin of wines from various regions of France and Spain, using the presence and concentration of lanthanides (rare earth elements).

The mineral elements used to authenticate the geographic origin of wines, by different authors, are presented in Table 1.

1.4. Analysis of stable isotopes and organic compounds of lead

Determination of stable isotopes and isotopic reports and subsequent interpretation of experimental data using chemometric methods (principal component analysis (PCA), linear discriminate analysis (LDA)), is another way to authenticate the geographical origin of wines.

Since the contents of stable isotopes of water and alcohol of wine, and their isotopic ratios (D/H, $^{18}O/^{16}O$, $^{13}C/^{12}C$) had variations caused mainly by climatic factors they may be used to locate areas of growing, especially in function of their climate (cold and dry, cold and wet, hot and humid, hot and dry).

Table 1. *Mineral elements used to authenticate the geographic origin of wines*

Year	**Country/region**	**Mineral elements**	**References**
1979	USA / France	Al, Ba, Ca, K, Mg, Sr	Kwan et al.
1987	Spain (Rioja)	Li, Mn, Rb	Gonzales - Larraina et al.
1988	France	Li, Mg, Rb	Etievant et al.
1993	France	Al, Ba, Fe, K, Rb, Sr, Zn	Day
1994	Spain (Galicia)	Li, Rb	Lattore et al.
2001	Greece	K, Na, Ca, Mg, Fe, Cu, Mn, Zn, P	Kallithraka et al.
2005	Slovakia	Ca, Mg, Rb, Sr, Ba, V	Korenôvska and Sohag

There was a decrease in content of oxygen isotopes (^{18}O) and of deuterium (^{2}H) of wine water, when they move from warmer areas to areas with a temperate climate and from West to East. The isotopic ratio value of $^{13}C/^{12}C$ is depending of the weather conditions, particularly the temperatures at which are grapes ripening. Recorded values of the ratio generate reliable information for elucidation of the area production of a wine (country, continent).

Moreover, because the values of isotopic ratios D/H and $H_2{}^{18}O/H_2{}^{16}O$ are dependent on soil water isotopic composition (and climatic conditions, especially precipitation), investigation of these ratios provide relevant information's to authenticate the geographic origin of wines. Determination of isotope ratio $^{18}O/^{16}O$ can be used to detect the geographical area in terms of latitude.

Organic lead compounds (trimethyl lead and triethyl lead) come from the decomposition of the substances used like gasoline additive (tetramethyl lead and tetraethyl lead). Trimethyl lead and triethyl lead pollute the atmosphere and soil. Although in the wines can be found in small quantities (trimethyl lead 10-500 ng/L and triethyl lead 0-50 ng/L), changes in their quantities provides useful information for recognition of geographical areas of wines origin as well as for finding the wines age.

The absence or very low doses of tetramethyl lead and tetraethyl lead, showing that wine comes from countries which not use additives containing lead for petrol (USA, Australia and in recent years and EU countries) or that the vineyards are located in rural areas or away from highways.

Nowadays, the process is less relevant for wines, because more countries use unleaded fuel.

Regarding the wine age, it can state that wine is either very old (before 1960 when began to use leaded gasoline), or younger (after 1980 if comes from U.S., or the last ten years if comes from Europe).

Similarly, to understand the presence of lead isotopes in wine, a general approach to determine the geographical origin of an unknown wine can be used:

- determination of lead isotopic ratios to locate the origin of the mainland;
- determination of the isotope ^{18}O or deuterium (^{2}H) to find the latitude (North or South);
- determination of elements such as lithium, rubidium, manganese etc. to locate large and small areas with vines planted.

Because of the multitude and variety of factors with direct influence on composition and sensory properties of wine, geographical origin authentication is still an object of study for specialists.

2. Authentication of grape variety

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

2.1. Sensory Analysis

Sensory analysis retains the privilege of being the most common method of assessing the biological characteristics of varieties. But the process is limited by the influence of several factors (ecological, agro and technological) that modify significantly the primary characteristics of the variety.

Although sensory analysis is still influenced by human subjectivity, statistical interpretation of results and using equipment such as "electronic nose" and "electronic tongue" improved the performance of sensory evaluation.

2.2. Mineral profile analysis

As the vine varieties selectively accumulate various metals, their identification can be achieved by the content of certain elements of the wine like: lithium, nickel, calcium, rubidium etc.

2.3. Amino acid and protein profile analysis

While soil, agro-technical and technological factors causes the large variations, the content and nature of amino acids are the subject of biological features of the plant and as a result may contribute to recognition of the vine variety.

Recent research has shown that molecular weights of proteins recorded small variations in wines by variety. Proteins are stable in must and can be found in wine and even those subject to stabilization. Protein quantification is relatively simple and can be done by conventional methods (electrophoresis) or by modern methods (mass spectroscopy etc.).

2.4. Analysis of polyphenolic profile

Variety vine clearly puts his mark on all of polyphenolic substances (Catharino et al., 2006).

Therefore, their evaluation is useful to authenticate individual wines by botanical origin. Investigation of phenolic compounds by multidimensional nuclear magnetic resonance allowed the differentiation of wines by variety, and even the clones of the same variety.

The most representative phenolic compounds of wines are the anthocyanins. There are like free form anthocyanidols/anthocyanidins (malvidol, delfinidol, cyanidol, peonidol and petunidol etc.) and as well as acyl and coumaryl compounds.

The acyl and coumaryl compounds, although they are in small amounts present interest as a feature of variety.

Cabernet Sauvignon is characterized by a higher content in malvidol and coumaryl anthocyanins while Merlot is highlighted by a higher content in peonidol and coumaryl anthocyanins (Gonzalez-Neves et al., 2004).

Therefore, resulting wine anthocyanins fingerprint may elucidate with sufficient certainty vine variety from which the wine originates. Initially assess the percentage of free anthocyanins and wine colour forming acyl. Because during the grapes processing and wine preservation acyl and coumaryl anthocyanins are more stable it was proposed that anthocyanins fingerprinting of red wines to express the amount of acyl anthocyanins + coumaryl anthocyanins and ratio of acyl anthocyanins/coumaryl anthocyanins (von Baer et al., 2008).

As noted in Table 2, the Cabernet Sauvingnon wine recorded the highest values of acyl and coumaryl anthocyanins, while in the case of Pinot Noir are missing. The process is not absolute because they are valid in related varieties (Cabernet Franc/Cabernet Sauvignon) in which differences are insignificant and during storage of wine anthocyanins spectrum is changing.

The process is inconclusive for wines that contain a percentage of 15% of another variety (which are allowed by the legislation to award the variety name), so the investigation is useful only to attest that the wine comes from a variety.

Table 2. *The fingerprint of red wine anthocyanins* (Tardea, 2007)

Grape variety	**Acyl anthocyanins + coumaryl anthocyanins**			**Acyl anthocyanins/ coumaryl anthocyanins**		
	minimum, %	**maximum, %**	**average, %**	**minimum, %**	**maximum, %**	**average, %**
Cabernet Sauvignon	21	34	26	3.5	5.8	4.6
Merlot	16	26	23	3.1	4.9	3.7
Fetească neagra	15	22	20	2.0	3.0	2.5
Zweigelt	13	22	17	1.1	1.7	1.4
Cadarca	11	16	13	1.0	1.2	1.1
Gamay	6	12	9	0.3	0.7	0.5
Pinot Noir	It contains acyl anthocyanins					

Table 3. *Variations in shikimic acid content of various wines* (Tardea, 2007)

Grape variety	Minimum value, mg/L	Maximum, mg/L
White wines		
Chardonnay	30	140
Pinot blanc	1	25
Pinot Gris	3	25
Riesling	16	209
Sauvignon Blanc	8	17
Red wines		
Cabernet franc	55	215
Cabernet Sauvignon	58	215
Merlot	27	77
Pinot Noir	4	26

Since the authentication variety by using the fingerprint anthocyanins is operational only in red wines, white wines, roses and even the red is investigating by the content of shikimic acid (Mardones et al., 2005, von Baer et al., 2007). Shikimic acid is found in small amounts in various fruits, including grapes. In wine is found in concentration of 10-150 mg/L. Research shows that red wines have a higher content of shikimic acid than white (table 3).

The variations are quite large, being dependent and other factors so the evaluation of this compound does not always lead to clear results. The content of shikimic acid is especially recommended for white wines authentication and as the additional indicator for red wines authentication (Makris et al., 2006).

2.5. *Analysis of volatile compounds profile*

The biosynthesis of odorant substances is connected by the biological characteristics of each grape variety, which manifests itself more strongly at aromatic varieties. The knowledge of content, structure and different correlations between volatile compounds is a valuable method to authenticate the grape variety.

Because the different biochemical and physico-chemical processes take place throughout the period of preparation and storage of the wine, the aromatic profile of wines undergo essential changes, which limits the possibility for grape variety authentication.

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

Sometimes, the combination between instrumental analysis and sensory evaluation using olfactometric method based on the selection of impact flavours depending on olfactometric index values (Tardea, 2007).

2.6. *Residual DNA analysis of grapes*

Since it was found that the wines have small amounts of DNA from grapes, their analysis is done in order to identify the variety of the vine (Baleiras-Couto and Eiras-Dias, 2006, Siret et al., 2002).

To develop techniques for assessing residual DNA is important to solve the impediments related to extremely low content of DNA in wine, the presence of similar compounds contamination (DNA from yeast, bacteria), the changes that occur during the grapes processing (especially in the alcoholic fermentation) and the existence of inhibitors factors (polyphenols) of polymerase chain reaction (PCR).

These difficulties were solved by using appropriate methods of DNA extraction and improving performance analysis using microsatellite PCR amplification. In conclusion, the method still remains safe and effective to authenticate the variety of vines and wine.

3. Authentication of wine age

By storage the wines during the time, a number of beneficial changes such as physical-chemical and even biochemical that causes the most refined sensory qualities are developed, so old wines are more valuable but also more expensive than young ones.

Moreover, the wines produced in a crop year which benefited from favourable weather conditions have great quality features appreciated by consumers which are also reflected in their market price. Because of this, there is the tendency of producers and sellers to misinform the consumers about this in order to obtain undeserved incomes.

Since the period of maturation and aging, the wines have changed dependent on the nature and quality, but also the storage conditions, sensory evaluation of age, in many cases, is not very useful.

The analytical method used frequently with clear results is to determine the radioactivity of the isotope ^{14}C of wine ethanol molecule.

Unlike the other isomers (^{2}H, ^{18}O), the isotope ^{14}C has a high distribution and its variations due to geographical or botanical origin are limited (± 5%).

For two centuries (during 1752-1952) radioactivity ^{14}C remained almost constant at a level of 13.6 dpm (disintegration per minute), after which, due to atomic bomb testing and particularly those with hydrogen increased reaching a peak in 1963, and after a decrease, as shows and Figure 1.

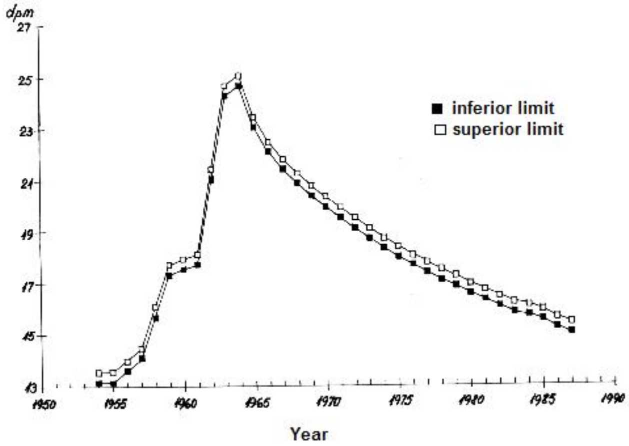

Figure 1. Evolution of ^{14}C activity with the year of wine production (Mongereau and Evin, 1993 cited by Medina, 1996)

The method is relatively simple and consists in determination of the ^{14}C isotope radioactivity of the concentrated solution (minimum 95%) of alcohol obtained by wine distillation or other alcoholic beverages. The process generates incorrect results if must and wine was with sucrose addition because the year cultivation of sugar beet or cane is different from that of the test sample.

For red wines, to increase certainty, it is recommended to combine this results with those obtained from analysis of polyphenolic compounds and colour indices. The method is valid for wine products produced in the period 1950-1995, the method accuracy is ± 3 years.

Determination of radioactivity by measuring the activity 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 radioactivity of isotopes have a high degree of reliability only for products with a considerable age.

4. Authentication technology for production

There are a variety of techniques and processes of winemaking, difficult to identify the occurrence conditions of modern technologies, especially the use of additives or the winemaking materials, 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.

4.1. Authentication of sparkling wines

Sparkling wines, which included class sparkling wines (sparkling), semi-sparkling, sparkling, pearl etc., are elite alcoholic beverages, much appreciated by consumers. There are a wide range, determined both by the diversity and quality of raw materials (wine based) but also technology development.

Besides the general aspects of wines authentication, as outlined above, where sparkling wines should be a clear distinction between products which contain CO_2 from endogenous origin (sparkling wine) and that where CO_2 is totally or partially exogenous.

It also requires identification technology for production (in bottles, the tanks, mixed, continuous flow), because it makes the quality of products and hence their trading price.

In addition to sensory evaluation, where the size, density and duration of release of CO_2 are among the most important and characteristic parameters, the instrumental analysis tool provides irrefutable data of recognition (Gonzalez-Martin et al., 1997, Martinelli et al., 2003).

The most information's are provided by the component amino acid analysis certainty being higher when is associated with the study of other compounds like: odorant substances, polyphenols content, carbohydrates, etc.

Isotopic analysis is generating the most rigorous investigation results by determining the amount of isotope ratio $^{13}C/^{12}C$ (Calderone et al., 2005). In this way, is precisely the origin of carbon dioxide in the product, if whether it comes from plants with C_3 metabolism (the vine) or C_4 (sugar beet etc.) or from other sources (industrial, synthesis etc.).

4.2. Authentication of oxidative type wines

Oxidative type wines, with the main representatives of Port wine, Madeira, Jeres etc. are characterized by sensorial properties, generated mainly by biochemical or physico-chemical 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, the carbohydrates (including the ratio of glucose and fructose), presence and content of amino acids etc. generate information's that compared with the reference, are useful to identify the original products.

With classical determinations and because the imitations are produced mainly with must fortified by alcohol with very little fermentation, the glucose/fructose ratio is above 0.9 for the imitations and below 0.8 for Port wine (Medina, 1996).

4.3. Authentication of rose wines

Rose wines have a low share in world wine production structure. Without fall within special wines, authentication raises some unresolved issues in their entirety until now. Rose wines are at the border 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 in the sense that comes from red grapes or a blend of white grapes and red or white and red wines, and secondly to assess the authenticity of colour, to detect possible fraud colour of white wines by oenocyanin addition.

Analysis of compounds and parameters such as polyphenols, sugars, volatile acidity, extract and especially the colour indices etc. and comparing the results with reference values provide a high degree of certainty.

The relevant results are obtained by determination of the colour intensity I (extinction at wavelengths λ = 420 nm, λ = 520 nm and λ = 620 nm) and T tone or hue (the ratio of light absorption at wavelengths λ = 420 nm and λ = 520 nm). The intensity colour for white and rosé wines has values of 0.3-0.6 and for the red wines red wines 15-20. Also the hue values are 0.5-0.6 and only old wine the recorded hue values are 1.0-1.5.

The recommended method for defining the colour is the spectrophotometric method in CIE-Lab coordinates Tristimulus-76, the reference method, which monitors the three indices colour: bright, chromaticity and purity (Garcia-Jares et al., 1993, cited by Medina, 1996).

Conclusions

Wine authenticity is very important, especially in relation to quality control and consumer information.

Since wine quality is dependent on the grapevine cultivars used, it is important to be able to detect and identify the grape varieties present in musts and wines. The characterisation and differentiation of musts have been based mostly on the analysis of chemical and biochemical parameters, namely protein and amino acid profiles, analysis of trace elements or phenolic compounds.

The mineral profile of wine is characteristic and unique to a specific wine geographical origin and can be used as proof of authenticity where a control exists.

However, these methods do not always give definitive results. Reliable results are obtained only by collating several analytical techniques, followed by statistical interpretation of results. Multifactorial approach by chemometrics methods of information from instrumental analysis provides the most rigorous results. The main problem still remains the creation of a database/databank for all, or even the main wines.

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