Original scientific paper
UDC 663.21:004.7.056.52

STUDIES ON THE POSSIBILITIES OF AUTHENTICATING THE GEOGRAPHICAL ORIGIN OF WINES

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Abstract

For some food products, as is the case with high-quality wines, the maturation and aging period determines their "ennoblement" with the development of the most refined qualities, but with consequences also on the economic value (price), a fact that requires the identification of the date (year) of obtaining. The purpose of this work is to complete the databases regarding the authentication of the geographical origin of the wines due to the specific conditions that the place of origin of the grapes gives the wines specific qualities and characteristics. A mapping of the provenance of a certain type of wine can thus be done.

The authentication of geographical origin can be investigated through a wide range of procedures, but there is no universal, direct scientific method, only indirect methods. Very faithful results are obtained only by corroborating several analytical techniques, followed by statistical processing and interpretation of the obtained results. The multifactorial approach through chemometric methods of processing the information provided by the instrumental analysis ensures the most rigorous results. The authentication and detection of possible fraud involve the completion of three important stages: sampling, analytical control, and data processing and interpretation. Fraudulent use of geographical indications is harmful to both legitimate producers and consumers. That is why the development of efficient (modern) investigative techniques for authenticating the geographical origin of food products is a challenge from an analytical point of view, which is currently being given special attention.

Interest in the authentication of food products has continuously increased, and is currently more current than ever, due to consumer pressure, as a result of animal diseases and the appearance of transgenic products on the market. To be able to confirm the authenticity of a product, considering its great diversity and the very small differences depending on the species and variety, it is indispensable to have a database (bank) where the main characteristics of the products sold can be found. The databases (banks) must be continuously dynamic and also correlated with the changes that occur in agriculture (climatic, biochemical, agrotechnical, etc.) and raw material processing technologies.

***Key words**: Authentication, Database, Wine, Quality, Geographical origin.*

1. Introduction

For some food products, as is the case with high-quality wines, the maturation and aging period determines their „ennoblement" with the development of the most refined qualities, but with consequences also on the economic value (price), a fact that requires the identification of the date (year) of obtaining.

Wine benefits from the most extensive and rigorous legislation, both in terms of production technologies and especially in terms of quality standards. All wine-growing countries have national legislation in the field of wine production, which is harmonized with the resolutions of the International Organization of Vine and Wine (OIV) and with the regulations of the European Union (EU). Romania, which is a member of the OIV and is part of the EU, through the Vine and Wine Law no. 244/2002 amended in 2006 by Lg 57, in 2015- Lg 164, and the Methodological Norms for the application of the law in 2016, in the system of the common organization of the market vitiviniculture, has aligned its wine production with EU requirements and

standards, primarily by increasing quality and applying international norms for analysis and technological control of viti-vini production.

The authenticity and typicality of the wine are basic attributes that guarantee the quality of a wine. First of all, the wine must meet the requirements of authenticity and typicality, since wines with a false identity cannot be offered to consumers.

The notion of authenticity refers to the variety from which the wine is produced and the vineyard from which it comes, and the notion of typicality, to the characteristics of the wine, in the sense of "benchmark wine" that meets the characteristics imprinted by the variety, the vineyard and the traditional wine production technology (Ţârdea, [6]).

The authenticity and typicality of the wines are highly valued by consumers and rigorously controlled during marketing. The criteria for controlling the authenticity of wines were established: the anthocyanin spectrum in red wines, the shikimic acid content in white wines, the amino acid footprint in wine, and the isotopic composition of alcohol and water in wine.

The notion of generic or semi-generic wine refers to registered trademarks for industrial and food products. In the case of wines, it refers to "branded wines", i.e. high quality for which there must be registered trademarks (Ţârdea, [6]).

A generic branded wine always carries a famous name of origin: "Bordeaux wine", "Malaga wine", "Tokay wine" and why not "Cotnari wine" or "Târnave wine". Through the wine legislation of each country, common elements are established that define branded wines and the preservation of reference samples in the wine cellar (Ţardea, [7]).

The purpose of this work is to complete the databases regarding the authentication of the geographical origin of the wines due to the specific conditions that the place of origin of the grapes gives the wines specific qualities and characteristics. A mapping of the provenance of a certain type of wine can thus be achieved.

2. Materials and Methods

The authentication of geographical origin can be investigated through a wide range of procedures, but there is no universal, direct scientific method, but only indirect methods. Very faithful results are obtained only by corroborating several analytical techniques, followed by statistical processing and interpretation of the obtained results. The multifactorial approach through chemometric methods of processing the information provided by the instrumental analysis ensures the most rigorous results(Ţârdea, [8]).

2.1 Materials

Investigations were carried out on Sauvignon Blanc, Chardonnay, and Italian Riesling wine varieties originating from two famous Pogdorii of Romania, namely Drăgăşani and Jidvei.

Soil characterization and exhibition of the vineyard areas as well as temperature dynamics in 2022 in the studied vineyards are presented in Tables 1 and 2, respectively.

2.2. Methods

2.2.1 Evaluation of the wines mineral profile

The following were determined: cadmium, lead, manganese, nickel, zinc, aluminum, barium, and copper, with the help of the atomic absorption spectrometer with graphite furnace ICP-MS Varian 820. Ultra-pure water, HNO_3 69% (w/v), concentrated with HF and HCl (Merck, Germany), and purified water, obtained from a Millipore Milli-Q system (Bedford, USA) were used. A small amount of sample or standard solution is placed inside the tubular graphite tube. This is heated in a temperature program to remove impurities. For quantitative determinations, a calibration curve was obtained for each element.

Table 1. Characterization of the soil and exhibition of the vineyard area (Toti, [9])

Vineyard	Exhibition	Soil type	Soil texture	Tillage
Vineyard Târnavelor -Jidvei	46°10'51,2" N, E-23°55'40,5", 330 m, exhibition E	Calcareous regosol, deep loosening – typical vertosol, vertic preluvosol, vertic luvosol, vertic regosol	Clay and with Sarmatian marl content, non-tagnoglazed	Black field (Ploughing + mechanical harrows per interval + manual harrows per row
Hills Olteniei - Drăgăşani	44°39'36,81" N 24°14'05,86" E, 201 m, exhibition E	Brown eroded eumezobasic soil 30%, heavily eroded brown eumezobasic soil 20%, podzolite pseudoglay brown soil 20%, typical regosol 10%, pseudoglay planosol 10%, typical alluvial soil 5%, typical vertisol 5%	Clayey-dusty clay, yellowish-brown, with small and medium frequent pores	Black field (Ploughing + mechanical harrows per interval + manual harrows per row

Table 2. Temperature dynamics in 2022 in the studied vineyards

Month	Air temperature			Rainfall (mm)	Index Huglin	Number of days with precipitation > 10 mm	Σ °t globe (°C)	Σ °t active (°C)	Σ °t helpful (°C)
	T med (°C)	Mediate T min (°C)	Mediate T max (°C)						
Dragasani									
April	11.92	6.53	17.83	39.9	146.25	1	357.5	314.5	64.5
May	14.08	9.42	19.06	14.9	203.67	-	436.5	436.5	166.6
June	22.81	17	29.23	139.2	480.6	7	684.5	684.5	384.5
July	22.82	15.84	30.16	63.8	511.19	3	707.5	707.5	397.5
August	25.13	17.39	32.87	1	589	-	779	779	469
Blaj									
April	11.4	5.03	17.83	456	138.45	14	343	239.3	43.4
May	12.4	8.16	16.65	396.4	140.28	20	385.2	272.8	153.2
June	21.1	14.77	27.47	345	428.55	15	633.6	633.6	300.6
Iuly	22	13	26.74	123	445.47	10	682	682	372
August	21.8	14.74	28.81	116	474.46	6	675.8	675.8	365.8

Legend: Index Huglin =[(T_{med} – 10)+(T_{max} - 10)]/2 x number of days per month; Σ°t global = sum of positive average daily temperatures; Σ°t active = sum of average daily temperatures > 10 °C; Σ°t useful = the sum of the differences between the average daily temperature > 10 °C and the biological threshold for starting the vine vegetation (10 °C)

2.2.2 Influence of the variety on the accumulation of volatile compounds in wines

The samples used were analyzed using the gas chromatograph coupled with a flame ionization detector (GC/FID) system, using the HeadSpace method beforehand.

The system included a Varian 450 GC gas chromatograph coupled to a Varian 240 MS model mass spectrometer (Varian, USA), equipped with a Thermo Scientific TG-WAXMS (Waltham, USA) capillary column (60 m x 0.32 x 0.25 pm).

2.2.3 Specific IRMS mass spectrometry analysis procedure

IRMS mass spectrometers are modern devices that usually record an ion current (proportional to the number of ions) in the form of a spectrum, depending on the mass of the ions and their relative abundance (concentration in percentage). The principle of mass spectrometry consists of ionizing the sample by electron bombardment in high vacuum, focusing and sending the ions and fragmentation products into an analyzer (depending on the mass/charge ratio by applying a magnetic and/or electric field), and then collecting and measuring the amounts of each selected ion in a detector.

2.2.4 Evaluation of wine authenticity and typicality using macromolecular wine fingerprinting techniques

Varietal evaluation methodologies for wine authentication are based on the study of proteins, metabolites, or DNA analysis. Protein analysis (immunological or electrophoretic assays) and determination of metabolite content (HPLC or NMR) are limited due to environmental conditions and industrial processing procedures, whereas DNA-based methodologies, even if limited by DNA degradation, are techniques independent of environmental conditions (Catalano, [2]).

Genotyping the must, or proving the origin of grapes from a certain variety, is a way of identifying the varietal composition that can be a way of product traceability and certification (Jobes, [4]).

For DNA extraction from wine samples, the Qiagen method and the Işçi *et al.*, [3], method can be used. For both methods, the wine samples must be concentrated according to the protocol recommended by Savazzini and Martinelli [10], respectively: sampling 45 mL samples, adding 5 mL of NaCl (1.2 M), homogenizing, and storing at -20°C until at the time of extraction.

3. Results and Discussion

The isotopic fingerprinting of wines involves several aspects, such as determining the geographical origin, the year of harvest, the wine grower, and the quality. That is why the proof of the authenticity of the wine must be based on the specific parameters of the origin that do not undergo changes during the vinification or that are difficult to falsify, namely the stable isotopes: oxygen 18 and carbon 13.

Unlike other cultures, viticulture today has precisely delimited areas, and within them, areas within which, following the model of large wine-growing countries, such as France, Italy, and Spain, wines with the right to

the designation of controlled origin can be produced. The grapevine can also be grown outside the demarcated viticultural areas which, according to the ecological conditions, are less favorable for obtaining higher-quality wines. As a result, the viticultural legislation in our country, and countries with developed viticulture is restrictive in terms of assigning the name of variety or area, as well as capitalizing on a higher price (Pomohaci, [5]).

The wine region comprises a large territory cultivated with vines, characterized by relatively similar natural climate and relief conditions, as well as by production directions and close assortments.

A vineyard is a natural and traditional territorial unit, characterized by specific conditions of climate, soil, and relief, by the cultivated soils, by the cultivation methods and winemaking processes used, which, as a whole, lead to the production of grapes and wines with specific characteristics.

The wine center is the territory that includes the vineyard plantations in one or more localities, which is or is not an integral part of a vineyard and which constitutes a territorial unit characterized by specific factors of climate, soil, and variety, as well as by similar agrotechnical and technological conditions. The wine center covers a smaller area than the vineyard.

The vineyard plot is the restricted territory within a viticultural center, which includes the vine plantations located on the same relief form. The natural factors, as well as the culture and technology conditions regarding the vineyard, are similar in the entire area cultivated with vines, determining the obtaining of products with specific quality characteristics.

Taking into account these particularities, in the last two decades, with the increase in the concern for the quality of wines and products based on must and wine, the concern for the evaluation of the degree of favorability of a wine-growing area has also increased, by introducing in the specialized literature the concept of "terroir" (Pomohaci, [5]).

The authentication and detection of possible fraud involves the completion of three important stages: sampling, analytical control, and data processing and interpretation. Fraudulent use of geographical indications is harmful to both legitimate producers and consumers. That is why the development of efficient (modern) investigative techniques for authenticating the geographical origin of food products is a challenge from an analytical point of view, which is currently being given special attention (Briciu, [1]).

The quantitative sequence of the studied and analyzed metals is as follows (Figures 1 and 2):

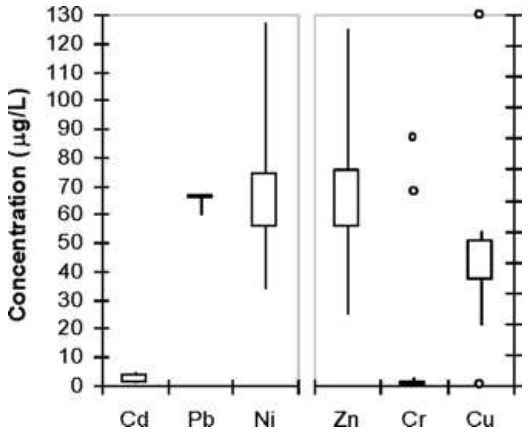

Figure 1. Global representation of the concentrations(p, g/L) of the elements in the wines produced in Jidvei

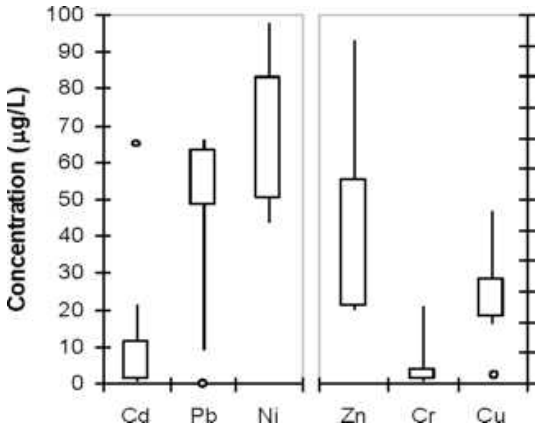

Figure 2. Global representation of the concentrations (p, g/L) of the elements in the wines produced in Drăgășani

The metal determination method using the graphite furnace atomic absorption spectrometer ICP-MS Varian 820 leads to very precise results in the order of micrograms. No elements leading to the hypothesis of soil contamination were found in any of the vineyards.

The higher alcohol content of the wines from the Drăgășani Vineyard is much higher than that of the wines from the Jidvei Vineyard, but as for the content of volatile fatty acids, the ratio is reversed. Esters, those that give the most pregnant aromas and aldehydes are found especially in the samples from the Jidvei Vineyard, and terpenic compounds, those that give floral aromas to the wines, are found in similar quantities.

Isotopic fingerprinting of wines involves several aspects, related to their geographical origin, the year

of harvest, the wine producer, and its quality. That is why the proof of the authenticity of the wine must be based on the specific parameters of the origin that do not undergo changes during the vinification or that are difficult to falsify, namely the stable isotopes of O_{18} and C_{13}. The results obtained through these determinations lead to the realization of the database of wine authentication from the regions under study.

3.1 Evaluation of characteristic markers in wine authentication

The identification of specific components of the area from which a wine originates is of major importance for its authentication, precisely because the constituent elements are typical.

Concentration in polyphenols depends on the variety, the ripening conditions of the grapes, the winemaking technologies applied, and especially the climate. The practices applied to the vines, specific works, and spraying, but also the composition of the soil and water table are also important.

Additions of alcohol to wine, sugar, or glycerol can be easily detected by isotopic fingerprinting, a method increasingly used in specialized laboratories. Authentication of geographical origin is an important desirability because certain wine-growing areas have a well-known reputation and producers are tempted to market cheap wines under a false name. The vine develops differently depending on the geographical area, so even the grapes, even if they are of the same variety, have different characteristics.

Isotopic fingerprinting leads to the exact establishment of the area of origin because it imprints a typical configuration on the wines, which can lead to their differentiation.

Heavy metal content is also a key element in the authentication of wines precisely because they can come from the vineyard as such (geographical area), but also from the use of containers of questionable or inappropriate quality. The concentration of mineral elements and microelements are specific to a wine in that they are involved in its color, present compositional particularities, and relevant discriminating elements.

Flavor compounds contribute relevantly to establishing the authenticity of wine through their concentration, but also through their variety. Each variety is specific to a set of aroma compounds that leads to their differentiation, some compounds are specific only to a segment of wines. This differentiation can arise from the concentration of terpenic compounds, but also from aromatic compounds in non-aromatic varieties.

International legislation provides for the harmonization and improvement of analytical methods to identify fraud and the efficiency of food control by establishing physicochemical characteristics consistent with natural potential, limiting or prohibiting the addition of various elements, establishing maximums in terms of the concentration of toxic compounds in wine but and identifying them according to the label.

Wine production technologies allow the use of selected enzymes and yeasts that ultimately lead to certain characteristics specific to each area.

4. Conclusions

- Interest in the authentication of food products has continuously increased, and is currently more current than ever, due to consumer pressure, as a result of animal diseases and the appearance of transgenic products on the market. To be able to confirm the authenticity of a product, considering its great diversity and the very small differences depending on the species and variety, it is indispensable to have a database (bank) where the main characteristics of the products sold can be found.
- More conclusions related to the specific results of this investigation and the purpose of this research can be obtained by mapping the provenance of a certain type of wine.
- The databases (banks) must be continuously dynamic and also correlated with the changes that occur in agriculture (climatic, biochemical, agrotechnical, etc.) and raw material processing technologies.

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