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Studies regarding the certification of the authenticity of wines and tracking their forgeries

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Abstract

The present work proposes a deepening of the main research carried out at international level on the issue of traceability and authenticity of food products, with a special focus on grapes and products derived from grapes (e.g. juices, compote, wines, distillates), in order to identify potential quality and origin certification markers as well as contaminants that can affect the quality of the fruits as well as the products resulting from them.

On the other hand, the authentication of food products must be based on chemical markers that show great stability during the processing of the raw materials, until the finished product is obtained and consumed.

Determining the natural composition in stable or radioactive isotopes of a wine is one of the high-performance applications of analytical chemistry, namely establishing the relationship between the finished product (wine) and the raw materials (water, CO_2) from their natural environment. 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 it is necessary that the proof of authenticity of the wine is based on the specific parameters of the origin that do not undergo changes during the vinification or that are difficult to falsify. The isotopic analyzes related to water and alcohol in wine are part of a global European program for establishing the authenticity of wines.

Keywords: authentication, forgery, wine, isotopic fingerprinting, markers.

1.Introduction

The authentication of food products must be carried out on the basis of chemical markers that show great stability during the processing of the raw materials, until obtaining the finished product and its consumption.

It was also found that if precipitation falls in the days preceding the harvest, the isotopic ratio of oxygen decreases significantly due to this dilution of the grape juice, just like in the cases of adding water to the wine, which is why it must also be taken into account meteorological data from a certain year when creating a database and evaluating the naturalness of a wine.

Foerstel (1985) [3] emphasized the potential of using the ratio $H_2{}^{18}O$/ $H_2{}^{16}O$, of the water from the grapes, as an indicator of the purity and geographical origin of the wine, considering that this ratio depends on the isotopic composition of the soil water in a certain area and of the average atmospheric humidity. Holbach et al confirmed the fact that the $^{18}O/^{16}O$ ratio in wine is an indicator of the geographical origin of the wine, from the point of view of latitude. This allows, to a certain extent, the detection of some frauds regarding the origin of the wine (the authors discovered wines that certainly came from a warmer area than the one indicated on the bottle), as well as the identification of some wines in which water was fraudulently added.

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2. Material and method

Determining the natural composition in stable or radioactive isotopes of a wine involves establishing the link between the finished product (wine) and the raw materials (water, CO_2) from their natural environment. That is why it is necessary that the proof of authenticity of the wine is based on the specific parameters of the origin that do not undergo changes during the vinification or that are difficult to falsify.

Isotopic analytical techniques are useful to objectively provide analytical parameters for the European wine protection system, such as:

- ✓ protection of the designation of origin (PDO Protected Designation of Origin, the requirements of the European regulation EEC no. 2081/92),
- ✓ protecting the geographical indication (PGI Protected Geographical Indication),
- ✓ the ways of applying controls in the wine sector.

The basic principle of the sample preparation tools in order to determine the isotopic ratio by mass spectrometry is the transformation of the sample into the corresponding elemental gases (e.g. CO_2 or CO for ^{13}C and /or ^{18}O, N_2 for ^{15}N, H_2 for deuterium and SO_2 or SF_6 for ^{34}S), while preserving the isotopic composition of the original sample. Currently, the conversion of samples into gases is done automatically (e.g. EA elemental analyzer, sample equilibration equipment with equilibration gases of known composition).

2.1. Sampling of samples

a) The collection, conservation, transport, storage and identification of water samples (drinking, spring water) are operations specified in the Romanian Standard SR ISO 5667-5 / June 1998 - "Water quality. Sampling. Part 5: Guidelines for the sampling of drinking water and water used in the food and beverage industry".

b) The sampling, preservation, transport, storage and identification of wine samples and products based on must and wine are operations specified in the Romanian Standard SR 7588, approved on April 30, 1999, with application from September 1999.

2.2. Preparation of samples for their isotopic analysis

Before any isotopic analysis, sample preparation is required.

a) *In the case of surface water (drinking, spring)* the sample does not undergo any additional preparation; in the case of precipitation, these samples are filtered through a filter paper to remove solid impurities that could clog the capillaries in the preparation systems.

b) *In the case of low-alcoholic beverages*, for example wine: the extraction of ethanol and water from wine is done according to European rules (Commission Regulation No. 2676/1999), namely by fractional distillation. According to them: any method for the extraction of ethanol can be used as long as it ensures the extraction of 98-98.5% of the total alcohol of a wine, into a distillate containing 92-93% by mass (95% volume) alcohol.

Specific fractional distillation procedure: Extraction of ethanol and water from wine: A sample of 300 ml of wine is introduced into the distillation flask and a distillation reflux rate of approximately 0.9 is ensured. Place a pre-calibrated 125 ml volumetric flask to collect the distillate. Collect the liquid between 78 and 78.2 until a volume of 40-60 ml is reached. If the temperature exceeds 78,5°C the collection is interrupted for about 5 minutes. When the temperature reaches 78°C again, distillate collection is resumed up to 78,5°C. This discontinuous collection operation is repeated until the temperature remains constant. Complete distillation takes about 5 hours.

3. Resultts and discussions

Isotopic ratios $\delta^{13}C/^{12}C$ and $\delta^{18}O/^{16}O$ of the wines obtained from grapes harvested in the study years varies *inversely proportional* to the active heat balance and to the precipitation during the grape ripening period and *directly proportional* to the duration of sunshine during the grape ripening period in the respective years. $^{12}C^{16}O_2$

Isotopic ratio $^{18}O/^{16}O$ is determined by mass spectrometry for isotopic ratios (IRMS) from the ion currents corresponding to the masses m/z = 46 ($^{12}C^{16}O^{18}O$) and m/z = 44 ($^{12}C^{16}O_2$) produced by the carbon dioxide obtained after the isotopic exchange with the sample, according to the reaction:

- $C^{16}O_2 + H_2{}^{18}O \leftrightarrow C^{16}O^{18}O + H_2{}^{16}O$

System settings for the determination of the $\delta^2H/^1H$ isotopic ratio in water originating from precipitation and springs in the studied area [1,2]:

Sample amount	***200 µl, in the presence of a Platinum fruit***
H_2/He	2 %
Equilibration time/ Vials temperature	60 min la 25°C
Column type	Pora Plot Q 25 m (24°C)
Primary standard	SMOW, SLAP, GISP

System settings for determination $\delta^{18}O/^{16}O$ from water extracted from wine and water from precipitation.

Sample amount	***500 µl***
CO_2/He	0.36 %
Equilibration time/ Vials temperature	20h la 25°C
Column type	Pora Plot Q 25 m (24°C)
Primary standard	SMOW, SLAP, GISP

Determination of Carbon 13**:** For the global and specific determination of the $^{13}C/^{12}C$ isotopic ratio in wine ethanol samples, the CF-IRMS Delta V Plus mass spectrometer is coupled to the EA 1112 HT elemental analyzer.

The purpose of the specific procedure is to measure the $^{13}C/^{12}C$ isotopic ratio of ethanol extracted from wine or derived products, originating from grapes following fermentation. The isotopic ratio $^{13}C/^{12}C$ can be expressed as a deviation from the working standard. The isotopic deviation of carbon 13 ($\delta^{13}C$) is then calculated on a delta per thousand (δ/ 1000) scale by comparing the results obtained for the measured sample with those for the working standard calibrated against the international primary standard.

$$\delta^{13}C_{sam/ref}‰ = \frac{R_{sam} - R_{ref}}{R_{ref}} 10^3$$

The values $\delta^{13}C$ are expressed against the working standard:

where R_{sam} and R_{ref} represent the isotopic ratios $^{13}C/^{12}C$ of the sample and the carbon dioxide used as a reference gas. Values $\delta^{13}C$ are expressed against V-PDB as follows:

Working parameters for the elemental analyzer [2,3].

Injection volume	**0,2µl**
Autosampler type	**AS 300**
Reactor temperature	**1010 °C**
Temperature GC	**45 °C**
Eluent flow rate (He)	**90 ml/min**
Oxygenflow rate 5.0	**250ml/min**
Oxygen injection time	**1 sec**
Type of syringe	**0,5µl**
Reference material BCR-660 (ethanol in water)	**$\delta^{13}C/^{12}C$ CvsPDB(‰) =- 26,72 ± 0,09**
Reference material BCR-656 (96% ethanol)	**$\delta^{13}C/^{12}C$ CvsPDB(‰) =- 26,91 ± 0,07**

Conclusions

Isotopic ratios $\delta^{13}C/^{12}C$ and $\delta^{18}O/^{16}O$ of the wines obtained from grapes harvested in the study years varies *inversely proportional* to the active heat balance and to the precipitation during the grape ripening period and *directly proportional* to the duration of sunshine during the grape ripening period in the respective years. Isotopic fingerprinting authenticates the vineyard, the year of harvest and the quality of the wine, if there is an up-to-date database of the vineyard and the rainfall of the respective years.

Compliance with Ethics Requirements: Authors declare that they respect the journal's ethics requirements. Authors declare that they have no conflict of interest and all procedures involving human or animal subjects (if exist) respect the specific regulation and standards.

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