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Study of the authenticity and regional origin of Romanian wines using Isotope Ratio Mass Spectrometry

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The measurement of natural abundance of isotopes has been mainly used in geochemistry and environmental research. Since a few years the isotopic techniques have also gained a growing interest for the control of food products and beverages. This paper presents the development of an analytic technique for the determination of isotope ratios as a tool for authenticity proof of wines.

Two analytical techniques are mainly used for the measurements of the stable isotope content in wines. These are the Isotope Ratio Mass Spectrometry (IRMS) for $^{13}C/^{12}C$, $^{18}O/^{16}O$, $^{2}H/^{1}H$ and the deuterium Nuclear Magnetic Resonance (^{2}H-NMR).

Wine has been one of the products analysed either for improvement of quality or for detection of possible frauds. Wine is obtained by fermentation of grape must and its alcohol grade is proportional to the initial sugar concentration of the must. An increase of the alcohol grade of wine can be obtained by addition of foreign sugars before or during fermentation. In the European Union this practice, called chaptalisation, must be in compliance with the European Regulation that stipulates maximum levels of enrichment for the various European wine growing areas. The chaptalisation with cane sugar is easily detectable by IRMS because of significant increase of the ^{13}C content of the ethanol resulting from the fermentation of the mixture of C_4 cane and C_3 grape sugar. On the other hand, because of the same C_3 metabolism of grape and beet, the chaptalisation with beet sugar can be detected by using quantitative deuterium NMR.

The content of ^{18}O in water from wine is performed by IRMS and is used for the detection of addition of water, for the characterisation of the geographical origin of wines and for the establishment of the year of vintage. The European Community has adopted the determination of ^{18}O from wine as an official method for analysis of wines and has included this parameter in the E.U.Wine Databank.

The $^{13}C/^{12}C$ –IRMS method is used for the detection of the geographical origin of wine, year of vintage, mixture of C_3 and C_4 sugars in wine, and for detection of addition of glycerol. This method is used for the characterisation of natural gasification of sparkling wines, too.

The method enables measurements of the $^{13}C/^{12}C$ isotope ratio in wine ethanol. The information on ^{13}C content enables the quantities of mixtures of sugar or alcohol derived from C_3 and C_4 plants to be determined.

The $^{13}C/^{12}C$ content is determined on carbon dioxide produced during the complete combustion of the ethanol. The ethanol must be extracted from the wine before isotopic analysis. This is carried out by distillation of wine.

The apparatus for extracting ethanol comprises an electric heating mantle with voltage regulator, one litre round-bottom flask with ground glass neck joint, a column filled with Dixon metallic rings, a flask for collecting the ethanol, and a distilling controller automatic controlled.

The ethanol is quantitatively converted into carbon dioxide in sealed glass bulb filled with copper oxide as an oxidation agent. The carbon dioxide is purified of all other combustion products including water.

All the process has to be without any isotopic fractionation. All steps of the preparation must be carried out without any significant ethanol loss through evaporation that would change the isotopic composition of the sample.

The isotopic analysis was performed with a mass spectrometer capable of determining the relative ^{13}C content of naturally occurring gas with an internal accuracy of 0,3‰ or better expressed as a relative value.

The ionic current for m/z=45 is corrected for the contribution of $^{12}C^{17}O^{16}O$ which is calculated according to the current intensity measured for m/z=46, while taking the relative abundance of ^{18}O and ^{18}O into account (Craig correction). Comparison with a reference calibrated against the international reference V-PDB permits calculation of carbon content on the $\delta^{13}C$ relative scale.

It was distilled 500ml wine to verify the parameters of the distillation column and the recoverable quantity of the ethanol from wine.

We found that a good reflux ratio (the ratio of the reflux to the distillate) was 20. The time needed for the distillation of the wine sample was about 4 hours. In this time it has collected three fractions from distillate:

- fraction I at 35 min, about 5ml distillate

- fraction II at 185 min, about 75ml distillate
- fraction III at 230 min, about 5ml distillate.

Every fraction was analyzed by gas chromatography to see its composition. The composition of the fraction I and II was carried out with a FID detector. The composition of fraction II and III was carried out with a thermal conductivity detector. The fraction I contained some impurities that are more volatile than ethanol (aldehydes and esters). The fraction II contained ethanol with very low level of impurities. The content of water from this fraction (6%) is normally because the ethanol is an azeotrop mixture with water in proportion of 95.6% ethanol and 4.4% water. The fraction II is good for isotopic analysis and we have used it for measuring $\delta^{13}C$ in ethanol.

The fraction III has a high content of water and low content of ethanol. The residuum of distillation contains water as major component and can be used to analyse ^{18}O in water from wine.

The samples of wine from the 2002 vintage and from six different wine-growing regions of Romania were analyzed.

The composition of ^{13}C, ^{18}O and D from 25 wine samples was established by analysis with a commercially modernized mass spectrometer respectively with a home made deuterium analysis mass spectrometer SMAD-1.

The results were presented in Table 1 and 2.

Table 1. The isotopic composition of the ^{13}C, ^{18}O and D from 11 white wine samples

Sample	Type of wine	$\delta^{18}O_{SMOW}$ (‰)		$\delta^{13}C_{PDB}$ (‰)	δD_{SMOW} (‰)
		wine	reziduu		
1.	Feteasca Alba, Tohani 2002	-0.57	+6.27	-25.75	23.8
2.	Feteasca Alba, Bucium 2002, final	-0.34	+3.12	-25.75	9.13
3.	Feteasca Alba, Cotnari 2002, start	+0.70	+1.89	-25.86	10.02
4.	Feteasca Alba, Cotesti 2002		+2.94	-25.16	16.56
5.	Feteasca Alba, Stefanesti 2002, final	+1.26	+2.51	-25.13	12.58

6.	Feteasca Alba, Aiud 2002, start	-2.60	+3.03	-25.61	26.24
7.	Feteasca Alba, Tohani 2002, final	+0.52	+7.34	-25.15	31.3
8.	Feteasca Alba, Bucium 2002, final	-3.58	+7.07	-26.84	26.76
9.	Feteasca Alba, Cotnari 2002, final	-0.61	-0.94	-26.05	7.64
10.	Feteasca Alba, Cotesti 2002	+3.28	+10.23	-26.22	48.02
11.	Feteasca Alba, Stefanesti 2002, Final	-0.68	+5.32	-25.61	41.13

Table 2. The isotopic composition of the ^{13}C, ^{18}O from 14 wine samples

Sample	Type of wine	$\delta^{18}O_{SMOW}$ (‰)	$\delta^{13}C_{PDB}$ (‰)
1.	Cabernet Sauvignon, Tg. Bujor, 2004, red wine	0.10	-26.74
2.	Cabernet Sauvignon, Murfatlar, 2004, red wine	0.23	-28.41
3.	Cabernet Sauvignon, Tohani, 2003, red wine	5.35	-24.67
4.	Cabernet Sauvignon, V. Calugareasca, 2004, red wine	-0.18	-27.48
5.	Cabernet Sauvignon, V. Calugareasca, 2003, red wine	4.16	-24.86
6.	Cabernet Sauvignon, Tohani, 2004, red wine	1.89	-27.05
7.	Cabernet Sauvignon, Murfatlar, 2003, red wine	1.13	-26.98
8.	Cabernet Sauvignon, Bujoru, 2003, red wine	3.40	-24.57
9.	Feteasca Regala, Copou, 2002, white wine	-5.87	-29.00
10.	Feteasca Regala, Aiud, 2002, white wine, final	-1.60	-25.56
11.	Feteasca Regala, Dragasani, 2002, white wine, start	-3.46	-28.18

12.	Feteasca Regala, Copou, 2004, white wine	-0.52	-26.22
13.	Feteasca Regala, Aiud, 2004, white wine	-1.15	-25.93
14.	Feteasca Regala, Dragasani, 2004, white wine	0.80	-27.89

In this study we have developed a method for measuring $^{13}C/^{12}C$ and $^{18}O/^{19}O$ in wine ethanol and water from wine and we have studied the possibility to extract the ethanol from wine by distillation, without isotopic fractionation. The most propitious parameter of the distillation column was determined. Also we have determined the composition of ^{13}C, ^{18}O and D from some wine samples from different regions of Romania. These methods will be further used for the constitution of a databank of isotope ratios of wine.

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