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Multivariate classification of wines from different Bohemian regions (Czech Republic)

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Abstract

Fifty-three samples of wines were analysed by inductively coupled plasma mass spectrometry and inductively coupled plasma optical emission spectrometry. The contents of 27 parameters were determined: Al, As, Ba, Ca, Ce, Co, Cr, Cs, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Rb, Sb, Sn, Sr, Th, U, V, Y and Zn. The best results for identification of sample origin were achieved when determining the following parameters: the contents of Al, Ba, Ca, Co, K, Li, Mg, Mn, Mo, Rb, Sr, V and element ratios Sr/Ba, Sr/Ca, Sr/Mg. With these parameters, a 97.4% correct classification was achieved for white wines and a 100% correct classification for red wines.

Keywords: Wine; ICP-MS; ICP-OES; Fingerprinting; Chemometrics

1. Introduction

Wine is a widely consumed beverage throughout the world and has an obvious commercial value. Determination of food authenticity is one of the most crucial issues in food quality control and safety. There are six vine-growing areas in Bohemia; four of them are important wine-production areas. The four biggest areas are named: Žernosecko (abbreviated as LI), Mělnicko (abbreviated as ME), Mostecko (abbreviated as MO), and Roudnicko (abbreviated as RO).

Wine is a complex matrix, which, besides water, sugar and alcohol, contains a great variety of components, inorganic as well as organic. The composition of wine is influenced by many factors related to the specific production area: grape varieties, soil and climate, culture, yeast, winemaking practices, transport and storage. The greatest risk for introduction of contamination to wines arises from the application of bentonites for purification from tarnishing components such as proteins.

Progress of multielement techniques in element analysis has quickly increased in recent years and also many publications about wine and its origin have been issued. Numerous articles have appeared involving chemical parameters such as elements (Augagneur, Médina, Szpunar, & Łobinski, 1996; Baxter, Crews, Dennis, Goodall, & Anderson, 1997; Day, Zhang, & Martin, 1994, 1995; Frías, Conde, Rodríguez-Bencomo, García-Montelongo, & Pérez-Trujillo, 2003; Greenough, Longerich, & Jackson, 1997; Jakubowski, Brandt, Stuewer, Eschnauer, & Görtges, 1999; Latorre, García-Jares, Medina, & Herrero, 1994; Moret, Scarponi, & Cescon, 1994; Pérez-Magariño, Ortega-Heras, & Gonzáles-San José, 2002; Rebolo et al., 2000; Thiel, Bauer, Danzer, & Eschnauer, 1998; Thiel & Danzer, 1997), their ratios (Thiel et al., 1998), isotopic ratios (Eschnauer, Hölzl, & Horn, 1994), volatile compounds (Moret et al.,

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1994; Rebolo et al., 2000), non-volatile organic compounds (Moret et al., 1994), phenolic compounds (Pérez-Magariño et al., 2002; Rebolo et al., 2000), amino acids, and stable isotopes (Day et al., 1994, Day, Zhang, & Martin, 1995).

The objective of this work was to develop a classification scheme that would confirm the authenticity of wines from Bohemia. Multi-element analysis of wines by inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectrometry (ICP-OES) was undertaken to ascertain whether or not these methods could provide data for determining the region of origin of the wine.

2. Materials and methods

2.1. Samples

Fifty-three samples were collected from the four most important Bohemian wine regions; 12 of them were red ones. Most collected samples (50) were of the same vintage 2000; the rest were of the 2001 vintage (the samples for checking the stability of measured parameters) and all samples were of high quality. The samples represent 13 vine varieties. The sampling procedure involved sampling of blank samples and duplicate samples (abbreviated as D). In order to ensure that we used authentic samples with a precisely known origin, the samples were collected directly from vinegrowers. The collected samples are summarised in Table 1.

2.2. Sample preparation

All chemicals were purchased from Analytika, Czech Republic, in SD quality. The wine samples were prepared for ICP-MS and ICP-OES analyses as follows; 70 ml of wine sample were evaporated in an open vessel on a hotplate nearly to dryness (thus eliminating ethanol which can affect analysis); the residue was taken up in 0.1 M HNO_3 and dissolved in a volume equal to half of the original volume, that is 35 ml.

Table 2
The dilution factors of all measured parameters

Parameter	Instrument	Sample dilution
Al, Ba, Mn, Rb, Sr, Zn	ICP-MS	10
As, Co, Cr, Cu, Ni, Pb, V		4
Ce, Cs, Li, Mo, Sb, Sn, Th, U, Y		2
Na, K	ICP-OES	20
Ca, Fe, Mg		10

2.3. Element determination

Twenty seven parameters were determined. The contents of Al, As, Ba, Ca, Ce, Co, Cr, Cs, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Rb, Sb, Sn, Sr, Th, U, V, Y and Zn were established. The major part of this work was carried out by ICP-MS – an Ultramass (Varian, Australia); for analysis of some macro elements (Ca, Fe, K, Mg, Na), ICP-OES – a Liberty (Varian, Australia) and a VISTA PRO (Varian, Australia) was used. The method was validated by spike recovery studies. Evaluation of uncertainties was also included. The prepared wine samples were diluted before analysis. The dilution factors of all measured parameters are summarised in Table 2.

2.4. Data analysis

Multivariate analysis, comprising principal component analysis (PCA) and discriminant analysis (DA), was employed in wine differentiation and classification according to the geographical origin. Most of the statistical computations were done using the statistical package XLSTAT Pro from Addinsoft.

The raw data were standardised by the usual procedure to eliminate the effect of the different size of the variables. This procedure standardises a variable k according to $y_{ik} = (x_{ik} - \bar{x}_k)/s_k$. where y_{ik} is the value i for the variable k before scaling, $\bar{x}_k$ is the mean of the variable, and s_k is the standard deviation of the variable. The result is a variable with zero mean and unit standard deviation.

The analysis of variance (ANOVA) was carried out in Microsoft Excel; the multivariate analysis of variance

Table 1
The collected samples from the 2000 vintage and 2001 vintages

Wine region	Number of collected samples			Number of vine-makers	Area of vineyards (ha)[a]
	2000 vintage		2001 vintage		
	White wines	Red wines	White wines		
LI	9 + 2D	1 + 1D	0	2	76
ME	9 + 2D	0	1 + 1D	3	173
MO	9 + 2D	5 + 1D	0	2	62
RO	4 + 1D	3 + 1D	1	1	57

D means duplicate samples.
[a] Vineyards registered in Bohemia in 2000.