Available online at www.sciencedirect.com

SCIENCE DIRECT®

Food Chemistry 93 (2005) 659–663

Food Chemistry

www.elsevier.com/locate/foodchem

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

Jaroslava Šperková [a,*], Miloslav Suchánek [b]

[a] Department of ICP, Ecochem a.s., U Elektry 650, Prague 9, 198 00, Czech Republic
[b] Department of Analytical Chemistry, Institute of Chemical Technology in Prague, Technická 5, Prague 6, 166 28, Czech Republic

Received 4 May 2004; received in revised form 20 October 2004; accepted 20 October 2004

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.,

* Corresponding author. Tel.: +420 732 920 155; fax: +420 281 866 012.
E-mail address: jaroslava.sperkova@seznam.cz (J. Šperková).

0308-8146/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.foodchem.2004.10.044

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.

Table 3
The results of the chemical determinations

Parameter [$\mu g\, l^{-1}$]	White wines – mean (standard deviation)				Red wines – mean (standard deviation)		
	LI	ME	MO	RO	LI	MO	RO
ρ(Al)	870 (170)	700 (380)	1600 (910)	470 (76)	430 (0.1)	420 (84)	170 (50)
ρ(As)	5.5 (3.2)	6.7 (5.3)	2.4 (0.58)	5.7 (0.88)	3.7 (0)	1.5 (0.30)	5.8 (1.0)
ρ(Ba)	38 (7.0)	62 (22)	120 (29)	40 (5.8)	100 (0.1)	89 (9.9)	65 (21)
ρ(Ca)	80000 (15000)	75000 (35000)	105000 (17000)	74000 (8200)	91000 (700)	75000 (14000)	69000 (8800)
ρ(Ce)	0.38 (0.28)	0.77 (0.75)	8.3 (6.4)	0.14 (0.051)	0.19 (0)	0.21 (0.19)	0.20 (0.049)
ρ(Co)	3.9 (0.88)	1.5 (0.55)	3.8 (3.1)	2.2 (0.57)	3.6 (0.058)	2.4 (0.26)	1.3 (0.28)
ρ(Cr)	21 (13)	32 (17)	18 (3.7)	26 (3.6)	32 (0.90)	19 (1.4)	28 (3.6)
ρ(Cs)	4.0 (1.5)	0.77 (0.75)	1.2 (3.4)	2.1 (1.9)	6.0 (0.044)	21 (18)	2.8 (1.2)
ρ(Cu)	180 (120)	130 (140)	130 (160)	170 (66)	260 (2.1)	45 (21)	220 (91)
ρ(Fe)	3500 (1100)	2500 (1800)	3200 (880)	2300 (300)	4600 (8.8)	3700 (910)	1800 (230)
ρ(K)	959000 (193000)	1149000 (195000)	789000 (236000)	1084000 (220000)	1459000 (4200)	1381000 (187000)	1384000 (154000)
ρ(Li)	11 (3.4)	4.7 (2.4)	240 (220)	10 (8.1)	12 (0.039)	160 (240)	14 (13)
ρ(Mg)	85000 (10000)	67000 (8400)	97000 (13000)	82000 (11000)	125000 (1100)	121000 (17000)	87000 (18000)
ρ(Mn)	870 (370)	310 (53)	1600 (740)	350 (57)	1100 (2.6)	1400 (420)	520 (40)
ρ(Mo)	8.7 (8.8)	14 (15)	1.2 (0.26)	12 (1.7)	7.0 (0.083)	0.55 (0.19)	8.3 (2.3)
ρ(Na)	18000 (3100)	13000 (5200)	32000 (15000)	10000 (1800)	8900 (64)	5800 (2700)	3500 (71)
ρ(Ni)	37 (13)	25 (9.1)	22 (7.1)	25 (8.7)	53 (0.41)	47 (5.7)	15 (1.0)
ρ(Pb)	24 (9.3)	31 (43)	48 (35)	22 (8.2)	26 (0.08)	11 (2.6)	11 (4.9)
ρ(Rb)	1200 (790)	240 (130)	1100 (1200)	1300 (440)	1400 (19)	5500 (2700)	1300 (180)
ρ(Sb)	0.78 (0.25)	2.0 (0.92)	0.86 (0.41)	0.63 (0.14)	0.45 (0.049)	0.089 (0.026)	0.14 (0.027)
ρ(Sn)	3.7 (2.9)	4.3 (8.7)	29 (44)	1.5 (0.49)	2.1 (0.19)	79 (120)	1.0 (0.43)
ρ(Sr)	470 (110)	310 (85)	430 (120)	500 (290)	1400 (1.3)	700 (130)	680 (260)
ρ(Th)	0.042 (0.014)	0.11 (0.095)	0.58 (0.57)	0.048 (0.012)	0.049 (0.007)	0.025 (0.017)	0.026 (0.012)
ρ(U)	0.25 (0.13)	0.45 (0.58)	0.32 (0.27)	0.18 (0.026)	0.11 (0.006)	0.028 (0.029)	0.18 (0.043)
ρ(V)	63 (58)	130 (160)	29 (6.9)	76 (7.9)	73 (0.65)	26 (4.4)	96 (24)
ρ(Y)	0.64 (0.44)	0.86 (0.64)	7.2 (3.5)	0.18 (0.048)	0.18 (0.003)	0.59 (0.50)	0.19 (0.079)
ρ(Zn)	540 (130)	530 (370)	290 (160)	400 (220)	1000 (12)	470 (81)	730 (340)
Sr/Ba	13 (3.0)	5.3 (1.6)	3.6 (1.4)	12 (5.6)	13 (0.025)	7.8 (0.80)	10 (2.5)
Sr/Ca	0.00599 (0.00168)	0.00975 (0.0135)	0.00419 (0.00132)	0.00721 (0.00546)	0.0150 (0.00013)	0.00954 (0.00159)	0.0103 (0.00507)
Sr/Mg	0.00551 (0.00104)	0.00474 (0.00145)	0.00442 (0.00071)	0.00607 (0.00345)	0.0110 (0.0001)	0.00584 (0.00085)	0.00846 (0.00476)
Number of s.	11	11	11	5	2	6	4

(MANOVA) was carried out according to Lawley–Hotelling procedure in Microsoft Excel too. The analyses elucidate the parameters and their combinations (groups) with the greatest power for differentiation of wine regions.

PCA was mainly used to achieve a reduction of dimensionality, i.e., to fit a j-dimensional subspace to the original p-variate ($p > j$) space of objects and it permits a primary evaluation of the between-category similarity. PCA is very useful for visual inspection of complex data matrices. The information is compressed into a few components or directions in multivariate space. In this way, PCA can be very useful for the identification of clusters, outliers and other structures in the data.

The DA classification procedure maximises the variances between categories and minimises the variances within categories. In order to measure the classification power of the analytical data, the number of individuals correctly predicted to belong to the assigned group is calculated; this number is expressed as a percentage of the group population. Classification power = (number of correctly classified individuals/sample population) × 100.

DA is used as a method for allocating samples to one of a number of groups. The goal is to find the allocation rule which gives the highest percentage of correct classification.

3. Results and discussion

The results of the instrumental analysis of 27 chemical variables for wines from four wine regions and the 2000 vintage are summarised in Table 3.

The ANOVA, performed on the different individuals ranged in four groups, indicates that 20 parameters are highly significant for distinguising between samples from two or more regions at the 99.9% confidence level. The variables are ranked in a decreasing order according to their experimental F values: Ba Y Sr/Ba Mn Mg Ce Sb Na Li Al Th K Cs Ni Co Ca Mo Rb Sr As Cr Sn Zn V Fe Sr/Mg Pb Sr/Ca U Cu.

According to the results of ANOVA and the knowledge about influences of wine practices to the concentration of some elements, several groups of parameters were created. These groups are summarised in Table 4.

PCA allows visualisation of the information of the data set in a few principal components retaining the maximum possible variability within that set. PCA was used, allowing more than 60% of the initial variance to be explained by the first three principal components for white wines and more than 80% for red wines.

The results of DA are extremely interesting, with 92.1–97.4% correct classification for created groups of parameters for white wines. All samples from MO and RO are 100% correctly classified. In the case of red wines, there was 100% correct classification for all groups of parameters. The projection of the samples in the new discriminate space is given in Fig. 1 for white wines.

Table 4
The tested groups of parameters

Group No.	Parameters	
	List of parameters	Total
1	Al, Ba, Ca, Cr, Co, K, Li, Mg, Mn, Ni, Pb, Rb, Sr, V, Sr/Ba, Sr/Ca, Sr/Mg	17
2	Al, Ba, Ca, Co, K, Li, Mg, Mn, Rb, Sr, V, Sr/Ba, Sr/Ca, Sr/Mg	14
3	Al, Ba, Ca, Co, K, Li, Mg, Mn, Mo, Rb, Sr, V, Sr/Ba, Sr/Ca, Sr/Mg	15
4	Al, As, Ba, Ce, Li, Mg, Mn, Mo, Na, Sb, Sn, Sr, Th, V, Y, Sr/Ba, Sr/Mg	17
5	Ba, Li, Mg, Mn, Mo, Na, Sb, Th, V, Y, Sr/Ba, Sr/Mg	12

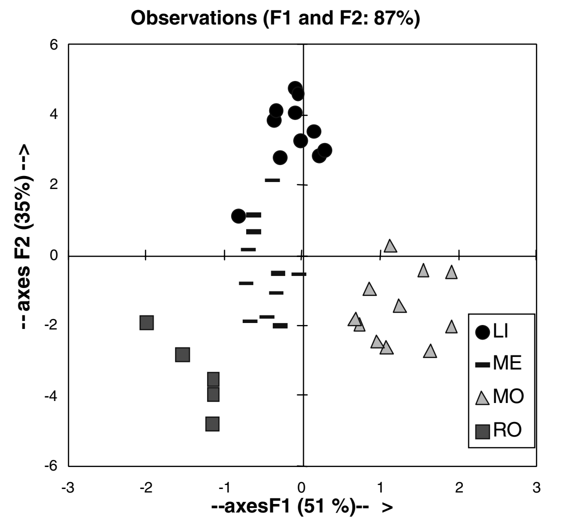

Fig. 1. The results of DA – white wines and the group of parameters No. 3.

Table 5
The results of DA, correct classification for white wines in %

Region	Group of parameters	Region		
		RO	MO	ME
LI	1	100	100	100
	2	100	100	100
	3	100	100	100
	4	100	100	95.4
	5	100	100	94.4
ME	1	100	100	
	2	100	100	
	3	100	100	
	4	100	100	
	5	93.7	100	
MO	1	100		
	2	100		
	3	100		
	4	100		
	5	100		

Upon comparison of wine regions, the results are interesting and are summarised in Table 5.

DA successfully showed element functions that separate the wines based on vineyard of origin. The wine samples from the 2001 vintage were classified according to the samples from the 2000 vintage. When the best group of parameters was used (group No. 3), 100% correct classification of three samples (2 + 1D) was achieved. With other groups of parameters, the correct classification was worse.

From the comparison of results of the same wine samples from the 2000 and 2001 vintages, it could be concluded that the element composition of wine is not dependent on the year of production. Of course this result must be confirmed with a larger number of samples and other vintages.

4. Conclusion

The contents of selected minerals and trace elements of wines from Bohemia were used to differentiate between wine samples of four Bohemian regions. PCA revealed the occurrence of groupings between the analysed samples according to their origin.

The content of elements in wine may be influenced by a few factors, such as the level of elements in soil, fertilizing practices and processing conditions.

This study has indicated that many measured parameters are not dependent on the year of production and that trace element analysis provides a good prospect for the determination of the region of origin of wines from Bohemia (Czech republic).

The best results for identification of sample origin were achieved with the following parameters: Al, Ba, Ca, Co, K, Li, Mg, Mn, Mo, Rb, Sr and V and element ratios Sr/Ba, Sr/Ca and Sr/Mg.

With these parameters, a 97.4% correct classification was achieved for white wines and a 100% correct classification for red wines.

Acknowledgement

We express our gratitude to all wine-makers, which enabled us to use samples of precisely known origin.

References

Augagneur, S., Médina, B., Szpunar, J., & Łobinski, R. (1996). Determination of rare earth elements in wine by inductively coupled plasma mass spectrometry using a microconcentric nebuliser. *Journal of Analytical Atomic Spectrometry, 11*, 713–721.

Baxter, M. J., Crews, H. M., Dennis, M. J., Goodall, I., & Anderson, D. (1997). The determination of the authenticity of wine from its trace element composition. *Food Chemistry, 3*, 443–450.

Day, M. P., Zhang, B., & Martin, G. J. (1994). The use of trace element data to complement stable isotope methods in the characterization of grape musts. *American Journal of Enology and Viticulture, 45*, 79–85.

Day, M. P., Zhang, B., & Martin, G. J. (1995). Determination of the geographical origin of wine using joint analysis of elemental and isotopic composition. II-Differentiation of the principal production zones in France for the 1990 vintage. *Journal of the Science of Food and Agriculture, 67*, 113–123.

Eschnauer, H., Hölzl, S., & Horn, P. (1994). Isotopensignaturen schwerer Elemente als Parameter zur Charakterisierung von Weinen: Isotopen-Vinogramme. *Viticulture Enology Science, 49*, 125–129.

Frías, S., Conde, J. E., Rodríguez-Bencomo, J. J., García-Montelongo, F., & Pérez-Trujillo, J. P. (2003). Classification of commercial wines from the Canary Islands (Spain) by chemometrics techniques using metallic contents. *Talanta, 59*, 335–344.

Greenough, J. D., Longerich, H. P., & Jackson, S. E. (1997). Element fingerprinting of Okanagan Valley wines using ICP-MS: relationships between wine composition, vineyard and wine colour. *Australian Journal of Grape and Wine Research, 2*, 75–83.

Jakubowski, N., Brandt, R., Stuewer, D., Eschnauer, H. R., & Görtges, S. (1999). Analysis of wines by ICP-MS: is the pattern of the rare earth elements a reliable fingerprint for the provenance?. *Fresenius Journal of Analytical Chemistry, 364*, 424–428.

Latorre, M. J., García-Jares, C., Medina, B., & Herrero, C. (1994). Pattern recogniction analysis applied to classification of wines from Galicia (Northwestern Spain) with certified brand of origin. *Journal of Agriculture and Food Chemistry, 42*, 1451–1455.

Moret, I., Scarponi, G., & Cescon, P. (1994). Chemometric characterization and classification of five Venetian white wines. *Journal of Agriculture and Food Chemistry, 42*, 1143–1153.

Pérez-Magariño, S., Ortega-Heras, M., & Gonzáles-San José, M. L. (2002). Multivariate classification of rosé wines from different Spanish protected designations of origin. *Analytica Chimica Acta, 458*, 187–190.

Rebolo, S., Peña, R. M., Latorre, M. J., García, S., Botana, A. M., & Herrero, C. (2000). Characterisation of Galician (NW Spain) Ribeira Sacra wines using pattern recognition analysis. *Analytica Chimica Acta, 417*, 211–220.

Thiel, G., Bauer, K. H., Danzer, K., & Eschnauer, H. (1998). Direktbestimmung und Gesamtgehalt von Erdalkalimetallen in Wein – Ansatzpunkt zur Herkunftsbestimmung. *Wein-Wissenschaft, 53*, 54–63.

Thiel, G., & Danzer, K. (1997). ICP-emissionspektrometrische und multivariat-statistische Untersuchungen zur Herkunftsbestimmung von Weinen. *Mengen-Spurenelem., Arbeitstagung, 17*, 635–643.