

## Chemometric prediction of wines affiliation with organic and conventional production systems through their elemental profiles

MÁRIA KOREŇOVSKÁ – MILAN SUHAJ

### Summary

Selected elements Ag, Ba, Ca, Cd, Cu, Fe, Hg, Mg, K, Na, Pb, Rb, Sr and Zn, determined by atomic absorption spectroscopy (AAS), were used for discrimination of Slovakian organic wines, musts and grapes from conventional counterparts. Results obtained by ANOVA proved to be significantly different in Cu and Fe concentrations in all examined wine and must varieties ( $P \leq 0.001$ ). In organic white wines, lower contents of these elements were found compared to the conventional ones. Rb, Sr, Zn, Mg, Ca and Cd had a selective discriminative ability only in some matched wine varieties. Organic grapes contained lower levels of Ba and K compared to the conventional counterparts. Elements P, K, C, Cu and Zn significantly discriminated organic soil samples from the conventional ones. The elemental data variation facilitated multivariate differentiation of samples and their classification according to production systems. Recognition and prediction ability testing by canonical discriminant analysis performed according to wines' affiliation to organic and conventional production resulted in 95.2% and 92.9% of correctly classified samples, respectively. Fe was found to be the most discriminating marker both by ANOVA and multivariate statistics.

### Keywords

organic wine; conventional wine; element; atomic absorption spectroscopy; chemometric prediction

Both genetic and environmental factors are essential to the grape and wine quality. Two different perspectives have emerged in worldwide wine production to indicate the origin and quality of grapes and wines. The first indicates the grape cultivar and the second is called “terroir” and is used to describe the complex of natural environmental factors, which include soil, climate and cultural practices [1]. These factors will be expressed in the final product, with the aid of various management decisions, resulting in distinctive wines with an identifiable origin [2]. At the end of 2006, more than 95 000 hectares of vineyards were managed organically in Europe, corresponding to around 2.3% of all vineyards. The biggest producers were Italy, France and Spain [3]. The only producer of organic wines in Slovakia is Víno Natural Domin & Kušický in Veľký Krtíš, which grows grapes on 40 ha in south-central Slovakia with Chardonnay, Cabernet Sauvignon, Pinot blanc, Pinot noir, Riesling and Traminer red varieties.

In the case of organic and conventional wines,

some comparative studies were published with respect to the different aspects of these types of wines production [4–8]. Overall, studies have found that vineyards with organic production have lower yields and the higher labour input than conventional vineyards. Costs of organic wines were found to be higher and were driven by higher labour costs [4]. Some published data bring information that, compared to conventional wines, organic wines contain higher levels of phenolic compounds, antioxidant activity and biogenic amines [9–12]. Similarly, higher levels of phenolics, polyphenol oxidase and a higher antioxidant activity was observed in the organic grapes by MICELLI [13], NÚÑEZ-DELICADO et al. [14] and DANI et al. [15]. Based on some enological parameters, TINTUNEN and LEHTONEN attempted, but unsuccessfully, to differentiate organic and conventional wines by principal components analysis [16]. Discriminant models based on middle infrared spectra were developed using principal component analysis, discriminant partial least squares regres-

---

Mária Koreňovská, Milan Suhaj, VÚP Food Research Institute, Department of Chemistry and Food Analysis, Priemyselná 4, SK – 824 75 Bratislava, Slovakia.

Correspondence author:

Milan Suhaj, e-mail: suhaj@vup.sk; Mária Koreňovská, e-mail: korenovska@vup.sk

sion and linear discriminant analysis [17]. Overall, these discriminant models correctly classified more than 75% of the wine samples according to organic and non-organic production systems. Some strategies for characterizing wines using compositional profiles of organic acids, volatile species, polyphenols, amino acids, biogenic amines and colour characteristics in combination with chemometrics were reviewed by SAURINA [18] with respect to wine authentication area.

Using elemental data and multivariate statistical techniques, wine identification or classification, mainly in terms of variety, geographical and environmental origin, has received increasing attention during previous years [19]. Wine multi-elemental composition reflects not only the geochemistry of provenance soil, but also other factors such as environmental contamination, agricultural practices, climatic changes and vinification processes, which may markedly change the composition of wine [9]. Trace elements have well assisted in typing the provenance of wines. The most frequently quantified elements used for wines geographical authentication are: K, Na, Fe, Yn, Rb, Ca, Cu, Cr, Co,

Sb, Cs, Br, As, Ag, Li, Ba, Sr, Mg, Al, Mn. Many of these elements, or their combination, were successfully used for multiregional differentiation of wines [20, 21]. The main advantages and drawbacks of various atomic spectrometry techniques for elemental wine analysis were well reviewed by GRINDLAY et al. [22].

The maximum acceptable limits for trace elements contents in wine have been established by the International Organization of Vine and Wine (OIV, Paris, France) [23].

In our work K, Ca, Mg, Na, Fe, Cu, Cd, Zn, Ag, Ba, Hg, Pb, Rb and Sr were selected and examined for discrimination of Slovakian organic wines, musts, grapes and soils from their conventional counterparts. We used atomic absorption spectroscopy (AAS) to describe the variability in the elemental composition of these products and statistically investigate the obtained data to differentiate and classify them according to their affiliation with the production systems. The aim of this study was to find the discriminating elemental markers to distinguish organic wines from the conventional ones.

**Tab. 1.** Analytical data of methods for the determination of elements in soil, wine and grapes.

Elements	Soil			Wine; Grape		
	$U_C$ [%]	$LOQ$ [mg·kg <sup>-1</sup> ]	Method	$U_C$ [%]	$LOQ$ [mg·kg <sup>-1</sup> ]	Method
Ag	2.5	0.2	F-AAS	6.2	0.0002	GF-AAS
Ba	2.5	10	XRF	13	0.005	GF-AAS
Ca	5	500	XRF	6.8	0.100	F-AAS
Cd	5	0.1	F-AAS	5.2	0.0001	GF-AAS
Cu	5	5	XRF	6.9	0.010	F-AAS
Fe	2.5	500	XRF	5.4	0.400	F-AAS
Hg	13	0.00003	AAS	13	0.00003	CV-AAS
K	2.5	500	XRF	10	0.060	F-AAS
Mg	2.5	500	XRF	3.5	0.090	F-AAS
Na	7.5	2000	XRF	6.4	0.090	F-AAS
Pb	7.5	5	XRF	7.8	0.006	GF-AAS
Rb	2.5	2	XRF	9.2	0.090	GF-AAS
Sr	2.5	5	XRF	4.7	0.080	F-AAS
Zn	5	5.0	XRF	7.5	0.740	F-AAS
C	5	0.01	EA	–	–	–
H	10	0.02	EA	–	–	–
N	10	0.01	EA	–	–	–
S	10	0.02	EA	–	–	–
P	5	0.01	XRF	–	–	–

$U_C$  - the combined standard uncertainty of measurement;  $LOQ$  – limit of quantification; AAS – atomic absorption spectrometry; GF – graphite furnace; F – flame, XRF – ray fluorescence spectrometry; EA – elemental analysis with a thermal conductive detector.

## MATERIALS AND METHODS

### Chemicals

All chemicals were of analytical grade. Stock solutions of each metal (Ag, Ba, Ca, Cd, Cu, Fe, Hg, Mg, K, Na, Pb, Rb, Sr and Zn at concentration of  $1.0 \text{ g}\cdot\text{l}^{-1}$ ) were from Merck (Darmstadt, Germany). Working standard solutions were prepared by suitable dilution of the stock solution. Nitric acid of suprapure quality was purchased from Merck and modification solution of Pd and  $\text{Mg}(\text{NO}_3)_2$  was also from Merck. Cesium chloride 99% as ionic suppressor for determination of Na, K, Rb and Sr was obtained from Serva (Heidelberg, Germany) and lanthanum chloride 5% as ionic suppressor for determination of Ca, and Mg was delivered from Slovak Institute of Metrology (Bratislava, Slovakia). Ultrapure water from Milli-Q system (Analyst HP, Wolf, United Kingdom) with conductivity of  $18 \text{ M}\Omega$  was used throughout the study.

### Wine samples

Fifteen Slovakian certified organic varietal dry wines (10 white and 5 red) and twenty-seven conventional wines (17 white and 10 red) with alcohol concentration of 11–13% (vol.) were sourced from three white wine varieties (Chardonnay, Pinot blanc and Traminer red) and two red wine varieties (Pinot noir and Cabernet Sauvignon). All the samples (soils, grapes, wines) originated from one vineyard sub-region (Modrý Kameň) in Central Slovakian wine-producing region. The proximity between the organic and conventional neighbouring vineyards varied within a radius of some kilometres, so the effects of differences in climate and soil quality should be minimal. Majority of wine samples with protected designation of origin were collected during the vintage periods 2007–2009, and were obtained from two wine neighbouring producers, the organic winemaker Víno Natural Domin & Kušický, and a conventional winemaker Agro-Movino (Veľký Krtíš, Slovakia). According to the Council Regulation (EC) No 834/2007 [24] and in accordance with Slovakian Regulation No. 189/2009 on organic production [25], all organic vineyards and products were under certified organic management for more than 6 years controlled by Naturalis SK (Bratislava, Slovakia).

### Wine and grape samples preparation for AAS

Sample of a wine (2 ml) after the addition of 1 ml  $\text{HNO}_3$  ( $1 \text{ mol}\cdot\text{l}^{-1}$ ) was filled with deionized water to 10 ml. Samples of a grape and must were digested by microwave digestion system MLS 1200 MEGA (Milestone, Sorisole, Italy). The grape

(2 g) and must (2 g) were introduced into a teflon microwave digestion vessel, and 3 ml of  $\text{HNO}_3$  were added. The microwave digestion programme was applied: 250 W (1 min), 0 W (1 min), 250 W (5 min), 400 W (5 min) and 650 W (5 min). The digested samples were adjusted to the volume of 10 ml with deionized water.

### Instrumentation

Samples were analysed for the concentration of elements Ag, Ba, Ca, Cd, Cu, Fe, Hg, Mg, K, Na, Pb, Rb, Sr and Zn, which were selected mainly according to their increased variability in soils of Slovakian vineyard regions [26]. A Perkin Elmer 4100 atomic absorption spectrometer (Perkin Elmer, Norwalk, Connecticut, USA) equipped with a deuterium lamp background-correction system and HGA 700 graphite tube atomizer with pyrolytically coated graphite tubes and flame was used for metal determination. Metals Ca, Mg, Na, K, Fe, Zn and Cu were determined from atomic spectrometry using an air/acetylene flame. Sr was determined using an acetylene/nitrous oxide flame. Metals Ag, Ba, Cd, Pb and Rb were measured on graphite tube atomizer. For the determination of mercury in wine, grape, must and soil, atomic absorption spectrometer AMA 254 (Altech, Prague, Czech Republic) was used. Analytical parameters are summarized in Tab. 1.

The accuracy of the results was verified by the standard addition method. Recovery of the method was assessed in wine and grape matrix by analysis of fortified samples at two concentration levels using standard solution of selected elements. Fortification of samples was performed before the microwave digestion. The mean recoveries of elements were 93–108%. Further instrumental conditions and analytical and validation parameters of the used methods were previously published [27, 28].

### Analysis of soil

The sample representing an average from a mixture of sub-samples of vineyard soil was taken with a probe of an area of  $100 \text{ m}^2$  from the depth horizon of 0–20 cm. In this way, composite samples of 2 kg were obtained. The samples were first dried to a constant weight. For the determination of total contents of chemical elements, the fraction with a particle size  $\leq 0.125 \text{ mm}$  was used. Silver and Cd were determined by F-AAS (flame AAS) after microwave digestion using the decomposition mixture of concentrated acids (HF,  $\text{HNO}_3$ , HCl). Elements Ba, Ca, Cu, Fe, K, Mg, Na, Pb, Rb, Sr and Zn were determined by X-ray fluorescence spectrometry (XRF) in Spectro Lab 2000

(Spectro, Kleve, Germany) from pressed tablets. Elemental analysis of the elements C, H, N and S was based on the quantitative combustion of the sample with the addition of an oxidation catalyst in an oxidizing atmosphere of O<sub>2</sub> (furnace at 1000 °C). This analysis was performed by Macro-elemental analyzer Macro Vario CHNS (Hanau, Germany) according to recommendations of the manufacturer.

### Statistical analysis

Multiple comparisons of elemental concentrations between organic and conventional wine samples were performed by ANOVA (Friedman two-way ANOVA, multiple comparison with *t*-distribution) with the accepted level of significance at  $P \leq 0.05$  [29]. From multidimensional pattern recognition techniques, the factor analysis (FA) and canonical discriminant analysis (CDA) were used. In order to find possible tendencies in the samples and the discriminant power of the variables, FA with quartimax rotation was applied. This orthogonal rotational criterion simplifies the rows of the factor loading matrix so that the large variable loadings are increased and the small ones decreased, the number of factors needed to explain a variable being minimized [29]. Canonical discriminant analysis is a classification supervised technique where the number of categories and the samples that belong to each category are previously defined. The recognizability of a discriminant model was determined as the percentage of correctly classified samples in the training data set. In addition, the predictability was tested as percentage of the samples correctly classified in the *k*-fold cross-validation approach (jack-knife method) by assigning samples randomly to a training set and a test set, the latter containing about 20% of samples [30]. The same process of data splitting was repeated 5 times to ensure that all the data were at least once in the position of test sample. Statistical processing of the elemental data enabling multivariate presentation, visualization and classification of wine, grape, must and soil samples was performed by Unistat statistical package v.6.0 for Windows (Unistat, London, United Kingdom).

## RESULTS AND DISCUSSION

The summarized results of selected mineral and trace element concentrations (Ag, Ba, Ca, Cd, Cu, Fe, Hg, Mg, K, Na, Pb, Rb, Sr and Zn) in Central Slovakian organic and conventional wine samples collected from two producers are given in Tab. 2. According to their mean concen-

tration in wine samples, the elements analysed by AAS showed the following decreasing order: K > Ca > Mg > Na > Fe > Zn > Rb > Sr > Cu > Ba > Pb > Cd > Ag > Hg, which was comparable to data published by RODRIGUES et al. [31]. The mean concentration levels for different elements were similar to those reported previously [32, 33]. The minor elements (Fe and Zn) showed levels similar to those reported by ÁLVAREZ et al. [34] and MORENO et al. [35]. All the elemental data were found to be in ranges of metal concentrations in wine samples originating in various countries, as referred by TARIBA [36]. OIV published maximum acceptable limits for Cu (1 mg·l<sup>-1</sup>), Pb (0.15 mg·l<sup>-1</sup>), Cd (0.01 mg·l<sup>-1</sup>) and Zn (5 mg·l<sup>-1</sup>) [23]. In the examined wines, the concentrations of these elements did not exceed the allowed maximum OIV limiting values with the exception of Cd and Cu in four wine samples (one organic – Cd, and three conventional – Cd, Cu). Higher over-limiting values of Cd and Cu in wines may be explained as a consequence of contamination from environment or winemaking process.

From Tab. 2 it can be seen that higher levels of Ag, Ba, Cd, Pb, Rb, Sr, K, Na and lower levels of Ca, Mg were present in red organic wine samples when compared with white organic wines. Zinc, Fe and Cu were of comparable concentrations. In the case of conventional wines, the higher levels of Rb, Sr, K and lower levels of, Ca, Cu, Fe, Na and Pb were observed in red wines compared to white wines. Silver, Ba, Cd, Hg, Mg and Zn were of comparable concentrations.

When all varieties of organic and conventional wines were statistically compared according to concentrations of major and minor elements using ANOVA statistics, Cu and Fe were of significantly different concentrations in examined wines ( $P \leq 0.001$ ) (Tab. 2). Although it was expected that higher Cu concentration will be found in organic wine samples, because of authorised copper fungicides most frequently used in organic viticulture, the results indicate that organic white wines had lower Cu concentration than conventional wines. It seems that in conventional viticulture, Cu-containing fungicide formulations are more extensively used compared to organic viticulture, due to lower resistance of conventional grapevines. However, found differences were not only a consequence of viticulture conditions. Concentration of Cu in wine may be changed due to the elimination of Cu during fermentation. Cu is reduced, forming insoluble sulfides, which are removed through sedimentation together with yeasts and lees [36]. Similarly, determination of Fe showed significantly lower levels of this element in organically pro-

**Tab. 2.** Comparison of mineral and trace elements concentrations in organic and conventional Slovakian wines (vintage 2007–2009).

Element	Units	Concentration	White wines		Red wines	
			Organic ( <i>n</i> = 10)	Conventional ( <i>n</i> = 17)	Organic ( <i>n</i> = 5)	Conventional ( <i>n</i> = 10)
Ag	[μg·l <sup>-1</sup> ]	mean	0.4	0.4	0.8	0.4
		min. – max.	0.2–1.0	0.2–1.9	0.2–2.0	0.2–2.3
Ba	[mg·l <sup>-1</sup> ]	mean	0.222	0.284	0.348	0.256
		min. – max.	0.113–0.294	0.123–0.884	0.203–0.570	0.159–0.351
Cd	[μg·l <sup>-1</sup> ]	mean	1.4	2.9	5.2	5.1
		min. – max.	0.4–2.3	0.6–10.3	0.6–21.0	0.4–23.6
Hg	[μg·l <sup>-1</sup> ]	mean	0.1	0.1	0.1	0.2
		min. – max.	0.1–0.3	0.1–0.2	0.1–0.1	0.1–0.5
Pb	[μg·l <sup>-1</sup> ]	mean	13.0	34.0	23.0	22.0
		min. – max.	8.0–42.0	6.0–100	12.0–40.0	8.0–39.0
Rb	[mg·l <sup>-1</sup> ]	mean	1.087	1.165	1.463	1.502
		min. – max.	0.480–1.672	0.745–2.041	1.036–2.138	1.206–2.137
Sr	[mg·l <sup>-1</sup> ]	mean	0.397	0.473	0.591	0.530
		min. – max.	0.191–0.497	0.212–0.693	0.366–0.896	0.333–0.807
Ca	[mg·l <sup>-1</sup> ]	mean	137	148	83.2	83.9
		min. – max.	65.8–176	93.6–205	67.5–101	60.6–108
Cu*	[mg·l <sup>-1</sup> ]	mean	0.106*	0.843*	0.124	0.266
		min. – max.	0.020–0.265	0.086–1.972	0.054–0.224	0.047–0.582
Fe*	[mg·l <sup>-1</sup> ]	mean	1.449*	5.427*	1.721*	4.221*
		min. – max.	0.673–2.679	1.304–10.6	1.364–2.173	1.001–6.427
K	[mg·l <sup>-1</sup> ]	mean	780	743	1128	1019
		min. – max.	567–902	573–1043	860–1537	710–1255
Mg	[mg·l <sup>-1</sup> ]	mean	103	109	94.2	102
		min. – max.	63.5–122	72.0–123	81.6–106	75.7–117
Na	[mg·l <sup>-1</sup> ]	mean	37.1	41.9	25.2	14.9
		min. – max.	23.7–57.1	11.3–86.4	5.14–51.0	1.00–26.7
Zn	[mg·l <sup>-1</sup> ]	mean	2.28	2.734	2.521	2.728
		min. – max.	1.15–2.97	1.017–5.147	1.612–3.230	2.007–3.082

\*– Significant differences (significance level  $P \leq 0.001$ ).

duced white and red wines compared to conventional counterparts. These findings are in a good accordance with data on Cu and Fe in some organic Croatian wine varieties [9].

Organically and conventionally produced wine samples were also individually compared in detail according to their varieties (Tab. 3). In samples of organically and conventionally produced Cabernet Sauvignon wines, no significant differences in concentrations of the examined elements were found. Found differences relating to concentrations of Cu and Fe were confirmed in Traminer red, Pinet blanc, Chardonnay and Pinot noir varietal wines. In Chardonnay wine variety, no other significant

differences were observed. In Traminer red variety, the concentrations of Sr, Rb and Zn were significantly different between the examined wine types ( $P = 0.0363$ ,  $P = 0.0104$  and  $P = 0.0027$ , respectively). In Pinot blanc wine variety, Mg and Ca were found as factors discriminating between organic and conventional origin of these wines ( $P = 0.0391$ ,  $P = 0.0065$ ) and in the Pinot noir variety, Ca, Sr and Cd were found to be the discriminating variables (for all  $P < 0.03$ ). Similar trends in concentrations of some of these elements between organic and conventional Traminer red and Chardonnay varietal wines were reported by VRČEK et al. [9].

**Tab. 3.** Significant differences in concentrations of selected elements between organically and conventionally produced wine varieties.

Element	Significance probability value (P)			
	Traminer red	Pinot blanc	Chardonnay	Pinot noir
Cu	< 0.0001	< 0.0001	0.0001	< 0.0001
Fe	0.0001	< 0.0001	0.0058	0.0004
Mg	–	0.0391	–	–
Ca	–	0.0065	–	0.0076
Sr	0.0363	–	–	0.0288
Rb	0.0104	–	–	–
Zn	0.0027	–	–	–
Cd	–	–	–	0.0288

For evaluation of significant differences between organic and conventional wines, it is necessary to know how the elemental compositional data of soils, grapes or musts correspond with the found differences in the examined wines. In the case of organic and conventional grapes (Tab. 4), differences for contents of Ba, Hg and K were observed and in the musts, Hg, Pb and Fe were different. In the vineyard soils, macroelements P, K and C, as well as minority elements Cu and Zn, discriminated the organic soils from conventional ones (Tab. 5). From these soil differencing markers, only K was significant for discrimination of organic grapes from conventional. Cu discriminated all the varietal red and white

**Tab. 4.** Comparison of mean contents of selected elements in organic and conventional grapes and musts (vintage 2010,  $n = 6$ ).

Element	Units	Content	Grape		Must	
			Organic	Conventional	Organic	Conventional
Ag	[ $\mu\text{g}\cdot\text{kg}^{-1}$ ]	mean	4.4	4.4	0.43	1.6
		min. – max.	2.5–6.7	3.1–6.7	0.39–0.51	0.5–3.8
Ba*	[ $\text{mg}\cdot\text{kg}^{-1}$ ]	mean	0.386*	0.746*	0.074	0.062
		min. – max.	0.324–0.425	0.351–1.18	0.058–0.100	0.028–0.092
Cd	[ $\mu\text{g}\cdot\text{kg}^{-1}$ ]	mean	2.4	2.3	13.0	11.5
		min. – max.	1.2–3.4	1.5–3.4	12.4–13.6	10.3–13.0
Hg*	[ $\mu\text{g}\cdot\text{kg}^{-1}$ ]	mean	7.6*	2.2*	0.06*	0.03*
		min. – max.	4.3–11.7	1.4–3.1	0.05–0.06	0.01–0.05
Pb*	[ $\text{mg}\cdot\text{kg}^{-1}$ ]	mean	0.228	0.209	0.062*	0.094*
		min. – max.	0.137–0.286	0.116–0.312	0.046–0.080	0.060–0.113
Rb	[ $\text{mg}\cdot\text{kg}^{-1}$ ]	mean	3.83	3.19	2.15	1.43
		min. – max.	2.43–4.66	2.67–3.46	1.23–2.82	1.03–1.96
Sr	[ $\text{mg}\cdot\text{kg}^{-1}$ ]	mean	0.577	1.14	0.188	0.150
		min. – max.	0.301–0.882	0.317–2.22	0.163–0.204	0.030–0.221
Ca	[ $\text{mg}\cdot\text{kg}^{-1}$ ]	mean	296	298	153	166
		min. – max.	264–325	208–410	120–186	117–227
Cu*	[ $\text{mg}\cdot\text{kg}^{-1}$ ]	mean	2.76	1.68	1.70*	1.06*
		min. – max.	2.53–2.97	0.94–3.12	1.25–2.00	0.602–1.83
Fe*	[ $\text{mg}\cdot\text{kg}^{-1}$ ]	mean	5.50	4.67	0.957*	1.48*
		min. – max.	4.18–7.96	4.17–5.17	0.630–1.28	1.26–1.99
K*	[ $\text{mg}\cdot\text{kg}^{-1}$ ]	mean	1340*	1483*	1652	1546
		min. – max.	1196–1458	1408–1578	1534–1851	1325–1858
Mg	[ $\text{mg}\cdot\text{kg}^{-1}$ ]	mean	100	102	88.0	103
		min. – max.	89–111	87–114	73.5–99.4	78.4–120
Na	[ $\text{mg}\cdot\text{kg}^{-1}$ ]	mean	17.6	15.9	20.6	27.9
		min. – max.	14.6–21.9	11.6–21.5	16.2–28.3	19.8–33.6
Zn	[ $\text{mg}\cdot\text{kg}^{-1}$ ]	mean	3.64	3.33	3.86	4.29
		min. – max.	3.51–3.77	2.67–3.93	2.76–4.90	3.00–6.48

\* – significant differences ( $P < 0.05$ )

**Tab. 5.** Comparison of the contents of elements in vineyard soils under organic and conventional management (vineyard sub-region Modrý Kameň).

Element	Units	Mean content in vineyard soils with grapevine					
		Organic			Conventional		
		Cabernet Sauvignon	Traminer red	Pinot Noir	Cabernet Sauvignon	Traminer red	Pinot Noir
N	[%]	0.14	0.19	0.21	0.22	0.24	0.20
P*	[%]	0.04	0.06	0.07	0.11	0.10	0.09
K*	[%]	1.44	1.34	1.58	1.79	1.71	1.69
C*	[%]	1.37	1.87	1.95	2.74	2.59	2.00
H	[%]	0.14	0.14	0.14	0.18	0.18	0.09
S	[%]	< 0.02	< 0.02	< 0.02	0.02	< 0.02	< 0.02
Ca	[%]	0.76	0.89	0.79	0.64	0.70	1.03
Fe	[%]	4.48	4.23	4.15	4.08	4.31	4.35
Mg	[%]	0.86	0.76	0.82	0.80	0.76	0.94
Na	[%]	0.57	0.53	0.55	0.55	0.55	0.72
Zn*	[mg·kg <sup>-1</sup> ]	82	85	85	94	97	104
Ag	[mg·kg <sup>-1</sup> ]	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
Hg	[mg·kg <sup>-1</sup> ]	0.042	0.058	0.039	0.049	0.036	0.030
Ba	[mg·kg <sup>-1</sup> ]	402	409	446	430	433	432
Cd	[mg·kg <sup>-1</sup> ]	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Pb	[mg·kg <sup>-1</sup> ]	23	28	30	27	29	24
Rb	[mg·kg <sup>-1</sup> ]	119	112	119	123	123	120
Sr	[mg·kg <sup>-1</sup> ]	87	84	94	93	86	89
Cu*	[mg·kg <sup>-1</sup> ]	29	33	41	63	75	57

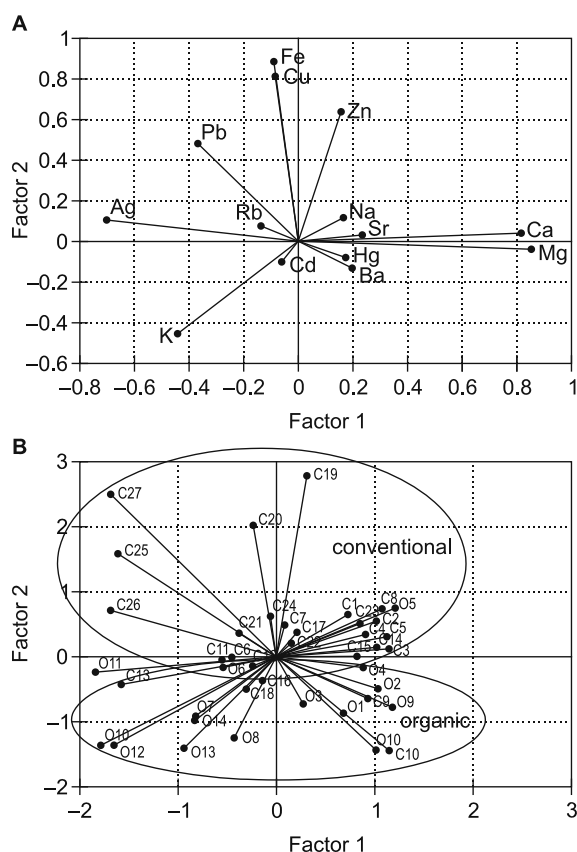
\* – found significantly different between organic and conventional vineyard soils ( $P < 0.05$ ).

organic and conventional wines with the exception of Cabernet Sauvignon variety. Zn differentiated only Traminer red wines. From these results it is obvious that Cu was the only marker showing a discrimination ability between organic and conventional origin for vineyard soils, grapes, musts and wines. Found differences in Cu contents in traditional and organic wines may have originated from specific soil characteristics (fertilizers) or were related to viticulture techniques (Cu bio-pesticide application). On the basis of information from both producers, similar winemaking technologies, mainly filtration techniques, were used for organic and conventional wine production.

Principal component factoring (PCF) with quartimax rotation was applied to detect differences between organically and conventionally produced red and white wines according to selected macro- and microelements. This method was used to see how all the 14 elemental variables contribute to positioning of wine samples on the plot of factors and factor score (Fig. 1). As can be

observed on this plot, the most of the variation (above 50%) in the data set can be explained by the first two factors. On the plot of factor score (Fig. 1B), the organic and conventional wines are well separated into two clusters in the upper and lower part of the plot. Ca and Mg were the best discriminating elements in the first factor, Cu and Fe in the second factor (Fig. 1A).

The multielemental marker data were elaborated by canonical discriminant analysis (CDA) procedure. Before analysis it was examined and confirmed that the data represented approximately normal within-class distribution, which is one of the requirements for efficient discrimination. Some of the distribution data were found to follow Laplacian distribution. This is similar to the normal distribution, but Laplace distribution has higher kurtosis than the normal one. A multiparametric approach of CDA was carried out in order to evaluate the influence of elemental variables on the classification of wines into the groups of organic and conventional wines. CDA recogni-

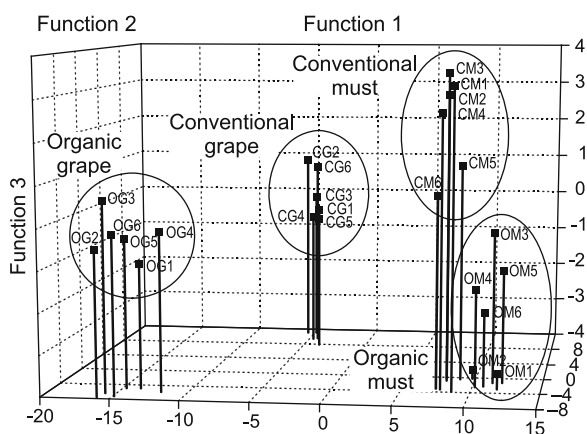


**Fig. 1.** Principal component factoring with quartimax rotation.

A – plot of factors, B – plot of factor score of organic (O1–O15) and conventional (C1–C27) white and red wines according to selected elements (Ag, Ba, Cd, Hg, Pb, Rb, Sr, Ca, Cu, Fe, K, Mg, Na and Zn).

tion ability testing gave evidence that 95.2% of the examined wines were correctly classified according to producing types. In this differentiating procedure, the most important discriminating elements were, in the descending order,  $Fe > Mg > K$  and Ca. Stepwise discriminant analysis selected as most important discriminating variables Fe, Ag and K. Kth-nearest neighbour discrimination was successful when  $K = 3$  was examined and resulted in 85.7% of correctly classified wine samples into the organic and conventional classes. Prediction ability testing performed by CDA resulted in 92.9% of correctly classified samples into the groups of organic and conventional wines. As already presented, the elemental profile of conventional and organic wines is not only derived from initial soil and grape mineral composition, but is significantly affected by wine-processing techniques. In general, wines derived from the two different viticulture and wine-making production systems contained macro- and microelements in concentrations within the expected intervals described in the literature. Results performed by ANOVA and multivariate statistics revealed certain significant differences in concentrations of some elements between organically and conventionally produced wines. The elemental data variation enabled multivariate visualization of wine samples and their classification according to production methods reflecting the different terroir and wine-making methods.

Similarly, organic and conventional grapes and musts were separated into four classes of samples (2 organic and 2 conventional) using the CDA method (Fig. 2). Thanks to the discriminating power of Ca, Cu, Rb and Ba, classification in the recognition ability testing resulted in 100% of correctly categorized grape and must samples. When organic and conventional wines, grapes and musts were classified simultaneously by CDA, the success of wine categorization decreased from 95.2% to only 92.4%.



**Fig. 2.** Differentiation of organic (O) and conventional (C) musts (M) and grapes (G) performed by canonical discriminant analysis of elemental data (Ag, Ba, Cd, Hg, Pb, Rb, Sr, Ca, Cu, Fe, K, Mg, Na and Zn).

## CONCLUSIONS

On the basis of results of this study, it can be concluded that some elemental markers, namely Fe and Cu, have a potential to be employed in differentiation between organic and conventional wines, in order to predict the authenticity of organic wines. These markers should be, however, combined with other discriminators, such as phenolics, antioxidants, anionic and aromatic profiles.



## Acknowledgements

This work is a part of national research project No. 2/PVV supported by the Ministry of Agriculture and Rural Development of the Slovak Republic. Víno Natural Domin & Kušický (Veľký Krtíš, Slovakia) and Agro-Movino (Veľký Krtíš, Slovakia) are gratefully acknowledged for providing samples.

## REFERENCES

1. Van Leeuwen, C. – Friant, P. – Chone, X. – Tregoat, O. – Koundouras, S. – Dubourdieu, D.: The influence of climate, soil and cultivar on terroir. *American Journal of Enology and Viticulture*, 55, 2004, pp. 207–217.
2. Conradie, W. J. – Carey, V. A. – Bonnardot, V. S. A. – Ayman, D. – Schoor, L. H. S.: Effect of different environmental factors on the performance of Sauvignon blanc grapevines in the Stellenbosch district of South Africa. I. Geology, soil, climate, phenology and grape composition. *South African Journal for Enology & Viticulture*, 23, 2002, pp. 78–91.
3. Willer, H. – Yussefi-Menzler, M. – Sorensen, N.: The world of organic agriculture. Statistics and emerging trends 2008. London : Earthscan, 2008. 238 pp. ISBN 978-1-84407-592-8.
4. Wheeler, S. A. – Crisp, P.: Evaluating a range of the benefits a costs of organic a conventional production in a Clare Valley vineyard in South Australia. In: Paper for the AARES conference workshop on The World's Wine Markets by 2030: Terroir, climate change, R&D and globalization, Adelaide Convention Centre, Adelaide, South Australia, 7–9 February 2010. Adelaide : The Adelaide University, 2010 [cited 1 October 2011]. Available at <www.adelaide.edu.au/cies/research/wine/pubs/Wheeler\_WC0210.pdf>
5. Niccolucci, V. – Galli, A. – Kitzes, J. – Pulselli, R. M. – Borsa, S. – Marchettini, N.: Ecological footprint analysis applied to the production of two Italian wines. *Agriculture, Ecosystems & Environment*, 128, 2008, pp. 162–166.
6. Plahutaa, P. – Raspor, P.: Comparison of hazards: Current vs GMO wine. *Food Control*, 18, 2007, pp. 492–502.
7. Desta, A.: Conventional versus environmentally-sensitive wines: the status of wine production strategies in California north coast counties. *Journal of Business a Public Affair*, 2, 2008, pp. 1–17.
8. Malusa, E. – Laurenti, E. – Ghibaudi, E. – Rolle, L.: Influence of organic a conventional management on yield a composition of grape cv 'Grignolino'. *Acta Horticulturae*, 640, 2004, pp. 135–141.
9. Vrček, I. V. – Bojić, M. – Žuntar, I. – Mendaš, G. – Medić-Šarić, M.: Phenol content, antioxidant activity a metal composition of Croatian wines deriving from organically a conventionally grown grapes. *Food Chemistry*, 124, 2011, pp. 354–361.
10. Otreba, J. B. – Berghofer, E.: Polyphenols a antioxidative capacity in Austrian wines from conventional a organic grape production. *Mitteilungen Klosterneuburg*, 56, 2006, pp. 22–32.
11. Yildirim, H. K. – Akcay, Y. D. – Guvenc, U. – Sozmen, E. Y.: Protection capacity against low-density lipoprotein oxidation a antioxidant potential of some organic a non-organic wines. *International Journal of Food Sciences a Nutrition*, 55, 2004, pp. 351–362.
12. Yildirim, H. K. – Üren, A. – Yücel, U.: Biogenic amines in organic a non-organic wines. *Food Technology and Biotechnology*, 4, 2007, pp. 62–68.
13. Micelli, A. – Negro, C. – Tommasi, L. – De Leo, P.: Polyphenols, resveratrol, antioxidant activity and ochratoxin a contamination in red table wines controlled denomination of origin (DOC) wines and wines obtained from organic farming. *Journal of Wine Research*, 14, 2003, pp. 115–120.
14. Núñez-Delicado, E. – Sánchez-Ferrer, A. – García-Carmona, F. F. – López-Nicolás, J. M.: Organic grapes contain higher levels of latent polyphenol oxidase than conventionally grown wine grapes. *Journal of Food Science*, 70, 2005, pp. C74–C78.
15. Dani, C. – Oliboni, L. S. – Vaerlinde, R. – Bonatto, D. – Salvador, M. – Henriques, J. A. P.: Phenolic content a antioxidant activities of white a purple juices manufactured with organically- or conventionally-produced grapes. *Food and Chemical Toxicology*, 45, 2007, pp. 2574–2580.
16. Tinttunen, S. – Lehtonen, P.: Distinguishing organic wines from normal wines on the basis of concentrations of phenolic compounds a spectral data. *Journal of European Food Research and Technology*, 212, 2001, pp. 390–394.
17. Cozzolino, D. – Holdstock, M. – Damberg, R. G. – Cynkar, W. U. – Smith, P. A.: Mid infrared spectroscopy a multivariate analysis: A tool to discriminate between organic a non-organic wines grown in Australia. *Food Chemistry*, 116, 2009, pp. 761–765.
18. Saurina, J.: Characterization of wines using compositional profiles and chemometrics. *Trends in Analytical Chemistry*, 29, 2010, pp. 234–245.
19. Pohl, P.: What do metals tell us about wine? *TrAC Trends in Analytical Chemistry*, 26, 2007, pp. 843–950.
20. Frías, S. – Conde, J. E. – Rodríguez, M. A. – Dohnal, V. – Trujillo, J. P. P.: Metallic content of wines from the Canary Islands (Spain). Application of artificial neural networks to the data analyses. *Nahrung/Food*, 46, 2002, pp. 370–375.
21. Szentmihályi, K. – Kiss, G. A. C. – Keszler, K. – Tai, L.: Method development for measurement of elements in Hungarian red wines by ICP-OES. *Acta Alimentaria*, 29, 2000, pp. 105–121.
22. Grindlay, G. – Mora, J. – Gras, L. – de Loos-Vollebregt, M. T. C.: Atomic spectrometry methods for wine analysis: A critical evaluation and discussion of recent applications. *Analytica Chimica Acta*, 691, 2011, pp. 18–32.
23. Compendium of international methods of wine and must analysis. Paris : Organisation Internationale de la Vigne et du Vin, 2006. 321 pp.
24. Council Regulation (EC) No 834/2007 of 28 June 2007 on organic production and labelling of

- organic products and repealing Regulation (EEC) No 2092/91. Official Journal of the European Union, *L 189*, 2007, pp. 1–28.
25. Zákon NR SR č. 189 z 29. apríla 2009 o ekologickej poľnohospodárskej výrobe. Zbierka zákonov, *73*, 2009, pp. 1400–1403.
26. Čurlík, J. – Šefčík, P.: Geochemical Atlas of the Slovak Republic. Part V: Soils. Bratislava: Soil Science and Conservation Research Institute, 1999. 182 pp. ISBN 80-88833-14-0.
27. Koreňovská, M. – Suhaj, M.: Identification of some Slovakian and European wines origin by the use of factor analysis of elemental data. *European Food Research and technology*, *221*, 2005, pp. 550–558.
28. Suhaj, M. – Koreňovská, M.: Study of some European cheeses geographical traceability by pattern recognition analysis of multielemental data. *European Food Research and Technology*, *227*, 2008, pp. 1419–1427.
29. Unistat 5.6 Statistical Package for Windows. User's Guide. London: Unistat, 2005. 953 pp.
30. Berrueta, L. A. – Alonso-Salces, R. M. – Heberger, K.: Supervised pattern recognition in food analysis. *Journal of Chromatography A*, *1158*, 2007, pp. 196–214.
31. Rodrigues, S. M. – Otero, M. – Alves, A. A. – Coimbra, J. – Coimbra, M. A. – Pereira, E. – Duarte, A. C.: Elemental analysis for categorization of wines and authentication of their certified brand of origin. *Journal of Food and Composition Analysis*, *24*, 2011, pp. 548–562.
32. Kment, P. – Mihaljevic, M. – Ettler, V. – Sebek, O. – Strnád, L. – Rohlova, L.: Differentiation of Czech wines using multielement composition – A comparison with vineyard soil. *Food Chemistry*, *91*, 2005, pp. 157–165.
33. Marengo, E. – Aceto, M.: Statistical investigation of the differences in the distribution of metals in Nebbiolo-based wines. *Food Chemistry*, *81*, 2003, pp. 621–630.
34. Álvarez, M. – Moreno, I. M. – Jos, A. M. – Cameán, A. M. – González, A. G.: Differentiation of two Andalusian DO 'fino' wines according to their metal content from ICP-OES by using supervised pattern recognition methods. *Microchemical Journal*, *87*, 2007, pp. 72–76.
35. Moreno, I. M. – Gonzalez-Weller, D. – Gutierrez, V. – Marino, M. – Camean, A. M. – Gonzalez, A. G. – Hardisson, A.: Determination of Al, Ba, Ca, Cu, Fe, K, Mg, Mn, Na, Sr and Zn in red wine samples by inductively coupled plasma optical emission spectroscopy: evaluation of preliminary sample treatments. *Microchemical Journal*, *88*, 2008, pp. 56–61.
36. Tariba, B.: Metals in wine – impact on wine quality and health outcomes. *Biologic Trace Elemental Research*, *144*, 2011, pp. 143–156.

Received 14 October 2011; revised 1 December 2011; accepted 9 January 2012.