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Chemometric comparison of mineral content in different grape fruits growing in Serbia

Chemometrischer Vergleich des Mineralgehalts verschiedener Traubensorten die in Serbien wachsen

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Summary

The aim of the work was the determination of the selected metals content (Fe, Zn, and Cu) in six varieties of grapes mainly consumed by the habitants of Serbia (Plovdina, Muscat, Hamburg, Cabernet Sauvignon, Prokupac and Afuzalija), chemometric analysis of the investigated samples and the estimation of the hazard which can be caused by the consumption of grapes. Selected metals were determined using AAS (Atomic Absorption Spectrometry), an experimental technique widely recognized as a suitable for the determination of metals in real samples. The average concentrations of iron, zinc and copper were 23.375 µg/g, 7.033 µg/g and 5.7 µg/g, respectively in all six investigated grape varieties (Methods I and III). The Hazard Quotient values for all the elements were below 1 (one), which can be considered safe. Performed statistics with Pearson correlation matrix on grape samples based on metals' content shows that there is a high positive correlation between ln-transformed data of iron and copper (0.697), and low positive correlation between ln-transformed data of iron and zinc (0.337) and Zn and Cu (0.554). The study represents the fast and efficacious approach to the determination of selected metals (Fe, Zn, and Cu) in grape varieties. It suggests that results of the determination depend on the extraction methods, and the best and the most reliable method was found.

Keywords: AAS, grapes, metals, Principal Component Analysis

Zusammenfassung

Ziel der Arbeit war die Bestimmung von ausgewählten Metallgehalten (Fe, Zn und Cu) in sechs Rebsorten (Plovdina, Muskat, Hamburg, Cabernet Sauvignon, Prokupac und Afuzalija), die hauptsächlich von den Einwohnern Serbiens konsumiert werden, die chemometrische Analyse der untersuchten Proben und die Abschätzung der Gefährdung durch den Verzehr von Trauben. Die ausgewählten Metalle wurden unter Verwendung von Atomabsorptionsspektrometrie (AAS) bestimmt, einer experimentellen Technik, die weithin als geeignet für die Bestimmung von Metallen in Proben anerkannt ist. Die durchschnittlichen Konzentrationen von Eisen, Zink und Kupfer betrugen 23,375 µg/g, 7,033 µg/g bzw. 5,7 µg/g in allen sechs untersuchten Rebsorten (Methoden I und III). Die Hazard Quotient-Werte für alle Elemente lagen unter 1, was als sicher angesehen werden kann. Die durchgeführte Statistiken mit dem Pearson-Korrelationskoeffizient zeigten, dass es eine hohe positive Korrelation zwischen transformierten Daten von Eisen und Kupfer (0,697) und eine geringe positive Korrelation zwischen transformierten Daten von Eisen und Zink (0,337) und Zink und Kupfer (0,554) gibt. Die Studie stellt den schnellen und effizienten Ansatz zur Bestimmung ausgewählter Metalle (Fe, Zn und Cu) in Rebsorten dar. Sie legt nahe, dass die Ergebnisse der Bestimmung von den Extraktionsmethoden abhängen und die effektivste und zuverlässigste Methode gefunden wurde.

Schlüsselwörter: AAS, Weintrauben, Metalle, Hauptkomponentenanalyse

Introduction

Most grapes come from cultivars of *Vitis vinifera* L., the European grapevine native to the Mediterranean and Central Asia (This et al., 2006). The first signs of grape cultivation came from Chalcolithic and Early Bronze Age (3500–2300 BC) sites in the Jordan Valley (Atak and Kahraman, 2012). According to the FAO statistics, around 7.5 million ha were dedicated to this crop in the world in 2007 (FAO, 2007). However, recently, extracts from leaf, seed, and skin have been used in the nutraceutical and cosmetic industries as well as for research purposes (Martinez-Esteso et al., 2011; Sat et al., 2002).

Grapes are valuable foods necessary to human body due to their complex composition: sugars (glucose, fructose) 12–25 %, organic acids (tartric, citric, malic) 1–2 %, mineral salts (Ca, Fe, K, P, etc.) about 1 %, nitrate compounds 0.15–0.2 %, vitamins (C, B1, B2, PP, A, E), enzymes, polyphenols, etc. (Dobrei et al., 2011).

Some of essential elements (K, Ca, Mg, Cr, Co, Fe, F, I, Cu, Mn, Ni, Se and Zn) are being gotten through fruits (Mitic et al., 2012). Previous investigations on metals content in grapes were performed in Slovenia (Kristl et al., 2003), Nigeria (Iyaka, 2007), and Jordan (Al Nasir et al., 2001). Various techniques have been used for the determination of selected metals in fruits: flame atomic absorption spectrometry (AAS) (Jalbany et al., 2010; Ortega et al., 1999), electrothermal atomic absorption spectrometry (Karadjova et al., 2002), and electrothermal atomic absorption spectrometry (ICP-OES) (Aceto et al., 2002; Bhat et al., 2010).

The content of selected elements in three varieties of table grapes from Serbia (Cardinal, Muscat Hamburg and Ribier) was determined using ICP-OES (Mitic et al., 2012). Also, our research group performed the chemometric analysis of grapes from different localities from Southeast Serbia (Sicevo, Brod, Aleksinac, Svrljig and Medosevac) on the basis of the determined heavy metals (Ranđelovic et al., 2015). The importance of the use of the combination of instrumental techniques and chemometrics is described in numerous publications with the application in food and wine industry such as Cozzolino and Dambergs (2010).

The aim of the present study was the determination of the metal content in six varieties of grapes from Serbia (Plovdina, Muscat, Hamburg, Cabernet Souvignon, Prokupac and Afuzalija) mainly use by habitants in Serbia, and the chemometric analysis with accent also on the potential hazard which can be caused by the consumption of investigated grapes. Three methods were used for the preparation of samples and obtained values were compared to previously published results. Statistical analysis including PCA (Principal Component Analysis)/FA (Factor Analysis) and CA (Cluster Analysis) was used for the determination of similarities/disimilarities among analyzed samples.

Materials and Methods

Instrumentation

Atomic absorption measurements were made using a Varian SpectraAA 10 with background correction and hollow cathode lamps. Air-acetylene flame was used for determination of all the elements. The calibration interval, wavelength, slit, and detection level are given in Table 1.

Grape analysis

Grape analysis was performed using three different methods, in order to compare efficacy and precision of the methods.

Different varieties of grapes were used from different territories taken in autumn 2007: Plovdina (Sicevo), Muscat (Svrljig), Hamburg (Aleksinac), Cabernet Sauvignon (Sicevo), Prokupac (Medosevac) and Afuzalija (Mokra).

Grapes were harvested at their optimum maturity. Approximately 500 berries were randomly snipped from cluster. The clusters were taken from three different vineyards from the same region of Southern Serbia. Samples (500 g) of grapes with skins, seeds, and pulps were homogenized in blender.

Method I

10 ml conc. nitric acid (JT Baker, 65 %, “Baker Analysed”) were added to the grape sample (1 g) and heated ~30 min. Afterwards, 8 ml perchloric acid (Merck, pa) were added and heated 15 min. Small amount of distilled water was added to the cooled sample, filtered through funnel and diluted with distilled water in the volumetric flask (50 ml).

Method II

10 ml HNO_3: H_2O (v/v = 1: 1) were added to the grape sample (1 g) and heated until yellow fumes released; afterwards, 10 ml HCl: H_2O (v/v = 1: 1) were added and heated 30 min. Obtained sample was filtered and diluted in the volumetric flask (25 ml).

Method III

The standard procedure described by Association of Official Analytical Chemists (AOAC) (2000) was followed for the preparation of the samples for the analysis of selected metals (AOAC, 2000). Accurately weighed (1 g) sample was transferred into a silica crucible and kept in a muffle furnace for ashing at 450 °C for 3 h and then 5 ml of 6 M HCl were added to the crucible. Care was taken to ensure that all the ash came into contact with acid. Further, the crucible containing acid solution was kept on a hot plate and digested to obtain a clean solution.

The final residue was dissolved in 0.1 M HNO_3 solution and made up to 50 ml. Working standard solutions were prepared by diluting the stock solution with 0.1 M nitric acid for linearity checking.

Data analysis and chemometric methods

The statistical data processing was performed employing XLSTAT 2014.2.03 using the original concentration data set. Multivariate analysis of the contents of selected metals was performed using PCA/FA and CA. The PCA and HCA were applied for the analysis of the distribution and spatial variations of present metals in grapes.

Principal component analysis, as a non-supervised technique, reduces the dimensionality of the original data matrix retaining the maximum amount of variability. It allows the relationship between variables, as well as recog-

TABLE 1: *Analytical characteristics of the AAS determination.*

Metal	Working range (mg/l)	Detection limit (mg/l)	Wave-length (nm)	Slit (nm)
Iron (Fe)	0.00–10.00	0.015	248.3	0.2
Zinc (Zn)	0.00– 5.00	0.021	324.8	0.5
Copper (Cu)	0.00– 1.00	0.007	213.9	1.0

nizing the data structure. PCA is usefully applied for assessment of water quality: surface (Raj Kannel et al., 2007; Ouyang, 2005; Simeonov et al., 2003; Kowalkowski et al., 2006), groundwater (Marengo et al., 2008), drinking water and marine water (Ruggieri et al., 2011; Astel et al., 2006; Stanimirova et al., 2007). PCA also has a significant role for the analysis of biomaterials and food (Razic et al., 2005; Skrbic and Onjia, 2007; Hron et al., 2012; Przybylowicz et al., 2012).

CA classifies objects (cases) into classes (clusters), so that each object is similar to the others within a class but different from those in other classes with respect to a predetermined selection criterion. Hierarchical agglomerative clustering is the most common approach typically illustrated by a dendogram. CA using the Ward method is regarded as a very efficient method and was applied to standardized data considering previous reports from the literature (Kowalkowski et al., 2006; Razic et al., 2005; Varol et al., 2012).

Calculation of oral intake of metals from soil through fruits

Calculation of oral intake of metals from soil through fruits was performed following Nahar Jolly et al. (2013).

Daily intake of metals (DIM) = daily fruit consumption x mean fruit metal concentrations (mg/day, fresh weight).

The required amount of fruit in our daily diet must be 300 g per person (Guenther et al., 2006).

Calculation of health risk index of metal contamination of fruits

Risk to human health by the intake of metal contaminated fruits was characterized using a Hazard Quotient (HQ) (US EPA, 1989). HQ is the ratio between exposure and the reference oral dose (R_fD). If the ratio is lower than one (1), there will be no obvious risk. An estimation of the potential hazard of metal to human health (HQ) through consumption of fruits is determined by the following equation:

$$HQ = (Div) \times (c_{metal}) / R_fD \qquad (1)$$

Where (Div) is the daily intake of fruits (kg/day), (c_{metal}) is the concentration of metal in the fruit (mg/kg), R_fD is the oral reference dose for the metal (mg/kg of body weight/day). Although the HQ-based risk assessment method does not provide a quantitative estimate for the probability of an exposed population experiencing a reverse health effect, it indeed provides an indication of health risk level due to exposure to pollutants (Nahar Jolly et al., 2013).

Results and discussion

Content of selected metals

According to the analysis of the investigated grapes using Method I, the concentration of iron was varied between 16.1 μg/g (Cabernet Sauvignon) and 35.6 μg/g (Muscat), the concentration of zinc between 1.5 μg/g (Plovdina) and 44.2 μg/g (Muscat), and the concentration of copper between 2.4 μg/g and 7.3 μg/g. Concentrations of zinc in the investigated grapes are similar, except Muscat with approximately 10 times higher zinc content than in others. We can presume that the cause is the soil contamination or grape treatment using chemicals of organometallic zinc complexes.

The presence and the concentrations of iron and zinc were determined using atomic absorption spectrometry (AAS) after sample preparation using Method II. Copper was not found using this method. The concentration of iron was in the interval from 5.5 μg/g (Prokupac) to 15.9 μg/g (Cabernet Sauvignon), and the concentration of zinc in the interval from 1.42 μg/g to 4.17 μg/g.

Samples obtained with the Method III show the concentration of iron between 15.5 μg/g (Prokupac) and 32.7 μg/g (Hamburg), the concentration of zinc between 3.5 μg/g and 5.6 μg/g, and the concentration of copper between 3.4 μg/g (Prokupac) and 13.6 μg/g (Hamburg).

Table 2 gives the presentation of results obtained using Methods I, II, III.

Comparing obtained data for iron using different preparation methods, we can draw conclusion that Methods I and III give similar results; Method II gives lower values. Demineralization procedure (mixture nitric and hydrochloric acid) gives lower values because of incomplete degradation of organic molecules, capable of complex formation with metals. All three methods give similar results for zinc. Method II was shown as unappropriate for the determination of copper in grape samples. Obtained results show that copper quantity was below detection limit for copper, which is contrary to obtained results using Methods I and III.

The investigation of metals content in grape samples from Slovenia (Kristl et al., 2003) show that the copper content varied between 1.3 and 8.0 mg/kg, which is very similar to our results (Table 2). Variation of copper content in grape varieties is caused by their individual characte-

TABLE 2: *Selected metals content (μg/g) in grape samples.*

Sample	Method	Fe (X±U[a]) (μg/g)	Zn (X±U[a]) (μg/g)	Cu (X±U[a]) (μg/g)
Plovdina	Method I	16.5±0.49	1.5 ±0.09	2.4±0.05
	Method II	7.8±0.23	2.17±0.13	–
	Method III	17.5±0.52	4.6 ±0.28	6.9±0.14
Muscat	Method I	35.6±1.07	44.2±2.65	4.7±0.09
	Method II	9.3±0.28	2.46±0.15	–
	Method III	22.4±0.67	5.2 ±0.31	5.3±0.11
Hamburg	Method I	23.1±0.69	2.4 ±0.14	7.3±0.15
	Method II	9.7±0.29	3.07±0.18	–
	Method III	32.7±0.98	5.6 ±0.34	13.6±0.27
Cabernet Sauvignon	Method I	16.1±0.48	2.6 ±0.16	4.6±0.09
	Method II	15.9±0.48	4.17±0.25	–
	Method III	18.4±0.55	3.5 ±0.21	3.6±0.07
Prokupac	Method I	33.8±1.01	3.3 ±0.19	5.4±0.11
	Method II	5.5±0.16	1.42±0.08	–
	Method III	15.5±0.46	3.7 ±0.22	3.4±0.07
Afuzalija	Method I	28.5±0.85	3.3 ±0.19	7.1±0.14
	Method II	6.0±0.18	2.15±0.13	–
	Method III	20.4±0.61	4.5 ±0.27	4.1±0.08

[a] U: expanded measurement uncertainty, X: average value, $U = 2 \cdot u_c$, u_c-combined measurement uncertainty

$$u_c = \sqrt{(bias)^2 + (u(bias))^2},\ bias = \frac{\bar{x} - x_{ref}}{\bar{x}} \cdot 100 \qquad (2)$$

$$u\,(bias) = \sqrt{(bias)^2 + u(c_{ref})^2 + \frac{S_{bias}}{\sqrt{n}}} \qquad (3)$$

$$u(c_{ref}) = \sqrt{x^2 + y^2 + z^2} \qquad (4)$$

x: purity of chemicals (%); y: balance uncertainty (%); z: uncertainty on the first dissolution (%)

TABLE 3: *Estimated daily intake of metal (DIM) through fruits.*

Trace elements	Average concentrations of 6 grape varieties (Method I and Method III) (µg/g)	Intake by human being (mg/g)	R_fD^a (mg/day)
Fe	23.375	7.012	10.0–60.0
Zn	7.033	2.11	15.0
Cu	5.7	1.71	2.0–3.0

^{a}: R_fD is the oral reference dose for the metal (mg/kg body weight/day)

ristics, and differences in the same grape varieties by different factors, such as soil, water, agrochemical protection, etc. However, zinc content in grapes from Slovenia (1.0–1.7 mg/kg) and Serbia is different. Higher zinc content in Serbia can be caused by the different concentration of zinc in soil and water, or use of pesticides containing zinc. Investigations of the contents of copper and zinc in fruits and vegetables from Nigeria using AAS showed copper content around 3.3 mg/kg, and zinc around 5 mg/kg (Iyaka, 2007). The zinc content in grape samples from Nigeria is several times higher than zinc content in samples from Serbia, which can be explained by different geographical origin. The investigations of copper and zinc content in grape samples from Jordan show that the average content of copper depending on territory varies between 109 and 2143 ppb, and zinc content varies between 145 and 192 ppb (Al Nasir et al., 2001). Copper concentrations of grape Chardonnay (500 µg/100 g) and Uva di Troia (1.70 µg/g) were detected by Provenzano et al. (2010).

Chemometric analysis of contents of selected metals in grapes

In the first step of the statistic evaluation, Kolmogorov-Smirnov test (the significance level α was 0.05) was preliminary used to test the normality of concentration distribution with each metal type. This test revealed that the original data set were normally distributed for the contents of iron and copper, but not for zinc. In contrast, the ln-transformed data were normally distributed for all metals (samples with concentrations equal to zero were expelled from all investigations-ln function is not defined for zero). Hereupon, all data analysis were performed using ln-transformed data.

In order to reveal the relations between elements, the obtained monitoring data set were subjected to PCA/FA. PCA performed reductions of data matrix by transforming the data into orthogonal components that were a linear combination of the original variables. Before applying PCA modelling, one should test the data matrix in order to detect outliers. Application of Grubb's test resulted in the detection of no outliers for all three metals (Grubbs, 1969). The critical value for α=0.05 and n=11 was 2.355.

Positive significant correlation were observed between ln-transformed data of Fe and Cu (0.697), and low correlations between ln-transformed data of Fe and Zn (0.337) and Zn and Cu (0.554) (Shrestha and Kazama, 2007; Varol et al., 2012).

Before proceeding with the PCA, the suitability of the data for factor analysis and the justification for its implementation were assessed. The Kaiser-Meyer-Olkun Measure of Sampling Adequacy (KMO) value indicator was 0.581, which is below the recommended value of 0.6 (Kaiser, 1960). The Bartlett test of sphericity (Bartlett, 1954) reached statistical significance p=0.037 (should be p<0.50), which indicates the suitability of the correlation matrix for factor analysis. From the shape of the scree plot, shown in Fig. 1a), the number of important components that will be used in further calculations can be observed.

PCA revealed the presence of one component with characteristic value (2.072) exceeding 1, explaining 69.072 %.

Correlations and similarities between the variables can be seen in Fig. 1b), which shows the loading plot of the first two components. Variables with low loadings have no significant impact on the structure of data, while the elements with high loadings have the most influence on the grouping and separation of grape samples. A high correlation was observed between ln-transformed data of Fe and Cu.

Observation plot based on the contents of metals are represented in Fig. 2a).

From Fig. 2a), it is visible that high content of iron is present in samples on the right side of the plot and low on the left side of the plot. Also, it can be concluded that high content of zinc is present in grape samples in the upper half of the plot and low on the opposite side of the plot.

Cluster analysis

HCA of the standardized variables using the Ward method as an amalgamation rule and the squared Euclidean

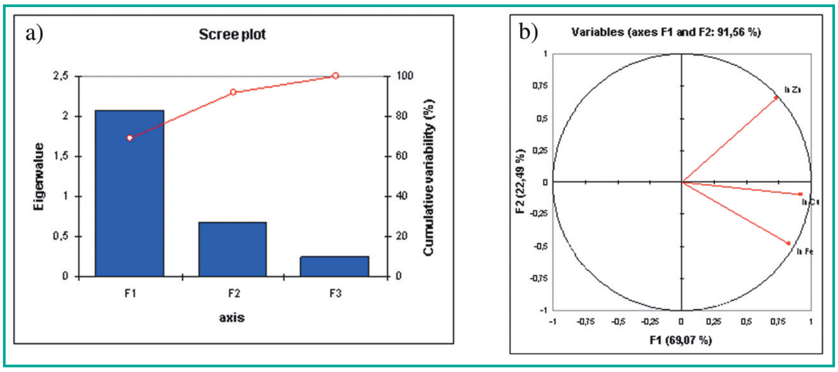

FIGURE 1: *a) Scree plot of Eigen values of the principal components; b) Loading plots of data in grape samples.*

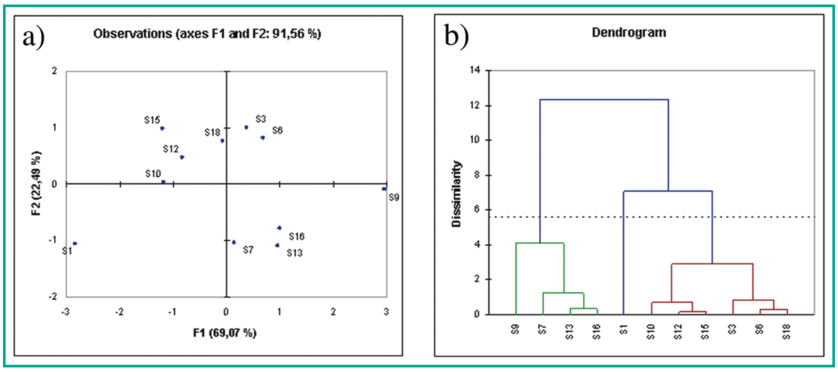

FIGURE 2: *a) Principal component score plot (F1 and F2) of the studied grape samples based on the content of metals (in order to understand labelling we are giving an example: S6 corresponds to Muscat (Method III) from Table 2); b) Dendrogram of grape samples by cluster analysis based on Ward Linkage and Euclidean Distance.*

distance as a measure of the proximity between the samples was performed. The obtained dendrogram presenting the clustering of the analyzed grape samples is presented in Fig. 2b).

The dendrogram shows that all the monitoring samples can be grouped into three main clusters. Cluster I is formed by sample S1; cluster II is formed by samples: S3, S6, S10, S12, S15, S18; cluster III is formed by samples: S7, S9, S13, S16.

Daily uptake of metals by human beings from mixed fruits

Table 3 shows approximate daily intake of metals by human beings from mixed fruits. The intake values are calculated by taking the average value of metals in samples obtained using Method I and III (Table 2) and considering that each person (assuming 70 kg of body weight) consumes approximately 300 g of fruits per day (Guenther et al., 2006). Because different fruits are consumed variably by different segment of population at different time throughout the year, so it may be a realistic estimate for the average intake of metals from fruits. It may be noticed from Table 3 that intake of selected metals is not high and within the permissible limits recommended by various agencies (Friberg et al., 1984; National Academy of Sciences, 2004; WHO, 1993; WHO, 2004; US EPA, 2010).

Potential hazard of metal to human health (HQ)

The Hazard Quotient (HQ) values for Fe, Zn and Cu were 0.117, 0.141, and 0.570, respectively. The sequence of HQ for the elements followed the decreasing order Cu>Zn>Fe. The HQ values for all the elements were below 1 (one), which can be considered safe.

Conclusions

The investigation of selected metals content in grape samples from Serbia shows that it is very similar to results obtained in other countries. Variation of metals content in grape varieties is caused by their individual characteristics, and differences in the same grape varieties by different factors, such as soil, water, agrochemical protection, etc. The average concentrations of iron, zinc and copper were 23.375 μg/g, 7.033 μg/g and 5.7 μg/g respectively in all six investigated grape varieties from Serbia (Methods I and III). Because Methods I and III give similar results, and obtained results according to Method II show that copper quantity was below detection limit for copper, which is contrary to obtained results using Methods I and III, only quantities of Fe, Zn and Cu obtained by Methods I and III were used for the calculation of intake by human being (mg g^{-1}) and Hazard Quotient values. The calculated Hazard Quotient values for all investigated elements were below 1 (one), which means that the investigated grape samples can be considered safe for use.

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Conflict of interest

No conflict of interest exist.

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