Journal of the Serbian Chemical Society

JSCS-info@shd.org.rs • www.shd.org.rs/JSCS

J. Serb. Chem. Soc. 82 (6) 711–721 (2017) UDC 628.1.033+683.51:543.3:54.061/.063(497.11)
JSCS–4998 *Original scientific paper*

Application of principal component and hierarchical cluster analyses in the classification of Serbian bottled waters and a comparison with waters from some other European countries

JELENA Đ. CVEJANOV* and BILJANA D. ŠKRBIĆ

University of Novi Sad, Faculty of Technology, Bulevar cara Lazara 1, 21000 Novi Sad, Serbia

(Received 19 February, revised 2 March, accepted 3 March 2017)

Abstract: The contents of major ions in bottled waters were analyzed by principal component (PCA) and hierarchical cluster (HCA) analysis in order to investigate if these techniques could provide the information necessary for classifications of the water brands marketed in Serbia. Data on the contents of Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-}, HCO_3^{-} and total dissolved solids (*TDS*) of 33 bottled waters was used as the input data set. The waters were separated into three main clusters according to their levels of TDS, Na^{+} and HCO_3^{-}; sub-clustering revealed a group of soft waters with the lowest total hardness. Based on the determined chemical parameters, the Serbian waters were further compared with available literature data on bottled waters from some other European countries. To the best of our knowledge, this is the first report applying chemometric classification of bottled waters from different European countries, thereby representing a unique attempt in contrast to previous studies reporting the results primarily on a country-to-country scale. The diverse character of Serbian bottled waters was demonstrated as well as the usefulness of PCA and HCA in the fast classification of the water brands based on their main chemical parameters.

Keywords: chemometrics; anions in bottled water; cations in bottled water; total dissolved solids.

INTRODUCTION

Water is essential for any living organism; without water, there would not be plant or animal life in the form that is known. The water consumed by human beings comes in various forms. Bottled water is widely consumed because it is readily available, tastes better, and contains fewer impurities.[1] Bottled waters contain many essential macro- and micro-elements that are responsible for the maintenance of underlying biochemical and physiological processes in the

* Corresponding author. E-mail: cvejanov@tf.uns.ac.rs
doi: 10.2298/JSC170219034C

human body, as the main ions in mineral waters are the main constituents of body fluids and cells.

The chemical composition of the bottled water is dependent on the environment from which it originates. The technological processing line from the producing well to the final bottling might alter the original water composition, but there are only few parameters affected (iron and sulphur compounds, nitrite, nitrate and ammonium).[2] The concentrations of the major dissolved components (such as, Ca^{2+}, Mg^{2+}, K^{+}, Na^{+} and Cl^{-}) in bottled water are unaffected by technological processing and could be considered to partially represent the original groundwater in the exploited aquifers.[2]

Several studies have been performed to analyze in more detail the composition and variation of the major and trace elements in bottled waters from different countries, presenting specific interpretations of the results, primarily on a more detailed, country-to-country scale.[3–12] Bertoldi *et al.* provided descriptive statistics on the chemical composition of 571 European bottled mineral waters marketed in 23 European countries;[13] however, similarities of the bottled water brands available on different markets have not hitherto been considered, even though it would provide useful information for consumers worldwide.

The objective of this study was to use principal component analysis (PCA) and hierarchical cluster analysis (HCA) to investigate the natural variation of the main chemical composition parameters of bottled waters. Thirty-three bottled waters produced in Serbia were classified based on the major ions in order to assess the water diversity, knowing that Serbia is one of the richest European countries regarding the availability of water resources. Currently, there are about 30 factories producing about 60 million L of bottled waters per year. Bottled water consumption in Serbia is about 75 L a year per inhabitant, which might be considered low with respect to the yearly Italian consumption rate of 200 L per inhabitant and to the European average rate of 150 litres per capita.[2,5] In this study, the Serbian bottled water brands were first characterized according to the existing EU Directive 2009/54/EC on natural mineral waters[14] taking into account the major ion contents and then they were evaluated by PCA and HCA in order to obtain their statistically based classification. Furthermore, the Serbian waters were compared with the relevant available literature data on bottled waters from Croatia, Estonia, Italy, Portugal and Slovenia, thereby providing the first simultaneous comparison of the bottled waters brands marketed in different countries and evaluating the similarities/differences among them.

EXPERIMENTAL

Data set used for chemometric classification of the Serbian bottled waters consisted of 7 variables for 33 waters available on the Serbian market. This set ("set 1") gathered 31 water brands in Serbia; two brands in the data set (Voda Vrnjci and Bivoda) were represented with waters of two mineralization degrees (*i.e.*, one water of low mineral content and one of high mineral content, later coded "2"). Eight most frequently used chemical composition parameters were taken for the chemometric evaluation of the Serbian bottled waters: total dissolved solids – *TDS*, and the contents of Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^{-}, Cl^{-} and SO_4^{2-}; their levels are presented in Table I.

TABLE I. Main chemical composition parameters (concentration in mg L^{-1}) of 33 bottled waters from the Serbian market

No	Brand	*TDS*	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	HCO_3^{-}	Cl^{-}	SO_4^{2-}
1	Jazak	389	76.5	43.3	7.7	3.4	427	4.9	29.3
2	Aqua Viva	377	83.0	19.0	9.9	1.6	317	11.5	21.2
3	Knjaz Miloš	1175	107	45.0	282	17.5	1256	13.0	39.0
4	Mivela	1621	26.6	335	121	9.1	2079	12.7	2.0
5	Rosa	58	10.0	0.9	2.7	0.5	42	0.5	5.3
6	Vlasina	48	5.7	2.7	2.3	0.3	32	0.05	3.7
7	Vrnjačko Vrelo	261	7.2	44.0	26.1	1.0	287	4.8	5.6
8	Zlatibor	272	62.7	30.5	4.51	0.9	13	1.4	17.6
9	Iva	245	58.4	20.2	2.9	0.8	268	2.4	6.8
10	Aqua Heba	3200	65.0	14.0	1059	56.0	3110	57.0	198
11	Baš Baš	248	48.3	11.1	15.9	0.8	198	11.1	16.5
12	Voda Voda	376	76.2	14.5	40.4	3.1	391	7.9	12.2
13	Voda Vrnjci[a]	295	36.8	22.3	40.2	3.4	292	5.0	18.5
14	Aqua Stilo	830	156	65.0	71.0	3.0	723	98	104
15	Bistrica	3282	87.7	20.7	1160	54.0	3233	46.6	173
16	Bivoda[a]	232	37.2	8.7	23.0	2.0	165	14.9	21.0
17	Duboka	847	238	18.9	56.6	5.2	966	15.0	11.0
18	Eko voda	293	48.0	15.1	26.6	2.9	189	21.8	42.1
19	Golijska Ledena	133	37.9	3.9	0.5	0.2	116	3.5	5.5
20	Karađorđe	1510	129	80.0	312	40.0	1560	56.0	50.0
21	Moja voda	163	33.7	7.9	9.9	0.8	119	8.3	12.1
22	Vujić voda	358	95.0	20.0	2.7	0.8	397	2.2	5.7
23	La Fantana	248	39.6	32.5	1.8	0.6	263	4.4	18.0
24	Aqua Gala	300	59.0	30.3	18.2	2.0	377	1.0	13.0
25	Prolom voda	150	2.0	0.05	48	0.3	80	2.0	2.5
26	Tron voda	364	83.0	38.7	1.8	0.6	401	1.4	22.2
27	Voda Kopaonik	1115	28.3	12.8	409	7.4	1183	18.9	0.3
28	Aqua Balkanika	394	78.5	28.3	33.9	2.1	440	5.2	18.0
29	Eva	202	47.8	15.2	3.1	1.0	200	1.9	15.8
30	Dar voda	637	90.6	22.6	92.4	17.2	521	28.4	80.5
31	Minaqua	1181	22.2	19.9	412	3.6	768	287	0.4
32	Voda Vrnjci2[a]	1174	76.3	55.4	241	35.1	1177	15.5	29.1
33	Bivoda2[a]	3401	85.4	20.6	1216	52.0	3290	54.1	173
Mean		769	64.8	33.9	174	10.0	754	24.8	35.5
Median		365	59.0	20.2	26.6	2.1	391	8.30	17.6
Minimum		48	2.00	0.05	0.5	0.2	13.3	0.05	0.3
Maximum		3401	238	335	1216	56.0	3290	287	198
Skewness		2.02	1.68	4.88	2.44	1.97	1.88	4.35	2.26
Kurtosis		3.45	4.73	26.0	5.11	2.55	2.73	21.3	4.23

[a]In the formed data set, the two brands, Voda Vrnjci and Bivoda, were represented with two different bottled waters regarding the mineralization degree, *i.e.*, with one water of low and one of high mineral content, later coded "2"

For the majority of the waters (coded 1–26, Table I), the data on the major ions were taken from the manufacturers' specifications, while the analytical results obtained elsewhere[15] were taken for the additional 7 brands (coded 27–11, Table I). These analytical results were obtained by different techniques:[15,16] contents of Ca^{2+}, Mg^{2+}, Na^{+} and K^{+} were determined by inductively coupled plasma atomic emission spectroscopy (with respective limits of detection (*LOD*) values in mg L^{-1}: 0.005, 0.005, 0.02 and 0.05), Cl^{-} and SO_4^{2-} by ion chromatography (both with *LOD* values of 0.01 mg L^{-1}) and HCO_3^{-} by the titration (alkalinity) method (with a limit of detection of 1 mg L^{-1}); the repeatability of the measurements was acceptable (below 5 %). Good agreement between the specified values and the analytical results was found by random comparison of data for the same brands.

In order to compare the selected major ions in the Serbian bottled waters with the ones in the waters marketed in different countries, comparable literature-based data were considered: 39 bottled waters from Portugal (samples Nos. 34–72),[3] 14 from Croatia (samples Nos. 73–86),[4] 5 from Estonia (samples Nos. 87–91),[5] 37 from Italy (samples Nos. 100–136)[6] and 22 from Slovenia (samples Nos. 137–158).[7] Hence, the second data set (*i.e.*, "set 2") used for comparison of the bottled waters from different countries consisted of the 7 major ion contents in 150 bottled waters.

For chemometric analysis, both data sets were arranged as follows: the rows refer to the bottled water samples, the while columns contain the ion concentrations.

Chemometric analysis

Basic univariate statistics have the capability of extracting precise characteristics from an examined population of data but information obtained in this way is necessarily one-sided and therefore limited.[17] For a more comprehensive insight into the data sets formed in this study, multivariate statistical analyses were required. Application of multivariate (chemometric) analysis to complex data sets has attracted high scientific interest in recent years and they are now used in a wide range of application.[18-24] Several chemometric-based studies have been performed to analyze bottled waters utilizing different physico-chemical parameters.[3,9,12]

In this study, PCA and HCA were used to elaborate the multidimensional data sets formed from the contents of major ions in the considered bottled waters (previously log-transformed and standardized). PCA can be summarized as a tool for transforming the original measured variables into new uncorrelated variables, *i.e.*, principal components, PCs. Each PC is a linear combination of the original variables. The results of PCA are presented in terms of the variable loadings and sample scores, which could be superimposed graphically in the form of a biplot graph. The number of extracted PCs from the data set was determined in accordance to the Kaiser rule.[25] In order to interpret the significance of the retained PCs in terms of original variables, only the loadings with absolute values greater than 60 % of the maximum loading for a particular PC were considered.

HCA was used to group bottled waters into statistically determined groups (*i.e.*, clusters). It differs from other classification tools (for example discriminant analysis) since the number and characteristics of the groups, which are derived from the data, are not usually known in advance. In this study, the Ward method as an amalgamation rule and the Euclidean distance as a measure of distance were used for HCA.

Throughout the study, the chemometric analyses were accomplished within the Statistica 6.0 computing environment (StatSoft Inc.).

RESULTS AND DISCUSSION

Classification of the Serbian bottled waters

In this study, chemometric characterization (classification) of 33 Serbian bottled waters (31 brands) was performed by means of eight important chemical composition parameters (see Table I). The skewness of all parameters was positive (Table I), indicating a right-skewed distribution with most values concentrated on the left of the means and the extreme values to their right. A kurtosis near 3 (obtained for HCO_3^- and K^+ (Table I) and also for *TDS*) showed a distribution similar to normal, while those greater than 3 (particularly high values of kurtosis were obtained for Mg^{2+} and Cl^-, Table I) suggested a distribution sharper than normal with thicker tails and a high probability for extreme values. Hence, due to presence of the extreme values (*i.e.*, outliers), the median values were used for the further discussion instead of simple means. Concerning the median values, the major cations in the Serbian bottled waters could be ordered in decreasing order as follows: $Ca^{2+} > Na^+ > Mg^{2+} > K^+$. The prevailing anion was HCO_3^- followed by SO_4^{2-} and Cl^-. This is in accordance with the most prevailing types of mineral waters in the large geotectonic units present in Serbia: HCO_3–Na type in the Pannonian Basin; HCO_3–Na or HCO_3–Ca–Mg type in the Dinarides; HCO_3–Na–Cl or HCO_3–Na–SO_4–Cl in the Serbian–Macedonian Massif; HCO_3–Ca or HCO_3–Na–SO_4–Cl type in the Carpatho-Balkanides.[26]

To gain a better insight into the selected Serbian bottled waters, they were classified following the criterion of the EU Directive 2009/54/EC.[14] The results of such classifications in accordance to the main cations and anions, as well as according to the *TDS* values, are presented in Table II.

PCA was used to reduce the dimensionality of the data set, identify the underlying structure of the data and the distributional structure of bottled waters in relation to the main chemical composition parameters. The application of the Kaiser rule led to the retention of two PCs with eigenvalues larger than one, which totally explained 79.6 % of total data variance. The first PC, PC1, accounted for 63.4 % of the data variance, and it was related to the concentrations of Na^+, *TDS*, K^+, HCO_3^- and Cl^- (with loadings of 0.966, 0.909, 0.870, 0.859 and 0.828, respectively); this observation suggested that higher contents of Na^+, K^+, HCO_3^- and Cl^- could be found in Serbian waters with higher mineral contents (*i.e.*, higher *TDS*). This is in agreement with the study of Peh *et al.*,[4] who reported dominant Na–K signature characterizing Croatian bottled waters of the mineral type, as well as their enrichment in Cl^-. The second PC, PC2, was responsible for an additional 16.2 % of the data variance and it was related to the concentration of Ca^{2+}, Mg^{2+} and SO_4^{2-} (with loadings of 0.895, 0.732 and 0.708, respectively). According to the parameters grouping, PC1 could be described as the component related to water mineralization (or dissolved salt content, *i.e.*, salinity), while PC2

TABLE II. Classification of the Serbian bottled waters according to EU directive 2009/54/EEC[14]

Mineral water type	Criterion	Brand name	%[b]
Cation and anion classification			
Contains bicarbonate	> 600	Knjaz Miloš, Mivela, Aqua Heba, Aqua Stilo, Bistrica, Duboka, Karađorđe, Voda Kopaonik, Minaqua, Voda Vrnjci 2, Bivoda 2	33
Contains sulphate	> 200	Aqua Heba (≈ 200)	3
Contains chloride	> 200	Minaqua	3
Contains calcium	> 150	Aqua Stilo, Duboka	6
Contains magnesium	> 50	Mivela, Voda Vrnjci 2	6
Contains iron	> 1	–	
Contains sodium	> 200	Knjaz Miloš, Aqua Heba, Bistrica, Karađorđe, Voda Kopaonik, Minaqua, Voda Vrnjci 2, Bivoda 2	24
Suitable for low sodium diets	< 20	Jazak, Aqua Viva, Rosa, Vlasina, Zlatibor, Iva, Baš Baš, Golijska Ledena, Moja voda, Vujić Voda, La Fantana, Aqua Gala, Tron Voda, Eva	45
TDS classification			
Very low mineral content	< 50	Vlasina	3
Low mineral content	50–500	Jazak, Aqua Viva, Rosa, Vrnjačko Vrelo, Zlatibor, Iva, Baš Baš, Voda Voda, Voda Vrnjci, Bi Voda, Eko Voda, Golijska Ledena, Moja voda, Vujić voda, La Fantana, Aqua Gala, Prolom, Tron, Aqua Balkanika, Eva	61
Intermediate mineral content	500–1500	Knjaz Miloš, Aqua Stilo, Duboka, Voda Kopaonik, Dar Voda, Minaqua, Voda Vrnjci 2	21
Rich in mineral salts	> 1500	Mivela, Aqua Heba, Bistrica, Karađorđe, Bivoda2	15

[a]All in mg L^{-1}; [b]percentage of the particular type of water relative to the total number of bottled waters considered in this work ($n = 33$)

might be related to the cations responsible for water hardness. The results of PCA in a two-dimensional biplot plane are depicted in Fig. 1. The first group of parameters correlating significantly with PC1 had an impact on the classification of bottled waters along PC1: waters located on the right side from the vertical dotted line (*i.e.*, samples distributed along the positive side of PC1, Fig. 1) had *TDS* values above 600 mg L^{-1} and these waters could be classified as intermediate and rich in mineral salts, whereas those on the left side of the vertical line (distributed along the negative side of PC1) had *TDS* values lower than 500 mg L^{-1} and could be classified as low mineral content waters (Table II). The second group of parameters correlating with PC2 influenced further the classification of the low mineralized waters along PC2, highlighting three brands of waters (Prolom Voda - No. 25, Vlasina - No. 6, Rosa - No. 5) separated from the others in Fig. 1. These waters had the lowest total hardness values (5.2–28.8 mg L^{-1}) calculated based on the concentrations of Ca^{2+} ($[Ca^{2+}]$) and Mg^{2+} ($[Mg^{2+}]$)

as 2.5[Ca^{2+}]+4.1·[Mg^{2+}].[12] Such waters with total hardness less than 50 mg L^{-1} could be classified as soft.[11]

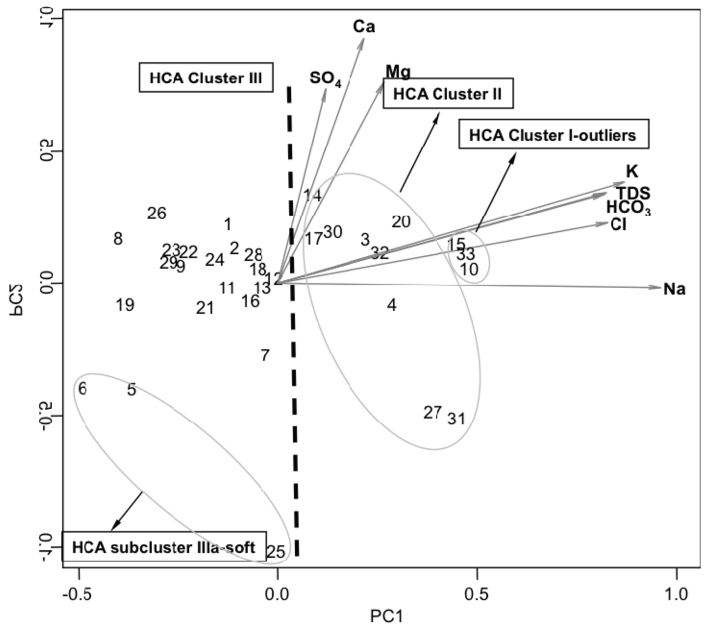

Fig. 1. The PCA biplot of PC1 *vs*. PC2 obtained for 33 Serbian bottled water ("set 1").

Additionally, HCA was used to find the natural grouping of the Serbian bottled water brands in accordance with the selected main chemical composition parameters. The results of HCA are presented in the form of a dendrogram (Fig. 2). Based on eight parameters, the HCA classified 33 Serbian bottled waters into the following main clusters. The first cluster (cluster "I-outliers", Fig. 2) comprised three brands with the highest values of *TDS* (>3000 mg L^{-1}, median 3282 mg L^{-1}), HCO_3^- (>3000 mg L^{-1}, median 3233 mg L^{-1}) and Na^+(>1000 mg L^{-1}, median 1160 mg L^{-1}), having also among the highest content of Cl^- (46.6, 54.1, 27.0 mg L^{-1}). The second cluster ("II") grouped nine brands that could also be found on the right side of PC1 (Fig. 1) with intermediate values of *TDS* (637–1621 mg L^{-1}, median 1175 mg L^{-1}), HCO_3^- (521–2079 mg L^{-1}, median 1177 mg L^{-1}) and Na^+ (92.4–412 mg L^{-1}, median 241 mg L^{-1}), having also pronounced Cl^- content (12.7–287 mg L^{-1}, median 18.9 mg L^{-1}). The third main cluster ("III", Fig. 2) contained the majority of the analyzed brands (21, *i.e.*, 64 %), which all could be classified as low in mineral salts, having *TDS* values less than 500 mg L^{-1} (Table II), *i.e.*, in the range 48–395 mg L^{-1}, with median 261 mg L^{-1}; additional common features for this cluster of waters were HCO_3^- levels (from 48 to 395 mg L^{-1} with median of 264 mg L^{-1}) less than 600 mg L^{-1} (the limit for the classification of water as "contains bicarbonate", Table II); Na^+ contents less than 50 mg L^{-1} (0.5–40.5 mg L^{-1} with median of 10 mg L^{-1}) and Cl^- contents less than 12 mg L^{-1} (except Bi voda – No. 16 and Eko voda – No. 18, see Table 1). Within cluster "III", further sub-clustering was observed; one of the sub-clusters, "IIIa-soft" (Fig. 2), gathered three waters with the lowest Mg^{2+} levels (0.05–2.7 mg L^{-1}), the lowest total hardness (5.2–28.8 mg L^{-1}; the total hardness of the remaining waters ranged from 110 to 1442 mg L^{-1}) and the lowest K^+ levels (0.3–0.5 mg L^{-1}).

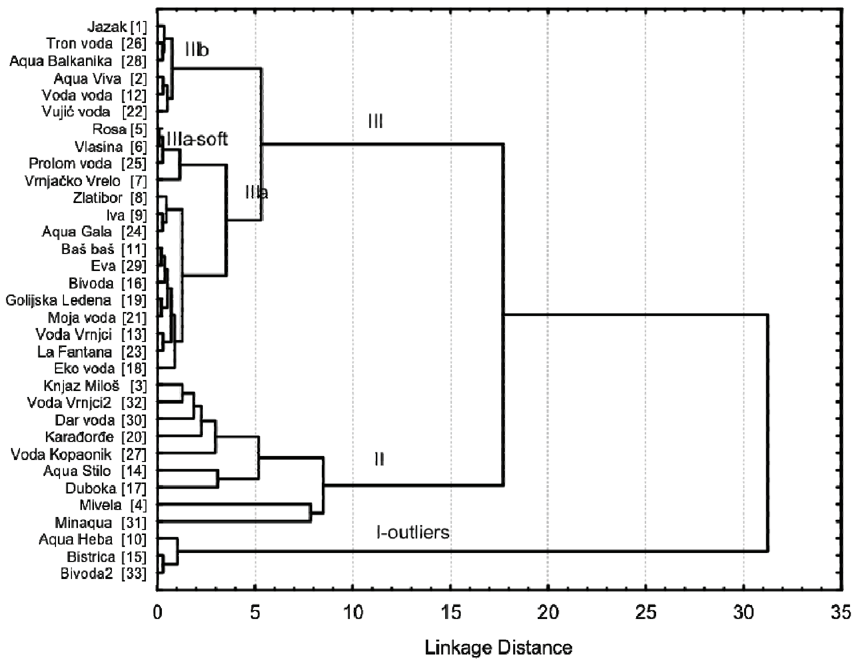

Fig. 2. The HCA dendrogram for the 33 Serbian bottled waters ("set 1").

Hence, the two applied multivariate chemometric tools gave results in good agreement (Fig. 1). In addition to the HCA dendrogram, PCA biplots visualized the relationship among the chemical compositional parameters and mineral water brands. The result of this study indicated that *TDS* and the contents of HCO_3^- and Na^+ are the most important variables for classification and separation of the investigated water brands. In a similar manner, Güler[9] and Oyebog *et al.*[11] mentioned *TDS* as the most discriminating variable in the grouping of water brands.

Comparison of the Serbian bottled waters with those marketed in other countries

HCA was applied to the data set ("set 2") consisting of available data for 7 major ions in 150 bottled waters produced in different countries, including 33 previously characterized Serbian waters. The groups (clusters) obtained by HCA contained waters with similar macrocomponent patterns listed in Table III. A description of the clusters (in terms of the origin of the waters within the particular cluster) is given in Table IV, from which it could be seen that the majority of the bottled water brands from Croatia, Italy, Serbia and Slovenia were grouped in cluster "1a". The Serbian waters in this cluster were those from cluster "III" mentioned above (Fig. 2). The exceptions were 3 waters that clustered together with the majority of the Portuguese brands in cluster "1b" (Table III). These three waters belong to the sub-cluster "IIIa-soft" (Fig. 2) with the lowest total hardness among the 33 considered Serbian brands. In cluster "2" (Tables III and IV), there were 12 Serbian waters of high and intermediate levels of *TDS*, HCO_3^- and Na^+ that were previously classified in clusters "I – outliers" and "II" (Fig. 2). Thus, the allocation of the Serbian waters in all three main clusters (Tables III and IV) suggested diversity of the marketed bottled waters, contrary to the Slovenian and Croatian waters not grouped in cluster "1b" with the lowest median values of the Ca^{2+} and Mg^{2+} contents.

TABLE III. The content of the clusters (marked 1a, 1b and 2) obtained by hierarchical cluster analysis (HCA) of the data "set 2" containing the concentration of 7 major ions in 150 bottled water brand marketed in different European countries. The clusters' content is given in the form of the bottled water sample numbers explained previously in the Experimental. The samples numbered 1–33 are from Serbia, 34–72 from Portugal,[3] 73–86 from Croatia,[4] 87–91 from Estonia,[5] 100–136 from Italy[6] and 137–158 from Slovenia[7]

1		2 (n = 50)
1a (n = 66)	1b (n = 34)	
1, 2, 7–9, 11–13, 16, 18, 19, 21–24, 26, 28, 29, 37, 58, 59, 64, 75–80, 82, 86, 85, 86, 89–100, 102, 107, 108, 109, 112, 115, 117, 118, 120, 123, 127–132, 134, 136, 140, 145, 146, 149–158	5, 6, 25, 34, 38–41, 43, 46, 48–51, 54, 55, 57, 60–63, 65–72, 91, 103, 106, 110, 113	3, 4, 10, 14, 15, 17,20, 27, 30–33, 35, 36, 42, 44, 45, 47, 52, 53, 56, 73, 74, 81, 84, 87, 88, 101, 104, 105, 111, 114, 116, 119, 121, 122, 124–126, 133, 135, 137–139, 141–144, 147, 148

TABLE IV. Origin of the bottled water samples grouped in the main HCA clusters from Table III: number of samples and percentage (in parentheses) of the bottled water from one country grouped in a particular cluster

Clusters	Croatia	Estonia	Italy	Portugal	Serbia	Slovenia	Total number of samples
2	4 (29)	2 (40)	14 (38)	9 (23)	12 (36)	9 (41)	50
1b	0 (0)	1 (20)	4 (11)	26 (67)	3 (9)	0 (0)	34
1a	10 (71)	2 (40)	19 (51)	4 (10)	18 (54)	13 (59)	66
Total number of samples	14	5	37	39	33	22	150

CONCLUSION

The main chemical composition parameters of 33 bottled waters available on the Serbian market were presented in the light of relevant EU legislation and they were evaluated by means of multivariate chemometric tools. The applied chemometric methods, *i.e.*, PCA and HCA, were shown to be effective tools in the identification of the principal interrelationships of the major ions of the studied bottled waters, thereby indicating their similarities and dissimilarities. High degree of correlations among examined chemical composition parameters was revealed: the group of parameters reflecting the water total mineralization (*TDS*, HCO_3^-, Na^+) was separated from the group of parameters reflecting the total hardness of the waters (Ca^{2+}, Mg^{2+}). Additionally, it is noteworthy that the application of PCA and HCA allowed a simple and meaningful classification of Serbian water brands into three main clusters primarily based on the parameters reflecting the water mineralization (*i.e.*, *TDS*, HCO_3^-, and Na^+). Moreover, the brands with the lowest total hardness were identified, providing valuable information for consumers. Simultaneous comparison of the waters from the Serbian markets with those marketed in Croatia, Estonia, Italy, Portugal and Slovenia by HCA revealed diversity of the domestic brands, which may represent competitive choices on the global market.

Acknowledgement. The results presented herein were obtained within Project No. 172050 supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia.

ИЗВОД

ПРИМЕНА АНАЛИЗЕ ГЛАВНИХ КОМПОНЕНАТА И КЛАСТЕРА У КЛАСИФИКАЦИЈИ ФЛАШИРАНИХ ВОДА ИЗ СРБИЈЕ И ЊИХОВОМ ПОРЕЂЕЊУ СА ВОДАМА ИЗ ИЗАБРАНИХ ЕВРОПСКИХ ЗЕМАЉА

ЈЕЛЕНА Ђ. ЦВЕЈАНОВ и БИЉАНА Д. ШКРБИЋ

Универзитет у Новом Саду, Технолошки факултет Нови Сад, Булевар цара Лазара 1, 21000 Нови Сад

Садржаји основних јона у флашираној води су обрађени применом анализе главних компонената и хијерархијеске кластер анализе са циљем испитивања могућности примене ових хемометријских техника при класификацији вода са српског тржишта. Подаци о хемијском саставу и то садржаји Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, SO_4^{2-}, HCO_3^- и суви остатак у 33 флаширане воде, чинили су улазну базу података. Уочене су три главне групе вода у складу на садржајима сувог остатка , Na^+ and HCO_3^-; даље груписање у оквиру једне од главних група указало је на групу „меких“ вода са најмањим степеном тврдоће. Уочене групе дају информације корисне за потрошаче при избору вода на тржишту. Додатно су ове српске воде на основу одређених хемијских параметара упоређене са релевантним подацима доступним у литератури о флашираним водама из иностранства; нова улазна база података у овом случају састојала се од садржаја 7 главних јона у 150 узорака флаширане воде из Србије и иностранства. Према нашим сазнањима, ово је први рад у ком се примењује истовремена (хемометријска) класификација флашираних вода из различитих земаља применом хијерархијске кластер анализе, представљајући јединствен покушај у односу на досадашње студије које су приказивале

првенствено резултате који се односе на једну земљу. Резултати су указали на разноликост флашираних вода из Србије, као и на корисност анализе главних компонената и хијерархијске кластер анализе за једноставну и брзу класификацију флашираних вода са тржишта на основу главних хемијских параметара.

(Примљено 19. фебруара, ревидирано 2. марта, прихваћено 3. марта 2017)

REFERENCES

1. A. Ikem, S. Odueyungbo, N. O. Egiebor, K. Nyavor, *Sci. Total Environ.* **285** (2002) 165
2. U. Fugedi, L. Kuti, G. Jordan, B. Kerek, *J. Geochem. Explor.* **107** (2010) 305
3. C. Lourenço, L. Ribeiro, J. Cruz, *J. Geochem. Explor.* **107** (2010) 362
4. Z. Peh, Š. Ajka, J. Halami, *J. Geochem. Explor.* **107** (2010) 227
5. L. Bityukova, V. Petersell, *J. Geochem. Explor.* **107** (2010) 238
6. R. Cidu, F. Frau, P. Tore, *J. Food Compos. Anal.* **24** (2011) 184
7. M. Brenčić, T. Ferjan, M. Gosar, *J. Geochem. Explor.* **107** (2010) 400
8. A. Astel, R. Michalski, Ł. Aleksandra, M. Jab, K. Bigus, S. Szopa, A. Kwieci, *J. Geochem. Explor.* **143** (2014) 136
9. C. Güler, *Chemom. Intell. Lab. Syst.* **86** (2007) 86
10. A. Baba, F. S. Ereeş, Ü. Hıçsönmez, S. Çam, H. Özdılek, *Environ. Monit. Assess.* **139** (2008) 277
11. S. A. Oyebog, A. A. Ako, G. E. Nkeng, E. C. Suh, *J. Geochem. Explor.* **112** (2012) 118
12. K. Y. Kermanshahi, R. Tabaraki, H. Karimi, M. Nikorazm, S. Abbasi, *Food Chem.* **120** (2010) 1218
13. D. Bertoldi, L. Bontempo, R. Larcher, G. Nicolini, S. Voerkelius, G. D. Lorenz, H. Ueckermann, H. Froeschl, M. J. Baxter, J. Hoogewerff, P. Brereton, *J. Food Compos. Anal.* **24** (2011) 376
14. *Off. J. Eur. Union* **L164** (2009) 45
15. T. Petrović, M. Zlokolica-Mandić, N. Veljković, D. Vidojević, *J. Geochem. Explor.* **107** (2010) 373
16. M. Birke, C. Reimann, A. Demetriades, U. Rauch, H. Lorenz, B. Harazim, W. Glatte, *J. Geochem. Explor.* **107** (2011) 217
17. E. Reisenhofer, G. Adami, P. Barbieri, *Water Res.* **32** (1998) 1193
18. B. Škrbić, K. Szyrwińska, N. Durišić-Mladenović, P. Nowicki, J. Lulek, *Environ. Int.* **36** (2010) 862
19. Z. Predojević, B. Škrbić, N. Đurišić-Mladenović, *J. Serb. Chem. Soc.* **77** (2012) 815
20. S. Ražić, A. Onjia, *Am. J. Enol. Vitic.* **61** (2010) 506
21. M. Savić Biserčić, L. Pezo, I. Sredović Ignjatović, L. Ignjatović, A. Savić, U. Jovanović, V. Andrić, *J. Serb. Chem. Soc.* **81** (2016) 813
22. N. Radosavljević-Stevanović, J. Marković, S. Agatović-Kustrin, S. Ražić, *Nat. Prod. Res.* **28** (2014) 511
23. T. Stafilov, B. Škrbić, J. Klánová, P. Čupr, I. Holoubek, M. Kočov, N. Durišić-Mladenović, *J. Chemom.* **25** (2011) 262
24. N. Đurišić-Mladenović, B. D. Škrbić, A. Zabaniotou, *Renew. Sustain. Energy Rev.* **59** (2016) 649
25. H. F. Kaiser, J. Rice, *Educ. Psychol. Meas.* (1974) 111
26. M. Martinović, M. Milivojević, in *Proceedings of World Geothermal Congress*, Bali, Indonesia, April 25–30, 2010.