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Chemometric expertise of Bulgarian mineral, spring and table waters

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Ten brands of Bulgarian bottled mineral, spring and table waters were subjected to chemometric expertise using cluster analysis and principal components analysis. The waters were classified into several patterns depending on their microelement composition. Groups of similarity between the chemical components of the potable waters were found and the specific indicators for the separate groups of waters were determined. The separation is obviously related to the specificity of the local origin of the waters, e.g. crustal and soil properties and composition. It is of interest to note that the chemical composition of spring waters strongly differs from that of the mineral waters from the same locations. The obtained results point to the stability of the chemical composition and lack of contamination of the bottled mineral waters in examination over a prolonged period of storage (up to 2.5 years after bottling).

Keywords: Bulgarian bottled potable waters; chemometric expertise; cluster analysis; principal components analysis

INTRODUCTION

Bulgaria is one of the countries in the world richest in mineral waters (more than 850 springs and boreholes), as well against its surface area, as *per capita* [1]. This natural richness has been known and exploited since antiquity. Nowadays, more than 50 brands of bottled mineral and spring waters are offered on the Bulgarian market. The major components of bottled Bulgarian drinking waters, such as K, Na, Ca, Mg, and Fe are monitored in accordance with European legislation [2,3], whereas only limited data are available about their trace element content. Information on the location, physico-chemical characteristics, element content, and medical applications of Bulgarian mineral and spring waters are reported by Pentcheva *et al.* [1], Vladeva and Kostadinov [4,5] and Vladeva *et al.* [6]. The quality of the waters, including their macro- and microelement content, as well as their stability during storage, is of paramount importance for the consumers.

The great variety of mineral water springs with respect to their location and chemical composition often requires a specific approach for expert assessment of mineral water origin and quality. Since careful monitoring of the chemical content of different mineral, spring and table waters creates large data sets, chemometric data classification, modelling and interpretation seems to be the most reliable assessment procedure [7-10].

Subject of the present work was the chemometric assessment of Bulgarian potable waters of the following ten brands: „Gorna Banya“ mineral, „Bankya“ mineral, „Kom“ mineral, „Thorn Springs“ mineral, „Hissar“ mineral, „Devin“ mineral and spring, „Mihalkovo“ mineral and spring and „Savina“ table using cluster analysis and principal components analysis. The „Savina“ table water was added to the sample list in order to assess the efficiency of the demineralization processing of this water prior to bottling. It was also of substantial interest to assess the water quality during a prolonged period after bottling.

Typical representatives of mineral waters of Southern and Western Bulgaria were selected for analysis among Bulgarian natural mineral waters recognised by the EC [11]. Commercial drinking waters in standard PET bottles of 0.5 L were subjected to chemical analysis. The microelement composition of the waters was determined in former works of the authors [12,13] using total reflection X-ray fluorescence spectrometry (Tables 1 and 2). The data for the microelement composition of the waters were treated in the present chemometric study in order to:

- find out groups of similarity between the chemical components of the waters, to which the local specificity of the potable waters may be related;
- find out groups of similarity between the different types of potable waters;
- find out the specific indicators for the separate groups of waters.

Two chemometric methods were employed in the study – cluster analysis and principal

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Table 1. Microelement content in bottled mineral waters analyzed in the year of bottling (samples C_1 - C_5) and about 2.5 years after bottling (samples C_6 – C_10), reported by Georgieva *et al*. (2013, 2014).

Element	"Gorna Banya"		"Kom"		"Thorn Spring"		"Devin"		"Mihalkovo"	
	(C_1)	(C_6)	(C_2)	(C_7)	(C_3)	(C_8)	(C_4)	(C_9)	(C_5)	(C_10)
S, mg L^{-1}	7.9 ± 0.4	6.4 ± 0.5	8.9 ± 0.2	8.8 ± 0.3	2.8 ± 0.4	2.2 ± 0.3	5.1 ± 0.8	4.5 ± 0.4	123 ± 13	96 ± 6
Cl, mg L^{-1}	2.4 ± 0.2	1.8 ± 0.2	1.2 ± 0.1	0.9 ± 0.1	2.9 ± 0.4	2.2 ± 0.3	3.4 ± 0.2	3.1 ± 0.2	47 ± 7	45 ± 7
K, mg L^{-1}	0.3 ± 0.1	0.3 ± 0.1	1.3 ± 0.2	1.0 ± 0.1	1.2 ± 0.2	1.5 ± 0.2	0.6 ± 0.1	0.6 ± 0.1	48 ± 7	46 ± 6
Ca, mg L^{-1}	1.3 ± 0.2	1.5 ± 0.2	1.4 ± 0.2	1.7 ± 0.2	78 ± 8	80 ± 6	1.5 ± 0.1	1.3 ± 0.1	215 ± 25	217 ± 29
Mn, µg L^{-1}	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	48 ± 7	38 ± 5
Fe, µg L^{-1}	25 ± 4	24 ± 3	10 ± 1	7.9 ± 1.0	6.8 ± 0.8	8.0 ± 1.0	15 ± 2	13 ± 2	15 ± 2	15 ± 2
Ni, µg L^{-1}	3.0 ± 0.5	< 1	12 ± 1	10 ± 1	5.0 ± 0.8	4.0 ±0.5	4.0 ± 0.5	3.0 ± 0.5	14 ± 2	13 ± 2
Cu, µg L^{-1}	6.0 ± 0.5	4.8 ± 0.5	6.0 ± 0.5	4.8 ± 0.1	< 2	< 2	3.0 ± 0.5	3.0 ± 0.5	< 10	< 10
Zn, µg L^{-1}	6.0 ± 0.5	4.9 ± 0.5	47 ± 4	50 ± 4	10 ± 1	13 ± 2	< 2	3.0 ± 0.5	< 9	< 9
As, µg L^{-1}	3.0 ± 0.5	3.0 ± 0.5	12 ± 2	9.0 ± 1.0	2.5 ± 0.2	< 1	< 1	< 1	< 7	< 7
Br, µg L^{-1}	8.0 ± 1.0	6.5 ± 1.0	37 ± 5	32 ± 3	5 ± 2	13 ± 2	6.0 ± 0.5	6.0 ± 0.5	400 ± 50	350 ± 50
Rb, µg L^{-1}	5.0 ± 0.5	4.0 ± 0.5	4.0 ± 0.5	4.0 ± 0.5	< 1	< 1	< 1	< 1	163 ± 25	160 ± 25
Ba, µg L^{-1}	45 ± 7	36 ± 1	30 ± 5	26 ± 4	8 ± 4	23 ± 2	38 ± 5	35 ± 2	< 100	< 100

Table 2. Microelement content in bottled table, mineral and spring waters analyzed in the year of bottling, reported by Georgieva *et al*. (2014).

Element	"Savina" table (C_11)	"Hissar" mineral (C_12)	"Bankya" mineral (C_13)	"Devin" spring (C_14)	"Mihalkovo" spring (C_15)
S, mg L^{-1}	0.20 ± 0.01	6.3 ± 1.1	14 ± 1	0.80 ± 0.05	2.6 ± 0.4
Cl, mg L^{-1}	2.2 ± 0.2	6.2 ± 0.8	9.8 ± 1.2	1.2 ± 0.2	1.4 ± 0.2
K, mg L^{-1}	1.1 ± 0.1	1.7 ± 0.1	0.7 ± 0.1	1.5 ± 0.2	10.6 ± 0.3
Ca, mg L^{-1}	6.1 ± 0.5	3. 6 ± 0.2	6.1 ± 0.7	7.9 ± 1.3	5.7 ± 0.8
Mn, µg L^{-1}	< 2	< 2	< 2	< 2	< 2
Fe, µg L^{-1}	18 ± 3	19 ± 1	20 ± 3	15 ± 2	16 ± 2
Ni, µg L^{-1}	< 1	< 1	< 1	< 1	< 1
Cu, µg L^{-1}	12 ± 2	19 ± 2	9 ± 1	8 ± 1	7 ± 1
Zn, µg L^{-1}	15 ± 2	29 ± 2	9 ± 1	9 ± 1	12 ± 2
As, µg L^{-1}	< 1	< 1	< 1	< 1	< 1
Br, µg L^{-1}	6 ± 1	30 ± 3	76 ± 6	9 ± 1	9 ± 1
Rb, µg L^{-1}	< 1	19 ± 1	< 1	< 1	< 1
Ba, µg L^{-1}	< 14	< 14	< 14	< 14	< 14

components analysis [14,15]. Both methods are well documented and find wide application.

Cluster analysis is a well-known and widely used classification approach for environmetric purposes with its hierarchical and non-hierarchical algorithms. In order to cluster objects characterized by a set of variables, one has to determine their similarity. The representation of the results of the cluster analysis is performed either by a tree-like scheme called dendrogram comprising a hierarchic structure (large groups are divided into small ones) or by tables containing different possible clusterings. *Principal components analysis (PCA)* is a typical display method which allows estimating the internal relations in the data set. There are different variants of PCA but basically, their common feature is that they produce linear combinations of the original columns in the data matrix (data set) responsible for the description of the variables characterizing the objects of observation. These linear combinations represent a type of abstract measurements (factors, principal components) being better descriptors of the data structure (data pattern) than the original (chemical or physical) measurements.

RESULTS AND DISCUSSION

Two data sets were treated: [10×12] including the mineral waters „Gorna Banya“ (samples C_1, C_6), „Kom“ (samples C_2, C_7), „Thorn Springs“ (samples C_3, C_8), „Devin“ (samples C_4, C_9), and „Mihalkovo“ (samples C_5, C_10), analyzed in the year of bottling and 2.5 years after bottling for 12 chemical parameters (As, Zn, Cu, Ba, Fe, Ni, Ca, Br, Mn, Rb, K, Cl), and [5×12] including the waters „Savina“ table (sample C_11), „Bankya“ mineral (sample C_12), „Hissar“ mineral (sample C_13), „Devin“ spring (sample C_14), and „Mihalkovo“ spring (sample C_15), analyzed in the year of bottling for the same chemical parameters.

Data set [10×12]

Figure 1 presents the hierarchic dendrogram for clustering of the 12 variables from the data set [10×12]. As can be seen, three clusters are formed at the significance level of 33.3 % D_{max}:

K1 (As, Zn)
K2 (Cu, Ba, Fe)
K3 (Ni, Ca, Br, Mn, Rb, K, Cl)

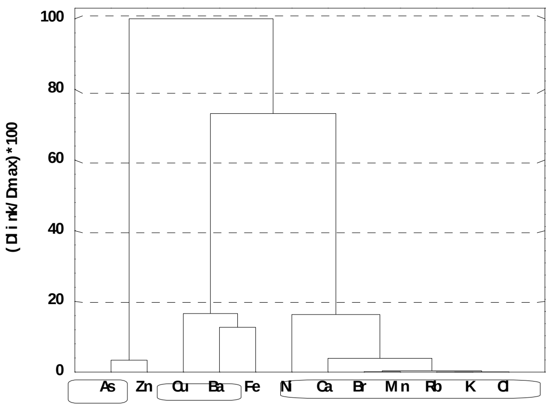

Fig. 1. Hierarchic diagram for clustering of 12 variables.

It follows from the results shown on Figure 1 that three main sources form the composition of all examined waters of the first data set, two of them being related to the microcomponents in the mineral waters (**K1** and **K2**), and the third one (**K3)** – mainly to the major components and the microcomponents Mn, Rb, Br, and Ni. This data structure is confirmed by the principal components (PC) analysis, where three latent factors appear to be responsible for the structure (Table 3). The first latent factor (PC1) is connected with all major components, while the other two (PC2 and PC3) – with characteristic combinations of microcomponents. Conditionally, one could define three latent factors responsible for the data structure: "soil mineral" factor, "strong As-Zn specific" factor and "rock mineral" factor.

Table 3. Factor loads for the data matrix [10×12].

Variables	PC1	PC2	PC3
Cl	0.99	0.06	0.14
K	0.99	0.02	0.13
Ca	0.96	0.15	-0.13
Mn	0.98	0.02	0.14
Fe	-0.06	0.29	0.94
Ni	0.76	-0.62	-0.12
Cu	0.20	-0.58	0.78
Zn	-0.23	-0.93	-0.26
As	-0.02	-0.99	0.04
Br	0.99	-0.04	0.12
Rb	0.98	0.01	0.16
Ba	0.67	0.21	0.68
Explained variance (%)	58	23	18

Figure 2 presents the hierarchic dendrogram for clustering of the mineral waters (firstly in the year of bottling and secondly – about 2.5 years later). Three clusters can be distinguished; there is a good correlation (grouping) between the results in the year of bottling and those about 2.5 years after bottling (samples 1 and 6, 2 and 7, 3 and 8, 4 and 9 and 5 and 10, respectively). This is an indication of the stability of the chemical composition and lack of contamination of all examined mineral waters even 2.5 years after bottling.

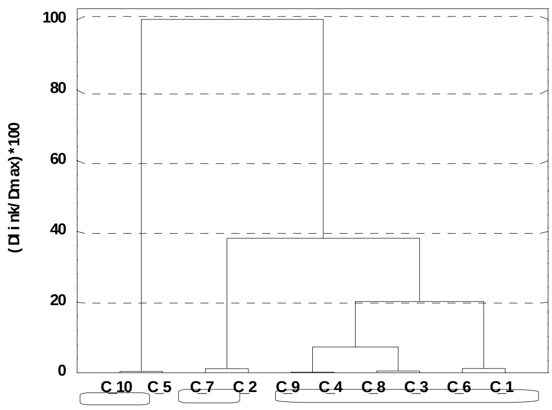

Fig. 2. Hierarchic dendrogram for clustering of the types of mineral waters analyzed in the year of bottling (samples C_1 - C_5) and about 2.5 years after bottling (samples C_6 – C_10).

On Figure 3 the diagram for the factor score is presented. The five brands of mineral waters included in the data set [10×12] ("Gorna Banya", "Kom", "Thorn Spring", "Devin" and "Mihalkovo") form three groups of similarity and the pairs (at the year of bottling and ~2.5 years after bottling) are very well distinguished. The three groups of similarity are described as follows:

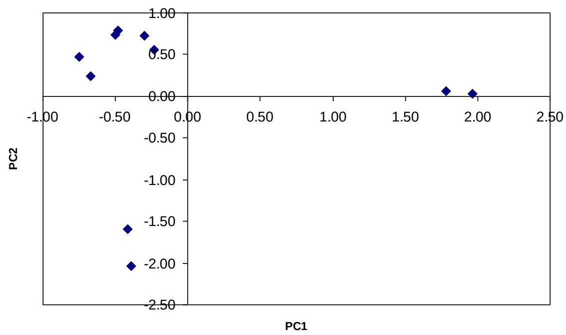

Fig. 3. Diagram for the factor scores (PC1 vs. PC2) for the data matrix [10×12].

- **„Mihalkovo"**: highest values of all major components (strong mineralization) and of the microcomponents manganese, nickel, copper, bromine and rubidium.

- **„Kom“**: highest values of zinc and arsenic (specific As-Zn mineralization) and lowest values of chlorides and calcium.
- **„Gorna Banya“, „Thorn Spring“, „Devin“**: mineral waters with similar chemical composition – lowest potassium content, significant content of calcium and iron.

Data set [5×12]

In this case four chemical variables were eliminated from the set, because they provided no chemical information – equal values were displayed for all examined samples. So the data set was reduced to **[5×8]**, the eliminated variables being the concentrations of manganese, nickel, arsenic and barium. The grouping of the chemical components yields three clusters at the significance level of 66.7% D_{max}, while at 33.3% D_{max} one of the clusters could be separated in two components (Figure 4).

K1 (Rb, Zn, Cu)
K2 (Ca, K) or (Ca) (K)
K3 (Fe, Br, Cl)

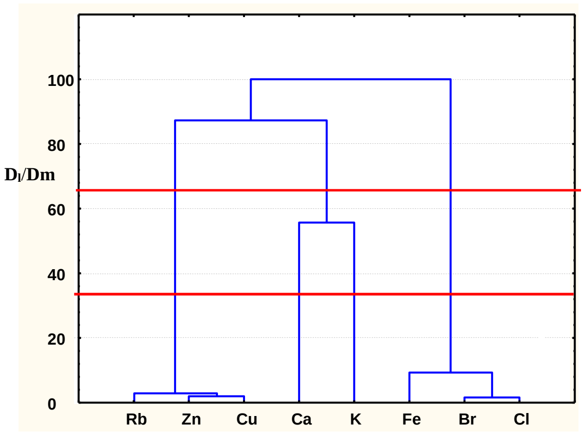

Fig. 4. Hierarchic dendrogram for clustering of 8 variables.

This clustering reveals that the microcomponents form similarity groups, while the major components (except for chloride) are of individual significance. The principal components analysis (Table 4) indicates the same grouping of the variables.

Table 4. Factor loads for the matrix [5×8].

Variables	PC1	PC2
Cl	0.15	0.98
K	-0.24	-0.51
Ca	0.01	-0.26
Fe	0.36	0.84
Cu	0.97	0.17
Zn	0.99	-0.003
Br	-0.10	0.98
Rb	0.94	0.14
Explained variance (%)	38	37

Two latent factors explain 75% of the total variance. Conditionally, they could be named “soil mineral” factor (strong correlations between Zn, Cu, Rb in PC1) and “rock mineral” factor (strong correlation for Cl, Fe, Br in PC2). Owing to their relatively low contents in the second set of water samples, Ca and K play a negligible role for the data structure (non-significant factor loadings).

The clustering of the water types (Figure 5) reveals a strong similarity only between the samples C_14 and C_15 (“Devin” spring and “Mihalkovo” spring), which are typical spring waters and display low concentrations of chlorides, bromides and iron.

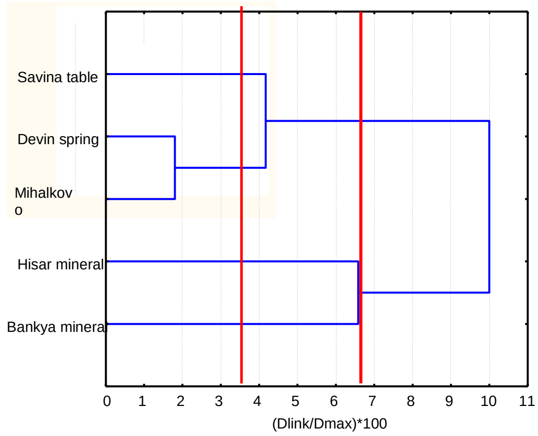

Fig. 5. Clustering of the investigated potable waters (samples C_11 - C_15).

The other three brands of waters differentiate (particularly at the first significance level and to a certain degree – at the second significance level). “Hissar” and “Bankya” form a group of mineralized waters with a high content of chlorides, iron, zinc and copper. The “Savina” table water forms a separate pattern owing to the demineralization processing of this water prior to bottling. However, calcium, iron, copper, and zinc are not removed - their contents are similar to those in the untreated mineral and spring water samples. These conclusions are confirmed by the principal component analysis (factor score diagram presented on Figure 6) where the separation of the five brands of waters can be observed.

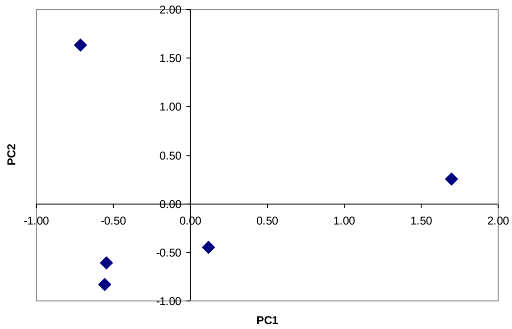

Fig. 6. Diagram for the factor scores (PC1 vs. PC2) for the data matrix [5×8].

CONCLUSIONS

The present study has indicated that the brands of mineral, spring and table waters in consideration could be classified into several patterns depending on their microelement composition. The separation is obviously related to the specificity of the local origin of the waters, e.g. crustal and soil properties and composition. In this relation it is of interest to note that the chemical composition of the spring waters „Devin“ and „Mihalkovo“ strongly differs from that of the mineral waters from the same locations. The separate pattern formed by the „Savina” table water may be related to the additional demineralization processing of this water prior to bottling. The results of the cluster analysis point to the stability of the chemical composition and lack of contamination of the bottled mineral waters even for a prolonged period of storage (2.5 years after bottling).

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ХЕМОМЕТРИЧНА ЕКСПЕРТИЗА НА БЪЛГАРСКИ МИНЕРАЛНИ, ИЗВОРНИ И ТРАПЕЗНИ ВОДИ

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(Резюме)

Десет вида бутилирани български минерални, изворни и трапезни води са изследвани хемометрично с помощта на кластерен анализ и анализ на главни компоненти. Водите са класифицирани в няколко категории в зависимост от елементния им състав. Намерени са групи на подобие между химичните компоненти на питейните води и са определени специфичните индикатори за отделните групи води. Това разделение очевидно се дължи на специфичността на локалните водни източници, като например свойствата и състава на земната кора и почвата. Интересно е да се отбележи, че химичният състав на изворните води се различава съществено от този на минералните води от същия район. Получените резултати свидетелстват за стабилността на химичния състав, както и за липсата на замърсяване на изследваните води за продължителен период на съхранение (до 2.5 години след бутилирането).