Multivariate statistical assessment of Bulgarian bottled mineral and spring waters

V. V. Mihaylova*, V. V. Lyubomirova, R. G. Djingova

Trace Analysis Laboratory, Department of Analytical Chemistry, Faculty of Chemistry and Pharmacy, Sofia University "St Kliment Ohridski", 1 J. Bourchier Blvd., 1164 Sofia, Bulgaria

Received: May 27, 2021; Revised: July 02, 2021

Water is essential to human life. Our bodies need a certain amount of water intake on a daily basis to function appropriately. Several health benefits have been attributed to the mineral and trace element content of mineral and spring waters. Although the quality of drinking water depends to a large extent on its microelement composition, only limited data are available about trace element content in Bulgarian bottled spring waters. In this study, using ICP-MS a simultaneous determination of 69 chemical elements in bottled spring waters has been performed and the results were compared to the previous analysis obtained for bottled mineral waters sold on the Bulgarian market. The data for both types of water (mineral and spring) prove that all determined elements are below Bulgarian Regulation No 9 of maximum admissible levels. Only Fe in one brand of spring water is slightly higher than Bulgarian health-based value but lower than EPA. Multivariate statistics (cluster, discriminant and factor analysis) were used to reveal groups of similarity among the investigated mineral and spring waters. For everyday use, along with the alternation of different brands of mineral water also change of the water type might be recommended.

Keywords: Spring waters, Mineral waters, Element composition, ICP-MS, Multivariate statistics.

INTRODUCTION

Water makes up 60-75% of human body weight and is the most consumed natural product. It is the only zero-calorie, zero-sugar and additive-free beverage that will ensure a healthy form of hydration. Most people in the EU have good access to high quality drinking water. According to the European Federation of Bottled Waters, the consumption of bottled water in 2019 in Bulgaria was 100 liters *per capita* for drinking purposes [1]. It is also worth mentioning that within the EU, the consumption of bottled mineral water surpasses more than five times that of spring waters [2].

The market of bottled waters is expanding worldwide thanks to health concerns and/or successful marketing [3]. According to the European Federation of Bottled Waters (EFBW) the three types of bottled water: natural mineral, spring and table water differ in respect to origin and applied legislation rules [4]. Both mineral and spring waters originate from recognized underground water sources. They are microbiologically safe. The main difference is that stable mineral balance is typical for natural mineral waters but is not required for spring waters and mineral composition is not demanded on the label of spring water bottles.

Investigations of the element concentrations in bottled waters are mainly directed to natural mineral waters and the number of publications is growing, covering all continents and countries [5−7]. The reason obviously is that mineral waters are mainly recommended for health reasons and the concentrations of major and some trace elements are object of national standards. Although also of natural origin spring waters are rarely investigated or not mentioned explicitly in the study. Many papers report results for bottled waters without description of the type of waters or separate discussion, using other types of classification of bottled waters [7]. In some cases, spring, mineral and table waters are analyzed and discussed together disregarding their different origin and pretreatment [8, 9].

Bulgaria is one of the richest countries in mineral water resources and the bottled mineral waters are certified and controlled [10]. Not so the spring waters although usually they are recommended for daily use because the mineral content is considered to be lower. On the bottle labels concentrations of major elements are given but information for trace elements concentrations is nowhere to be found [11, 12].

Detcheva *et al.* [13] compared the concentrations of 13 elements in a random selection of 7 mineral, 2 spring and 1 table waters. The results indicted stability in the composition with the time of bottling and certain similarity in the composition of some of the samples.

The aim of the present paper is to perform a comparison of the chemical composition of eight spring waters with previously published data for mineral waters [14] available on the Bulgarian market for a maximum number of elements and

*To whom all correspondence should be sent:
E-mail: ahvm@chem.uni-sofia.bg

provide basis for the correct choice of suitable drinking water, both for daily needs and after medical recommendation.

EXPERIMENTAL

Bottled mineral and spring water samples

Fig. 1 presents a map of Bulgaria with the mineral and spring water deposits where production of bottled water is allowed. Seventeen brands of mineral waters were subjected to analysis and the results are discussed in details in Lyubomirova *et al*. [14]. Additionally, eight brands of spring water available in the commercial network were purchased: three brands (Devin, Baldaran and Billa) are originating from the same spring (spring Baldaran, village Fotinovo, Rhodope mountains), Bachkovo (spring "Badjova cheshma", village Bachkovo, Rhodope mountain), Rilana (drilling Rilana No 962, Stob village, Rila mountain), H_2O pure (source Puknatinni vodi – Peshtera-Dospat, Bratsigovo village, Rhodope mountains), Mihalkovo (Natural source Peshtera – Chiflika, Rhodope mountains) and Zeolite water (spring Balkan mountains, filtered through natural zeolites).

Fig. 1. Simplified map of Bulgaria with the locations of the registered mineral (in blue) and spring (in pink) water deposits.

ICP-MS analysis

The spring waters were analyzed using ICP-MS (Perkin-Elmer SCIEX Elan DRC-e) with cross-flow nebulizer. The concentration of 69 elements (Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, In, Ir, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, Os, P, Pb, Pd, Pr, Pt, Rb, Re, Rh, Ru, Sb, Sc, Se, Si, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, Zr) were determined as described in Lyubomirova *et al.* [14]. The macroelement (Na, Mg, Si, K and Ca) concentrations were determined by the application of a Dynamic Bandpass Tuning parameter – RPa as described in Lyubomirova *et al.* [15]. The concentrations of arsenic and selenium were determined in a DRC mode [16] for the elimination of Ar-based polyatomic interferences.

Analytical characteristics of the method

The accuracy of the method was checked by analysis of two water SRMs: SPS-SW2 (Reference Material for Measurement of Elements in Surface Waters, Spectrapure Standards, Norway) and NWTM-23.5 (Environmental matrix reference material, a trace element-fortified sample, Environment and Climate Change, Canada). The experimental results were in very good agreement with the certified values. The average recovery for each element concentration was calculated based on the obtained results and the certified values. The results showed that the current method had good recovery (from 98.9 % to 101.6 % for macroelements, from 99.6 % to 100.4 % for microelements and from 99.5 % to 101.3 % for trace elements).

All samples were analyzed in triplicate to assess the precision of the analysis, which is in the interval 1-9 %.

Statistical analysis

The statistical analyses were performed by STATISTICA 7.0 software package. The analytical data were subjected to cluster, discriminant and factor analysis. Although 69 elements were determined, not all of them were used in the statistical analysis. The concentrations of Ag, Au, Be, Cd, Dy, Er, Eu, Gd, Ho, In, Ir, La, Lu, Nb, Nd, Os, Pb, Pd, Pr, Pt, Re, Rh, Ru, Se, Sm, Sn, Ta, Tb, Tm and Yb which exhibited values usually lower than the limit of detection (LOD) of the method were excluded. A data matrix with 17 mineral water and 8 spring water samples and 39 variables was formed. The data were treated by hierarchical cluster analysis, based on the Ward's method algorithm and the squared Euclidean distance. To verify the correct classification of the mineral and spring samples obtained by cluster analysis, a discriminant analysis with the same 39 variables was performed. The posterior probability for the samples to belong to each group was automatically calculated by the STATISTICA 7.0 statistical software programme.

Factor analysis was also used in the current investigation as a multivariate exploratory technique, which can be used to uncover the latent structure of a set of variables. The Kaiser criterion [17] was applied to determine the total number of factors for each dataset in this analysis. Under this criterion, only factors with eigenvalues greater than or equal to 1 are accepted as possible sources of variance in the data, with the highest priority ascribed to the factor that has the highest eigenvector sum. The rationale for choosing 1 is that a factor must have a variance at least as large as that of a single standardized original variable to be acceptable.

RESULTS AND DISCUSSION

Element concentrations

The concentrations of 55 elements in the spring waters are presented in Table 1 and the mineral water content is presented in [14].

The data for both types of water (mineral and spring) prove that all determined elements are below Bulgarian Regulation No 9, 2001 [18], WHO, 2017 [19] and EPA, 2018 [20] maximum admissible levels. Only Fe in Bachkovo (see Table 1) spring water is slightly higher than Bulgarian health based value but lower than EPA. The concentrations of Dy, Er, Gd, Ir, Lu, Pb, Pd, Pt, Re, Ru, Sm, Ta, Tm, Os, were below the LODs in all the samples of the spring waters and are not presented in the table. The experimentally determined LODs for Dy, Er, Gd, Ir were 0.001 µg/L, for Lu, Os, Pb, Pt, Re and Ru were 0.002 µg/L and for Sm, Ta, Tm were 0.003 µg/L.

Table 1. Element concentrations (µg/L) in Bulgarian spring waters.

Element	Billa	Bach-kovo	Rilana	Devin	Baldaran	H_2O pure	Mihal-kovo	Zeolitna	BG-Reg N9	WHO	EPA
Ag	0.042	0.026	0.011	0.005	<0.003	0.005	0.005	<0.003		100**	
Al	5.18	1.08	0.34	20.2	25.8	2.69	5.89	<0.011	200*	900**	50-200***
As	0.27	1.83	0.20	0.27	0.29	0.89	0.27	0.14	10	10	10
Au	0.02	0.05	0.02	0.02	0.03	0.01	<0.001	<0.001			
B	1.08	41.3	1.31	1.94	2.62	16.1	2.62	0.68	1000	2400	
Ba	0.53	19.2	23.3	1.29	1.08	16.5	5.53	2.71		1300	2000
Be	<0.008	0.066	<0.008	<0.008	<0.008	<0.008	<0.008	<0.008			4
Bi	1.66	1.76	0.19	0.37	0.29	0.36	0.078	0.047			
Ca mg/L	5.83	74.5	18.4	6.02	5.97	51.5	20.7	0.70	150*		
Cd	0.003	0.010	<0.001	<0.001	0.024	<0.001	<0.001	<0.001	5	3	5
Ce	0.004	<0.001	<0.001	0.043	0.032	<0.001	<0.001	<0.001			
Co	0.014	0.15	0.055	0.007	0.010	0.058	0.027	<0.001			
Cr	1.24	2.49	1.47	0.39	0.46	1.73	1.42	1.41	50	50	100
Cs	<0.001	10.6	0.002	<0.001	0.005	0.019	<0.001	0.048			
Cu	<0.011	<0.011	0.36	<0.011	<0.011	0.40	0.038	0.049	2000	2000	1300
Eu	<0.001	0.005	0.007	<0.001	<0.001	0.002	<0.001	<0.001			
Fe	23.1	258	72.0	27.9	37.3	119	65.9	<0.014	200*		300***

Ga	0.060	0.078	0.018	0.014	<0.003	0.051	0.028	0.058			
Ge	<0.001	0.67	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001			
Hf	0.14	0.35	0.035	0.079	0.053	0.52	0.011	0.93			
Hg	0.02	0.05	0.02	0.02	0.03	0.01	0.03	0.05	1	6	2
Ho	0.002	0.003	<0.001	0.003	<0.001	0.002	0.002	<0.001			
In	0.002	0.005	<0.001	<0.001	<0.001	<0.001	<0.001	0.026			
K mg/L	0.84	3.73	2.99	0.93	0.95	3.63	1.67	13.8			
La	<0.001	0.002	0.008	0.007	0.004	0.004	0.008	<0.001			
Li	3.37	61.6	0.83	2.73	2.82	4.71	0.53	0.024			
Mg mg/L	0.32	8.50	2.69	0.29	0.34	6.56	0.64	0.099	80*		
Mn	<0.007	<0.007	<0.007	0.039	<0.007	<0.007	0.86	0.025	50*	400**	50***
Mo	0.23	0.42	0.10	0.045	0.055	0.096	0.036	0.26		70**	
Na mg/L	5.26	25.4	3.96	5.78	5.75	28.9	3.59	0.87	200*	50	
Nb	0.01	0.03	0.01	0.02	<0.001	0.03	<0.001	<0.001			
Nd	0.012	<0.003	0.024	0.009	0.004	<0.003	<0.003	<0.003			
Ni	<0.008	5.79	0.21	<0.008	0.10	1.34	0.62	<0.008	20	70	
P	73.8	1.50	80.2	73.3	96.5	34.4	68.1	20.6			
Pr	0.003	0.003	<0.002	0.004	0.003	<0.002	<0.002	<0.002			
Rb	0.60	11.4	0.27	0.65	0.71	3.56	1.33	2.42			
Rh	<0.001	0.01	<0.001	<0.001	<0.001	0.02	0.01	<0.001			
Sb	1.29	1.68	0.93	0.94	0.52	0.82	0.50	1.37	5	20	6
Sc	13.34	5.11	4.83	12.93	13.26	18.8	9.93	0.24			
Se	1.57	1.56	0.44	0.68	<0.012	0.45	<0.012	0.87	10	40	50
Si mg/L	13.4	5.52	4.94	13.3	14.1	23.4	11.8	0.15			
Sn	0.11	0.15	<0.007	0.07	<0.007	0.11	<0.007	0.16			
Sr	27.6	243	89.9	30.5	29.3	229	47.5	5.84			
Tb	0.002	0.002	<0.001	<0.001	<0.001	<0.001	0.003	<0.001			
Te	0.23	0.64	0.19	0.045	0.14	0.23	0.23	0.70			
Th	0.14	0.098	0.012	0.050	0.043	0.038	0.012	0.73			
Ti	1.20	352	87.4	2.78	9.85	184	73.6	1.07			
Tl	0.009	0.030	<0.006	<0.006	0.009	<0.006	0.013	0.050			2
U	0.19	5.29	0.025	0.20	0.24	1.56	0.17	0.006	30	30	30
V	0.57	0.57	0.47	0.53	0.64	0.39	0.60	0.11			
W	9.44	21.1	1.79	3.03	1.98	2.85	1.39	22.1			
Y	<0.001	<0.001	0.007	0.003	0.003	<0.001	0.006	<0.001			
Yb	<0.003	<0.003	<0.003	0.006	<0.003	0.004	<0.003	0.004			
Zn	0.17	1.90	0.66	<0.002	<0.002	1.20	<0.002	<0.002	4000*		5000***
Zr	0.18	0.65	0.012	0.10	0.042	0.22	0.018	1.12			

*- Indicator value, **- Health-based value, *** - Secondary Drinking Water Regulation

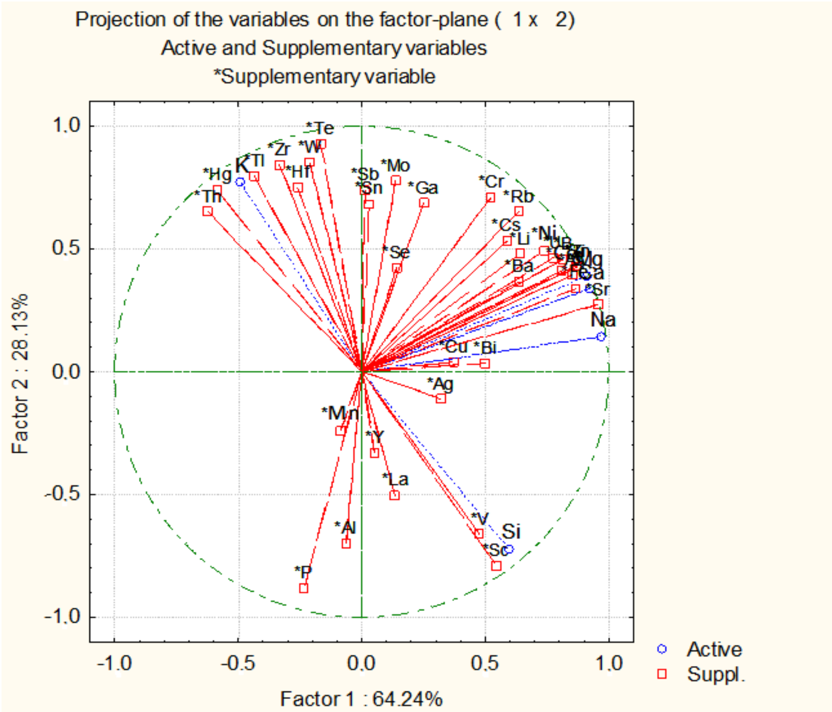

Fig. 2. Two-dimensional plot of projection of the elements on the factor plane

Statistical assessment of the data

Factor analysis was applied to investigate interelement and geochemical correlations among the determined elements in all investigated water samples. The performed factor analysis of the data set revealed three latent factors, explaining 92.37% variance. Figure 2 presents two-dimensional plot projections on the factor plane.

Highest factor loadings in Factor 1 have alkali (without K) and alkaline earth elements, Ti, Fe, Cr, Co, Ni, Zn, As, U and B. Factor 2 includes K, Si, P, V, Zr, Hf, W, Tl, Th, Sc, Sn. Members of Factor 3 are Ag, Cu, Bi, Se. Factor 1 reflects the presence of elements in Fe-Ti oxide minerals and sedimentary carbonate rocks which are widespread in Northern Bulgaria [21]. The Moesian Platform of Northern Bulgaria originates from Hercynian deformation and is mantled by shelf-type Mesozoic and Tertiary carbonate rocks. The elements in Factor 2 are usually present in different combinations in potassium silicates distinctive for the Rhodope massif of southern Bulgaria, which is a mountainous terrain of Precambrian and Paleozoic crystalline rocks [21, 22]. The combination in Factor 3 indicates polymetallic veins [23, 24].

To establish groups of similarity in the chemical composition of the analyzed samples cluster analysis was performed and the respective dendrogram is presented on Fig. 3. A data matrix with 17 mineral water and 8 spring water samples and 39 variables was formed, as described in the experimental part. The samples were combined in two groups and one outlier. The statistical validity of the classification was confirmed by discriminant analysis and the result is presented on Fig. 4.

Cluster 1 includes all mineral waters with the exception of Voditsa and Dragoynovo which join cluster 2 where all spring waters are grouped. The Zeolite water is an outlier. The two-dimensional plot after discriminant analysis (Fig. 4) confirmed the results from the cluster analysis.

The elements responsible for this grouping of the samples are the macroelements - Na, Ca, K, Si and Mg. This result indicates that the major difference between mineral and spring water is the concentration of major elements. Fig. 5 presents the ratio of the average concentrations in the obtained clusters. Na and Si are substantially higher in cluster 1 where the majority of mineral waters are grouped while K, Ca and Mg are higher in cluster 2 including all spring waters and two mineral waters. It is worth noting the differences between Na and Ca, whose average concentrations differ significantly not only in the obtained clusters, but also in the average concentrations of the mineral [14] and spring waters. The average concentrations of K and Mg are also higher in the spring waters compared to the majority of the mineral waters. The only exception is the mineral water Mihalkovo with acidic pH and higher mineral content. The higher average K, Ca and Mg concentration in the group of the spring waters contradicts to a certain extent the accepted opinion that spring waters are much more suitable for everyday use compared to mineral waters due to lower mineral content.

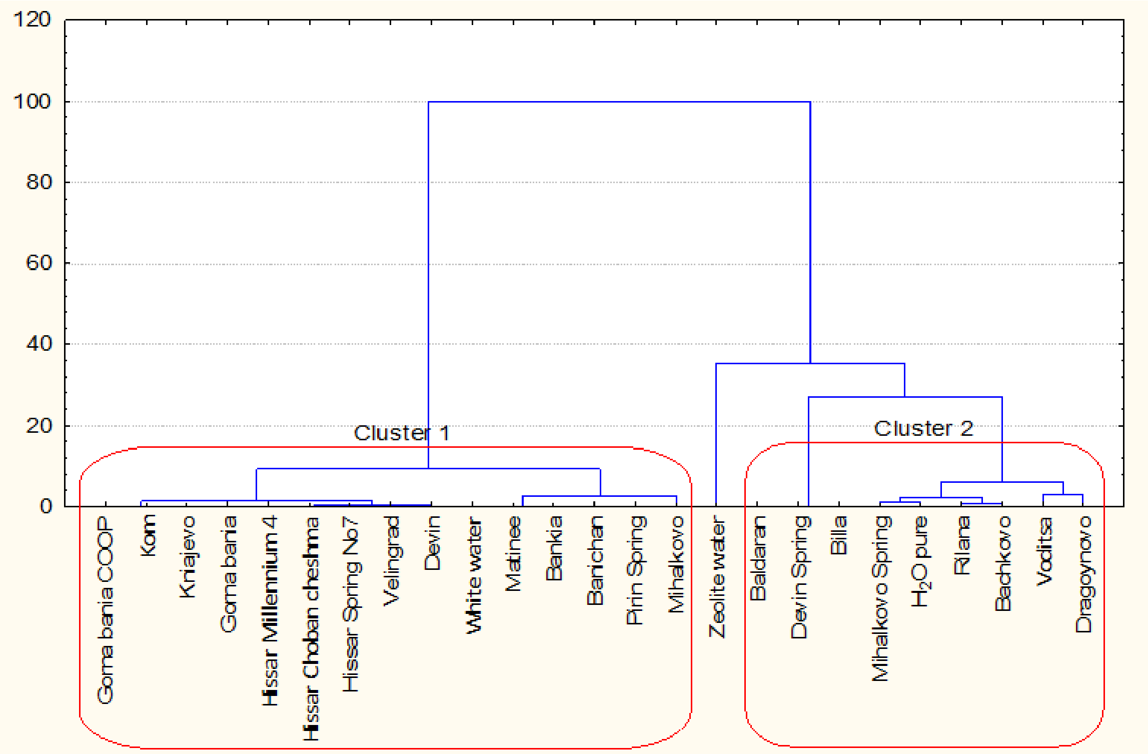

Fig. 3. Dendrogram from the cluster analysis of Bulgarian mineral and spring waters.

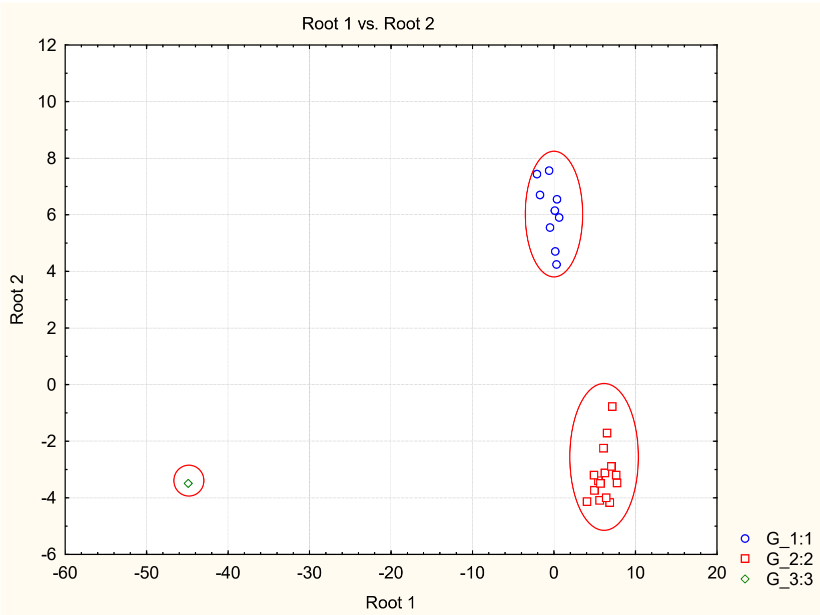

Fig. 4. Two-dimensional plot after discriminant analysis of Bulgarian mineral and spring waters.

Higher mineral content however does not mean that the water has more harmful effects because the concentrations are lower than the maximum permissible level [14], moreover, the effect on an organism depends on their form. For instance, Na in bicarbonate form is considered to have a beneficial effect on blood pressure and metabolic activity [24, 25] while NaCl might show some negative effect. Bulgarian mineral waters are mainly of the $NaHCO_3$ type and may be considered having positive influence on the organisms [14].

The finding about the difference in the concentrations of spring to mineral waters is justified specifically for Bulgarian waters. The lack of information for European bottled spring waters hinders the possibility to conclude whether such tendencies in the element concentrations exist in other regions as well.

However, it is not the total mineral concentration that is important but there is a specific tendency in the element distribution. The microelements' contents are an important part of healthy human diet. Their concentrations in mineral waters are controlled in respect to toxicity while in spring waters the content of microelements is not officially under control.

To compare the concentration of microelements in the analyzed waters and look for similarity groups cluster analysis of the samples was performed. The resulting dendrogram is shown on Fig. 6.

The result from the cluster analysis of microelements showed the formation of four clusters. Cluster 1 includes the mineral waters Kniajevo, Gorna Bania COOP, Gorna Bania - all three samples are from Sofia region where host rocks contain up to 1.1 % Ti, 11.6% Al, 10.5 % Fe, 0.52% P, 0.5 % Sr, 160 µg/g Zn, 70 µg/g Li, which were the elements corresponding to the clustering results [26]. Cluster 2 includes Banichan, Pirin Spring, Kom, Devin, Hissar Choban cheshma, Hissar Millennium 4, Hissar Spring № 7, White water, Velingrad, Mihalkovo. The mineral water deposits are located in the Rhodope, Rila and Pirin mountain regions in Southern Bulgaria region where the host metabasic rocks contain up to 10.3 % Al, 6.7 % Fe, 0.46 % Ti and 0.052 % P [27]. Cluster 3 includes 3 spring waters (Baldaran, Devin Spring and Billa) all of them originating from the same source but bottled by different suppliers and the outlier Zeolite water. Cluster 4 combines 4 mineral (Matinee, Bankia, Voditsa and Dragoynovo) and 4 spring waters (Mihalkovo, Rilana, H_2O pure and Bachkovo) in one group indicating significant similarity in the chemical composition irrespective of the difference in their type and origin.

The spring waters in cluster 4 originate from the Rhodope - Rila mountain region and have similar geochemical background [27]. Obviously, they have different microelement concentrations from the mineral waters from the same region members of the second cluster. The mineral waters in cluster 4 originate from different regions which are not geologically similar. The elements responsible for the grouping are Al, P, Li, Sr, Ti, W and Fe.

There is direct connection between Al, Fe and P during the process of their release from soils and sediments to water depending on acidification and redox processes. It is considered that P may be liberated by reductive dissolution of $Fe(OH)_3$ but remains absorbed on $Al(OH)_3$ [28, 29]. Thus the established similarity in the microelement concentrations of the mineral and spring waters in cluster 4 might be attributed to local redox processes influencing the release of microelements.

CONCLUSION

The results from the present investigation indicate quantitative and qualitative difference in the macroelement concentrations of spring and the majority of mineral waters in spite of the similarity established between certain mineral brands and spring waters. The comparison of microelements also established mixed similarity groups mineral/spring waters. Thus for daily use except the change between types of water (mineral/spring), a change of the water brands may be recommended. Additionally, attention should be paid to the water source since a single source is used by several producers for bottling different brands of water.

The results however confirm that the element concentrations in Bulgarian bottled waters meet all national and international safety standards.

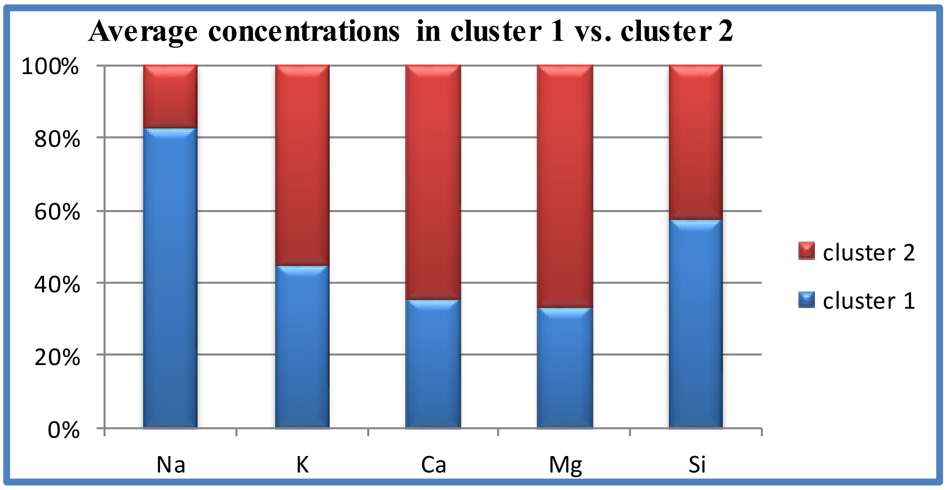

Fig. 5. Ratio of the average concentrations in the clusters.

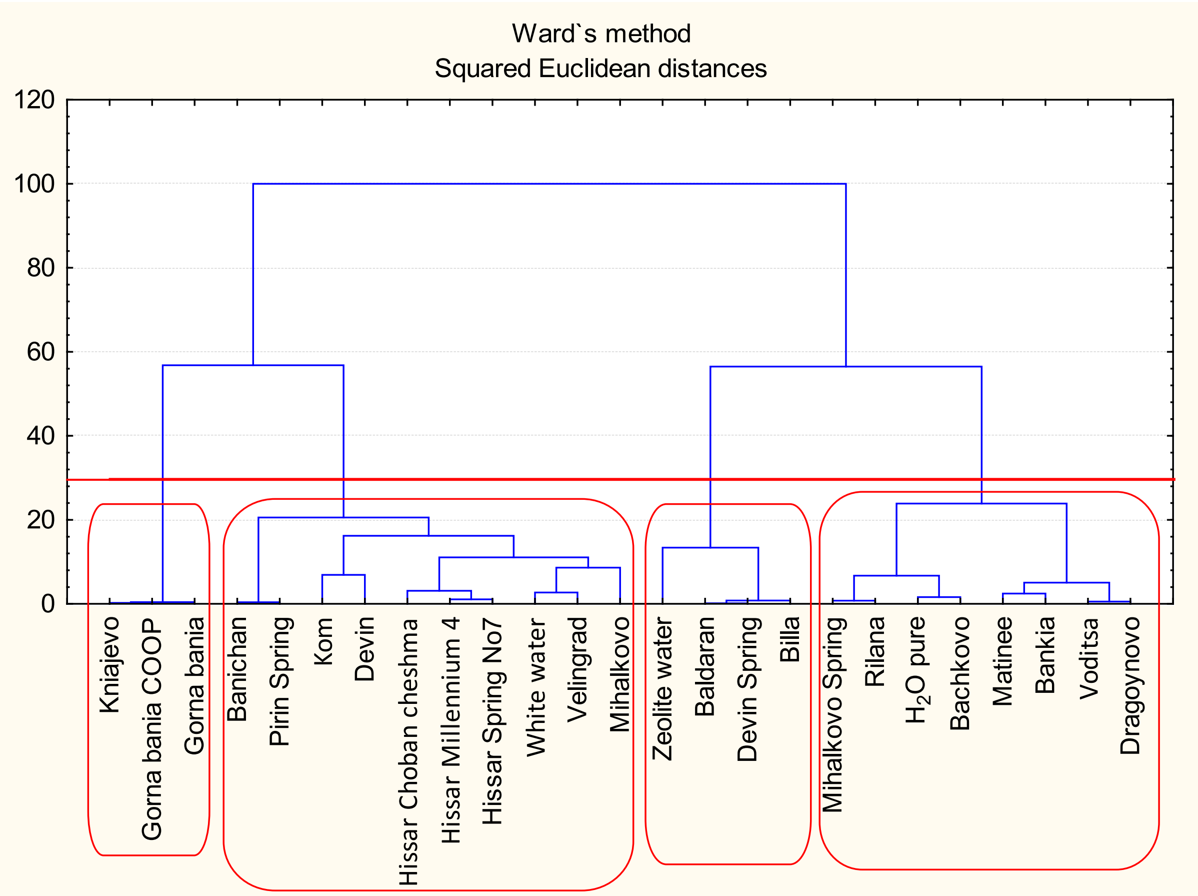

Fig. 6. Similarity groups based on microelement composition of the water samples

Acknowledgement: *This work is part of project BG05M2OP001-1.002-0019: „Clean technologies for sustainable environment – water, waste, energy for circular economy" (Clean&Circle) 2018 – 2023, for development of a Centre of Competence, financed by the Operational programme "Science and Education for Smart Growth" 2014-2020, co-funded by the European Union through the European structural and investment funds.*

Research equipment of Distributed Research Infrastructure INFRAMAT, part of Bulgarian National Roadmap for Research Infrastructures, supported by the Bulgarian Ministry of Education and Science was used in this investigation.

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