SHORT COMMUNICATIONS

Major Inorganic Ions in Bottled Waters from Several Polish and Romanian Mineral Waters

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Abstract

Mineral waters are important sources of micro- and macroelements for humans, thus its composition ought to be supported with good knowledge on their chemical composition and be controlled systematically. The aim of the study was to analyze the content of common inorganic cations in 9 Romanian and 9 Polish bottled waters, and compare the results of the analyses with the product label's data. The novelty was the application of new analytical method (atomic emission spectrometry with microwave plasma) for this approach. A short chemometric evaluation of the obtained results was carried out, highlighting in many cases significant differences between the values declared by the producers and the obtained results; possible reasons of this situation are discussed.

Keywords: calcium, magnesium, mineral water, potassium, sodium

Introduction

Depending on its source, mineral water contains various amounts of macro and microelements that have a significant impact on living organisms. Among them very important are Na, K, Mg and Ca. Sodium salts are found in virtually all food as well as in different water types (e.g. drinking and mineral water). No firm conclusions can be drawn concerning the possible association between sodium in mineral water and the occurrence of hypertension, therefore no health-based guideline value is proposed (Bertoldi et al., 2011).The same is with potassium which is an essential element in humans and is seldom found in mineral water at levels that could be a concern for healthy humans. Both calcium and magnesium are essential to human health. While the concentrations of calcium and magnesium in drinking and mineral water vary markedly from one supply to another, mineral rich waters may provide substantial contributions to total intakes of these nutrients in some populations. Magnesium is the fourth most abundant cation in the body and the second most abundant cation in intracellular fluid (Cabot, 2004). Inadequate intakes of calcium have been associated with increased risks of osteoporosis, nephrolithiasis, colorectal cancer, hypertension and stroke, coronary artery disease, insulin resistance and obesity (Diduch et al., 2011). If the contents of these elements in the organism are not appropriate, several imbalances may occur. Mineral water can be admitted for consumption only when the concentrations of its constituents do not exceed the standards specified in various legal regulations, if any (EU 2003/40/EC).

To increase the consumption of mineral waters some companies emphasize therapeutic values of the specific brand, and although it is expected that the content of minerals, trace minerals and other constituents must fit declared composition, it is common that declared and analyzed composition may differ. Therefore, widespread and frequent monitoring surveys should be carried out on one side to monitor the levels of dissolved constituents, and on the other side to check an agreement between factual and declared composition. Analysis of alkaline and alkaline earth metals may be difficult, due to: low levels of individual compounds present in samples; complex compositions (high mineralization degree); interactions between the constituents present in samples; and possible changes in the composition during transport and storage resulting from reactions and potential desorption of constituents from the packaging materials (Kończyk et al, 2019). Although there are many papers dealing with mineral water quality, only a few of them, relatively old papers were devoted for alkaline and alkaline earth metals in mineral waters (Astel et al., 2014; Gros and Gorenc, 1995; Birke et al., 2010; Carstea et al., 2016).

Materials and methods

The subject of the study was 18 mineral water available in Polish and Romanian markets. Waters were divided into non-carbonated, lightly carbonated and carbonated. The PET bottle volume was usually 0.5 L or 1.5 L, however there were also 0.33-L and 1.0-L bottles. Sodium, potassium, magnesium and calcium were determined by using microwave plasma – atomic emission spectroscopy (MP-AES). MP-AES is relatively new instrumental method, which is applied for metal and metalloids analysis mainly in complex matrices samples. It allows for fast, relatively cheap and reliable analysis of several elements (Tanabe et al., 2016).

Studies were performed using microwave plasma atomic emission spectrometer Agilent Technologies type MP 4200-AES. The plasma within an MP-AES atomizes and partially ionizes a stream of nitrogen gas that is laden with an aerosol of the solution being analyzed. Accordingly, the spectrum of light being radiated by the plasma contains wavelengths that are emitted by the nitrogen plasma and vaporized solvent, which yields the background signal; and also contributions from the solutes and suspended solids that include the elements of interest.

The sparkling and lightly sparkling mineral water samples were degassed in a ultrasonic bath (Labindex, Poland) before the analysis. The examined water samples were filtered through a 0.2-μm nitrocellulose filter (Whatman, USA). Samples which contained high concentration of analytes had been diluted appropriately by deionized water.

Standard solutions of specific elements were made with the Fluka reference materials (Steinheim, Switzerland); their concentrations amounted to 1000 ± 2 mg/L. Water used for standards and eluents preparation came from a Millipore deionizer (Merck, Germany); its electrical conductivity was < 0.07 μS/cm. Calibration solutions were made by diluting appropriate standard solutions right before their application. All solutions were kept in glass or high-density polyethylene (HDPE) containers at room temperature.

The calibration was performed in compliance with currently accepted procedures (ISO 8466-1). Six standard solutions which contained various concentrations of given metals were prepared

Table 1. The validation parameters of applied MP-AES method.

Element	Wavelength [nm]	The type of the calibration curve	The range of the calibration curve	Limit of Detection LOD	Limit of quantification LOQ	Corellation coefficient (r)
			[mg/L]	[μg/L]^3	[μg/L]^3	
Na	588.995	linear	1.0 – 10.0	1.7	5.2	0.99934
K	766.491	linear	1.0 – 20.0	2.6	7.8	0.99912
Ca	393.366	linear	1.0 – 5.0	3.1	9.3	0.99952
Mg	403.076	linear	1.0 – 20.0	1.9	5.8	0.99998

for validation purposes. Each solution were analysed in triplicate. The obtained data were used to calculate: standard deviation, variation coefficient, limits of detection and quantification, and correlation coefficient. The validation results are given in Table 1.

The data matrix was prepared and processed in Excel (Microsoft, USA), then principal component analysis (PCA) and cluster analysis were performed using MatLab (The Mathworks, USA) after mean center preprocessing.

Results and discussion

In Table 2 are given obtained average results (from three replicates) for results obtained by MP-AES method and producer data (PD), if any.

Chemometric analysis of experimental data was based on principal component analysis (PCA). The following models were built on seven variables (concentrations of sodium, potassium, magnesium and calcium) having two principal components. Besides outlining similarities in the composition of the studied mineral water samples, this approach helps in a fast identification of potentially "harmful" mineral waters.

PCA of the experimental data lead to a four variables model, having the cations' concentrations as variables, which explains 94.63% of data variability; the biplot from figure 1 highlights a close correlation between the concentrations of magnesium and calcium in the analysed samples. PCA reveals two classes (figure 2), confirmed by cluster analysis (Ward's method, using PCA – figure 3) and one outlier.

Table 2. Producer's data and obtained results for MP-AES methods

Water name	Na		K		Ca		Mg	
	MP-AES	PD	MP-AES	PD	MP-AES	PD	MP-AES	PD
Non-carbonated waters								
Nałęczowianka	11.97	10.00	4.51	2.40	30.59	114.20	19.23	21.30
Dobrowianka	3.54	2.00	1.25	0.00	27.77	58.10	25.55	33.42
Polanicka	54.52	56.79	6.03	4.97	38.79	161.10	20.01	15.31
Aqua Carpatica	2.11	0.78	1.29	-	45.77	44.90	17.25	14.30
Azuga	2.68	2.40	0.86	0.74	51.40	47.40	7.36	5.98
Dorna	1.75	0.92	0.55	0.40	25.09	63.65	2.46	1.20
Lightly-carbonated waters								
Kinga Pienińska	19.48	9.20	5.24	3.46	12.96	87.00	16.80	12.82
Polaris	9.24	6.85	3.45	2.20	55.50	94.20	14.50	14.00
Muszynianka	125.48	98.00	12.54	9.00	22.59	240.00	134.69	120.00
Borsec	82.29	86.50	22.18	-	29.61	349.80	110.58	107.04
Perla Harghitei	63.17	61.92	12.64	10.57	22.41	112.90	40.71	40.91
Valea Izvoarelor	104.52	92.50	10.40	-	24.73	47.42	15.18	9.42
Vâlcele	302.06	409.30	18.84	13.00	13.74	304.60	242.81	257.80
Carbonated waters								
Ustronianka Biała	7.60	7.24	1.65	1.17	53.78	95.40	19.46	16.70
Polanicka	53.99	56.79	6.43	4.79	27.22	161.10	19.90	15.31
Selenka	13.09	13.35	1.90	1.92	56.90	98.20	17.35	36.46
Zizin	2.26	0.65	0.54	-	54.90	63.30	1.69	2.74
Bucovina	30.63	26.72	6.66	4.32	26.19	264.50	72.52	76.73
Cheile Bicazului	17.54	13.25	8.38	7.00	15.01	95.80	18.91	14.13

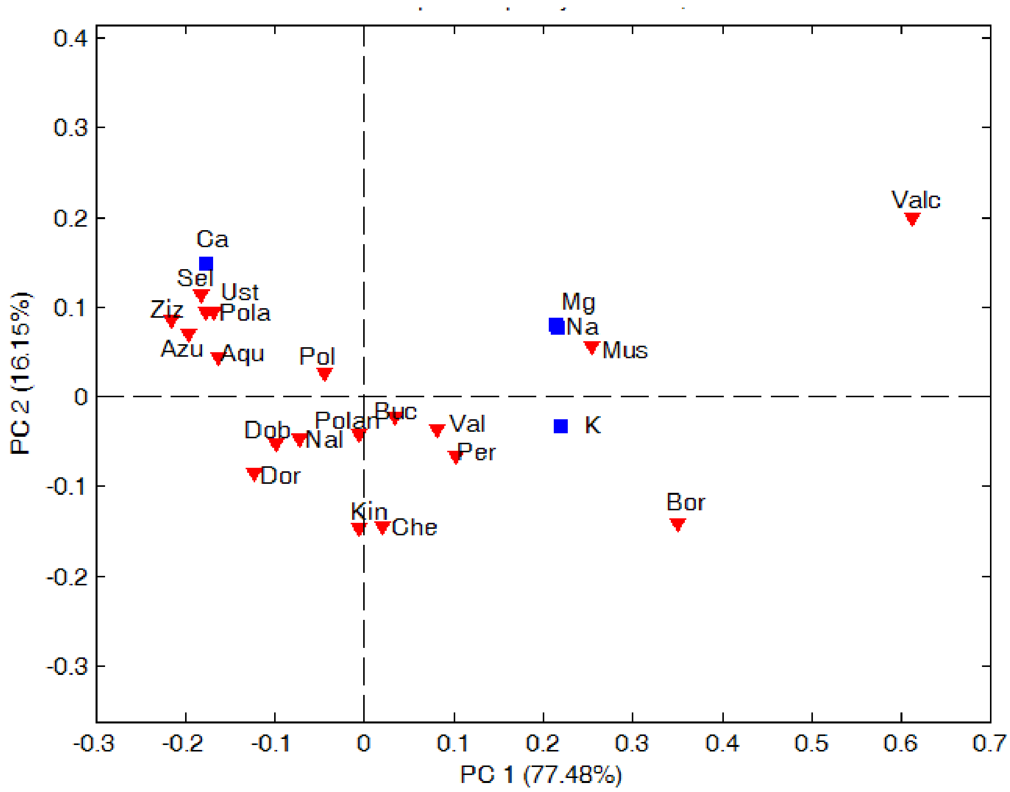

Figure 1. Biplot for the experimental dataset

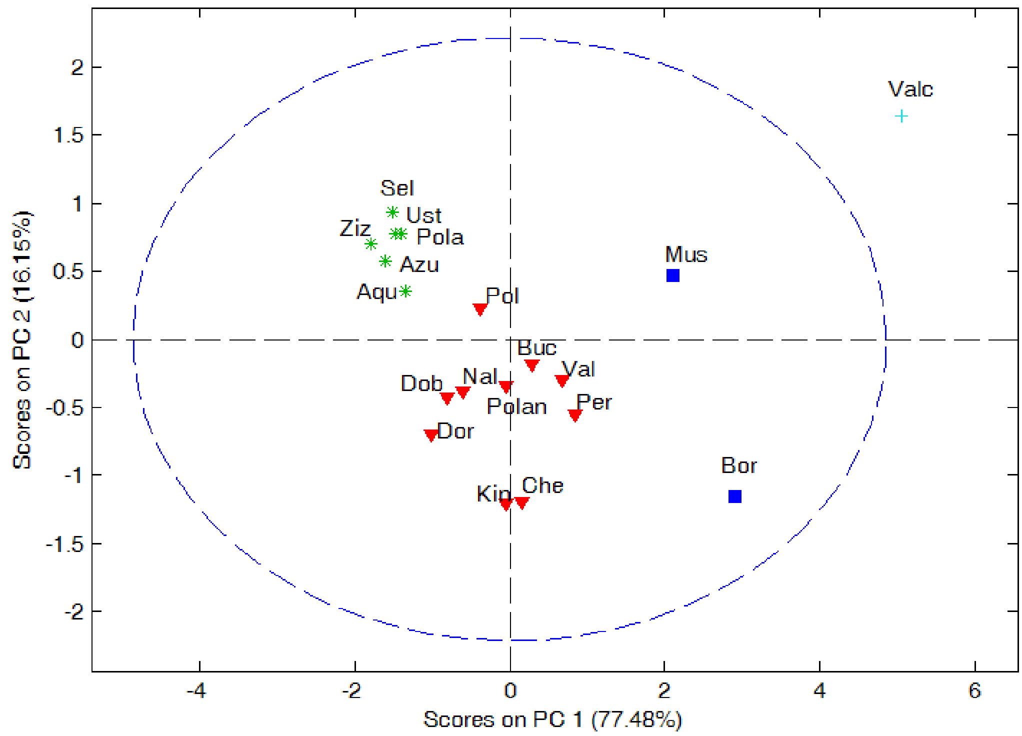

Figure 2. Score's plot for the experimental dataset

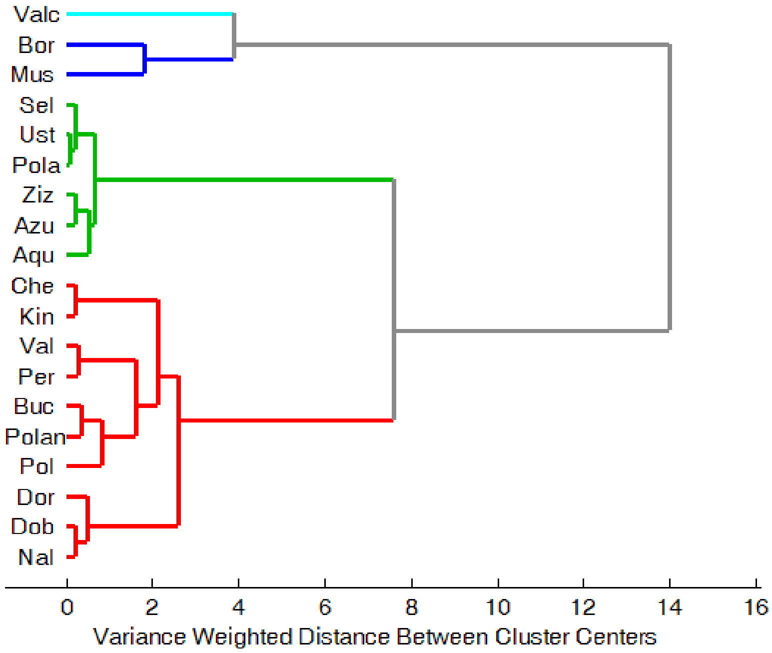

Figure 3. Dendrogram for the experimental dataset (Ward's method)

The smaller cluster consists from three Romanian (Aqua Carpatica and Zizin,) and two Polish (Selenka and Ustronianka Biała) mineral waters with highest calcium concentrations, the bigger one joining most of the analyzed samples. The Vâlcele brand is an outlier in this dataset given its very high concentrations for the analyses parameters.

According to research hypothesis in some cases significant differences (> 20%) between the ions' concentrations declared by producers and obtained in our research were found. Some important examples are: for sodium (Kinga Pienińska and Zizin); for potassium (Nałęczowianka); for calcium (Nałęczowianka, Muszynianka, Polanicka, Valea Izvoarelor and Cheile Bicazului, and for magnesium (Selenka). The highest differences concern the determination of calcium, which may be related to the specificity of the applied MP-AES method. Some other possible reasons for this can be: the method and duration of water storage, the impact of the applied technologies of water preparation and the use of analytical methods without validation. Moreover, the quality of bottled water is highly dependent both of the geochemical features and the anthropogenic pollution. Unfortunately, due to the lack of data, it is not possible to precisely determine the geological and geographical impact on analysed waters. This would require a much wider range of research.

Conclusion

There are opinions that if the chemical content of mineral water and drinking water is similar, so that we can overpay unnecessarily buying certain brands of expensive mineral waters. Due to the large time variability (annual variability) and randomness (meteorological phenomenon), the waters' sources should be supervised and controlled as often as it is required by the current situation, not necessarily according to legislator's requirement(s). The majority of mineral water's producers do not inform about the specific water composition, because regulations do not require it. Contrary to inorganic anions, mineral water producers often give the information about the content of sodium, potassium, calcium and magnesium on the labels, praising their own water. It is because these metals have a positive influence on our health and it is very good from the marketing point of view to add that information. As a common question arises frequently from consumers: "which mineral water is the best?", it is difficult to give a generally valid answer, since it depends both on consumers' preferences and on their health status.

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