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Characterization of some bottled Romanian mineral waters on the basis of the total mineral content

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Abstract. Romania has many mineral water sources due to its geological features. In the present study, bottles of 26 Romanian mineral water brands were purchased from the market to make a characterization based on the pH, conductivity, and fixed residue content. Focusing on the total fixed residue, the distribution of low, medium, and highly mineralized water was 43.9%, 41.46%, and 14.63% respectively. The mean of fixed residue concentration was 763.3 mg/L, ranging from 40.37 mg/L to 2,603 mg/L. The pH values of the still mineral waters varied between 6.86 and

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7.91, while the pH values of the sparkling mineral waters were the lowest (4.7). The conductivity was strongly related to the concentration of the ions, so the maximum measured conductivity for the still waters was 573 μS/cm, for the partially sparkling waters 2,133 μS/cm, and for the sparkling mineral waters 3,079 μS/cm. The chemical composition of the mineral waters was highly dependent on the rock types. Using the hierarchical cluster analysis, two different clusters were detected according to the main characteristics of mineral waters.

1 Introduction

Romania owns 60% of the hydro-mine sources in Europe, but only one-fifth of these resources are exploited (*FRD Center Market*, 2016). According to the EU legislation (80/777/EEC): "mineral water is microbiologically wholesome water from an underground aquifer tapped via one or more natural or drilled wells" (*The Council of the European Communities*, 1980). According to the definition of the Food and Drug Administration, mineral water contains at least 250 mg/L of dissolved solids originated from a biologically and physically protected underground water source (*Sharma*, 2017).

According to the literature, the most significant mineral water source with high CO_2 content is found in the Eastern Carpathians due to the Oaş-Gutâi-Călimani-Harghita volcanic chain (*Ionete et al.*, 2015; *Vaselli et al.*, 2002).

The World Health Organization's (WHO) recommendations for the average daily water requirements for women, men, and children are 2.2 L, 2.9 L, and 1.0 L respectively. In the case of hard physical work at elevated temperature, this requirement may be increased to 4.5 L. For a woman in pregnancy and lactation period, the daily water intake should be 4.8 L and 3.3 L respectively (WHO, 2005). Besides body hydration, mineral water consumption supports essential macro-nutrients (Ca^{2+}, Cl^{-}, PO_4^{3-}, Mg^{2+}, K^{+}, Na^{+}, SO_4^{2-}) and micro-nutrients at trace levels (Co^{2+}, Co^{3+}, Cr^{3+}, Fe^{2+}, Fe^{3+}, F^{-}) (*Ingegerd*, 2014; *Quattrini et al.*, 2016; *Whelton et al.*, 2007).

The mineral water bottling process consists of the following operation series: extraction of water from the well, drilling, water filtration, water treatment (iron and manganese removal), carbon dioxide enrichment, and, finally, bottling (*Galanakis*, 2020). The total soluble mineral content of the mineral waters is strongly dependent on CO_2 concentration because the acidulated water dissolves more components from the rocks (*Misund et al.*, 1999). The chemical composition and the mineral variety of water are strongly dependent on the original geological state, the rock types, and some other parameters:

temperature, CO_2 concentration, redox conditions, and adsorption complex type (*Kis & Baciu*, 2014; *van der Aa*, 2003).

The consumption of mineral water types is recommended to different types of meat; therefore, the consumption of CO_2-saturated mineral water is recommended with fatty foods, and the consumption of still mineral water is suitable for fish (*Feru*, 2012). Based on the dissolved mineral content, mineral water with low mineral content is more proper for newborns, and rich mineral water is suitable for sportsmen to compensate the minerals lost in transpiration (*Feru*, 2012).

The chemical composition of natural mineral waters in Romania collected from the original springs was analysed by many researchers (*Kis et al.*, 2013; *Papp & Niţoi*, 2006; *Szakács & Krézsek*, 2006); however, bottled mineral waters were analysed by only a few (*Levei et al.*, 2016).

The main objective of the present research is to investigate the fixed residue, pH, and electrical conductivity of some commercially available bottled mineral waters from the Romanian market and to group them according to the abovementioned properties in order to provide supplementary information for the customers.

2 Materials and methods

In order to determine the pH and the conductivity of the mineral waters, a portable laboratory equipment was used (HI 9828 multimeter, Hanna Instruments). The measurements were carried out at room temperature (20 °C).

For the determination of the fixed residue, the water was evaporated entirely at 180 °C, and the fixed residue was measured using an analytical balance with four decimal precision. For the calculated fixed residue, the following equation was used:

$$\mathrm{Rez}_{fix} = [(m_{sp-dry} - m_{wa-em})/(m_{sp-weet} - m_{wa-em})] \cdot \mathrm{CF}, \qquad (1)$$

where: Rez_{fix} – fixed residue at 180 °C (mg/L); m_{sp-dry} – the weight of the ampoule with samples (solid) after the evaporation (g); m_{wa-em} – the weight of the empty ampoule (g); $m_{sp-weet}$ – the weight of the ampoule with the sample (liquid) (g); CF – conversion factor (10^6).

In order to add the confidence interval to the results, all samples were measured in triplicate. After the determination of the fixed residues, the mineral water brands were categorized into four groups, based on the European legislation: 1 – very low mineral content (< 50 mg/L), 2 – low mineral content

(50–500 mg/L), 3 – medium mineral content (500–1500 mg/L), and 4 – rich mineral content (> 1500 mg/L) waters (*EU Commission Directive*, 2003). According to the CO_2 content indicated on the label of the bottles, the waters were marked with st – still, spp – partially sparkling, and sp – sparkling.

In the local market (Miercurea Ciuc), the following 26 brands were available: *Apa Craiului sp*, *AQUA Carpatica Forte sp*, *AQUA Carpatica st*, *Aquatique st*, *Artesia st*, *Azuga sp*, *Azuga st*, *Borsec sp*, *Bucovina st*, *Cezara light spp*, *Dorna st*, *Harghita Tiva sp*, *Izvorul Zăganului sp*, *K-classic sp*, *K-classic spp*, *Perla Harghitei sp*, *Perla Harghitei spp*, *Poiana Negri cump. sp*, *Siculaqua sp*, *Spring Harghita sp*, *Stânceni sp*, *Tuşnad sp*, *Tuşnad spp*, *Vâlcele sp*, *Wonder Spring st*, and *Zizin st.*

Using the IBM SPSS Statistics 22 version, the hierarchical cluster analysis was used to classify the mineral water brands based on their similarities (centroid clustering method and Euclidean distance), and the results were presented in a dendrogram.

3 Results and discussion

The statistical description of mineral water characteristics based on CO_2 content

The main characteristics of all studied brands are presented in *Table 1.* According to the CO_2 content, the mineral waters were classified into three categories: still mineral waters, partially sparkling mineral waters, and sparkling mineral waters. Still mineral waters had higher pH values, ranging between 6.86 and 7.91. It is well-known that there is a strong correlation between electrical conductivity and mineral concentration – namely, high conductivity indicates a high ion and mineral concentration. The highest fixed residue was measured in the case of highly carbonated mineral water brands (Vâlcele sp – 2604 mg/L, K-classic sp – 2384 mg/L, Borsec sp – 1553 mg/L). Based on the pH value, the partially sparkling mineral waters were situated between the still and sparkling mineral waters, with values between 5.72 and 6.19, while the lowest pH value (Azuga sp – 4.7) was detected in the case of the sparkling mineral water brands. On average, the mineral content of the sparkling and partially sparkling mineral waters was quite similar, exhibiting 1008 mg/L and 987 mg/L respectively.

Table 1. Statistical description of the studied mineral waters

		N	Min.	P(25)	Mean	Med.	P(75)	Max.
Still mineral water	pH	8	6.86	7.49	7.59	7.73	7.83	7.91
	Cond. μS/cm		93	182	298	296	365	573
	Fix res. mg/L		40	68	148	137	179	345
Partially sparkling	pH	4	5.72	5.74	5.91	5.88	6.06	6.19
	Cond. μS/cm		1003	1148	1507	1447	1807	2133
	Fix res. mg/L		756	788	1008	939	1160	1402
Sparkling	ph	14	4.7	5.27	5.45	5.39	5.88	6.33
	Cond. μS/cm		254	421	1216	1024	1813	3079
	Fix res. mg/L		104	480	987	711	1360	2604

Abbreviations: **N** – number of samples; **Min.** – minimum; **P(25)** – 25^{th} percentile; **Mean** – average; **Med.** – median; **P(75)** – 75^{th} percentile; **Max.** – maximum; **Cond.** – conductivity; **Fix res.** – fixed residue.

Characterization of mineral waters based on the pH value

As it can be observed in *Figure 1*, the dissolved CO_2 content highly influences mineral waters' pH. Three sparkling mineral waters, Azuga, Izvorul Zăganului, and Apa Craiului, had pH values lower than 5. For 12 types of mineral waters (46.15%), pH values varied between 5 and 6, while 4 and 7 types of mineral waters exhibited pH values in the range of 6–7 and 7–8 respectively.

Characterization of mineral waters based on electrical conductivity

The relationship between the fixed residue and the conductivity of the mineral waters was strong (Pearson correlation: r = 0.96). The conductivity varied between 92 and 3078 μS/cm (*Figure 2*).

For 14 mineral water brands, conductivity was lower than 600 μS/cm; from these brands, 8 were still mineral waters and 6 were sparkling. The conductivity of the other 12 mineral waters was higher than 1000 μS/cm, including eight sparkling and four partially sparkling mineral waters.

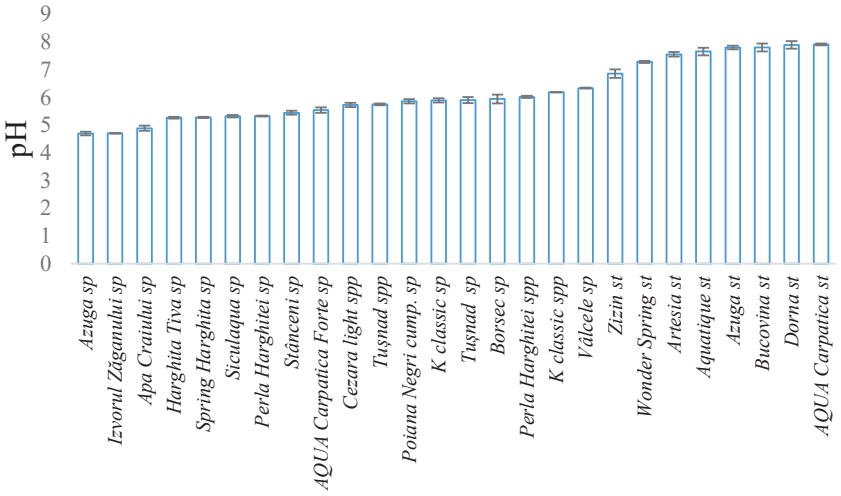

Figure 1. The pH values of the studied mineral waters

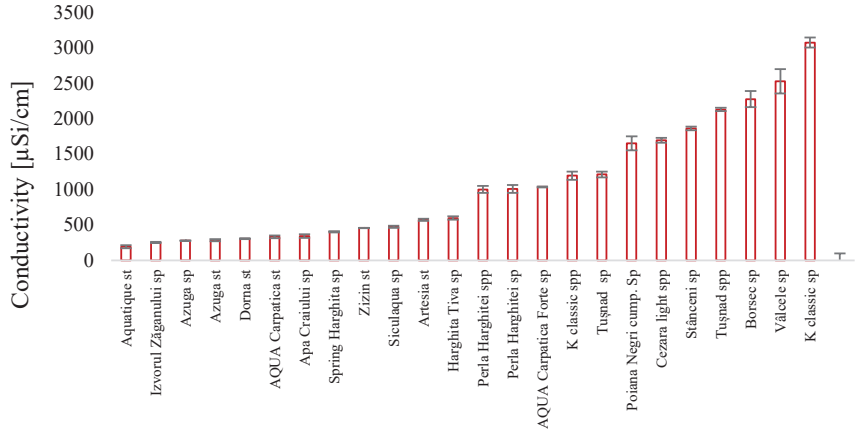

Figure 2. Electrical conductivity of the mineral waters

Classification of mineral waters based on the fixed residue

According to the results obtained for the 26 studied brands for the fixed residue, we can emphasize that in the case of 12 brands (46.2%) the fixed residue was between 50 and 500 mg/L, which corresponds to a low mineral

content, followed by 10 brands (38.5%) with medium mineral content. However, one brand was detected as having a very low mineral content, while brands with rich mineral content represented 11.5% of the samples, namely Borsec sp, K-classic sp, and Vâlcele sp (*Table 2*).

Table 2. Mineral water classification based on the fixed residue

Fix res. at 180 °C	No.	%	Brand description
Very low (< 50 mg/L)	1	3.85	Wonder Spring st
Low (50–500 mg/L)	12	46.2	Bucovina st, Aquatique st, Azuga sp, Dorna st, Izvorul Zăganului sp, Azuga st, AQUA Carpatica st, Apa Craiului sp, Zizin st, Artesia st, Siculaqua sp, Spring Harghita sp
Medium (500–1500 mg/L)	10	38.5	Harghita Tiva sp, Perla Harghitei sp, AQUA Carpatica Forte sp, Perla Harghitei spp, K-classic spp, Cezara light spp, Poiana Negri cump. sp, Stânceni sp, Tuşnad spp, Tuşnad sp
Rich (> 1500 mg/L)	3	11.5	Borsec sp, K-classic sp, Vâlcele sp

Two categories were identified based on the fixed residue values as follows: very low and low (*Figure 3*) and medium and rich mineral content (*Figure 4*). The lowest fixed residue was detected in the case of Wonder Spring and the highest in Vâlcele mineral waters.

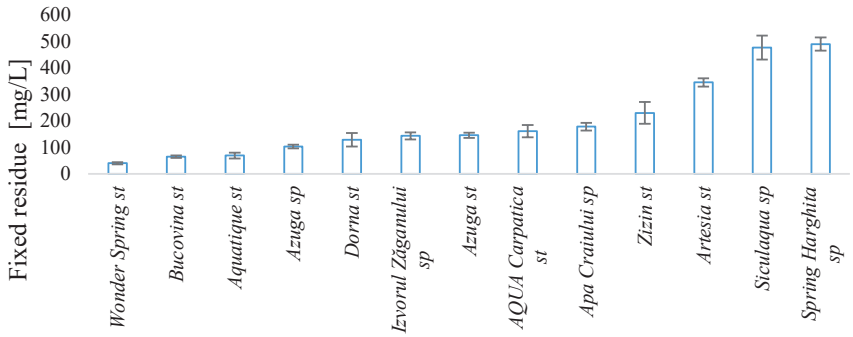

Figure 3. Very low and low fixed residue mineral water brands

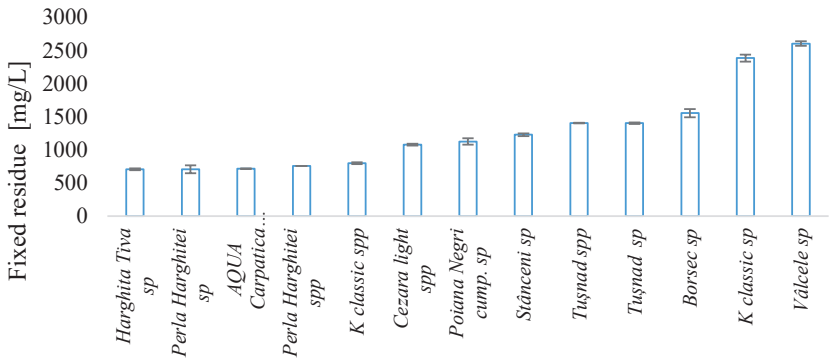

Figure 4. Medium and rich fixed residue mineral water brands

Comparison of the studied waters with some European waters

The measured parameters were compared to other European mineral waters (*Table 3*). The lowest and highest pH values were registered in Italy (4.1, 8.8), while the measured conductivity varied on a large scale from 18 to 26000 μS/cm. Based on pH values, the Romanian mineral waters' variability (4.7–7.91) was similar to that of Estonian mineral waters (4.7–7.76). The maximum value of measured electrical conductivity in Romanian waters (3079 μS/cm) was almost identical to the one measured in Italian mineral waters (3020 μS/cm).

Table 3. The pH and the electrical conductivity of mineral waters from Europe

	pH	**Cond, μS/cm**	**Reference**
Romania	4.7–7.91	92–3079	
Serbia	5.6–7.5	340–4560	(*Petrović et al.*, 2010)
Italy	4.1–8.8	18–3020	(*Dinelli et al.*, 2010)
Estonia	4.7–7.76	175–4370	(*Bityukova & Petersell*, 2010)
Poland	4.7–8.3	188–6510	(*Astel et al.*, 2014)
Hungary	5.3–8.3	250–26000	(*Fugedi et al.*, 2010)
Spain	6–8.1	30–1257	(*Devesa et al.*, 2012)
Slovakia	6–6.75		(*Dušan et al.*, 2010)
Croatia	6–7.9	340–3680	(*Peh et al.*, 2010)
Germany	3.8–8.10	38.1–6340	(*Birke et al.*, 2010)

Comparison of the studied parameters with the reported ones on the labels

The comparative analysis between the determined and the reported values on the labels is presented in *Table 4*. We would like to mention that not all studied brands displayed the pH values and fixed residues on the labels.

Table 4. The comparison of the measured ^{m} and the reported ^{r} values

	pH^{m}	**pH^{r}**	**Fix res^{m}**	**Fix res^{r}**
Apa Craiului sp	4.89	5.00	178	194
Aquatique st	7.66	7.8	70	90
Artesia st	7.55		345	465.5
Azuga sp	4.70		104	191
Azuga st	7.80		146	191
Borsec sp	5.94	5.64	1554	1655
Bucovina st	7.80	7.27	65	78
Cezara light spp	5.72	6.11	1079	
Dorna st	7.89	7.71	129	192
Izvorul Zăganului sp	4.70		144	147
K-classic sp	5.89		2384	2453
K-classic spp	6.19		798	920
Poiana Negri cump. Sp	5.86	5.65	1125	1173
Spring Harghita sp	5.28	5.3	490	510
Stânceni sp	5.45	5.37	1229	1375
Tuşnad sp	5.90		1403	1674
Tuşnad spp	5.75		1402	1674
Vâlcele sp	6.33	6.55	2604	2440
Wonder Spring st	7.28		40	81.4
Zizin st	6.86		230	202

Hierarchical Cluster Analysis

In order to find similarities and differences among the studied samples, the hierarchical cluster analysis was carried out, taking into consideration the pH, the electrical conductivity, and the fixed residue. The results showed two main clusters with sub-clusters (*Figure 5*). Cluster 1 contained two sub-clusters. The sub-cluster 1.1 contained 8 still mineral waters, characterized by average high pH (7.59) and low electrical conductivity (298 μS/cm) and fixed residue (148 mg/L). The 1.2 sub-cluster covers the majority of the studied brands (16), represented by partially sparkling and sparkling mineral waters. In comparison with cluster 1.1, lower pH (5.49), higher electrical conductivity (1090 μS/cm) and fixed residue (804 mg/L) were observed. Two brands, K-classic st and

Vâlcele sp, appeared in cluster 2, which formed a group of waters with very high fixed residue and electrical conductivity (2494 mg/L, 2805 μS/cm).

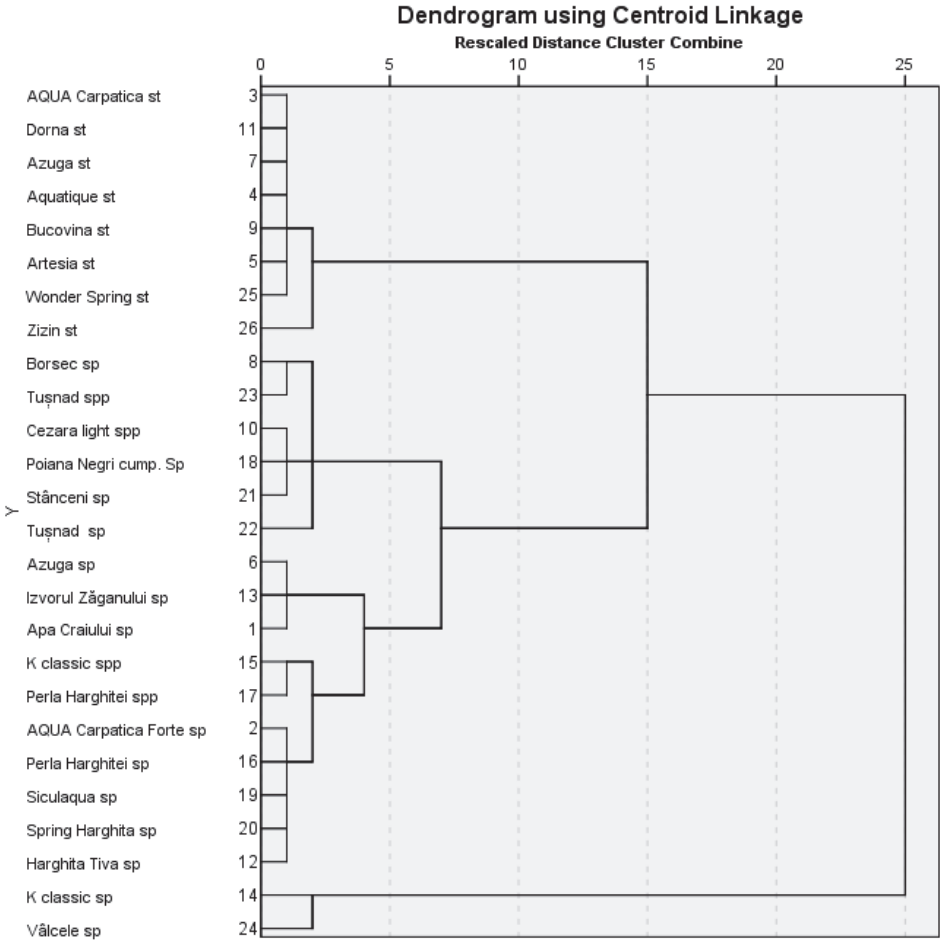

Figure 5. Classification of the mineral waters by hierarchical cluster analysis

4 Conclusions

In this study, three parameters (pH, electrical conductivity, and fixed residue) were determined for selected commercialized mineral waters and analysed in more detail using descriptive statistics. The results revealed that the mineral

content was very low for 3.84%, low for 46.2%, medium for 38.5%, and rich for 11.5% of the selected waters. The total mineral content of sparkling and partially sparkling mineral waters was remarkably close, as we found close values for the electrical conductivity. According to the hierarchical cluster analysis, cluster 1.1 covers the still mineral waters with high pH and low fixed residue. Cluster 1.2 was represented by the medium mineral content, and in cluster 2 two brands were observed with very high fixed residue. There were no considerable differences between the reported values on the labels of the bottles and the values determined by our team.

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