STUDIA UBB CHEMIA, LXI, 3, Tom II, 2016 (p. 391-400)
(RECOMMENDED CITATION)

Dedicated to Professor Emil Cordoș on the occasion of his 80th anniversary

CHEMICAL COMPOSITION OF SOME ROMANIAN BOTTLED NATURAL MINERAL WATERS

ERIKA ANDREA LEVEI[a,*], MARIA-ALEXANDRA HOAGHIA[a], MARIN SENILA[a], MIRELA MICLEAN[a], CLAUDIU TANASELIA[a], ELFRIDA MARIA CARSTEA[b]

ABSTRACT. Considering the increase of bottled mineral water consumption all over Europe, there is a growing interest related to its chemical composition and quality, especially for the elements that are not regularly monitored. This study reports the chemical composition of 21 bottled natural mineral waters available on the Romanian market. The studied mineral waters have low mineral contents (50-500 mg/l), except one, that was found to be rich in salts (>1500 mg/l). Generally, high bicarbonate contents (>600 mg/l) were found in the carbonated and partially degassed mineral waters, while the contents of sulfates and chlorides were low. The Piper diagram revealed that most of the waters are $Ca-HCO_3$ type. Compared to the threshold limits, all samples comply with the legislated limits for natural mineral waters and the majority complies also with the requested standards for drinking water. The determined parameters were found to be in good agreement with those reported on the label.

Keywords: *bottled natural mineral water, chemical composition, major and trace elements*

INTRODUCTION

Water may contain essential, non-essential or toxic substances with beneficial or harmful effects on consumers' health [1, 2]. Although more expensive than tap water, the consumption of bottled water increased considerably in the last decades, due to its association with purity and naturalness, to supposed good quality, taste and odor, and to effective advertising campaigns [3-7].

[a] *INCDO INOE 2000 Research Institute for Analytical Instrumentation, 67 Donath Street, RO-400293, Cluj-Napoca, Romania*
[b] *National Institute of R&D for Optoelectronics, 409 Atomistilor, RO-077125, Magurele, Romania*
** Corresponding author: erika.levei@icia.ro*

Therefore, in addition to data available on the products label, detailed information on the chemical composition of water would help consumers to make an informed choice among products and brands.

The average per capita consumption of bottled waters in Europe has an increasing trend, the most consumed being natural mineral and spring waters, representing about 97 % of the market volume in 2012 [8, 9]. Bottled waters available on market are classified as natural mineral, spring and table water. Natural mineral waters are microbiologically wholesome waters, characterized by their purity at source and their mineral content [10]. It may be subjected to separation of undesirable elements by filtration, decanting or treatment with ozone-enriched air and to total or partial elimination of free carbon dioxide by physical methods, but the addition of bacteriostatic substances or disinfecting treatments are prohibited [10]. Similar to natural mineral water, spring water must come from a specified underground source, be microbiologically safe at source without disinfection and must comply with the drinking water standards [9]. Table waters may originate from groundwater, surface water or municipal supply and are generally treated or disinfected to comply with drinking water standards [9].

Romania holds about 60 % of Europe's mineral water resources, although only about 20 % of these resources are exploited [8]. The tradition of mineral waters in these region dates back to Roman times, but its consumption is first mentioned in a 16th century document. Starting from 1806 the mineral waters from Borsec were bottled at industrial scale. Presently, in Romania, 66 varieties of natural mineral waters are recognized [11, 12], but five brands cover more than half of the market share [13].

The chemical composition of mineral waters has a large natural variation, determined mainly by the different geological settings, but different compounds may leach from the bottle material [14-16]. As bottled water consumption increased, several studies were conducted to determine the composition of mineral waters all over the world [4, 5, 17-28].

The objective of the study was to determine and compare the chemical composition of some bottled natural mineral waters available on the Romanian market in order to provide consumers information that may assist them in choosing the type of water for their daily consumption.

RESULTS AND DISCUSSION

The certified and measured values for the analyzed certified reference materials (CRMs) SRM 1643e: trace elements in water (NIST) and ERM-CA015 Hard drinking water–anions (LGC) are presented in Table 1. The measured values were found to be in agreement with the certified values, the recoveries ranging between 95-108 %.

The pH, electrical conductivity (EC), major elements and total mineral content determined as dry residue (R), together with the threshold limits established by the Romanian legislation [29] harmonized with the European legislation [30] are reported in Table 2, while the micro and trace elements contents in Table 3.

Table 1. Measured and certified concentration of metals in the certified reference materials

Parameter	Certified value	Measured value	Recovery (%)
SRM 1643e trace elements in water / (µg/l)			
Ca	32300±1100	32800±1400	102
Mg	8037±98	7990±420	99
Na	20740±260	20500±550	99
K	2034±29	2030±140	100
Al	141.8±8.6	135±11	95
As	60.45±0.72	59.8±2.2	99
B	157.9±3.9	165±8	104
Ba	544.2±5.8	583±28	107
Cd	6.568±0.073	6.4±0.4	97
Cr	20.40±0.24	19.8±1.2	97
Co	27.06±0.32	27.1±2.0	100
Cu	22.76±0.31	23.0±1.5	101
Li	17.4±1.73	18.4±1.1	106
Mn	38.97±0.45	39.6±2.9	102
Ni	62.41±0.69	63.1±4.6	101
Pb	19.63±0.21	19.2±1.1	98
Se	11.97±0.14	11.4±0.7	95
Sr	323.1±3.6	333±22	103
Zn	78.5±2.2	80.1±4.6	102
ERM-CA015 hard drinking water / (mg/l)			
Cl^-	247±8	241±8	98
F^-	1.3±0.1	1.4±0.1	108
NO_3^-	45±3	43±3	96
SO_4^{2-}	247±7	251±15	102

The charge balance errors based on the percentage difference between the total positive charge and the total negative charge, calculated according to Guller [3] was below ± 5 % for each sample.

Generally, the majority of parameters vary up to two orders of magnitude, and a few up to three orders of magnitude. The pH ranged between 6.22-7.72 and 4.46-5.85 for still and carbonated waters, respectively. In case of mineral waters with pH <6.5, corrosion may occur, favoring the release of metals from pipes [19, 21]. The EC ranged from 85 to 2440 µS/cm, indicating a high variability of the total dissolved solids content in the studied mineral waters, thus suggesting their different source. According to dry residue, all studied mineral waters have low mineral contents (50-500 mg/l), except for one, that was found to be rich in mineral salts (>1500 mg/l). Generally, high bicarbonate contents (>600 mg/l) were found in the carbonated and partially degassed mineral waters, while high contents of sulfate (200 mg/l) and chloride (>200 mg/l) were not found.

Table 2. Dominant chemical composition (mg/l), pH, electrical conductivity (µS/cm) and dry residue (mg/l) of bottled natural mineral waters together with the threshold limits

Sample	pH	EC	R	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Cl^{-}	HCO_3^{-}	NO_3^{-}	F^{-}	SO_4^{2-}
1	5.85	1630	990	257	77.6	4.30	2.50	2.36	1196	0.10	0.15	17.1
2	7.49	344	167	47.2	15.5	0.59	1.29	0.12	220	0.71	0.05	5.81
3	5.77	1650	998	163	56.2	93.8	33.4	23.7	1098	4.20	1.10	5.88
4	6.22	94	82	9.66	3.13	3.01	2.27	0.46	49	3.70	<0.01	6.70
5	6.05	2440	1580	326	101	77.5	16.2	17.3	1806	0.56	0.35	13.7
6	7.21	495	258	56.4	28.6	3.16	0.92	0.97	305	4.51	0.22	8.64
7	5.66	1090	640	152	45.9	19.3	3.64	4.10	732	2.10	0.38	12.0
8	6.92	85	66	9.80	3.11	3.00	1.30	0.45	49	4.55	<0.01	5.72
9	5.75	1450	930	296	11.2	24.3	3.80	7.76	976	0.95	0.32	31.7
10	7.72	315	140	62.5	1.73	1.11	0.57	0.17	171	3.21	0.03	7.40
11	4.46	124	61	18.8	3.67	1.47	0.78	0.72	66	3.20	<0.01	2.51
12	7.19	116	68	15.8	3.52	1.24	0.84	0.35	64	2.93	<0.01	2.70
13	5.28	1080	665	78.3	28.9	88.0	3.21	25.3	598	0.24	<0.01	36.7
14	5.76	1070	660	79.0	29.3	89.2	3.35	24.3	606	6.20	<0.01	32.8
15	5.20	507	282	92.0	7.39	2.73	0.55	1.28	336	2.40	0.03	15.2
16	7.20	477	264	85.0	7.73	1.56	0.39	0.83	293	2.46	<0.01	13.9
17	5.61	1060	681	93.0	41.1	60.3	9.07	12.7	703	2.04	<0.01	1.20
18	5.83	1030	676	91.5	40.3	58.2	8.51	12.0	693	2.20	<0.01	2.00
19	5.77	2050	1360	215	34.5	181	20.8	56.0	1361	3.24	<0.01	13.8
20	5.33	1070	623	45.6	12.1	140	7.14	118	375	18.2	0.12	31.6
21	7.55	984	574	49.2	12.6	132	7.26	107	368	22.8	<0.01	34.5
ML*	**-**	**-**	**-**	**-**	**-**	**-**	**-**	**-**	**-**	**50**	**5**	**-**
MAC**	**6.5-9.5*** **	**2500**	**-**	**-**	**-**	**200**	**-**	**250**	**-**	**50**	**-**	**250**

*ML-maximum limit for natural mineral waters according to Directive 2003/40/EC [30],
**MAC-maximum admitted concentration according to Directive 98/83/EC [31],
***For bottled still water pH>4,5 while for bottled waters naturally rich in or artificially enriched with carbon dioxide, the minimum value may be lower [31].

Table 3. Trace metals content (μg/l) of bottled natural mineral waters together with the threshold limits

Sample	Li	Cr	Mn	Co	Ni	Cu	Zn	Se	Sr	Ba
1	6.9	<0.6	7.80	0.6	14.7	<2.0	2.8	2.2	350	47.4
2	<1.2	<0.6	<1.0	<0.4	<0.9	<2.0	<2.2	<1.4	49.6	6.9
3	400	<0.6	114	<0.4	<0.9	<2.0	24.0	1.6	536	943
4	1.3	<0.6	<1.0	<0.4	<0.9	<2.0	<2.2	<1.4	33.6	2.7
5	199	<0.6	119	0.8	2.5	<2.0	14.5	3.4	509	215
6	5.3	<0.6	<1.0	<0.4	<0.9	<2.0	<2.2	<1.4	73.5	17.3
7	63.1	<0.6	13.3	<0.4	<0.9	<2.0	20.0	<1.4	460	70.4
8	1.4	<0.6	<1.0	<0.4	<0.9	<2.0	<2.2	<1.4	57.8	4.5
9	92.6	<0.6	18.0	0.6	4.1	<2.0	48.8	2.9	1020	152
10	<1.2	<0.6	<1.0	<0.4	<0.9	<2.0	<2.2	<1.4	318	70.9
11	<1.2	<0.6	<1.0	<0.4	<0.9	<2.0	30.6	<1.4	14.0	17.1
12	<1.2	<0.6	<1.0	<0.4	<0.9	<2.0	7.1	<1.4	14.5	16.5
13	34.4	<0.6	213	0.7	<0.9	<2.0	7.3	<1.4	443	87.9
14	35.4	<0.6	200	0.7	<0.9	<2.0	<2.2	<1.4	424	83.7
15	1.4	<0.6	1.8	<0.4	<0.9	<2.0	66.4	<1.4	51.1	17.8
16	<1.2	<0.6	1.2	<0.4	<0.9	<2.0	<2.2	<1.4	43.1	14.7
17	190	<0.6	1.6	<0.4	1.0	<2.0	32.6	<1.4	652	136
18	181	<0.6	1.5	<0.4	<0.9	<2.0	4.6	<1.4	675	140
19	405	<0.6	3.2	<0.4	1.4	<2.0	3.7	2.4	1320	2.0
20	271	<0.6	18.6	<0.4	<0.9	<2.0	11.7	2.2	247	134
21	229	<0.6	25.0	<0.4	<0.9	<2.0	3.0	1.9	255	136
ML*	**-**	50	500	-	20	1000	-	10	-	1000
MAC**	**-**	50	50	-	20	2000	-	10	-	-

*ML-maximum limit for natural mineral waters according to Directive 2003/40/EC [30],
**MAC-maximum admitted concentration according to Directive 98/83/EC [31].

The high bicarbonate content was generally correlated with calcium contents above 150 mg/l. The high Ca content found in samples 1, 3, 5 and 9 acts as a buffer against the pH lowering in these waters. The Mg contents were below 50 mg/l, except for two samples. No samples were found with Na contents higher than 200 mg/l, thus none of the samples had salty taste. In one of the samples, the F^- content was higher than 1, without exceeding the threshold (1.5 mg/l) that requests mentioning on the label. The nitrites and phosphates were below 0.02 mg/l.

Besides the mineralogical sources, some metals may originate in the packaging material, storage tanks or pipelines [16, 32]. However, our data indicates that toxic metals (Al, As, Cd, Cr, Cu and Pb) were below the detection limits in all samples. Generally, B is present in trace concentration in groundwater, thus higher concentrations indicate a possible anthropogenic contamination as boron compounds are used in detergents, bleaches, wood preservatives, fertilizers, herbicides, astringents, antiseptics [25], however no limit has been set for B in bottled water. In our study the highest B concentration was found both in the carbonated and in the partially degassed sorts of Roua Muntilor mineral water (8.9 and 5.8 mg/l), while values above 0.5 mg/l were found in six other samples. The low Mn contents found in the majority of samples are probably due to the Mn elimination by aeration, as increased Mn contents may cause undesirable taste and odor.

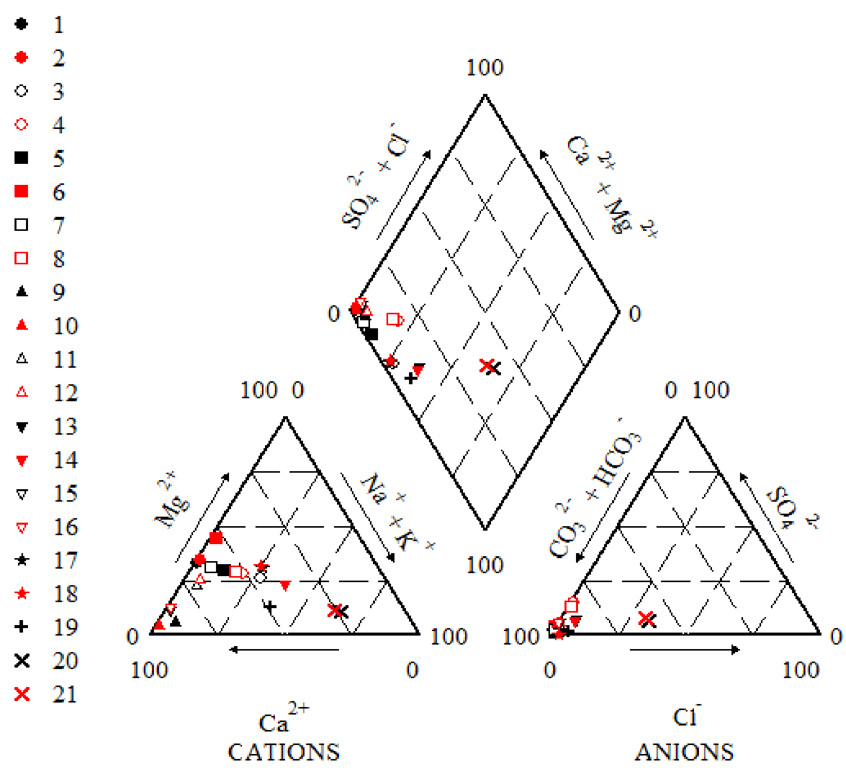

Figure 1. Piper diagram of the studied natural mineral waters

In order to identify the different water types, the main components (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, CO_3^{2-} and HCO_3^-) expressed in mEq/l were plotted on the Piper diagram (fig.1). The diagram shows that all waters are Ca-HCO_3 types, except for samples 20 and 21 which were found to be of Ca-Na-HCO_3 type.

Compared to the threshold limits, all analyzed samples comply with the legislated limits for natural mineral [30] and for drinking waters [31], except Mn that exceeded the threshold for drinking water in 4 samples.

The measured values were found to be in good agreement with those reported on the label, indicating a stable chemical composition of these waters. Values regarding trace metal contents were not provided on the label of the studied mineral waters.

CONCLUSIONS

The chemical composition of 21 bottled natural mineral waters available on the Romanian market was studied. All mineral waters have low mineral contents except for one that was found to be rich in minerals. Generally, the carbonated and partially degassed mineral waters had high bicarbonate contents. No samples were found to be with Na contents higher than 200 mg/l, thus none of the samples had salty taste. In one of the samples, the F^- content was higher than 1, without exceeding the threshold (1.5 mg/l) that requests mentioning on the label. The Piper diagram revealed that most of the waters are Ca-HCO_3 type and two are Ca-Na-HCO_3 type. The majority of waters comply with the legislated limits for natural mineral and for drinking waters, except 4 samples that exceed the Mn threshold for water intended for human consumption. The measured values were in good agreement with those reported on the label.

EXPERIMENTAL SECTION

During 2015, twenty one bottled natural mineral waters (Table 4) were bought from the Romanian varieties available on the market in Cluj-Napoca town.

Table 4. General information of the studied bottled natural mineral waters

Sample	Brand name	Source	Type*
1	Aqua Carpatica	F2 Paltinis	C
2	Aqua Carpatica	Blajenaru	S
3	Bilbor	F1	C
4	Bilbor	Q1	S
5	Borsec	Borsec	NC
6	Borsec	Borsec Faget	S
7	Bucovina	F2-Rosu, C7 Secu	C

Sample	Brand name	Source	Type*
8	Bucovina	F2-Rosu, C7 Secu	S
9	Dorna	Poiana Vinului	C
10	Dorna	Izvorul Alb	S
11	Izvorul Minunilor	Stana de vale	C
12	Izvorul Minunilor	Stana de vale	S
13	Lipova	F9bis, 8E	C
14	Lipova	F9bis, 8E	D
15	Perenna Premier	Calina-Muntii Dognecei	C
16	Perenna Premier	Calina-Muntii Dognecei	S
17	Perla Harghitei	Sancraieni	C
18	Perla Harghitei	Sancraieni	D
19	Poiana Negrii	Foraj FD	C
20	Roua Muntilor	S1, S2 Covasna	C
21	Roua Muntilor	S1, S2 Covasna	D

*NC=natural carbonated natural mineral water; C=carbonated natural mineral water; S=still natural mineral water; D=partial degassed natural mineral water.

Certified standard solutions, high purity reagents (Merck) and ultrapure water (Millipore, Milli-Q) were used for sample preparation and analyses. Certified reference materials SRM 1643e: trace elements in water (NIST) and ERM-CA015 Hard drinking water–anions (LGC) were used for the quality control of the determination of metals and anions, respectively.

The pH and EC were determined immediately after opening the bottles using a WTW 350i multiparameter. For the determination of dry residue, bicarbonates and anions, the samples were degassed by ultrasonication. For the determination of major and trace elements the samples were degassed by ultrasonication and acidified by adding 1 ml 63 % HNO_3. The HCO_3^- content was determined by titration with HCl, against methyl orange indicator, the dry residue (R) by gravimetric method while the anions (Cl^-, F^-, NO_2^-, NO_3^-, SO_4^{2-}, PO_4^{3-}) using a 761 ion chromatograph (Methrom). The major elements (Ca, Mg, Na, K) were determined by inductively coupled plasma optical emission spectrometry (ICP-OES), using an Optima 3500 DV (Perkin Elmer) spectrometer and the trace metals (Al, As, B, Ba, Cd, Cr, Co, Cu, Li, Mn, Ni, Pb, Se, Sr, Zn) by inductively coupled plasma mass spectrometry (ICP-MS) using an ELAN DRC II (Perkin Elmer) spectrometer. To avoid polyatomic interferences methane was used as reaction gas for of Ba, Cd, Co, Mn, Ni, Pb, Se, Sr and Zn, ammonia for Cr and Cu, and oxygen for As determination. No reaction gas was used for the determination of Al, B and Li [33].

ACKNOWLEDGMENTS

This work was funded by Core Program, under the support of ANCSI, project no. PN 16.40.02.01 and by Sectoral Operational Programme "Increase of Economic Competitiveness", Priority Axis II, project no. 1887, INOVAOPTIMA, code SMIS-CSNR 49164.

REFERENCES

1. D. Varrica, E. Tamburo, G. Dongarra, *Applied Geochemistry*, **2013**, *34*, 102.
2. M. C. Albertini, M. Dacha, L. Teodori, M. E. Conti, *International Journal of Environmental Health*, **2007**, *1*, 153.
3. C. Guler, *Chemometrics and Intelligent Laboratory Systems*, **2007**, *86*, 86.
4. R. Cidu, F. Frau, P. Tore, *Journal of Food Composition and Analysis*, **2011**, *24*, 184.
5. V. Naddeo, T. Zarra, V. Belgiorno, *Journal of Food Composition and Analysis*, **2008**, *21*, 505.
6. M. Brencic, T. Ferjan, M. Gosar, *Journal of Geochemical Exploration*, **2010**, *107*, 400.
7. M. Guadayol, M. Cortina, J. M. Guadayol, J. Caixach, *Water Research*, **2016**, *92*, 149.
8. M. J. Dumitrescu, "Mineral waters", Romanian Trade and Invest, **2012**, Available online at: http://ukrexport.gov.ua/i/imgsupload/file/Romania%20-%20Mineral%20Waters%202012r.pdf
9. The European Federation of Bottled Waters (EFBW), Available online at: http://efbw.eu/index.php
10. Directive 2009/54/EC of the European Parliament and of the Council of 18 June 2009 on the exploitation and marketing of natural mineral waters, *The Official Journal of the European Union,* **2009**, *L164*, 45.
11. B. M. Kis, C. Baciu, *Ecoterra, Journal of Environmental Research and Protection*, **2013**, *36*, 9.
12. List of natural mineral waters recognised by member states, *The Official Journal of the European Union,* **2013**, *C315*, 66.
13. A. Feru, *Environmental Geology*, **2004**, *46*, 670.
14. A. Misund, B. Frengstad, U. Siewers, C. Reimann, *Science of The Total Environment*, **1999**, *243–244*, 21.
15. C. Reimann, M. Birke, P. Filzmoser, *Applied Geochemistry*, **2010**, *25*, 1030.
16. A. Guart, F. Bono-Blay, A. Borrell, S. Lacorte, *Food Chemistry*, **2014**, *156*, 73.
17. Z. Peh, A. Sorsa, J. Halamic, *Journal of Geochemical Exploration*, **2010**, *107*, 227.
18. E. Dinelli, A. Lima, B. De Vivo, S. Albanese, D. Cicchella, P. Valera, *Journal of Geochemical Exploration*, **2010**, *107*, 317.
19. B.S. Frengstad, K. Lax, T. Tarvainen, O. Jeager, B.J. Wigum, *Journal of Geochemical Exploration*, **2010**, *107*, 350.
20. L. Bityukova, V. Petersell, *Journal of Geochemical Exploration*, **2010**, *107*, 238.

21. M. A. Saleh, F. H. Abdel-Rahman, B. B. Woodard, S. Clark, C. Wallace, A. Aboaba, W. Zhang, J. H. Nance, *Journal of Environmental Science and Health Part A*, **2008**, *43*, 335.
22. R. W. Dabeka, H. B. Conacher, J. F. Lawrence, W. H. Newsome, A. Mckenzie, H. P. Wagner, R. K. Chadha, K. Pepper, *Food Additives & Contaminants*, **2002**, *19*, 721.
23. D. Bertoldi, L. Bontempo, L. Roberto, G. Nicolini, S. Voerkelius, G.D. Lorenz, H. Ueckermann, H. Froeschl, M. J. Baxter, J. Hoogewerff, P. Brereton, *Journal of Food Composition and Analysis*, **2011**, *24*, 376.
24. U. Fugedi, L. Kuti, G. Jordan, B. Kerek, *Journal of Geochemical Exploration*, **2010**, *107*, 305.
25. M. Birke, U. Rauch, B. Harazim, H. Lorenz, W. Glatte, *Journal of Geochemical Exploration,* **2010***, 107*, 245.
26. A. Astel, R. Michalski, A. Lyko, M. Jablonska-Czapla, K. Bigus, S. Szopa, A. Kwiecinska, *Journal of Geochemical Exploration*, **2014**, *143*,136.
27. M. Felipe-Sotelo, E. R. Henshall-Bell, N.D.M. Evans, D. Read, *Journal of Food Composition and Analysis*, **2015**, *39*, 33.
28. D. T. Udagedara, D. T. Jayawardana, *Environmental Earth Sciences*, **2015**, *73*, 7957.
29. Romanian Government Decision No. 1020/2005 for the approval of technical norms for natural mineral waters exploitation and commercialization, *The Official Gazette of Romania*, **2005**, 854 [in Romanian].
30. Commission Directive 2003/40/EC of 16 May 2003 establishing the list, concentration limits and labelling requirements for the constituents of natural mineral waters and the conditions for using ozone-enriched air for the treatment of natural mineral waters and spring waters, *The Official Journal of the European Union,* **2003***, L 126*, 34.
31. Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption, **1998**, *Official Journal of the European Communities*, *L330*, 32.
32. P. L. Smedley, *Applied Geochemistry*, **2010**, *25*, 1872.
33. T. W. May, R .H. Wiedmeyer, *Atomic Spectroscopy*, **1998**, *19*, 150.