Bulgarian Chemical Communications, Volume 46, Number 4 (pp. 840 – 844) 2014

Determination of the trace element content in Bulgarian bottled potable waters by total reflection X-ray fluorescence analysis

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Received January 13, 2014; Revised February 28, 2014

The content of S, Cl, K, Ca, Mn, Fe, Ni, Cu, Zn, As, Br, Rb and Ba in several brands of Bulgarian bottled potable waters ("Savina" table, "Gorna Banya" mineral, "Bankya" mineral, "Kom" mineral, "Thorn Spring" mineral, "Hissar" mineral, "Devin" spring and mineral and "Mihalkovo" spring and mineral) was determined by total reflection X-ray fluorescence (TXRF) analysis using gallium as internal standard. The spring waters generally displayed lower mineralization (total dissolved solids, TDS content) than the mineral waters, even those originating from the same location. The content of S, Cl, K and Ca was at the mg L^{-1} level, while that of Mn, Fe, Ni, Cu, Zn, As, Br, Rb and Ba - at the lower µg L^{-1} level. The trace element content of the mineral waters did not considerably change (less than ±30 % difference) over a storage period of approx. 2.5 years after bottling.

Keywords: Bulgarian bottled potable waters; total reflection X-ray fluorescence analysis; essential and toxic elements

INTRODUCTION

Bulgaria is one of the countries in the world richest in mineral and spring waters (more than 850 boreholes and springs) [1]. At present, more than 50 brands of bottled mineral, spring and table 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, e.g. [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 can be found in [1,4-6].

During the last two decades the total reflection X-ray fluorescence (TXRF) has turned out to be a well-established analytical tool and has found many applications owing to the fact that quantification procedures are very simple and practically no sample preparation is required [7,8]. Further benefits of TXRF are: no need of external calibration; multi-element analysis including halogenides; low analytical operation and maintenance costs; portability. TXRF methods for trace element analysis in different kinds of natural waters including mineral waters after separation and preconcentration of the analytes [9,10], as well as direct TXRF methods [11-15] are reported in the literature. In a former work of the present authors [16], the conditions for the direct TXRF determination of both major and trace elements in mineral waters of total dissolved solids (TDS) content in a broad range – from 160 to 2900 mg L^{-1} were optimized.

The purpose of the present work was to apply the optimized TXRF procedure [16] for direct trace element analysis of several brands of bottled potable waters offered on the Bulgarian market: the mineral waters "Hissar" and "Bankya", the spring waters "Devin" and "Mihalkovo" and the table water "Savina". Furthermore, the trace element content in the formerly analyzed mineral waters "Gorna Banya", "Kom", "Devin", "Thorn Spring" and "Mihalkovo" [16] was again determined in the present work in order to find out whether any changes have taken place in their composition and characteristics over a storage period of approx. 2.5 years after bottling.

EXPERIMENTAL

Instrumentation

The TXRF analyser S2 PICOFOX (BRUKER AXS GmbH Karlsruhe, Germany) was used for the measurements. This instrument was equipped with an air-cooled low power X-ray tube (Mo target), a Ni/C monochromator with 80% reflectivity and a liquid nitrogen-free Silicon Drift Detector (SDD) of 10 mm^2 area with an energy resolution of < 159 eV

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(Mn Kα). The sample holders were quartz optical plates of 30 mm diameter and 3 mm thickness (Perspex Distribution LTD, UK). The power was 50 kV and the current was 1000 μA. Prior to each series of measurements gain correction was performed to compensate for the drift of the channel/energy dependence by measuring at As Kα – 10.53 keV.

Cleaning of the lab ware

The quartz plates used as sample holders were cleaned with 10% (v/v) nitric acid (p.a., Merck, Darmstadt, Germany) at a temperature of 80 °C for 1 h on a hot plate. They were subsequently flushed with water from a Cole-Parmer deionizer model 01503-20, Germany, conductivity 15 MΩ/cm, and were let to dry in the air.

Sample preparation and analysis

Sample preparation was performed according to [16]. The water sample (1.0 mL) was transferred to an Eppendorf® tube of 1.5 mL volume and was mixed with 20 μL of the internal standard (a 10 mg L^{-1} Ga solution). Three aliquots (each of 5 μL) of the water sample, mixed with the internal standard, were consecutively pipetted and dried on a siliconized quartz holder. The dry residue was measured for 1000 s at two perpendicular positions of the sample holder. Several blank quartz holders were measured to determine the blank value.

For the evaluation of the TXRF spectra, the Spectra 5.1® software (Bruker AXS Microanalysis GmbH, Berlin, Germany) was used. The quantification was performed as described in [17].

RESULTS AND DISCUSSION

Several brands of bottled Bulgarian mineral, spring and table waters were selected for analysis. Some of the characteristics of the waters, as given on the bottle labels, are presented in Table 1.

As can be seen, all selected waters are neutral to slightly alkaline (pH from 7.2 to 9.0) and of low mineralization (TDS content between 50 and 240 mg L^{-1}). The waters were analyzed within one year after bottling. As Table 1 shows, the spring waters are of lower TDS content than the mineral waters. The lowest TDS content is manifested by the “Savina” table water, which may be attributed to its treatment by reverse osmosis prior to bottling. The TDS content of the mineral waters analyzed in [16] was as follows: “Gorna Banya” ~160 mg L^{-1}, “Kom” and “Devin” ~260 mg L^{-1}, “Thorn Spring”~ 420 mg L^{-1} and ”Mihalkovo” ~2900 mg L^{-1}. In the present work the pH values of these waters were measured again ~2.5 years after bottling. No changes in the pH values of these waters with respect to the original values were registered, except for the ”Mihalkovo” mineral water: the presently measured pH value was ~ 7 (original value 6.4). This increase in pH was attributed to the removal of CO_2, naturally contained in the ”Mihalkovo” mineral water, which diffused out of the bottle during the prolonged storage.

It was further of interest that mineral and spring waters from the same location displayed different TDS values, e.g., ”Mihalkovo” mineral water (2900 mg L^{-1}) – “Mihalkovo” spring water (72 mg L^{-1}); “Devin” mineral water (260 mg L^{-1}) – “Devin” spring water (82 mg L^{-1}).

The content of the trace elements S, Cl, K, Ca, Mn, Fe, Ni, Cu, Zn, As, Br, Rb (Kα line) and Ba (Lα line) in the water samples was determined. Light elements (Li, Na, Be, B) were not detectable in the water samples with the present instrumentation [18]. Ag, Cd, Sb, Sr, Mo were excluded from the list of analytes as discussed in [16]. The TXRF lower limits of detection (LLD), determined according to the 3σ criterion [18] in low- and high-TDS waters, are shown in Table 2.

Table 1. Characteristics of bottled mineral, spring and table waters, analyzed in the present work, according to the certificates of the Ministry of Health of Bulgaria, given on the bottle labels. Bottle volume is 0.5 L.

Characteristic	“Savina” table water	“Hissar” mineral water	“Bankya” mineral water	“Devin” spring water	“Mihalkovo” spring water
Bottled in	10.2012	03.2012	09.2012	11.2012	11.2012
TDS content, mg L^{-1}	< 50	240	247	82	72
pH	7.2-7.6	9.0	8.9	7.8	7.4
Source	Busmanci (Sofia district)	Hissar (Plovdiv district)	Ivanyane (Sofia district)	Devin (Smolian district)	Mihalkovo (Smolian district)
Na, mg L^{-1}	< 0.002	60.3	53.0	5.4	2.8
K, mg L^{-1}		1.1	0.67		11.3
Ca, mg L^{-1}		2.7	4.61	7.14	5.1

Table 2. TXRF lower limits of detection (LLD, µg L^{-1}) of the analytes in waters of low and high TDS content, obtained under the conditions given in the Experimental.

Analyte	LLD, µg L^{-1} for low-TDS waters (TDS ‹50-420 mg L^{-1})	LLD, µg L^{-1} for high-TDS waters (TDS 2900 mg L^{-1})
S	90	970
Cl	70	800
K	20	300
Ca	18	200
Mn	2	20
Fe	2	14
Ni	1	10
Cu	2	10
Zn	2	9
As	1	7
Br	1	6
Rb	1	7
Ba	14	100

As can be seen, the LLD values in high-TDS waters are higher by a factor of 5-15 than those in low-TDS waters, which may be related to the increased X-ray excitation scattering and the higher background in the former case.

The results for the trace element content in the analyzed table, spring and mineral waters are shown in Table 3. S, Cl, K and Ca are at the mg L^{-1} level; Fe, Cu, Zn and Br are at the µg L^{-1} level, while Mn, As, Ni and Ba are not detected (below the corresponding LLD). Rb is detected only in the "Hissar" mineral water, which agrees with literature data for waters of the same location [1].

The results for the trace element content in mineral waters, stored for approx. 2.5 years after bottling, are shown in Table 4.

The upper values refer to the analysis carried out in 2011 [16], while the lower ones are obtained in the present work. As can be seen, the concentrations of the analytes are not significantly changed over the period of 2.5 years (differences below ± 30 %). This is an evidence for the stability of the trace element content of the bottled waters during prolonged storage.

The precision of the TXRF results for the trace element content in the analyzed waters is characterised by an RSD of 5–16%.

Table 3. Data for the trace element content in bottled table, mineral and spring waters of low TDS content (50-260 mg L^{-1}). The results are presented as mean ± SD of six replicates.

Analyte	"Savina" table water	"Hissar" mineral water	"Bankya" mineral water	"Devin" spring water	"Mihalkovo" spring water
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

Table 4. Data for the trace element content in bottled mineral waters. The first row of values is obtained in the year of bottling [16]; the second one – approx. 2.5 years after bottling. The results are presented as mean ± SD of six replicates.

Analyte	"Gorna Banya" mineral water	"Kom" mineral water	"Thorn Spring" mineral water	"Devin" mineral water	"Mihalkovo" mineral water
S, mg L-1	7.9 ± 0.4	8.9 ± 0.2	2.8 ± 0.4	5.1 ± 0.8	123 ± 13
	6.4 ± 0.5	8.8 ± 0.3	2.2 ± 0.3	4.5 ± 0.4	96 ± 6
Cl, mg L-1	2.4 ± 0.2	1.2 ± 0.1	2.9 ± 0.4	3.4 ± 0.2	47 ± 7
	1.8 ± 0.2	0.9 ± 0.1	2.2 ± 0.3	3.1 ± 0.2	45 ± 7
K, mg L-1	0.35 ± 0.02	1.3 ± 0.2	1.2 ± 0.2	0.6 ± 0.1	48 ± 7
	0.31 ± 0.05	1.0 ± 0.1	1.5 ± 0.2	0.6 ± 0.1	46 ± 6
Ca, mg L-1	1.3 ± 0.2	1.4 ± 0.2	78 ± 8	1.5 ± 0.1	215 ± 25
	1.5 ± 0.2	1.7 ± 0.2	80 ± 6	1.3 ± 0.1	217 ± 29
Mn, µg L-1	< 2	< 2	< 2	< 2	48 ± 7
	< 2	< 2	< 2	< 2	38 ± 5
Fe, µg L-1	25 ± 4	10 ± 1	6.8 ± 0.8	15 ± 2	15 ± 2
	24 ± 3	7.9 ± 1.0	8.0 ± 1.0	13 ± 2	15 ± 2
Ni, µg L-1	3.0 ± 0.5	12 ± 1	5.0 ± 0.8	4.0 ± 0.5	14 ± 2
	< 1	10 ± 1	4.0 ± 0.5	3.0 ± 0.5	13 ± 2
Cu, µg L-1	6.0 ± 0.5	6.0 ± 0.5	< 2	3.0 ± 0.5	< 10
	4.8 ± 0.5	4.8 ± 0.1	< 2	3.0 ± 0.5	< 10
Zn, µg L-1	6.0 ± 0.5	47 ± 4	10 ± 1	< 2	< 9
	4.9 ± 0.5	50 ± 4	13 ± 2	3.0 ± 0.5	< 9
As, µg L-1	3.0 ± 0.5	12 ± 2	2.5 ± 0.2	< 1	< 7
	3.0 ± 0.5	9.0 ± 1.0	< 1	< 1	< 7
Br, µg L-1	8.0 ± 1.0	37 ± 5	15 ± 2	6.0 ± 0.5	400 ± 50
	6.5 ± 1.0	32 ± 3	13 ± 2	6.0 ± 0.5	350 ± 50
Rb, µg L-1	5.0 ± 0.5	4.0 ± 0.5	< 1	< 1	163 ± 25
	4.0 ± 0.5	4.0 ± 0.5	< 1	< 1	160 ± 25
Ba, µg L-1	45 ± 7	30 ± 5	28 ± 4	38 ± 5	< 100
	36 ± 1	26 ± 4	23 ± 2	35 ± 2	< 100

CONCLUSIONS

The trace element content in several brands of bottled Bulgarian potable waters ("Savina" table, "Gorna Banya" mineral, "Bankya" mineral, "Kom" mineral, "Thorn Spring" mineral, "Hissar" mineral, "Devin" spring and mineral and "Mihalkovo" spring and mineral) was determined by direct TXRF analysis using gallium as internal standard. The spring waters generally displayed a lower TDS content than the mineral waters, even those from the same location. The trace elements S, Cl, K and Ca were found to be at the mg L^{-1} level, while Mn, Fe, Ni, Cu, Zn, As, Br, Rb and Ba - at the lower µg L^{-1} level. It was of interest that the trace element content of the examined mineral waters remained rather constant over a period of storage of 2.5 years (differences below ± 30 %). The natural purity and the stable trace element content of Bulgarian mineral, spring and table waters make them a high-quality product on the Bulgarian and the European market of potable waters. It follows from the obtained results that TXRF is a suitable method for the routine trace element analysis (including S, Cl and Br) of bottled potable waters of various type and mineral composition.

Acknowledgement: *The authors thank the National Science Fund at the Ministry of Education, Youth and Science of Bulgaria for the financial support (Contract DTK 02-5/2010).*

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ОПРЕДЕЛЯНЕ НА СЛЕДИ ОТ ЕЛЕМЕНТИ В БЪЛГАРСКИ БУТИЛИРАНИ ПИТЕЙНИ ВОДИ С ПОМОЩТА НА РЕНТГЕНОФЛУОРЕСЦЕНТЕН АНАЛИЗ С ПЪЛНО ВЪТРЕШНО ОТРАЖЕНИЕ

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(Резюме)

Съдържанието на S, Cl, K, Ca, Mn, Fe, Ni, Cu, Zn, As, Br, Rb и Ba в различни марки български бутилирани питейни води (“Савина” трапезна, “Горна баня” минерална, “Банкя” минерална, “Ком” минерална, “Трънска банкя” минерална, “Хисар” минерална, “Девин” изворна и минерална и “Михалково” изворна и минерална) е определено чрез рентгенофлуоресцентен анализ с пълно вътрешно отражение с вътрешен стандарт галий. Изследваните изворни води са с по-ниска обща минерализация от минералните води, дори от едно и също находище. Съдържанието на S, Cl, K и Ca е на ниво mg L^{-1},а това на Mn, Fe, Ni, Cu, Zn, As, Br, Rb и Ba – на ниво µg L^{-1}. Установено е, че съдържанието на елементи в минералните води не се променя съществено (по-малко от ± 30 %) при съхранението им за период от 2.5 години след бутилиране.