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Professional paper

Application of an ion chromatographic method for determination of selected cations of group IA and IIA in bottled water

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Abstract

Bottled waters are an important source of essential minerals for the human body. This study presents the results from the determination of four cations (sodium, potassium, magnesium and calcium) in commercially available bottled waters in Republic of North Macedonia using ion chromatography with conductometric detection. First, the performance of the standard ISO 14911 ion chromatographic method was verified, evaluating the linearity, accuracy, and precision. Then, the verified method was applied on water samples from 4 different parts of the country (Bitola, Debar, Gevgelija and Kratovo). Sodium concentrations in the analyzed samples ranged between 1.94 and 17.01 mg/L. Potassium concentrations were between 0.32 and 4.01 mg/L. Magnesium concentrations varied between 1.87 and 7.53 mg/L, whereas calcium concentrations were between 10.79 and 44.96 mg/L. The concentrations of the investigated cations were in accordance with the requirements given in the Official Gazette for quality and safety of drinking water.

Key words: bottled water, cations, ion chromatography, method verification, quality

Introduction

Water is a basic substance supporting life and the natural environment, a primary component for the industry, a consumer item for humans and animals and a vector for domestic and industrial pollution (Brima, 2017; Michalski, 2006; Michalski et al*.,* 2018). It contains different components such as inorganic cations, anions, trace elements or dissolved organic carbon which are naturally present, and it may contain different hazardous compounds or contaminants. Water quality depends on geochemical characteristics of the region and anthropogenic pollution (Konczyk et al*.,* 2019).

Some of the most important elements that contribute to the water quality are sodium, potassium, magnesium and calcium, major cations present in all type of waters, including bottled water. Sodium and potassium are elements essential for humans and they usually occur in relatively small concentrations in bottled water. On the other hand, calcium and magnesium are minerals whose concentration can vary significantly. These minerals are

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very important for the normal functioning of the human body, "performing" numerous physiological functions. Since bottled waters are usually rich in these minerals they can provide a significant contribution to these minerals total daily intake (Michalski et al., 2018; Konczyk et al., 2019). Therefore, there is a general preference to drink bottled water instead of tap water due to hygienic and health reason (De Beaufort, 2007; Lyubomirova et al., 2020).

The determination of sodium, potassium, magnesium and calcium can be performed by various analytical methods such as complexometric titrations or flame atomic absorption spectrometry, FAAS, however, they suffer from several disadvantages such as interferences and limited sensitivity, and can be laborious, intensive and difficult to automate (Michalski, 2006). In comparison, ion chromatography (IC) is especially suitable for identification and quantification of organic and inorganic ions in complex matrices, simultaneous determination of multiple analytes in a single run, at the same time saving time and resources. It is very selective and a sensitive technique (Michalski, 2006).

The growing popularity of bottled water has resulted in the issuing of specific national and international regulations for the quality and monitoring the quality of these products (Lyubomirova et al., 2020). Laboratories can monitor bottled water quality using their own methods, developed in the laboratory, or chose, for example a standard method proposed by International Organization for Standardization, ISO. If a standard ISO method is chosen, prior application on real samples, the method must be verified. Method verification studies are typically less extensive than those required for method validation. Nevertheless, the facility would be expected to demonstrate the ability to achieve the published performance characteristics of the standard method under their own test conditions and with the matrices to which the method is being applied (Kotsiuba, 2022).

The aim of our study was to conduct a method performance verification on a standard ISO 14911:1998 ion chromatographic method for determination of cations in water and waste water and to apply the verified method for determination of the concentration of the four cations (Na^+, K^+, Mg^{2+}, and Ca^{2+}) in bottled waters manufactured in 4 different parts of the country (Bitola, Debar, Gevgelija and Kratovo).

Material and methods

Chemicals and reagents

Commercially available Dionex Six Cation-II certified Standard containing 50 mg/L Li^+, 203 mg/L Na^+, 252 mg/L NH_4^+, 505 mg/L K^+, 253 mg/L Mg^{2+} and 506 mg/L Ca^{2+}, used as a calibration standard was purchased from Merck (Germany). Methanesulfonic acid (MSA, HPLC grade), used as an eluent (mobile phase) in the chromatographic analysis, was also purchased from Merck, Germany. Water used for the standard and eluent preparation was from the Millipore deionizer Direct Q with an electrical conductivity < 0.05 μS/cm. For obtaining the results for precision and accuracy, the certified reference materials (CRMs) for Na^+ and K^+ were purchased from CPA Chem, Bulgaria whereas $Mg^{2+}$and Ca^{2+} CRMs were purchased from Merck, Germany.

Standard and sample solutions

Working standards of the investigated ions for calibration, were prepared by further dilution of the Dionex Six Cation-II certified Standard before analysis. Each standard solution was analyzed in triplicate. The final concentration of the standard solutions was ranging from 0.1015 to 20.3 mg/L for sodium, 0.252 to 50.5 mg/L for potassium, 0.1265 to 25.3 mg/L for magnesium and 0.253 to 50.6 mg/L for calcium.

The mobile phase was prepared by dissolving methanesulfonic acid in Milli-Q grade water to obtain concentration of 0.03 mol/L (30 mM). All standard solutions were prepared in glass volumetric flasks and kept at ambient temperature.

Four brands of commercially available bottled waters consisting of natural mineral waters manufactured in different regions of North Macedonia were tested each month during the whole year. All the samples analyzed in this work are commercially available in the supermarkets around the country. Before analysis, 5 ml of the sample were transferred into the plastic vials compatible for the ion chromatography system. Samples that had conductivity values higher than 1000 μS cm^{-1} were suitably diluted before analysis. Ultrapure water was used as blank.

Instrumentation and chromatographic conditions

The selected cations were determined on an Ion Chromatography system IC Dionex Aquion equipped with an autosampler and a conductivity detector. The separation was performed on Dionex IonPac CS16 Analytical chromatographic column (5 x 250 mm, 5.5 μm particle size). The column temperature, the flow rate and the injected volume were set at 40 °C, 1.0 mL/min and 5000 μL respectively. The IC column needs to be conditioned at least 30 min with the eluent and after that, all the standard samples, control materials and unknown samples can be measured. Identification of the analytes is performed through the retention time of the analytes and comparison of the absorption spectra of the unknown compound with the standard substance. Data acquisition and instrument settings were performed using Chromeleon 7 software.

Verification of the method

The verification of the method was performed in terms of, selectivity, linearity, accuracy and precision, according to the requirements of Guidelines for the validation and verification of quantitative and qualitative test methods (ISO 17025, 2012).

Results and discussion

The chemical composition of natural waters depends on many factors such as environmental factors, topography and climate (Guler et al., 2002; Mokthar et al., 2009). Hence, each bottled water brand has its own physical characteristics and chemical properties defined by unique combination of these factors (Aris et al., 2013). Nowadays, the chemical composition and the related properties of bottled waters are being used in their promotion and advertisement. To make the products more attractive, some manufacturers emphasize therapeutic properties of the specific bottled waters and although the content of minerals should fit the declared composition, it is common that the declared and the analyzed composition differ (Konczyk et al., 2019; Rey-Salgueiro et al., 2013). In this study, a method performance verification of the standard ISO 14911:1998 method for determination of cations was conducted and the verified method was applied for determination of Na^+, K^+, Mg^{2+} and Ca^{2+} concentrations in bottled waters available on the market.

Selectivity/specificity – Selectivity, as the ability of the method to differentiate the analyte of interest from other components of the matrix, was investigated by analysis of blank water sample (conductivity < 0.05μS/cm), standard solution containing 5 mg/L of each cation and the sample solutions. All the peaks were well separated and no interferences from the matrix were observed. Despite being not a mandatory parameter for the method's performance verification, selectivity/specificity were investigated to confirm that the instrument used does not affect specificity (ALACC, 2007). Representative chromatograms from a blank sample, standard solution containing 5 mg/L of each cation, Sample solution (Bitola), Sample solution (Debar), Sample solution (Gevgelija) and Sample solution (Kratovo), are presented in Fig. 1.

System suitability - As a part from the qualification of the chromatographic system, system suitability was evaluated in terms of resolution between the investigated peaks of Na^+, K^+, Mg^{2+} and Ca^{2+}. The resolution between the investigated peaks of Na^+ and K^+ was 5.2, the resolution between the investigated peaks of K^+ and Mg^{2+} was 5.2 and the resolution between the investigated peaks of Mg^{2+} and Ca^{2+} was 5.9, respectively. The obtained results for the resolution were in accordance with the requirements of *Rs* > 1.3 (ISO 14911:1998). Also, the number of theoretical plates was > 2000, for all investigated peaks.

Table 1. Linearity and precision

Cation	Regression equation (y)		Correlation coefficient	Method precision (RSD, %)	Intermediate precision (RSD, %)	
	Slope (b)	Intercept (a)				ISO criterion
Na^+	0.0215	0.2538	0.999	0.54	2.41	< 3.7%
K^+	-0.0019	0.1626	0.999	0.40	3.38	<6.3%
Mg^{2+}	-0.0352	0.4518	0.999	0.16	2.65	<3.6%
Ca^{2+}	-0.0338	0.2707	0.999	1.09	3.01	<3.2%

Table 2. Results from the testing of the accuracy of the method

Amount spiked	% Recovery*			
	Na	K	Mg	Ca
50%	101.50± 1.61	104.6 ± 1.16	103.67 ± 4.65	101.87 ± 3.48
100%	100.3± 0.54	100.93 ± 0.40	104.4 ± 0.16	100.80 ± 1.09
150%	99.83 ± 0.71	100.5 ± 0.09	103.83 ± 0.14	100.13 ± 0.83

*Results are expressed as mean ± RSD (%) for three determinations at each level

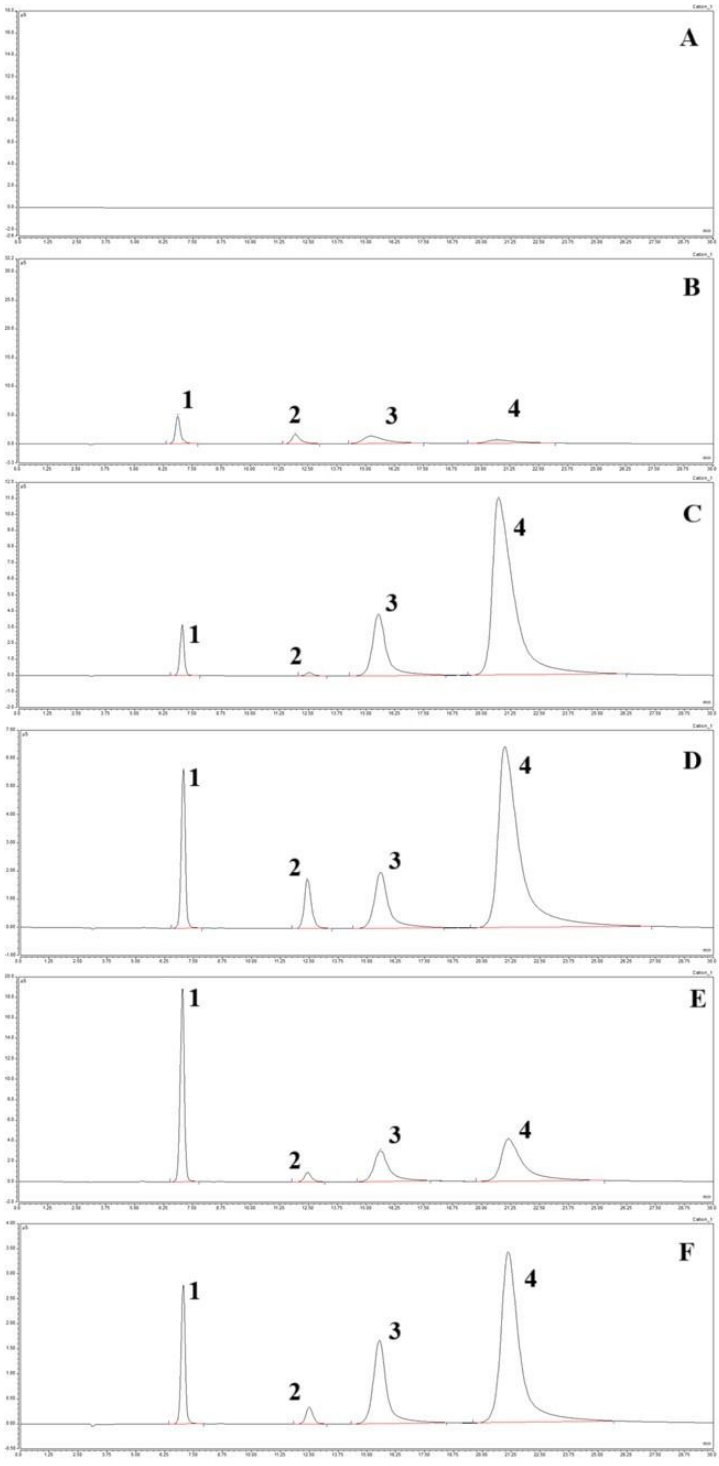

Fig. 1. Representative chromatograms: A) blank, b) Standard solution containing 5 mg/L of each cation (1-sodium, 2-potassium, 3-magnesium and, 4-calcium), c) Water sample from Bitola, d) Water sample from Debar, e) Water sample from Gevgelija, f) Water sample from Kratovo.

Linearity - In our study, the linearity was determined in the range from 0.253 mg/L to 50.6 mg/L for Ca^{2+}, 0.1265 mg/L to 25.3 mg/L for Mg^{2}, 0.252 mg/L to 50.5 mg/L for $K^{+,}$ and 0.1015 mg/L to 20.3 mg/L for Na^{+}. The calibration standards were prepared at 6 concentration levels and each measurement was performed in triplicate. The obtained

results were evaluated using linear regression analysis using the least squares regression method. The results are presented in Table 1.

The results confirmed the linear relationship between peak areas of the examined analytes and the respective concentrations. The correlation coefficient was greater than 0.999 for all the cations. The results indicate very good linearity.

Precision – Method precision was verified and evaluated through repeatability (system and method repetability) and intermediate precision. The repeatability of the system was evaluated by six determinations of the peak areas of standard solutions containing each investigated cation (10 mg/L Na^+, 25 mg/L K^+, 12 mg/L Mg^{2+} and 25 mg/L Ca^{2+}). System precision as well as method precision values were below 2%, thus the method is precise. The intermediate precision assessed on two consecutive days, by two different analysts showed that the RSD value of the entire determination is not more than the recommended value for RSD given in ISO 14911:1998 allowed for intermediate precision, thus the method is precise (Table 1).

Accuracy - Accuracy of the method was verified through the study of analytical recovery, at 3 concentration levels (50, 100 and 150%) for each examined cation. For Na^+, accuracy was investigated at the following concentration levels (5, 10 and 15 mg/L), for K^+ (12, 25 and 37 mg/L), Mg^{2+} (6, 12 and 18 mg/L) and 12, 25 and 37 mg/L for Ca^{2+}. The results are shown in Table 2. The percentages of the obtained recoveries are in the range 99.83-104.60%, indicating and verifying good accuracy of the method (Little, 2016).

Analysis of bottled water samples

Table 3 shows the results obtained by analyzing the bottled water samples over the 12 months (from May 2023 to April 2024) manufactured in 4 different parts of the country (Bitola, Debar, Gevgelija and Kratovo).

Na^+ concentrations in the analyzed samples ranged between 1.94 and 17.01 mg/L. The highest concentrations were observed in the region of Bitola and the lowest in Debar. K^+ concentrations were between 0.32 and 4.01 mg/L, with the highest concentration in Gevgelija and the lowest concentration in Debar. Mg^{2+} concentrations varied between 1.87 and 7.53 mg/L. The highest concentration of Mg^{2+} were present in the region of Debar and the lowest in the region of Kratovo. Ca^{2+} concentrations were between 10.79 and 44.96 mg/L. Lowest concentrations were characteristic for the region of Kratovo and the highest concentrations for the region of Debar. The determined values were in accordance with the national legislation (Official Gazette of Republic of North Macedonia, Rulebook n.184, 2018).

There are no significant changes in the cation composition of the investigated bottled waters during the year. The concentrations of Na^+ and Ca^{2+} ions were in the range of 10-100 mg/Land the concentrations of K^+ and Mg^{2+} were in the range of 1-10 mg/L in the bottled water. The comparison of the obtained ranges for the content of the examined cations in our study differed from the labeled content of the corresponding cations. This finding may be due to the natural fluctuations of major cation levels in the water sources (Konczyk et al., 2019).

Table 3. Results obtained by analyzing the bottled water samples over the 12 months

Analyte	Region	Results obtained (mg/L)		Data declared by the manufacturer (mg/L)
		min	max	
Na	Bitola	13.57	17.01	12.40
	Debar	1.94	2.90	2.50
	Gevgelija	2.35	5.20	4.30
	Kratovo	1.97	3.52	2.18
K	Bitola	1.70	2.43	1.53
	Debar	0.33	0.46	< 1.00
	Gevgelija	3.21	4.02	3.50
	Kratovo	0.69	0.92	0.93
Mg	Bitola	5.57	7.53	6.50
	Debar	4.31	6.31	7.00
	Gevgelija	2.41	3.42	3.70
	Kratovo	1.88	2.69	2.99
Ca	Bitola	14.06	18.48	20.60
	Debar	34.61	44.96	44.00
	Gevgelija	23.06	26.90	26.30
	Kratovo	10.74	14.16	11.60

Conclusion

In this study, the results of the method performance verification and application of the ISO 14911:1998 method for determination of cations by ion chromatography are shown. The concentrations of the four investigated cations in bottled waters (Na^+, K^+, Mg^{2+} and Ca^{2+}) of the 4 brands of bottled water from North Macedonia were determined. According to the results, the cation concentration did not exhibit significant variability of the composition during the investigated period. However, small differences were observed due to natural fluctuations. The method presented in this study could be used for future investigations regarding bottled water quality in order to ensure its safety and to promote public health.

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Резиме

Примена на јонска хроматографија за определување на одбрани катјони од IA и II A група во пакувани води

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Клучни зборови: пакувана вода, катјони, јонска хроматографија, верификација на метод, квалитет

Пакуваните води се важен извор на есенцијални минерали за човечкото тело. Ова истражување ги прикажува резултатите од определувањето на 4 главни катјони (натриум, калиум, магнезиум и калциум) во комерцијално достапни пакувани води во Република Северна Македонија со помош на јонска хроматографија со кондуктометриски детектор. Прво, беше направена верификација на методот ISO 14911, каде што бепе пресметана линеарноста, точноста и прецизноста. Верификуваниот метод за јонска хроматографија, беше применет на примероци од вода од 4 различни делови на земјата (Битола, Дебар, Гевгелија и Кратово). Концентрацијата на натриум во анализираните примероци се движи помеѓу 1,94 и 17,01 mg/L. Концентрацијата на калиум е помеѓу 0,32 и 4,01 mg/L. Концентрацијата на магнезиум варира помеѓу 1,87 и 7,53 mg/L, додека концентрацијата на калциум е помеѓу 10,79 и 44,96 mg/L. Концентрациите на испитуваните катјони се во согласност со барањата на правилникот за безбедност и квалитет на водата за пиење.