Quantification of inorganic anions in surface and drinking waters using ion chromatography

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The Republic of Bulgaria regulates the quality of surface waters for drinking and domestic purposes, monitoring anions like F^-, Cl^-, Br^-, I^-, BrO_3^-, NO_2^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, and SCN^-. The presence of NO_3^- and NO_2^- in water is undesirable, as they have a harmful effect on human health. It is also well known that CN^- as opposed to SCN^- has acute toxic and lethal effects on living organisms including humans.

In the present study, an instrumental method was developed and optimized for the separation and quantification of inorganic anions in surface and drinking water using ion chromatography. The analytical characteristics of the proposed instrumental method were determined. The oxidation of CN^- to OCN^- was investigated, and the optimal experimental conditions for the oxidation were established. The achieved low LOD and LOQ of the analyzed inorganic anions allows their detection and quantification in surface and drinking waters.

The applicability of the proposed chromatographic method was determined in the analysis of surface and bottled waters. The analyzed anions in bottled waters were close to the label's values, only one spring water showed significant deviations.

Keywords: Inorganic anions, Ion chromatography, Surface waters, Drinking waters.

INTRODUCTION

For all living organisms including humans, water is vital. It is widely used in many industries, including the mining and energy sectors, in addition to being used for drinking and domestic requirements. Naturally, this results in a decline in the water basins' quality. The anions that prevail in waters from natural sources are chloride (Cl^-), sulfate (SO_4^{2-}), carbonate (CO_3^{2-}), and hydrogen carbonate (HCO_3^-). Apart from them, nitrate (NO_3^-), nitrite (NO_2^-), bromide (Br^-), iodide (I^-), phosphate (PO_4^{3-}), thiocyanate (SCN^-), and cyanide (CN^-) can also be found. NO_3^-, a plant nutrient, can reach surface water due to agricultural activities, wastewater disposal, and oxidation of nitrogenous waste products. NO_2^-, a stable oxidation state, is less common in reducing environments. Excess free ammonia can lead to nitrification and increase NO_3^-, and NO_2^- in drinking water [1]. Br^- is commonly found in nature along with sodium chloride owing to their similar physical and chemical properties, but in smaller quantities. Br^- concentrations in fresh water varies from trace amounts to about 0.5 mg/L and in desalinated waters up to 1 mg/L [1]. Most of the natural surface waters have total I^- concentrations between 0.5 and 100 µg/L [2]. Phosphate treatment of drinking water increases phosphate concentrations to prevent corrosion and metal leaching in distribution systems, typically adding orthophosphate to reduce metal solubility in pipe work systems [3]. CN^-, found in some foods and drinking water, can be high in concentrations due to industrial spills. SCN^- contamination threatens aquatic ecosystems and pollutes freshwater supplies, a widespread global issue caused by industrial processes like gold mines and coal coke processing [4].

Maximum permissible concentrations according to Bulgarian Regulation No. 9 (2001) on the quality of water intended for drinking and household purposes are: F^-—1.5 mg/L, Cl^-—250 mg/L, BrO_3^-—0.01 mg/L, NO_2^-—0.5 mg/L, NO_3^-—50 mg/L, CN^-—0.05 mg/L, SO_4^{2-}—250 mg/L, and PO_4^{3-}—0.5 mg/L. According to Bulgarian Regulation No. 12 (2002) on the quality of surface water intended for drinking and household purposes for water with the best indicators (category A1), the maximum permissible concentrations for F^-, NO_3^-, CN^- and SO_4^{2-} are the same as in Regulation No. 9, but a difference is observed for Cl^-—200 mg/L and PO_4^{3-}—0.7 mg/L. The rest of the anions are not mentioned in the regulations.

Ion chromatography (IC) is a suitable instrumental technique for the separation and determination of inorganic anions. Various

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characteristics of IC, such as its simple operation, speed, available reagents, and high sensitivity [5], make it suitable for environmental sample analyses. IC has become a rapid analytical technique for analyzing complex mixtures of ions [6]. In addition, it is a relatively cheap method and, in many cases, requires simple sample preparation. IC has been successfully applied for the determination of different species of inorganic anions in environmental samples such as water, plants, soils, sediments, and wastewater [7-9]. Stefanović applied IC with a conductometric determination without suppression for analyses of six anions: F^-, Cl^-, NO_2^-, NO_3^-, Br^- and SO_4^{2-} in drinking water [10]. BrO_3^- anions can be found in water as a result of ozonation. They have been found to be carcinogenic. Dhillon and Statler [11] developed a methodology for determining μg/L concentrations of BrO_3^- in ozonated waters. In the European standard EN ISO 10304-1:2009 [12], there is a method for the separation and quantification of F^-, Cl^-, Br^-, NO_2^-, NO_3^-, SO_4^{2-}, and PO_4^{3-} in natural, waste, drinking, surface, underground, and other types of water, but it does not include BrO_3^- and CN^-. However, the use of IC with conductivity detection makes it difficult to detect CN^-, mainly because HCN is too weak acid with a dissociation constant pKa=9.2. Weak acids with a pKa larger than 6 cannot be detected with a conductivity detector [13]. An analytical solution is the conversion of CN^- to OCN^- (the dissociation constant of hydrogen cyanate is high enough, pKa=3.66) because OCN^- can be measured with a conductivity detector [14].

In the present study, a method for the separation and quantification of F^-, Cl^-, Br^-, I^-, BrO_3^-, NO_2^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, and SCN^- in surface and drinking water using IC was established and optimized. An efficient procedure for the oxidation of CN^- to OCN^- and their subsequent quantification is proposed. The method was applied to real samples of surface, drinking, and bottled water.

MATERIALS AND METHODS

Reagents and standards

All standard solutions of F^-, Cl^-, Br^-, I^-, BrO_3^-, NO_2^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, and SCN^- were prepared from analytical reagent grade chemicals (purchased from Merck, Darmstadt, Germany) using deionized water. All salts were in the sodium form with the exception of SCN^- (ammonium form). A stock standard solution of each anion with a concentration of 1000 mg/L, was prepared, from which working solutions were subsequently prepared by appropriate dilution. To simulate the matrix of the analyzed samples, the calibration standard solutions were

mixed in the concentration range of 0.1-30 mg/L for BrO_3^-, Br^-, Cl^-, F^-, I^-, NO_2^-, NO_3^-, and SCN^-, and in the range of 1-75 mg/L for SO_4^{2-}, and 10-60 mg/L for PO_4^{3-}. External calibration with multi-anion standard solution was performed.

Instrumentation

The chromatographic analysis was performed with an ion chromatograph model CIC-D160, SHINE (Qingdao Shenghan Chromatograph Technology Co., Qingdao, China), equipped with an anion-exchange column SH-AC-11 (size 4.6×250 mm) purchased from SHINE (Qingdao, China). The separation was performed at the following operating parameters - mobile phase: 15 mM KOH, column temperature: 35 °C and flow rate: 1.0 mL/min (isocratic elution). The volume of the injected sample was 25 μL. Ultrapure water purified by Milli-Q purification system (Millipore purification system Synergy, France, 18.2 MV cm), was used throughout the experiments.

Accuracy and precision of the method

To evaluate the accuracy and precision of the proposed chromatographic method, a reference material SPS-NUTR-WW2 (Reference Material for Measurement of Ions in Waste Waters, Oslo, Norway), was used, to which the missing inorganic anions were added in appropriate concentrations.

Limit of detection (LOD) and limit of quantification (LOQ)

LOD of the analyzed inorganic anions was calculated by preparing spiked solutions of F^-, Cl^-, Br^-, I^-, BrO_3^-, NO_2^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, and SCN^- at low concentrations that were expected to produce a response 3-10 times the noise of baseline. LOQ was determined in the same way and selected as the concentration of the anions that gives an S/N ratio of 10-20 [15].

Oxidation of cyanide to cyanate

A volume of 4.5 mL of 0.1 M NaOH (pellets pure, min. 97%) solution was added to 5 mL of a 5 mg/L CN^- solution in 50 mL volumetric flasks and diluted to the mark with deionized water. 5 μL of concentrated H_2O_2 and Cu-lamina to catalyze the reaction were added to the flask, stoppered, and mixed well. The solution was kept in a water bath at 65 °C for 30 min. Then the hot solution was left in the water bath to reach room temperature. After that, the solution was filtered through 0.45 μm filter before loading into the autosampler vial for IC analyses to evaluate the conversion rate of CN^- to OCN^-. After oxidation, determination of the

accuracy, precision, and LOD and LOQ was done in the same manner as for the other anions.

Sampling and sample preparation

Water samples were taken from 6 locations: the lower reaches of the Beli Iskar River, Rila mountain (Station 1), at the mouth of the Vladaiska River (Station 2), at the mouth of the Lesnovska River (Station 3), at the mouth of the Batuliyska River (Station 4), at the mouth of the Bebresh River, Malki Iskar (Station 5), Perlovska River, Sofia (Station 6). Water samples were collected in polypropylene containers. The containers were rinsed with deionized water before use and then with real samples. The surface waters were filtered through a 0.45 µm filter and then were cooled to 4 °C and analyzed within 48 h [16]. For the determination of CN$^-$ anions, individual parallel samples were spiked with NaOH to adjust pH>12, then were stored at 4 °C. Samples preserved in this way can be stored for up to 14 days [16]. Additionally, three brands of spring water (Devin, Baldaran, and Ledina) and one mineral water (Devin) available in the commercial network were purchased and analyzed without sample pretreatment.

RESULTS AND DISCUSSION

IC method development

At the beginning of method development, a 30 mM KOH mobile phase and 1.5 mL/min flow rate of eluting solvent were used to achieve shorter analysis times and higher throughput. But this leads to overlapping of nearby anion peaks. Virtually no separation was achieved between BrO$_3^-$ and Cl$^-$ due to their equal retention times. The subsequent stages of method development involved decreasing the concentration of the mobile phase and the flow rate. Complete separation of F$^-$, Cl$^-$, Br$^-$, I$^-$, BrO$_3^-$, NO$_2^-$,

NO$_3^-$, SO$_4^{2-}$, PO$_4^{3-}$ and SCN$^-$ was achieved at 15 mM KOH and a flow rate of 1 mL/min. At these conditions the total analysis time is less than 25 min. The resulting chromatogram of anion separation with the following concentrations: 0.3 mg/L F$^-$, 1.0 mg/L Cl$^-$, 0.5 mg/L Br$^-$, 1.0 mg/L I$^-$, 0.5 mg/L BrO$_3^-$, 0.3 mg/L NO$_2^-$, 0.3 mg/L NO$_3^-$, 4.0 mg/L SO$_4^{2-}$, 10.0 mg/L PO$_4^{3-}$, and 1.0 mg/L SCN$^-$ and the respective retention times (min) is presented in Figure 1.

Linearity and linear ranges

Calibration was performed over the whole linear dynamic ranges, and calibration curves of different anions were prepared at eight levels assorted evenly from lowest to highest concentration. The calibration ranges, regression equation, correlation coefficient (r) and coefficient of determination (R^2) were calculated according to Juradoa *et. al.* [17] and are presented in Table 1.

The low sensitivity and the narrow linear concentration interval of PO$_4^{3-}$, are due to the low degree of dissociation, which makes it difficult to be detected with a conductivity detector. At concentrations less than 6.5 mg/L, the chromatographic peak is not well defined and phosphate ions cannot be quantified. Nevertheless, this result indicates that the studied anions can be determined in environmental samples in a wide concentration range.

Accuracy and precision

To evaluate the accuracy of the proposed instrumental method, a reference material, SPS-NUTR-WW2, was used, to which the missing anions were added in appropriate concentrations. Table 2 shows the experimental and certified concentrations of detectable anions.
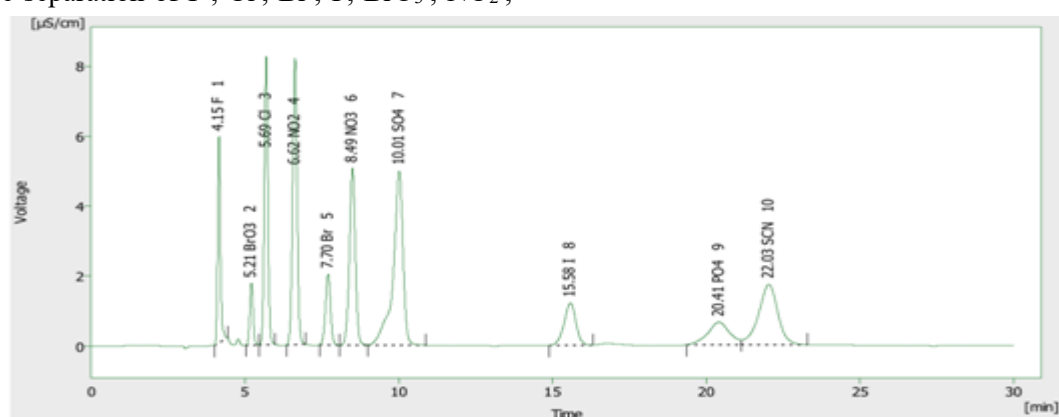

Figure 1. Ion chromatogram of F$^-$, Cl$^-$, Br$^-$, I$^-$, BrO$_3^-$, NO$_2^-$, NO$_3^-$, SO$_4^{2-}$, PO$_4^{3-}$, and SCN$^-$.

Table 1. Summarized calibration data of different anions in standard solution by IC.

Anion	Range (mg/L)	Regression equation	Coefficient of determination (R^2)	Correlation coefficient (r)
F^-	0.1-30	f(x)=41.1085x - 1.8759	0.99976	0.99987
Cl^-	0.1-30	f(x)=27.4809x - 4.1323	0.99963	0.99981
Br^-	0.1-30	f(x)=11.7850x - 3.4116	0.99906	0.99952
I^-	0.1-30	f(x)=7.2621x - 0.7403	0.99971	0.99985
BrO_3^-	0.1-30	f(x)=6.6614x - 0.9527	0.99982	0.99991
NO_2^-	0.1-30	f(x)=19.2124x - 1.4932	0.99993	0.99996
NO_3^-	0.1-30	f(x)=15.3541x - 2.4743	0.99950	0.99975
SO_4^{2-}	1-75	f(x)=8.3461x - 4.1825	0.99966	0.99983
PO_4^{3-}	10-60	f(x)=3.2604x - 0.9108	0.99893	0.99946
SCN^-	0.1-30	f(x)=13.5511x - 0.9104	0.99990	0.99995

Table 2. Accuracy of inorganic anions measurement with IC based on analysis of certified reference material SPS-NUTR-WW2.

Anion (mg/L)	Experimental value	Certified value	Anion (mg/L)	Experimental value	Certified value
F^-	10.1±0.1	10.0±0.1	NO_3^-	5.03±0.04	5.00±0.05
BrO_3^-	5.0±0.1	5*	SO_4^{2-}	101±2	100±1
Cl^-	49.8±0.3	50.0±0.5	I^-	4.8±0.3	5*
NO_2^-	4.9±0.3	5*	SCN^-	4.9±0.3	5*
Br^-	5.1±0.2	5*	PO_4^{3-}	7.45±0.04	7.50±0.08

* added to SPS-NUTR-WW2.

Table 3. Limit of detection and limit of quantification of F^-, Cl^-, Br^-, I^-, BrO_3^-, NO_2^-, NO_3^-, SO_4^{2-}, PO_4^{3-} and SCN^- (mg/L).

Anion (mg/L)	LOD	LOQ	Anion (mg/L)	LOD	LOQ
F^-	0.01	0.03	NO_3^-	0.06	0.17
BrO_3^-	0.06	0.35	SO_4^{2-}	0.08	0.26
Cl^-	0.03	0.1	I^-	0.07	0.83
NO_2^-	0.03	0.1	SCN-	0.06	0.85
Br^-	0.06	0.35	PO_4^{3-}	2.17	6.54

The comparison of the experimentally obtained values of the analyzed anions with the data from the certificate showed that the proposed method is characterized by good accuracy and is applicable for the determination of F^-, Cl^-, Br^-, I^-, BrO_3^-, NO_2^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, and SCN^- in surface and drinking water.

The precision of the current method for determining the inorganic anions was evaluated by calculating the relative standard deviation (RSD, %) of the peak areas of six replicate injections of standard solutions with three concentrations (10, 20 and 30 mg/L for SO_4^{2-} and PO_4^{3-} and 1.0, 10.0, and 15 mg/L for the other anions), which was found to be less than 7.0%.

Limit of detection (LOD) and limit of quantification (LOQ)

The LOD and LOQ of each anion were determined, and the obtained results are presented in Table 3.

Most of the proposed methods in the literature are restricted to the determination of a limited number of anions F⁻, Cl⁻, Br⁻, NO₂⁻, NO₃⁻, SO₄²⁻, PO₄³⁻ [7, 9], while in the present study BrO₃⁻, I⁻, and SCN⁻ were also determined. The achieved LODs are sufficiently low for the determination of the target anions in the concentrations they present in water. Also, the maximum permissible concentrations of the analyzed anions in the water intended for drinking and household purposes according to Bulgarian Regulation No. 9 (F⁻—1.5 mg/L, Cl⁻— 250 mg/L, BrO₃⁻—10 µg/L , NO₂⁻—0.5 mg/L, NO₃⁻—50 mg/L, and SO₄²⁻—250 mg/L) and EPA, 2018 (F⁻—2,0 mg/L, Cl⁻— 250 mg/L, BrO₃⁻—10 µg/L, NO₂⁻—1 mg/L, NO₃⁻—10 mg/L, and SO₄²⁻—250 mg/L) are much higher than the LOQs. As expected, the highest LOD and LOQ were observed for phosphate anions. The obtained values do not permit its determination in concentrations lower than the maximum permissible concentrations (0.5 mg/L). The rest of the anions are not mentioned in the Bulgarian regulations.

Oxidation of cyanide to cyanate

The use of an IC with a conductivity detector is not suitable to detect CN⁻ anions, mainly because HCN is a weak acid. A method that uses NaOCl to oxidize free CN⁻ to OCN⁻ before chromatographic separation with conductivity detection was reported in the literature [18], but a highly tailed chloride ion peak was observed. In another study, a method for determination of CN⁻ in drinking and seawater was developed based on the oxidation of CN⁻ with chloramine-T [14]. In the current study, the proposed procedure was based on the oxidation of CN⁻ to OCN⁻ with H₂O₂ at an alkaline pH and heating. The working temperature (25-85 °C) was optimized during the experiment.

To optimize the operating temperature, the CN⁻ solutions, prepared as described in the experimental part, were heated in a water bath from 25 °C to 85 °C in steps of 10 degrees. At each temperature, the heating time was 60 min. The peak retention time of the OCN⁻ was 6.86 min (Figure 2) using experimental conditions under which the other anions were determined. After the chromatographic analysis, it was found that the maximum degree of oxidation to OCN⁻ is achieved at 65 °C (Figure 3a). After establishing the optimal temperature required for oxidation, the time was optimized to reduce heating and sample preparation time. The time required was found to be 30 min. After this time, no increase in chromatographic peak area was observed (Figure 3b). The OCN⁻ calibration standard solutions were prepared in the concentration range from 0.1-25 mg/L. A plot of the peak areas of the OCN⁻ *versus* concentration (in mg/L) was found to be linear in the range of 0.1-30 mg/L, the same as F⁻, Cl⁻, Br⁻, I⁻, BrO₃⁻, NO₂⁻, NO₃⁻ and SCN⁻. The LOD and LOQ were 0.03 mg/L and 0.1 mg/L, respectively. The oxidation efficiency was verified by using standard addition at three concentration levels (0.05 mg/L, 5.0 mg/L, 15.0 mg/L) to real water samples, which showed a recovery between 98.9-101.5 %.
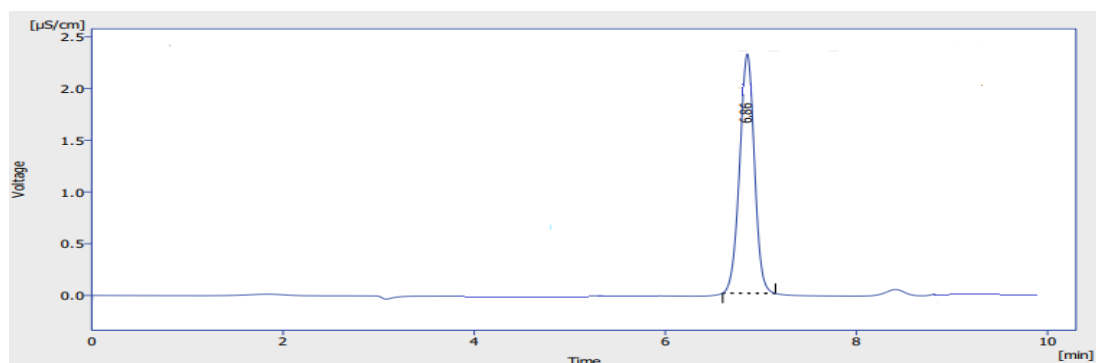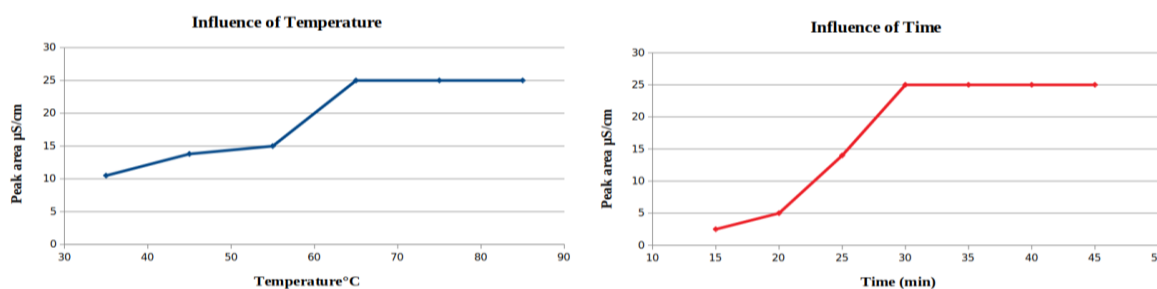

Figure 2. Chromatogram of OCN⁻anion.

Figure 3. Dependence of temperature (3a) and heating time (3b) on CN⁻ to OCN⁻ oxidation.

Table 4. Concentration of analyzed anions in surface waters

Anion (mg/L)	Reg. №12 (mg/L)	Station 1	Station 2	Station 3	Station 4	Station 5	Station 6
F^-	1.5	0.051±0.003	0.054±0.002	0.068±0.003	0.102±0,005	0.145±0.007	0.076±0.004
Cl^-	200	4.87±0.24	22.9±1.2	4.98±0.25	6.91±0.35	2.91±0.15	34.6±1.7
NO_3^-	50	3.10±0.16	18.6±0.9	3.36±0.17	4.33±0.22	2.60±0.13	6.45±0.32
SO_4^{2-}	250	20.9±1.5	41.1±2.8	21.5±1.5	25.8±1.8	35.5±2.5	20.9±1.5
NO_2^-	0.5	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	0.18±0.09

Table 5. Measured concentrations of the anions present in drinking water by IC.

Anion (mg/L)	Reg. №9 (mg/L)	Spring waters						Mineral waters	
		Devin		Baldaran		Ledina		Devin	
		Exp.value	Label	Exp.value	Label	Exp.value	Label	Exp.value	Label
F^-	1.5	<0.01	< 0.1	< 0.01	< 0.1	0.077±0.004	< 0.1	3.86±0.19	3.69
Cl^-	250	0.85±0.04	< 1	0.84±0.04	2.3	13.1±0.6	4.3	1.08±0.05	2.9
NO_3^-	50	0.19±0.01	< 0.064	1.27±0.06	< 5	22.4±1.1	3	< 0.06	< 0.064
SO_4^{2-}	250	2.50±0.17	2.7	2.42±0.17	3.29	23.5±1.7	10.7	17.7±1.2	19.75

Application of the method to real water samples

The applicability of the proposed chromatographic method was determined in the analysis of surface and bottled waters. The chromatographic results obtained for surface waters are presented in Table 4.

F^-, Cl^-, NO_3^- and SO_4^{2-} were found in the surface waters from the sampling points of stations 1–5. In station 6, apart from them, NO_2^- were also present. The measured anion concentrations from the various sampling points did not exceed the maximum permissible values described in the Bulgarian regulations. The remaining anions - I^- Br^-, BrO_3^-, PO_4^{3-}, SCN^-, were below the LODs of the chromatographic method. CN^- anion was 0.21 mg/L in the sample from Perlovska River.

The chromatographic method was also applied to bottled waters purchased from the commercial network in Bulgaria. Table 5 presents the measured concentrations of the anions present in three spring waters and one mineral water and they are compared with the concentrations given on the label of the respective water.

The content of the analyzed anions was close to those indicated on the label for most of the bottled waters. Serious deviations in the concentrations of the experimentally determined and those indicated on the label were observed in "Ledina" spring water. Although the anion concentrations are within the limits of the maximum permissible values mentioned in the Regulation No. 9 (2001) on the quality of water intended for drinking and domestic purposes, they significantly exceed the values described on the label. Cl^- anions were about 3 times higher, NO_3^- more than 7 times, and sulfates nearly 2 times higher than the label values.

CONCLUSION

An ion chromatographic method was developed and optimized for the separation and quantification of F^-, Cl^-, Br^-, BrO_3^-, I^-, NO_2^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, and SCN^- in water samples. The method is characterized by good analytical characteristics, which makes it applicable and reliable. Good accuracy and precision were achieved for all detectable inorganic anions. The low values of LOD and LOQ satisfy the requirements specified by the relevant regulations controlling the quality of water for drinking and domestic needs in the Republic of Bulgaria. Also, a methodology for the quantitative determination of CN^- anions was developed, which without prior oxidation, cannot be determined with an ion chromatograph equipped with a conductometric detector. The developed chromatographic method was successfully applied to real surface and drinking water samples.

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