Quantification of Trace and Major Anions in Water by Ion Chromatography in a High-Throughput Laboratory

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Introduction

Ion chromatography (IC) hyphenated to a conductivity detector (CD) is a well-established and accepted technique for the quantitative analysis of inorganic anions in drinking water. It allows the routine determination of chloride, fluoride, nitrate, and nitrite as well as bromide, phosphate, and sulfate. In 1993, the World Health Organization (WHO)[1] set a guideline of 25 µg/L for bromate in drinking water and the Council Directive 98/83/EC[2] set this parametric value at 10 µg/L bromate and a limit of detection (LOD) of 2.5 µg/L for the analytical performance of the method. However, the analytical performance of the IC-CD method is not sufficient to routinely reach such a low LOD for bromate analysis.

The bromate detection limit can be improved to the sub-µg/L level by using preconcentration after sample pretreatment,[3,4] but this methodology is very time consuming for high-throughput laboratories. Other methods based on a large sample volume injection and the use of postcolumn reaction (PCR) in conjunction with IC followed by a UV-vis detector (IC-PCR-UV-vis) allow a low LOD for trace bromate analysis (usually sub-µg/L).[5-8]

The use in series of a CD and a postcolumn reaction system followed by a UV-vis detector allows the determination of inorganic anions and trace concentrations of bromate.[9] However, a large sample volume injection is required which dramatically affects the peak symmetry, the width, and the resolution (sometimes causing co-elution) of some inorganic anion peaks such as chloride, nitrate, and sulfate, which can be present in drinking water at concentrations 100,000 times higher than bromate.

In summary, good resolution for the major inorganic anion peaks and a low LOD for bromate determination is a difficult compromise to achieve. It dictates that laboratories split their method, which is time consuming and increases costs.

For this reason, we present in this paper a method for the determination of fluoride, chloride, chlorite, chlorate, bromide, bromate, nitrite, nitrate, sulfate, and phosphate in different types of water samples without compromise between the sample volume injected in the chromatographic system and a low limit of quantification suitable for trace bromate determinations.

Experimental

The method is composed of two sets of chromatographic conditions used in parallel (chromatographic conditions 1 and chromatographic conditions 2) on a Dionex ICS-3000 ion chromatography system (Thermo Scientific, Sunnyvale, CA, USA). The detailed schematic of this method is presented in Figure 1. The Dionex ICS-3000 system used in this study incorporates an electrolytic eluent generator (for KOH production), dual-piston pump with vacuum degas, two six-port injection valves fitted with two loops in series (25 and 250 µL), heated conductivity cell, column heater, and a postcolumn reaction system. A Thermo Scientific Dionex AS50 Autosampler was used for sample processing. Thermo Scientific Dionex Chromeleon 6.8 Chromatography Data System software was used for system control and data processing.

Thermo Scientific Note: Today one would purchase a Dionex ICS-5000 dual system with a Dionex AS-AP Autosampler to execute this method.
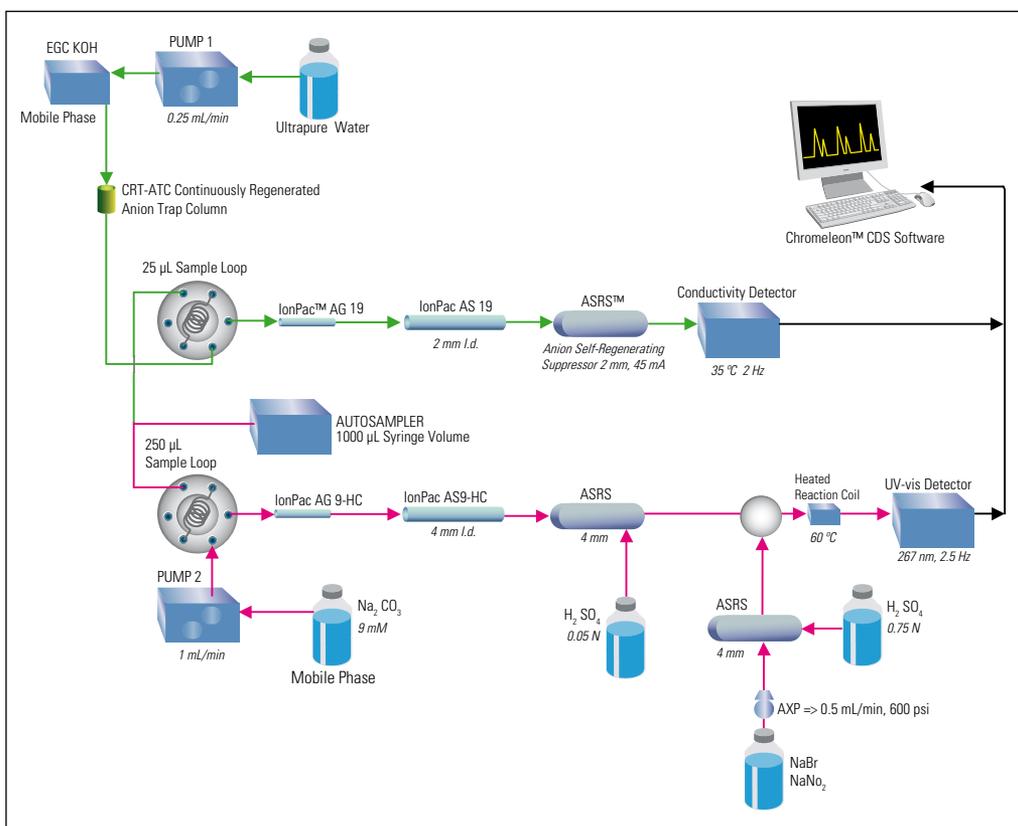
Figure 1. General representation of the chromatographic system.

Chromatographic conditions 1

A Thermo Scientific Dionex IonPac AS19 (250 mm × 2 mm i.d.) analytical column and its respective guard column, the Dionex IonPac™ AG19 (50 mm × 2 mm i.d.), were used for the separation of fluoride, nitrite, bromide, phosphate, chlorate, nitrate, chloride, and sulfate. The mobile phase gradient program is presented in Table 1. Suppression was achieved using a Dionex ASRS™ electrolytic suppressor, supplied with external ultrapure water. Inorganic anions were detected using a suppressed conductivity detector.

Table 1. Selected mobile phase program for chromatographic conditions 1

Time (min)	KOH Concentration (mM)
0–10	10
18.5	45
18.5–22.5	60
23–26	10

Chromatographic conditions 2

A Dionex IonPac AS9-HC (250 mm, 4 mm i.d.) and its guard column, the Dionex IonPac AG9-HC (50 mm, 4 mm i.d.), were used for the separation of chlorite and bromate. The mobile phase was 9 mM sodium carbonate (Na_2CO_3).

A pressurized postcolumn delivery module (Dionex AXP Auxiliary Pump) was used to deliver the postcolumn reagent at a flow rate of 0.50 mL/min. A 500 µL knitted reaction coil was placed in a postcolumn heater, set at 60 °C, to mix the effluent and postcolumn reagent. The postcolumn reaction mixture consists of 0.5 mM sodium nitrite and 1 M sodium bromide. Acidification of the PCR reagent is realized using an ASRS suppressor which is regenerated with 0.75 M sulfuric acid. Chlorite and bromate were detected with an UV-vis detector at a wavelength of 267 nm.

2.2. Standard solutions and samples

All solutions were prepared in ultrapure water with a specific resistance of 18.2 MΩ•cm (Millipore, Molsheim, France). Commercially available 1000 mg/L certified solutions of nitrate, sulfate, chloride, phosphate, bromide, nitrite, and fluoride (Merck, Darmstadt, Germany) and chlorite, chlorate, and bromate (Spex CertiPrep, Metuchen, NJ), were used to prepare working standard solutions.

The concentrations of inorganic anions used for the calibration curve and the quality control of the analysis of drinking water are presented in Table 2.

Table 2. Concentrations of the anions used for the calibration curve and the quality control. Certified solutions used to prepare the quality control and the working standards were different.

Anion	Concentration of Anions (mg/L)					
	Calibration Curve					Quality Control
Fluoride	2	1	0.5	0.2	0.1	1
Nitrite	1	0.5	0.25	0.1	0.05	0.5
Bromide	1	0.5	0.25	0.1	0.05	1
Phosphate	1	0.5	0.25	0.1	0.05	1
Chlorite	0.02	0.01	0.005	0.002	0.001	0.02
Bromate	0.02	0.01	0.005	0.002	0.001	0.02
Chlorate	0.2	0.1	0.05	0.02	0.01	0.1
Nitrate	100	50	25	10	5	50
Chloride	200	100	50	20	10	50
Sulfate	200	100	50	20	10	50

Results And Discussion

3.1 Method characteristics

As presented in Figure 1, two sample loops (25 and 250 µL) were filled in series. The selected volumes were compatible with the selection of a 2 mL vial. A larger volume would require the use of vial with a higher capacity (i.e., 5 mL). This would reduce the number of vials in the autosampler.

Once the sample loops are filled, the valve switches to the inject position. On the one side, potassium hydroxide (KOH) mobile phase carries the content of the 25 µL sample loop to the Dionex IonPac AG19 guard column, the Dionex IonPac AS19 analytical column, ASRS suppressor, and then to the conductivity detector. On the other side, the Na_2CO_3 mobile phase carries the content of the 250 µL sample loop to the Dionex IonPac AG9-HC guard column, the Dionex IonPac AS9-HC analytical column, the postcolumn reaction system, and then to the UV-vis detector.

The use of different sample loop sizes, mobile phases, and detection systems for the simultaneous determination of the major inorganic anions and trace oxhalides (bromate and chlorite) presents the following main advantages.

Advantages for the method for trace oxyhalide determinations (bromate and chlorite):
- A large injected volume (250 µL instead of 25 µL) improves the response for bromate and chlorite.
- Postcolumn reaction followed by UV-vis detection is selective for trace bromate and chlorite analysis. This improves the limit of quantification for these analytes.
- The resolution between chlorite and bromate under the applied chromatographic conditions appeared to be better on the Dionex IonPac AS9-HC column than on the Dionex IonPac AS19 column.

Advantages for the method for major inorganic anions analysis:
- The injected volume (25 µL) allows good resolution. Larger injection volumes could result in unwanted peak-broadening and partial coelutions.
- KOH mobile phase is suitable for a good chromatographic resolution. As the mobile phase was electrolytically generated, only one isocratic pump was required to deliver the deionized water needed for the Dionex Reagent-Free™ Ion Chromatography (RFIC™) system, even for gradient elution.

3.2 Anion chromatograms

Figure 2 shows representative chromatograms of a mixed anion solution (quality control) containing 20 µg/L bromate and chlorite, 0.1 mg/L chlorate, 0.5 mg/L nitrite, 1 mg/L fluoride, bromide, and phosphate, and 50 mg/L nitrate, chloride, and sulfate. The bromate peak is baseline-resolved from chlorite with a resolution of 1.54 and 1.59 for chromatographic conditions 1 and 2 respectively. These resolutions meet the ISO 11206:2011 requirement, which set a resolution of 1.3 or better. Although both chromatographic systems allow a good resolution of bromate with its closest peak (chlorite), the bromate peak shows a significantly enhanced response with postcolumn reaction followed by a UV-vis detector. For example, Figure 3 shows that the bromate peak at a concentration of 1 µg/L is not quantifiable with the CD while the postcolumn reaction and the UV-vis detector permits bromate quantification.

So, the proposed method allows the determination of 10 inorganic anions including both trace (i.e., bromate, chlorite) and major inorganic anions (i.e., chloride). This method of simultaneously analyzing the same sample under two chromatographic conditions avoids compromise between the injected volume and analyte peak resolution.
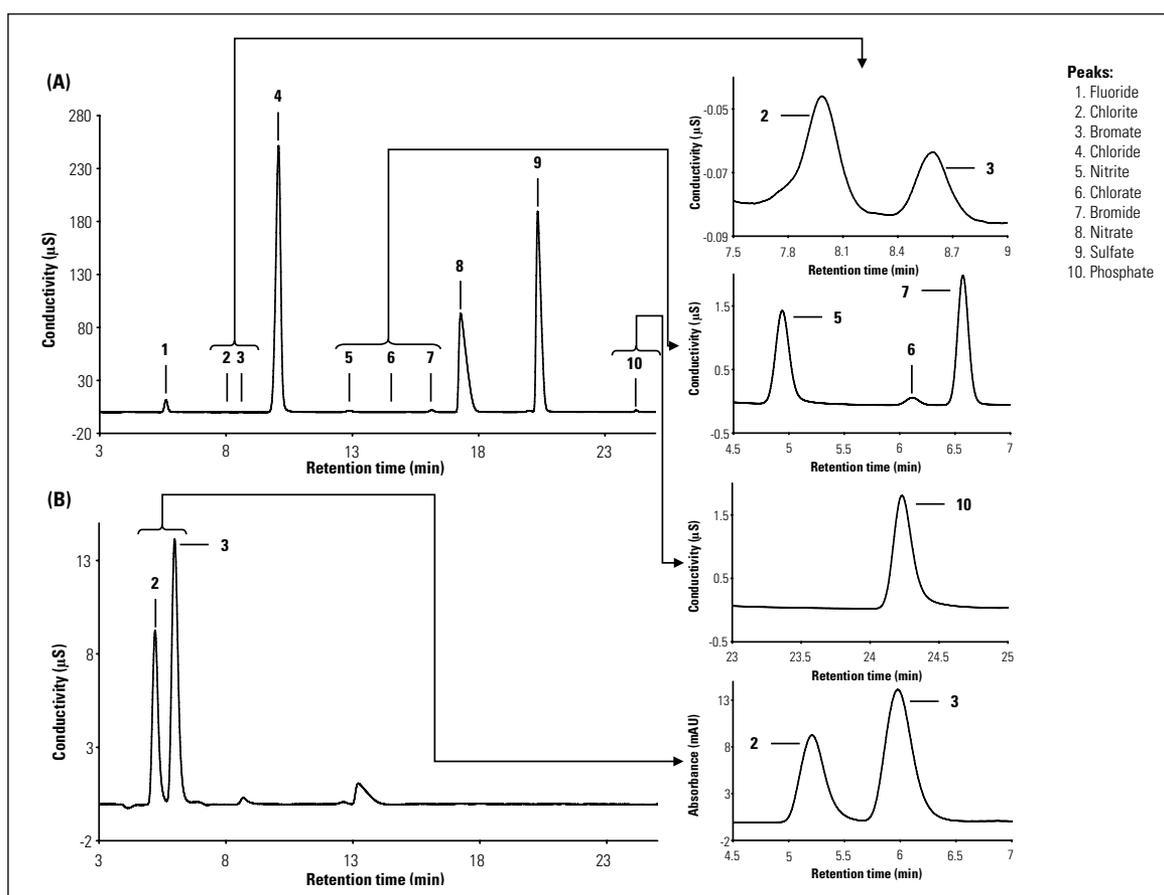

Figure 2. Chromatograms of (A) 25 µL injected standard solution containing 20 µg/L chlorite, bromate; 0.1 mg/L chlorate; 0.5 mg/L nitrite; 1 mg/L fluoride, bromide, and phosphate; and 50 mg/L nitrate, chloride, and sulfate. (B) 250 µL injected standard solution containing 20 µg/L chlorite and bromate.
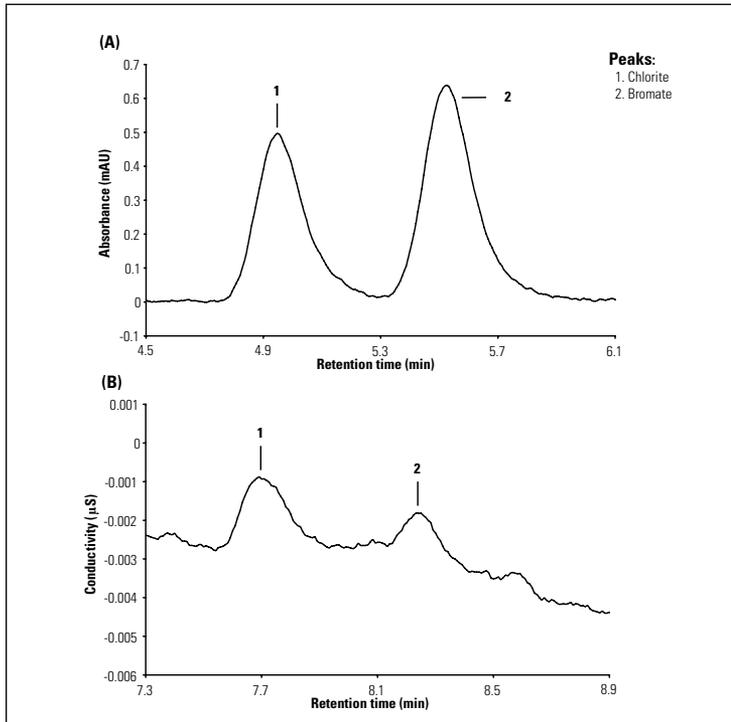
Figure 3. (A) Chromatograms of ultrapure water containing 1 µg/L bromate and 1 µg/L chlorite with postcolumn reaction system and UV-vis detection (chromatographic condition 2). (B) Chromatograms of ultrapure water containing 1 µg/L bromate and 1 µg/L chlorite with conductivity detection (chromatographic condition 1).

3.3 Limit of quantification (LOQ)

LOQs were determined according to the NFT 90-210, a French norm based on the ISO 5725 accuracy measurements methodology. This methodology analyzes trueness and precision of the determination for a sample containing inorganic anions at a concentration close to the supposed limit of quantification. This test ensures that accuracy (trueness and precision) does not exceed ± 60% of the supposed LOQ (Equations 1 and 2).

$$\overline{\overline{z}}_{LOQ} - 2 \cdot s_{LOQ} > LOQ - 60\% \cdot LOQ \quad \text{(Equation 1)}$$

$$\overline{\overline{z}}_{LOQ} + 2 \cdot s_{LOQ} < LOQ + 60\% \cdot LOQ \quad \text{(Equation 2)}$$

With $s_{LOQ} = \sqrt{s_r^2 + s_R^2}$ (Equation 3)

Where:

$\overline{\overline{z}}_{LOQ}$ is the general mean;

s_{LOQ} is the reproducibility standard deviation;

s_r^2 is the repeatability variance; and

s_R^2 is the inter-series variance.

For more details about calculation of s_r^2 and s_R^2, please refer to ISO 5725 and NFT-90210.

Table 3 summarizes the LOQ for each anion in drinking water. They were obtained for inorganic anions using chromatographic conditions 1 (CD) and chromatographic conditions 2 (UV-vis detection after postcolumn reaction).

Table 3. LOQs of anions in drinking water with CD or UV-vis detection after postcolumn reaction.

Anion	Conductivity Detection LOQ (µg/L)	UV-vis Detection LOQ (µg/L)
Fluoride	25	-
Nitrite	12.5	-
Bromide	10	-
Phosphate	150	-
Chlorite	-	0.25
Bromate	-	0.12
Chlorate	5	-
Nitrate	50	-
Chloride	500	-
Sulfate	125	-

Postcolumn reaction followed by UV-vis detection of bromate and chlorite allows an LOQ of 0.12 and 0.25 µg/L, respectively. Major and trace anions can be analyzed simultaneously using a gradient elution and CD detection for the major components, and large-loop injection, PCR, and UV-vis for saving time and being cost effective.

3.4 Uncertainty measurement

In routine analysis, the quality control is prepared daily from the 1000 mg/L certified solution. Table 4 presents the mean ($\bar{x}$) and the standard deviation (s) which are useful in establishing warning limits ($\bar{x} \pm 2s$) and control limits ($\bar{x} \pm 3s$) of a control chart. Data were obtained from 310 quality controls which correspond to the analysis of around 3000 samples.

The detection system used (CD or UV-vis) has a significant impact on the uncertainty measurement of trace inorganic anions such as bromate. Figure 4 presents the control chart of bromate at a concentration of 20 µg/L.

For bromate determinations, the warning limit ($\bar{x} \pm 2s$) and the control limit ($\bar{x} \pm 3s$) were significantly reduced when postcolumn reaction with UV-vis detection was used ($\bar{x} = 19.0$; s = 0.89 µg/L) compared to CD ($\bar{x} = 21.6$; s = 2.80).
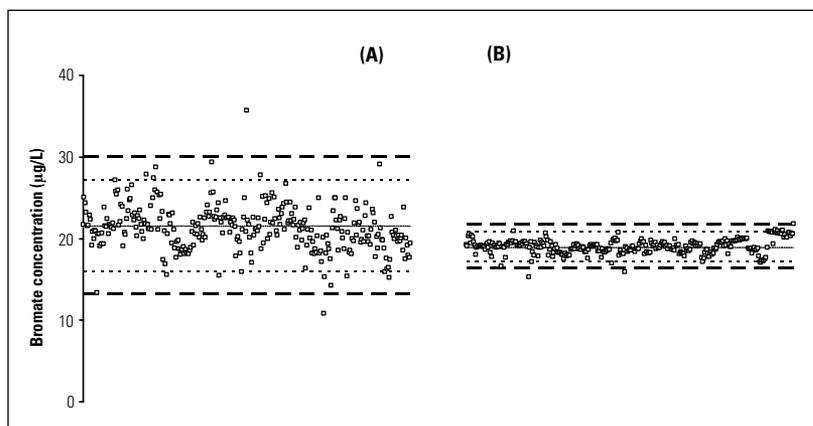

Figure 4. Control chart for bromate at a concentration of 20 µg/L. (A) Conductivity detection (chromatographic conditions 1); (B) Postcolumn reaction and UV-vis detection (chromatographic conditions 2).

Table 4. Mean ($\bar{x}$) and standard deviation (s) of 310 quality controls analyzed with CD or UV-vis detection.

Anion	Conductivity Detection			UV-vis Detection		
	$\bar{x}$	s	Unit	$\bar{x}$	s	Unit
Fluoride	1.04	0.05	mg/L	-	-	-
Nitrite	0.50	0.03	mg/L	-	-	-
Bromide	1.01	0.05	mg/L	-	-	-
Phosphate	0.99	0.07	mg/L	-	-	-
Chlorite	-	-	-	20.5	1.4	µg/L
Bromate	(21.6)	(2.80)	(µg/L)	19.0	0.9	µg/L
Chlorate	97.2	4.4	µg/L	-	-	-
Nitrate	50.4	1.2	mg/L	-	-	-
Chloride	50.9	1.0	mg/L	-	-	-
Sulfate	50.1	1.0	mg/L	-	-	-

3.5 Inter-laboratory tests

The method has been used for the Aquacheck® proficiency tests (Aquacheck Ltd, Bury Greater Manchester, England) for the determination of both major and trace inorganic anions. The selected proficiency schemes were "chlorination and disinfection by-products", "major inorganic components in hard water", "major inorganic components in soft water", and "nutrients and other compounds". The range of the expected values for these inter-laboratory schemes were: 0.456–1.572 µg/L (fluoride); 23.1–95.8 µg/L (chlorite); 2.82–10.82 µg/L (bromate); 9.70–279 mg/L (chloride); 0.086–7.56 mg/L (nitrite); 23.2–77.7 µg/L (chlorate); 43.8–80.7 µg/L (bromide); 5.20–27.2 mg/L (nitrate); 11–49.10 mg/L (sulfate) and 2.041–25.65 mg/L (phosphate).

Table 5 shows that from January 2010 to June 2011, the laboratory had very satisfying results. The average deviation from the assigned value was always well below ± 20%, highlighting the high reliability of our approach. The method, therefore, is efficient for the simultaneous determination of major and trace inorganic anions in water.

Table 5. Proficiency test results for anion determinations with the postcolumn reaction and UV-vis detection system. Results are expressed in percentage of error compared to the expected value.

Round of the proficiency scheme	F^-	ClO_2^-	BrO_3^-	Cl^-	NO_2^-	ClO_3^-	Br^-	NO_3^-	SO_4^{2-}	PO_4^{3-}
379 (01/2010)				-4.80	1.90			-3.40		-4.40
381 (03/2010)	0.60			0.20	6.10			3.70	3.30	
382 (03/2010)		3.60	-5.80			7.90	-10.30			
385 (06/2010)	-1.20			0.80	-7.20			3.10	0.20	
386 (06/2010)		2.80	-9.80			-10.80	-8.70			
389 (07/2010)	2.10			2.60	16.00			1.30	0.50	
390 (08/2010)		2.60	-10.40			-0.80	-9.10			
391 (09/2010)				1.40	1.80			-4.40		-6.70
393 (10/2010)	-2.30			-1.60	-7.00			0.10	-1.70	
394 (10/2010)		-12.80	2.00			-12.80	-7.30			
397 (12/2010)	7.10			3.20	1.70			1.80	2.00	
398 (12/2010)		-9.20	-7.80			-5.20	-11.50			
399 (01/2011)				-4.00	5.40			0.00		-4.10
401 (03/2011)	1.90			1.40	-9.50			1.00	1.50	
402 (03/2011)		-1.30	-2.40			-2.10	-12.90			
405 (06/2011)	1.00			1.40	-10.80			-1.40	2.60	

Conclusion

A method for the determination of trace and major inorganic anions in water was developed. It allows in a single run the simultaneous analysis of fluoride, bromide, phosphate, nitrate, chloride, sulfate, chlorite, and bromate with limit of quantification suitable for drinking water analysis. In comparison with the use of two methods for the determination of both major and trace inorganic anions, the proposed method is powerful and is time saving (and thus cost effective) which is suitable for laboratories doing high volume routine analysis.

References

1. WHO. Guidelines for Drinking Water Quality. World Health Organization. Geneva, Switzerland. 1993.

2. Council Directive 98/83/EC of 3 November 1998 on the Quality of Water Intended for Human Consumption. *Official Journal of the European Communities.*

3. Joyce R.J., Dhillon H.S. Trace Level Determination of Bromate in Ozonated Drinking Water Using Ion Chromatography. *J. Chromatogr. A.* **1994**, *671*, 165–171.

4. Weinberg. H. Pre-Concentration Techniques for Bromate Analysis in Ozonated Waters. *J. Chromatogr. A.* **1994**, *671*, 141–149.

5. Weinberg H.S., Yamada H., Joyce R.J. New, Sensitive, and Selective Method for Determining Sub-μg/L Levels of Bromate in Drinking Water, *J. Chromatogr. A.,* **1998**, *804*, 137–142.

6. Achilli M., Romele L. Ion Chromatographic Determination of Bromate in Drinking Water by Post-Column Reaction with Fuchsin. *J. Chromatogr. A.* **1999**, *847*, 271–277.

7. Delcomyn C.A., Weinberg H.S., Singer P.C. Use of Ion Chromatography with Post-Column Reaction for the Measurement of Tribromide to Evaluate Bromate Levels in Drinking Water. *J. Chromatogr. A.* **2001**, *920*, 213–219.

8. Matsis V.M., Nikolaou E.C. Determination of Inorganic Oxyhalide Disinfection By-Products in Bottled Water by EPA Method 326.0 for Trace Bromate Analysis. *Desalination*, **2008**, *224*, 231–239.

9. Thermo Fisher Scientific. Determination of Inorganic Oxyhalide Disinfection Byproduct Anions and Bromide in Drinking Water Using Ion Chromatography with the Addition of a Postcolumn Reagent for Trace Bromate Analysis. Dionex Application Note 136.

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