

New ion-chromatography method for detection of chlorite, chlorate, and bromate in drinking water

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Abstract

A direct ion chromatographic method for the determination of chlorite, chlorate, and bromate in the presence of fluoride, chloride, nitrate, nitrite, and bromide in treated drinking waters was described. Separation of target analytes was achieved using an ASI9-HC analytical column (250 mm x 4 mm), AG 19-HC guard column (50 mm x 4 mm), and KOH 25 mmol/L as mobile phase. Inorganic analytes were eluted using a flow rate of 1 mL/min. The column temperature was set up and maintained at 30°C. The analyte ions were quantified using a suppressed conductivity detector.

Keywords: *chlorite, chlorate, bromate, ion chromatography, drinking water*

INTRODUCTION

Drinking water is obtained by raw water disinfection treatments (surface water and groundwater). The most common disinfectants for drinking water are chlorine, chloramines, ozone, and chlorine dioxide. During the disinfection procedure, due to the existence of some organic matter or halides (mainly bromide) in the raw water, inorganic (chlorates, chlorites, and bromates) and organic (especially trihalomethanes) disinfection by-products may occur [1]. Chlorite and chlorate are formed when chlorine dioxide is used to disinfect raw water. Also, chlorate is formed in hypochlorite treated water and it is the result of a complex interaction between ozone and chlorine ion in aqueous solution [2]. Bromate is produced when raw water is treated with ozone if contains bromide anion [3].

International regulations and guidelines also defined maximum concentrations allowed for chlorite, chlorate, and bromate in drinking water. The maximum concentration of chlorate and chlorite have been limited at 0.7 mg/L by many organizations such as World Health Organization [4], Iranian national standard [5], Japanese standard [6], and Chinese standard [7] while in Canadian guidelines the maximum allowed limit for both chlorate and chlorite

anion concentrations is 1 mg/L [8]. In the United States and Australia, only the chlorite concentration is limited to 1 mg/L [9] and 0.8 mg/L respectively [10].

Bromate, a possible human carcinogen, is regulated at 10 µg/L in many countries around the world.

World Health Organization has estimated that 2 µg/L bromate in drinking water poses a lifetime cancer risk of 1 in 10,000 [11].

Considerable efforts have focused on the development of new ion chromatographic methods for determining the concentrations of inorganic disinfection by-products (chlorate, chlorite and bromate) in drinking water to meet current limitations from environmental legislation. Ion chromatography with suppressed conductivity detector is an efficient technique for the simultaneous determination of chlorite, chlorate, and bromate ions in the presence of common inorganic anions in drinking water. Several analytical methods have been developed for the determination of these disinfection by-products (chlorate, chlorite, and bromate) using ion chromatography with a conductivity detector and UV detector. The columns, mobile phases, and suppressor/detectors are presented in Table 1.

Table 1. The columns, mobile phases, and suppressors/detectors used in different ion chromatographic methods for determination of chlorate, chlorite, and bromate

Column	Mobile Phase (mM)	Suppressor/ Detector	Reference
Ion Pac AS23 /Guard AG23	Na ₂ CO ₃ :NaHCO ₃ =4.2 : 1	Suppressed conductivity Supp 5 (4 x 250 mm) Conductivity detector model732,	[1]
Ion Pac AS9-HC analytical column (250 mm x 4 mm I.D.), AG9-HC guard column (50 mm x 4 mm I.D.)	8.0 mmol/L Na ₂ CO ₃	Suppressed conductivity, ASRS-ULTRA auto-suppression with external water mode, 80 mA current,	[12]
Ion Pac AS19 (250mmx4 mm), AG19 (50mmx4 mm) hydroxide-selective column	10mM KOH, 0-10 min, 10-45 mM 10-25 min	ASRS TM ULTRA II operated 130 mA, Suppressed conductivity	[13]
Carbonate selective Ion Pac AS9-HC column	9 mM Na ₂ CO ₃	ASRS ULTRA II operated in the external water mode	[13]
IonPacAS27 column (250 mm x 4 mm), AG 27(50 mm x 4 mm)	20 mM KOH	AERS TM 500 (4mm), water, Conductivity cell, water	[14]
IonPac AS9-HC (250mmx4mm), AG9-HC (50mm x4 mm)	9 mM Na ₂ CO ₃	AERS TM 500 (4mm), water, Conductivity cell, water	[14]
Ion Pac AS19 (250mmx4 mm), AG19 (50mmx4 mm) hydroxide-selective column	10mM KOH, 0-10 min, 10-45 mM 10-25 min	ASRS TM ULTRA II operated 130 mA, Suppressed conductivity	[15]
Ion Pac AS19 (250mmx4 mm), AG19 (50mmx4 mm)	10mM KOH, 0-10 min, 10-45 mM 10-25 min	ASRS 300 Anion Regenerating Suppressor, external water mode Absorbance detector, 352 nm	[16]
IonPac AS9-HC (250mmx4mm), AG9-HC (50mm x4 mm)	9 mM Na ₂ CO ₃	ASRS-I, external water mode ,100 mA current, Suppressed Conductivity detector CD 20	[17]
IonPac AS9-HC (250mmx4mm), AG9-HC (50mm x4 mm)	9 mM Na ₂ CO ₃	ASRS-I, external water mode, 100 mA current, Suppressed Conductivity detector CD 20 PCR suppressor ASRS-I with sulfuric acid regenerant to acidify the PCR Absorbance detector 10 mm cell path length, set at 352 nm (deuterium lamp)	[18]

In this study, a direct ion chromatographic method that allows a quantitative analysis of

chlorite, chlorate, and bromate ions in drinking water was established.

MATERIALS AND METHODS

Chemicals and reagents

The inorganic disinfection by-products are marketed in the form of sodium salt: sodium bromate, purity 99.5 % and sodium chlorite, purity 80 %, (Sigma-Aldrich, Steinheim, Germany) and sodium chlorate, 98 % purity (Merck, Darmstadt, Germany).

The other common anions of drinking water were purchased as standard substances from Merck (Darmstadt, Germany): chloride standard

solution 1000 mg /L, fluoride standard solution 1000 mg/L, nitrite standard solution 1000 mg/L, bromide standard solution 1000 mg/L, and nitrate standard solution 1000 mg/L.

Potassium hydroxide used for the mobile phase was acquired from Merck (Darmstadt, Germany). Ultrapure water (DI) used during the experiments was produced in-house. Ultrapure water was solutions preparation.

Ion Chromatographic equipment

The Thermo Scientific Dionex ICS-5000 Ion Chromatography System is equipped with a conductivity detector. Chromatographic separation was achieved using a Dionex IonPac AS19 (4 x 250 mm) chromatographic column

with AG19 (4 x 50 mm) guard column. Data collection and processes were conducted using the Thermo Scientific Dionex Chromeleon™ 7 Software.

Method analysis

Stock solutions of bromate, chlorite, and chlorate were prepared by solving 0.119 g NaBrO_3 , 0.1337 g NaClO_3 , and 0.160 g NaClO_2 in 100 ml ultrapure water. The concentration of each solution was 1000 mg/L.

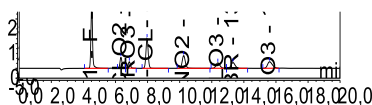
Intermediate stock solutions of 50 mg/L of bromate, chlorate, chlorite, chloride, fluoride, nitrate, nitrite, and bromide were prepared from individual solutions. Calibration standard solutions were prepared at concentration ranges from 0.1 to 25 mg/L from the intermediate stock solution.

The mobile phase used for anions elution was potassium hydroxide. A mobile phase

concentration of 25 mM KOH was prepared by dissolving 1.4 g KOH in 1000 ml ultrapure water. The solution was degassed and filtered through a 0.45 μm nylon membrane filter.

The flow rate and temperature were set up at 1 ml/min and 30°C respectively. The parameters of the chromatographic separation were optimized for performing the best responses for the quantification of each anion.

Figure 1 shows a typical chromatogram of target anions: bromate, chlorate, chlorite, chloride, fluoride, nitrate, nitrite, and bromide standard.



retention times (min)

Fig. 1. Chromatogram of anions: bromate (BrO_3^-), chlorate (ClO_3^-), chlorite (ClO_2^-), chloride (Cl^-), fluoride (F^-), nitrate (NO_3^-), nitrite (NO_2^-), and bromide (Br^-).

RESULTS AND DISCUSSION

The eight anions were separated by 25mM KOH eluent and the elution orders are given in

Figure 1. The corresponding retention times are indicated in Table 2.

Table 2. Retention times for interested anions

Anions	tR (min)	Anions	tR (min)
Fluoride	4.52	Nitrite	10.25
Chlorite	6.34	Chlorate	12.38
Bromate	6.86	Bromate	13.32
Chloride	7.96	Nitrate	15.60

The parameters evaluated in the validation process of the ion chromatographic method for inorganic disinfection by-products detection in the presence

of common anions were linearity, repeatability, intermediate precision, detection limit, the limit of determination (quantification), and accuracy.

Linearity

The calibration curves were obtained for each analyte, at the same time, obtaining a linear

domain for all anions as seen in Figure 2.

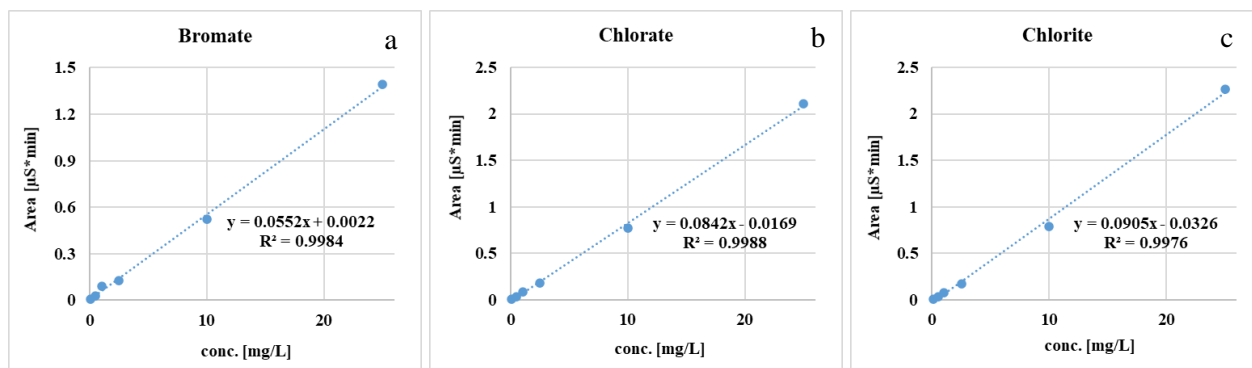


Fig. 2. Calibration curves for bromate (a), chlorate (b) and chlorite (c)

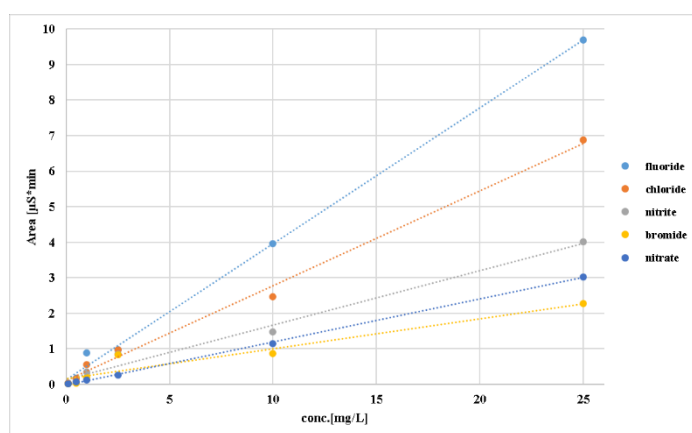


Fig. 3. Calibration curves for the common anions

The working range, correlation coefficients (R^2), and relative standard deviation values (RSD, %) are presented in Table 3. As can be

seen, the method proved to be precise, the RSD % values being lower than 10 %.

Table 3. Working range (mg/L), correlation coefficient (R^2), and RSD (%) values for the developed method

Anion	Working range (mg/L)	Correlation Coefficient (R^2)	RSD (%)
Fluoride	0.1-25.0	0.9997	2.52
Chlorite	0.1-25.0	0.9965	9.01
Bromate	0.1-25.0	0.9984	6.09
Chloride	0.1-25.0	0.9977	7.07
Nitrite	0.1-25.0	0.9986	5.50
Chlorate	0.1-25.0	0.9984	5.98
Bromide	0.1-25.0	0.9986	5.49
Nitrate	0.1-25.0	0.9992	4.17

Detection and quantification limits

Detection (LOD) and quantification (LOQ) limits for common anions and inorganic disinfection products were determined by measuring the standard solution with a

concentration of 0.5 mg/L each for five times and were calculated at a 95% confidence level. The LOQ and LOD calculated values are presented in Table 4.

Table 4. Detection and quantitation limits

Anion	LOD (mg/L)	LOQ (mg/L)	Anion	LOD (mg/L)	LOQ (mg/L)
Fluoride	0.06	0.20	Nitrite	0.03	0.09
Chlorite	0.07	0.20	Chlorate	0.02	0.05
Bromate	0.08	0.30	Bromide	0.03	0.10
Chlorite	0.08	0.30	Nitrate	0.02	0.06

Method repeatability

Repeatability gives information on the accuracy of the method when successive measurements of the same sample are performed (same analyst, same sample, same equipment, in a short period).

Five determinations were performed for two solutions of two concentration levels (0.5 mg/L and 10 mg/L) for each analyte. The obtained

results are presented in Table 5.

Analyzing the results from Table 5, it was observed that among the analyzed inorganic disinfection by-products, the lowest relative standard deviation was obtained for chlorate while the highest relative standard deviation was obtained for bromate, for both concentration levels.

Table 5. Repeatability results

Anion	Real concentration (mg/L)	Mean concentration (mg/L)	SR (mg/L)	Min.	Max.	Median	RSD %	Repeatability (r)
Fluoride	0.50	0.49	0.022	0.46	0.53	0.48	4.41	0.606
Chlorite	0.50	0.49	0.024	0.45	0.52	0.48	4.97	0.678
Bromate	0.50	0.48	0.028	0.43	0.51	0.47	5.77	0.782
Chloride	0.50	0.48	0.018	0.47	0.51	0.48	3.61	0.494
Nitrite	0.50	0.49	0.009	0.47	0.50	0.48	1.89	0.258
Chlorate	0.50	0.47	0.005	0.47	0.48	0.47	1.07	0.142
Bromide	0.50	0.48	0.011	0.47	0.50	0.47	2.30	0.311
Nitrate	0.50	0.48	0.006	0.47	0.49	0.48	1.23	0.166
Fluoride	10.0	9.98	0.104	9.80	10.06	9.98	1.04	0.291
Chlorite	10.0	8.98	0.104	8.80	9.05	8.98	1.16	0.381
Bromate	10.0	9.07	0.136	8.89	9.24	9.07	1.50	0.368
Chloride	10.0	9.09	0.131	8.87	9.22	9.09	1.45	0.317
Nitrite	10.0	9.26	0.113	9.06	9.33	9.29	1.22	0.305
Chlorate	10.0	9.24	0.109	9.05	9.30	9.26	1.18	0.308
Bromide	10.0	9.30	0.110	9.11	9.37	9.32	1.18	0.618
Nitrate	10.0	9.36	0.221	9.02	9.54	9.36	2.36	0.290

Intermediate precision

Intermediate precision gives information on the variability of the method in reproducibility conditions (same method, same sample, same laboratory, same equipment, but different analysts and a longer time interval).

Five determinations were performed for two consecutive days for a 10 mg/L standard solution for each anion. The obtained results are given in Table 6.

Table 6. Intermediate precision results

Anion	Real concentration (mg/L)	Mean concentration (mg/L)	SR (mg/L)	Min.	Max.	Median	RSD (%)	Intermediate precision (R)
Fluoride	10.0	9.93	0.415	9.09	10.71	10.01	4.17	1.161

Chlorite	10.0	9.13	0.207	8.80	9.44	9.04	2.27	0.580
Bromate	10.0	9.20	0.167	8.89	9.37	9.26	1.82	0.468
Chloride	10.0	9.28	0.326	8.87	10.11	9.24	3.51	0.912
Nitrite	10.0	9.39	0.179	9.06	9.66	9.32	1.91	0.503
Chlorate	10.0	9.31	0.320	9.05	10.18	9.24	3.44	0.896
Bromide	10.0	9.29	0.114	9.06	9.39	9.34	1.23	0.320
Nitrate	10.0	9.52	0.229	9.02	9.71	9.60	2.41	0.643

The values of relative standard deviations were varied between 1.23 and 4.17 %.

Method accuracy

To determine the method accuracy, two different types of water matrices (tap water and groundwater) were spiked with a known amount of the chlorate, chlorite, and bromate (5 mg/L each). For tap water and groundwater

containing chlorate, chlorite, and bromate the recoveries ranges were presented in Table 7. The values of recovery were situated between 79.9 and 81.8 % for chlorite, 81.8 and 84.6 % for bromate, 91.8 and 93 % for chlorate.

Table 7. Recovery values

Sample	Chlorite		Bromate		Chlorate	
	Value added (mg/L)	Recovery (%)	Value added (mg/L)	Recovery (%)	Value added (mg/L)	Recovery (%)
Tap water 1	5	80.2	5	84.4	5	93.0
Tap water 2	5	79.8	5	84.6	5	92.2
Tap water 3	5	81.8	5	81.8	5	92.2
Ground water 1	5	80.0	5	84.2	5	93.0
Ground water 2	5	81.2	5	84.2	5	91.8
Ground water 3	5	80.0	5	84.2	5	92.6

Application to municipal drinking waters

The developed method was successfully tested on real water samples. Tap water samples were collected from 45 sampling points from the municipal drinking water distribution system.

Chlorate, chlorite, and bromate concentrations were not determinate in none of the investigated drinking water samples, while the other anions were found to be in normal concentration levels.

CONCLUSIONS

The direct ion-chromatographic method with a conductivity detector was developed and fully validated in the laboratory. The new IC method was used to determine the inorganic disinfection by-products resulting from chlorination/disinfection of drinking water (chlorate and chlorite) in presence of common water ions (fluoride, chloride, bromide, nitrate, nitrite). The IC method was linear over a large concentration range (0.1-25 mg/L), with correlation coefficients higher than 0.9965. The RSD values corresponding to method repeatability were in the range of 1.04 ÷ 5.77 %, while the RSD values determined for

intermediate precision were situated between 1.23 and 4.17 %. Good recoveries were obtained for each inorganic disinfection by-products: up to 81.8 % for chlorite, up to 84.6 % for bromate, and up to 93 % for chlorate. The method quantification limits were situated between 0.05 and 0.3 mg/L. After validation, the IC method was applied to real water samples, without any sample preparation step (separation or concentration).

The results demonstrate that this simple and rapid method can be used to monitor the quality of drinking water subjected to chlorination/disinfection.

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