Determination of Trace Concentrations of Oxyhalides and Bromide in Municipal and Bottled Waters Using a Compact Ion Chromatography System

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Key Words
Dionex IonPac AS19-4µm column, Disinfection byproducts, Drinking water, Suppressed conductivity detection, Bromate

Goal
To demonstrate that oxyhalides and bromide can be run successfully using a Thermo Scientific™ Dionex™ Integrion™ HPIC™ system combined with a Thermo Scientific™ Dionex™ IonPac™ AS19-4µm column, featuring smaller resin particles, to achieve faster analysis without compromising data quality

Introduction
Most municipal water authorities must treat their water to provide their communities with safe drinking water. Disinfection of the water supply protects public water systems from potentially dangerous microbes. The most common chemical disinfectants are chlorine, chlorine dioxide, chloramine, and ozone.[1] However, the disinfectants themselves can react with naturally occurring materials in the water to form unintended disinfection byproducts (DBPs), which may pose health risks. For example, chlorination of drinking water can produce trihalomethanes, haloacetic acids, and chlorate. Similarly, chlorine dioxide treatment generates inorganic oxyhalides, DBPs, chlorite, and chlorates. Chlorate may also be generated in the presence of chloramine.[2] Ozone reacts with natural sources of bromide, which may be found at various levels in water supplies, to produce bromate. To date, there are no practical methods for removing bromide or its bromate byproduct from water. Currently, the only solution to the problem is to limit bromate formation during the water treatment process. Limiting bromate formation requires careful monitoring of bromate concentration to ensure that it does not exceed safe drinking water standards.

Bromate has been identified by the International Agency for Research on Cancer as an animal carcinogen and potential human carcinogen.[3] Major regulatory bodies worldwide, including the U.S. Environmental Protection Agency (EPA), European Commission (EC), U.S. Food and Drug Administration (FDA), and World Health Organization (WHO), have set the maximum allowable concentration for bromate in drinking water at 10 µg/L.[4,5]

In Europe, the limit was lowered to 3 µg/L for bottled natural mineral and spring waters disinfected by ozonation.[6]

The work presented here is based on the method published in Application Note 167, which uses a Thermo Scientific™ Dionex™ ICS-2100 Integrated IC System with a Dionex IonPac AS19 column.[7] In this application note, the method is performed using a Thermo Scientific Dionex Integrion HPIC system with a Dionex IonPac AS19-4 µm column.

The Dionex Integrion HPIC system is a robust, easy-to-use system that includes features such as eluent generation, temperature control, easy access to consumables, high-pressure capability, consumables tracking, and low-void-volume Thermo Scientific™ Dionex™ IC PEEK Viper™ fittings. The Dionex Integrion HPIC system can therefore take advantage of the high-efficiency separations offered by smaller-particle-size separation columns.

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The Dionex IonPac AS19-4µm column, in combination with the Dionex IonPac AG19-4µm guard column, is designed for the determination of inorganic anions and oxyhalides using an isocratic or gradient hydroxide eluent delivered by an Eluent Generator.

In comparison to the Dionex IonPac AS19 column, the Dionex IonPac AS19-4µm column exhibits higher peak efficiency while maintaining the same selectivity.[8] This application update shows that using a Dionex IonPac AS19-4µm column saves 5 min per injection, thereby improving productivity in oxyhalide and bromide determinations in drinking water.

Equipment and Consumables

- A Thermo Scientific™ Dionex™ Integrion™ HPIC™ system including:
  - Eluent Generator
  - Pump
  - Degasser
  - Conductivity Detector
  - Column oven temperature control
  - Detector-suppressor compartment temperature control
  - Tablet control
- Thermo Scientific™ Dionex™ AS-AP Autosampler, with 5000 µL syringe (P/N 074308), 8500 µL buffer line assembly (P/N 075520), 250 µL injection loop (P/N 042953) and 10 mL vial trays
- Thermo Scientific™ Dionex™ EGC 500 KOH Cartridge (P/N 075778)
- Thermo Scientific™ Dionex™ CR-ATC 600 Continuously Regenerated Anion Trap Column (P/N 088662)
- Thermo Scientific™ Dionex™ AERS™ 500 Anion Electrolytically Regenerated Suppressor, 4 mm (P/N 082541)
- Dionex IC PEEK Viper Fitting Tubing Assembly Kits (P/N 088798)
- Dionex AS-AP Autosampler Vials 10 mL (P/N 074228)
- Thermo Scientific™ Dionex™ Chromeleon™ 7.2 SR4 Chromatography Workstation
- Thermo Scientific™ Nalgene™ Syringe Filters, PES, 0.2 µm (Fisher Scientific 13 mm, P/N 720-1320 or 25 mm, P/N 09-740-113)
- AirTite™ All-plastic Norm-Ject® Syringes, 5 mL (Fisher Scientific P/N 14-817-28)

Reagent and Standards

- Degassed deionized (DI) water, 18 MΩ-cm resistance or better
- Sodium and potassium salts, A.C.S. reagent grade or better, for preparing anions standards
- Ethylenediamine, 99% (Sigma-Aldrich)

Conditions	
Columns:	Dionex IonPac AS19-4µm Analytical Column, 4 × 250 mm (P/N 083217) Dionex IonPac AG19-4µm Guard Column, 4 × 50 mm (P/N 083221)
Eluent:	10 mM KOH from 0–10 min, 10-30 mM KOH from 10–18 min, 100 mM from 18–25 min*
Eluent Source:	Dionex EGC 500 KOH cartridge with CR-ATC 600
Flow Rate:	1 mL/min
Injection Volume:	250 µL in Push-Full mode
Column Temperature:	30 °C
Detection:	Suppressed conductivity, Dionex AERS 500 (4mm) Suppressor, recycle mode, 248 mA current
Detection/Suppressor Compartment:	15 °C
Cell Temperature:	35 °C
Background Conductance:	<0.5 µs
System Backpressure:	~4000 psi
Noise:	<5 nS/min
Run Time	25 min

*Method returns to 10 mM KOH for 3 min prior to injection

Preparation of Solutions and Reagents

Stock Standard Solutions

Stock standard solutions (1000 mg/L) can be prepared by dissolving the appropriate amounts of the required analytes in 100 mL of DI water according to Table 1. Stock standards for most anions are stable for at least 6 months at 4 °C. The chlorite standard is stable for only two weeks when stored protected from light at 4 °C. The nitrite and phosphate standards are only stable for one month when stored at 4°C.

Table 1. Masses of compounds used to prepare 100 mL of 1000 mg/L ion standards.

Analyte	Compound	Amount (mg)
Fluoride	Sodium fluoride (NaF)	221.0
Chlorite	Sodium chlorite ($NaClO_2$), 80%	167.6
Bromate	Sodium bromate ($NaBrO_3$)	118.0
Chloride	Sodium chloride (NaCl)	164.9
Nitrite	Sodium nitrite ($NaNO_2$)	150.0
Chlorate	Sodium chlorate ($NaClO_3$)	127.5
Bromide	Sodium bromide (NaBr)	128.8
Nitrate	Sodium nitrate ($NaNO_3$)	137.1
Sulfate	Sodium sulfate (Na_2SO_4)	147.9
Phosphate	Potassium phosphate, monobasic (KH_2PO_4)	143.3
Carbonate	Sodium carbonate (Na_2CO_3)	176.6

Table 2. Calibration standards preparation (µg/L).

Analyte	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7	Level 8
Chlorite	500	400	300	200	100	50	20	10
Bromate	50	40	30	20	10	5	2	1
Chlorate	500	400	300	200	100	50	20	10
Bromide	500	400	300	200	100	50	20	10

Working Standard Solutions

Calibration standard level and preparation method

Diluted working standard solutions were prepared using the 1000 mg/L stock standards. Working standards containing less than 100 µg/L anions should be prepared fresh daily. Eight levels of calibration standards were used in this study for chlorite, bromate, chlorate, and bromide to cover the expected concentration range found in typical environmental samples (Table 2). Additional anions, listed in Table 1, were used to prepare a simulated drinking water sample containing 1 ppm fluoride, 50 ppm chloride, 0.1 ppm nitrite, 10 ppm nitrate, 100 ppm carbonate, 50 ppm sulfate, and 0.1 ppm phosphate.

Sample Preparation

For this analysis, bottled water samples were purchased from a local supermarket and drinking water samples were collected from three locations in Northern California: Sunnyvale, San Mateo, and Milpitas.

Filter sample, as necessary, through a 0.2 µm PES syringe filter, discard the first 300 µL of effluent. Treat samples with the preservation solution as described below.

Preservation Solution (EDA)

Dilute 2.8 mL of ethylenediamine (EDA) to 25 mL with DI water according to section 7.4 in U.S. EPA Method 300.1 to prepare a 100 mg/mL EDA solution. Preserve the standards or samples by adding 50 µL of EDA preservation solution (100 mg/mL) per 100 mL of sample.

Results and Discussion

Separation

The Dionex IonPac AS19-4µm hydroxide-selective anion-exchange column was specifically designed for high resolution separation of trace oxyhalides and inorganic anions in drinking water. Its high resolution, high capacity, and selectivity allow the determination of bromate in drinking water at the low µg/L level. Compared to the Dionex IonPac AS19 column, this anion-exchange column uses smaller resin particles for more efficient separations resulting in more accurate peak integration and more reliable results.

Figure 1 shows a separation of common anions and disinfection byproduct anions separated within 25 min using the Dionex IonPac AS19-4µm column. As this figure shows, chlorite, bromate, chlorate, and bromide were resolved from other common inorganic anions. The excellent resolution between bromate and chloride makes it ideal for determining low concentrations of bromate in municipal and bottled water samples. Compared to the IonPac AS19 column, the Dionex IonPac AS19-4µm demonstrates better resolution between oxyhalide and inorganic anion peaks under the same conditions. As a result, a shorter gradient method (25 min)), which still resulted in excellent separation of oxyhalides and bromide, was used in this study compared to the 30 min method described in AN 167 . In the shorter gradient method, the eluent was 10 mM KOH for 10 min to allow excellent separation between chlorite, bromate, and chloride, increased to 30 mM from 10–18 min to separate chlorate and bromide, and changed to 100 mM from 18–25 min to elute the remaining inorganic anions.

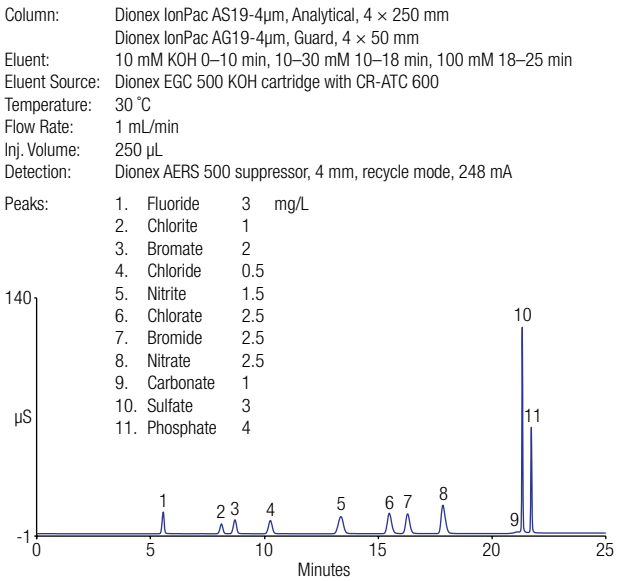

Figure 1. Separation of common anions and disinfection byproduct anions using a Dionex IonPac AS19 4-µm column.

Linearity

An eight-point calibration range was used for chlorite, bromate, chlorate, and bromide. Table 3 shows the linear concentration ranges, the coefficients of determination (r^2), and retention time and peak area precisions of three replicate injections. The excellent retention time stability and peak area precision are consistent with results typically obtained when using an electrolytically generated high-purity potassium hydroxide eluent. The use of an electrolytically generated potassium hydroxide eluent further simplifies the method by eliminating the time required to manually prepare eluents and reducing the time required for method development.

Table 3. Linearity, retention time, and peak area precision obtained using the Dionex IonPac AS19-4µm column (n=3).

Analyte	Range (µg/L)	Linearity (r^2)	Retention Time Precision (RSD)	Peak Area Precision (RSD)
Chlorite	10–500	0.9999	<0.1	<0.5
Bromate	1–50	0.9998	<0.1	1.09
Chlorate	10–500	0.9999	<0.1	<0.5
Bromide	10–500	0.9999	<0.1	<0.5

Method Detection Limit (MDL)

MDLs were determined by performing seven replicate injections of standards at a concentration of three to five times the estimated instrument detection limits. In addition, the MDLs were determined by preparing the same concentration of anions in a simulated drinking water sample. Table 4 shows typical calculated MDLs in DI water and simulated drinking water using the Dionex IonPac AS19-4 µm column combined with an electrolytic eluent generator and a 250 µL injection. In comparing the detection limits in the two matrices, the results showed no significant difference. The low detection limits result from the excellent peak efficiencies of the Dionex IonPac AS19-4µM column combined with low noise and exceptionally low suppressed background conductivities obtained using a thermally regulated environment detector compartment. Figure 2 shows the separation of a low-level calibration standard. As shown, a bromate concentration as low as 1 µg/L is easily detected using this method.

Table 4. Method detection limits for oxyhalides and bromide in DI water and simulated drinking water using a Dionex IonPac AS19-4µm column.

Analyte	MDL Standard (µg/L)	Calculated MDL in DI H_2O (µg/L)	Calculated MDL in Simulated Drinking Water (µg/L)
Chlorite	1.0	0.20	0.27
Bromate	1.0	0.20	0.28
Chlorate	1.0	0.31	0.25
Bromide	1.0	0.31	0.24

MDL = (t) × (S)

Where t= Student's t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom (t= 3.14 for seven replicates)

S=standard deviation of the replicate analyses

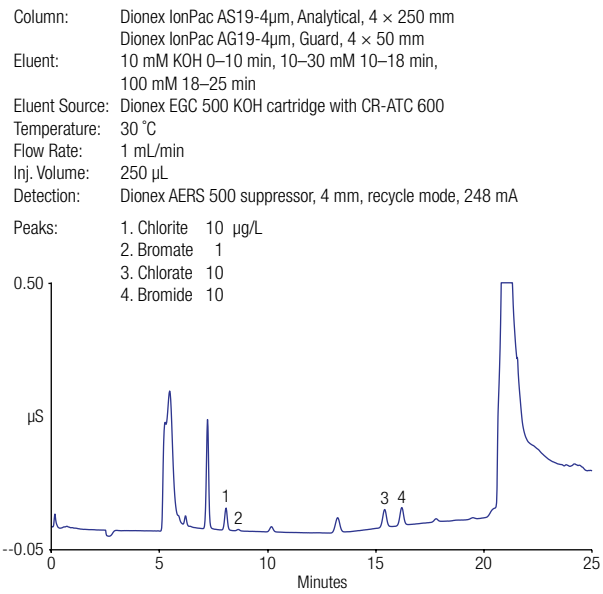

Figure 2. Separation of DBP anions and bromide, low-level calibration standard.

Sample Accuracy and Precision

The performance of the method featuring the Dionex IonPac AS 19-4µm column was also evaluated through recovery studies using spiked bottled and drinking water samples. Three different brands of bottled water were obtained from a local supermarket and three residential tap water samples were collected from Sunnyvale, San Mateo, and Milpitas, CA. Table 5 shows the amount detected and the recoveries obtained using a Dionex IonPac AS19-4µm column for trace concentrations of DBPs, anions, and bromide spiked in bottled waters.

Table 6 shows the recoveries for DBPs, anions, and bromide spiked in drinking waters. All anions demonstrate acceptable recoveries (85–115%) according to the criteria outlined in U.S. EPA Method 300.1.[9] Figure 3 shows an overlay of chromatograms of unspiked and spiked bottled water sample #3. Figure 4 shows an overlay of chromatograms of unspiked and spiked drinking water sample #2. As the two figures show, the Dionex IonPac AS19-4µm achieves excellent resolution and sensitive detection for oxyhalides and bromide.

Table 5. Recoveries of trace oxyhalides and bromide spiked in bottled waters.

Analyte	Bottled Water 1			Bottled Water 2			Bottled Water 3		
	Amount Found (µg/L)	Amount Added (µg/L)	Recovery (%)	Amount Found (µg/L)	Amount Added (µg/L)	Recovery (%)	Amount Found (µg/L)	Amount Added (µg/L)	Recovery (%)
Chlorite	<MDL	20	108.6	<MDL	20	100.3	<MDL	20	109.0
Bromate	<MDL	5	92.3	<MDL	5	101.8	<MDL	5	104.7
Chlorate	<MDL	20	109.5	<MDL	20	109.8	11.6	20	92.6
Bromide	<MDL	20	107.5	32.4	20	99.3	4.50	20	95.9

Table 6. Recoveries of trace oxyhalides and bromide spiked in drinking waters.

Analyte	Drinking Water 1			Drinking Water 2			Drinking Water 3		
	Amount Found (µg/L)	Amount Added (µg/L)	Recovery (%)	Amount Found (µg/L)	Amount Added (µg/L)	Recovery (%)	Amount Found (µg/L)	Amount Added (µg/L)	Recovery (%)
Chlorite	10.8	20	90.3	11.6	20	91.8	<MDL	20	105.2
Bromate	<MDL	5	90.6	<MDL	5	90.5	<MDL	5	99.0
Chlorate	146.3	100	106.3	138.2	100	104.5	108.3	100	103.0
Bromide	13.5	20	103.7	11.6	20	102.0	90.3	100	104.8

Column: Dionex IonPac AS19-4µm, Analytical, 4 × 250 mm
Dionex IonPac AG19-4µm, Guard, 4 × 50 mm
Eluent: 10 mM KOH 0–10 min, 10–30 mM 10–18 min, 100 mM 18–25 min
Eluent Source: Dionex EGC 500 KOH cartridge with CR-ATC 600
Temperature: 30 °C
Flow Rate: 1 mL/min
Inj. Volume: 250 µL
Detection: Dionex AERS 500 suppressor, 4 mm, recycle mode, 248 mA

Samples (A): Bottled water
(B): Spiked bottled water

Peaks (A): 3. Chlorate 11.7 µg/L
4. Bromide 4.29

Peaks (B): 1. Chlorite 21.5 µg/L
2. Bromate 5.10
3. Chlorate 31.7
4. Bromide 24.5

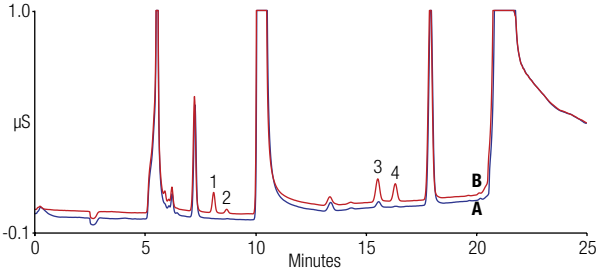

Figure 3. Determination of oxyhalides and bromide spiked in bottled water #3.

Column: Dionex IonPac AS19-4µm, Analytical, 4 × 250 mm
Dionex IonPac AG19-4µm, Guard, 4 × 50 mm
Eluent: 10 mM KOH 0–10 min, 10–30 mM 10–18 min, 100 mM 18–25 min
Eluent Source: Dionex EGC 500 KOH cartridge with CR-ATC 600
Temperature: 30 °C
Flow Rate: 1 mL/min
Inj. Volume: 250 µL
Detection: Dionex AERS 500 suppressor, 4 mm, recycle mode, 248 mA

Samples (A): Drinking water
(B): Spiked drinking water

Peaks (A): 1. Chlorite 11.1 µg/L
3. Chlorate 137
4. Bromide 11.0

Peaks (B): 1. Chlorite 29.8 µg/L
2. Bromate 4.64
3. Chlorate 238
4. Bromide 31.7

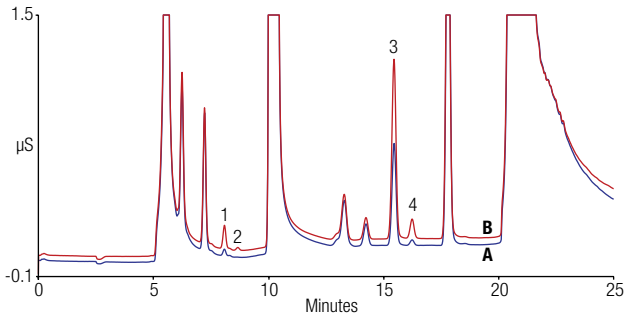

Figure 4. Determination of oxyhalides and bromide spiked in drinking water #2.

The precision of the method using a Dionex IonPac AS19-4µm column on a Dionex Integrion system was determined by performing 10 replicate injections of spiked bottled water #2. As shown in Table 7, the calculated peak area precision varied from 0.23 to 1.81 with retention time precisions <0.04% for all target anions. The high precision of this method is consistent with results typically found with an RFIC system.

Table 7. Retention time and peak area precisions of sample analysis (ten injections of spiked bottled water #2).

Analyte	Retention Time Precision (RSD)	Peak Area Precision (RSD)
Chlorite	0.03	0.55
Bromate	0.03	1.81
Chlorate	0.02	0.39
Bromide	0.01	0.23

Conclusion

This study demonstrates that oxyhalides and bromide can be determined accurately in municipal drinking water and bottled water using a Dionex IonPac AS19-4µm column and a Dionex Integrion HPIC system. The excellent resolution of the 4 µm small-particle column allows for faster analysis without compromising data quality. The Dionex Integrion HPIC system provides excellent reproducibility, thereby yielding greater quantification accuracy and consistently reliable results.

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