

## Environmental

## Determination of trace concentrations of oxyhalides and bromide in municipal and bottled waters

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### Keywords

Inorganic disinfection by-products, DBPs, Dionex IonPac AS23-4 $\mu$ m column, suppressed conductivity detection, Dionex Inuvion system, peristaltic pump, RFIC, U.S. EPA Method 300.1, Safe Drinking Water Act (SDWA), Clean Water Act (CWA), bromate

### Introduction

Ion chromatography (IC) is a well-accepted technique for monitoring inorganic anions in water, including surface, ground, drinking, and wastewater. In the U.S., water quality is regulated through the Safe Drinking Water Act (SDWA) and the Clean Water Act (CWA) and enforced through the United States Environmental Protection Agency (U.S. EPA)<sup>1</sup>. Ion chromatography methods have been approved by the U.S. EPA for compliance monitoring of inorganic anions and oxyhalides in drinking water since the 1980s through U.S. EPA Method 300.0, which was updated in 1997 to U.S. EPA Method 300.1.<sup>2</sup> Various IC methods for water analysis have been demonstrated in Thermo Scientific Application Notes using standard or microbore flow rate columns with carbonate/bicarbonate and hydroxide eluents.<sup>3</sup>

U.S. EPA Method 300.1 Part B describes the method and guidelines for inorganic Disinfection By-products (DBPs, oxyhalides) and bromide monitoring. Thermo Scientific Application Note 72209 demonstrated a sensitive IC method for the determination of trace concentrations of oxyhalides and bromide in drinking water using a Thermo Scientific™ Dionex™ ICS-5000+ HPIC system with carbonate/bicarbonate eluent generated by the Reagent-Free Ion Chromatography (RFIC) System.<sup>4</sup>

The method used a Thermo Scientific™ Dionex™ IonPac™ AS23-4µm column,<sup>5</sup> a Thermo Scientific™ Dionex™ AERS™ 500 Carbonate anion electrolytically regenerated suppressor,<sup>6</sup> and a Thermo Scientific™ Dionex™ CRD 300 Carbonate Removal Device in vacuum mode.<sup>7</sup> This work demonstrates a similar method on a Thermo Scientific™ Dionex™ Inuvion™ ion chromatography system, a new integrated, single-channel compact IC system. Here, the Dionex CRD 300 device is operated in the chemical regenerant mode with the regenerant conveniently delivered by the Dionex Inuvion system's peristaltic pump.

## Method

### Reagent, sample, and standard

- Degassed deionized (DI) water, 18 MΩ·cm resistance or better
- Municipal drinking water
- Sodium and potassium salts, A.C.S. reagent grade or better, for preparing anion standards

### System preparation and setup

Figure 1 shows the flow diagram of a Dionex Inuvion IC system using the peristaltic pump to deliver regenerant for the carbonate removal device (CRD).

## Instrument method parameters

Instrument	Dionex Inuvion system (P/N 22185-60108)
Autosampler	Thermo Scientific™ Dionex™ AS-DV autosampler (P/N 068907) with 5 mL Thermo Scientific™ Dionex™ PolyVials™ and filter caps (P/N 038141)
Columns	Thermo Scientific™ Dionex™ IonPac™ AS23-4µm and AG23-4µm, 4 mm i.d. column set (P/N 302555 and P/N 302556)
Eluent	4.5 mM Na <sub>2</sub> CO <sub>3</sub> / 0.8 mM NaHCO <sub>3</sub>
Eluent source	Thermo Scientific™ Dionex™ EGC K <sub>2</sub> CO <sub>3</sub> (Analytical) eluent generator cartridge (P/N 102-60008) with Thermo Scientific™ Dionex™ EPM 500 pH modifier (P/N 088471), Thermo Scientific™ Dionex™ RFI eluent degasser (P/N 106-60001), and Thermo Scientific™ Dionex™ EGC Carbonate Mixer Kit (P/N 088468)
Eluent flow rate	1.0 mL/min
Inj. volume	250 µL (full loop)
Column temp.	30 °C
Detection	Suppressed conductivity with a Dionex CRD 300 device. Dionex AERS 500 Carbonate suppressor, (4 mm, P/N 085029), ambient, 40 mA, recycle mode; Dionex CRD 300 Carbonate Removal Device (4 mm, P/N 064637), ambient, chemical regenerant mode, 200 mM NaOH (peristaltic pump at 20%, ~2.2 mL/min)
Background conductance	~1.3 µS/cm
System backpressure	~4,300 psi (100 psi = 0.6894 MPa)
Run time	30 min
Software	Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software version 7.3.3

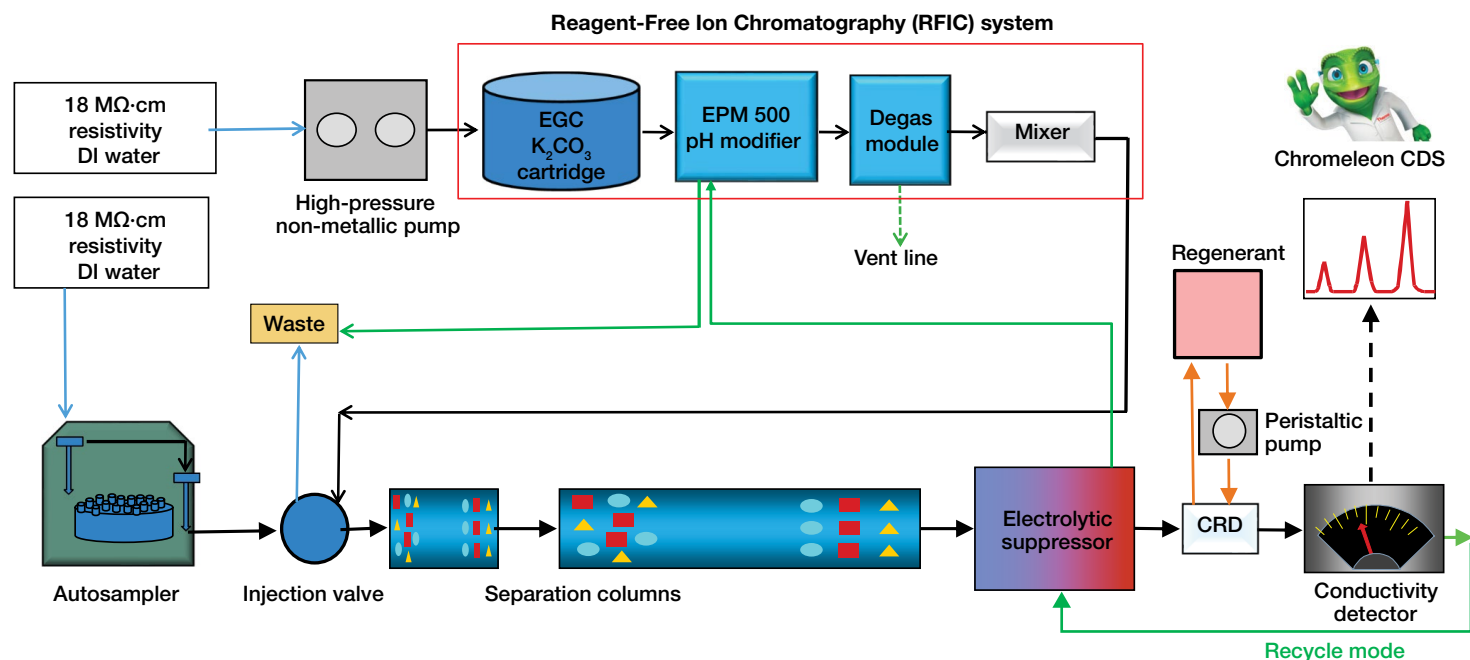


Figure 1. Illustration of the IC system flow diagram

## Results and discussion

Figure 2 shows a separation of inorganic anions within 30 min using a Dionex IonPac AS23-4 $\mu$ m column set. Ten inorganic anions, including oxyhalides, are resolved. The Dionex IonPac AS23-4 $\mu$ m column can be used for compliance monitoring of these inorganic anions in drinking and bottled waters.

Figure 3 shows the chromatograms of a drinking water sample and spiked drinking water samples containing trace concentrations of oxyhalides and bromide. Chlorite and bromate are currently regulated with maximum contaminant levels of 1 ppm (1,000  $\mu$ g/L) and 10 ppb ( $\mu$ g/L).<sup>1</sup> In the U.S., chlorate has

Columns:	Dionex IonPac AG23-4 $\mu$ m, 4 $\times$ 50 mm and Dionex IonPac AS23-4 $\mu$ m, 4 $\times$ 250 mm	
Eluent:	4.5 mM K <sub>2</sub> CO <sub>3</sub> / 0.8 mM KHCO <sub>3</sub>	
Eluent source:	Dionex EGC K <sub>2</sub> CO <sub>3</sub> (Analytical) cartridge with Dionex EPM 500 pH modifier, Dionex RFIC eluent degasser, and Dionex EGC carbonate mixer	
Flow rate:	1.0 mL/min	
Inj. volume:	250 $\mu$ L (full loop)	
Column temp.:	30 $^{\circ}$ C	
Detection:	Suppressed conductivity with a Dionex CRD 300 device. Dionex AERS 500 Carbonate suppressor, (4 mm), ambient, 40 mA, recycle mode; Dionex CRD 300 Carbonate Removal Device (4 mm), ambient, chemical regenerant mode, 200 mM NaOH (peristaltic pump at 20%, ~2.2 mL/min)	
Sample:	Mixed standards	
Peaks:	Min	mg/L (ppm)
1. Fluoride	4.8	0.15
2. Chlorite	6.5	0.5
3. Bromate	6.8	1.0
4. Chloride	7.8	0.3
5. Nitrite	9.8	0.75
6. Chlorate	11.0	1.25
7. Bromide	12.0	1.25
8. Nitrate	13.8	1.25
9. Phosphate	19.9	2.0
10. Sulfate	22.1	1.5

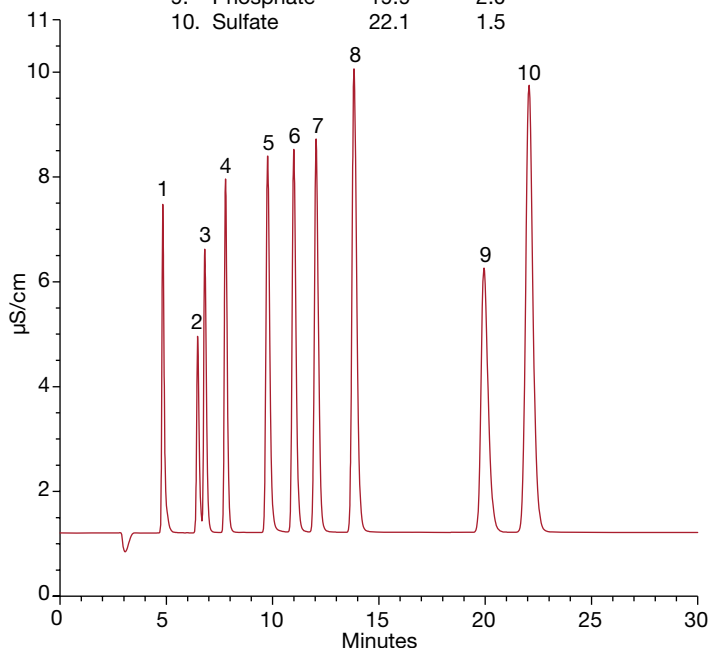


Figure 2. Separation of inorganic anions using a Dionex IonPac AS23-4 $\mu$ m column

not been regulated yet, but public water systems were required to monitor it during the period of Unregulated Contaminant Monitoring Rule 3 (UCMR 3).<sup>8</sup> In the EU, the default maximum residue level (MRL) of chlorate at 0.01 ppm was applicable for all food products.<sup>9</sup> The results show that the method can detect trace concentrations of oxyhalides and bromide for regulatory monitoring. This drinking water sample contains chlorite (5.4  $\mu$ g/L), chlorate (77.1  $\mu$ g/L), bromide (13.3  $\mu$ g/L), and no detectable bromate, which meet the regulatory criteria.

Columns:	Dionex IonPac AG23-4 $\mu$ m, 4 $\times$ 50 mm and Dionex IonPac AS23-4 $\mu$ m, 4 $\times$ 250 mm		
Eluent:	4.5 mM K <sub>2</sub> CO <sub>3</sub> / 0.8 mM KHCO <sub>3</sub>		
Eluent source:	Dionex EGC K <sub>2</sub> CO <sub>3</sub> (Analytical) cartridge with Dionex EPM 500 pH modifier, Dionex RFIC eluent degasser, and Dionex EGC carbonate mixer		
Flow rate:	1.0 mL/min		
Inj. volume:	250 $\mu$ L (full loop)		
Column temp.:	30 $^{\circ}$ C		
Detection:	Suppressed conductivity with a Dionex CRD 300 device. Dionex AERS 500 Carbonate suppressor, (4 mm), ambient, 40 mA, recycle mode; Dionex CRD 300 Carbonate Removal Device (4 mm), ambient, chemical regenerant mode, 200 mM NaOH (peristaltic pump at 20%, ~2.2 mL/min)		
Sample:	A: Municipal drinking water B: A + 10 $\mu$ g/L of oxyhalides and bromide C: A + 50 $\mu$ g/L of oxyhalides and bromide		

Peaks:	A	B	C	$\mu$ g/L (ppb)
1. Fluoride	-	-	-	
2. Chlorite	5.4	14.9	51.3	
3. Bromate	0	7.6	48.0	
4. Chloride	-	-	-	
5. Nitrite	-	-	-	
6. Chlorate	77.1	87.4	128	
7. Bromide	13.3	22.8	60.7	
8. Nitrate	-	-	-	
9. Phosphate	-	-	-	
10. Sulfate	-	-	-	

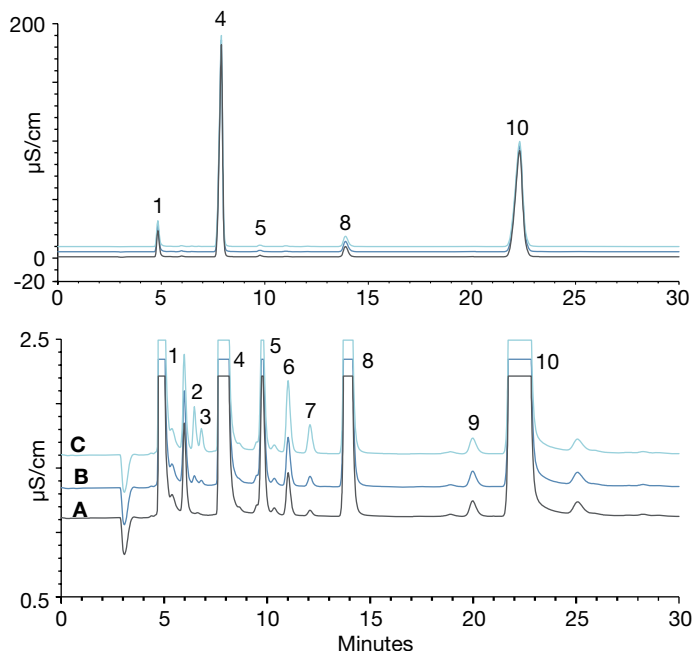


Figure 3. Determination of trace concentrations of oxyhalides and bromide in drinking water samples

## Conclusion

This work shows a method for the determination of trace concentrations of oxyhalides and bromide in drinking water in 30 min using a Dionex Inuvion RFIC system. The method uses Dionex IonPac AS23-4 $\mu$ m columns, a Dionex AERS 500 Carbonate anion electrolytically regenerated suppressor, and a Dionex CRD 300 Carbonate Removal Device, which was operated in the chemical regenerant mode with the regenerant conveniently delivered by the Dionex Inuvion system's peristaltic pump. The Dionex Inuvion RFIC system, coupled with a Thermo Scientific™ Dionex™ AS-DV autosampler, provides an economical compact setup for compliance monitoring of oxyhalides and bromide in drinking water.

## References

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