



Fast determination of oxyhalides and bromide in drinking water using a compact ion chromatography system coupled with a single quadrupole mass spectrometer

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Keywords

IC-MS, isocratic, Dionex Integrion HPLC, Dionex IonPac AS19-4 μ m column, disinfection byproducts, US EPA Method 300.1 Part B, bromate, chlorite, chlorate, ISQ EC mass spectrometer, AERS 500e suppressor, drinking water, RFIC system

Goal

To develop a fast, isocratic method to determine oxyhalides and bromide in drinking water by coupling IC with single quadrupole mass spectrometry (IC-MS)

Introduction

Most municipal water authorities disinfect their water in order to provide their communities with safe drinking water. The most common chemical disinfectants are chlorine, chlorine dioxide, chloramine, and ozone.¹ However, these disinfectants can react with naturally occurring material 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, chlorite, chlorate, and other DBPs. 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. Of these DBPs, bromate has been identified by the International Agency for Research on Cancer as an animal carcinogen and potential human carcinogen.³ The World Health Organization (WHO) has estimated an excess lifetime cancer risk of 10^{-4} , 10^{-5} , 10^{-6} for drinking water containing bromate at levels of 20, 2, and 0.2 μ g/L, respectively.⁴ 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 μ g/L.⁵ In Europe, the limit was lowered to 3 μ g/L for bottled natural mineral and

spring waters disinfected by ozonation. Recently there has been a discussion of lowering the 10 µg/L limit, and this could require more sensitive analytical methods.⁶

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. Careful monitoring of the bromate concentration is necessary to ensure that it does not exceed safe drinking water standards.

For the determination of oxyhalides in drinking water, ion chromatography (IC) coupled with conductivity detection (CD) is the analytical method of choice, as previously demonstrated and as described in US EPA Method 300.1 Part B.⁷⁻⁹ However, under certain circumstances where more sensitivity and selectivity is needed, the conductivity detector can be replaced or augmented with a mass spectrometer (MS). This study describes a method to determine oxyhalides and bromide in water by coupling IC with single quadrupole mass spectrometry (IC-MS).

The new, easy-to-use Thermo Scientific™ ISQ™ EC Single Quadrupole Mass Spectrometer seamlessly integrates IC with MS, taking advantage of the strengths of both techniques. Anion exchange chromatography using eluent generation and suppressed conductivity detection provides chromatographic selectivity, analytes in the ionic form, and compatibility with MS. Electrospray ionization (ESI) is used to introduce the liquid IC stream (after suppression) as a fine spray into the MS source. The Heated ESI (HESI II) probe improves the ESI interface by allowing the use of high temperatures and voltage to deliver better desolvation and enhanced sensitivity; thus, a make-up solvent is not needed.

Application Note 72866 (AN72866) describes a method to determine oxyhalides and bromide in water by IC-MS¹⁰, which extends US EPA Method 300.1 Part B. Adding the single quadrupole mass spectrometer to Method 300.1 Part B provides advantages by delivering improved sensitivity and selectivity. IC-MS also offers positive analyte identification, which is particularly useful for complex matrices.

US EPA Method 300.1 Part B uses CD detection, and thus chlorite, bromate, chlorate, and bromide must be completely resolved from other common inorganic anions using gradient eluent conditions with an analysis time of 30 min. MS detection can resolve co-eluting peaks using their mass-to-charge ratio, allowing a shorter (15 min) isocratic run. The results for bromate, chlorite, chlorate, and bromide determinations in drinking water were compared with the results of AN72866.

Experimental Equipment

- Thermo Scientific™ Dionex™ Integrigon™ HPIC™ system* (P/N 22153-60208) including:
 - Eluent Generator
 - Pump
 - Degasser
 - Conductivity Detector
 - Second 6-port injection valve (P/N 22153-62027) used as a diverter valve
 - Thermo Scientific™ Dionex™ IC PEEK Viper™ Fitting Tubing Assembly Kit (P/N 088798)
 - Column Oven Temperature Control
 - Detector-Suppressor Compartment Temperature Control
 - Tablet Control
- Thermo Scientific™ Dionex™ AS-AP Autosampler (P/N 074926), with 5000 µL syringe (P/N 074308), 8500 µL buffer line assembly (P/N 075520), 60 µL injection loop and 10 mL vial trays
- Thermo Scientific™ ISQ™ EC single quadrupole mass spectrometer (P/N ISQEC-IC) including Thermo Scientific™ HESI-II probe (P/N 70005-60155)
- Thermo Scientific™ Dionex™ AXP-MS auxiliary pump (used to deliver suppressor external water) (P/N 060684)
- Thermo Scientific™ Dionex™ SRD-10 Suppressor Regenerant Detector (P/N 074395) (Optional)

* This method can also be run on a Dionex ICS-5000+ or Dionex ICS-6000 dual system using the second pump to deliver suppressor external water in place of the AXP-MS auxiliary pump.

Software

Thermo Scientific™ Dionex™ Chromeleon™ Data System (CDS) Version 7.2.8

Consumables

- 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 500e Anion Electrolytically Regenerated Suppressor, 2 mm (P/N 302662)
- Thermo Scientific™ Dionex™ AS-AP Autosampler Vials 10 mL (P/N 074228)
- Fisherbrand™ Narrow-Mouth field sample bottles, high-density polyethylene (HDPE), 125 mL, 250 mL sizes for storage of standards and samples (Fisher Scientific P/N 02-895A, B)

Reagents and standards

- Deionized (DI) water, Type 1 reagent grade, 18 MΩ·cm resistivity or better
- Sodium and potassium salts, A.C.S. reagent grade or better, for preparing anion standards
- Ethylenediamine, 99% (Sigma-Aldrich)
- Potassium bromate (90-95% chemical purity) (¹⁸O₃, 98%) 100 µg/mL in ¹⁸O-water (Cambridge Isotope Laboratories P/N OLM-8283-18O-1.2)

Samples

Three different brands of bottled water were obtained from a local supermarket (BW#1-3), and three residential tap water samples were collected from different cities in the San Francisco Bay Area (DW#1-3).

Chromatographic conditions

Columns:	Thermo Scientific™ Dionex™ IonPac™ AG19-4µm Guard Column, 2 × 50 mm (P/N 083225) Thermo Scientific™ Dionex™ IonPac™ AS19-4µm Analytical Column, 2 × 250 mm (P/N 083223)
Eluent:	40 mM KOH
Eluent Source:	Dionex EGC 500 KOH cartridge with CR-ATC 600
Flow Rate:	0.25 mL/min
Injection Volume:	60 µL in Push-Full mode
Column Temp.:	30 °C
Detection 1:	Suppressed Conductivity
Suppressor:	Dionex AERS 500e (2mm) Suppressor, external water mode (flow 0.5 mL/min), 62 mA current
Detection/Suppressor Compartment:	15 °C
Cell Temp.:	35 °C
Background Conductance:	<1 µS/cm
System Backpressure:	~3200 psi
Noise:	<1 nS/cm
Run Time	15 min

The Thermo Scientific Dionex™ DRS 600 Suppressor can be used for this application in either dynamic or legacy mode.

Chromatographic conditions (continued)

Detection 2:	Mass Spectrometry
MS Detector:	ISQ EC single quadrupole MS
Ionization Interface:	Electrospray Ionization (ESI), negative mode
Diverter Valve Switch Times:	0–2 min to waste, 2–8 min to MS, 8–15 min to waste
Sheath Gas Pressure:	45 psi
Aux Gas Pressure:	4.5 psi
Sweep Gas Pressure:	1 psi
Source Voltage:	-2500 V
Vaporizer Temp:	450 °C
Ion Transfer Tube Temp:	200 °C
Chrom. Filter Peak Width:	Off
Scan Mode:	Table 1
MS Processing Method	Table 2

Table 1. MS scan mode

Time (min)	Scan Name	Mass List (amu)	Dwell or Scan Time (s)	SIM Width (amu)	Ion Polarity	Spectrum Type	Source CID Voltage
3–7.5	Bromate 127	126.90	0.24	0.1	Negative	Centroid	40
3–7.5	Bromate 129	128.90	0.24	0.1	Negative	Centroid	40
3–7.5	Bromate ISTD 133	132.92	0.24	0.1	Negative	Centroid	40
3–7.5	Bromate ISTD 135	134.91	0.24	0.1	Negative	Centroid	40
3–7.5	Chlorite 67	66.96	0.24	0.1	Negative	Centroid	40
3–7.5	Chlorite 69	68.96	0.24	0.1	Negative	Centroid	40
3–7.5	Bromide 79	78.92	0.36	0.1	Negative	Centroid	40
3–7.5	Bromide 81	80.92	0.36	0.1	Negative	Centroid	40
3–7.5	Chlorate 83	82.95	0.36	0.1	Negative	Centroid	40
3–7.5	Chlorate 85	84.95	0.36	0.1	Negative	Centroid	40

Table 2. MS processing method

Component	MS Quantitation Ion (<i>m/z</i>)	MS Confirmation Ion (<i>m/z</i>)
Bromate	126.90	128.90
Bromate ISTD	132.92	134.91
Chlorite	66.96	68.96
Bromide	78.92	80.92
Chlorate	82.95	84.95

System preparation and setup

The system preparation and setup are the same as AN72866. Figure 1 shows the flow diagram of IC-CD/MS. The Integrion HPIC system is plumbed as a Reagent-Free IC (RFIC) system using eluent generation following the Dionex Integrion installation and operator's manual.¹¹ Install the suppressor in external water mode using a Dionex AXP-MS pump to provide the DI water needed for regeneration.¹² The AXP-MS can be added in the instrument configuration and thus be controlled by Chromeleon CDS. The ISQ EC mass spectrometer is installed according to the installation guide.¹³

A 6-port diverter valve is placed between the CD and mass spectrometer. The diverter valve can be operated in two positions (Figure 2). A small piece of red PEEK tubing called a "jumper" is installed in the IC diverter valve connecting port 1 to 3. In position A, eluent flows from the CD to the MS, and the AXP delivers water to the suppressor "Regen In" port. In position B, eluent flow is in recycle mode for the suppressor, and the AXP delivers water to the MS. Configure the diverter valve in the instrument method script editor to divert everything to waste except the compounds of interest.

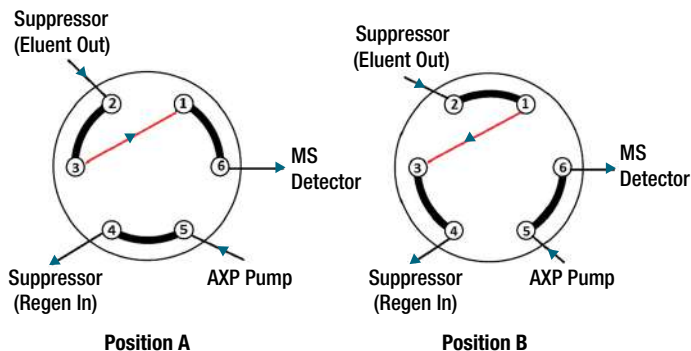


Figure 2. Diverter valve positions

The Dionex SRD-10 Suppressor Regenerant Detector is an optional device that can be placed between Regen Out port of the suppressor and the Regen In port of the Dionex CR-ATC trap column. The Dionex SRD-10 device automatically disables the eluent pump if the suppressor regenerant flow stops or slows, preventing damage to the suppressor and the mass spectrometer.

Detailed instructions for configuring the IC-MS system, including the addition of the Dionex SRD-10 device, are shown in Technical Note 72611.¹⁴

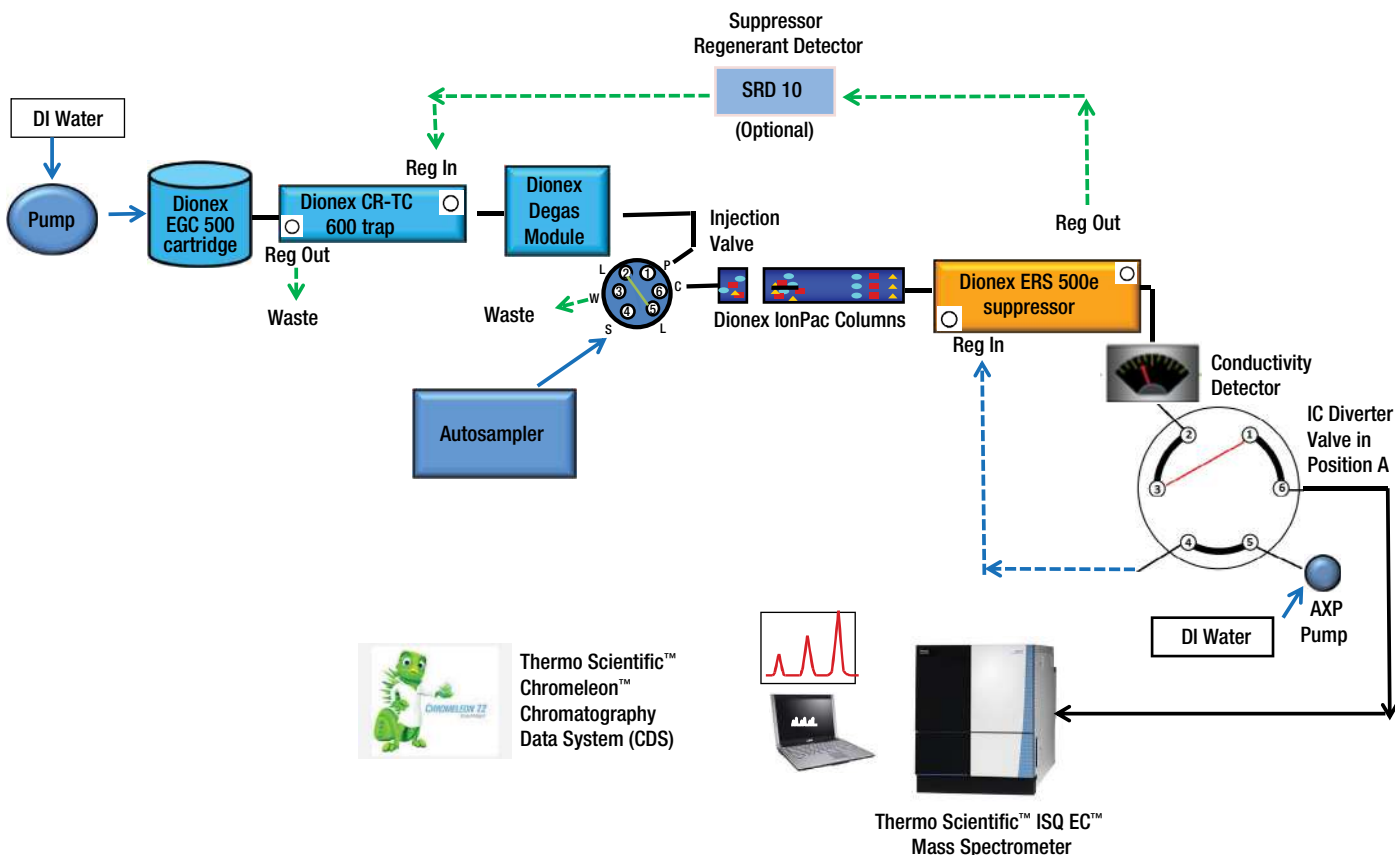


Figure 1. Flow diagram for IC-CD/MS with diverter valve in "A" position

Precautions

1. Allow the system to equilibrate until the total conductivity is <1.5 µS/cm before connecting the IC flow to an operating MS. In other words, keep the diverter valve at position B, with flow from the Dionex AXP-MS auxiliary pump going to the MS until the background conductivity is below 1.5 µS/cm. This can prevent the non-volatile eluent from precipitating inside ESI capillary.
2. The column used in this application has an inner diameter of 2 mm. Red PEEK tubing (0.005 in. i.d.) from CD to MS detector should be used to improve MS sensitivity. However, keep this tubing as short as possible to minimize backpressure on the suppressor. High backpressure can cause irreversible damage to the suppressor.
3. The MS needs to be “baked out” when the system is idle for over a day or when the MS peak area reproducibility becomes poor. To bake out the MS, set the vaporizer temperature to 500 °C, ion transfer temperature to 400 °C, sheath gas to 50 psi, aux gas to 10 psi, and sweep gas to 1 psi. Then, deliver DI water to the mass spectrometer at 0.1 mL/min with the Dionex AXP-MS auxiliary pump. Allow the system to bake out for at least 2 h.

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 3.

Stock standards for most anions are stable for at least 6 months at 4 °C. The chlorite standard is only stable for 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.

Bromate internal standard solution (ISTD)

The potassium bromate ($^{18}\text{O}_3$) standard from Cambridge Isotope Laboratories contains 77.4 mg/L of bromate ^{18}O . Dilute to 1 mg/L bromate ^{18}O with DI water.

Working standard solutions

Diluted working standard solutions were prepared using the 1000 mg/L stock standards. Concentrations of calibration standard mixtures used for chlorite, bromate, chlorate, and bromide were 0.25, 0.5, 1, 2, 5, 10 µg/L.

HIW (high ionic strength water)

Additional anions listed in Table 3 were used to prepare a simulated high ionic strength drinking water sample containing 1 mg/L fluoride, 50 mg/L chloride, 0.1 mg/L nitrite, 10 mg/L nitrate, 100 mg/L carbonate, 50 mg/L sulfate, and 0.1 mg/L phosphate. Dilute oxyhalide standards with HIW for determining the limit of detection (LOD) in HIW.

MDL standard solutions

MDL standard solutions were prepared using the 1000 mg/L stock standards. Concentrations of MDL standard mixtures used for MDL determination were 0.15 µg/L. Prepare MDL standard solution in both DI water and HIW.

Table 3. 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

Preservation solution

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

Sample preparation

Water samples are treated with the EDA preservation solution and kept in HDPE bottles at 4 °C.

Standard and sample with ISTD

Add 40 μ L 1 mg/L of ISTD to each 8 mL of calibration standard or sample.

Results and discussion

Separation

The Dionex IonPac AS19-4 μ m hydroxide-selective anion-exchange column was specifically designed for high-resolution separation of 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 μ g/L concentrations.¹⁵ Figure 3 shows a separation of common anions and disinfection byproduct anions within 15 min using a 40 mM KOH eluent. The top chromatogram displays the CD profiles of all anions. The bottom chromatogram displays the MS profiles of

the four analytes of interest: chlorite, bromate, chlorate, and bromide. As Figure 3 shows, chlorite, bromate, chlorate, and bromide were not completely resolved from other common inorganic anions. Chlorite coelutes with bromate, and chlorate coelutes with sulfate. Because of the coelution, CD detection should not be used for the quantification under these elution conditions. MS detection can resolve co-eluting peaks using their mass-to-charge ratio and is used for the quantification in this application, and isocratic elution increases the sample throughput due to a shorter cycle time between injections compared to gradient elution.

A delay time of 0.17 min is applied to the MS profile to match the CD profile. The delay time is the time required for the analyte to travel from one detector to another when they are in series. Here, the analyte goes through CD cell before going into MS. The delay time can be set in Chromeleon CDS in: Processing Method-Advanced Setting-Delay Time.

Limits of detection (LOD) and method detection limits (MDL)

Several approaches for determining the detection limit are possible. Here two methods were used. The LOD method is based on the signal-to-noise (S/N) ratio. Determination of the S/N ratio is performed by comparing measured signal from standard with low concentrations of analyte with those of blank samples and establishing the minimum concentration at which the analyte can be reliably detected. A S/N=3 is used for estimating the detection limit (LOD) and S/N=10 is used for estimating the quantification limit (LOQ).¹⁶ In this study, the baseline noise was first determined by measuring the peak-to-peak noise in a representative 1-min segment of the baseline where no peaks elute, but close to the peak of interest. The signal was determined from the average height of three injections of standard (0.1 μ g/L).

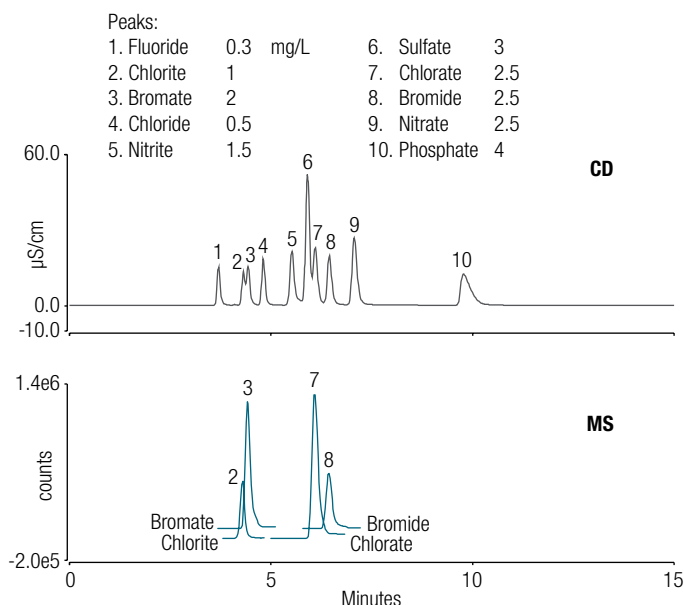


Figure 3. Separation of common anions and disinfection byproduct anions

The MDL method is based on the standard deviation of the response. EPA Method 300.1 uses the MDL method as the quality control.⁹ MDLs were determined by performing seven replicate injections of standards at a concentration of three to five times the estimated instrument detection limits (0.15 μ g/L). Calculate the MDL as follows: $MDL = (t) \cdot (S)$, where t represents the Student's value for a 99% confidence level and a standard deviation estimate with $n-1$ degrees of freedom ($t = 3.14$ for seven injections), S =standard deviation of the replicate analysis.

The LOD and MDL in HIW were also determined by preparing the same concentration of standard mixture in a simulated drinking water sample.

The estimates of MDL and LOD for chlorite, bromate, chlorate, and bromide are summarized in Table 4. The amount calculated is similar to that found in AN72866, which uses gradient elution. The LODs of chlorate and bromide in HIW were not determined due to the presence of trace amounts of those compounds in HIW. Figure 4 shows the chromatographic profiles (CD and MS) of a 0.25 µg/L calibration standard (No ISTD). The four anions of interest are all sensitively detected by MS while they are not detected by CD. Figure 5 shows the mass autofilter of a 0.25 µg/L calibration standard with bromate ¹⁸O internal standard (5 µg/L), which shows that chlorite, bromate, chlorate, and bromide are all detected well at 0.25 µg/L using MS detection.

Table 4. MDL and LOD using MS detection

Analyte	MDL (µg/L)	MDL in HIW (µg/L)	LOD (µg/L)	LOD in HIW (µg/L)
Chlorite	0.030	0.036	0.025	0.029
Bromate	0.038	0.033	0.035	0.031
Chlorate	0.036	0.045	0.028	N/A
Bromide	0.049	N/A	0.050	N/A

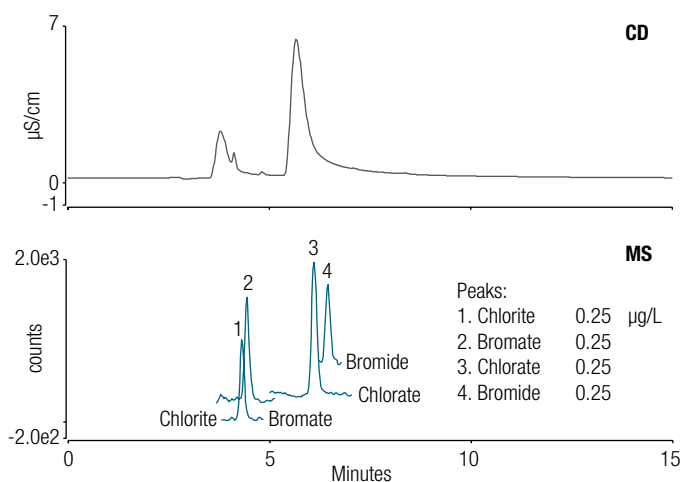


Figure 4. CD (top) and MS profile (bottom) of a 0.25 µg/L calibration standard (No ISTD)

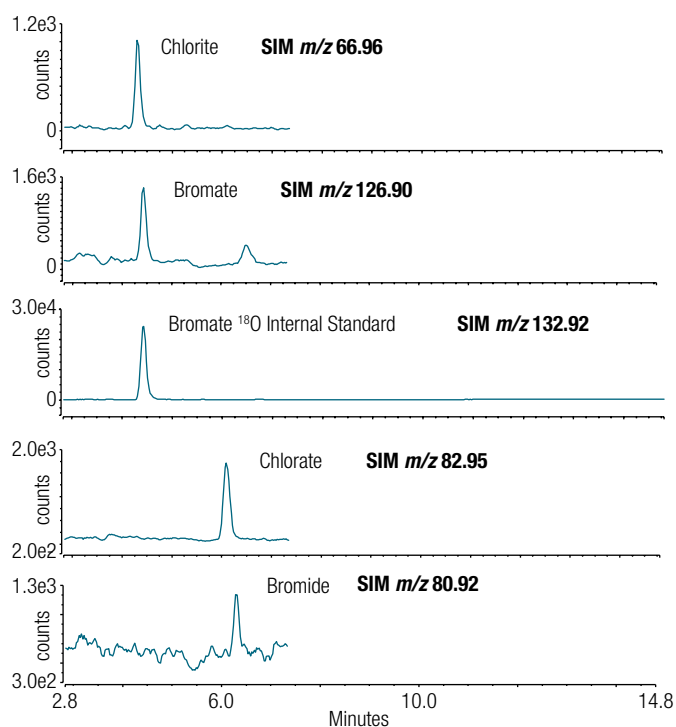


Figure 5. Mass autofilter of a 0.25 µg/L calibration standard with ISTD (5 µg/L)

Calibration

Calibration standard mixtures (chlorite, bromate, chlorate, and bromide) in the range of 0.25 to 10 µg/L were prepared in DI water, and then EDA was added as a preservative. The bromate ISTD was spiked into each calibration standard at a concentration of 5 µg/L. The internal standard method provides a means to account for losses in ionization efficiencies due to components of the matrix that may compete for ion formation in the source. The use of isotopically labeled internal standards ensures that both compound identification and compound quantification are of the highest degree of precision and accuracy possible. Table 5 summarizes the calibration results. Calibration curves were generated using internal standard calibration for MS detection in the range of 0.25 to 10 µg/L (Figure 6). The coefficient of determination is greater than 0.999 for all components.

Table 5. Calibrations using MS detection

Analyte	Range (µg/L)	Calibration Type	Coefficient of Determination (r ²)
Chlorite	0.25–10	Internal, Linear	0.9993
Bromate	0.25–10	Internal, Linear	0.9999
Chlorate	0.25–10	Internal, Linear	0.9991
Bromide	0.25–10	Internal, Linear	0.9994

Sample analysis

Three different brands of bottled water were obtained from a local supermarket, and three residential tap waters were collected from three cities in the San Francisco Bay Area, California. The samples used for this study are the same samples used in AN72866. If the target analyte concentration in the sample was greater than 10 µg/L it was diluted with DI water to be less than 10 µg/L. Table 6 shows the chlorite, bromate, chlorate, and bromide concentrations obtained. The concentrations are similar to those reported in AN72866 that used gradient elution.

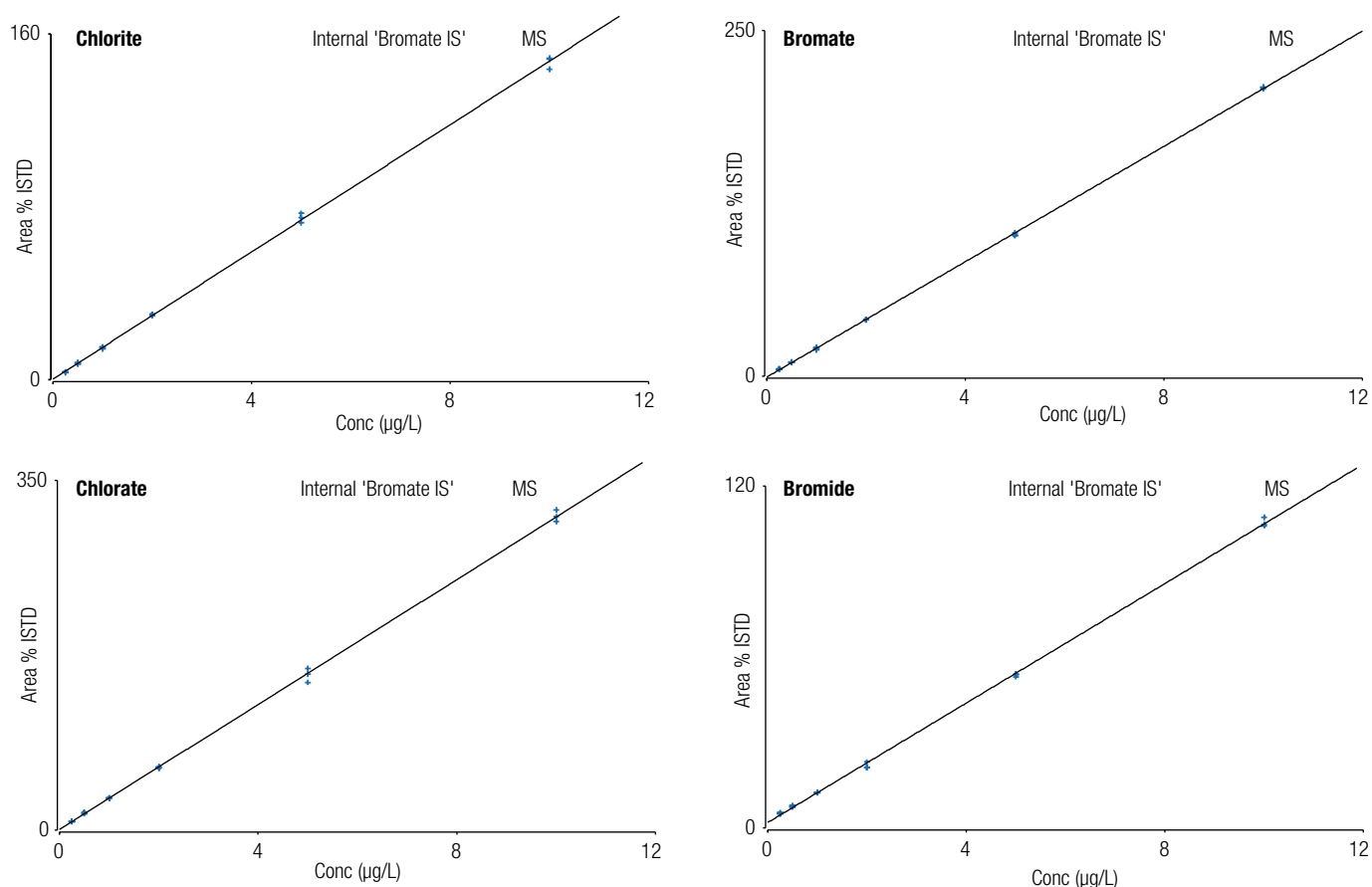
Figure 6. MS Calibration curves of chlorite, bromate, chlorate and bromide using bromate ¹⁸O as the internal standard

Table 6. Concentration of oxyhalides and bromide in drinking water determined using MS detection (µg/L)

Sample	Chlorite	Bromate	Chlorate	Bromide
BW1	<MDL	0.264	0.546	<MDL
BW2	<MDL	1.11	2.66	0.815
BW3	<MDL	0.565	0.165	1.87
DW1	4.91	<MDL	84.2	3.68
DW2	<MDL	0.248	61.7	109
DW3	<MDL	2.78	439	73.1

Method accuracy

Method accuracy was evaluated through recovery studies using spiked bottled and drinking water samples. Table 7 shows recovery of trace oxyhalides and bromide spiked in water samples using MS detection. EPA defines that MRL (minimum reporting limit) concentration can be no lower than the concentration of the lowest calibration standard. In the recovery study a 1 µg/L bromate spike was used. This is four times the MRL. Bromate recovery ranged from 97% to 104% in the six samples, all acceptable recovery according to U.S. EPA Method 300.1 Part B, i.e., 75% to 125% for the range from 1 to 10 times of the MRL. Recoveries were also good for the other anions except for chlorite in BW#3. The low recovery of chlorite in BW#3 is most likely due to the instability of chlorite at low concentration. Figure 7 shows an overlay of neat and spiked bottled water #2 chromatograms using MS detection.

Peaks:	A	B
1. Chlorite	<MDL	0.809 µg/L
2. Bromate	1.11	2.11
3. Chlorate	2.66	3.68
4. Bromide	0.815	1.83

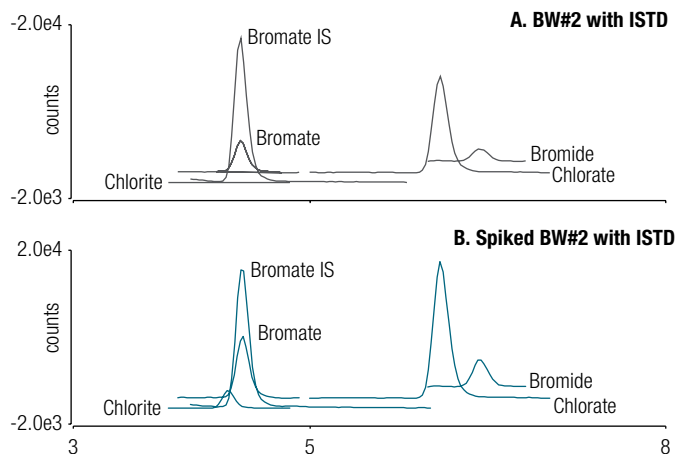


Figure 7. MS Profile of BW#2 (ISTD 5 µg/L) and spiked BW#2 (ISTD 5 µg/L)

Precision

The precision of the method was determined by triplicate injections of the 10 µg/L calibration standard on three separate days. As shown in Table 8, the calculated peak area precision varied from 0.33% to 1.93% with retention time precision <0.41% for all target anions. The high precision of this method is consistent with results typically found with a Reagent-Free IC (RFIC) system.

Table 8. Retention time and peak area precisions

Component	Retention Time (RSD)	MS Relative Peak Area to ITSD (RSD)
Chlorite	0.34	1.93
Bromate	0.33	0.33
Chlorate	0.41	1.88
Bromide	0.39	1.50

Table 7. Recoveries of trace oxyhalides and bromide spiked in drinking water samples using MS detection

Sample	Chlorite			Bromate			Chlorate			Bromide		
	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 (%)	Amount Found (µg/L)	Amount Added (µg/L)	Recovery (%)
BW1	<MDL	1	87.5	0.264	1	97.3	0.546	1	108	0.000	1	105
BW2	<MDL	1	80.9	1.11	1	101	2.66	1	102	0.815	1	102
BW3	<MDL	1	63.2	0.565	1	104	0.165	1	79.3	1.87	1	106
DW1	4.91	5	87.0	<MDL	1	101	84.1	40	103	3.68	5	91.5
DW2	<MDL	5	76.1	0.248	1	102	61.7	40	81.6	109	50	93.8
DW3	<MDL	5	75.8	2.78	1	98.2	439	200	88.0	73.1	40	108

Conclusion

This study demonstrates that oxyhalides and bromide can be determined accurately in municipal drinking water and bottled water using a fast isocratic 15-min IC-MS method. The method provides an advantage over the traditional IC-CD method concerning sensitivity and selectivity, offering positive analyte-identification, particularly for complex samples.

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