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APPLICATION NOTE 72886

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, Dionex Integrion HPIC, Dionex IonPac AS19-4µm column, disinfection byproducts, US EPA Method 300.1 Part B, bromate, chlorite, chlorate, ISQ EC mass spectrometer, AERS 500e suppressor, drinking water

Goal

To develop a 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 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 1 in 10,000 (i.e., in a population of one million, an additional one hundred people are expected to contract cancer over their lifetime) for drinking water containing bromate at 20 µg/L.[4]

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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.[5] In Europe, the limit was lowered to 3 µg/L for bottled natural mineral and spring waters disinfected by ozonation. In the last decade, there has been a discussion of lowering the limit even further, 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 suppressed 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 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 permits seamless integration of 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 HESI-II probe improves the ESI interface by using high temperature and voltage to deliver better desolvation and enhanced sensitivity; thus, a make-up solvent is not needed.

The method presented here is based on the conductivity detection method published in Application Update 203, which used a 4 mm Thermo Scientific™ Dionex™ IonPac™ AS19-4µm column with the suppressor in recycle mode. In this application note, a single quadrupole mass spectrometry detector (ISQ EC) is coupled to an HPIC system to deliver both CD and MS detections. A 2 mm Dionex IonPac AS19-4µm column is used to optimize the flow rate for MS. In this setup, the liquid stream passes through the suppressor and the CD cell before going into the mass spectrometer, with the suppressor in external water regeneration mode. The CD results for bromate, chlorite, chlorate, and bromide determinations in drinking water (i.e., Method 300.1 Part B results) were compared with the results from MS detection obtained in the same injection.

Experimental

Equipment

- A Thermo Scientific™ Dionex™ Integrion™ HPIC™ system* (P/N 22153-60208) including:
  - Eluent Generator
  - Pump
  - Degasser
  - Conductivity Detector
  - Second 6-port injection valve (P/N 22153-62027) used as 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

*This method can also be run on a Thermo Scientific™ Dionex™ ICS-5000+ system or Thermo Scientific™ Dionex™ ICS-6000 dual system using the second pump to deliver suppressor external water.

- 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
- ISQ EC single quadrupole mass spectrometer (P/N ISQEC000IC) including Thermo Scientific™ HESI-II probe (P/N 70005-60155)
- Thermo Scientific™ Dionex™ AXP-MS auxiliary pump (P/N 060684)

Software

- Thermo Scientific™ Chromeleon™ Chromatography 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)
- Thermo Scientific™ Dionex™ SRD-10 Suppressor Regenerant Detector (P/N 074395) (Optional)
- 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 anions standards
- Ethylenediamine, 99% (Sigma-Aldrich)
- Potassium bromate (90–95% chemical purity) ($^{18}O_3$, 98%) 100 µg/mL in ^{18}O-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:	Dionex IonPac AG19-4µm Guard Column, 2 × 50 mm (P/N 083225) Dionex IonPac AS19-4µm Analytical Column, 2 × 250 mm (P/N 083223)
Eluent:	10 mM KOH from 0–10 min, 10–30 mM KOH from 10–18 min, 100 mM KOH from 18–25 min, 10 mM KOH from 25–30 min
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 (2 mm) 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	30 min

The Thermo Scientific™ Dionex™ DRS 600 Suppressor can also 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 Time:	0–5 min to waste, 5–18 min to MS, 18–30 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

Mass spectrometry conditions

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
7–12	Bromate 127	126.90	0.24	0.1	Negative	Centroid	40
7–12	Bromate 129	128.90	0.24	0.1	Negative	Centroid	40
7–12	Bromate ISTD 133	132.92	0.24	0.1	Negative	Centroid	40
7–12	Bromate ISTD 135	134.91	0.24	0.1	Negative	Centroid	40
7–12	Chlorite 67	66.96	0.24	0.1	Negative	Centroid	40
7–12	Chlorite 69	68.96	0.24	0.1	Negative	Centroid	40
14–18	Bromide 79	78.92	0.36	0.1	Negative	Centroid	40
14–18	Bromide 81	80.92	0.36	0.1	Negative	Centroid	40
14–18	Chlorate 83	82.95	0.36	0.1	Negative	Centroid	40
14–18	Chlorate 85	84.95	0.36	0.1	Negative	Centroid	40

Table 2. MS processing method

Component	MS Quantitation Ion *(m/z)*	MS Confirmation Ion *(m/z)*
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

Figure 1 shows the flow diagram of IC-CD/MS system. The Integrion HPIC system is plumbed as a Reagent-Free IC (RFIC) system using eluent generation following the Thermo Scientific Dionex Integrion Installation and Operator's Manual.[10] Install the suppressor in external water mode using the Dionex AXP-MS pump to provide the DI water regenerant.[11] The Dionex AXP-MS pump can be added in the instrument configuration and thus be controlled by Chromeleon software. The ISQ EC mass spectrometer is installed according to the installation guide.[12]

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. 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 be placed in position B except when the compounds of interest are eluting.

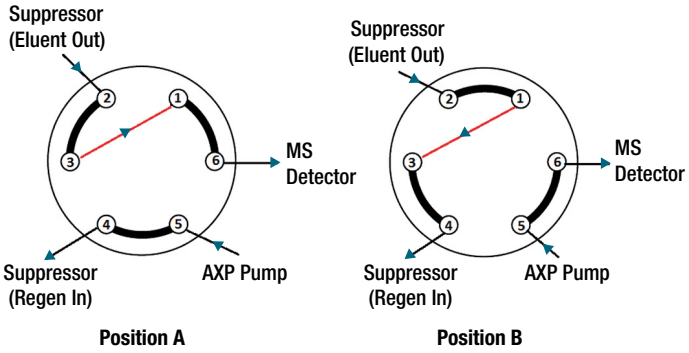


Figure 2. Diverter valve position

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 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 can be found in Technical Note 72611.[13]

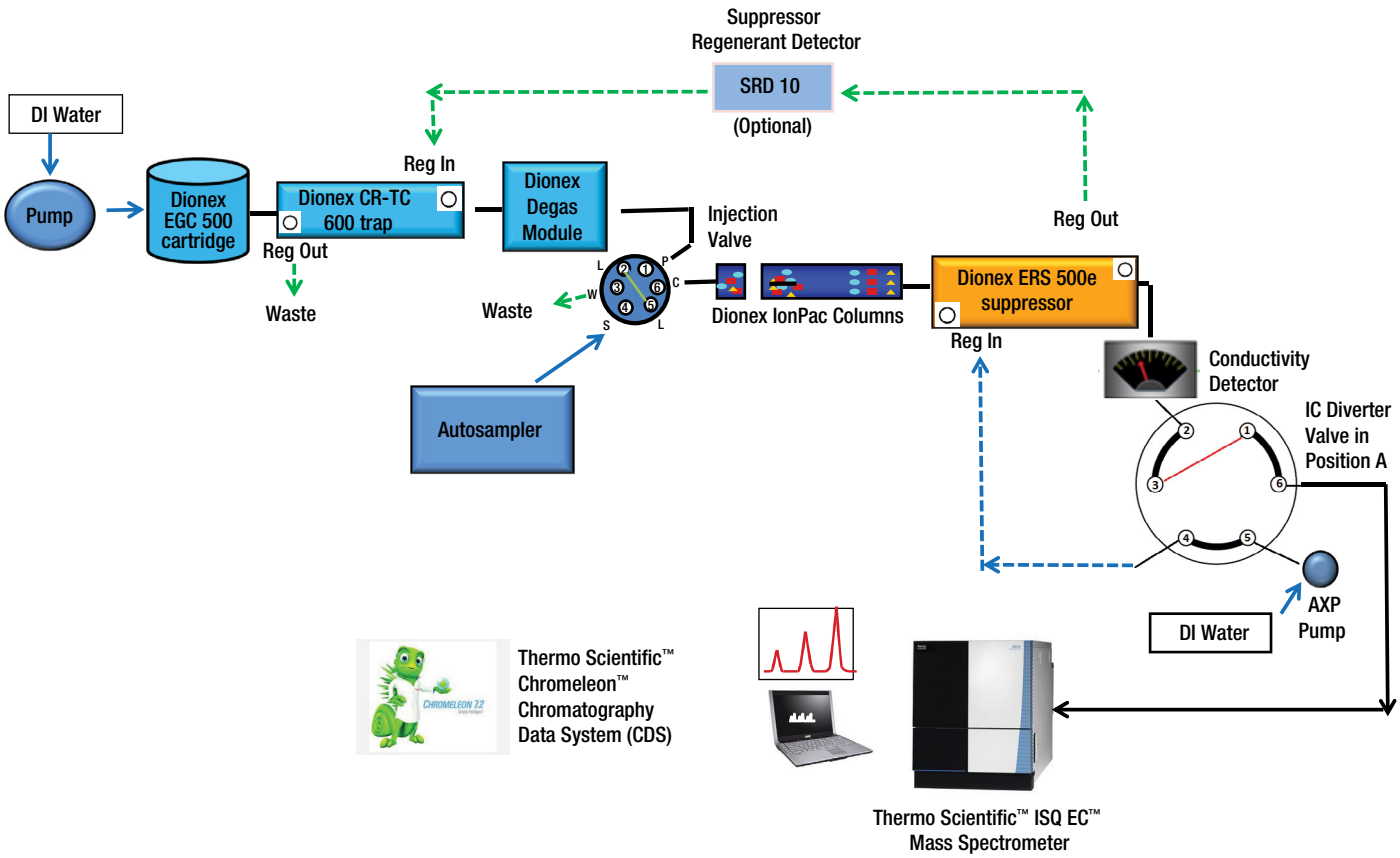


Figure 1. Flow diagram for IC-CD/MS with diverter valve in "A" position

Precautions

1. Allow the system to equilibrate until the total conductivity is <1.5 µS/cm. Then it is safe to connect the IC flow to an operating mass spectrometer. In other words, keep the divert valve at position B, with flow from the Dionex AXP-MS Auxiliary pump flow to the mass spectrometer until the background conductivity is below 1.5 µS/cm. This can prevent the non-volatile eluent from precipitating inside the ESI capillary.

2. The column used in this application has an inner diameter of 2 mm. Red 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 the backpressure (<150 psi; <10 bar), which can cause irreversible damage to the suppressor.

3. The mass spectrometer needs to be "baked out" when the system is idle for more than 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 AXP 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 ($^{18}O_3$) standard from Cambridge Isotope Laboratories (ULM-8451-1.2) 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. Levels of calibration standard mixture from 0.25, 0.5, 1, 2, 5, 10, 20, 50, 100, 200, 300, 400, and 500 µg/L were used in this study for chlorite, bromate, chlorate, and bromide to cover the expected concentration range found in typical environmental samples. A range of 0.25 to 20 µg/L was used for MS calibration, and 1 to 500 µg/L was used for CD calibration.

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 LOD in HIW.

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 µL of EDA preservation solution (100 mg/mL) per 100 mL of sample.

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

Sample preparation
Drinking water samples are treated with the EDA preservation solution and kept in HDPE bottles at 4 °C.

Standard and sample with ISTD
Add 40 µL of 1 mg/L ISTD to each 8 mL of calibration standard or sample.

Results and discussion
Separation
The Dionex IonPac AS19-4µm 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 low µg/L concentrations.[14] Figure 3 shows a separation of common anions and disinfection byproduct anions within 30 min using the Dionex IonPac AS19-4µm column. The top chromatogram displays the CD profile 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 resolved from other common inorganic anions. The excellent resolution between bromate and chloride makes this column ideal for determining low concentrations of bromate in municipal and bottled water samples.

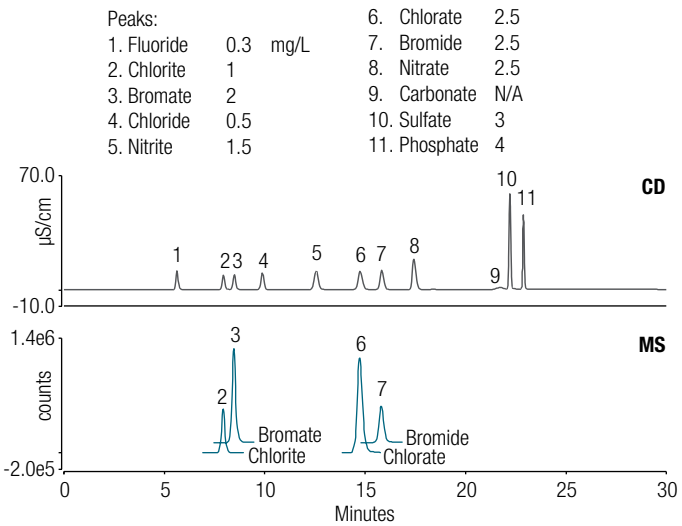


Figure 3. Separation of common anions and disinfection byproducts anions

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 a CD cell before going into the mass spectrometer. 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 standards 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).[15] 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 µg/L for MS detection, 1 µg/L for CD detection).

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 µg/L for MS detection, 1 µg/L for CD detector). Calculate the MDL as follows: MDL=(t) x (S), where t = 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. In comparison to CD detection, the LODs are 5–10-fold lower with MS detection for all anions. The LODs of

Table 4. MDL and LOD using CD and MS detections

Analyte	CD Detection				MS Detection			
	MDL (µg/L)	MDL in HIW (µg/L)	LOD (µg/L)	LOD in HIW (µg/L)	MDL (µg/L)	MDL in HIW (µg/L)	LOD (µg/L)	LOD in HIW (µg/L)
Chlorite	0.24	0.17	0.19	0.22	0.038	0.035	0.028	0.029
Bromate	0.33	0.43	0.33	0.37	0.039	0.032	0.037	0.028
Chlorate	0.23	0.22	0.36	0.32	0.047	0.037	0.034	N/A
Bromide	0.34	N/A	0.27	N/A	0.044	N/A	0.035	N/A

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 more sensitively detected by MS than CD. Figure 5 shows the mass autofilter of a 0.25 µg/L calibration standard with bromate ^{18}O internal standard (5 µg/L), which shows that chlorite, bromate, chlorate, and bromide are all detected well at 0.25 µg/L.

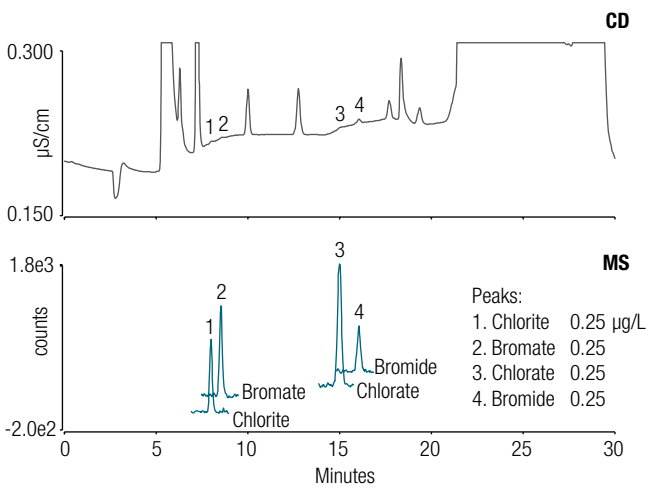


Figure 4. CD (top) and MS profile (bottom) of a 0.25 µg/L calibration standard (No ISTD)

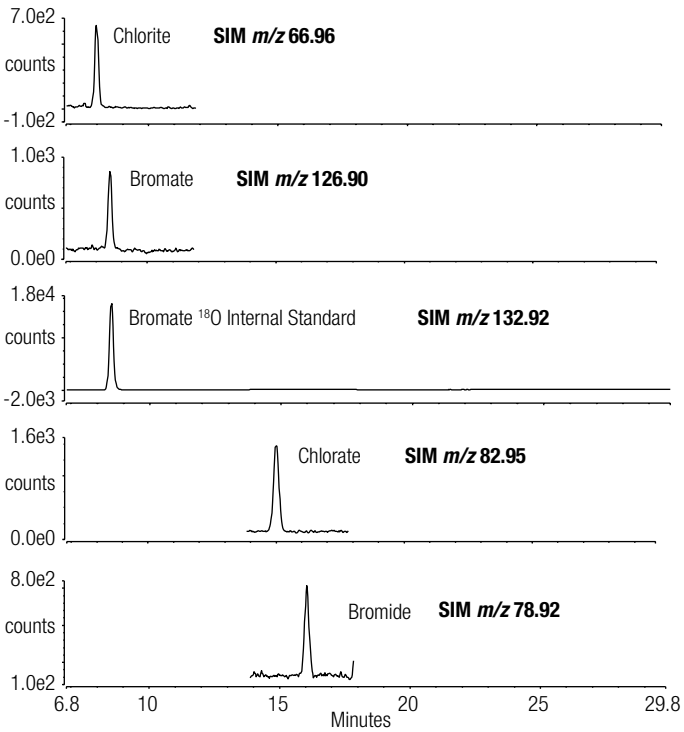


Figure 5. Mass autofilter of a 0.25 µg/L calibration standard with ISTD (5 µg/L)

Calibration

Calibration standard mixtures (chlorite, bromate, chlorate, and bromide) in the range of 0.25 to 500 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 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 20 µg/L (Figure 6), and external standard calibration for CD detection in the range of 1 to 500 µg/L (Figure 7). The coefficient of determination is greater than 0.999 for all components. Conductivity detection has a wider linear range than MS detection. In this application, conductivity detection was coupled with mass spectrometry detection. Thus we can take advantage of the benefit of both detectors: the high sensitivity of the MS detector and the wider linear range of the CD detector.

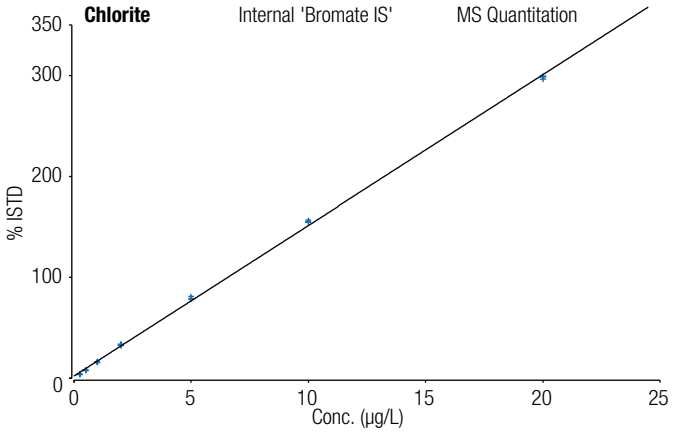
During method development, a bromate calibration curve for MS detection using 0.25–20 µg/L standards (without ISTD) was created as shown in Figure 8. Peak area variation is higher at 20 µg/L, and the result is that the calibration deviates from linearity. The calibration curve is more linear using a range of 0.25 to 10 µg/L. After adding an internal standard, the bromate calibration curve becomes linear in the range of 0.25 to 20 µg/L as shown in Figure 6. At 20 µg/L bromate, ion suppression is experienced by both the internal standard and bromate. Therefore the response factor (% ISTD) changes little. Although the linearity for a range 0.25 to 20 µg/L using the internal standard is good, for best accuracy, a calibration curve for MS detection should be kept at a range of 0.25 to 10 µg/L.

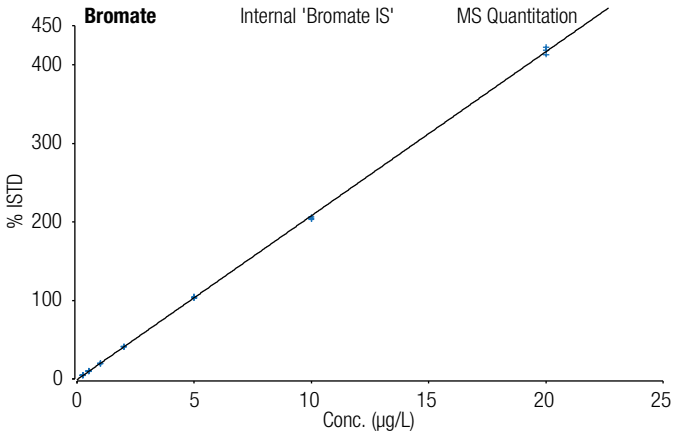
During method development, a bromate calibration curve for CD detection using calibration standards without ISTD was also created as shown in Figure 9. Here, the positive intercept caused by the presence of the ISTD in Figure 7 is absent.

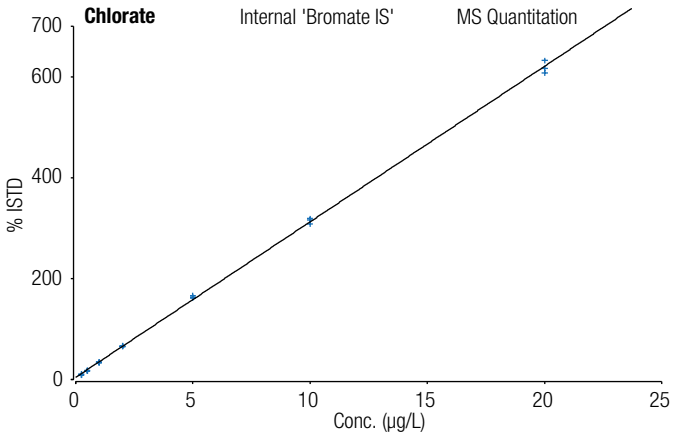
Although CD exhibits linearity up to 500 µg/L when the amount of oxyhalides in the sample is less than 50 µg/L (typical), a calibration range of 1 to 50 ppb should be used for best accuracy.

Table 5. Calibrations using CD and MS detections

Analyte	CD Detection			MS Detection		
	Range (µg/L)	Calibration Type	Coefficient of Determination (r^2)	Range (µg/L)	Calibration Type	Coefficient of Determination (r^2)
Chlorite	1–500	External, Linear	0.9999	0.25–20	Internal, Linear	0.9994
Bromate	1–50	External, Linear	0.9997	0.25–20	Internal, Linear	0.9998
Chlorate	1–500	External, Linear	0.9998	0.25–20	Internal, Linear	0.9994
Bromide	1–500	External, Linear	0.9999	0.25–20	Internal, Linear	0.9993







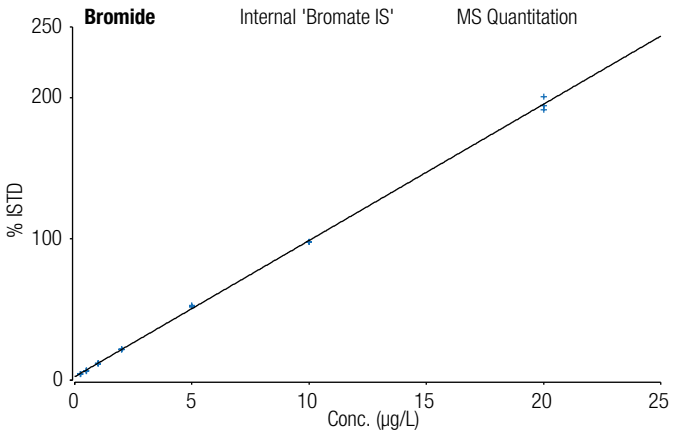
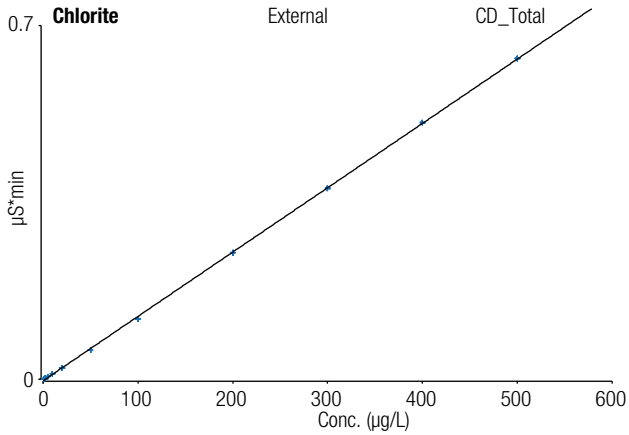
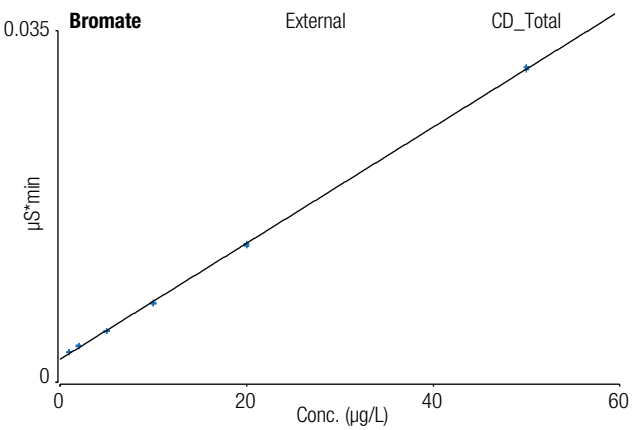
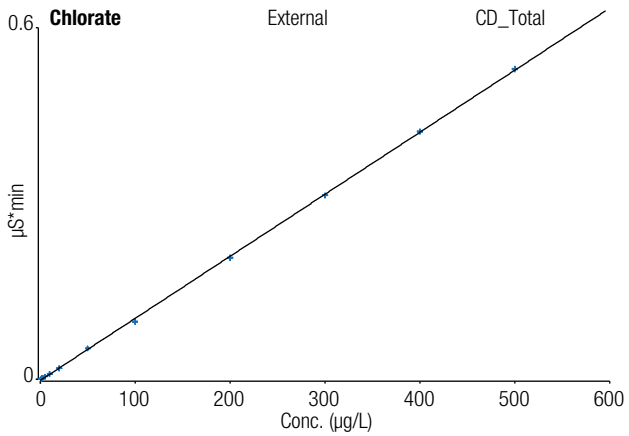


Figure 6. MS calibration curves of chlorite, bromate, chlorate, and bromide using bromate ^{18}O as internal standard







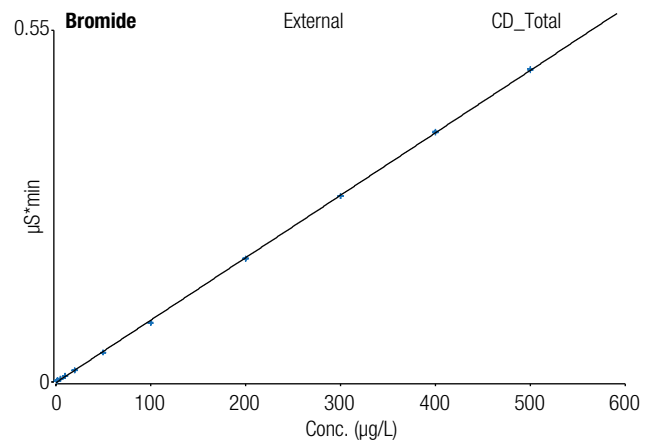


Figure 7. CD calibration curves of chlorite, bromate, chlorate, and bromide

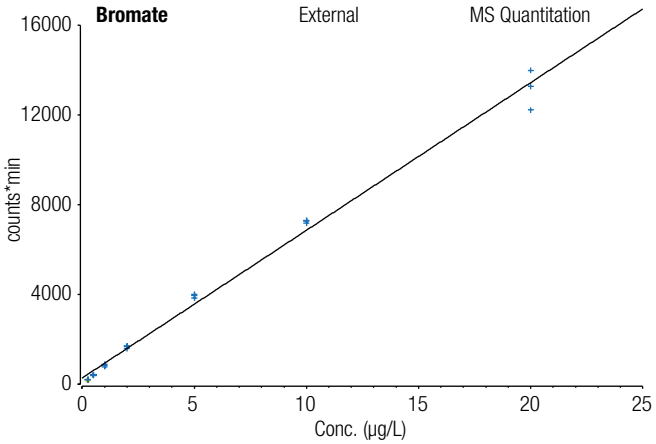


Figure 8. Bromate calibration curve, 1-20 ppb (No ISTD)

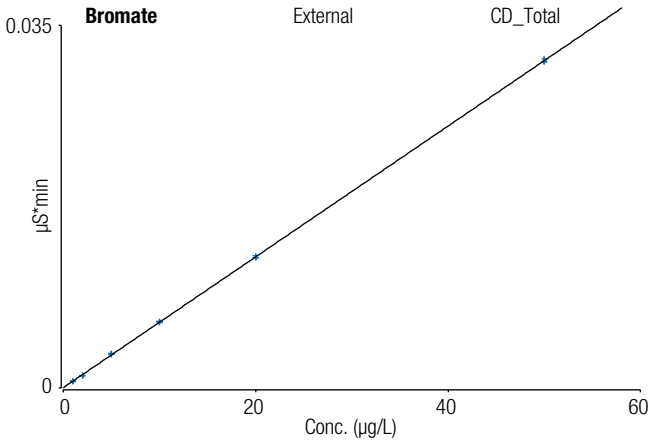


Figure 9. Bromate calibration curve, 1-50 ppb (No ISTD)

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. For MS detection, if the target analyte concentration in the sample is greater than 10 µg/L, dilute with DI water to be less than 10 µg/L. Table 6 compares the chlorite, bromate, chlorate, and bromide amounts obtained using CD and MS detections. The amounts calculated by the two methods of detection are similar. Bromate in bottled water #1 and drinking water #2 can be quantified by MS detection due to the higher sensitivity but not by CD. Figure 10 shows the chromatographic profiles (CD and MS) of bottled water #3 (ISTD is not added to demonstrate sensitivity difference.). Bromate is 5–10 times more sensitively detected by MS than CD.

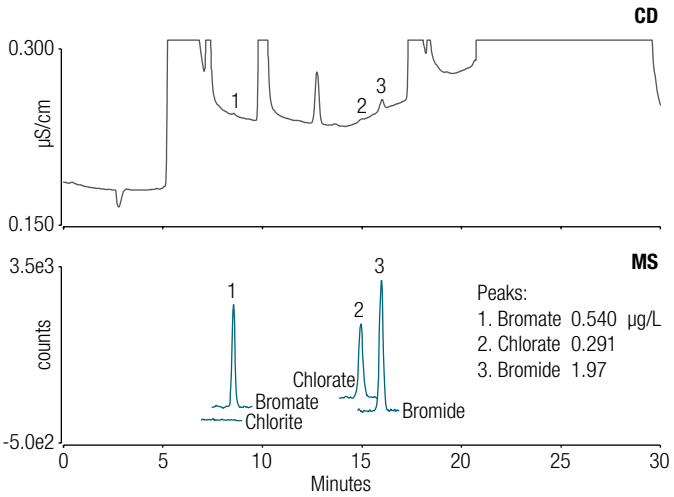


Figure 10. CD profile (top) and MS profile (bottom) of bottled water #3

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

	CD Detection				MS Detection			
Sample	Chlorite	Bromate	Chlorate	Bromide	Chlorite	Bromate	Chlorate	Bromide
BW1	<MDL	<MDL	<LOQ	0.416	<MDL	0.251	0.509	<MDL
BW2	<MDL	0.975	2.43	0.692	<MDL	1.08	2.70	0.685
BW3	<MDL	<LOQ	<LOQ	1.89	<MDL	0.540	0.291	1.97
DW1	6.69	<MDL	78.1	4.05	3.89	<MDL	78.1	3.59
DW2	<MDL	<MDL	80.6	104	<MDL	0.236	78.2	104
DW3	<MDL	2.06	478	67.2	<MDL	2.73	456	70.7

In addition to higher sensitivity, MS detection can be used to confirm analyte identity. Figure 11A and Figure 11B (magnified) show the chromatographic profile of drinking water #3. The CD channel chromatogram (top) overlays the sample with a 5 µg/L standard, and the MS channel (bottom) displays the sample only. The CD channel shows an unknown peak at a retention time close to that of chlorite; however, the MS indicates that this is not chlorite.

MS detection can resolve co-eluting peaks by taking advantage of differing mass-to-charge (*m/z*) ratios. Figure 12A and Figure 12B (magnified) show the chromatographic profile of drinking water #1. The CD channel chromatogram (top) is overlaid with a 5 µg/L standard, while the MS channel (bottom) displays the sample only. The CD channel shows an unknown peak that partially coelutes with the chlorite peak, affecting its integration and therefore the accuracy of chlorite quantitation. The MS channel is able to remove this interference by selecting only for chlorite's *m/z* ratio.

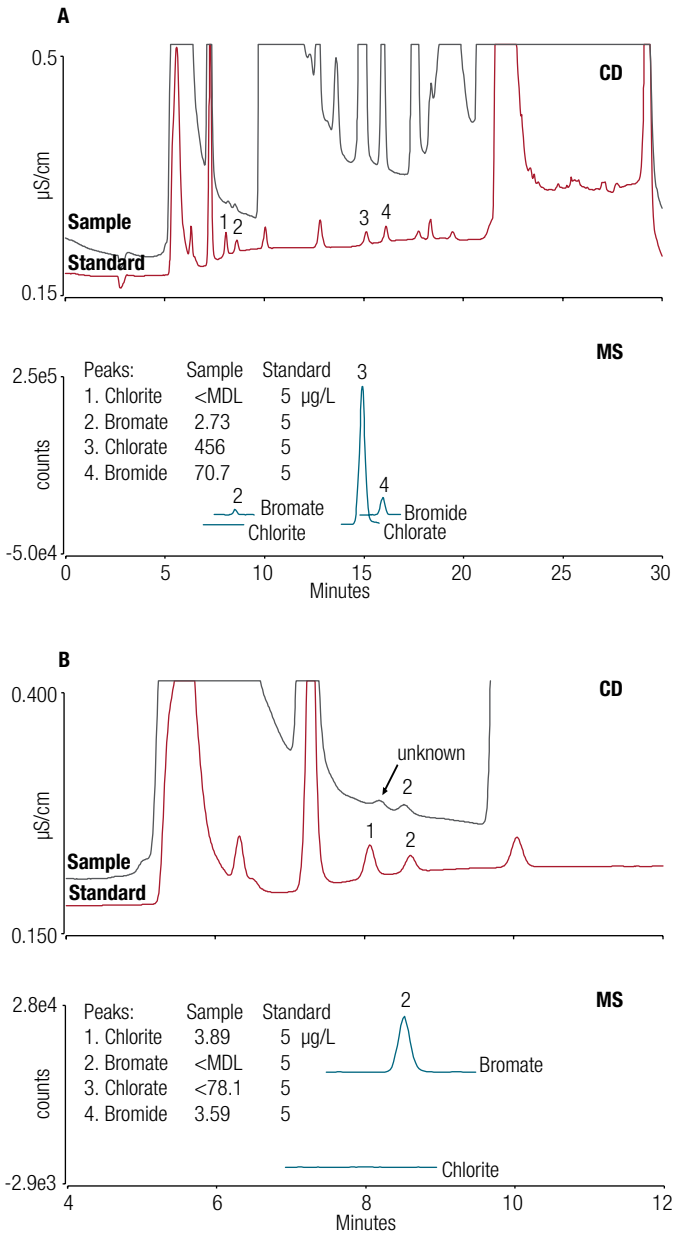


Figure 11. (A) CD profile (top) and MS profile (bottom) of drinking water #3 and (B) CD profile (top) and MS profile (bottom) of drinking water #3 (zoomed in)

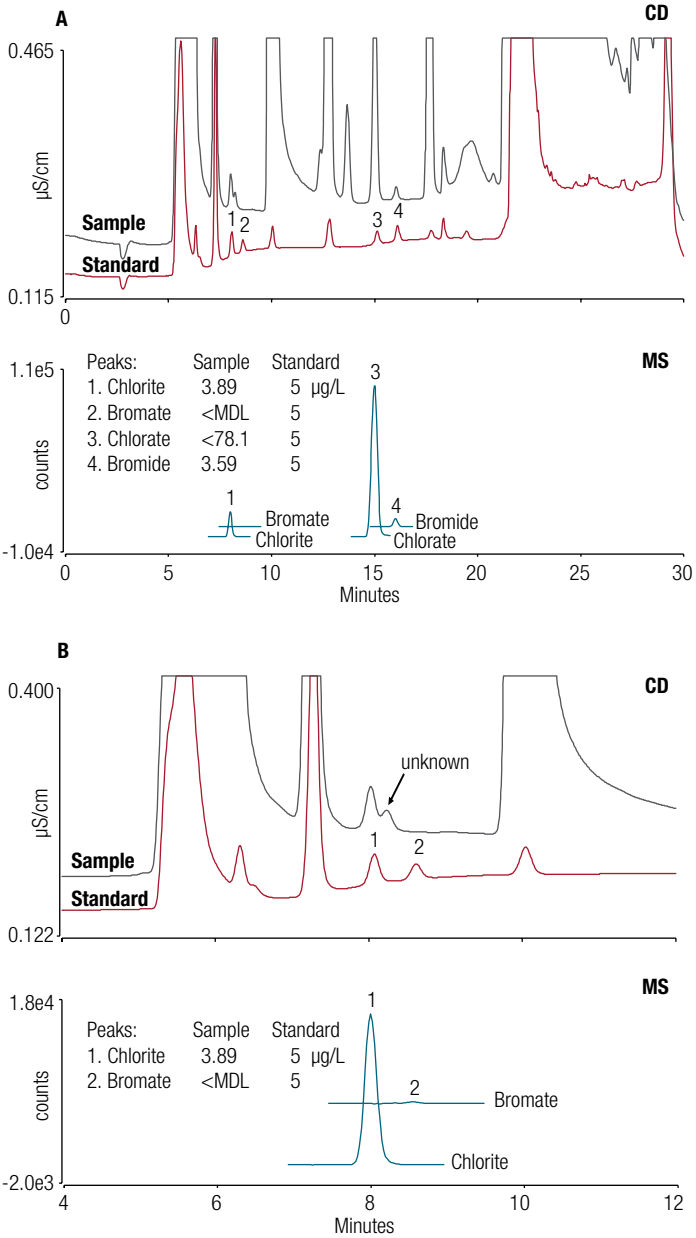


Figure 12. (A) CD profile (top) and MS profile (bottom) of drinking water #1 and (B) CD profile (top) and MS profile (bottom) of drinking water #1 (zoomed in)

MS provides greater selectivity for analytes in complex matrices. Figure 13 shows the chromatographic profile of bottled water #1. Baseline drift in CD around the chlorate and bromide peaks affects the quantification of those two peaks. However, MS can accurately determine those two peaks without interference.

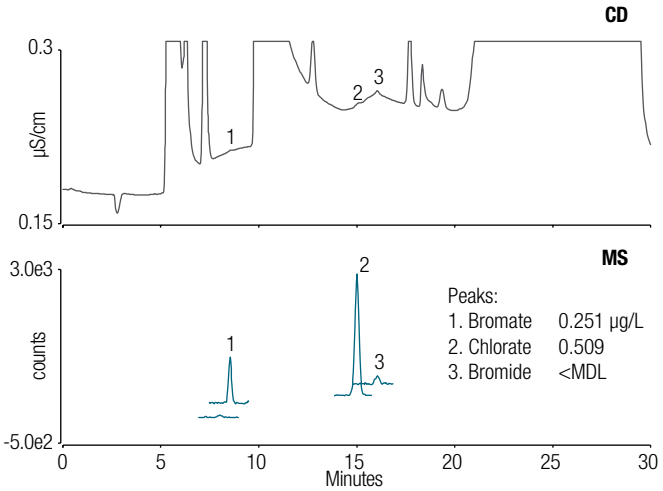


Figure 13. CD profile (top) and MS profile (bottom) of bottled water #1

Dual detection takes advantage of the strengths of each detector. When oxyhalides are present at low concentrations (<10 µg/L), MS detection can be used for the quantification due to the higher sensitivity. When oxyhalides are present at high concentrations (10–500 µg/L), CD detection can be used for the quantification due to its wider linear range. CD detection is also able to quantify oxyhalides from 1 to 10 µg/L.[7]

Method accuracy

Method accuracy was evaluated through recovery studies using spiked bottled and drinking water samples. Tables 7 and 8 show recovery of trace oxyhalides and bromide spiked in water samples using the MS detector and CD detector, respectively. The recovery for bromate in all six samples is in the range of 95 to 102% using MS detection and 78 to 113% using CD detection. The spike amount in the recovery study is less than 10 × MRL (minimum report limit). All anions demonstrate acceptable recovery (75–125%) according to the criteria outlined in U.S. EPA Method 300.1.

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

MS Detection	Chlorite			Bromate		
Sample	Amount Found (µg/L)	Amount Added (µg/L)	Recovery (%)	Amount Found (µg/L)	Amount Added (µg/L)	Recovery (%)
BW1	<MDL	1	98.3	0.251	1	95.6
BW2	<MDL	1	90.5	1.08	1	102
BW3	<MDL	1	77.1	0.540	1	100
DW1	3.89	5	82.0	<MDL	1	102
DW2	<MDL	5	80.0	0.236	1	101
DW3	<MDL	5	80.2	2.73	1	95.9
BW1	0.509	1	98.2	0.685	1	85.7
BW2	2.70	1	105	1.97	1	110
BW3	0.291	1	99.4	3.59	1	107
DW1	78.1	40	88.8	104	5	80.9
DW2	78.2	40	89.1	70.7	50	92.1
DW3	456	200	86.4	<MDL	40	107

Table 8. Recoveries of trace oxyhalides and bromide spiked in drinking water samples using CD detection

CD Detection	Chlorite			Bromate		
Sample	Amount Found (µg/L)	Amount Added (µg/L)	Recovery (%)	Amount Found (µg/L)	Amount Added (µg/L)	Recovery (%)
BW1	<MDL	1	100	<MDL	1	113
BW2	<MDL	1	109	0.975	1	103
BW3	<MDL	1	82.8	<LOQ	1	85.4
DW1	6.69	5	97.1	<MDL	1	78.7
DW2	1.19	5	86.3	<MDL	1	88.7
DW3	<MDL	5	87.2	2.06	1	82.0
BW1	<LOQ	1	90.8	0.416	1	93.4
BW2	2.43	1	87	0.692	1	77.7
BW3	<LOQ	1	75.9	1.89	1	83.1
DW1	78.1	40	102	4.05	5	117
DW2	80.6	40	98.2	104	50	113
DW3	478	200	105	67.2	40	99.9

Figure 14 shows an overlay of unspiked and spiked bottled water #2 chromatograms using CD detection. Figure 15 shows an overlay of unspiked and spiked bottled water #2 chromatograms using MS detection.

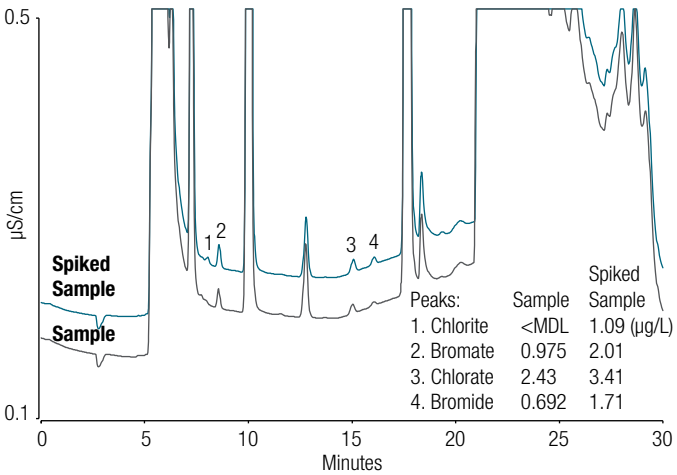


Figure 14. CD profile of BW#2 (IS 5 µg/L) and spiked BW#2 (IS 5 µg/L)

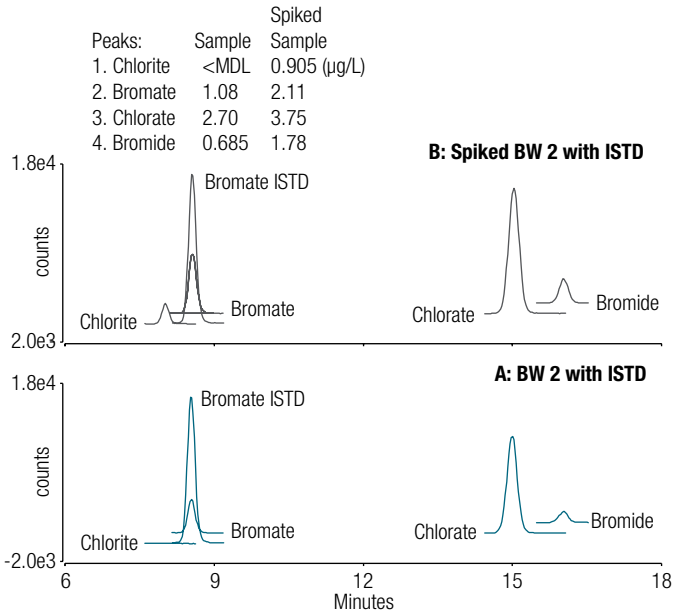


Figure 15. MS profile of BW#2 (ISTD 5 µg/L) and spiked BW#2 (ISTD 5 µg/L)

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Precision

The precision of the method was determined by triplicate injections of the 10 µg/L calibration standard on three separate days and calculating the relative standard deviation across all nine injections. As shown in Table 9, the calculated peak area precision varied from 0.16 to 1.8% with retention time precision <0.09% for all target anions. The high precision of this method is consistent with results typically found with an RFIC system.

Table 9. Retention time and peak area precisions

Component	Retention Time (RSD)	CD Peak Area (RSD)	MS Relative Peak Area to ITSD (RSD)
Chlorite	0.05	1.44	1.04
Bromate	0.06	0.63	0.69
Chlorate	0.06	1.28	1.80
Bromide	0.09	0.66	0.16

Conclusion

The IC-MS method described here augments US EPA Method 300.1 Part B (IC-CD) for bromate analysis. Adding the single quadrupole mass spectrometer to the Method 300.1 Part B setup provides advantages over the traditional setup regarding sensitivity and selectivity. IC-MS also offers positive identification of analytes, which is particularly advantageous for complex matrices. This method can simultaneously determine other oxyhalides (chlorite, chlorate) and bromide and thus can deliver Method 300.1 Part B data, confirm peak identification, and provide more sensitive and accurate detection of bromate. Coupling MS with CD takes advantage of the strengths of each detector.

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