APPLICATION NOTE

AN43227

Speciation of Bromine Compounds in Ozonated Drinking Water using Ion Chromatography and Inductively Coupled Plasma Mass Spectrometry

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Key Words
Bromate, Drinking Water, EPA 321.8, Inductively Coupled Plasma Mass Spectrometry, Ion Chromatography, Speciation

Goal

Speciate and quantify bromine (Br) species in drinking water by means of ion chromatography (IC) coupled with Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Applying the Environmental Protection Agency (EPA) method 321.8 for bromate detection in drinking water.

Introduction

Bromine speciation in drinking water is required worldwide by major regulatory bodies. A maximum contaminant level (MCL) of 10 $\mu g \cdot L^{-1}$ in the US for bottled drinking water and in the EU of 3 $\mu g \cdot L^{-1}$ for natural mineral water and spring water treated with ozonation are stipulated for the bromate anion. As a result of the ozonation process, a common water disinfection method, bromate can be formed via the oxidation of the naturally occurring bromide. Whereas bromide is non-toxic, bromate is toxic and carcinogenic.

Differentiating bromate from bromide is therefore important due to the toxicity differences between the two species.

Bromine analysis with ICP-MS is challenging because the ionization potential of bromine is relatively high and it lowers sensitivity in ICP based techniques. Additionally, there are a number of isobaric interferences on *m/z* 81 and 79 (the two Br stable isotopes) as shown in Table 2.

The United States Environmental Protection Agency (EPA) and the International Organization for Standardization have developed several methods for bromate determination in drinking water (EPA 300, 300.1, 302.0, 317, 326: ISO 10304-4 and 15061) all of which have been validated in Thermo Scientific™ Dionex™ application notes (AN167, AN168, AN171, AN184, AN187).

The EPA Method 321.8 provides an analytical procedure for bromate determination in drinking water using IC-ICP-MS. This method significantly reduces the risk for contamination and has the advantage of a stable and quantitative bromate recovery (Table 1, Figure 6) through the IC column and it tolerates high salt conditions. The method also provides guidance for reducing polyatomic interferences that overlap with the two most abundant Br isotopes.

For this method, a Thermo Scientific™ Dionex™ ICS-5000 IC can be coupled to a Thermo Scientific™ iCAP™ RQ ICP-MS (data presented was acquired with a Thermo Scientific™ iCAP™ Q ICP-MS.). The iCAP RQ ICP-MS is equipped with a collision/reaction cell, the Thermo Scientific™ QCell™, which enables a single interference reduction approach using He-KED (Kinetic Energy Discrimination). This measurement mode filters out polyatomic interferences on bromine and allows for the accurate quantification of bromide and bromate species, all without the need for additional interference correction steps. Additionally, the QCell design maintains high transmission and high sensitivity so that quantification at the sub-ppb levels required by the EPA method can be easily achieved.

General Analytical Conditions

All data collection was performed according to the protocols outlined in EPA 321.8 for "Determination of bromate in drinking waters by Ion Chromatography – Inductively Coupled Plasma – Mass Spectrometry". The QCell, operated in He-KED mode, provides simple and accurate quantification of Br at both *m/z* 79 and 81. However, in accordance with EPA 321.8, ^{81}Br was only measured to screen for potential interferences. All bromate results were quantified based upon the isotope at mass 79. The KED measurements were conducted with a mixture of 7% H_2/He as collision gas.

Table 1. Acquisition parameters for the IC-ICP-MS method.

Parameter	IC
Columns	Thermo Scientific™ Dionex™ IonPac™ AS19 Analytical, 2 × 250 mm (P/N 062886) Dionex IonPac AG19 Guard, 2 × 50 mm (P/N 062888)
Eluent	10 mM KOH from 0–25 min, 45 mM from 25–30 min, 10 mM from 35 min*
Flow Rate	300 µL·min^{-1}
Sample Loop	100 µL
System back pressure	2300 psi
Run Time	35 min
Conditions	**ICP-MS**
Measurement Mode	KED, STD
Isotopes Measured (Dwell Time)	^{79}Br (200 ms), ^{81}Br (200 ms)
Gas Flow For QCell (He/H_2)	4.5 mL·min^{-1}
Cool Gas	14 L·min^{-1}
Auxiliary Flow	0.8 L·min^{-1}
Nebulizer	1.13 L·min^{-1}
Analysis Mode	tQuant
Spray Chamber	2.6 °C
Forward Power	1550 W
Injector	2 mm i.d.
KED Voltage	2.5 V

*Method returns to 10 mM KOH for 5 min re-equilibration prior to injection.

Equipment

- Thermo Scientific™ Dionex™ ICS-5000 (or Thermo Scientific Dionex ICS-2100) HPIC System consisting of:
  - DP Dual Pump or SP single Pump
  - EG Eluent Generator module
  - Injection Loop, 100 µL
- Thermo Scientific™ Dionex™ Eluent Generator KOH Cartridge
- Polystyrene Autoselect vials with caps and septa 10 mL
- Thermo Scientific™ iCAP™ Q ICP-MS

Autosampler and Software

- Thermo Scientific™ Dionex™ AS-AP Autosampler
- Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Data System
- Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution (ISDS)

Preparing Standards and Samples

Six samples of bottled water and tap water (numbered 1 through 6) were analyzed for this application. The samples came from various sources in the US, where the ozonation approach for water disinfection is still commonly applied.

Bromide and bromate stock standards were diluted with deionized water acidified with 2% HNO_3 to produce calibration standards containing 1, 5, 10 and 25 µg·L^{-1} of each Br species. The blank was prepared by dissolving NaOH in deionized water in order to increase the pH of the solution to 10. Standards and water samples were also brought to a pH of 10 and measured without further sample preparation. The samples and standards were analyzed using the Dionex ICS-5000 IC system for chromatographic analysis (although the Dionex ICS-2100 IC system with KOH cartridge would be a suitable alternative). The method could be followed using KOH as per EPA recommendation with no ICP-MS compatibility issues. A solution containing 100 ppm of PO_4^{3-} and SO_3H^- was prepared and analyzed to check for interferences at *m/z* 79 and 81. Several potential plasma- and solution-based interferences are listed in Table 2.

Table 2. Possible sources of isobaric interference.

Interferent Source	MASS 79	MASS 81
Plasma	$^{40}Ar^{38}Ar^{1}H^+$	$^{40}Ar^{40}Ar^{1}H^+$
Sulfate		SO_3H^+
Phosphate	$^{31}P^{16}O_3^+$	$^{31}P^{16}O_3{}^{1}H_2^+$
Potassium	$^{40}Ar^{39}K^+$	

Results and Discussion

Data sets were collected over three consecutive days. On each day of analysis the blanks and standards were analyzed. Samples were quantified against the external calibrations. On each day of analysis the correlation coefficient was always better than 0.999 (Figure 1).

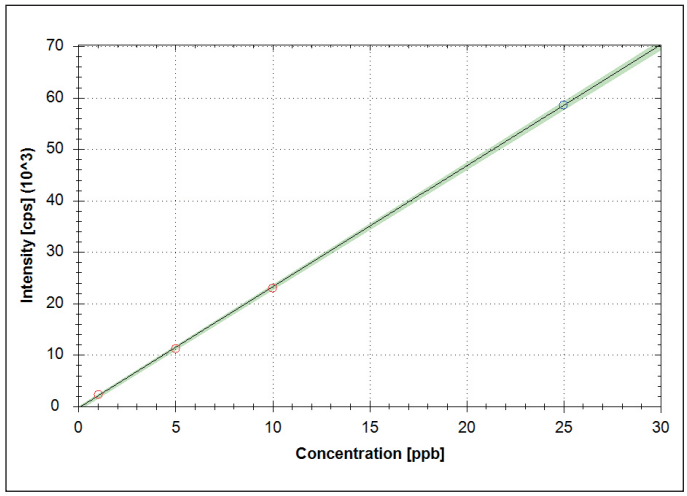


Figure 1. Calibration curve for bromate standards measured at ^{79}Br in He-KED mode.

As per EPA 321.8, each sample was prepared in quadruplicate. One of the replicate preparations was spiked with 1 µg·L^{-1} of bromate and 5 µg·L^{-1} of bromide for determining spike recoveries. The remaining three preparations were analyzed without further modification. Spike recoveries were calculated according to the following equation:

$$\%R = \frac{\text{(spiked sample result – unspiked sample result)}}{\text{(known spike added concentration)}} \times 100$$

For purposes of comparison, Br was measured at *m/z* 79 and 81 in both He KED and STD modes (STD mode data not shown). Due to increased accuracy using KED mode, quantitative results for mass 79 in KED mode only are shown (Table 3).

Table 3. Results for bromate in KED mode of the six water samples (spiked and unspiked).

Water	Average Unspiked Sample Result ($\mu g \cdot L^{-1}$)	Samples Spiked with 1 $\mu g \cdot L^{-1}$ Bromate ($\mu g \cdot L^{-1}$)	Recovery %
1	N/A	0.999	99.9
2	1.218	2.221	100.3
3	1.732	2.729	99.7
4	N/A	1.000	100.0
5	N/A	0.999	99.9
6	1.127	2.124	99.7

Results in Table 3 indicate that recovery for bromate is quantitative and reproducible. The average recovery is 99.8% with a SD of 0.4%.

A Method Detection Limit (MDL) was calculated for bromate according to the EPA method instructions (3.14 × s.d. of 7 replicates of 5 $\mu g \cdot L^{-1}$ target species). Figure 2 shows the chromatographic overlay of the 7 replicates. Based on those results, a bromate MDL of 0.014 $\mu g \cdot L^{-1}$ was achieved. This is significantly below the maximum contamination level (MCL) for bromate in water (3 $\mu g \cdot L^{-1}$) and twenty times lower than the required EPA MDL of 0.3 $\mu g \cdot L^{-1}$. Figure 3 shows the chromatographic elution of bromate at the EPA MDL concentration of 0.3 $\mu g \cdot L^{-1}$. To demonstrate the necessity of He KED mode for the accurate analysis of bromine, a 25 ppb standard of both bromate and bromide were analyzed in standard mode (STD). The baseline offset for mass 81 is due to the isobaric interference from $^{40}Ar^{40}ArH^+$ detected in STD mode. This interference is completely eliminated using He KED, as shown in Figure 5 where the baseline signals for ^{79}Br and ^{81}Br overlap perfectly.

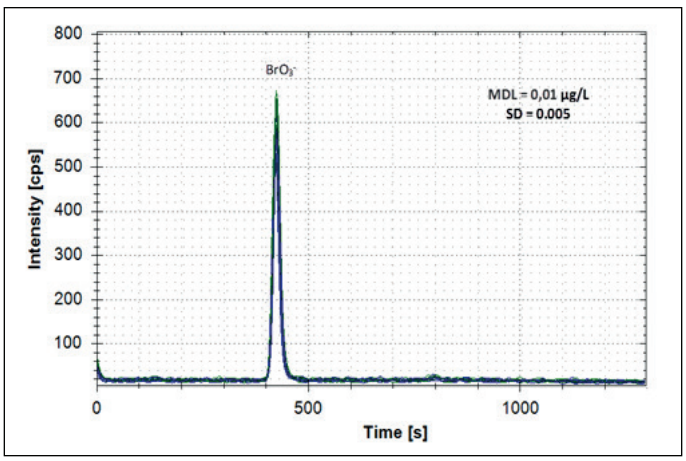


Figure 2. Overlay of chromatograms from 7 repeated injections of 5 ppb standard are shown in He- KED mode.

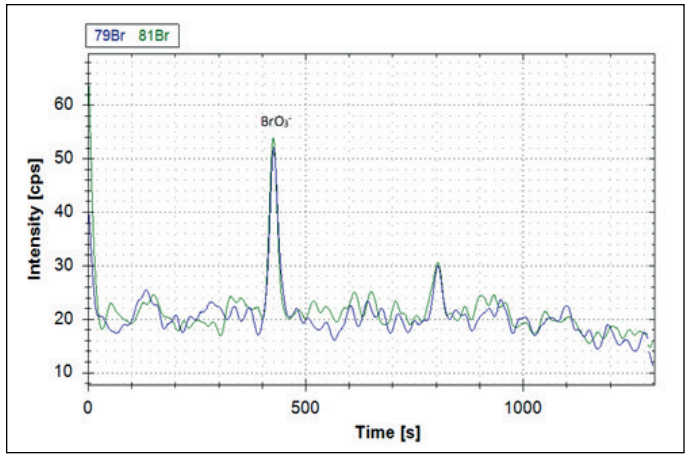


Figure 3. Test for EPA recommended MDL of bromate at 0.3 $\mu g \cdot L^{-1}$.

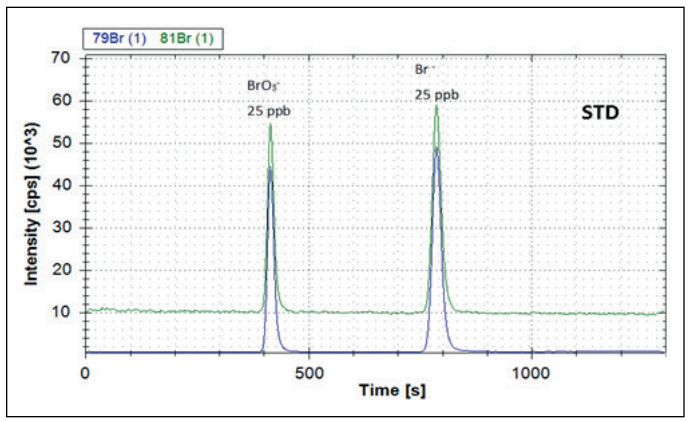


Figure 4. Signal for 25 ppb bromate and 25 ppb bromide in STD mode. Green upper trace is ^{81}Br, blue lower trace is ^{79}Br.

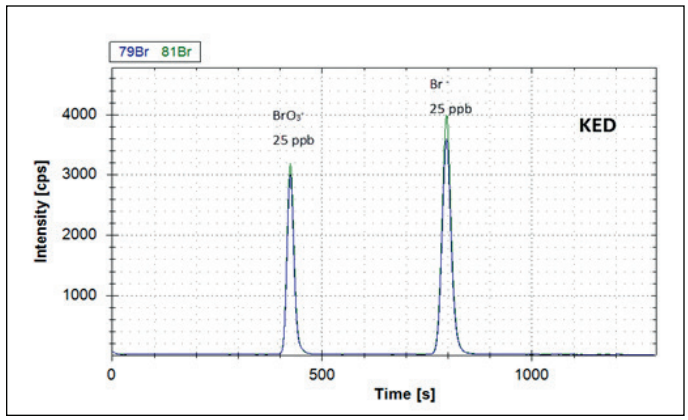
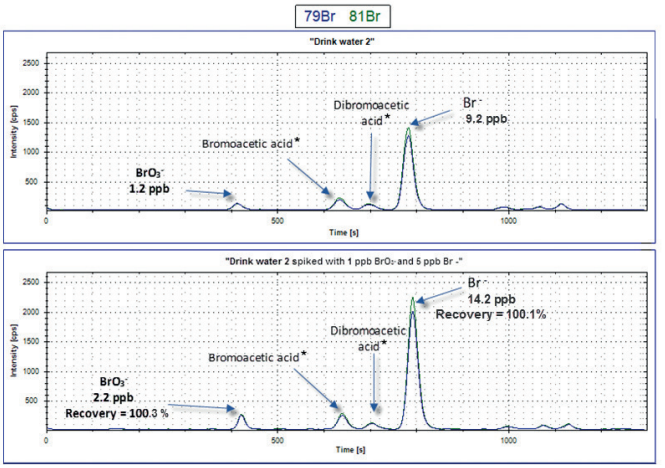


Figure 5. Signal for 25 ppb bromate and 25 ppb bromide in He-KED mode. Green trace is ^{81}Br, blue trace is ^{79}Br.



*likely identity.

Figure 6. Separation for Br species in water sample 2 (upper trace) and the same sample with a 1 µg·L^{-1} bromate and 5 µg·L^{-1} bromide spike (lower trace). Note the consistency in elution times for all the species detected, the excellent separation and quantitative recovery.

The chromatographic separation (Figure 6) demonstrates that the measured analytes are effectively eluted from the column with baseline resolution, even in the presence of other brominated species and the sample matrix. This chromatographic separation coupled with the effective KED interference removal ensures that the detected peaks correspond only to the target analytes giving highly precise and accurate results. Results for bromate in samples 2 (Figure 6), and 3 (not shown) corroborate that both samples were collected from a municipality which ozonates its drinking water as part of the disinfection treatment process. Bromate concentrations are reasonably close to each other, as they come from the same supply although different locations within the same city.

Based on the results of the interference check with sulfate and phosphate and from the isotope ratios, the two peaks at 630 and 700 s were identified as bromine-containing species. Following the order of elution outlined in the EPA methods, it is likely that these two species are bromoacetic acid and dibromoacetic acid respectively, although this was not unequivocally confirmed (via spiking experiments or other approaches).

Sample 6 (not shown) is a bottled water from a company that does not state the purification method adopted, but according to the bromate content it is reasonable to assume that it is ozonation.

Samples 1, 4 and 5 are all bottled waters, but any bromate present was below the MDL.

Conclusion

Combining the resolving capability of IC with the detection power of ICP-MS allows fast, easy and reliable analysis of bromine species in drinking waters. Low background and He-KED interference removal permit robust conditions so that sample preparation is virtually eliminated and analysis of the water can be performed from the tap to the vial after simple alkalinization. This method enables robust and reliable speciation of bromine containing species in drinking water, with no salinity-related recovery issues. Thanks to the high sensitivity and completely metal free sample and mobile phase flow paths, the application complies to EPA 321.8 quality control requirements and provides MDLs well below the values necessary for accurate monitoring of water from various sources.

References

1. ISO method 11206
2. EPA Method 326.0 and 317.0 “Determination of inorganic oxhalide disinfection by-products in drinking water using ion chromatography incorporating the addition of a suppressor acidified postcolumn reagent for trace bromate analysis”
3. EPA Method 300.0 and 300.1 “Determination of inorganic anions by ion chromatography.”
4. EPA Method 321.8 “Determination of bromate in drinking waters by Ion Chromatography – Inductively Coupled Plasma – Mass Spectrometry”.

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