Determination of Bromate by ISO Method 11206

Jules Djoukeng and Detlef Jensen, Thermo Scientific, Olten, Switzerland

Key Words
Triiodide, Acidic Eluent, Ion Chromatography (IC), Ozonation

Background

Drinking and bottled waters are commonly disinfected with ozone. Ozone is highly effective and, unlike many other disinfectants, does not remain in the water or change its taste. When bromide is present during ozonation, it is converted to bromate. Bromate is recognized as a potential human carcinogen, which has led to the regulation of its concentration in drinking and bottled waters. Major regulatory bodies worldwide (e.g., U.S. EPA and the European Commission) have set a maximum allowable bromate concentration in drinking water of 10 µg/L. In Europe, the limit was reduced to 3 µg/L for bottled natural mineral and spring waters disinfected by ozonation.[1,2]

Our Methods Embraced by Standards Organizations

Over the past two decades, we worked with regulatory agencies and international standards organizations to develop a number of ion chromatography (IC) products and techniques that improve the sensitivity and ruggedness of determining bromate and other oxyhalides, such as chlorite and chlorate, and increase the types of samples that can be directly injected.

U.S. EPA Methods 300 and 300.1, as well as International Organization for Standardization (ISO™) 10304-4 and 15061 use Thermo Scientific Dionex IonPac AS9-SC and AS9-HC columns along with suppressed conductivity detection for bromate, chlorite, and chlorate determination in drinking water.[3]

The Dionex IonPac™ AS9-HC column and our suppression technology for conductivity detection of oxyhalides, combined with the postcolumn derivatization and absorbance detection for enhanced determination of bromate, were instrumental in the development of the U.S. EPA Method 317, per Application Note (AN) 136[4], and U.S. EPA Method 326, per AN 149[5].

To improve the sensitivity for bromate using direct injection, the Dionex IonPac AS19 column was developed for use with hydroxide eluents (as described in AN 167[6]). Besides providing superior sensitivity for suppressed conductivity detection, hydroxide eluents can be generated easily with Reagent-Free™ IC (RFIC™) systems. RFIC systems improve reproducibility and simplify analysis. The Dionex IonPac AS19 column can also replace the Dionex IonPac AS9-HC column in EPA Methods 317 and 326, as documented in AN 168[7] and AN 171.[8]

The Dionex IonPac AS19 column was also used with an isocratic hydroxide eluent rather than the gradient for analysis of bromate in drinking water. As described in Application Update (AU) 154[9], this method cannot determine all the common inorganic anions in a single injection that the gradient method in AN 167 can, but is a cost-effective way for determining just bromate. To determine sub-µg/L concentrations of bromate in drinking water and higher ionic strength matrices without postcolumn derivatization, a two-dimensional IC technique (AN 187[10]) was developed that uses a Dionex IonPac AS19 column in the first dimension, and a Dionex IonPac AS24 column in the second dimension, followed by conductivity detection.

Thermo SCIENTIFIC

AN 184[11] demonstrated that the Dionex IonPac AS19 column method in AN 167 can be used to meet the 3 µg/L European maximum limit for bromate in natural mineral and spring waters disinfected by ozonation. The same application note compared the chromatography of the Dionex IonPac AS19 column with that of the Dionex IonPac AS23 column, which uses carbonate eluents and was developed to replace the Dionex IonPac AS9-HC column. The Dionex IonPac AS23 column has a higher capacity than the Dionex IonPac AS9-HC column, and a different selectivity for the carbonate ion. Therefore, it is less likely to interfere with bromate determinations and can provide improved analysis of phosphate and sulfate. AN 184 showed that lower sensitivity associated with using carbonate eluents when compared to hydroxide eluents made the method using the Dionex IonPac AS19 column superior to that using the Dionex IonPac AS23 column. An overview of the existing methods for bromate determination is shown in the Determination of Bromate in Water Using Ion Chromatography brochure.[12]

ISO Method 11206

In order to meet the 3 µg/L European maximum limit for bromate in natural mineral and spring waters disinfected by ozonation, ISO recently published a new standard, ISO 11206.[13] This standard describes two approaches for a postcolumn derivatization, also known as the Triiodide Method. Sensitivity for bromate is improved by more than a factor of 10 as compared to U.S. EPA Methods 300 and 300.1 and ISO 10304-4 and ISO 15061. This method uses a postcolumn reaction in which hydroiodic acid (HI) generated in situ from potassium iodide (KI) reacts with bromate in the column effluent to form the triiodide anion (I_3-), as shown in the following set of reactions:

$$BrO^-_3 + 3\ I^- + 3\ H^+ \Leftrightarrow 3\ HOI + Br^-$$

$$3\ HOI + 3\ I^- + 3\ H^+ \Leftrightarrow 3\ I_2 + 3\ H_2O$$

$$3\ I_2 + 3\ I^- \Leftrightarrow 3\ I_3^-$$

Triiodide is then detected by its absorbance at 352 nm.

Equipment

- Thermo Scientific Dionex ICS-5000 IC system including:
  - DP Dual Pump
  - DC Detector/Chromatography Compartment
  - VWD Variable Wavelength Detector
  - AS-AP Autosampler
- Thermo Scientific Dionex Chromeleon 7.1 Chromatography Data System software or higher

Analytical Conditions

Column:	Thermo Scientific Dionex CarboPac PA1, 4 × 250 mm, (P/N 035391)
Eluent:	200 mM Methanesulfonic acid
Flow Rate:	1.0 mL/min
System Pressure:	1700 psi (11.72 MPa)
Detection:	UV at 352 nm
Injection Volume:	500 µL
Temperature:	30 °C
Sample Preparation:	None

Postcolumn Reagent (PCR):

PCR:	0.27 M potassium iodide containing 0.05 mM of ammonium heptamolybdate tetrahydrate
Flow Rate:	0.3 mL/min
System Pressure:	1150 psi (7.93 MPa)
Reaction Coil:	375 µL (P/N 043700)

The first approach mentioned in ISO 11206 uses a high pH eluent, as reflected in AN 149 and EPA Method 326. The postcolumn derivatization can be coupled with suppressed conductivity, allowing the simultaneous determination of both the major inorganic anions with suppressed conductivity, and oxyhalides like bromate and chlorite after derivatization followed by UV detection.

The second approach uses a low pH eluent and is tailored for the selective trace determination of only bromate in presence of chlorite. The respective evaluations of the ISO committee showed that using an acidic eluent and maintaining the pH of the derivatization solution below or equal to pH 1 eliminated the need to heat the reaction coil. Also, chlorite ions do not interfere, even if present at a large excess, as they do with other methods that detect bromate as the triiodide ion.

The method described in ISO 11206 uses sulfuric acid as the eluent, limiting the application to a small set of commercially available columns. During our studies we found that if methanesulfonic acid is used as the eluent, more columns of different chemical and chromatographic properties can be used, offering the benefit of greater application flexibility. Bromate was separated on a Thermo Scientific Dionex CarboPac™ PA1 column in less than 18 min using isocratic conditions and detected by UV at 352 nm after derivatization.

Using methanesulfonic acid as the eluent, KI is added postcolumn using the second system pump, and is directly acidified once it is mixed with the eluent. Applying these conditions, HI is produced and it reacts with bromate in the reaction coil to form the triiodide anion (I_3^-), which absorbs light at 352 nm.

The limits of detection (LODs) were calculated as three times signal to noise, whereas the limits of qualification (LOQs) were calculated as ten times signal to noise.

Column:	Dionex CarboPac PA1 (4 × 250 mm)	PCR:	0.27 M KI, 0.05 mM $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$
Eluent:	200 mM MSA	Flow Rate:	0.3 mL/min
Flow Rate:	1 mL/min	Reaction Coil:	375 µL
Injection Vol.:	500 µL		
Temperature:	30 °C	Peaks:	1. Bromate 1.2 µg/L
Detection:	UV 352 nm (after PCR)		

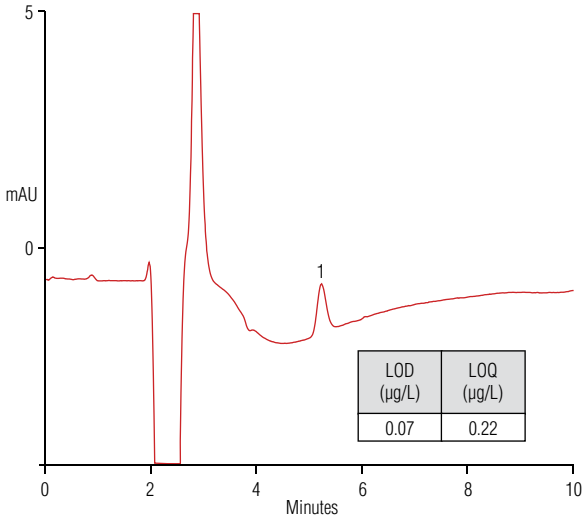

Figure 1. This chromatogram of a drinking water sample shows a bromate peak with a concentration of 1.2 µg/L. The trace ends at 10 min, although the run time is extended to 18 min due to a later-eluting component.

Conclusion

Described here is an alternate strategy for a trace analysis of bromate by IC. Bromate is separated using a latex-based anion exchanger and a methanesulfonic acid eluent, followed by a simplified postcolumn reaction to form triiodide. This is subsequently detected by its UV-absorption. Because the reaction takes place at lower pH than other methods, no heating of the reaction coil is needed. These conditions prevent interference from chlorite, which is known to interfere in other bromate determination methods.

References

1. U.S. EPA. National Primary Drinking Water Regulations: Disinfectants and Disinfection Byproducts. Federal Register **1998**, *63* (241) 69389–69476.
2. Commission Directive 2003/40/EC. Official Journal of the European Union, Establishing the List, Concentration Limits and Labeling Requirements for the Constituents of Natural Mineral Waters and the Conditions for Using Ozone-Enriched Air for the Treatment of Natural Mineral Waters and Spring Waters, 2003.
3. Dionex (now part of Thermo Scientific) Application Note 81: Ion Chromatographic Determination of Oxyhalides and Bromide at Trace Level Concentrations in Drinking Water Using Direct Injection, 1997 [Online]. www.dionex.com/en-us/webdocs/4171-AN81_LPN0965.pdf (accessed Mar. 16, 2012).
4. Dionex (now part of Thermo Scientific) Application Note 136: Determination of Inorganic Oxyhalide DisinfectionByproduct Anions and Bromide in Drinking WaterUsing Ion Chromatography with the Addition of a Postcolumn Reagent for Trace Bromate Analysis, 2004 [Online]. www.dionex.com/en-uswebdocs/4087-AN136_LPN1229-01.pdf (accessed Mar. 16, 2012).
5. Dionex (now part of Thermo Scientific) Application Note 149: Determination of Chlorite, Bromate, Bromide, and Chlorate in Drinking Water by Ion Chromatography with an On-Line-Generated Postcolumn Reagent for Sub-µg/L Bromate Analysis, 2003 [Online]. www.dionex.com/en-us/webdocs/4100-AN149_LPN1523.pdf (accessed Mar. 16, 2012).
6. Dionex (now part of Thermo Scientific) Application Note 167: Determination of Trace Concentrations of Oxyhalidesand Bromide in Municipal and Bottled Waters Using a Hydroxide-Selective Column with a Reagent-Free™ IonChromatography System, 2004 [Online]. www.dionex.com/en-us/webdocs/10376-AN167_released121506.pdf (accessed Mar. 16, 2012).
7. Dionex (now part of Thermo Scientific) Application Note 168: Determination of Trace Concentrations of Disinfection By-Product Anions and Bromide in Drinking Water Using Reagent-Free™ Ion Chromatography Followed by Postcolumn Addition of o-Dianisidine for Trace Bromate Analysis, 2005 [Online]. www.dionex.com/en-us/webdocs/34036-AN168_V27_releasedJC112105.pdf (accessed Mar. 16, 2012).
8. Dionex (now part of Thermo Scientific) Application Note 171: Determination of Disinfection Byproduct Anions and Bromide in Drinking Water Using a Reagent-Free Ion Chromatography System with Postcolumn Addition of an Acidified On-Line Generated Reagent for Trace Bromate Analysis, 2009 [Online]. www.dionex.com/en-us/webdocs/34585-AN171-IC-DisinfectByprod-DrinkWater-26May2009-LPN1767-01.pdf (accessed Mar. 16, 2012).
9. Dionex (now part of Thermo Scientific) Application Update 154: Determination of Bromate in Drinking and Mineral Water by Isocratic Ion Chromatography with a Hydroxide Eluent, 2006 [Online]. www.dionex.com/en-us/webdocs/40786-AU154_V30_released091406.pdf (accessed Mar. 16, 2012).
10. Dionex (now part of Thermo Scientific) Application Note 187: Determination of Sub-µg/L Bromate in Municipal and Natural Mineral Waters Using Preconcentration with Two-Dimensional Ion Chromatography and Suppressed Conductivity Detection, 2007 [Online]. www.dionex.com/en-us/webdocs/60294-AN187_2DIC_Bromate_Water_13Aug2007_LPN1943_02.pdf (accessed Mar. 16, 2012).
11. Dionex (now part of Thermo Scientific) Application Note 184: Determination of Trace Concentrations of Chlorite, Bromate, and Chlorate in Bottled Natural Mineral Waters, 2007 [Online]. www.dionex.com/en-us/webdocs/56257-AN184_released02Apr2007.pdf (accessed Mar. 16, 2012).
12. Dionex (now part of Thermo Scientific) Environmental Brochure: Determination of Bromate in Water Using Ion Chromatography, 2007 [Online]. www.dionex.com/en-us/webdocs/62038-Bro_Bromate_Water_19Sep07_LPN1970.pdf (accessed Mar. 16, 2012).
13. ISO 11206:2011, Water Quality — Determination of Dissolved Bromate - Method Using Ion Chromatography (IC) And Post Column Reaction (PCR), Beuth Verlag, Berlin, www.beuth.de.

U.S./Canada	(847) 295 7500	**Brazil**	(55) 11 3731 5140	**India**	(91) 22 2764 2735	**Singapore**	(65) 6289 1190
Australia	(61) 2 9420 5233	**China**	(852) 2428 3282	**Ireland**	(353) 1 644 0064	**Sweden**	(46) 8 473 3380
Austria	(43) 1 616 51 25	**Denmark**	(45) 36 36 90 90	**Italy**	(39) 02 51 62 1267	**Switzerland**	(41) 62 205 9966
Benelux	(31) 20 683 9768	**France**	(33) 1 39 30 01 10	**Japan**	(81) 6 6885 1213	**Taiwan**	(886) 2 8751 6655
	(32) 3 353 42 94	**Germany**	(49) 6126 991 0	**Korea**	(82) 2 3420 8600	**United Kingdom**	(44) 1276 691722

Thermo SCIENTIFIC

Part of Thermo Fisher Scientific

TN70067E_ 09/16S