# Comparison of Regulated Methods Using Ion Chromatography for Bromate Analysis in Drinking Water

Richard F. Jack, Thermo Fisher Scientific, Sunnyvale, California, USA.

### Introduction

Ozone is a powerful drinking water disinfectant that is effective in treating chlorine resistant organisms, such as Cryptosporidia [1]. For bottled water, ozonation is generally preferred over other available disinfection treatment methods because it does not leave a taste or residual disinfectant, due to the short lifetime of ozone [2,3]. Ozone also improves the quality of finished drinking water, by reducing filtered water turbidity and decreasing the formation of many halogenated disinfection by-products. However, ozonation of drinking water containing bromide can result in the formation of the disinfection by-product bromate, a potential human carcinogen even at low µg/L concentrations [4]. The US EPA and European Commission have established a regulatory maximum contaminant level (MCL) of 10 µg/L bromate in drinking waters [5,6]. In the

US, bottled water is considered a food product and is, therefore, regulated by the US Food and Drug Administration (FDA) under the Federal Food, Drug and Cosmetic Act [7].

In 2001, the US FDA also established an MCL of 10  $\mu$ g/L bromate in bottled drinking water [7]. More recently, the European Commission set a lower MCL of 3  $\mu$ g/L bromate for natural mineral waters and spring waters treated by ozonation [8]. However, these limits were based on the feasibility of detection and removal, even though studies suggest concentrations lower than 1  $\mu$ g/L pose increased lifetime cancer risks [4,9].

Ion chromatography (IC) plays an important role in the analysis of ozone-treated drinking water. Bromate can be separated using different IC column chemistries and detected using a variety of detection techniques. Which one to use primarily depends on the sample and detection limits required. When matrix conditions allow, suppressed conductivity detection is the easiest method to use. Otherwise, several strategies can be used to increase signal and deal with interfering anions by a combination of eluent, column and detection methods as summarized in Table 1.

EPA Methods 300.0 and 300.1 / ISO 15061: Ion Chromatography with Suppressed Conductivity Detection EPA Method 300.0 was written in 1993 and served as the original standard using ion chromatography for inorganic anion analysis in reagent, ground, surface, drinking and wastewater. This method was divided into two parts: Part A for the seven common anions and Part B for the disinfection by-product (DBP) anions chlorate, chlorite and bromate. Through use of a manually prepared carbonate eluent, a column (Dionex AS9), and suppressed conductivity detection, a method detection limit (MDL) of 20 ug/L was obtained for bromate in drinking water. Due to growing concerns of the potential carcinogenicity of bromate at lower ug/L levels, the EPA lowered the bromate MCL to 10 ug/L in 1998. This subsequently led to the publishing of Method 300.1 for the determination of common anions and DPBs in drinking, ground and surface water. This method again used manually prepared carbonate eluent but used a higher capacity analytical column (Dionex AS9-HC) and suppressed conductivity detection to lower the bromate MDL to 1.4 ug/L in drinking water. Since Method 300.1 was written over ten years ago, bromate determination using suppressed





conductivity detection has been the preferred application in low ionic strength matrices. While carbonate eluents have commonly been used for this method, hydroxide eluents have also been demonstrated to meet the requirements of Method 300.1. Both of these eluents can be manually prepared or electrolytically generated using reagent free ion chromatography.

#### Manually Prepared Eluents

While EPA Method 300.1 specifies the use of an AS9-HC column,

recent advancements in column technology have provided a more suitable replacement. A high-capacity anion-exchange column (lonPac AS23) is specifically designed to be used with carbonate eluents for the determination of trace bromate, chlorite, and chlorate together with common inorganic anions. This column was developed using a unique polymer technology to achieve a capacity of 320 ueq/ column, higher than the AS9-HC column (190 ueq/column) described in Method 300.1. The combination



Figure 2: Determination of trace DBP anions and bromide in tap water using: A) suppressed conductivity detection; and B) UV absorbance after postcolumn reaction with acidified KI..

of optimized selectivity for DBP anions with high anion exchange capacity makes this column an ideal replacement for the AS-9HC column. The use of hydroxide eluents has also proven effective in the determination of trace bromate in drinking water. Since the suppression product of hydroxide is water, use of this eluent results in lower background conductance and greater analyte sensitivity than carbonate eleuents. The hydroxide-selective column (Dionex AS19) has been shown to meet or exceed the requirements of Method 300.1 for bromate.

#### Reagent Free Ion Chromatography While EPA Methods 300.0 and

While EPA Methods 300.0 and 300.1 have traditionally used a manually prepared eluent, analytical sensitivity and reproducibility have been demonstrated to improve with the use of reagent free ion chromatography (RFIC). RFIC systems eliminate the need to manually prepare and degas eluent, combining electrolytic eluent generation with self-regenerating suppression. By electrolytically producing high-

Flow Rate: Reaction Coil: 375 uL 1 mL/min Injection Vol.: 500 µL Temperature: 30 °C Peaks 1. Bromate 1.2 µg/L UV 352 nm (after PCR) Detection: 5 mAU 0 LOD LOQ  $(\mu g/L)$ (µg/L) 0.22 0.07 0 8 10 6 Minutes Figure 3: 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-

quality eluents from deionzed water, RFIC systems have demonstrated improved performance for bromate detection.

eluting component.

Column

Eluent:

Dionex CarboPac PA1

 $(4 \times 250 \text{ mm})$ 

200 mM MSA

PCR

Flow Rate:

0.27 M KI, 0.05 mM

(NH4)6M07024 • 4H20

0.3 mL/min

Figure 1 demonstrates how the uses of electrolytically generated hydroxide eluents facilitate both an improved separation of bromate and an improved limit of detection. This application provides greater sensitivity than conventional IC with manually prepared eluents and can determine bromate at sub-ppb levels. Electrolytically generated eluents are approved for use with EPA Methods 300.0 and 300.1 to determine bromate and the seven inorganic anions required for regulation. Electrolytically generated potassium hydroxide (KOH) is available for use with the lonPac AS19 column. Precise control of current allows repeatable concentrations and gradients for improved reproducibility over manually prepared eluents. The lonPac AS23 column can be used with electrolytically generated potassium



carbonate to automatically and reproducibly generate carbonate/ bicarbonate eluent at the desired concentration.

Figure 4

#### EPA Methods 317.0/326.0 and ISO 11206: Ion Chromatography with Post Column Reaction and Visible Detection

Determining low concentrations of bromate in high ionic strength matrices using suppressed conductivity detection is subject to potential interferences and loss of sensitivity. Since surface and ground waters can contain chloride and sulphate in excess of 50 ppm each, the resolution of bromate diminishes due to interference from these two salts. In order to achieve good chromatographic resolution in these circumstances, the use of postcolumn reagent with absorbance detection may be required.

The EPA and ISO organizations have validated the use of ion chromatography with post-column derivitization techniques combined



Technique	U.S. EPA Method	ISO Method	Application Note	Drinking Water
IC Suppressed Conductivity	300.0 B	15061	167, 184	Low salt conditions
IC Suppressed Conductivity	300.1	15061	167, 184	Low salt conditions
IC Suppressed Conductivity with Postcolumn ODA	317.0	11206	168	Tolerates higher salt conditions
IC Suppressed Conductivity with Postcolumn Acidified Kl	326.1	11206	171	Tolerates higher salt conditions
2D-IC Suppressed Conductivity	302.0		187	Tolerates higher salt conditions
IC-ICP-MS	321.8			Tolerates higher salt condition:

Table 1: Bromate brochure Table 1 (compares IC Technique with EPA Method and Matrix conditions).

with UV detection of bromate in high salt matrices in Methods 317.0 and 326.0 and ISO 11206. These methods are extensions of EPA 300.1 that combine suppressed conductivity detection and post-column addition of o-dianisidine (ODA) followed by visible detection. EPA 326.0 and ISO 11206 combine suppressed conductivity detection and post column addition of potassium iodide (KI) and detection of triiodide by visible detection. By using the IonPac AS19 column and applying an electrolytically generated hydroxide eluent combined with the post column potassium iodide reaction, an MDL of 0.04 ug/L can be achieved. Figure 2 demonstrates the sensitivity of post-column derivatization and UV detection at 352 nm for disinfection by-products (DBPs) compared with suppressed conductivity detection on the IonPac AS19 column.

Table 1

The second approach described in ISO 11206, and shown in Figure 3, uses a low pH eluent and is tailored for the selective trace determination of only bromate in the 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 trijodide 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 methanesulphonic 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 column (Thermo Scientific Dionex CarboPac PA1) in less than 18 min using isocratic conditions and detected by UV at 352 nm after derivatization. Using methanesulphonic acid as the eluent, KI is added postcolumn using the second system pump, and is directly acidified once it is mixed with the eluent. It should be mentioned that a major limitation to this method is that anions such, as bromide, cannot be determined as in EPA 317 and 326.

EPA Method 302.0: Two Dimensional Ion Chromatography with Suppressed Conductivity Detection Although post-column reaction methods do not generally suffer from interferences by common anions, column overloading with high ionic strength samples can still cause peak broadening and an associated loss of response. In particular, natural mineral waters typically contain elevated levels of common anions that can significantly exceed the concentrations present in most municipal drinking water samples, presenting an additional challenge for the currently available methods to determine  $<1 \mu g/L$ bromate. EPA Method 302.0 provides another strategy for bromate determination in high salt matrices by using two dimensional IC (2D-IC). 2D-IC combines two separate RFIC systems into a single footprint. There are several advantages of the 2-D matrix diversion approach. First, initial sample loading onto the 4 mm column allows a large sample injection volume (large amount of sample) due to the high capacity of the analytical column and higher selectivity for analytes of interest relative to the matrix ions. Second, it is possible to focus the analyte peak that is partially resolved in the first dimension onto a concentrator column in the second dimension. The suppressed effluent with hydroxide eluent is water, which provides the ideal environment for ion-exchange retention and focusing. Third, the second dimension column has a smaller cross-sectional area relative to the first dimension, thereby enhancing the detection sensitivity. Finally, this approach allows the potential of combining two different chemistries in two dimensions, which enables selectivity not possible when

using a single chemistry dimension.

In EPA 302.0 a water sample is injected onto a high-capacity column (Dionex IonPac AS19) using a potassium hydroxide eluent gradient. Bromate is partially resolved from matrix ions and a cut volume containing the bromate is transferred to the second dimension while the matrix ions are flushed to waste. In the second dimension, the sample is collected on a concentrator column and subsequently resolved on a column (Dionex IonPac AS24). Figure 4 show the results of a 2D-IC separation of bromate in a high-salt matrix. The upper chromatogram shows that the bromate is not resolved from chloride in this sample. The lower chromatogram shows the results after the reinjection of the cut volume onto a concentrator column, and separation on an IonPac AS24. The bromate that was undetectable in the first dimension is fully resolved in the second. Using this 2D-IC technique, an MDL of 0.036 ug/L can be achieved in high-salt matrices.

## Recent Ion Chromatography Developments

Since the development of reagent free ion chromatography (RFIC) and its utility for 2D IC, the need to improve performance, resolution and sensitivity has led to the evolution of smaller scale, capillary IC systems. Capillary IC scales down traditional IC from 10- to 100-fold by using 0.4 mm columns and 10 µL/min flow-rates. The benefit of this scale down is the ability to use less eluent and make leaving the system constantly running much more practical and economical. This makes the system continuously available for unplanned, last minute samples. Capillary IC falls under the scope of the EPA's flexibility rule and is, therefore, accepted for compliance monitoring.

#### Conclusion

Over the course of the last 20 years, bromate has gained considerable attention as a potential carcinogen in drinking water treated with ozone for disinfection. This has prompted regulatory bodies throughout the world to regulate the level of bromate present in finished drinking water at trace levels. Since the ionic strength of drinking water can vary, monitoring at low µg/L levels can become challenging. The use of ion chromatography has been demonstrated as a versatile technique for compliance monitoring of bromate in drinking water. Through the use of suppressed conductivity detection, post-column derivitization with UV detection, or two dimensional IC for matrix elimination, ion chromatography has been proven as an effective technique for bromate detection and has been validated and approved by the EPA for compliance monitoring.

#### References

1. T.A. Bonacquisti, Drinking Water Utility's Perspective on Bromide, Bromate and Ozonation, *Toxicology*, 221, 145-148 (2006).

2. US Environmental Protection Agency, WaterHealth Series: Bottled Water Basics, Sept 2005.

3. US Environmental Protection Agency,
Occurrence Assessment for the Final Stage 2
Disinfectants and Disinfection Byproducts Rule,
Document No. 815-R-05-011, December 2005.
4. World Health Organization, Bromate in
Drinking Water–Background document for the
development of WHO Guidelines for Drinking
Water Quality, 2005.

 US EPA. National Primary Drinking Water Regulations. Disinfectants and Disinfection By-Products. Fed. Reg. 63 (241), 69389–69476 (1998).
 J. Fawell and M. Walker, Approaches to Determining Regulatory Values for Carcinogens with Detington Defermine to Determining Regulatory Values for Carcinogens

with Particular Reference to Bromate, *Toxicology*, , 221, 149–153 (2006).

7. Food and Drug Administration. Beverages: Bottled Water. Fed. Reg., 66(60), 16858–16868 (2001).

8. European Parliament and Council Directive No. 2003/40/EC, 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).

9. Toxicological Review of Bromate, US Environmental Protection Agency, Washington, D.C., (2001). Richard Jack is currently the North American Environmental Marketing Manager at Thermo Fisher Scientific Inc. He works with regulatory agencies around the world to develop analytical methods compliance monitoring. Richard is a coauthor for EPA 557 and has also drafted several ASTM methods. Richard received his PhD in biochemistry and anaerobic microbiology from Virginia Tech University in Blacksburg, Virginia, USA and his Masters in ecology from the University of Tennessee in Knoxville, Tennessee, USA.

First published in SeparationScience PREMIER LEARNING FOR ANALYTICAL CHEMISTS Separation Science, Vol. 5, Iss. 5 (May 2013)

by Eclipse Business Media Ltd Frederick House, Princes Court, Beam Heath Way Nantwich CW5 6PQ, UK