

ENVIRONMENTAL

Determination of Bromate in Water Using Ion Chromatography

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 ozone's short lifetime.^{2,3}

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 $\mu\text{g/L}$ concentrations. If ozone is used for disinfection, the finished product should be tested to assure that bromate levels are safe for human consumption.

The World Health Organization (WHO) has estimated excess lifetime cancer risks of 10^{-4} , 10^{-5} , and 10^{-6} for drinking water containing bromate at 20, 2, and $0.2 \mu\text{g/L}$, respectively, and have suggested a guideline of $10 \mu\text{g/L}$ bromate in drinking water.⁴ The U.S. EPA, European Commission, and Japanese Ministry of Health, Labor, and Welfare have established a regulatory maximum contaminant level (MCL) of $10 \mu\text{g/L}$ bromate in municipal drinking waters,⁵⁻⁷ and the European Commission has further established

an MCL of $3 \mu\text{g/L}$ bromate for natural mineral waters and spring waters treated by ozonation.⁸ Limits of detection required by the European Commission for bromate analysis are 25% of the MCL, or as low as $2.5 \mu\text{g/L}$ for drinking waters and below $1.0 \mu\text{g/L}$ for bottled mineral waters.⁵

Determining low concentrations of bromate in high ionic strength matrices can be very challenging. 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 determination of $<1 \mu\text{g/L}$ bromate.

The determination of bromide and bromate in chemicals used in water disinfection is also critical in order to prevent contamination before it occurs.

Dionex has developed a variety of methods, utilizing different column chemistries, detectors, and system capabilities to provide drinking water suppliers with choices customizable for their analytical requirements. Many of these methods are also suitable for detecting other disinfection by-products (DBPs) and common anions.



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Separation Methods

Carbonate/bicarbonate eluents have commonly been used for bromate analysis. However, recent methods have been developed utilizing hydroxide eluents. Dionex has designed columns for the determination of trace concentrations of bromate using both these eluents.

The IonPac® AS23 is a high-capacity anion-exchange column designed to be used with carbonate/bicarbonate eluent and a large loop injection for the determination of the trace DBPs chlorite, bromate, and chlorate, together with common inorganic anions, including bromide (precursor to bromate), in drinking waters. The IonPac AS23 column was developed using a unique polymer technology to achieve a capacity of 320 µeq/column, higher than the IonPac AS9-HC column (190 µeq/column) described in ASTM D 6581-00 (2005)⁹ and EPA Method 300.1.¹⁰ The combination of an optimized selectivity for DBP anions, high anion-exchange capacity, and improved selectivity of carbonate from inorganic anions and oxyhalides, makes this column an ideal replacement for the AS9-HC column. Figure 1 shows the use of a large loop injection and separation on an IonPac AS23 with an isocratic carbonate-bicarbonate eluent coupled with suppressed conductivity detection.

The high capacity IonPac AS19 is designed to be used with hydroxide eluents. The suppression product of KOH is water, which exhibits the lowest possible background conductivity in IC. Hydroxide eluents also allow the use of gradients, which provide more control over separation. The 240 µeq/column capacity of the AS19, coupled with the low noise provided by eluent suppression, allows this column to meet and exceed the performance requirements specified in ASTM D 6581-00 (2005) and U.S. EPA Method 300.1 for the determination of oxyhalides produced as disinfection by-products in drinking water. Column selectivity and detection performances of these two columns are compared in Figure 2.

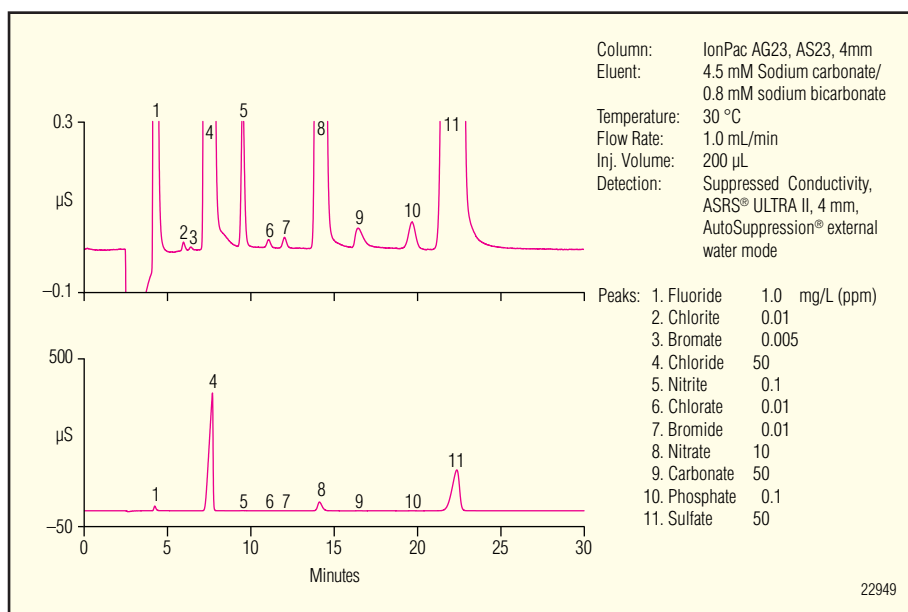


Figure 1. Determination of trace concentrations of bromate using the IonPac AS23 column with a large-loop injection.

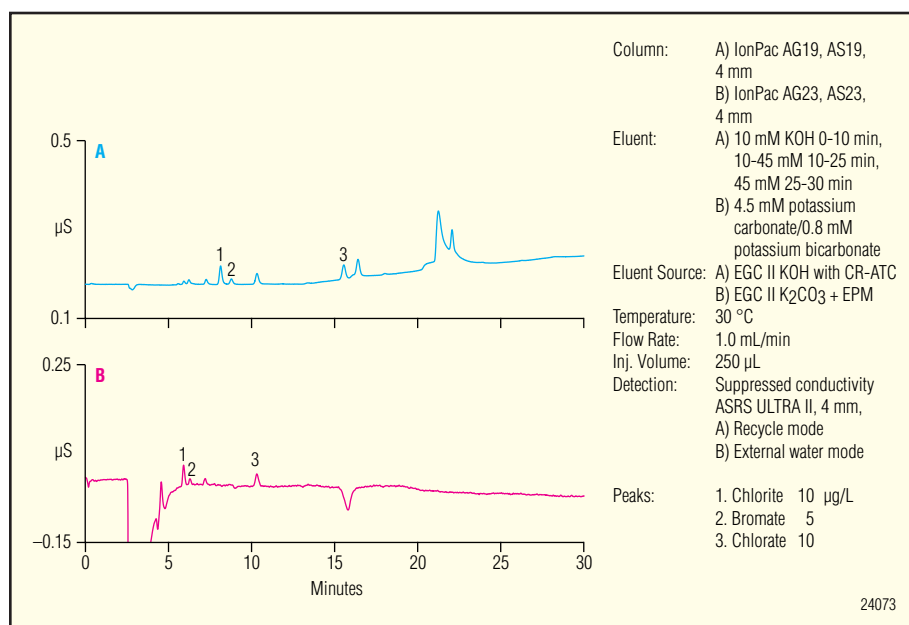


Figure 2. Different column selectivities in the separation of disinfection by-products: A) IonPac AS19 column, B) IonPac AS23 column.

Table 1 compares the performance of the IonPac AS19 with an electrolytically generated hydroxide eluent to the IonPac AS23 with an electrolytically generated carbonate/bicarbonate eluent, both methods using suppressed conductivity detection. The calculated MDL of bromate with the IonPac AS19 column was 0.31 µg/L, compared to 1.63 µg/L using the IonPac AS23 column. Hydroxide eluents improve the sensitivity for bromate compared to carbonate-based eluents and are therefore more suitable to meet the current European Commission regulatory requirement of 3 µg/L for the quantification of bromate in natural mineral waters.

Detection Methods

IC separations can be combined with various detection schemes as described by Fischer et al.² Suppressed conductivity using continuously regenerated suppressors is by far the most popular detection technique in IC, as background conductivity is reduced and the sensitivity for analytes is increased. Unlike most manufacturers' detectors, the use of Dionex auto-ranging detectors allows the simultaneous detection of disparate chloride/bromate concentrations without changing detection ranges.

Postcolumn derivatization techniques combined with UV detection increase the specificity of bromate detection while yielding very low detection limits, and can also be used to quantify bromate at sub-µg/L concentrations.^{11,12} This method, as described in US EPA Method 326.0,¹³ uses a postcolumn reaction that generates hydroiodic acid (HI) in situ from an excess of potassium iodide (KI). The HI combines with bromate from the column effluent to form the triiodide anion (I₃⁻) that is detected by absorbance at 352 nm. Figure 3 compares the analysis of drinking water using suppressed conductivity and postcolumn derivatization after separation on an AS9-HC column with a carbonate/bicarbonate eluent. The

| Table 1. Calibration Data, Retention Time Precisions, Peak Area Precisions, and Method Detection Limits for DBP Anions | | | | | | |
|--|--------------|-----------------------------|-------------------------------------|-------------------|---------------------|-----------------------|
| IonPac AS19 Column | | | | | | |
| Analyte | Range (µg/L) | Linearity (r ²) | Retention Time ^a RSD (%) | Peak Area RSD (%) | MDL Standard (µg/L) | Calculated MDL (µg/L) |
| Chlorite | 2-50 | 0.9999 | 0.04 | 1.20 | 1.0 | 0.18 |
| Bromate | 1-25 | 0.9995 | 0.03 | 1.40 | 2.0 | 0.31 |
| Chlorate | 2-50 | 0.9999 | 0.01 | 0.54 | 1.0 | 0.28 |
| IonPac AS23 Column | | | | | | |
| Chlorite | 10-50 | 0.9999 | 0.07 | 2.20 | 5.0 | 1.02 |
| Bromate | 5-25 | 0.9998 | 0.07 | 2.63 | 5.0 | 1.63 |
| Chlorate | 10-50 | 0.9998 | 0.11 | 2.48 | 9.0 | 2.05 |

^aRSD= relative standard deviation, n = 10 for a standard consisting of 10 ppb bromate and 20 ppb each of chlorite and chlorate.

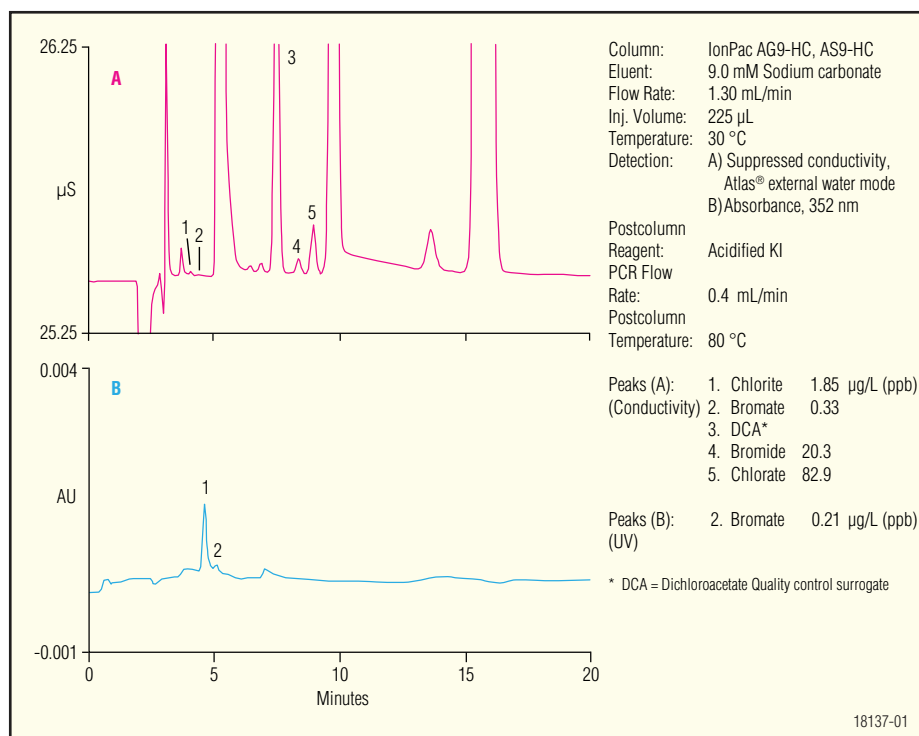


Figure 3. Determination of DBP anions in drinking water using (A) suppressed conductivity detection and (B) UV absorbance detection after postcolumn reaction with acidified KI.

postcolumn technique reduces the calculated bromate MDL to 0.06 µg/L,¹¹ which exceeds even the low detection limits specified by the European Commission for bottled mineral waters. Use of the AS19 column, applying an electrolytically generated hydroxide eluent combined with the postcolumn KI reaction, further reduces the MDL to 0.04 µg/L.¹³ Figure 4 compares the detection of DBPs using suppressed conductivity and UV after separation on an AS19 column. Typical MDLs for both suppressed conductivity and postcolumn UV detection are summarized in Table 2.

Bromate Analysis Using RFIC

Reagent-Free™ IC (RFIC™) systems allow the application of IC without manually prepared eluents, combining electrolytic eluent generation and self-regenerating suppression. By electrolytically producing high quality eluents from deionized water, RFIC improves both the ease of use and method performance of IC systems used for bromate detection. As shown in Figure 5, electrolytically generated hydroxide eluents allow for both an improved separation of bromate from the major component chloride and an improved LOD. The latter is obtained due to the improved S/N ratio resulting from the low background conductivity after suppression.

RFIC systems are flexible enough to be used with a variety of column chemistries. Electrolytically generated KOH is available for use with the IonPac AS19 column. Precise control of current allows repeatable concentrations and gradients for improved reproducibility over manually prepared eluents and standard proportioning valves. The AS23 column can be used with electrolytically generated potassium carbonate that is modified by an Electrolytic pH Modifier (EPM) to automatically and reproducibly generate carbonate/bicarbonate eluent at the desired concentration.

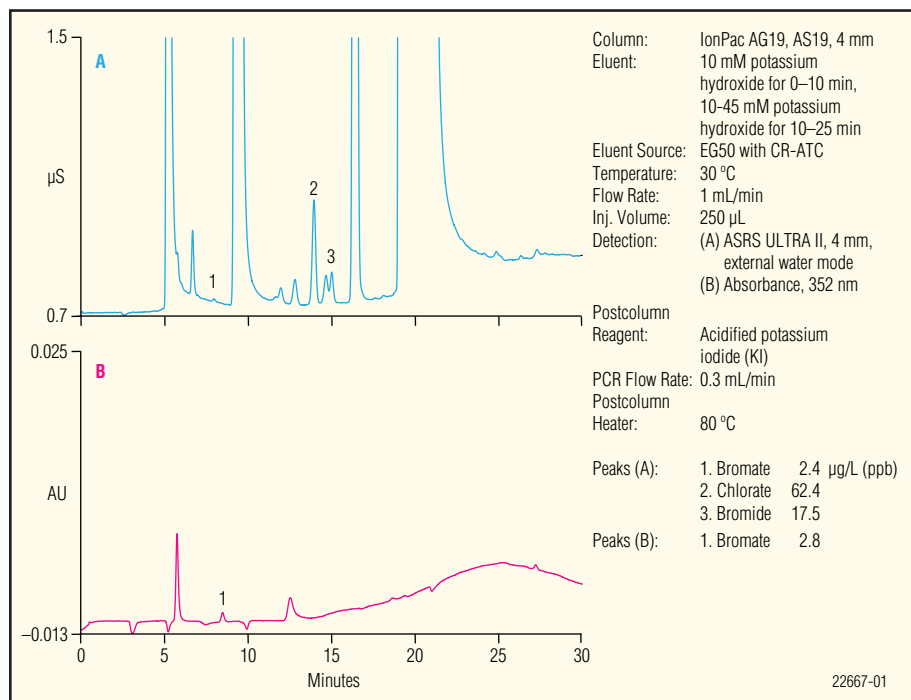


Figure 4. Determination of trace DBP anions and bromide in tap water using (A) suppressed conductivity detection and (B) UV absorbance after postcolumn reaction with acidified KI.

| Table 2. Linearity and MDLs for Disinfection By-Products and Bromide Using the IonPac AS19 Column | | | | |
|---|--------------|-----------------------------|---------------------|-----------------------|
| Analyte | Range (µg/L) | Linearity (r ²) | MDL Standard (µg/L) | Calculated MDL (µg/L) |
| Chlorite | 5–500 | 0.9995 | 1.0 | 0.17 |
| Bromate (conductivity) | 1–40 | 0.9999 | 1.0 | 0.29 |
| Bromate (UV) | 0.5–15 | 1.0000 | 0.2 | 0.04 |
| Chlorate | 5–500 | 0.9991 | 1.2 | 0.37 |
| Bromide | 5–500 | 0.9998 | 2.0 | 0.45 |

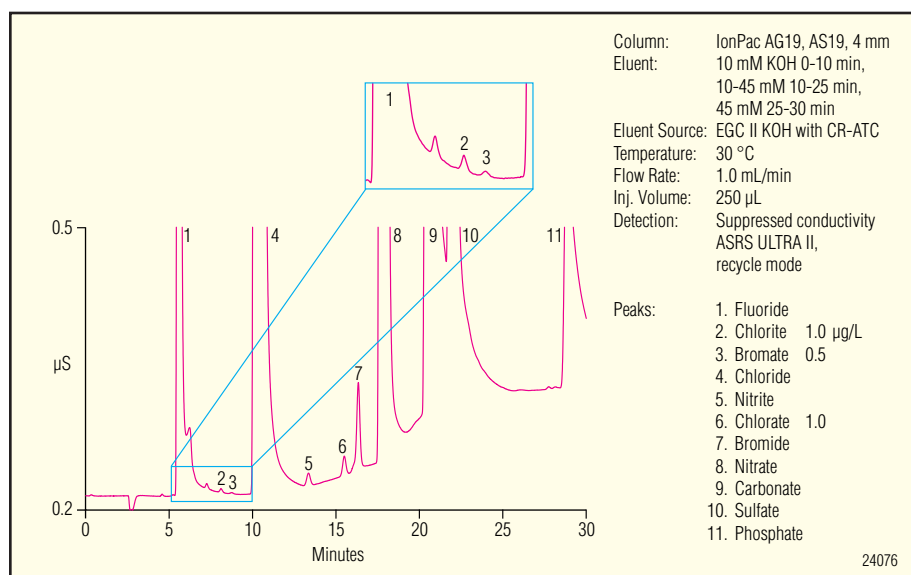


Figure 5. Chromatogram of mineral water spiked with 1 µg/L each chlorite and chlorate and 0.5 µg/L bromate.

Two-Dimensional IC and Suppressed Conductivity

Another strategy for the determination of bromate in high ionic strength matrices is two-dimensional ion chromatography (2-D IC).¹⁵ Figure 6 shows a diagram of a 2-D IC configuration. Automated column switching, facilitated by the ICS-3000 system and Chromeleon® software, makes it possible to remove matrix ions before analysis. A high-volume water sample is injected onto a high capacity 4-mm IonPac AS19 column using a KOH gradient. Bromate is partially resolved from matrix ions, and a cut volume containing the bromate is transferred to the second dimension. Matrix ions are flushed to waste, preventing potential column overloading by high ionic strength matrices. In the second dimension, the sample is further concentrated on a TAC-ULP1 concentrator column and resolved on an IonPac AS24, 2-mm column. The smaller cross-sectional area of the 2-mm column increases selectivity compared to the 4-mm AS19. The use of two different column chemistries also increases selectivity over one-dimensional IC. This method is fully automated using the ICS-3000 RFIC system.

Figure 7 shows the results of a 2-D IC separation of bromate in a high ionic strength matrix. The upper chromatogram shows that the bromate is not resolved from the chloride in this sample by the AS19, 4-mm column. The lower chromatogram shows the results after separation on an AS19 column, re-injection of a cut sample onto a TAC-ULP1 concentrator column, and separation on an AS24, 2-mm column. The bromate that was undetectable in the first dimension is fully resolved in the second. Using this 2-D IC technique, an MDL of 0.036 µg/L can be achieved in high ionic strength matrices without the need for postcolumn derivatization.

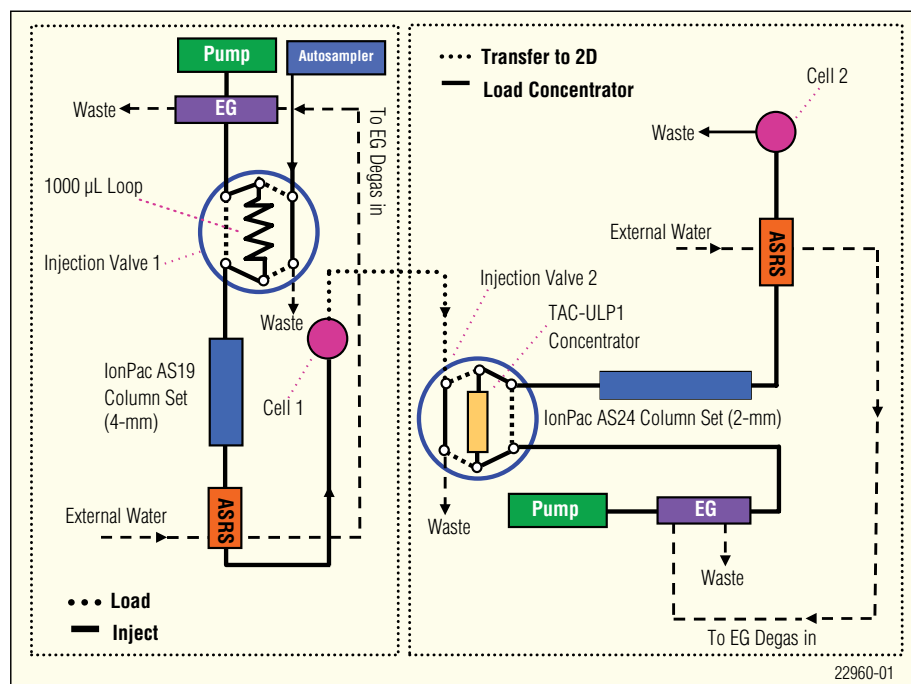


Figure 6. Diagram of a two-dimensional IC system for detection of bromate.

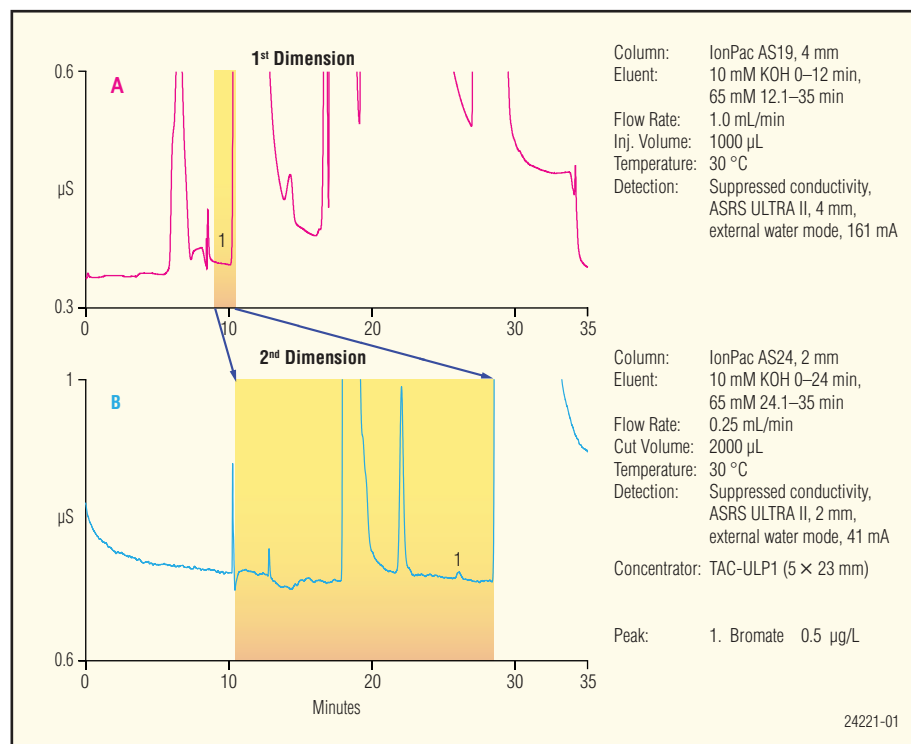


Figure 7. Two dimensional bromate analysis using (A) a 4-mm IonPac AS19 column in the first dimension, and (B) a 2-mm IonPac AS24 column in the second dimension.

IC/MS for Trace Bromate Determination

In combination with continuously regenerated suppressors, MS detection with ion-chromatographic separations provides optimal sensitivity, selectivity, and specificity. Figure 8 shows the application of IC/MS for the determination of bromate. The Selected Ion Monitoring (SIM) trace at $m/z = 127$ shows a second peak beside bromate which was identified as dichloroacetic acid.

Bromate Determination in Chemicals

Hypochlorite salts are often used for the disinfection of drinking water and swimming pool water since they are safer and easier to handle than chlorine or ClO_2 . Sodium hypochlorite is produced by the reaction of chlorine gas and high quality NaOH. Because chlorine gas is produced from natural salt sources that may contain trace amounts of bromide, bromine contamination is possible. As a result, unintended byproducts such as bromate and other oxohalides may be formed during the hypochlorite synthesis.

IC can be used to determine the bromate content in hypochlorite solutions,¹⁶ as can be seen in Figure 9. Prior to injection, the sample is treated with hydrogen peroxide followed by the removal of the excess of chloride with an OnGuard® Ag cartridge.

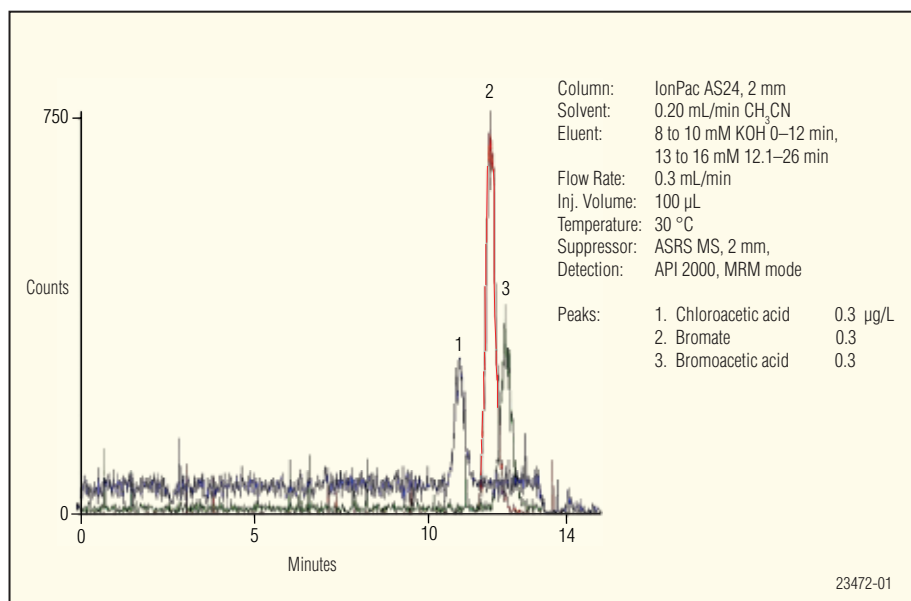


Figure 8. IC-MS determination of bromate in tap water.

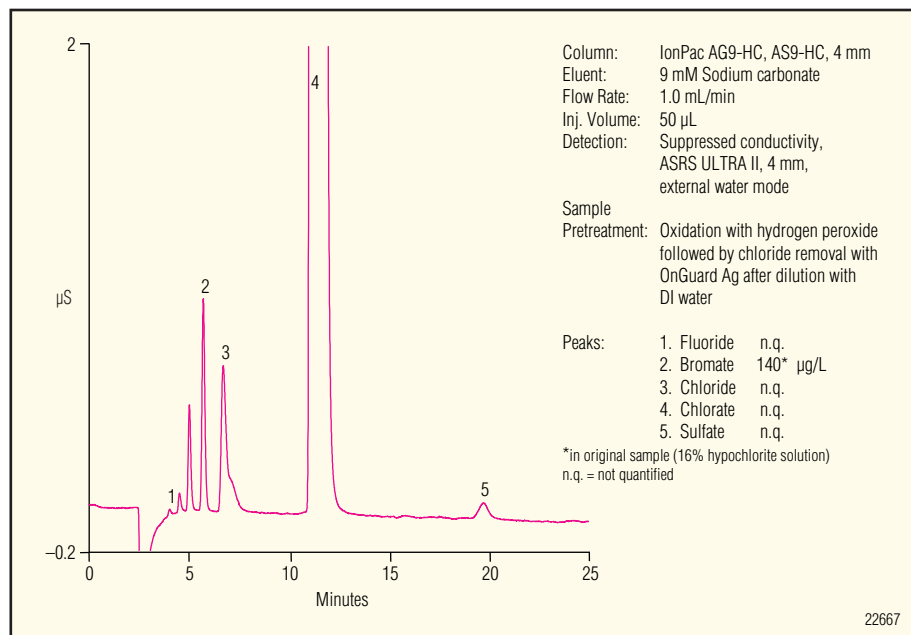


Figure 9. Determination of bromate in hypochlorite solution.

| IC USING SUPPRESSED CONDUCTIVITY DETECTION | IC USING POSTCOLUMN REAGENT AND UV DETECTION | 2-D IC USING SUPPRESSED CONDUCTIVITY DETECTION | IC USING MS DETECTION |
|--|---|--|---|
| Suitable for compliance monitoring of drinking water. Can be used for ground- and wastewaters depending on salt (anion) concentration. | Suitable for compliance monitoring of drinking, ground-, and waste-waters. | Suitable for compliance monitoring of drinking, ground-, and wastewaters. | Suitable for compliance monitoring of drinking, ground-, and wastewaters. |
| Specificity depending on retention time. | Specific due to a chemical reaction and signal enhanced using absorbance detection. | Specific due to use of two columns with different selectivity and signal enhanced due to a smaller column in the second dimension. | Specific and sensitive using MS detector. |
| Easy to use with either hydroxide or carbonate eluents. | More complex system that requires two pumps. | More complex installation with two pumps and dual valves. Does not require a second eluent type; RFIC can be used for both dimensions. | Highly complex and high costs associated with initial investment and operation. |
| Matrix conditions are addressed using hydroxide eluent and columns with increasing capacity that allow bromate separation from other anions. | Matrix conditions are addressed using a post-column reagent that does not react with matrix ions that typically interfere with bromate. | Matrix conditions are addressed by matrix elimination using a heart cut technique; bromate is refocused onto a concentrator column. | |
| High concentration matrices can reduce method sensitivity. | Good sensitivity except in very high concentration matrices. | Good sensitivity regardless of matrix concentration. | Generally not required for compliance monitoring. |

Bromate Detection Method Selection

Bromate can be separated using different column chemistries and detected using a variety of detection techniques. Which one to use primarily depends on matrix conditions and the 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 method. These techniques are summarized above.

Summary

As a leader in ion chromatography technology, Dionex is developing new techniques for important environmental contaminants such as bromate. Regulations are continually being established and updated in order to protect human health. Consequently, the analytical methods are subject to change. Dionex is ready to partner with you to ensure the compliance of your bromate method with the latest requirements.

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LPN 1970 8M 09/07
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