APPLICATION UPDATE 73278

# Improved ion chromatography column for separation of ethylenediamine carbamate and fluoride, and carbonate and sulfate in drinking water

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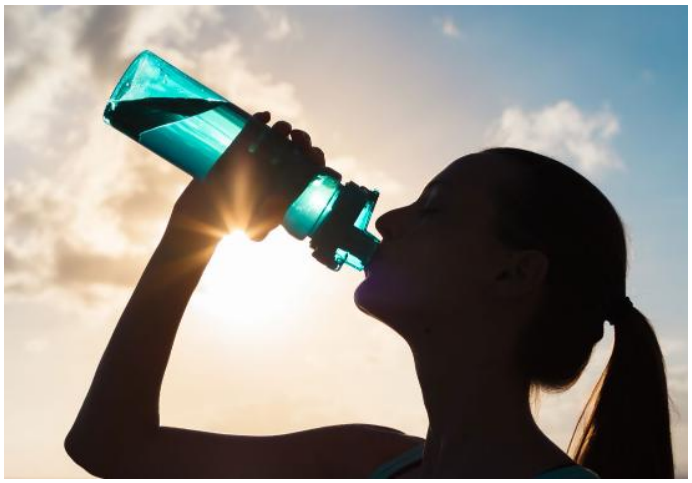


## Goal

To demonstrate the ability of the Thermo Scientific™ Dionex™ IonPac™ AS30 column to separate ethylenediamine (EDA) carbamate and fluoride as well as carbonate and sulfate in order to determine trace concentrations of oxyhalides and bromide in drinking water containing the EDA preservative.

## Introduction

Disinfection treatment is used to protect municipal water from potentially dangerous microbes. The most common chemical disinfectants are chlorine, chlorine dioxide, chloramine, and ozone.[1,2] These chemical disinfectants can react with natural organic and inorganic matter in the source water to produce disinfection byproducts (DBPs) that are potentially harmful to humans. For example, chlorine dioxide treatment generates the inorganic oxyhalide DBPs chlorite and chlorate, whereas ozone reacts with naturally occurring bromide to produce bromate.[2] In addition, bromate can also be formed when chlorinated water is exposed to the UV rays in sunlight.[3]

Of these DBPs, bromate has received the most attention due to its potential negative health effects. The World Health Organization (WHO) has estimated an excess lifetime cancer risk of $10^{-4}$, $10^{-5}$, and $10^{-6}$ for drinking water containing bromate at levels of 20, 2, and 0.2 µg/L, respectively, and has suggested a guideline level of 10 µg/L bromate in drinking water.[4] The U.S. Environmental Protection Agency (EPA); European Commission; and Japanese Ministry of Health, Labor, and Welfare have established a regulatory maximum contaminant level (MCL) of 10 µg/L bromate in municipal drinking water.[5-7]

The determination of trace concentrations of bromate and other oxyhalides in drinking water preserved with EDA can be very challenging. The EDA preservative is required in all standards and samples to preserve the integrity of chlorite and bromate. Chlorite is susceptible to degradation through catalytic reactions with dissolved iron, but EDA prevents this reaction by chelating iron and other destructive metal cations. EDA also preserves bromate by binding with hypobromous acid/hypobromite, which is an intermediate

formed as a byproduct of the reaction of either ozone or hypochlorous acid/hypochlorite with bromide. However, $CO_2$ absorption into aqueous EDA solution forms EDA carbamate/bicarbamate which cannot be fully resolved from fluoride on the Thermo Scientific™ Dionex™ IonPac™ AS27 and the Thermo Scientific™ Dionex™ IonPac™ AS19 columns that are high-capacity, hydroxide-selective, and anion-exchange columns recommended for the determination of trace concentrations of chlorite, bromate, chlorate, and bromide in drinking water samples.[8-9]

This study demonstrates the Dionex IonPac AS30 high capacity, hydroxide-selective column that offers improved separation of inorganic anions and oxyhalides in samples preserved with EDA. The Dionex IonPac AS30 column was specifically developed to resolve the EDA carbamate artifact and fluoride as well as carbonate and sulfate better than the Dionex IonPac AS27 and the Dionex IonPac AS19 columns, and provide good resolution of dichloracetate (DCA, a surrogate anion) from potentially interfering matrix anions.

## Equipment

- Thermo Scientific™ Dionex™ Integrion™ HPIC RFIC system* including:
  - Eluent generator
  - Pump
  - Degasser
  - Conductivity detector
  - Column oven temperature control
  - Detector-suppressor compartment temperature control
  - Tablet control
- Thermo Scientific™ Dionex™ AS-AP Autosampler with Sample Syringe, 250 µL (P/N 074306) and Buffer line, 1.2 mL (P/N 074989)

* This application can be run on any Thermo Scientific Dionex RFIC system.

## HPIC consumables

- Thermo Scientific™ Dionex™ EGC 500 KOH Eluent Generator Cartridge (P/N 075778)
- Thermo Scientific™ Dionex™ CR-ATC 600 Continuously Regenerated Anion Trap Column (P/N 088662)
- Thermo Scientific™ Dionex™ ADRS 600 Anion Dynamically Regenerated Suppressor, 2 mm, (P/N 088667)
- Dionex IC PEEK Viper Fitting Tubing Assembly Kits (P/N 088798)

## Software

- Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software version 7.2

## Reagents and standards

- Deionized (DI) water, Type I reagent grade, 18 MΩ-cm resistivity or better
- Chlorite Standard, 1000 mg/L (P/N 303167)
- Bromate Standard, 1000 mg/L (P/N 303168)
- Nitrite Standard, 1000 mg/L (P/N 303169)
- Chlorate Standard, 1000 mg/L (P/N 303170)
- Phosphate Standard, 1000 mg/L (P/N 303172)
- Nitrate Standard, 1000 mg/L (P/N 056497)
- Sodium Bromide, (Granular/Certified ACS), Fisher Chemical (Fisher Scientific P/N S255-500)
- Ethylenediamine, 99+%, extra pure, ACROS Organics™ (Fisher Scientific P/N AC22042-2500)
- Potassium Dichloroacetate, 98%, Sigma-Aldrich Fine Chemicals Biosciences (Fisher Scientific P/N NC0349258)
- Sodium Carbonate Anhydrous, ≥99.5%, (Powder/Certified ACS), Fisher Chemical (Fisher Scientific P/N S263-500)
- Sodium Chloride, (Crystalline/Certified ACS), Fisher Chemical (Fisher Scientific P/N S271-500)
- Sodium Fluoride, (Powder/Certified ACS), Fisher Chemical (Fisher Scientific P/N S299-500)
- Sodium Sulfate Anhydrous, (Granular/Certified ACS), Fisher Chemical (Fisher Scientific P/N S421-500)

| IC Conditions (Applicable to Figures 2 and 7) | |
|---|---|
| Columns | • Thermo Scientific™ Dionex™ IonPac AG30 Guard, 2 × 50 mm (P/N 303162)<br>• Dionex IonPac AS30 Analytical, 2 × 250 mm (P/N 303161) |
| Eluent source | Dionex EGC 500 KOH Eluent Generator Cartridge with CR-ATC 600 trap column |
| Eluent | • Equilibration - 6 min with 1 mM KOH<br>• At 0 min: 1 mM KOH<br>• At 8 min: 8 mM KOH<br>• At 17 min: 25 mM KOH<br>• At 21 min: 30 mM KOH<br>• At 23 min: 66 mM KOH<br>• At 35 min: 66 mM KOH<br>• At 35 min: 1 mM KOH<br>• At 36 min: Stop Run |
| Flow rate | 0.38 mL/min |
| Column temperature | 30 °C |
| Injection volume | 50 µL (Full Loop) |
| Detection | Suppressed Conductivity, Dionex ADRS 600 Suppressor (2 mm), recycle mode, Use recommended voltage |
| System backpressure | 2900 psi (100 psi = 0.6894 MPa) |
| Background conductance | 0.3 µS/cm |
| Run time: | 42 min |

## Preparation of solutions and reagents

### Standard solution

Deionized (DI) water was used for eluent and standard preparation and for diluting samples. For several of the anions of interest, 1000 mg/L standard solutions can be purchased from Thermo Fisher Scientific or other commercial sources. When commercial standards are not available, prepare 1000 mg/L individual stock standard solutions by dissolving the appropriate amounts of the required analyte in 100 mL of DI water as specified in Table 1. A mixed standard solution was prepared by diluting the individual stock standard solutions into a 100 mL volumetric flask with DI water. Calibration standards were prepared similarly by diluting the stock standards in DI water. Mix thoroughly and store at 4 °C.

Table 1. Amounts of compounds used to prepare 100 mL of 1000 mg/L stock solutions.

| Anion | Compound | Mass (mg) |
|---|---|---|
| Fluoride | Sodium Fluoride | 221.01 |
| Bromide | Sodium Bromide | 128.77 |
| Chloride | Sodium Chloride | 164.85 |
| Carbonate | Sodium Carbonate | 176.67 |
| Sulfate | Sodium Sulfate | 147.87 |
| DCA | Potassium DCA | 130.46 |

### Ethylenediamine (EDA) preservation solution, 100 mg/mL

Dilute 2.8 mL of ethylenediamine (99%) (CASRN 107-15-3) to 25 mL with reagent water. Prepare fresh monthly.

### Sample preparation

Filter samples, as necessary, through a 0.45 µm syringe filter and discard the first 300 µL of the effluent. To prevent degradation of chlorite or formation of bromate from hypobromous acid/hypobromite, preserve the samples by adding 50 µL of EDA preservation solution per 100 mL of sample so the final concentration of EDA will be 50 mg/L. All samples require a final fortified concentration of 1 mg/L DCA, so add 0.1 mL of 1000 mg/L DCA stock solution per 100 mL of sample. The recovery of DCA must fall between 90 and 115%.

## Recovery study

The recovery of chlorite, bromate, chlorate, and bromide was assessed in this study. To be certain that our measurement is accurate, the samples were spiked with appropriate known amounts of stock standard solutions.

## Results and discussion

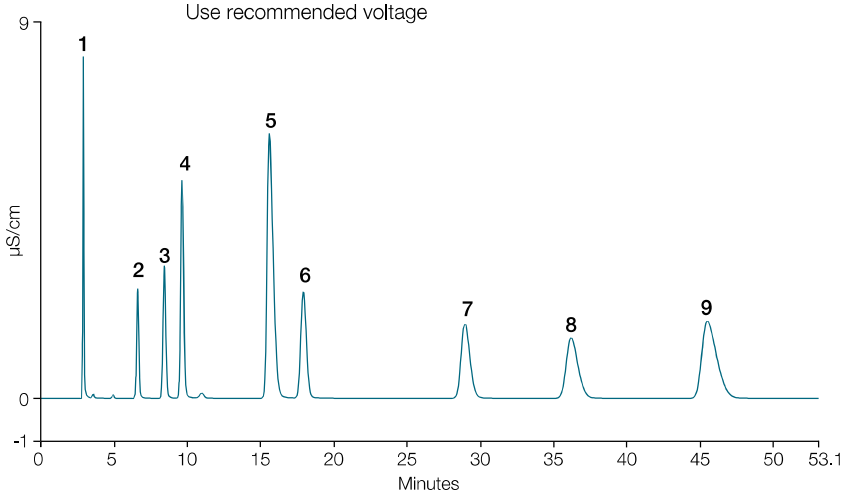
### Separation

The Dionex IonPac AS30 column is a high capacity, hydroxide-selective, anion-exchange column specifically developed for the improved separation of the EDA carbamate artifact and fluoride as well as carbonate and sulfate in samples preserved with EDA. The EDA preservative can react with carbonate and produce artifacts that interfere with early eluting analytes, such as fluoride. In comparison to the Dionex IonPac AS27 and Dionex IonPac AS19 columns, the Dionex IonPac AS30 column has the ability to determine trace bromate with good resolution of DCA from potentially interfering matrix, but also offers good resolution of EDA carbamate artifact and fluoride, as well as improved resolution of carbonate and sulfate.

When installing a new column, we strongly recommend reproducing the quality assurance report (QAR) that is included in the column packaging. Figure 1 shows a separation of six common inorganic anions, chlorite, bromate, and chlorate, following the QAR conditions. As shown, all target analytes are well resolved using an isocratic elution.

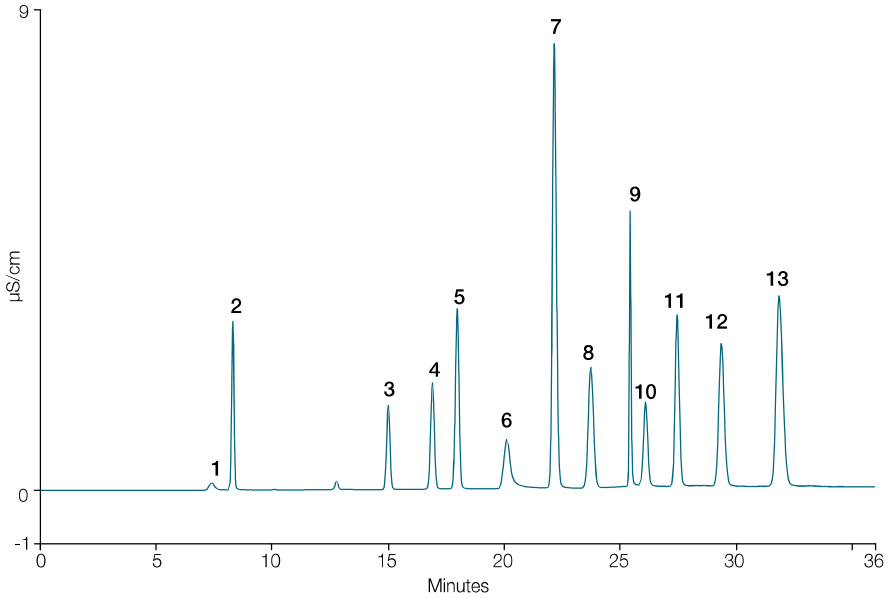
The separation was then optimized using a multistep hydroxide gradient to resolve chlorite, bromate, chlorate, bromide, DCA, and EDA carbamate from common inorganic anions found in drinking water samples. The optimized separation developed for this application (Figure 2) shows that the Dionex IonPac AS30 column provides good resolution of the DBP anions, bromide, DCA, and EDA carbamate from common anions using a hydroxide gradient.

| | |
|---|---|
| Column: | Dionex IonPac AG30 Guard, 2 × 50 mm<br>Dionex IonPac AS30 Analytical, 2 × 250 mm |
| Eluent: | 18 mM KOH |
| Eluent source: | Dionex EGC 500 KOH cartridge with CR-ATC 600 |
| Temperature: | 30 °C |
| Flow rate: | 0.38 mL/min |
| Injection volume: | 2.5 µL |
| Detection: | Dionex ADRS 600 suppressor, 2mm, recycle mode,<br>Use recommended voltage |




| Peak | mg/L |
|---|---|
| 1. Fluoride | 3 |
| 2. Chlorite | 10 |
| 3. Bromate | 20 |
| 4. Chloride | 6 |
| 5. Sulfate | 30 |
| 6. Nitrite | 15 |
| 7. Bromide | 25 |
| 8. Chlorate | 25 |
| 9. Nitrate | 25 |

**Figure 1. Dionex IonPac AS30 column QAR separation using an isocratic KOH eluent.**




| Peak | mg/L |
|---|---|
| 1. EDA carbamate | – |
| 2. Fluoride | 0.15 |
| 3. Chlorite | 0.5 |
| 4. Bromate | 1 |
| 5. Chloride | 0.3 |
| 6. Carbonate | – |
| 7. Sulfate | 1.5 |
| 8. Nitrite | 0.75 |
| 9. Phosphate | 1 |
| 10. DCA | 1 |
| 11. Bromide | 1.25 |
| 12. Chlorate | 1.25 |
| 13. Nitrate | 1.25 |

**Figure 2. Separation of common anions, DBPs, DCA, and EDA carbamate using a Dionex IonPac AS30 column with a hydroxide gradient.**

## Linearity and method detection limits (MDLs)

Before analyzing samples, the linear calibration range and minimum detection limits (MDLs) were determined; and acceptable performance of a quality control sample (QCS) was demonstrated. A seven-point calibration range was used for chlorite (1–100 µg/L), whereas a six-point calibration range was used for bromate (1.25–30 µg/L), chlorate (10–500 µg/L), and bromide (10–500 µg/L). The results yielded a linear relationship of peak area to concentration with a coefficient of determination ($r^2$) ranging from 0.9995–0.9999 (Figures 3–6, Table 2).

The initial demonstration of performance is used to characterize instrument performance (determination of accuracy through the analysis of the QCS) and laboratory performance (determination of MDLs) prior to performing analyses by this method. A QCS consisting of 50 µg/L each of chlorite, chlorate, and bromide; 5 µg/L bromate; and 1000 µg/L DCA was prepared and seven replicate injections were performed. The recoveries from these injections ranged from 98.5–103%, the peak area precisions ranged from 0.06–1.15%, and retention time precisions ranged from 0–0.02%, respectively (Table 3). The recoveries and precisions demonstrate good initial performance of the method for the determination of oxyhalides and bromide.

The MDLs for chlorite, bromate, chlorate, and bromide were determined by performing seven replicate injections of reagent water fortified at a concentration of 3× to 5× the estimated instrument detection limits. Table 2 shows typical calculated MDLs in reagent water using the Dionex IonPac AS30 column combined with an electrolytic eluent generator and a 50 µL injection.

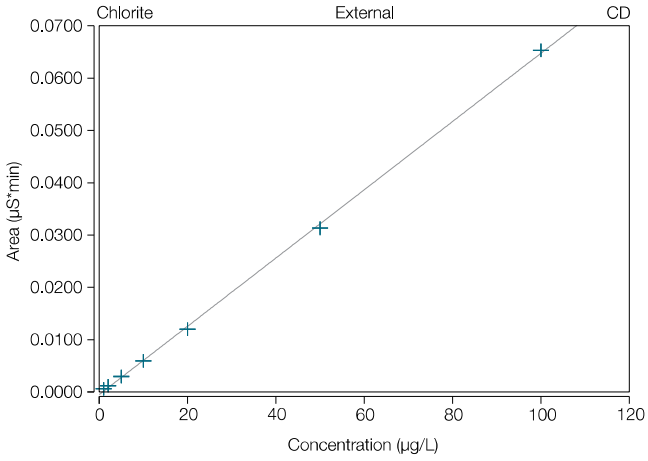



Figure 3. Linearity of chlorite response to concentration (1–100 µg/L).

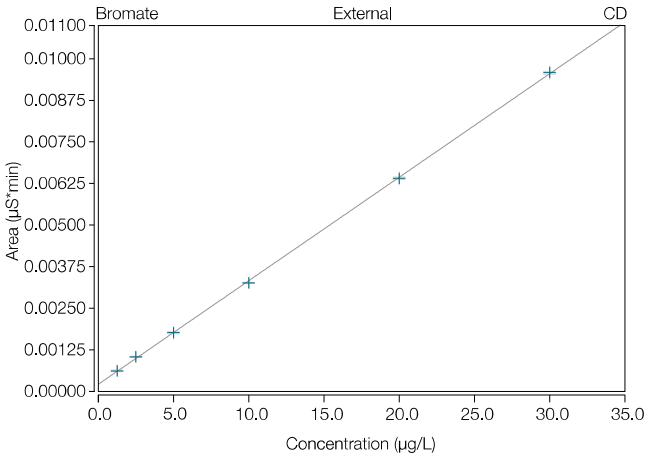



Figure 4. Linearity of bromate response to concentration (1.25–30 µg/L).

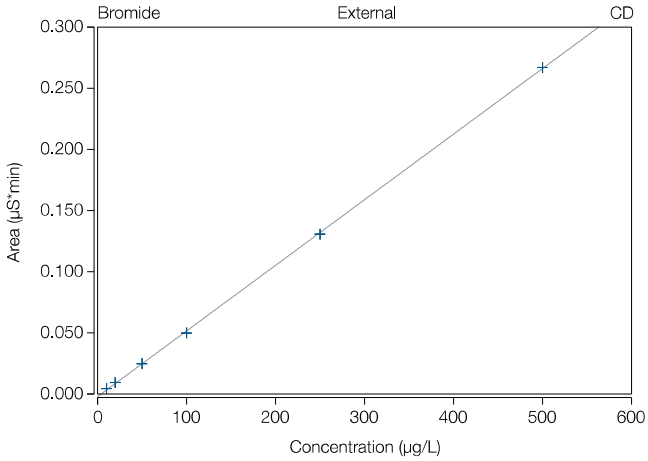



Figure 5. Linearity of bromide response to concentration (10–500 µg/L).

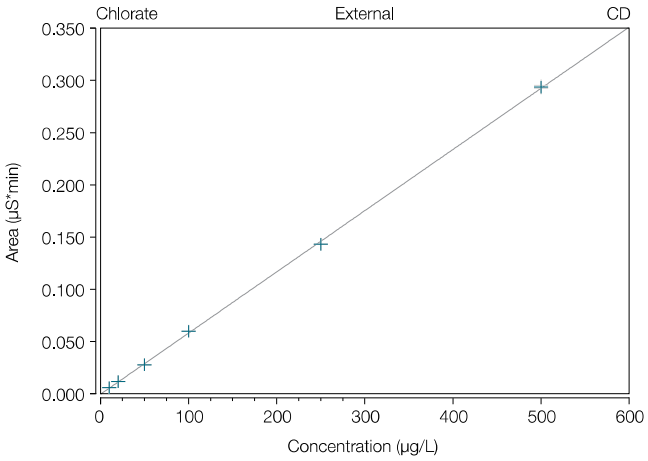



Figure 6. Linearity of chlorate response to concentration (10–500 µg/L).

Table 2. Linearity and detection limits obtained using a Dionex IonPac AS30 column

| Analyte | Range (µg/L) | Coefficient of Determination ($r^2$) | MDL Standard (µg/L) | Calculated MDL[a,b] (µg/L) |
|---|---|---|---|---|
| Chlorite | 1–100 | 0.9995 | 0.5 | 0.15 |
| Bromate | 1.25–30 | 0.9999 | 1.0 | 0.29 |
| Bromide | 10–500 | 0.9999 | 2.5 | 0.58 |
| Chloride | 10–500 | 0.9998 | 2.5 | 0.60 |

[a]50 µL injection volume
[b]MDL= σtS,99 where $t_{S,99}$ = 3.14 for n = 7

Table 3. Recovery and precision of the QCS sample

| Analyte | Recovery (%) | Peak Area RSD | Retention Time RSD |
|---|---|---|---|
| Chlorite | 101 | 0.19 | 0.02 |
| Bromate | 99.5 | 1.15 | 0.02 |
| Bromide | 98.5 | 0.36 | 0.00 |
| Chlorate | 103 | 0.47 | 0.01 |
| DCA | 99.1 | 0.06 | 0.01 |

## Accuracy and precision

The performance of the Dionex IonPac AS30 column was also evaluated through a single-operator precision and bias study using spiked water samples. The three water samples were a commercial bottled water (drinking water A), a municipal water (drinking water B), and 1 to 1 dilution of synthetic high-ionic-strength matrix (½ HIW) (drinking water C) containing 50 mg/L chloride, 50 mg/L carbonate, 5 mg/L nitrate, 5 mg/L phosphate, and 50 mg/L sulfate. The synthetic HIW is described in the U.S. EPA's Method 300.1.[10]

Figure 7 shows the separation of common anions, DBPs, DCA, and EDA carbamate in drinking water on the Dionex IonPac AS30 column. As shown, DBPs and common anions are resolved from EDA preservative artifact, sulfate is well resolved from carbonate, and DCA has a good resolution from potentially interfering matrix anions.

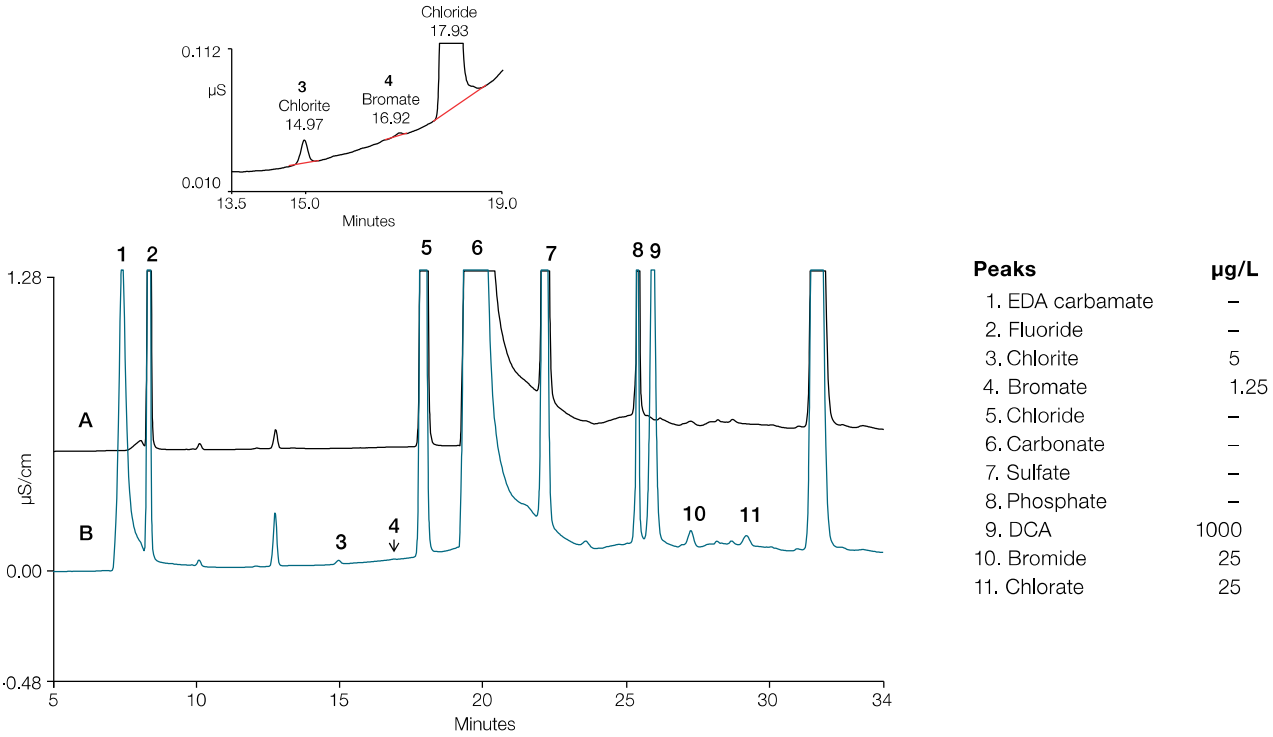



Figure 7. Drinking Water A fortified with DBPs, bromide, DCA and EDA carbamate; A) Unfortified sample, and B) Fortified sample.

Table 4. Recoveries of trace oxyhalides and bromide spiked into water samples.

| Analyte | Drinking Water A | | | Drinking Water B | | | ½ HIW | | |
|---|---|---|---|---|---|---|---|---|---|
| | Amount Found (µg/L) | Amount Added (µg/L) | Recovery (%) | Amount Found (µg/L) | Amount Added (µg/L) | Recovery (%) | Amount Found (µg/L) | Amount Added (µg/L) | Recovery (%) |
| Chlorite | <MDL | 5.0 | 95.0 | 6.99 | 10 | 109 | <MDL | 10 | 90.1 |
| Bromate | <MDL | 2.5 | 109 | <MDL | 5 | 76.6 | <MDL | 5 | 78.1 |
| Bromide | <MDL | 25.0 | 117 | <MDL | 50 | 115 | 31.7 | 50 | 88.3 |
| Chlorate | <MDL | 25.0 | 80.9 | 50.9 | 50 | 106 | <MDL | 50 | 85.5 |
| DCA | – | 1000 | 97.4 | – | 1000 | 103 | – | 1000 | 99.8 |

Table 4 summarizes the recoveries of the DBP anions, bromide, and DCA spiked into three different samples, then separated on the Dionex IonPac AS30 column. Overall, the recoveries ranged from 76.6 to 117%, which is within the acceptable range of 75 to 125%. All samples were fortified with 1 mg/L DCA surrogate, for which recovery ranges from 97.4% to 103%, all within 90 to 115%.

The precision of the method using the Dionex IonPac AS30 column in combination with electrolytic eluent generation was determined from seven replicate injections of Drinking water A spiked with trace concentrations of DBPs and bromide. Overall, the calculated peak area precisions varied from 0.48 to 4.39% for the target analytes.

## Limitation

The Dionex IonPac AS30 column is overloaded by a HIW sample containing 100 mg/L chloride, 100 mg/L carbonate, 10 mg/L nitrate, 10 mg/L phosphate, and 100 mg/L sulfate that the Dionex IonPac AS27 and the Dionex IonPac AS19 columns can analyze at the same injection volume. Figure 8 shows chromatograms comparing bromate and chloride separation of HIW and ½ HIW samples on a Dionex IonPac AS30 column. Due to the column capacity, bromate cannot be detected with the high chloride concentration in the HIW sample, but it can in the sample with half the ionic strength of the HIW. Therefore, while the Dionex IonPac AS30 is an excellent column for determining low bromate concentrations in most drinking water and environmental water samples, the analyst should exercise caution when analyzing high ionic strength water samples.

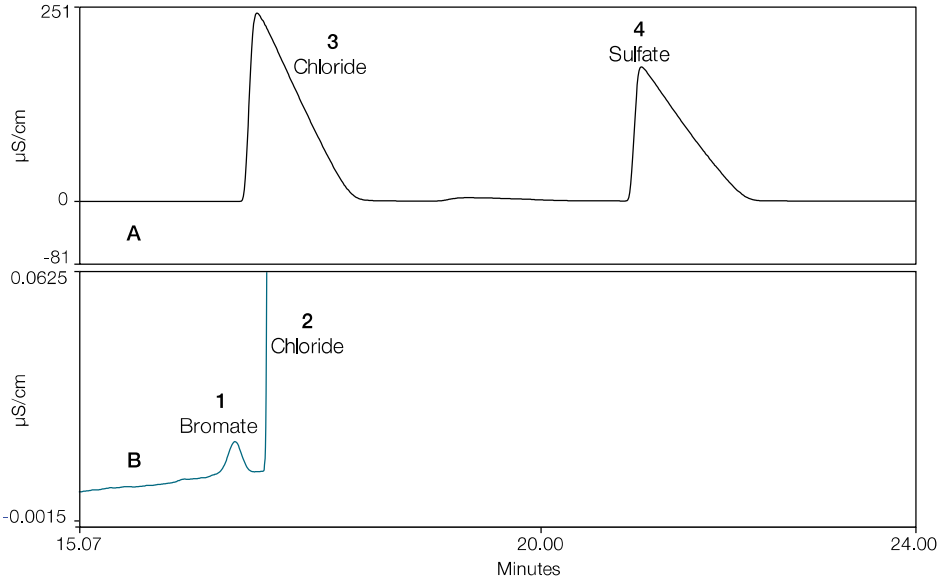



Figure 8. Separation of bromate and chloride on a Dionex IonPac AS30 column in A) HIW sample, and B) ½ HIW sample.

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This study introduced and validated a new IC column that is proposed to determine trace concentrations of bromide and DBP anions, including bromate, in municipal drinking water samples using a hydroxide eluent. The Dionex IonPac AS30 column also offers good resolution of DCA from potentially interfering matrix, offers good resolution of EDA carbamate artifact and fluoride, as well as improved resolution of carbonate and sulfate compared to the Dionex IonPac AS27 and Dionex IonPac AS19 columns. But this column has less resolution between bromate and chloride in HIW sample than the Dionex IonPac AS27 and Dionex IonPac AS19 columns. Besides providing superior sensitivity by suppressed conductivity detection, hydroxide eluents can be easily generated with Reagent-Free™ ion chromatography (IC) (RFIC™) systems. These systems simplify analysis and improve reproducibility when transferring methods between laboratories.

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