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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

INTRODUCTION

Public drinking water municipalities routinely disinfect their water supplies to protect the public from potentially dangerous microorganisms. Chlorine dioxide, chloramine, and ozone are common disinfection compounds used to treat public water supplies.[1] These treatments produce byproducts that expose the public to potentially harmful chemicals. For example, the use of chlorine dioxide for disinfection treatment can generate the oxyhalide disinfection byproducts (DBPs) chlorite and chlorate, while the use of chloramine can produce chlorate.[2] Although ozonation of water supplies is a particularly effective disinfection treatment, bromate may be generated if the source water contains elevated levels of naturally occurring bromide. Bromate has been identified as an animal carcinogen and a potential human carcinogen by the International Agency for Research on Cancer.[3]

The US EPA has estimated a potential cancer risk of 1 in 10^4 for a lifetime exposure to drinking water containing 5 µg/L bromate and a potential risk of 1 in 10^5 for 0.5 µg/L bromate.[4] The EPA promulgated the Stage 1 Disinfectants/Disinfection Byproducts (D/DBP) Rule in 1998 that established a maximum contaminant level (MCL) for bromate at 10 µg/L and for chlorite at 1000 µg/L.[5] At the same time, the agency set a maximum contaminant goal of zero for bromate. In a European Union (EU) directive, the EU also proposed a regulatory value of 10 µg/L bromate that must be met within 10 years after entry into the EU.[6] The World Health Organization has reduced their bromate guideline from 25 µg/L to a provisional value of 10 µg/L.[7]

Considerable efforts have focused on developing improved analytical methods for determining trace concentrations of inorganic DBPs in drinking water to meet current regulatory requirements. Traditionally, ion chromatography (IC) with suppressed conductivity detection has been used to determine chlorite, bromate, and chlorate in environmental waters, as described in Method 300.0 (B).[8] This method describes the use of an IonPac® AS9-SC column with a reported method detection limit (MDL) of 20 µg/L bromate. Method 300.1 (B) was published in the Stage 1 D/DBP Rule as an update to Method 300.0 to further reduce the bromate MDL from 20 to 1.4 µg/L.[9] Method 300.1 describes the use of an IonPac AS9-HC column with a carbonate eluent and a large volume injection followed by suppressed conductivity detection. The bromate detection limit can be reduced to <1 µg/L by using preconcentration after sample pretreatment.[10,11]

Postcolumn derivatization methods can also be used to quantify bromate at sub-µg/L concentrations. The Stage 2 D/DBP Rule published two methods that combine Method 300.1 (B) with a postcolumn reagent (PCR) to further improve the sensitivity of bromate determinations in environmental waters.[12] EPA Method 317.0 combines suppressed conductivity and the postcolumn addition of *o*-dianisidine (ODA) followed by visible detection to achieve a bromate MDL of 0.1 µg/L with a practical quantitation limit (PQL) of 0.5 µg/L.[3,13] Because the ODA reagent is a potential human carcinogen,[14] EPA Method 326.0 was developed as an alternative to Method 317.0. Method 326.0 uses a postcolumn reaction that generates hydroiodic acid (HI) in situ from an excess of potassium iodide (KI), which combines with bromate from the column effluent to form the triiodide anion (I_3^-); which is then detected by absorbance at 352 nm.[15]

Most published EPA methods specify the IonPac AS9-HC column and 9 mM sodium carbonate eluent for determination of DBP anions in drinking water. No hydroxide-selective column had been used for this application due to the lack of a column with suitable selectivity for the target anions (chlorite, bromate, and chlorate). The introduction of the IonPac AS19 column—a hydroxide-selective column—not only improved the selectivity for disinfection byproducts, but also provided the typical advantages observed when using a hydroxide eluent for trace applications, such as lower baseline noise and improved sensitivity. For example, the use of the AS19 column combined with electrolytically generated potassium hydroxide eluent resulted in a bromate MDL that is approximately three times less than with the AS9-HC column and carbonate eluent.[16,17] The AS19 can also be substituted for the AS9-HC in EPA Method 317.0.[18] In this application note, the authors demonstrate the performance of the AS19 column for EPA Method 326.0. This method allows quantification of bromate to 1 µg/L using suppressed conductivity detection with hydroxide eluent and postcolumn reaction with UV detection. The linearity, method detection limits, and quantification of the target DBP anions and bromide in municipal and bottled drinking waters are discussed.

EQUIPMENT

Dionex ICS-3000 Reagent-Free™ Ion Chromatography System (RFIC) consisting of:

- DP Dual Pump or SP Single Pump
- DC Dual Compartment with CD Conductivity Detector and Automation Manager (PN 061962)
- RCH-1 Postcolumn Reaction Heater (Dionex P/N 079944)
- VWD UV/Vis Absorbance Detector with PEEK® analytical flow cell (PN 6074.0200)
- AS Autosampler
- EG Eluent Generator with EluGen® EGC II KOH Cartridge (Dionex P/N 058900)
- Continuously-Regenerated Anion Trap Column, CR-ATC (Dionex P/N 060477)
- PC10 Postcolumn Pneumatic Delivery Module (Dionex P/N 050601)
- Knitted Reaction Coil, 500 µL, potted (for RCH-1) (Dionex P/N 039349)
- PEEK Mixing Tee (Dionex P/N 048227)
- 4 L plastic bottle assemblies (Four each) (Dionex P/N 063292)
- Three bottles for external water mode of suppression
- One bottle for 0.3 N sulfuric acid for online conversion of KI to I_3^-.

Chromeleon® Chromatography Data System

Polystyrene Autoselect™ vials with caps and septa, 10 mL (Dionex P/N 055058)

Nalgene Filter Unit, 0.2 µm nylon membrane, 1000 mL (VWR P/N 28198-514)

REAGENTS AND STANDARDS

Deionized water, Type I reagent grade, 18 MΩ-cm resistivity or better

Potassium Iodide (KI) (VWR P/N BDH0264-500g)

Ammonium Molybdate Tetrahydrate [$(NH_4)_6Mo_7O_{24}•4H_2O$] (Sigma-Aldrich, A7302)

Ethylenediamine (EDA) (Aldrich, 24,072-9)

Sulfuric Acid, 36 N (J.T. Baker INSTRA-ANALYZED 9673-33)

Bromide Standard, 1000 mg/L, 100 mL (Ultra Scientific, VWR P/N ICC-001)

Sodium Chlorite ($NaClO_2$) (Fluka 71388, 80% pure)

Bromate Standard, 1000 mg/L, 100 mL (Ultra Scientific, VWR P/N ICC-010)

Sodium Bromate ($NaBrO_3$) (EM SX 03785-1)

Sodium Chlorate ($NaClO_3$) (Aldrich, 24,414-7)

DL-Malic Acid, Disodium salt (Sigma-Aldrich, M6773)

CONDITIONS

Columns:	IonPac AS19 Analytical, 4 × 250 mm (Dionex P/N 062885) IonPac AG19 Guard, 4 × 50 mm (Dionex P/N 062887)
Eluent:	10 mM KOH from 0–10 min, 10–45 mM from 10–25 min, 45 mM from 25-30 min*
Eluent Source:	EGC II KOH with CR-ATC
Flow Rate:	1.0 mL/min
Temperature:	30 °C
Inj. Volume:	250 µL
Detection:	Suppressed conductivity, ASRS® 300, 4 mm (Dionex P/N 064554) AutoSuppression® external water mode 112 mA current
Background Conductance:	<1 µS
Noise:	~1 nS
System Backpressure:	~2400 psi
Run Time:	30 min

Postcolumn Reaction Conditions

UV Detection:	Absorbance @ 352 nm (deuterium lamp)
PCR Flow:	0.26 M potassium iodide at 0.3 mL/min
AMMS III:	0.3 N sulfuric acid at 2.5 mL/min
Postcolumn Heater Temp:	80 °C
UV Noise:	<0.1 mAU

*Eluent concentration returns to initial conditions 5 min prior to next injection.

PREPARATION OF SOLUTIONS AND REAGENTS

Deionized Water Preparation

Deionized water should be degassed prior to use in the RFIC system. The presence of oxygen in the system can adversely affect the baseline in the postcolumn system and it must be removed. Water can be degassed by filtering it through a 1 L, 0.2 µm nylon filter unit (Nalgene) then sonicating the solution under vacuum for 15 min. For larger volumes of water, a vacuum-safe glass container may be used by applying vacuum to the container while sonicating for 15 min.

Ethylenediamine (EDA) Preservation Solution

Dilute 2.8 mL of 99% EDA to 25 mL with DI water according to Section 7.1.3 in EPA Method 326.0 to prepare a 100 mg/mL solution. Use 50 µL of 100 mg/mL EDA per 100 mL of standard or sample so the final EDA concentration is 50 mg/L. Store this solution at <6°C and prepare fresh monthly.

Sulfuric Acid Solution (0.3 N)

Add 33.3 mL concentrated sulfuric acid to ~ 1000 mL DI water in a 2 L glass volumetric flask. Bring to volume with DI water. Transfer this solution (0.6 N sulfuric acid) to a 4 L plastic eluent bottle assembly. Fill the volumetric flask with an additional 2 L of DI water and add to the 4 L plastic eluent bottle to form a 0.3 N sulfuric acid solution.

Ammonium Molybdate Solution (2.0 mM)

Add 0.247 g ammonium molybdate $[(NH_4)_6Mo_7O_{24}•4H_2O]$ to approximately 50 mL DI water in a 100 mL volumetric flask according to Section 7.1.4 in EPA Method 326.0. Dissolve and bring to volume with DI water. This solution is stored in an opaque plastic bottle at <6 °C and prepared fresh monthly.

Postcolumn Reagent (PCR) (0.26 M KI with 43 µM Ammonium Molybdate Tetrahydrate)

Prepare the PCR by adding 43.1 g potassium iodide (KI) to a 1 L volumetric flask containing approximately 500 mL DI water and mixing to completely dissolve the solid. Bring to volume with DI water and mix. Filter and degas this solution by vacuum filtration through a 0.2 µm nylon filter unit and add 215 µL 2 mM ammonium molybdate solution. Immediately place the solution in the PC-10 reagent delivery vessel and pressurize with helium. Protect the solution from light by covering the PC-10 with aluminum foil. Properly protected from light, this reagent is stable for 24 h.

Stock Standard Solutions

Prepare 1000 mg/L stock standard solutions by dissolving the corresponding mass of the salt in 100 mL DI water (Table 1). Alternatively, commercially available 1000 mg/L standards may be used. Stock standards for most anions listed in Table 1 are stable for at least six months when stored at <6 °C. Chlorite is only stable for two weeks when stored at <6 °C and protected from light.

Prepare a secondary stock standard containing 5 mg/L each of chlorite, chlorate, and bromide by combining 0.5 mL of each anion in a 100 mL volumetric flask and bringing to volume with DI water. Prepare a separate secondary stock standard containing 1 mg/L of bromate only by adding 0.1 mL of the 1000 mg/L bromate stock to a 100 mL volumetric flask and bring to volume with DI water.

Table 1. Mass of Compounds Used to Prepare Stock Standard Solutions

Analyte	Compound	Amount (g)
Chlorite	Sodium chlorite ($NaClO_2$), 80%	0.1676
Bromate	Sodium bromate ($NaBrO_3$)	0.1180
Chlorate	Sodium chlorate ($NaClO_3$)	0.1275
Bromide	Sodium bromide (NaBr)	0.1288

Working Standard Solutions

Prepare dilute working standards by performing appropriate dilutions of the secondary stock solutions with deionized water containing EDA at a final concentration of 50 mg/mL. Dilute working standards should be prepared monthly, except those that contain chlorite which must be prepared every two weeks or earlier if evidence of degradation is indicated by repeated QC failures as discussed in Method 326. Store all working standard solutions at <6 °C.

Surrogate (Sodium Malate) Stock Solution

Prepare a 1000 mg/L solution of malate by dissolving 135 mg sodium malate in 100 mL of DI water. Add 100 µL of this solution to 100 mL sample for a spike level of 1 mg/L of surrogate.

SAMPLE PREPARATION

Filter samples, as necessary, through a 0.45 µm syringe filter, discarding the first 300 µL of the effluent. To prevent degradation of chlorite or the formation of bromate from hypobromous acid/hypobromite, preserve the samples by adding 50 µL of EDA preservation solution per 100 mL of sample. If a sample contains an excess amount of chlorite, follow the chlorite removal procedure described in Section 11.1.4.1 in Method 326.0 and reanalyze for bromate. The holding time for preserved samples stored at <6 °C is 28 days for bromate, chlorate, and bromide and 14 days for chlorite.

Use of dichloroacetic acid (DCA) or trichloroacetic acid (TCA) as a surrogate is not recommended. Instead, add 100 µL of a 1000 mg/L malate solution to 100 mL sample to obtain 1 mg/L malate surrogate.

SYSTEM PREPARATION AND SETUP

Prepare the ASRS 300 (Dionex P/N 064554) for use by hydrating the suppressor. Use a disposable plastic syringe and push approximately 3 mL degassed DI water through the Eluent Out port, followed by 5 mL degassed DI water through the Regen In port. Allow the suppressor to stand for approximately 20 min to fully hydrate the suppressor screens and membranes. Install the ASRS 300 for use in External Water mode by connecting the Regen Out of the suppressor to the Regen In of the CR-ATC. Connect the Regen In of the suppressor should directly to the external water source. Connect the Regen Out of the CR-ATC to the SRS Waste In of the EG degasser. This configuration allows the effluent of the analytical column to be connected to the conductivity detector after the suppressor then to the mixing tee of the PCR system. Adjust the head pressure on the external water to achieve a total flow of 4-6 mL/min. Depending on the backpressure of the installed components, the pressure on

the external water reservoir should fall between 7–10 psi. Lower noise may be achieved if the total external water flow rate is as close to 6 mL/min as possible.

Prepare the AMMS 300 (P/N 064558) for use by hydrating the suppressor. Using a disposable plastic syringe, push approximately 3 mL 0.3 N sulfuric acid through the Eluent Out port, followed by 5 mL 0.3 N sulfuric acid through the Regen In port. Allow the suppressor to stand for approximately 20 min. Install the suppressor in the chemical regeneration mode. Adjust the pressure on the 0.3 N sulfuric acid reservoir to deliver a flow rate of 2–3 mL/min. Attach a piece 0.010" ID PEEK tubing approximately 45 cm in length to the end of the tubing attached to the AMMS 300 Regen Out port to yield a backpressure of ~10–15 psi.

Install the EGC II KOH cartridge in the EG and configure it with the CR-ATC according to the CR-TC Quickstart (LPN 031911). Use the Chromeleon system configuration to set up and control the EGC II KOH cartridge. Condition the cartridge as directed by the EGC II Quickstart (LPN 031909) with 50 mM KOH at 1 mL/min for 30 min. Install a 4 × 50 mm AG19 and 4 × 250 mm AS19 column. Confirm the pressure displayed by the pump is at or near the optimal pressure of ~2300 psi when 45 mM KOH is delivered at 1 mL/min. This allows the EG degas assembly to effectively remove hydrolysis gases from the eluent. If necessary, install additional backpressure tubing to adjust the pressure to 2300 ± 200 psi.

Configure the ICS-3000 with the PCR system as shown in Figure 1. Orange PEEK tubing (Dionex P/N 042855, 0.020" ID) should be used between the PC-10 and the AMMS and between the AMMS and the mixing tee. The orange PEEK line from the AMMS should join the mixing tee directly opposite the black PEEK line from the conductivity detector. Black PEEK tubing (Dionex P/N 042690, 0.010" ID) should be used from the postcolumn reactor to the UV flow cell. The waste line from the UV flow cell should be made of a length of green PEEK tubing (Dionex P/N 044777, 0.030" ID) which is directed to a waste container. If noise greater than 0.1 mAU is consistently observed after system equilibration, a short piece of black PEEK tubing can be inserted between the cell and the waste line tubing to reduce trapped bubbles in the cell and lower the noise.

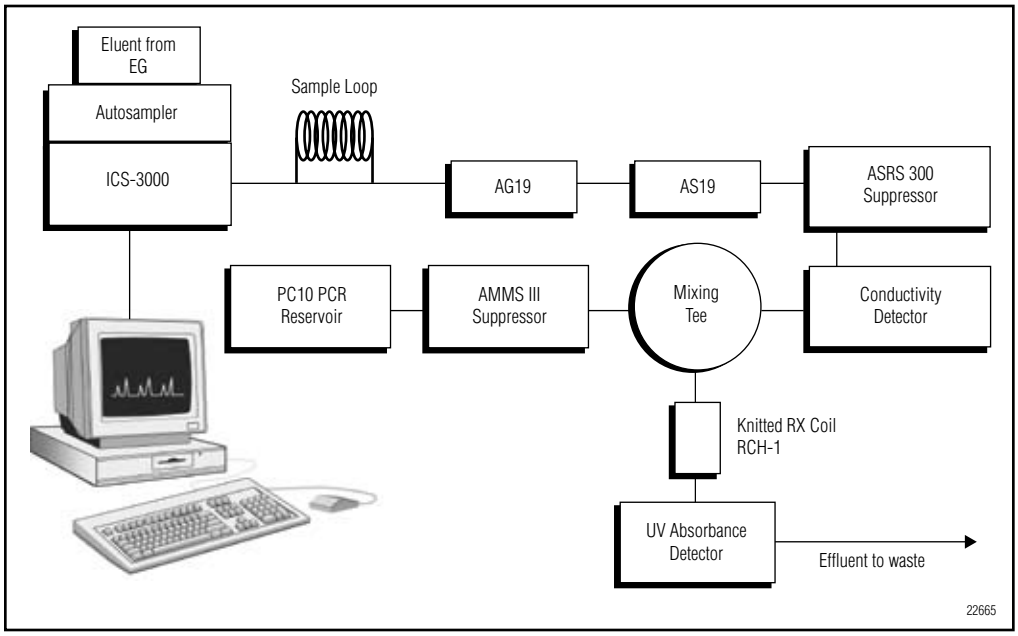

Figure 1. IC system configuration for EPA Method 326.0.

The PCR flow rate for this application was determined based on the analytical/PCR flow rate ratio provided in EPA Method 326.0. For the system used here, a 0.3 mL/min PCR flow rate was required. Set the temperature on the RCH-1 to 80 °C and the wavelength on the VWD to 352 nm. Allow both the suppressed conductivity and visible detection baselines to stabilize. Measure the PCR flow rate by collecting the combined effluent from the IC pump and PCR system in a pre-weighed vial for at least 5 min. After 5 min, weigh the collected solution. The mass of the solution is divided by the collection time (e.g., 5 min) to determine the total flow rate of the system. The PCR flow rate is equal to the difference between the measured total flow rate and the flow rate delivered by the IC pump. Adjust the pressure of the postcolumn delivery module (PC10) and measure the flow rate again until the correct flow rate of 0.3 mL/min is achieved. Acceptable values for this flow rate range between 0.28 mL/min to 0.33 mL/min. The delivery pressure can range between 26-50 psi. If the pressure needed to reach 0.3 ml/min of PCR is greater than 50 psi, check the system for leaks or possible restrictions in flow, such as crimped or clogged tubing. It is critical to confirm the flow rate daily, in addition to whenever the PCR is changed, or if the quality control standard deviates from the EPA's acceptance criteria. Prior to sample analysis, inject 250 µL DI water/method blank. No peaks should elute at the same retention times as the target analytes. An equilibrated system should display a suppressed background conductivity <1 µS, and peak-to-peak noise of ~1–2 nS per min (UV peak-to-peak noise <0.1 mAU per min). Upon initial installation and configuration of the system it may require 8 h to allow the conductivity detection to equilibrate and 48 h for the postcolumn UV detection to achieve a noise level of <0.1 mAU. For systems that are being restarted after a short shutdown, such as overnight or for a weekend, this equilibration may require 2–3 hours.

SYSTEM SHUTDOWN

The following steps should be taken to protect the system components and ensure smooth startup.

1: With the PCR and IC eluent flowing, wearing latex or other suitable protective gloves and safety glasses, remove the line at the mixing tee that leads back to the AMMS Eluent Out port and plug this port on the tee. Turn off the pressure at the PC10. Allow eluent flow (10 mM KOH at 1 mL/min) for 30 min through the system with the Reaction Coil Heater (RCH) at 80 °C.

2: While the system is flushing with eluent, remove the PCR from the PC10 and flush the reservoir with DI water. Fill the reservoir with DI water and install in the PC10. Remove the line from the Eluent In port of the AMMS and flush this line with DI water from the PC10. Re-install this line to the Eluent In port of the AMMS and flush the AMMS with DI water.

3: At the mixing tee, disconnect the tubing leading from the Cell Out of the conductivity detector. Connect this line to a separate waste line of green PEEK tubing. The conductivity detection portion of the system is now separate from the postcolumn detection portion of the system and can be shut down. The pressure for the external water can be shut off and the water reservoirs vented to stop flow. If the conductivity system will be shut down for several days, remove the Eluent In line from the ASRS and plug the port on the ASRS to protect the suppressor from dehydration. Turn on the PC10 using the same pressure that was used for delivering the PCR. Flow through the AMMS should be approximately 1–1.5 mL/min. Connect the line from the Eluent Out® port of the AMMS to the mixing tee. Flush acidified DI water from the AMMS through the RCH at 80 °C. Flush for 30 min to remove the residual hydroxide eluent from the UV cell.

4: Turn off the UV lamp and the RCH. Allow the RCH to cool to <50 °C and then turn off the PC10 pressure. Turn off pressure to the external H_2SO_4 and vent the H_2SO_4 reservoir.

PRECAUTIONS

- When the application is configured to run this method for the first time, and whenever an AMMS 300 is replaced, it will require 48-72 h of operation for the PCR system to equilibrate and the noise on the VWD to fall below 0.1 mAU. Detection of 0.5 µg/L bromate should not be attempted until after the system has equilibrated. After this initial equilibration, the system should equilibrate and be ready to run samples in 2–3 h after shutdown.
- To achieve the lowest noise and drift, maintain consistent flow rates of the PCR, the external water, and 0.3 N sulfuric acid. A dual-stage regulator is highly recommended between the source gas (helium or nitrogen, grade 4.6 or better) and the regulators for the individual pressurized bottles. Use of house-supplied compressed gas is not recommended.
- Movement of the waste line leading from the UV flow cell can impact the noise observed in the UV. Secure this line so that it is not located where it can be disturbed.
- Daily checks of the pressures and flow rates for all pneumatically fed solutions are recommended. If the pressure needed to deliver 0.3 mL/min of PCR continually increases, the UV flow cell should be backflushed with eluent to remove any potential particulates not removed by filtration. To backflush the cell, remove the PCR line from the mixing tee and plug the tee at that port. Reverse the flow into the UV cell. Allow the eluent to flow for 1–2 min. Reconnect the line to the cell inlet and reconnect the waste line to the cell outlet.
- The presence of oxygen in the eluent will increase the background signal observed at the VWD detector. It is strongly recommended that the DI water be thoroughly degassed by vacuum and sonication prior to use.
- Filtration of the potassium iodide reagent through a Nalgene 0.2 µm nylon filter unit is strongly recommended to remove insoluble material. The membrane will discolor to yellow upon initial use. This discoloration will not affect the PCR that has been filtered and it can be used for bromate analysis. If desired, the filter unit can be reused if promptly rinsed with DI water and an additional 1000 mL of DI water is flushed through to clean the nylon membrane. Successive filtration with this filter unit should not further discolor the membrane.

RESULTS AND DISCUSSION

US EPA Method 326.0 specifies the use of an IonPac AS9-HC column with 9 mM sodium carbonate eluent for determination of chlorite, chlorate, and bromide by suppressed conductivity detection and bromate by suppressed conductivity and UV absorbance detection after postcolumn reaction with acidified potassium iodide.[15] Method 326.0 reports a detection limit of 1.2 µg/L for bromate using a 225 µL injection with suppressed conductivity detection and 0.17 µg/L by UV absorbance detection. Previously, the authors demonstrated bromate detection limits by suppressed conductivity can be reduced further to 0.34 µg/L using electrolytically generated hydroxide eluent and a hydroxide-selective IonPac AS19 column.[16] In addition, it was demonstrated that suppressed conductivity detection in conjunction with *o*-dianisidine postcolumn reagent may be used with electrolytically generated hydroxide eluent and the AS19 column to achieve a bromate detection limit equivalent to that reported in Method 317.0[13] using visible detection. In this application note, the authors examine the feasibility of using the IonPac AS19 column with the combination of suppressed conductivity detection and a postcolumn reaction system for UV absorbance detection. The use of a suitable hydroxide-selective column for this application allows for lower detection limits for the target disinfection byproduct anions by suppressed conductivity detection while providing the improved sensitivity and selectivity for bromate obtained by the postcolumn reaction system.

Figure 2 shows chromatograms of 1 µg/L bromate and 10 µg/L each of chlorite, chlorate, and bromide. The top chromatogram shows the response obtained using suppressed conductivity detection and the bottom chromatogram using UV detection after postcolumn reaction with acidified KI. Bromate is well-resolved from chlorite. Although bromate is easily detected at this concentration using suppressed conductivity detection, enhanced response is observed after postcolumn reaction with acidified KI followed by UV detection.

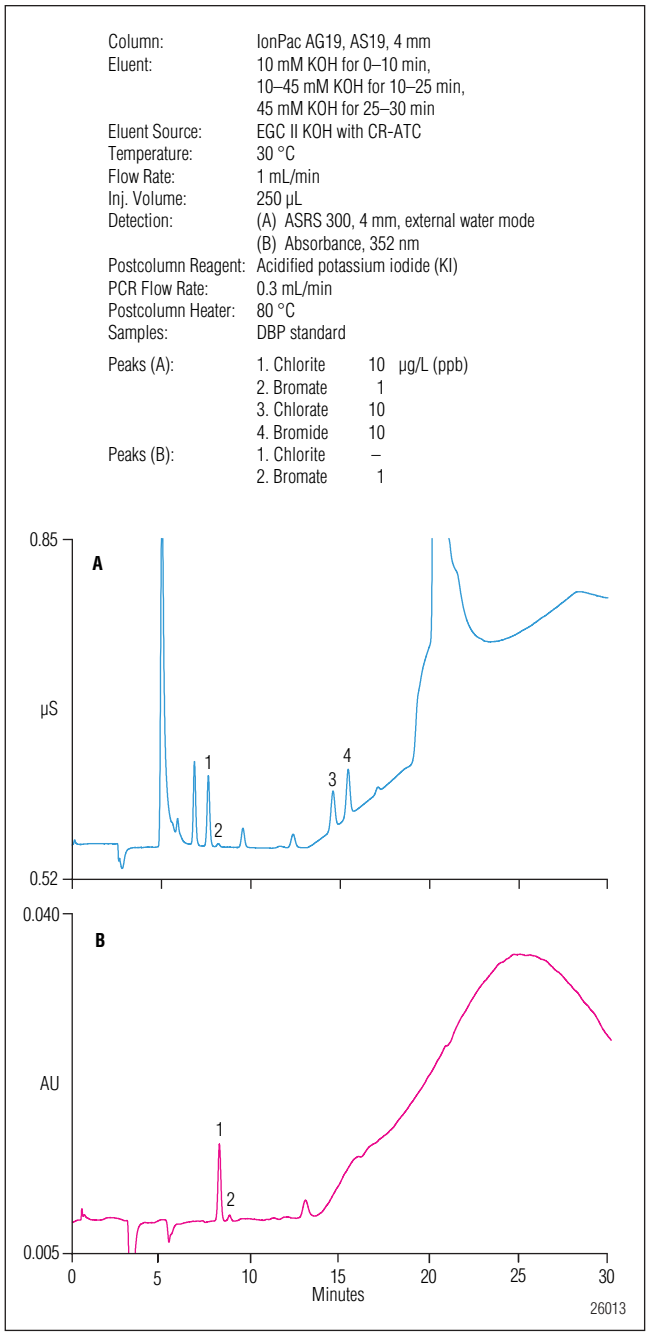

Figure 2. Separation of low ppb DBP anions and bromide on the IonPac AS19 column using suppressed conductivity detection and UV absorbance after PCR with acidified potassium iodide.

Table 2 summarizes the calibration data and method detection limits (MDLs) obtained for the DBP anions and bromide using the AS19 column and electrolytically generated hydroxide eluent with suppressed conductivity and UV detection modes. MDLs for the target analytes were determined by performing seven replicate injections of reagent water fortified at a concentration of three to five times the estimated instrument detection limit.[15] The calculated MDLs for bromate using suppressed conductivity detection followed by postcolumn reaction and UV detection were 0.12 µg/L and 0.18 µg/L, respectively. During the determination of the MDLs, the noise observed in the suppressed conductivity detection channel was unusually low (0.3-0.5 nS.) In addition, these MDLs were determined by injection of standards with minimal interference from other components that may be present in samples. The detection limit of 0.12 µg/L should not be expected in environmental samples. This method allows quantification of bromate at 1 µg/L using suppressed conductivity, and 0.5 µg/L with UV detection using an AS19 column with electrolytically generated potassium hydroxide eluent. Accordingly, bromate was calibrated from 1–50 µg/L with suppressed conductivity and 0.5–15 µg/L with UV detection. Chlorite, chlorate, and bromide were each calibrated from 5–500 µg/L. These calibration ranges are expected to cover the typical concentrations found in environmental samples.

Table 2. Linearity and MDLs for DBP Anions and Bromide

Analyte	Range (µg/L)	Linearity (r^2)	MDL Standard (µg/L)	Calculated MDL (µg/L)
Chlorite	5–500	0.9993	0.6	0.33
Bromate (conductivity)	1–50	0.9997	0.5	0.12
Bromate (UV)	0.5–15	0.9999	0.5	0.17
Chlorate	5–500	0.9991	1.0	0.40
Bromide	5–500	0.9991	1.9	0.29

EPA Method 326.0 requires an initial demonstration of capability to characterize the instrument and laboratory performance of the method prior to performing sample analyses, as described in Section 9.2.15 An initial demonstration of precision, accuracy, and analysis of a quality control sample (QCS) are part of the criteria used for this characterization. To evaluate the precision and accuracy of the conductivity detector, Method 326.0 recommends using 20 µg/L each of the four target anions. However, because electrolytically generated hydroxide eluent improves the overall sensitivity of the method, the authors determined that 5 µg/L bromate and 10 µg/L each of chlorite, chlorate, and bromide standards were suitable for characterizing the instrument and laboratory performance. For the absorbance detector, 2 µg/L bromate was used. EPA Method 326.0 lists an RSD ≤20% and an average recovery of ±15% as acceptable performance. The precision of our replicate analyses was <5.8% RSD and the accuracy was 92–102%, well within EPA's acceptance criteria. A QCS should be analyzed after the calibration curves are initially established, on a quarterly basis, or as required to meet data quality needs. All QCS analyses in our experiments met the EPA's ±15% recovery criteria.

Table 3 summarizes the method performance for the determination of trace DBP anions and bromide in municipal and bottled drinking water samples. For samples fortified with low concentrations of the target analytes, recoveries ranged from 90–112%, well within the 75–125% acceptance criteria of EPA Method 326.0. Figures 3–6 illustrate the performance for the determination of DBP anions and bromide in municipal tap waters and bottled drinking waters using the IonPac AS19 column. Figure 3 shows chromatograms of a 250 µL injection of tap water sample B using suppressed conductivity and UV detection at 352 nm after postcolumn reaction with acidified KI. Bromide was not

Table 3. Recoveries of Trace DBP Anions in Spiked Water Samples

Analyte	Amount Found (µg/L)	Amount Added (µg/L)	Recovery (%)
Tap Water Sample A			
Chlorite	4.6	6.9	95.9
Bromate (conductivity)	0.32	1.0	95.5
Bromate (UV/Vis)	0.35	1.0	98.1
Chlorate	74.7	80.1	97.5
Bromide	34.6	39.9	95.4
Tap Water Sample B			
Chlorite	< MDL	4.6	108.0
Bromate (conductivity)	2.4	3.0	102.8
Bromate (UV/Vis)	2.8	3.0	94.7
Chlorate	62.4	69.7	96.7
Bromide	17.5	19.9	92.3
Bottled Water Sample A-1			
Chlorite	< MDL	4.9	105.3
Bromate (conductivity)	9.5	9.7	101.1
Bromate (UV/Vis)	10.8	9.7	97.3
Chlorate	< MDL	6.2	99.8
Bromide	19.0	19.9	95.0
Bottled Water Sample A-2			
Chlorite	<MDL	6.4	95.9
Bromate (conductivity)	8.7	9.7	95.7
Bromate (UV/Vis)	8.5	9.7	98.4
Chlorate	< MDL	6.4	107.6
Bromide	3.2	6.4	111.8
Bottled Water Sample B			
Chlorite	< MDL	4.9	108.3
Bromate (conductivity)	< MDL	1.0	102.4
Bromate (UV/Vis)	< MDL	1.0	104.5
Chlorate	< MDL	5.2	101.5
Bromide	10.4	9.9	90.8

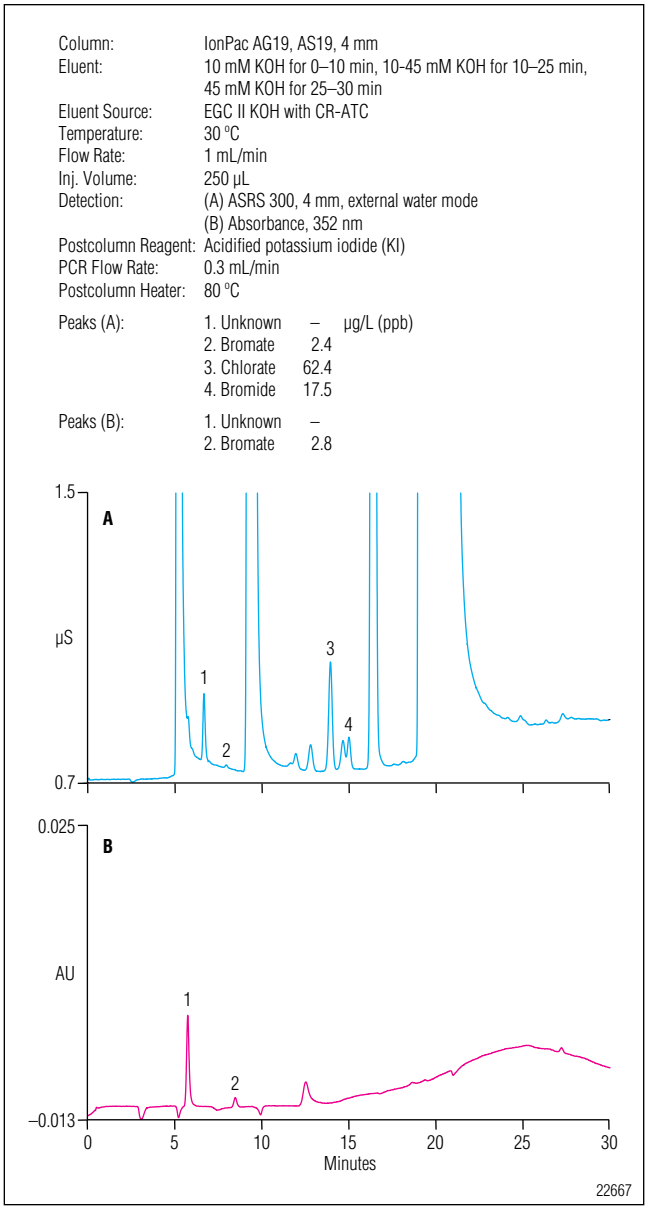

Figure 3. Determination of trace DBP anions and bromide in tap water sample B using suppressed conductivity detection and UV absorbance after PCR with acidified iodide.

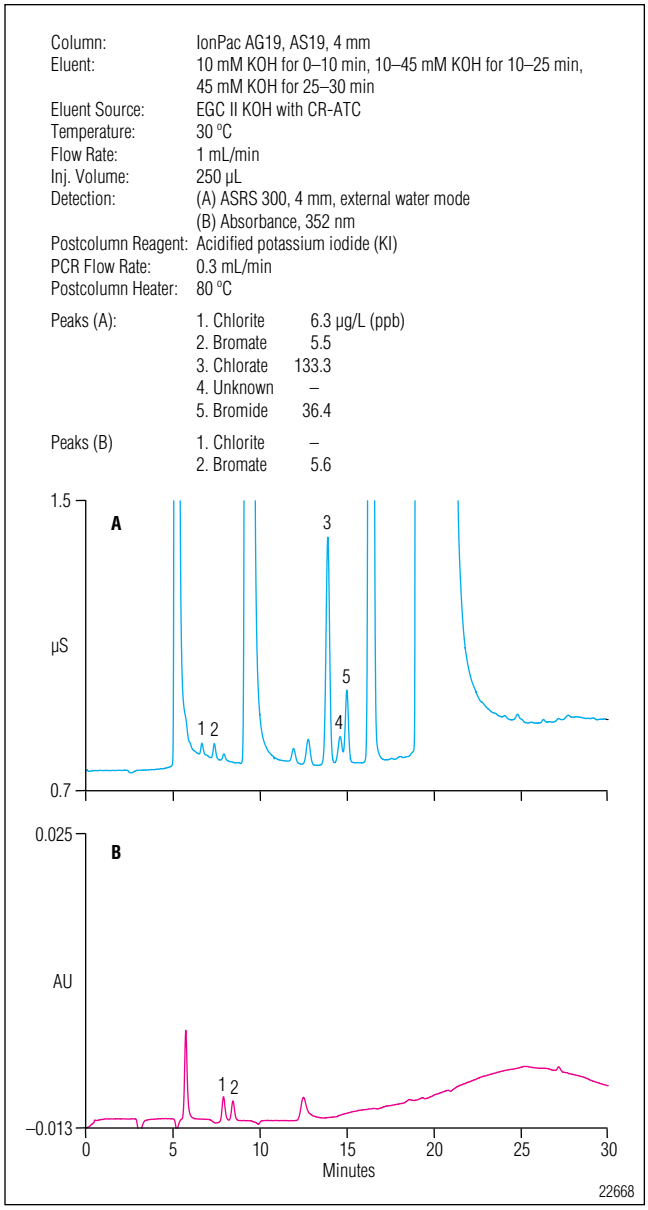

Figure 4. Determination of DBP anions spiked into tap water sample B using suppressed conductivity detection and UV absorbance after PCR with acidified potassium iodide.

completely resolved from the earlier eluting unknown analyte. However, fortification of the sample with 20 µg/L bromide produced good recovery (92%.) Bromate is clearly visible at approximately 3 µg/L with the absorbance detector; however, this concentration was also easily determined using suppressed conductivity detection with the AS19 column. Figure 4 shows the same sample spiked with chlorite, bromate, chlorate, and bromide at concentrations ranging from 3–70 µg/L. Analyte recoveries for this sample ranged from 92–108%.

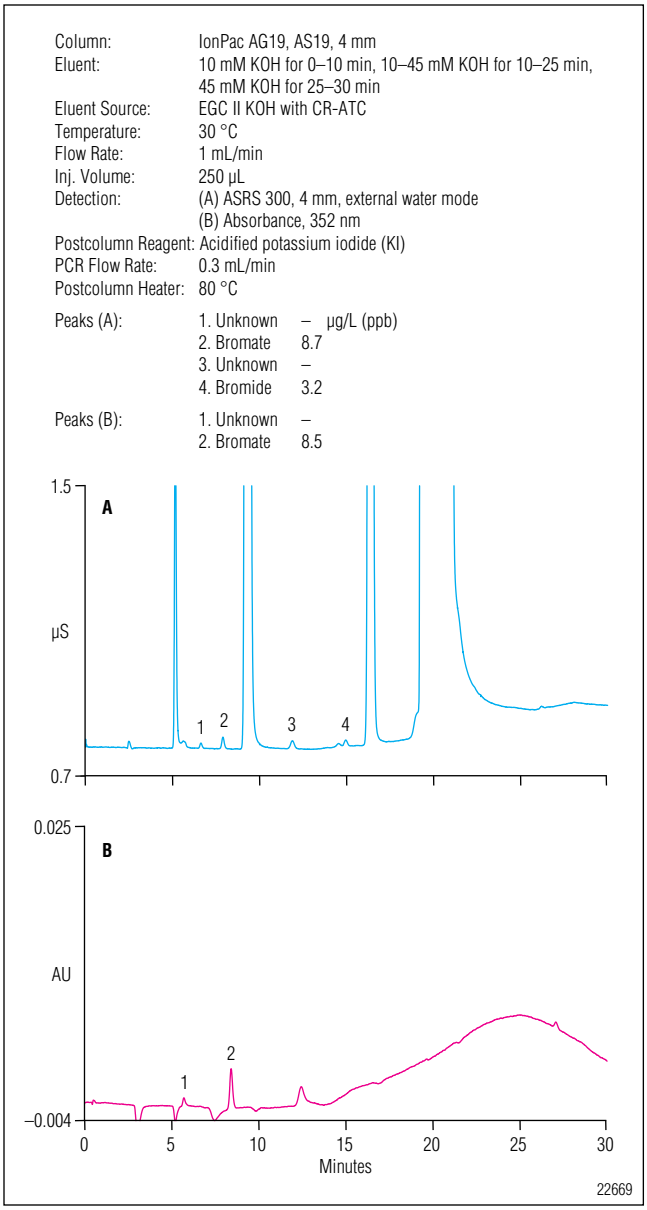

Figure 5. Determination of DBP anions and bromide in bottled water sample A-2 using suppressed conductivity detection and UV absorbance after PCR with acidified potassium iodide.

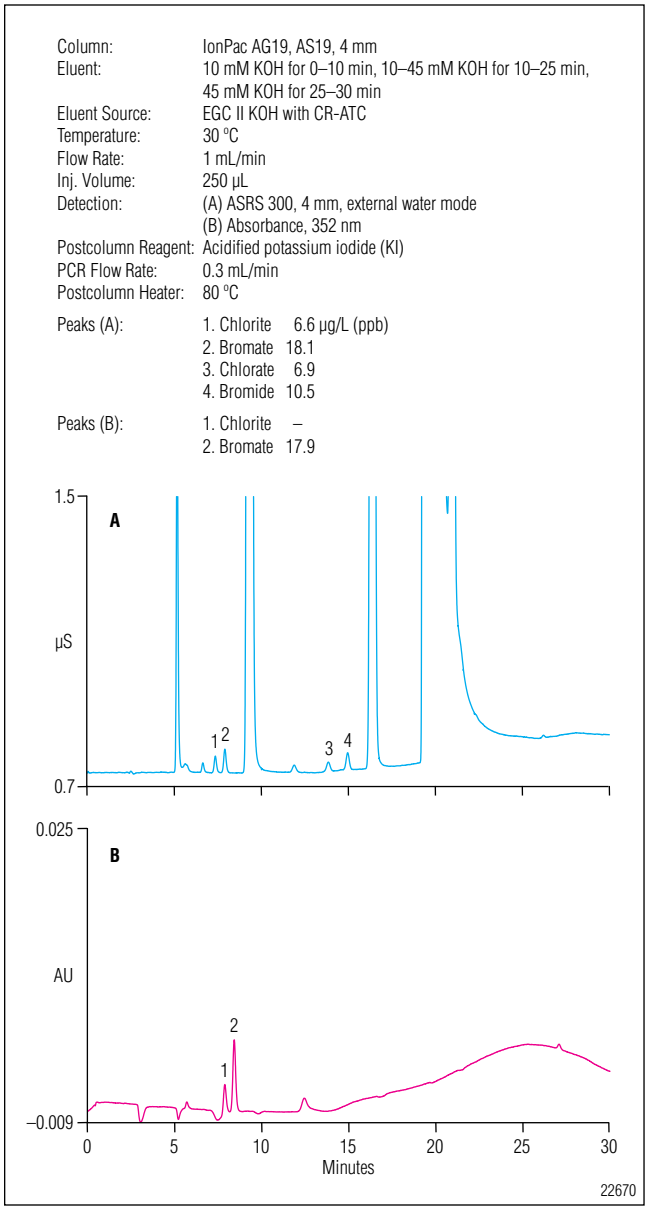

Figure 6. Determination of DBP anions and bromide in spiked bottled water sample A-2 using suppressed conductivity detection and UV absorbance after PCR with acidified potassium iodide.

Bottled Water sample A-2 is the same brand of bottled water product as A-1, except it was purchased approximately seven months later. The initial bromate concentration detected in A-1 was 10 µg/L, the current EPA regulatory limit. The bromate concentration found in sample A-2 was ~8.7 µg/L. Figure 5 shows chromatograms of the ozonated bottled drinking water sample A-2 containing 8.7 µg/L bromate and 3.2 µg/L bromide. The top chromatogram (Figure 5A) shows the response of the target analytes obtained by suppressed conductivity detection, and the bottom chromatogram (Figure 5B) was obtained by UV detection after postcolumn reaction with acidified KI. The bromate response is easily observed on both detector channels; however, the response using UV detection is enhanced compared to the conductivity detector. Figure 6 shows the same bottled drinking water sample spiked with 6–10 µg/L of the target DBP anions and bromide.

EPA Method 326.0 stipulates use of a surrogate to be added to a sample before filtration and other processing to monitor method performance. This surrogate should: 1) Chemically resemble the target analytes, 2) Be commercially available at a defined purity, 3) Be stable in solution when properly stored, 4) Be unlikely to be found in the sample, and 5) Not coelute with the analytes of interest. The choice of surrogate used can be made by the analyst, but data must be maintained to show that the surrogate used meets the requirements listed above. The recommended surrogate in EPA 326.0 is dichloroacetic acid (DCA). This surrogate interferes with quantification when using hydroxide eluent, therefore, trichloroacetic acid (TCA) has been suggested as a replacement for DCA as a surrogate. If samples have high amounts of carbonate, the carbonate can interfere with determination of TCA, making it a poor surrogate for this method. To minimize this peak overlap between carbonate and the surrogate, sodium malate was investigated for use in this capacity. None of the above-mentioned options for use as a surrogate are detected by UV using the PCR. Malate is not typically present in drinking water samples and it is also well-separated from the analytes of interest and from the carbonate peak without obscuring other peaks. Figure 7 shows analysis of a municipal tap water sample containing chlorate, bromate, and bromide. The malate peak is separated from the carbonate peak and is therfore suitable for use as an internal surrogate. Eight sequential injectons of 1 mg/L malate in a DBP standard showed an RSD of 0.73 for peak area and an RSD of 0.01 for retention time. Given this data, malate is shown to be an appropriate surrogate for samples with high carbonate concentrations when using these conditions.

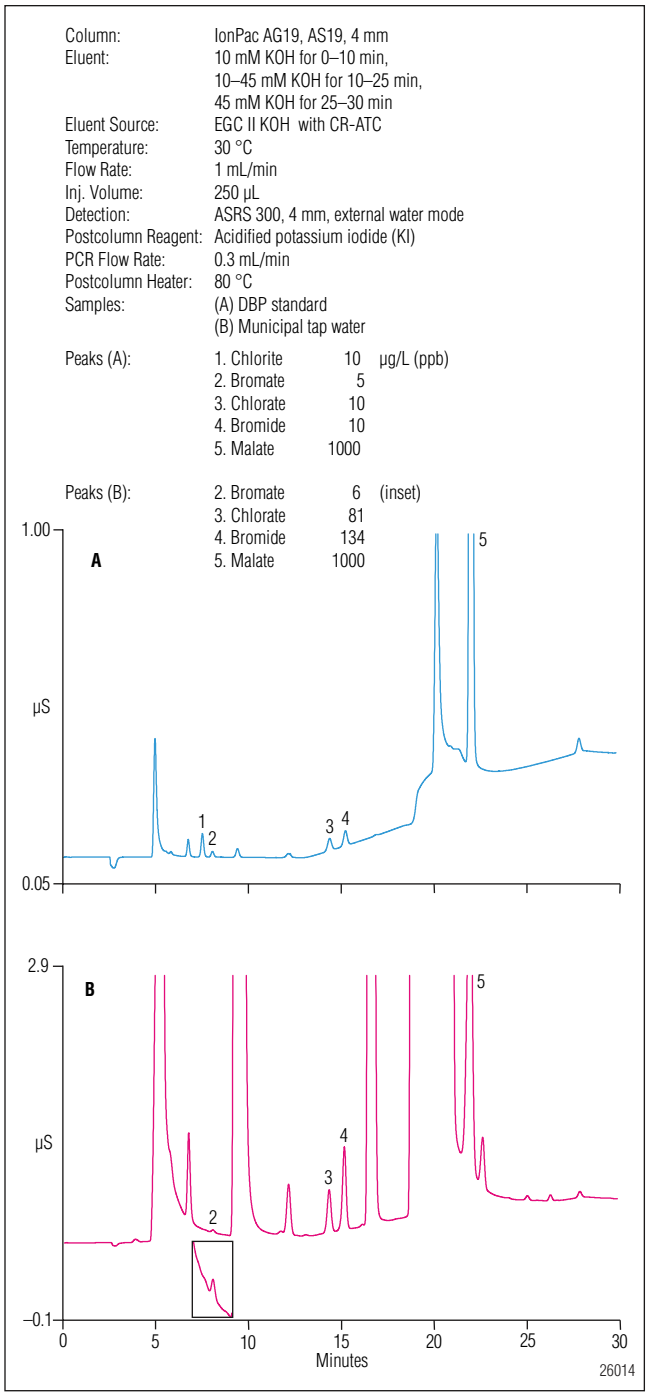

Figure 7. Determination of DBP anions in water using malate as a surrogate.

RUGGEDNESS

The method was run for several weeks to confirm ruggedness. With a range of PC10 delivery pressures between 26–54 psi, and PCR flow rates ranging between 0.28–0.33 mL/min, the peak area determined for a bromate standard of 1 ppb had an RSD of 9.2 over 21 business days of analysis with a peak retention time RSD of 0.89. During this period, two AMMS suppressors and two different flow cells were used to evaluate the effect of changes to the system on the response. Aside from the equilibration time required when changing the AMMS, no significant effect of the individual suppressor or flow cell was observed.

Low peak area responses in individual injections during this 21 day period were observed when the pressure required to deliver 0.3 mL/min of PCR from the PC10 increased when no other changes were made. For this reason, it is recommended that any increase or decrease in the delivery pressure required after initial system equilibrium be immediately investigated and corrected. Backpressure increases from the UV flow cell can be corrected by flushing the cell as described in the precautions section. Restrictions in the PCR tubing can lead to poor results due to potential clogging and eventual changes in the flow of the reagent. Replace any crimped PEEK tubing to ensure consistent flow rates of all solutions.

Changes in the flow rate of the external water or the 0.3 N sulfuric acid will also change the baseline observed in the UV detection channel. Changes in the delivery pressures—and therefore flow rates—of these reagents can lead to baseline drift in the UV detection channel. If these flow rates are held constant, a stable baseline can be achieved. If baseline drift is observed, confirm that no tubing is crimped or blocked before making changes to the consumables on the ICS-3000.

CONCLUSION

This application note describes an IC method using electrolytically generated potassium hydroxide eluent combined with a hydroxide-selective IonPac AS19 column for determination of trace DBP anions and bromide using suppressed conductivity detection followed by postcolumn addition of acidified KI with UV detection. The postcolumn reaction improves the selectivity and sensitivity for the determination of bromate in environmental waters. The use of hydroxide eluent improved the sensitivity for bromate using suppressed conductivity and UV detection compared to using 9 mM carbonate eluent with the AS9-HC column, as described in Method 326.0.

The use of postcolumn addition and UV detection with the AS19 column allowed quantification of bromate from 0.5–15 µg/L without compromising the suppressed conductivity detection of chlorite, bromate, chlorate, and bromide. However, the significant improvement in bromate detection by suppressed conductivity using electrolytically generated hydroxide eluent may eliminate the need for postcolumnn reaction for some environmental samples. Finally, this method demonstrates that the hydroxide-selective AS19 column combined with hydroxide eluent can be successfully used in place of the AS9-HC column for compliance monitoring by US EPA Method 326.0.

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