Determination of Disinfection Byproduct Anions and Bromide in Drinking Water Using a Reagent-Free Ion Chromatography System Followed by Postcolumn Addition of an Acidified On-Line Generated Reagent for Trace Bromate Analysis

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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 treatments 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, whereas 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 U.S. Environmental Protection Agency (EPA) has estimated a potential cancer risk of 1 in 104 for a lifetime exposure to drinking water containing 5 µg/L bromate and a potential risk of 1 in 105 for 0.5 µg/L bromate.[4] The U.S. 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 an MCL for chlorite of 1000 µg/L.[5] At the same time, the U.S. EPA set a maximum contaminant goal of zero for bromate. In an EU (European Union) 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 a Thermo Scientific™ Dionex™ 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 a Dionex 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] However, the ODA PCR is a potential human carcinogen.[14] Therefore, 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), that combines with bromate from the column effluent to form the triiodide anion (I_3^-) that is detected by absorbance at 352 nm.[15]

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Most published EPA methods specify the use of a Dionex IonPac AS9-HC column and a 9 mM sodium carbonate eluent for determining DBP anions in drinking water. A hydroxide-selective column had not been used for this application due to the lack of a suitably selective column for the target DBP anions, chlorite, bromate, and chlorate. The introduction of the Dionex IonPac AS19, a hydroxide-selective column, not only improved the selectivity for disinfection byproducts, but also provided the typical advantages observed when using hydroxide eluent for trace applications, such as lower baseline noise and improved sensitivity. For example, the use of the Dionex IonPac AS19 column combined with electrolytically generated potassium hydroxide eluent resulted in a bromate MDL approximately three times lower than with the IonPac AS9-HC column and carbonate eluent.[16,17] The Dionex IonPac AS19 can also be substituted for the IonPac AS9-HC in EPA Method 317.0.[18] In this application note, we demonstrate the performance of the Dionex IonPac AS19 column for EPA Method 326.0. This method allows quantification of bromate to 1 µg/L by suppressed conductivity detection with a hydroxide eluent and 0.5 µg/L using 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

- Thermo Scientific™ Dionex™ ICS-3000 Reagent-Free™ Ion Chromatography (RFIC™) consisting of:
  - DP Dual Pump or SP Single Pump
  - DC Dual Compartment with a CD conductivity detector and an Automation manager (PN 061962) equipped with a RCH-1 Postcolumn Reaction Heater (P/N 079944)
  - VWD UV/Vis Absorbance Detector with a PEEK™ analytical flow cell (PN 6074.0200)
  - AS Autosampler
  - EG Eluent Generator with a Thermo Scientific™ Dionex™ EluGen™ EGC II KOH Cartridge (P/N 058900)
  - Thermo Scientific™ Dionex™ CR-ATC Continuously Regenerated Anion Trap Column (P/N 060477)
  - PC10 Postcolumn Pneumatic Delivery Module (P/N 050601)
  - Knitted Reaction Coil, 500 µL, potted (for RCH-1) (P/N 039349)
  - PEEK Mixing Tee (P/N 048227)
  - Four 4 L plastic bottle assemblies (P/N 063292)
  - Three bottles for external water mode of suppression
  - One bottle for 0.3 N sulfuric acid for the online conversion of KI to I_3^-.
- Thermo Scientific™ Dionex™ Chromeleon™ Chromatography Management Software
- Polystyrene Autoselect vials with caps and septa, 10 mL (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 MW-cm resistivity or better
- Potassium Iodide (KI) (VWR P/N BDH0264-500g)
- Ammonium Molybdate Tetrahydrate [$(NH_4)_6Mo_7O_{24}\bullet 4H_2O$] (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:	Dionex IonPac AS19 Analytical, 4 × 250 mm (P/N 062885) Dionex IonPac AG19 Guard, 4 × 50 mm (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:	Dionex IEGC II KOH with Dionex CR-ATC
Flow Rate:	1.0 mL/min
Temperature:	30 °C
Inj. Volume:	250 µL
Detection:	Suppressed conductivity, Thermo Scientific™ Dionex™ ASRS™ 300 Anion Self-Regenerating Suppressor™, 4 mm (P/N 064554) auto-suppression, 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 at 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

*Method returns to 10 mM KOH for 5 min prior to 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 will 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) and then sonicating the solution while it is 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 of concentrated sulfuric acid to ~ 1000 mL of DI water in a 2 L glass volumetric flask. Dilute the solution to 2 L 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 this water 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 of ammonium molybdate [$(NH_4)_6Mo_7O_{24}\bullet 4H_2O$] to about 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)

The PCR is prepared by adding 43.1 g of potassium iodide (KI) to a 1 L volumetric flask containing approximately 500 mL DI water and mixing to completely dissolve the solid. Dilute 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 of 2.0 mM ammonium molybdate solution. Immediately place the solution in the PC10 reagent delivery vessel and pressurize with helium. Protect the PC10 from light by covering with aluminum foil. If 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 diluting 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 dilute 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 of sodium malate in 100 mL of DI water. Add 100 µL of this solution to 100 mL of sample to spike the sample with 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 then the chlorite removal procedure described in Section 11.1.4.1 in Method 326.0 must be followed and the sample must then be reanalyzed 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 dichloroacetate (DCA) or trichloroacetate (TCA) as a surrogate is not recommended. Instead, add 100 µL of a 1000 mg/L malate solution to 100 mL of sample to obtain 1 mg/L of the malate surrogate.

System Preparation and Setup

Prepare the Dionex ASRS 300 Anion Self-Regenerating Suppressor (P/N 064554) for use by hydrating the suppressor. Use a disposable plastic syringe and push approximately 3 mL of degassed DI water through the Eluent Out port and 5 mL of 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 Dionex ASRS 300 for use in the external water mode by connecting the Regen Out of the suppressor to the Regen In of the Dionex CR-ATC column. The Regen In of the suppressor should connect directly to the external water source. The Regen Out of the Dionex CR-ATC column is then connected to the SRS Waste In of the EG degasser. This configuration allows the eluent out of the analytical column to be connected to the conductivity detector after the suppressor and 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 should fall between 7–10 psi. Lower noise will be achieved if the total external water flow rate is as close to 6 mL/min as possible.

Prepare the Thermo Scientific™ Dionex™ AMMS™ 300 Anion MicroMembrane™ Suppressor (P/N 064558) for use by hydrating the suppressor. Use a disposable plastic syringe and push approximately 3 mL of 0.3 N sulfuric acid through the Eluent Out port and 5 mL of 0.3 N sulfuric acid through the Regen In port. Allow the suppressor to stand for approximately 20 min to fully hydrate the suppressor screens and membranes. 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. The pressure needed will be ~10–15 psi if an approximately 45 cm piece of 0.010" i.d. PEEK tubing is connected to the end of the tubing attached to the Dionex AMMS 300 suppressor Regen Out port.

Install the Dionex EGC II KOH cartridge in the EG and configure it with the Dionex CR-ATC column according to the Dionex CR-TC Quickstart (LPN 031911). Use the Chromeleon system configuration to set up the Dionex EGC II KOH cartridge with the software. Condition the cartridge as directed by the Dionex EGC II Quickstart (LPN 031909) with 50 mM KOH at 1 mL/min for 30 min. Install a 4 × 50 mm Dionex IonPac AG19 and 4 × 250 mm Dionex IonPac AS19 column. Make sure the pressure displayed by the pump is at an 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 Dionex ICS-3000 with the PCR system as shown in Figure 1. Orange PEEK tubing (P/N 042855, 0.020" i.d.) should be used between the PC10 and the Dionex AMMS suppressor and the mixing tee. The orange PEEK line from the Dionex AMMS suppressor should join the mixing tee directly opposite the black PEEK line from the conductivity detector. Black PEEK tubing (P/N 042690, 0.010" i.d.) 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 (P/N 044777, 0.030" i.d.) that is directed to a waste container. If noise above 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, and therefore, noise in the cell.

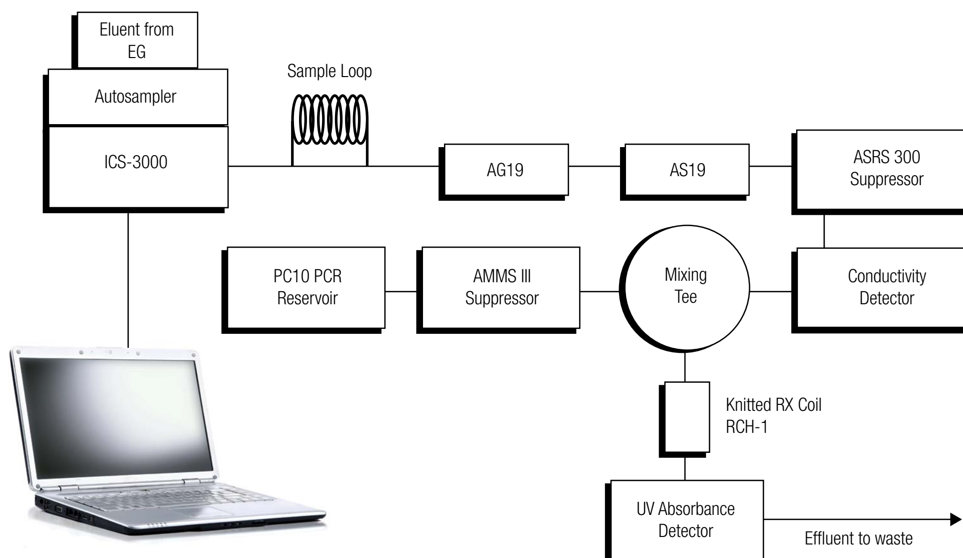

Figure 1. IC system configuration for EPA Method 326.0.

The PCR flow rate for this application was determined based on the analytical to PCR flow rate ratio provided in EPA Method 326.0. For our system, this resulted in the use of a 0.3 mL/min PCR flow rate. 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 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 that 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 analyzing any samples, inject 250 µL of DI water using the described method. This is the method blank. No peaks should elute at the same retention times as the target analytes. An equilibrated system has a suppressed background conductance <1 µS and peak-to-peak noise of ~1–2 nS per min and a UV peak-to-peak noise of <0.1 mAU per min. For the initial setup of the system it may take overnight for the conductivity detection to equilibrate and 2 days 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 will take 2–3 hours.

System Shutdown

If the system needs to be shut down, such as for a weekend, the following steps should be taken to protect the system components and ensure a smooth startup when the system is needed.

1. While the PCR and IC eluent are flowing, wearing latex or other suitable protective gloves and safety glasses, remove the line at the mixing tee that leads back to the Dionex AMMS suppressor 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 wash 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 Dionex AMMS suppressor and flush this line with DI water from the PC10. Re-install this line to the Eluent In port of the Dionex AMMS and flush the Dionex AMMS with DI water.
3. At the mixing tee, disconnect the tubing leading from the Cell Out of the conductivity detector to the mixing tee. 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 Dionex ASRS suppressor and plug the port on the Dionex ASRS to protect the suppressor.

   Turn on the PC10 using the same pressure that was used for delivering the PCR. Flow through the Dionex AMMS suppressor should be approximately 1–1.5 mL/min. Connect the line from the Eluent Out port of the Dionex AMMS suppressor to the mixing tee. Flow acidified DI water from the Dionex AMMS suppressor through the RCH at 80 °C. Allow this to flow for 30 min to remove the residual hydroxide eluent from the UV cell.
4. Turn off the UV lamp and turn off 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 set up for the first time, and whenever a Dionex AMMS 300 suppressor is replaced, it will require 2–3 days of flow for the PCR system to equilibrate and the noise on the VWD to fall below 0.1 mAU. The detection of 0.5 µg/L of bromate should not be attempted until after the PCR system has equilibrated. After this initial equilibration, the system should equilibrate and be ready to run samples in 2–3 h after a shutdown.
- The noise and drift present in the system will be highly dependent on maintaining consistent flow rates of the PCR, the external water, and the 0.3 N sulfuric acid. A high quality dual-stage regulator is highly recommended between the source gas (Helium or Nitrogen of grade 4.6 or better) and the regulators for the individual pressurized bottles. Use of a house compressed gas system is not recommended.
- Movement of the waste line leading from the UV flow cell will impact the noise observed in the UV. Be sure to secure this line so that it is not located where it can be disturbed.
- Daily checks of the pressures and flows for all pneumatically fed solutions are recommended. If the pressure of the PC10 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 that may have passed through the filtering process. 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 observed in 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 through a Nalgene 0.2 µm nylon filter unit is strongly recommended to remove insoluble material. The first time a filter unit is used, the membrane will turn yellow. This discoloration in the membrane will not affect the PCR that has been filtered and the PCR 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 filtered to clean the nylon membrane. Successive filtration with this filter unit will not further discolor the membrane.

Results and Discussion

U.S. EPA Method 326.0 specifies the use of a Dionex IonPac AS9-HC column with a 9 mM sodium carbonate eluent for the 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 bromate detection limit of 1.2 µg/L for a 225 µL injection by suppressed conductivity and 0.17 µg/L by UV absorbance (225 µL injection). Previously, we demonstrated that the bromate detection limit by suppressed conductivity can be reduced further to 0.34 µg/L using an electrolytically generated hydroxide eluent and a novel hydroxide-selective Dionex IonPac AS19 column.[16] Furthermore, we demonstrated that suppressed conductivity detection and postcolumn reaction with *o*-dianisidine may be used with an electrolytically generated hydroxide eluent and the Dionex IonPac AS19 column to achieve a bromate detection limit by visible detection equivalent to that reported in Method 317.0.[13] In this application note, we examine the feasibility of using the Dionex 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 still 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 was obtained 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, an enhanced response for bromate is observed after postcolumn reaction with acidified KI followed by UV detection.

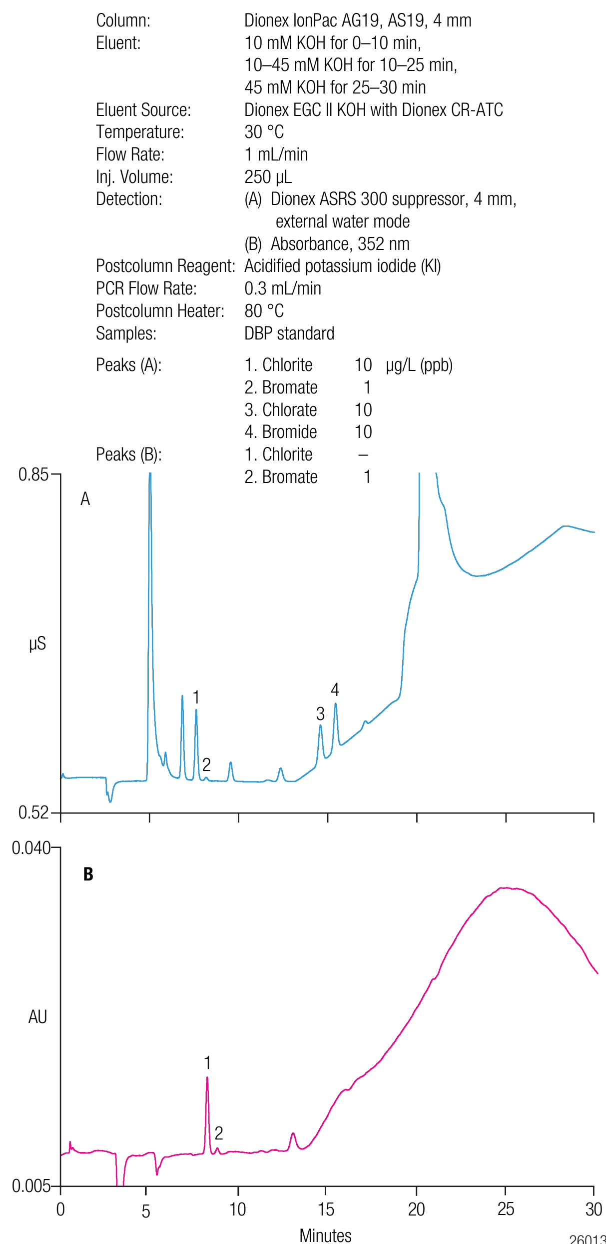

Figure 2. Separation of low-ppb DBP anions and bromide on the Dionex IonPac AS19 column using suppressed conductivity detection and UV absorbance after PCR with acidified potassium iodide.

Table 2 summarizes the calibration data and method detection limits (MDLs) obtained for the DBP anions and bromide using the Dionex IonPac AS19 column and an electrolytically generated hydroxide eluent with suppressed conductivity and UV detections. The 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, at 0.3–0.5 nS. Additionally, these were determined by injection of standards with minimal interference from other components that may be present in samples. The determined detection limit of 0.12 µg/L should not be expected in environmental samples. This method allows quantification of bromate to 1 µg/L using suppressed conductivity and 0.5 µg/L with UV detection using a Dionex IonPac AS19 column with an electrolytically generated potassium hydroxide eluent. Therefore, bromate was calibrated from 1–50 µg/L with suppressed conductivity and 0.5–15 µg/L using 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. For evaluating the precision and accuracy of the conductivity detector, Method 326.0 recommends using 20 µg/L each of the four target anions. However, because an electrolytically generated hydroxide eluent improves the overall sensitivity of the method, we 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 considers an RSD ≤20% and an average recovery of ±15% to be acceptable performance. The precision of our replicate analyses was <5.8% RSD and the accuracy was 92–102%, well within the 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. Recoveries of trace DBP anions spiked into water samples.

Analyte	Amount Found (µg/L)	Amount Added (µg/L)	Recovery (%)
Tap Water 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 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 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 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 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

Table 3 summarizes the method's 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 Dionex IonPac AS19 column. Figure 3 shows chromatograms of a 250 µL injection of Tap Water B using suppressed conductivity and UV detection at 352 nm after postcolumn reaction with acidified KI. Bromate, chlorate, and bromide were detected in the tap water. Bromide was not completely resolved from the earlier eluting unknown analyte. However, fortification of the sample with 20 µg/L bromide still produced good recovery of 92%. Bromate is clearly visible at approximately 3 µg/L with the absorbance detector; however, this bromate concentration was also easily determined using suppressed conductivity detection with the Dionex IonPac AS19 column. Figure 4 shows the same tap water 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%.

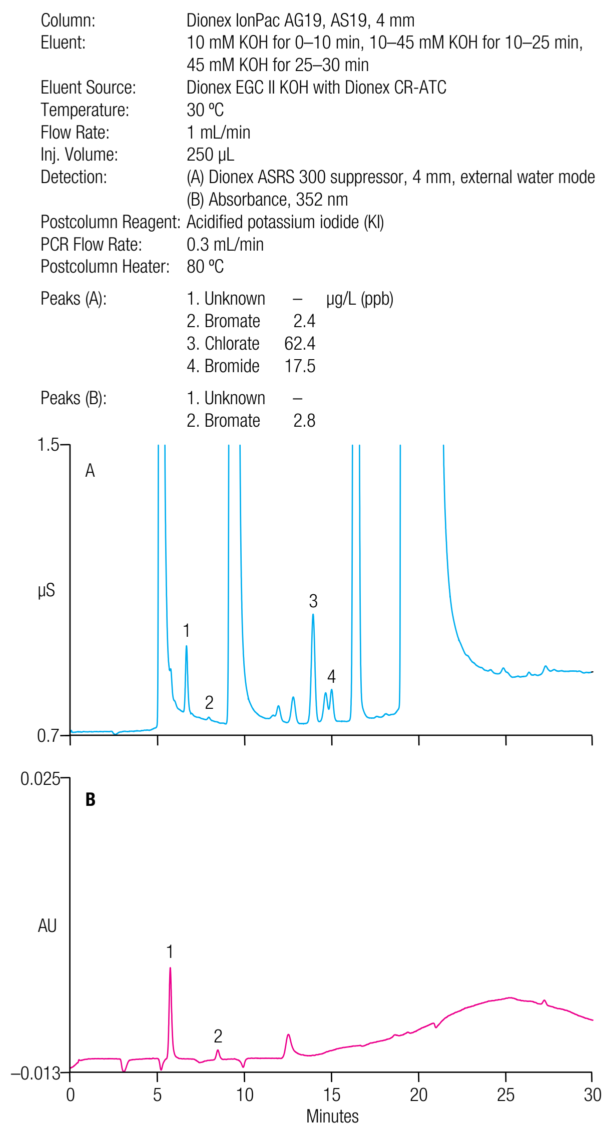

Figure 3. Determination of trace DBP anions and bromide in tap water B using suppressed conductivity detection and UV absorbance after PCR with acidified iodide.

Column: Dionex IonPac AG19, AS19, 4 mm
Eluent: 10 mM KOH for 0–10 min, 10–45 mM KOH for 10–25 min, 45 mM KOH for 25–30 min
Eluent Source: Dionex EGC II KOH with Dionex CR-ATC
Temperature: 30 °C
Flow Rate: 1 mL/min
Inj. Volume: 250 µL
Detection: (A) Dionex ASRS 300 suppressor, 4 mm, external water mode
(B) Absorbance, 352 nm
Postcolumn Reagent: Acidified potassium iodide (KI)
PCR Flow Rate: 0.3 mL/min
Postcolumn Heater: 80 °C

Peaks (A): 1. Chlorite 6.3 µg/L (ppb)
2. Bromate 5.5
3. Chlorate 133.3
4. Unknown –
5. Bromide 36.4

Peaks (B) 1. Chlorite –
2. Bromate 5.6

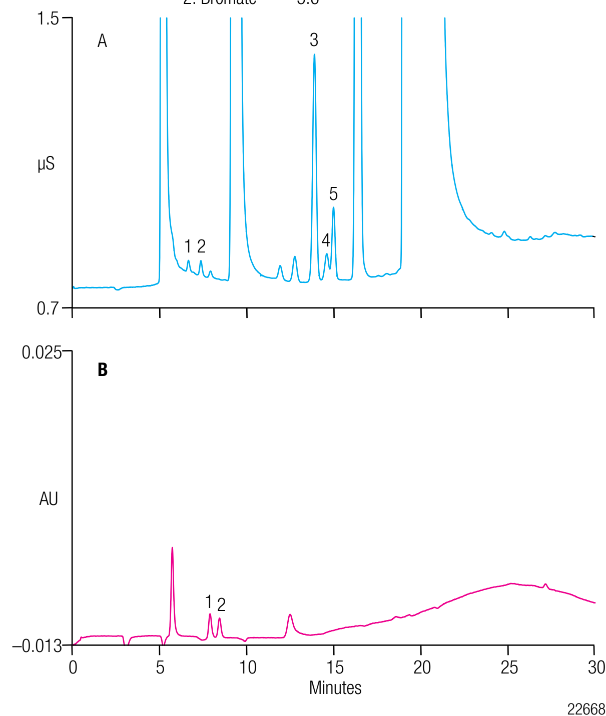

Figure 4. Determination of DBP anions spiked into tap water B using suppressed conductivity detection and UV absorbance after PCR with acidified potassium iodide.

Bottled Water 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 at the current EPA regulatory limit of 10 µg/L. However, the bromate concentration found in the second purchase (A-2) was ~8.7 µg/L, slightly below the regulatory limit. Figure 5 shows chromatograms of the ozonated bottled drinking water 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; 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 extremely 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 above. The recommended surrogate in EPA Method 326.0 is DCA. This surrogate interferes with quantification when using a hydroxide eluent. Trichloroacetic acid (TCA) has been suggested as a replacement for DCA as a surrogate. For samples with high amounts of carbonate, the carbonate interferes 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

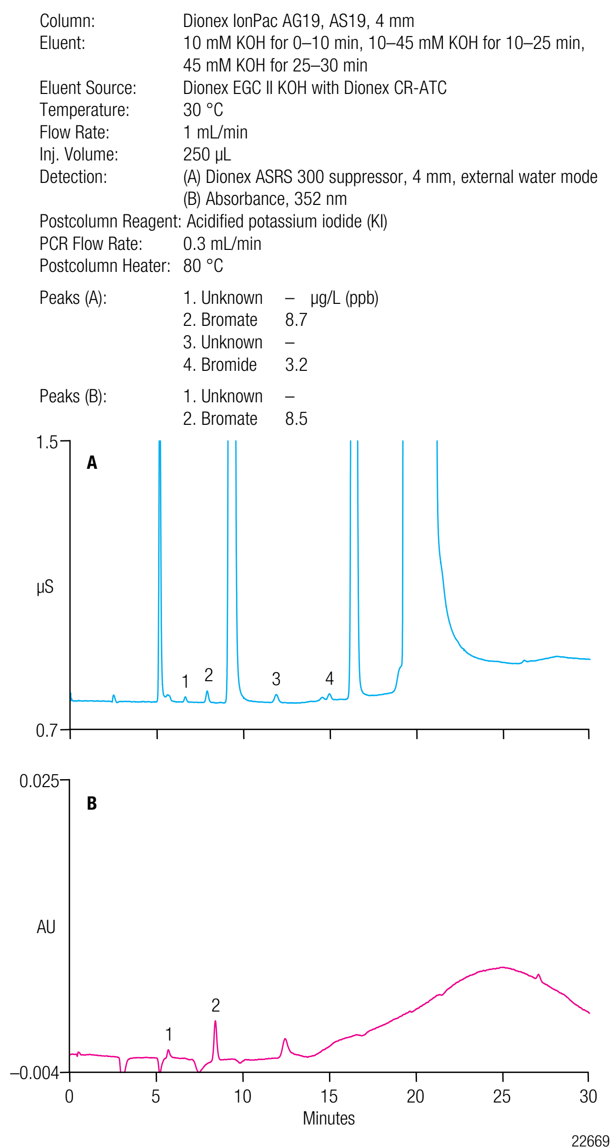

Figure 5. Determination of DBP anions and bromide in bottled water A-2 using suppressed conductivity detection and UV absorbance after PCR with acidified potassium iodide.

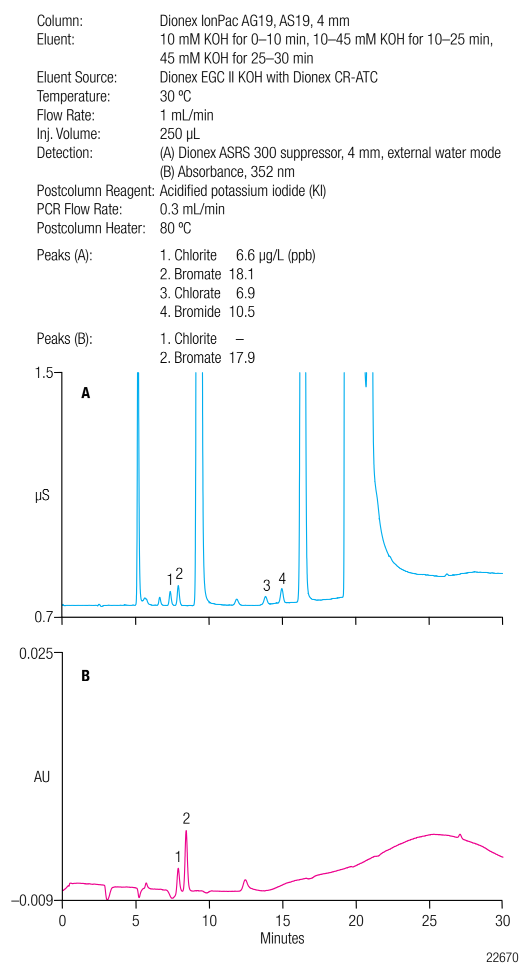

Figure 6. Determination of DBP anions and bromide in spiked bottled water A-2 using suppressed conductivity detection and UV absorbance after PCR with acidified potassium iodide.

investigated. None of these 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 peak resulting from carbonate without obscuring other peaks. Figure 7 shows the resolution possible when analyzing a municipal tap water sample containing chlorate, bromate, and bromide. The malate peak is separated from the carbonate peak, and is 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. Malate is an appropriate surrogate for samples with high carbonate concentrations when using these conditions.

Ruggedness

In order to test the method for ruggedness, it was repeated for several weeks. With a range of PC10 delivery pressures of 26–54 psi and PCR flow rates ranging 0.28–0.33 mL/min, the peak area determined for a 1.0 ppb bromate standard had an RSD of 9.2 over 21 business days of analysis with a peak retention time RSD of 0.89. During this time period, two Dionex 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 a Dionex AMMS suppressor, no significant effect of the individual suppressor or flow cell was observed.

Low area responses in individual injections during this 21-day period were observed when the PC10 pressure required to deliver 0.3 mL/min of PCR increased when no other changes were made. For this reason, it is recommended that any increase in the PC10 delivery pressure from the pressure after initial system equilibrium, or any decrease in PCR flow 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 tubing for the PCR will 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 will lead to baseline drift in the UV detection channel. As long as these flow rates are constant, a stable baseline will be achieved. If baseline drift is observed, confirm that no tubing is crimped or blocked before making changes to the consumables on the Dionex ICS-3000.

Column: Dionex IonPac AG19, AS19, 4 mm
Eluent: 10 mM KOH for 0–10 min,
10–45 mM KOH for 10–25 min,
45 mM KOH for 25–30 min
Eluent Source: Dionex EGC II KOH with Dionex CR-ATC
Temperature: 30 °C
Flow Rate: 1 mL/min
Inj. Volume: 250 µL
Detection: Dionex ASRS 300 suppressor, 4 mm, external water mode
Postcolumn Reagent: Acidified potassium iodide (KI)
PCR Flow Rate: 0.3 mL/min
Postcolumn Heater: 80 °C
Samples: (A) DBP standard
(B) Municipal tap water

Peaks (A):
1. Chlorite 10 µg/L (ppb)
2. Bromate 5
3. Chlorate 10
4. Bromide 10
5. Malate 1000

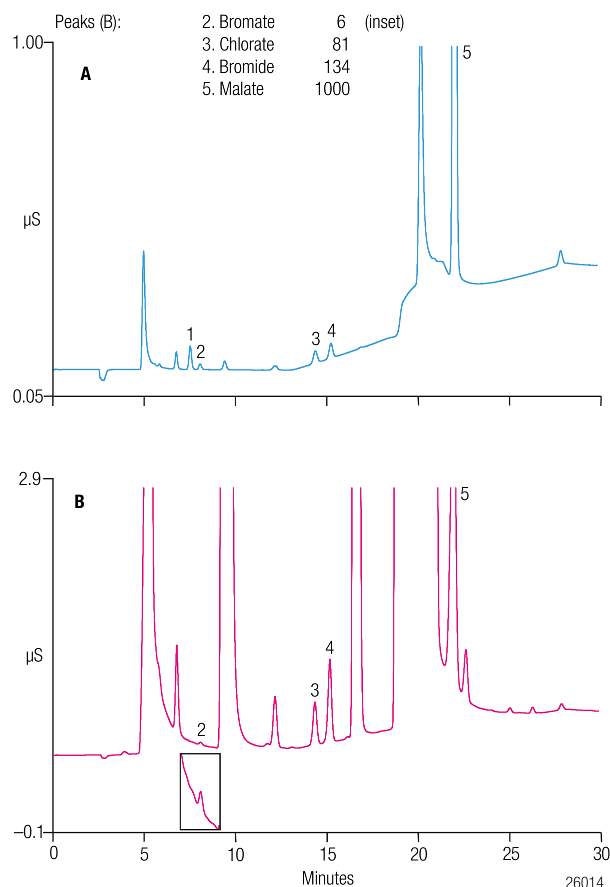

Figure 7. Determination of DBP in water using malate as a surrogate.

Conclusion

This application note describes an IC method using an electrolytically generated potassium hydroxide eluent combined with a hydroxide-selective Dionex 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 water samples. The use of a hydroxide eluent improved the sensitivity for bromate using suppressed conductivity and UV detection compared to using a 9 mM carbonate eluent with the Dionex IonPac AS9-HC column, as described in Method 326.0. Furthermore, the use of postcolumn addition and UV detection with the Dionex IonPac AS19 column allowed quantification of bromate from 0.5–15 µg/L without compromising the 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 application demonstrates that the hydroxide-selective Dionex IonPac AS19 column combined with a hydroxide eluent can be successfully used in place of the IonPac AS9-HC column for compliance monitoring by U.S. EPA Method 326.0.

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- VWR, 1310 Goshen Parkway, West Chester, PA, 19380 USA. Tel: 800-932-5000. www.vwr.com

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