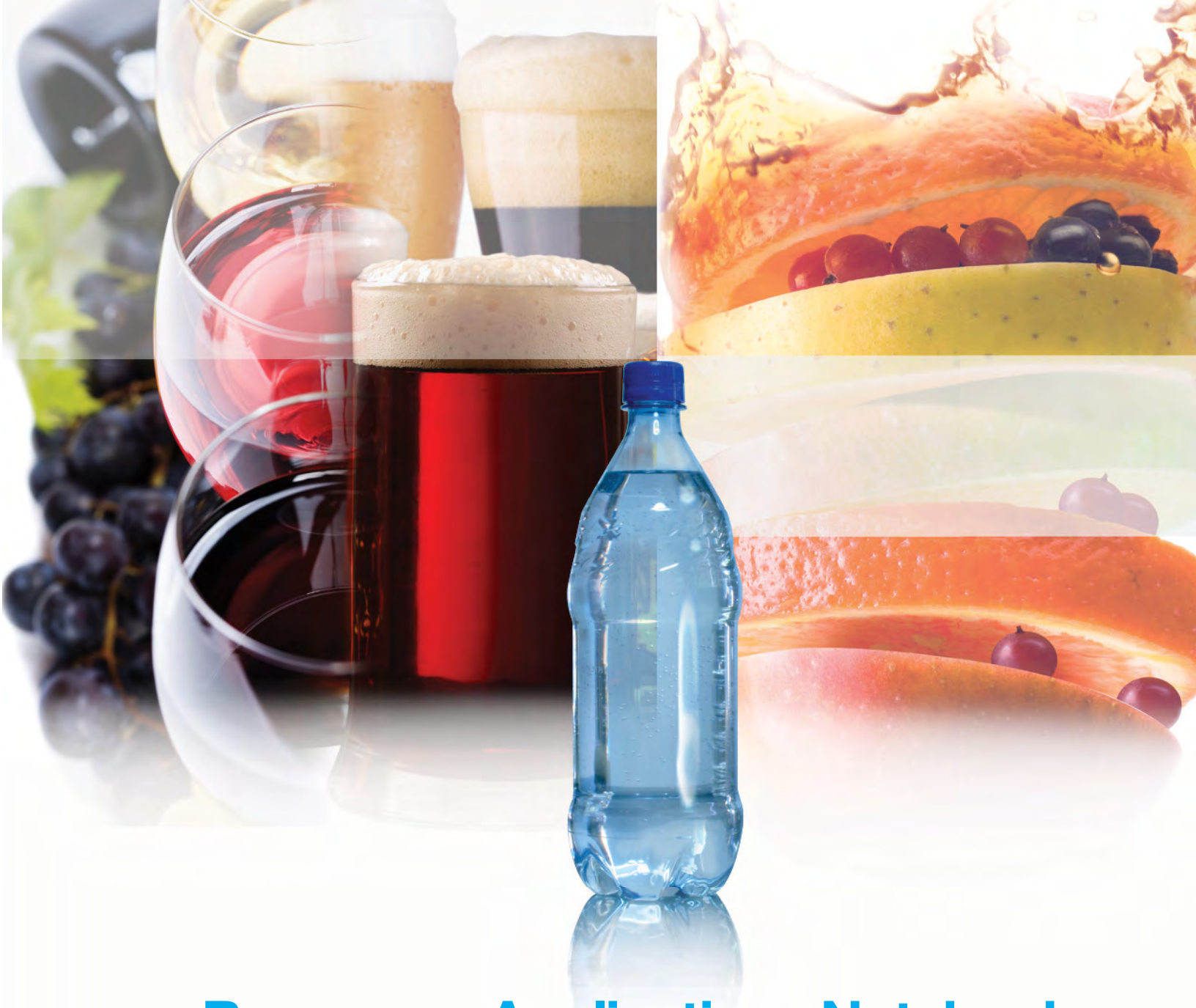

Beverages Applications Notebook

Bottled Water

Thermo SCIENTIFIC

Table of Contents

Index of Analytes

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Introduction to Beverages

The global beverage industry is growing each year with the introduction of new products, such as vitamin-fortified water, energy drinks, anti-aging water, and herbal nutritional supplements. With this growth, come many more analytical challenges. These challenges are compounded by the continuing and new needs to analyze classic favorites such as sodas, fruit juices, milk drinks, alcoholic beverages, and bottled water. One such example would be the melamine contamination in milk and infant milk formula.

For all beverages, the compositional quality and safety must be monitored to help track contamination, adulteration, product consistency, and to ensure regulatory compliance from raw ingredients (water, additives, and fruits) to the final product.

Thermo Fisher Scientific is a recognized leader in providing analytical solutions for sample preparation, liquid chromatography for compositional testing, and chromatography data management for compliance and quality testing of beverages. From inorganic ions, organic acids, biogenic amines, glycols and alcohols, carbohydrates and sugar alcohols, to vitamins, additives, and sugar substitutes, we are unique in our commitment to provide fast, accurate testing and labeling information for all applications in this industry.

Thermo Scientific and Dionex Integrated Systems

Dionex Products are now a part of the Thermo Scientific brand, creating exciting new possibilities for scientific analysis. Now, leading capabilities in liquid chromatography (LC), ion chromatography (IC), and sample preparation are together in one portfolio with those in mass spectrometry (MS). Combining Dionex's leadership in chromatography with Thermo Scientific's leadership position in mass spec, a new range of powerful and simplified workflow solutions now becomes possible.

For more information on how the new lineup of Thermo Scientific products can expand your capabilities and provide the tools for new possibilities, choose one of our integrated solutions:

- Ion Chromatography and Mass Spectrometry
- Liquid Chromatography and Mass Spectrometry
- Sample Preparation and Mass Spectrometry

UltiMate 3000 UHPLC+ Systems

Best-in-class HPLC systems for all your chromatography needs

Thermo Scientific Dionex UltiMate 3000 UHPLC+ Systems provide excellent chromatographic performance while maintaining easy, reliable operation. The basic and standard analytical systems offer ultra HPLC (UHPLC) compatibility across all modules, ensuring maximum performance for all users and all laboratories. Covering flow rates from 20 nL/min to 10 mL/min with an industry-leading range of pumping, sampling, and detection modules, UltiMate™ 3000 UHPLC+ Systems provide solutions from nano to semipreparative, from conventional LC to UHPLC.

- Superior chromatographic performance
- UHPLC design philosophy throughout nano, standard analytical, and rapid separation liquid chromotography (RSLC)
- 620 bar (9,000 psi) and 100 Hz data rate set a new benchmark for basic and standard analytical systems
- RSLC systems go up to 1000 bar and data rates up to 200 Hz
- ×2 Dual System for increased productivity solutions in routine analysis
- Fully UHPLC compatible advanced chromatographic techniques
- Thermo Scientific Dionex Viper and nanoViper–the first truly universal, fingertight fitting system even at UHPLC pressures

Thermo Fisher Scientific is the only HPLC company uniquely focused on making UHPLC technology available to all users, all laboratories, and for all analytes.

Rapid Separation LC Systems: The extended flow-pressure footprint of the RSLC system provides the performance for ultrafast high-resolution and conventional LC applications.

RSLCnano Systems: The Rapid Separation nano LC System (RSLCnano) provides the power for high-resolution and fast chromatography in nano, capillary, and micro LC.

Standard LC Systems: Choose from a wide variety of standard LC systems for demanding LC applications at nano, capillary, micro, analytical, and semipreparative flow rates.

Basic LC Systems: UltiMate 3000 Basic LC Systems are UHPLC compatible and provide reliable, high-performance solutions to fit your bench space and your budget.

IC and RFIC Systems

A complete range of ion chromatography solutions for all customer performance and price requirements

For ion analysis, nothing compares to a Thermo Fisher Scientific ion chromatography system. Whether you have just a few samples or a heavy workload, whether your analytical task is simple or challenging, we have a solution to match your needs and budget. And with your IC purchase, you get more than just an instrument—you get a complete solution based on modern technology and world-class support.

- Thermo Scientific Dionex ICS-5000: The world's first capillary IC system
- Dionex ICS-2100: Award-winning integrated Reagent-Free™ IC system
- Dionex ICS-1600: Standard integrated IC system
- Dionex ICS-1100: Basic integrated IC system
- Dionex ICS-900: Starter line IC system

Ranging from the Dionex ICS-900 to the ICS-5000, these IC systems cover the entire range of IC needs and budgets and come with superior support and service worldwide.

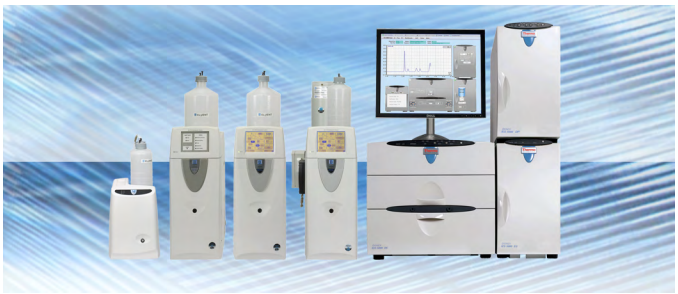
Dionex ICS-5000: Developed with flexibility, modularity, and ease-of-use in mind, the Dionex ICS-5000 combines the highest sensitivity with convenience

Dionex ICS-2100: An integrated Reagent-Free IC (RFIC™) system for electrolytically generated isocratic and gradient separations with conductivity detection, now with electrolytic sample preparation.

Dionex ICS-1600: The Dionex ICS-1600 combines high sensitivity with convenience. Now ready for eluent regeneration, with available dual-valve configuration for automated sample preparation.

Dionex ICS-1100: With dual-piston pumping and electrolytic suppression. Now ready for eluent regeneration, with available dual-valve configuration for automated sample preparation.

Dionex ICS-900: Can routinely analyze multiple anions and cations in 10–15 min—fully automated with Displacement Chemical Regeneration (DCR).



MS Instruments

Single-point control and automation for improved ease-of-use in LC/MS and IC/MS

Thermo Fisher Scientific provides advanced integrated IC/MS and LC/MS solutions with superior ease-of-use and modest price and space requirements. UltiMate 3000 System Wellness technology and automatic MS calibration allow continuous operation with minimal maintenance. The Dionex ICS-5000 instrument and the family of RFIC systems automatically remove mobile phase ions for effort-free transition to MS detection.

- Thermo Scientific MSQ Plus mass spectrometer, the smallest and most sensitive single quadrupole on the market for LC and IC
- Self-cleaning ion source for low-maintenance operation
- Thermo Scientific Dionex Chromeleon Chromatography Data System software for single-point method setup, instrument control, and data management
- Compatible with existing IC and LC methods
- The complete system includes the MSQ Plus™ mass spectrometer, PC datasystem, electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI) probe inlets, and vaccum system

You no longer need two software packages to operate your LC/MS system. Chromeleon™ LC/MS software provides single-software method setup and instrument control; powerful UV, conductivity, and MS data analysis; and fully integrated reporting.

MS Systems and Modules: MSQ Plus Mass Spectrometer; MSQ18LA nitrogen gas generator; Thermo Scientific Dionex AXP-MS digital auxiliary pump

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Chromeleon 7 Chromatography Data System Software

The fastest way to get from samples to results

Discover Chromeleon software version 7, the chromatography software that streamlines your path from samples to results. Get rich, intelligent functionality and outstanding usability at the same time with Chromeleon software version 7—the Simply Intelligent™ chromatography software.

- Enjoy a modern, intuitive user interface designed around the principle of operational simplicity
- Streamline laboratory processes and eliminate errors with eWorkflows, which enable anyone to perform a complete analysis perfectly with just a few clicks
- Access your instruments, data, and eWorkflows instantly in the Chromeleon Console
- Locate and collate results quickly and easily using powerful built-in database query features
- Interpret multiple chromatograms at a glance using MiniPlots
- Find everything you need to view, analyze, and report data in the Chromatography Studio
- Accelerate analyses and learn more from your data through dynamic, interactive displays
- Deliver customized reports using the built-in Excel-compatible speadsheet

Chromeleon software version 7 is a forward-looking solution to your long-term chromatography data needs. It is developed using the most modern software tools and technologies, and innovative features will continue to be added for many years to come.

The Cobra™ integration wizard uses an advanced mathematical algorithm to define peaks. This ensures that noise and shifting baselines are no longer a challenge in difficult chromatograms. When peaks are not fully resolved, the SmartPeaks™ integration assistant visually displays integration options. Once a treatment is selected, the appropriate parameters are automatically included in the processing method.

Chromeleon software version 7 ensures data integrity and reliability with a suite of compliance tools. Compliance tools provide sophisticated user management, protected database stuctures, and a detailed interactive audit trail and versioning system.

Process Analytical Systems and Software

Improve your process by improving your process monitoring with a Thermo Scientific Dionex on-line IC or HPLC system

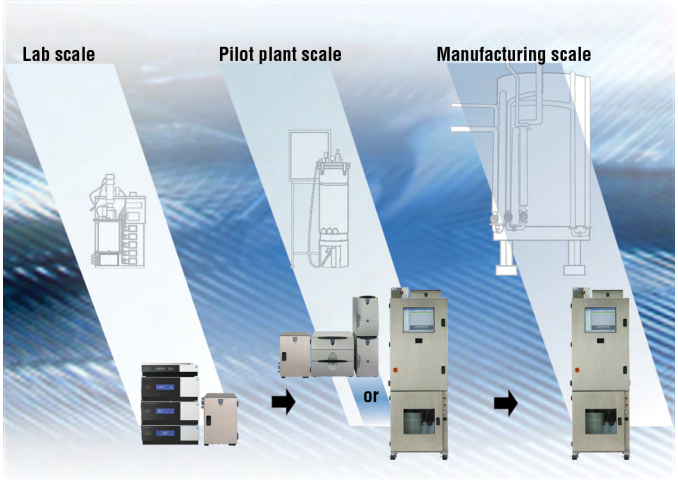
Our process analytical systems provide timely results by moving liquid chromatography-based measurements on-line. Information from the Thermo Scientific Dionex Integral process analyzer can help reduce process variability, improve efficiency, and reduce downtime. These systems provide comprehensive, precise, accurate information faster than is possible with laboratory-based results. From the lab to the factory floor, your plant's performance will benefit from the information provided by on-line LC.

- Characterize your samples completely with multicomponent analysis
- Reduce sample collection time and resources with automated multipoint sampling
- Improve your process control with more timely results
- See more analytes with unique detection capabilities
- 25 years of experience providing on-line IC and HPLC capabilities to a wide range of industries
- The Thermo Scientific Integral Migration Path approach lets you choose the systems that best meets your needs

The Integral Migration Path™ approach enables on-line IC/HPLC to generate timely, high-resolution information when monitoring a small-scale reactor in a process R&D lab, in a pilot plant, or improving current manufacturing plant processes. No matter what the application, the Integral™ process analyzer has the versatility to place a solution using on-line IC/HPLC, whenever and wherever it is needed.

Integral: The Integral Migration Path approach: System solutions wherever you need them: lab, pilot plant, or manufacturing

Chromeleon Process Analytical (PA) Software: Chromeleon PA software provides unique capabilities to support on-line IC or HPLC analysis



Automated Sample Preparation

ACCELERATED SOLVENT EXTRACTORS

Two new solvent extraction systems with pH-hardened Dionium components

We offer two solvent extraction systems. The Thermo Scientific Dionex ASE 150 Accelerated Solvent Extractor is an entry-level system with a single extraction cell, for laboratories with modest throughput. The Dionex ASE™ 350 system is a sequential extraction system capable of automated extraction of up to 24 samples. Both systems feature chemically inert Dionium components that allow the extraction of acid- or base-pretreated samples.

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SOLID-PHASE EXTRACTION SYSTEMS

Faster, more reliable solid-phase extraction while using less solvent

The Thermo Scientific Dionex AutoTrace 280 Solid-Phase Extraction (SPE) instrument unit can process six samples simultaneously with minimal intervention. The instrument uses powerful pumps and positive pressure with constant flow-rate technology. Current analytical methods that require SPE sample preparation include gas chromatography (GC), GC-MS, LC, and LC-MS, IC and IC-MS. The Dionex AutoTrace™ 280 instrument is approved or adapted for U.S. EPA clean water methods and safe drinking water methods (600 and 500 series) and can extract the following analytes:

- PCBs (polychlorinated biphenyls)
- OPPs (organophosphorus pesticides), OCPs (organochlorine pesticides), and chlorinated herbicides
- BNAs (base, neutral, acid semivolatiles)
- Dioxins and furans
- PAHs (polyaromatic hydrocarbons)
- Oil and grease or hexane extractable material

With SPE, large volumes of liquid sample are passed through the system and the compounds of interest are trapped on SPE adsorbents (cartridge or disk format), then eluted with strong solvents to generate an extract ready for analysis. Automated SPE saves time, solvent, and labor for analytical laboratories.

Dionex AutoTrace Systems: The new Dionex AutoTrace 280 system provides fast and reliable automated solid phase extraction for organic pollutants from liquid samples

Dionex AutoTrace Accessories: High-quality parts and accessories are available for Dionex AutoTrace 280 instruments

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Analysis of Bottled Water

Determination of Trace Concentrations of Oxyhalides and Bromide in Municipal and Bottled Waters Using a Hydroxide-Selective Column with a Reagent-Free Ion Chromatography System

INTRODUCTION

All drinking water municipalities share the same goal of providing their communities with a reliable source of safe drinking water. To achieve this goal, most water systems must treat their water. The type of treatment used varies depending on the size, source, and water quality.[1] Disinfection protects public water systems (PWSs) 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 by-products (DBPs) that are potentially harmful to humans. For example, chlorination of drinking water can produce trihalomethanes, haloacetic acids, and chlorate. While chlorine dioxide treatment generates the inorganic oxyhalide DBPs chlorite and chlorate, and the presence of chloramine has also been known to generate chlorate.[2] Ozone reacts with naturally occurring bromide to produce bromate. The International Agency for Research on Cancer has identified bromate as an animal carcinogen and potential human carcinogen.[3] The World Health Organization (WHO) has estimated[4] an excess lifetime cancer risk of 10^{-5} for drinking water containing bromate at 3 µg/L.*

* Probable increase in deaths due to a cancer, 10^{-5} = 1 in 100,000 people

From July 1997 to December 1998, the U.S. Environmental Protection Agency (EPA) documented the occurrence of bromate and other DBPs through a comprehensive collection of sampling data mandated by the Information Collection Rule (ICR).[5] The ICR required that PWSs serving 100,000 or more connections report the concentration of target microorganisms present, the removal process used, and the concentration of DBPs present in their drinking water. In 1998, the EPA set the maximum contaminant level (MCL) for bromate at 10 µg/L and chlorite at 1000 µg/L under the Disinfectants/Disinfection By-Products (D/DBP) Stage 1 Rule.[6] This rule resulted in the promulgation of EPA Method 300.1 as an update to Method 300.0. Method 300.1 reduced the detection limit for bromate from 20 to 1.4 µg/L to allow the PWSs' laboratories to meet the MCL requirement set by the EPA.[7] The European Union (EU Directive 98/83/EC) also proposed the same regulatory value of 10 µg/L bromate (previously at 50 µg/L) in drinking water.[8]

The U.S. EPA reconvened in 2003 to establish the Stage 2 Rule of the D/DBP. Based on a thorough evaluation, the EPA could not estimate the additional benefits of reducing the MCL for bromate. Therefore, this rule resulted in no changes to the current MCL for either chlorite or bromate. However, additional methods for de-

termining low µg/L bromate were promulgated under the Stage 2 Rule and included ion chromatography (IC) with postcolumn reaction (EPA Methods 317.0 and 326.0) and IC/ICP-MS (EPA Method 321.8). The addition of these methods resulted in improved sensitivity and selectivity for bromate.[9] Recently, the WHO reduced their bromate guideline value from 25 µg/L to a provisional value of 10 µg/L bromate.[4] This change resulted from the availability of improved analytical methods capable of determining low-µg/L concentrations of bromate in environmental waters.

Unlike tap water, bottled water is treated as a food product in the U.S. and therefore regulated by the U.S. Food and Drug Administration (FDA). Bottled water is an increasingly popular product in the U.S. From 1997 to 2002, bottled water sales increased from roughly 6% to 13% per year of total beverage sales, according to the Beverage Marketing Corporation.[10] Because some bottled water companies use ozone or other disinfection treatments, the FDA adopted the EPA's MCLs for chlorite and bromate and the analytical methods used to monitor these contaminants in public drinking water.[11] The FDA also requires that bottled water manufacturers monitor their finished product for these contaminants at least once each year under current good manufacturing practice as stated in part 129 of the Code of Federal Regulations (21 CFR part 129).

Previous methods developed for determining low-µg/L concentrations of bromate by direct injection have focused primarily on using columns specifically designed for carbonate eluents.[12,13] Columns designed for use with hydroxide eluents have not been widely used for the determination of trace bromate in environmental waters due to their lack of appropriate column selectivity and the difficulty in preparing contaminant-free hydroxide eluents. The introduction of electrolytic eluent generation has not only eliminated the difficulty in preparing hydroxide eluents, but has simplified the development of optimized methods. In this application note, we use the IonPac® AS19, a column specifically designed for use with hydroxide eluents and developed with an optimized selectivity for the determination of trace DBPs and bromide in environmental waters. We describe the linearity, method detection limits, and the recovery and precision of spiked municipal and bottled waters.

EQUIPMENT

A Dionex ICS-2000 Reagent-Free Ion Chromatography (RFIC™)* System was used in this work. The ICS-2000 is an integrated ion chromatograph and consists of:

Eluent Generator

Column Heater

Pump with Degasser

EluGen® EGC II KOH Cartridge (Dionex P/N 058900)

CR-ATC (Dionex P/N 060477)

AS50 Autosampler

Chromeleon® Chromatography Workstation

*This application note is also applicable to other RFIC systems.

REAGENTS AND STANDARDS

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

Sodium and Potassium salts, ACS reagent-grade or better, for preparing anion standards (VWR or other)

Fluoride standard 1000 mg/L, 100 mL (Dionex P/N 037158)

Chloride standard 1000 mg/L, 100 mL (Dionex P/N 037159)

Sulfate standard 1000 mg/L, 100 mL (Dionex P/N 037160)

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

Sodium Chlorite, 80% (Fluka Chemical Co.)

Sodium Bromate (EM Science, VWR P/N EM SX0385-1)

Ethylenediamine, 99% (Sigma-Aldrich)

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 to 10 min, 10–45 mM from 10 to 25 min*
Eluent Source:	ICS-2000 EG with CR-ATC
Flow Rate:	1.0 mL/min
Temperature:	30 °C
Injection:	250 µL

Detection:	Suppressed conductivity, ASRS® ULTRA II, 4 mm (Dionex P/N 061561) AutoSuppression® Recycle Mode 130 mA current
Background Conductance:	<1 µS
System Backpressure:	~2200 psi
Run Time:	30 min

*Method returns to 10 mM KOH for 3 min prior to injection

PREPARATION OF SOLUTIONS AND REAGENTS

Stock Standard Solutions

For several of the anions of interest, 1000-mg/L standard solutions can be purchased from Dionex or other commercial sources. When commercial standards are not available, 1000-mg/L standards can be prepared by dissolving the appropriate amounts of the required analytes in 100 mL of deionized water according to Table 1. Stock standards for most anions are stable for at least 6 months when stored at 4 °C. The chlorite standard is only stable for two weeks when stored protected from light at 4 °C. The nitrite and phosphate standards are only stable for one month when stored at 4 °C.

Table 1. Masses of Compounds Used to Prepare 100 mL of 1000-mg/L Ion Standards

Analyte	Compound	Amount (g)
Fluoride	Sodium fluoride (NaF)	0.2210
Chlorite	Sodium chlorite ($NaClO_2$), 80%	0.1676
Bromate	Sodium bromate ($NaBrO_3$)	0.1180
Chloride	Sodium chloride (NaCl)	0.1649
Nitrite	Sodium nitrite ($NaNO_2$)	0.1500
Chlorate	Sodium chlorate ($NaClO_3$)	0.1275
Bromide	Sodium bromide (NaBr)	0.1288
Nitrate	Sodium nitrate ($NaNO_3$)	0.1371
Sulfate	Sodium sulfate (Na_2SO_4)	0.1479
Phosphate	Potassium phosphate, monobasic	0.1433

Working Standard Solutions

Dilute working standard solutions were prepared using the 1000-mg/L stock standards. Working standards containing less than 100 µg/L anions should be prepared fresh daily. Seven levels of calibration standards were used in this study for chlorite, chlorate, and bromide to cover the expected concentration range found in typical environmental samples. The bromate calibration curve was prepared using eight calibration standards. Additional anions listed in Table 1 were used to prepare a simulated drinking water sample containing 1 ppm fluoride, 50 ppm chloride, 0.1 ppm nitrite, 10 ppm nitrate, 100 ppm carbonate, 50 ppm sulfate, and 0.1 ppm phosphate.

Preservation Solution

Dilute 2.8 mL of 99% ethylenediamine (EDA) to 25 mL with deionized water according to section 7.4 in EPA Method 300.1 to prepare a 100-mg/mL solution of EDA. Use 50 µL of this solution per 100 mL of standard or sample so that the final concentration is 50 mg/L.

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.

RESULTS AND DISCUSSION

EPA Method 300.1 Part B currently specifies an IonPac AS9-HC column using a carbonate eluent and suppressed conductivity detection for the determination of trace DBP anions and bromide in environmental waters, such as drinking water, surface water, and groundwater.[7] The use of the IonPac AS9-HC column in EPA Method 300.1 (B) significantly improved the determination for trace bromate compared to the AS9-SC specified in Method 300.0, Part B.[14] The AS9-HC allowed for detection limits to 1.4 µg/L bromate with a 200-µL injection volume, even in the presence of excess chloride. However, the use of a hydroxide eluent for the determination of trace bromate is more appealing than carbonate eluents. Hydroxide eluent has significantly lower suppressed background conductivity, lower noise, and therefore lower detection limits compared to carbonate eluents. Previously, we described the advantages of hydroxide over carbonate eluents for the determination of common anions.[15] Therefore, similar advantages for bromate should be expected using a column with an appropriate selectivity combined with a hydroxide eluent.

The IonPac AS19 is a high-capacity, hydroxide-selec-

tive column specifically designed for the determination of trace bromate and other oxyhalides using a large-volume injection. The novel polymer chemistry of the AS19 yields a higher capacity of 240 µequiv/column compared to the AS9-HC (190 µeq/column). The AS19 stationary phase is based on a new hyper-branched anion-exchange condensation polymer that is electrostatically attached to the surface of a wide-pore polymeric substrate. The AS19 selectivity and capacity are optimized to achieve good resolution between bromate and chloride. Unlike previous IonPac columns, the anion-exchange resin of the AS19 contains alternating treatments of epoxy and amines to produce a coating that grows directly off the surface-sulfonated substrate. The number of alternating coating cycles results in a carefully controlled ion-exchange capacity with an extremely hydrophilic polymer. Therefore, the column has excellent selectivity for hydroxide eluents, allowing lower concentrations of hydroxide to be used.[16] Figure 1 shows a separation of common anions and disinfection by-product anions separated within 30 min using the AS19 column with a hydroxide gradient. As this figure shows, the AS19 achieves excellent resolution between bromate and chloride, making it ideal for determining low concentrations of bromate in municipal and bottled water samples.

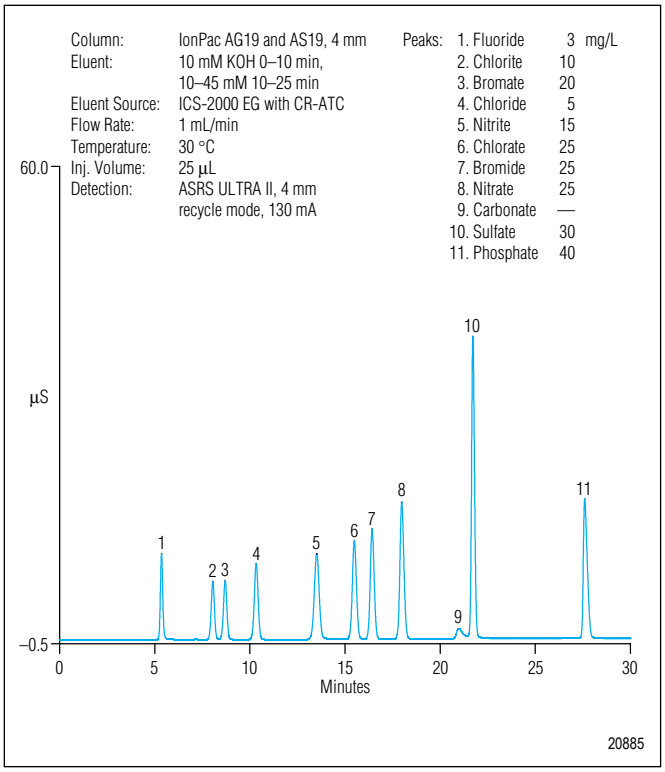

Figure 1. Separation of common anions and disinfection by-product anions on the IonPac AS19 column.

Linearity and Method Detection Limits

Before conducting any sample analyses, the linear calibration range, MDLs, and acceptable performance of a quality control sample (QCS) should be demonstrated. Initially, a seven-point calibration range was used for chlorite, chlorate, and bromide, whereas eight calibration points were used for bromate. MDLs for each anion listed in EPA Method 300.1, Part B were determined by performing seven replicate injections of reagent water fortified at a concentration of three to five times the estimated instrument detection limits. In addition, the MDLs were also determined by fortifying the same concentration of anions in a simulated drinking water sample. Table 2 shows typical calculated MDLs in reagent water and simulated drinking water using the IonPac AS19 column combined with an electrolytic eluent generator and a 250-µL injection. In comparing the detection limits in the two matrices, the results showed no significant difference. The only exception was the calculated MDL for bromate in simulated drinking water was only slightly greater, as expected, because increasing concentrations of chloride will affect the determination of low concentrations of bromate. The calculated MDL for bromate using this method was 0.34 µg/L, approximately 70% lower than previously reported with the AS9-HC column at comparable injection volumes.[12] The lower detection limit results from the excellent peak efficiencies of the AS19 combined with low noise and exceptionally low suppressed background conductivities obtained by using an electrolytically generated hydroxide eluent. These results demonstrate the significant advantages of using an RFIC system for the determination of trace bromate.

Table 2. Method Detection Limits for Oxyhalides and Bromide in Reagent Water and Simulated Drinking Water Using the IonPac AS19 Column[a]

Analyte	MDL Standard (µg/L)	Calculated MDL[b] in Reagent Water (µg/L)	Calculated MDL[b] in Simulated Drinking Water (µg/L)
Chlorite	1.0	0.23	0.26
Bromate	1.5	0.34	0.42
Chlorate	1.3	0.32	0.30
Bromide	2.0	0.54	0.52

[a] 250-µL injection volume
[b] MDL = $\sigma t_{s,99}$ where $t_{s,99}$ = 3.14 for n = 7

Figure 2 shows a separation of an MDL standard prepared in reagent water. As shown, bromate concentrations as low as 1.5 µg/L are easily detected by this method.

Table 3 shows the linear concentration ranges investigated, the coefficients of determination (r^2), and the retention time and peak area precisions of a QCS based on 10 replicate injections. The excellent retention time stability and peak area precisions are consistent with results typically encountered when using an electrolytically generated high-purity potassium hydroxide eluent. The data presented in Table 3 demonstrate the advantages of using a hydroxide-selective column for routine applications, such as the determination of oxyhalides and bromide in environmental waters. The advantages of using IC with a hydroxide eluent are improved linearity, lower background conductivity, and improved method detection limits when compared with "conventional" IC columns that use carbonate eluents, such as the IonPac AS9-HC. The use of an electrolytically generated potassium hydroxide eluent further simplifies the method by eliminating the time required to manually prepare eluents and by reducing the time required for method development.

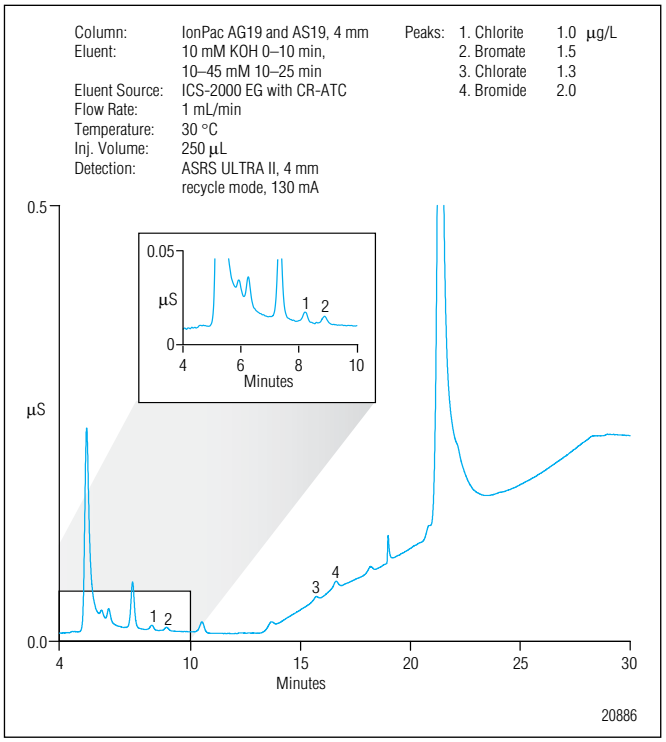

Figure 2. Separation of DBP anions and bromide method detection limit standard.

Effect of Column Overloading

The effect of sample overload on the IonPac AS19 column was evaluated as part of this study. One of the many challenges encountered when determining trace concentrations of bromate is the potential presence of a high sample chloride concentration. In addition to chloride, a high concentration of other anions can together reduce the amount of bromate recovered from a sample. For most environmental samples, chloride, sulfate, and carbonate are generally present at the greatest amounts with respect to other common anions. For this study, we chose a 250-µL sample injection for the analyses because this volume provided us the sensitivity necessary to achieve low-ppb detection of bromate and reduced the likelihood of overloading the column when analyzing high-ionic-strength samples.

To determine the effect of chloride on bromate recovery, a series of increasing concentrations of chloride was added to Sunnyvale drinking water. Figure 3 illustrates the effect of increasing concentrations of chloride on the recovery of 5 µg/L bromate. As shown, the recovery of bromate is acceptable in the presence of ~150 ppm chloride. Above this concentration, the bromate significantly decreases to an unacceptable recovery (e.g., <75%). Based on this analysis, the IonPac AS19 can tolerate up to ~150 ppm chloride, resulting in a bromate-to-chloride

Table 3. Linearity and Retention Time and Peak Area Precisions Obtained Using the IonPac AS19 Column[a]

Analyte	Range (µg/L)	Linearity (r^2)	Retention Time Precision (%RSD[b])	Peak Area Precision (%RSD)
Chlorite	20–500	0.9997	<0.03	0.44
Bromate	1–40	0.9995	<0.03	1.09
Chlorate	20–500	0.9996	<0.03	0.12
Bromide	20–500	0.9997	<0.03	0.11

[a] Dionex ICS-2000 Reagent-Free IC system with a 250-µL injection volume

[b] RSD = relative standard deviation, n = 10

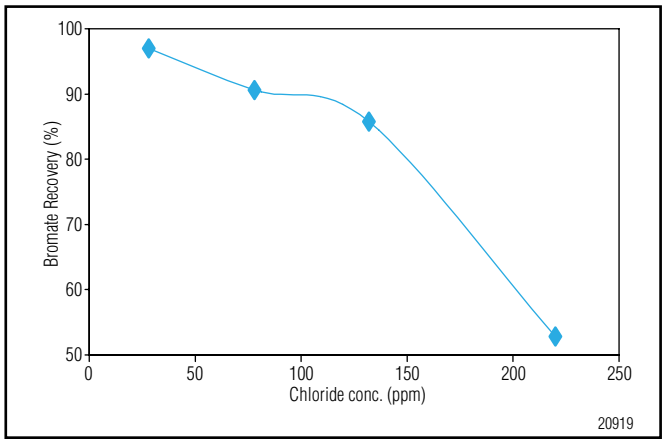

Figure 3. Effect of increasing the chloride concentration on the recovery of 5 µg/L bromide.

ratio of 1:30,000, comparable to the AS9-HC column.[12] A similar experiment was performed by increasing the sulfate concentration without any additional chloride added. This experiment demonstrated very little change in the bromate recovery for up to 200 ppm sulfate (results not shown). However, high concentrations of chloride and sulfate can combine to have a greater impact on reducing the bromate recovery. Equal concentrations of chloride and sulfate (up to 120 ppm each) were added to Sunnyvale drinking water, resulting in a 75% bromate recovery. However, most drinking water samples contain significantly less chloride and sulfate than the concentrations included in this study. For example, 18 of the samples examined contained chloride concentrations ranging from <0.1 to 70 ppm and sulfate from <0.1 to 60 ppm. Therefore, almost all samples can be easily analyzed using a 250-µL injection volume, while the column can tolerate 500-µL injections of low- to moderate-ionic-strength samples. Figure 4 shows a chromatogram of a 500-µL injection of Sunnyvale drinking water spiked with oxyhalides and bromide. As shown, bromate was well resolved from chloride with bromate recovered at nearly 100%. Figure 5 compares 250- to 500-µL injection volumes for a simulated drinking water sample. The 500-µL injection volume caused some column overloading and therefore a lower bromate recovery of ~74%. However, a 250-µL injection of the same sample significantly improved the recovery of bromate to 92%. Therefore, a 250-µL injection is recommended for most sample analyses. The effect of column overloading is most prevalent on early-eluting peaks, observed by increased peak broadening and lower recoveries, as demonstrated in this example.

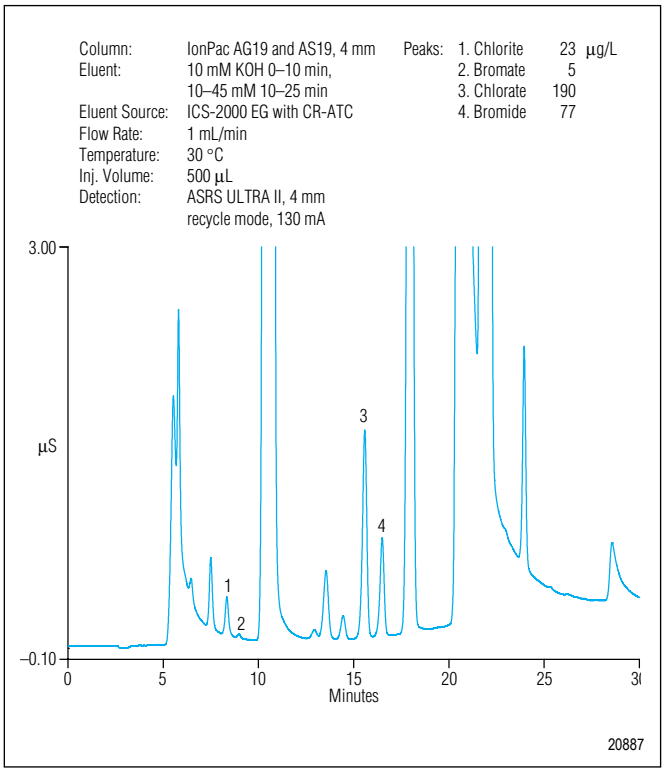

Figure 4. Determination of DBP anions and bromide spiked in drinking water A using a 500-µL injection volume.

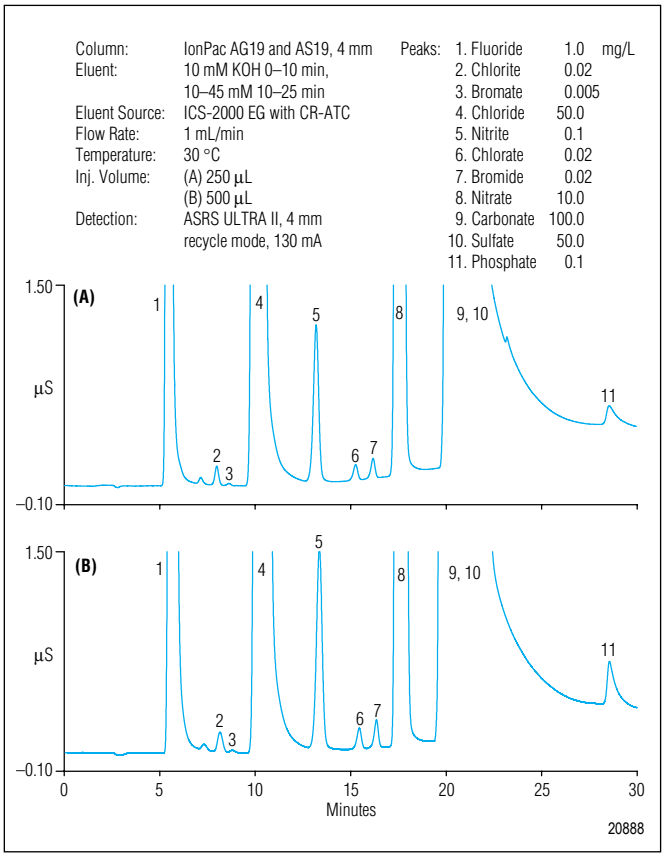

Figure 5. Comparison of simulated drinking water using (A) 250-µL injection and (B) 500-µL injection.

Table 4. Recoveries of Trace Oxyhalides and Bromide Spiked into Environmental Waters												
Analyte	**Drinking Water A**			**Drinking Water B**			**Drinking Water C**			**Drinking Water D**		
	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 (%)**	**Amount Found (μg/L)**	**Amount Added (μg/L)**	**Recovery (%)**
Chlorite	8.8	10.0	95.3	<MDL	21.0	105.6	11.6	10.0	95.7	<MDL	20.0	108.0
Bromate	<MDL	5.0	92.2	<MDL	5.1	95.6	<MDL	5.0	96.8	1.3	4.9	93.9
Chlorate	81.9	106.0	96.9	120	144.0	104.4	85.3	90.7	97.6	73.6	79.4	98.2
Bromide	26.3	30.0	99.6	202	200.0	99.8	1.2	25.0	94.2	9.7	10.0	107.4
Analyte	**Drinking Water E**			**Surface Water**			**Shallow Well Water[b]**			**Well Water[b]**		
	Amount Found (μg/L)	**Amount Added (μg/L)**	**Recovery (%)**	**Amount Found (μg/L)**	**Amount Added (μg/L)**	**Recovery (%)**	**Amount Found[c] (μg/L)**	**Amount Added (μg/L)**	**Recovery (%)**	**Amount Found[c] (μg/L)**	**Amount Added (μg/L)**	**Recovery (%)**
Chlorite	4.6	14.0	93.4	<MDL	20.0	95.7	<MDL	21.0	103.1	<MDL	20.0	101.4
Bromate	<MDL	5.0	100.5	<MDL	5.0	94.7	16.0	9.8	101.1	<MDL	5.0	86.5
Chlorate	136.0	151.0	99.9	<MDL	20.0	96.8	<MDL	30.0	96.8	10.6	20.0	93.0
Bromide	<MDL	20.0	24.8[a]	<MDL	20.0	103.3	381.0	200.0	104.0	452.0	230.0	100.7

[a] Suspect/matrix

[b] Sample diluted 1:1

[c] Calculated amounts

Accuracy and Precision

The performance of the IonPac AS19 was also evaluated through a single-operator precision and bias study using spiked municipal and bottled water samples. Table 4 shows typical recoveries for single-operator data obtained using the IonPac AS19 column for trace concentrations of DBPs and bromide in environmental waters. Most anions demonstrated acceptable recoveries (i.e., 75–125%) according to the criteria outlined in EPA Method 300.1. However, drinking water E resulted in an exceptionally lower recovery for bromide, regardless of the amount of bromide spiked in the sample. Section 9.4.1.5 of EPA Method 300.1 states, "If the recovery of any analyte falls outside the LFM [Laboratory Fortified Matrix] recovery range and the laboratory performance for that analyte is shown to be in control, the recovery problem encountered with the LFM is judged to be either matrix or solution related, not system related." Therefore, the sample was labeled as "suspect/matrix" to indicate that the poor recovery of bromide was sample related and not system related.

Due to the high ionic strength of the well water samples, both were diluted 1:1 to avoid column overloading. The estimated chloride and sulfate concentrations were 160 and 270 ppm, respectively, for the shallow well water, and 150 and 170 ppm, respectively, for the well water prior to dilution. These concentrations exceed the limits determined for this column during the sample overload study. Section 4.1.2 in EPA Method 300.1 states that "sample dilution will alter your Minimum Reporting Limit (MRL) by a proportion equivalent to that of the dilution." In this study, dilution of the well water samples increased the bromate MRL from 1 to 2 μg/L. However, the adjusted MRL was still sufficient to report the 8 μg/L bromate detected in the diluted sample. Because this well water sample is not known to be treated, the presence of bromate was unexpected. The detection of bromate in the well water may result from contamination by a nearby site that originally contained a high concentration of the anion.

Figure 6A shows a chromatogram of diluted shallow well water. Figure 6B shows the same well water sample spiked with 10–20 µg/L of DBP anions and 200 µg/L of bromide. As shown, bromate was well resolved from the high concentration of chloride, resulting in a recovery of 101.1%.

Figure 7 shows chromatograms of an unspiked and spiked drinking water B. This sample also demonstrates the excellent resolution and accuracy of analysis for the determination of trace DBP anions and bromide using an RFIC system. The calculated recoveries of the target analytes ranged from 96 to 106%.

This study also included the analysis of a variety of bottled water samples randomly obtained from a local supermarket. A previous study conducted from 1997–1998 in Canada found many bottled waters contained bromate, some at concentrations greater than 25 µg/L.[17] These results in combination with the increasing popularity of bottled water, led us to examine the presence of bromate in several different brands of bottled waters. More than half of the bottled waters tested in this study reported using ozonation as a form of treatment according to the bottle's label or company's web site (Table 5).

Table 5. Treatments Used for Different Bottled Waters

Bottled Water	Treatment
1	Natural spring water (no treatment)
2	UV light, RO[a], ozonation
3	Ozonation
4	Natural mineral water (no treatment)
5	RO
6	Microfiltration, UV light, ozonation
7	Filtration
8	Microfiltration, ozonation
9	Natural spring water (no treatment)
10	Microfiltration, ozonation
11	Microfiltration, RO, DI[b], ozonation
12	Ozonation

[a] RO = reverse osmosis

[b] DI = deionization

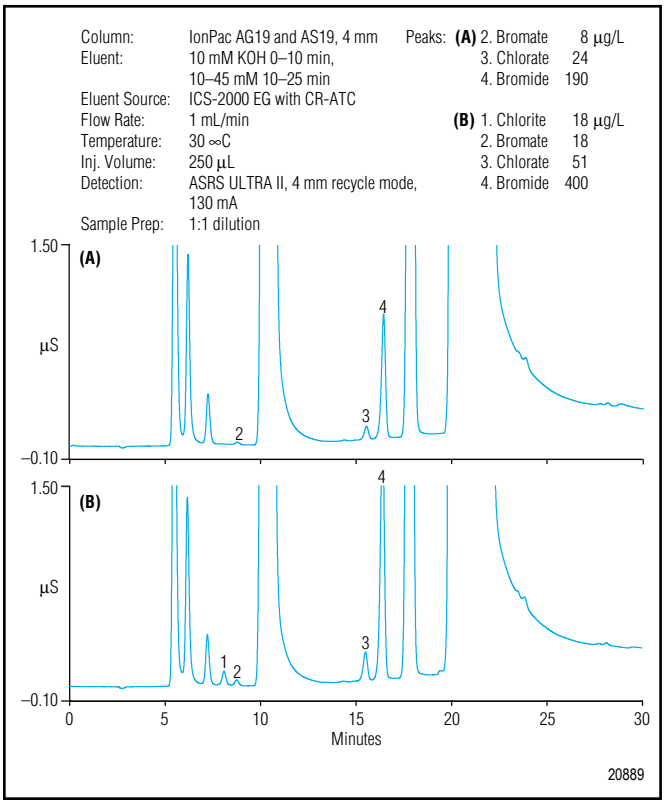

Figure 6. Determination of DBP anions and bromide in (A) shallow well water and (B) spiked shallow well water using the IonPac AS19 column.

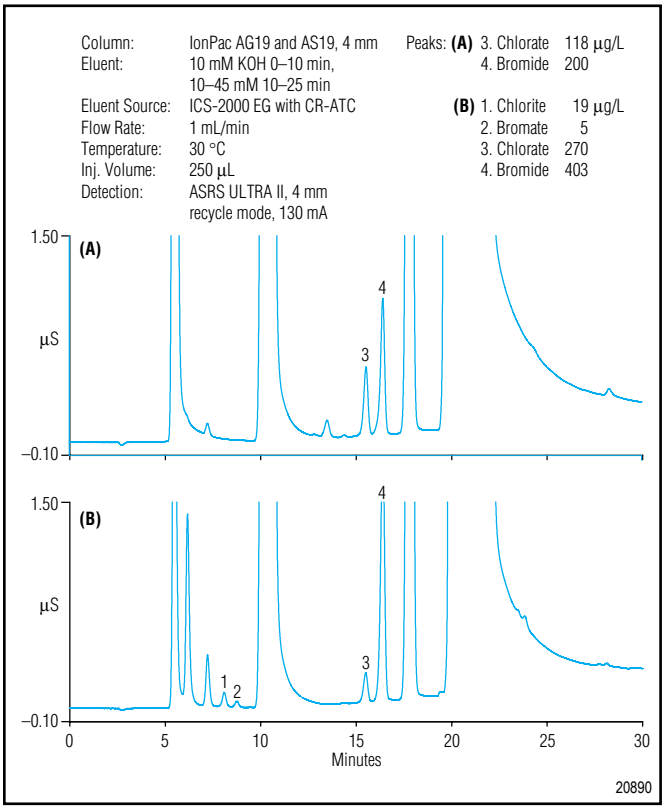

Figure 7. Determination of DBP anions and bromide in (A) drinking water B and (B) spiked drinking water B using the IonPac AS19 column.

Table 6 shows the amount found and the recoveries obtained using the AS19 column for trace concentrations of DBP anions and bromide spiked in the bottled waters. All target analytes demonstrated acceptable recoveries according to U.S. EPA Method 300.1. Only four bottles tested contained some amount of bromate, with two of these near or slightly above the bromate MCL of 10 µg/L. No correlation was observed between the concentrations of bromide in the samples versus the amount of bromate detected. For example, bottled water #10 contained approximately 4 µg/L bromate, but no bromide was detected in the sample. However, the conversion of bromide to bromate upon ozonation is affected by several factors, such as the presence of natural organic matter, pH, temperature, and other variables.[2] As expected, most bottled waters analyzed contained appreciably less chloride and sulfate than tap water with estimated maximum concentrations of 8 and 30 ppm, respectively. The low ionic content of most bottled waters allows the use of larger injection volumes

Table 6. Recoveries of Trace Oxyhalides and Bromide Spiked into Bottled Waters

Analyte	Bottled Water 1			Bottled Water 2			Bottled Water 3			Bottled Water 4		
	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 (%)	Amount Found (µg/L)	Amount Added (µg/L)	Recovery (%)
Chlorite	<MDL	20.0	108.1	<MDL	20.0	102.9	<MDL	20.0	99.8	<MDL	20.0	90.2
Bromate	<MDL	5.0	96.1	<MDL	5.0	100.7	10.2	9.8	104.6	<MDL	5.0	83.5
Chlorate	2.4	20.0	107.7	<MDL	20.0	106.5	<MDL	20.0	102.8	10.2	20.0	103.5
Bromide	7.5	20.0	105.0	<MDL	20.0	106.5	19.4	20.0	92.9	95.5	105.0	
Analyte	**Bottled Water 5**			**Bottled Water 6**			**Bottled Water 7**			**Bottled Water 8**		
	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 (%)	Amount Found (µg/L)	Amount Added (µg/L)	Recovery (%)
Chlorite	<MDL	20.0	101.2	<MDL	20.0	101.5	<MDL	20.0	106.7	<MDL	20.0	102.2
Bromate	<MDL	5.0	95.9	9.2	9.8	106.6	<MDL	5.0	92.3	<MDL	5.0	93.7
Chlorate	1.6	20.0	108.6	375.0	150.0	97.3	<MDL	25.0	90.6	<MDL	20.0	105.4
Bromide	1.2	20.0	95.6	2.5	20.0	100.9	31.8	30.0	98.9	18.7	20.0	
Analyte	**Bottled Water 9**			**Bottled Water 10**			**Bottled Water 11**			**Bottled Water 12**		
	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 (%)	Amount Found (µg/L)	Amount Added (µg/L)	Recovery (%)
Chlorite	<MDL	20.0	106.1	<MDL	20.0	98.2	<MDL	20.0	104.8	<MDL	20.0	95.2
Bromate	<MDL	5.0	98.4	4.4	5.0	101.1	<MDL	5.0	96.4	0.98	5.0	102.1
Chlorate	<MDL	20.0	105.7	<MDL	20.0	107.7	<MDL	23.0	98.3	4.2	20.0	98.5
Bromide	<MDL	20.0	104.1	<MDL	20.0	105.3	6.3	23.0	94.5	<MDL	20.0	

(500 µL or more). Figure 8 shows a 250-µL injection of an unspiked and spiked bottled water sample. The disinfection treatment used for this bottled water was UV radiation and ozonation. An unusually high amount of chlorate was detected in the sample, indicating that some form of chlorination may also be used for treatment. Bromate was detected at a slightly lower concentration than the EPA's MCL, possibly indicative of elevated levels of bromide in the source water. The recoveries for oxyhalide DBPs and bromide spiked in the sample ranged from ~97 to 107%, well within EPA Method 300.1 specifications.

The precision of the method using the AS19 column in combination with an electrolytic eluent generation was determined by performing 10 replicate injections of randomly selected samples spiked with trace concentrations of DBPs and bromide. Overall, the calculated peak area precisions varied from 0.21 to 1.78% with retention time precisions <0.04% for most target analytes. For bromate, the worst peak area precision observed was 1.78%. This number represents a deviation of only ±0.09 µg/L based on a sample containing 5 µg/L bromate. The high precision of this method is consistent with results typically found with an RFIC system.

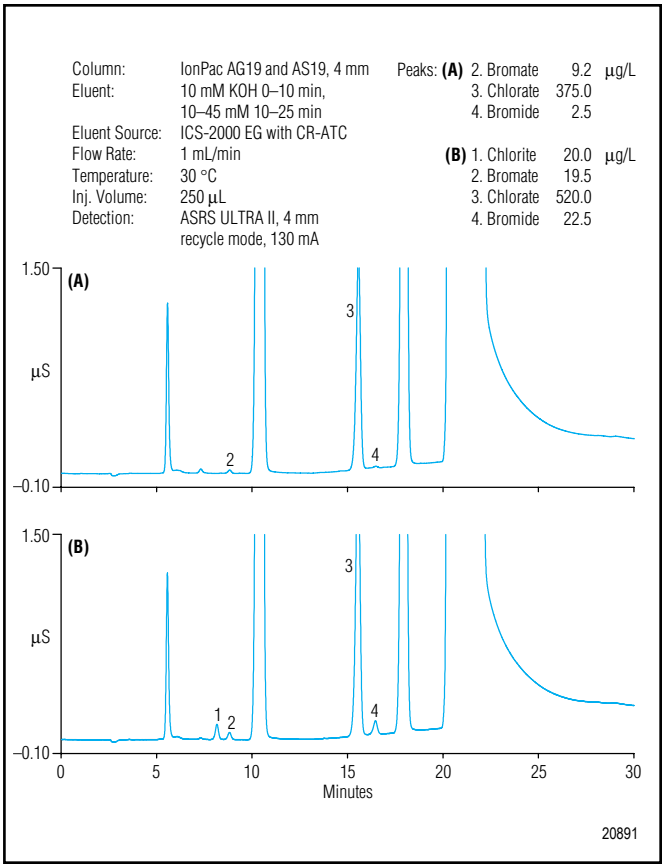

Figure 8. Determination of DBP anions and bromide in (A) bottled water 6 and (B) spiked bottled water 6 using the IonPac AS19 column.

CONCLUSION

IC with a hydroxide-selective IonPac AS19 column and an electrolytic eluent generator is an improved approach for determining trace concentrations of DBP anions and bromide in municipal and bottled water samples. The high-capacity AS19 column can be used with large-volume injections to detect low-ppb concentrations of bromate, a potential human carcinogen, in many municipal and bottled waters. In addition, electrolytic generation of an ultrapure potassium hydroxide eluent, combined with the AS19 column, improves linearity, MDLs, precision, and resolution between bromate and chloride compared to the AS9-HC column described in EPA Method 300.1. This approach also eliminates the need to manually prepare eluents and thereby increases the automation, ease of use, and reproducibility between analysts and laboratories. The U.S. EPA, Office of Water, has determined that the use of hydroxide eluents in EPA Method 300.1 is acceptable for compliance monitoring under the Clean Water Act and Safe Drinking Water Act.[18]

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Determination of Trace Concentrations of Chlorite, Bromate, and Chlorate in Bottled Natural Mineral Waters

INTRODUCTION

Bottled water has been one of the fastest growing beverage markets in the last five to ten years. Global consumption approached 41 billion gallons in 2004, an increase of 6.5% from 2003.[1] The bottled water industry markets to health conscious consumers as an alternative not only to tap water, but also to carbonated soft drinks and juice drinks.[1] Regardless of whether the water is delivered from a local municipality or is prepackaged in a bottle, the consumption of safe and reliable drinking water is essential to maintain a healthy lifestyle.

Bottled water must be disinfected to remove pathogenic microorganisms and ensure it is safe for human consumption. Water companies prefer ozone as a disinfectant because it is one of the most effective treatments available, it does not leave a taste, and there is no residual disinfectant in the bottled water.[2,3] Some bottlers, however, use ultraviolet light or chlorine dioxide as alternative treatment methods.[2] Reactions between disinfectants and natural organic and inorganic matter in the source water can result in the production of undesirable disinfection byproducts (DBPs), such as chlorite, bromate, and trihalomethanes, that are potentially harmful to humans.[4] Bromate, for example, can be formed by ozonation of water containing naturally occurring bromide, or may be present as an impurity in sodium hypochlorite used for treatment.[5]

Results from toxicological studies led the International Agency for Research on Cancer to conclude that bromate is a potential human carcinogen, even at low µg/L (ppb) concentrations.[6] The World Health Organization (WHO) estimated excess lifetime cancer risks of 10^{-4}, 10^{-5}, and 10^{-6} for drinking water containing bromate at 20, 2, and 0.2 µg/L, respectively.[9] The U.S. EPA,[7] European Commission,[8] and the WHO[9] set a maximum permissible limit of 10 µg/L bromate in tap water. The U.S. FDA[10] adopted the same regulatory limit for bottled water. In Europe, natural mineral waters and spring waters treated by ozonation have a maximum permissible limit of 3 µg/L bromate.[11]

Traditionally, ion chromatography (IC) with suppressed conductivity detection has been used for determination of bromate and other DBPs in drinking water, as described in EPA Method 300.1.[12] This method describes the use of a high-capacity IonPac AS9-HC column with a carbonate eluent and large loop injection to achieve a method detection limit (MDL) of 1.4 µg/L bromate. In early 2006, the U.S. EPA enacted stage 2 of the disinfectants/disinfection byproducts (D/DBP) rule, maintaining the maximum permissible limit for bromate but adding three additional analytical methods to further improve the selectivity and sensitivity for bromate.[13] U.S. EPA Methods 317.0 and 326.0 combine suppressed conductivity detection and absorbance detection after postcolumn addition to achieve bromate MDLs less than 0.2 µg/L.[14,15] IC coupled to inductively coupled plasma mass spectrometry has also been demonstrated for the determination of low concentrations of bromate in environmental waters, permitting a bromate MDL of 0.3 µg/L.[16]

A high-capacity IonPac® AS19 column with an electrolytically generated hydroxide eluent, large loop injection, and suppressed conductivity detection can achieve a calculated bromate MDL of 0.34 µg/L.[17] Absorbance detection after postcolumn addition can reduce this MDL to less than 0.2 µg/L, using EPA Methods 317.0 and 326.0.[18,19] In this application note, we compare the IonPac AS19 using an electrolytically generated hydroxide eluent to the IonPac AS23 column using an electrolytically generated carbonate/bicarbonate eluent for the determination of chlorite, bromate, and chlorate in natural mineral waters. We compare the linearity, method detection limits, precisions, and recovery for three mineral waters obtained from three European countries to determine whether these columns have the sensitivity required to meet current EPA and EU requirements.

EQUIPMENT

A Dionex ICS-2000 Reagent-Free™ Ion Chromatography (RFIC™) system was used in this work. The ICS-2000 is an integrated ion chromatograph and consists of:

- Eluent generator
- Pump with in-line vacuum degas
- Column heater
- Hydroxide system:
  - EluGen® EGC II KOH cartridge (Dionex P/N 058900)
- CR-ATC (Dionex P/N 060477)
- Carbonate system:
  - EluGen EGC II K_2CO_3 cartridge (Dionex P/N 058904)
- EPM Electrolytic pH Modifier to generate the carbonate/bicarbonate eluent (Dionex P/N 063175)
- EGC Carbonate Mixer (Dionex P/N 079943)
- Two 4-L plastic bottle assemblies (for external water mode of suppression)
- AS Autosampler
- Chromeleon® Chromatography Management Software

REAGENTS AND STANDARDS

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

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

Sodium bromate ($NaBrO_3$, EM SX 03785-1)

Sodium chlorate ($NaClO_3$, Fluka 71370)

CONDITIONS

Columns:	(A) IonPac AS19 Analytical, 4 × 250 mm (Dionex P/N 062885) IonPac AG19 Guard, 4 × 50 mm (Dionex P/N 062887)
	(B) IonPac AS23 Analytical, 4 × 250 mm (Dionex P/N 064149) IonPac AG23 Guard, 4 × 50 mm (Dionex P/N 064147)
Eluent:	(A) 10 mM KOH from 0–10 min, 10–45 mM from 10–25 min, 45 mM from 25–30 min*
	(B) 4.5 mM K_2CO_3/0.8 mM $KHCO_3$
Eluent Source:	(A) EGC II KOH with CR-ATC
	(B) EGC II K_2CO_3 with EPM
Flow Rate:	1.0 mL/min
Temperature:	30 °C
Injection:	250 µL
Detection:	(A) Suppressed conductivity, ASRS® ULTRA II, 4 mm (Dionex P/N 061561) AutoSuppression® recycle mode 130 mA current
	(B) Suppressed conductivity, ASRS ULTRA II, 4 mm AutoSuppression external water mode 25 mA current
CRD:	(A) 4-mm format (P/N 062983)
Background Conductance:	(A) <1 µS
	(B) 18–20 µS
System Backpressure:	~2200 psi
Run Time:	30 min

*Method returns to 10 mM KOH for 3 min prior to injection.

PREPARATION OF SOLUTIONS AND REAGENTS

Eluent Solution for the AS23 Column

4.5 mM Carbonate/0.8 mM Bicarbonate

Generate the carbonate/bicarbonate eluent on-line by pumping high quality deionized water (18 M -cm resistivity or better) through the EluGen EGC II K_2CO_3 Cartridge and EPM. Chromeleon will track the amount of eluent used and calculate the remaining lifetime.

Alternatively, prepare the eluent solution by adding 10 mL of the AS23 Eluent Concentrate (Dionex P/N 064161) to a 1-L volumetric flask containing

approximately 700 mL of degassed deionized water. Bring to volume and mix thoroughly. The 0.45 M sodium carbonate/0.08 M sodium bicarbonate concentrate can also be prepared from the salts by combining 47.7 g sodium carbonate (MW=106 g/mole) and 6.72 g sodium bicarbonate (MW=84 g/mole) in a 1-L volumetric flask containing approximately 700 mL of degassed deionized water. Bring to volume and mix thoroughly.

Stock Standard Solutions

Prepare 1000 mg/L stock standard solutions of chlorite, bromate, and chlorate by dissolving 0.1676 g, 0.1180 g, and 0.1275 g, respectively, of the corresponding sodium salts in separate 100 mL volumetric flasks of DI water.

Calibration Standard Solutions

Prepare a secondary stock solution containing 1 mg/L each of chlorite and chlorate and a separate secondary stock solution containing 1 mg/L bromate by performing the appropriate dilutions of the 1000 mg/L stock standards. Calibration standards can then be prepared from the secondary solutions using the appropriate dilutions. Dilute working standards should be prepared monthly, except those that contain chlorite, which must be prepared every two weeks, or sooner if evidence of degradation is indicated by repeated QC failures. Concentration ranges used in this application note are shown in Table 1.

SAMPLE PREPARATION

For the present analysis, mineral waters B and C were degassed for 10–15 min under vacuum due to an excess amount of bicarbonate in the samples. Increased amounts of bicarbonate in the sample can produce shifts in retention times as shown in Figures 1A and 1B. In addition, due to the presence of significantly high concentrations of sulfate in mineral water C, the sample was diluted 1:5 with DI water prior to analysis.

Table 1. Calibration Data, Retention Time Precisions, Peak Area Precisions, and Method Detection Limits For DBP Anions

Analyte	Range (µg/L)	Linearity (r^2)	Retention Time[a] RSD (%)	Peak Area RSD (%)	MDL Standard (µg/L)	Calculated MDL (µg/L)
IonPac AS19 Column						
Chlorite	2-50	0.9999	0.04	1.20	1.0	0.18
Bromate	1-25	0.9995	0.03	1.40	2.0	0.31
Chlorate	2-50	0.9999	0.01	0.54	1.0	0.28
IonPac AS23 Column						
Chlorite	10-50	0.9999	0.07	2.20	5.0	1.02
Bromate	5-25	0.9998	0.07	2.63	5.0	1.63
Chlorate	10-50	0.9998	0.11	2.48	9.0	2.05

[a]RSD= relative standard deviation, n = 10 for a standard consisting of 10 ppb bromate and 20 ppb each of chlorite and chlorate.

RESULTS AND DISCUSSION

The IonPac AS23 is a high-capacity anion-exchange column specifically designed to be used with carbonate /bicarbonate eluent for the determination of the trace DBPs, chlorite, bromate, and chlorate, together with common inorganic anions, including bromide (precursor to bromate), in drinking waters. To simplify the method and avoid manual eluent preparation, this column can be used with electrolytically generated potassium carbonate that is modified by an Electrolytic pH Modifier (EPM) to automatically generate the carbonate/bicarbonate eluent that is required for analyte separation. The IonPac AS23 column was developed using a unique polymer technology to achieve a capacity of 320 µeq/column, higher than the IonPac AS9-HC column (190 µeq/column) described in EPA Method 300.1. The combination of an optimized selectivity for DBP anions, high anion exchange capacity, and improved selectivity of carbonate from inorganic anions and oxyhalides, makes this column an ideal replacement for the AS9-HC column.

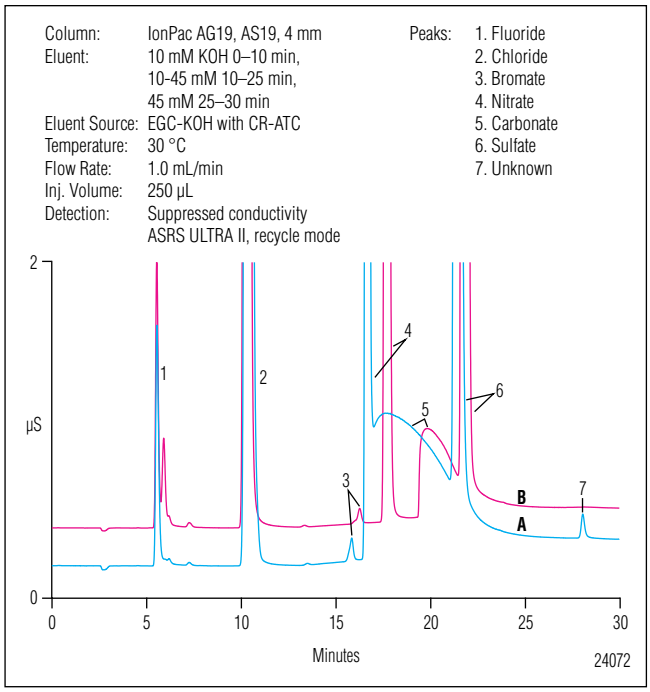

Figure 1. Comparison of mineral water B
A) before vacuum degas and B) after vacuum degas.

In this application, we compare the IonPac AS23 column to the hydroxide-selective IonPac AS19 column for the determination of trace DBP anions in natural mineral waters. Figure 2 compares the separation for chlorite, bromate, and chlorate on the IonPac AS19 and AS23 columns. As shown, both columns provide good selectivity for the target DBP anions.

The linear calibration ranges, MDLs, and quality control standard (QCS) performances were evaluated for the hydroxide and carbonate eluent systems. The hydroxide eluent system was calibrated using four increasing concentrations of chlorite and chlorate (2-50 µg/L) and five increasing concentrations of bromate (1-25 µg/L). For the carbonate-based system, chlorite and chlorate were calibrated from 10-50 µg/L whereas bromate was calibrated from 5-25 µg/L using three different concentrations. Each system produced a linear response in its respective range with a correlation coefficient greater than 0.999. The improved sensitivity of the hydroxide eluent system, however, allowed a lower minimum reporting limit (MRL) than the carbonate-based system. The MDLs for the target DBPs were determined for each system by performing seven replicate injections of reagent water fortified with the calibration standards at concentrations of three to five times the estimated instrument detection limits.

Table 1 compares the calibration data, retention time and peak area precisions for a QCS, and MDLs for the IonPac AS19 with an electrolytically generated hydroxide eluent to the IonPac AS23 with an electrolytically generated carbonate/bicarbonate eluent. The calculated MDL of bromate with the IonPac AS19 column was 0.31 µg/L compared to 1.63 µg/L using the IonPac AS23 column. This demonstrates that hydroxide eluents improve the sensitivity for bromate compared to carbonate-based eluents and are therefore more suitable to meet the current European regulatory requirement of 3 µg/L bromate in natural mineral waters. Either the AS19 or AS23 based IC systems are capable of measuring the 10 µg/L requirement of bromate for tap water or U.S. bottled water according to the regulations established by the U.S. EPA, U.S. FDA, WHO, and European Commission.

In the U.S., mineral water is defined as water that contains no less than 250 ppm total dissolved solids (TDS) and that originates from a geologically and

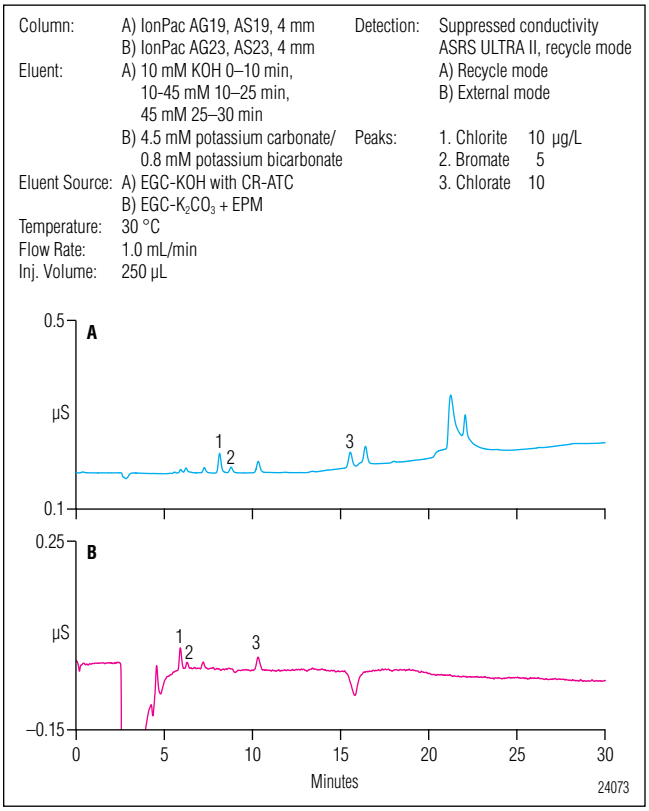

Figure 2. Separation of disinfection byproducts using the A) IonPac AS19 column and B) IonPac AS23 column.

physically protected underground water source. Mineral content must be maintained at a constant level and no minerals may be added to the water.[18] In Europe, mineral water is defined as microbiologically wholesome water, originating from an underground water table or deposit and emerging from a spring tapped at one or more natural or bored exits. It can contain less than 50 ppm TDS.[19] The total mineral content of the waters can vary significantly, with higher mineral concentrations generally appearing in Russia, the Baltic States, and Germany. The differences between regions are most likely a result of differences in the overall compositions of the waters and the geological locations.[20]

In this application, three natural mineral waters from different European countries with TDSs that varied significantly from 136 to 2359 ppm were evaluated. The properties of the investigated water samples are summarized in Table 2. As shown, the ionic strength of mineral water C is significantly higher than observed in typical drinking waters. The absence of bromate in the bottled mineral waters analyzed indicated that ozonation was not used for disinfection.

Tables 3 and 4 summarize typical recoveries for single-operator data obtained using the IonPac AS19 and AS23 columns, respectively, for trace concentrations of DBP anions in three European natural mineral water samples. As shown, chlorite and bromate were not detected in any of the samples analyzed,whereas only a trace concentration of chlorate was detected in mineral water A. To determine the accuracy of the method, the samples were spiked with 5 µg/L bromate and 10 µg/L each of chlorite and chlorate. Calculated recoveries for the spiked mineral water samples were in the range of 86–97% and 84–111% using the IonPac AS19 and AS23 columns, respectively. The analyte recoveries using either a hydroxide or carbonate/bicarbonate eluent were within the acceptable range of 75–125% according to the criteria described in EPA Method 300.1. Figure 3 compares chromatograms of mineral water A using the IonPac AS19 and AS23 columns. Figure 4 shows the same chromatograms spiked with 5 µg/L bromate and 10 µg/L each of chlorite and chlorate, which resulted in good recoveries for both eluents. Although bromide was not quantified in this study, the estimated concentrations were approximately 16 µg/L in mineral waters A and B and 2 µg/L in mineral water C. Therefore, ozonation of mineral waters A and B could potentially produce bromate. To demonstrate the applicability of detecting bromate at concentrations significantly less than the 3 µg/L European regulatory limit for ozonated mineral waters, mineral water A was spiked with 0.5 µg/L bromate (Figure 5). As shown, bromate can be observed easily at this concentration, with good peak-to-peak baseline noise of 0.3–0.5 nS.

Table 2. Concentrations in mg/L of Cations and Anions in the Investigated Mineral Water Samples

Mineral water	Na^+	K^+	Mg^{2+}	Ca^{2+}	F^-	Cl^-	NO_3^-	HCO_3^-	SO_4^{2-}
A	11.8	6.2	8	11.5	–[a]	13.5	6.3	71	8.1
B	4.5	0.5	8	32.0	–[a]	5.0	< 2	133	7.0
C	4.2	–[a]	117	510	1.8	3.0	< 0.1	278	1445

[a]Not specified.

Table 3. Recoveries of Disinfection Byproduct Anions in Natural Mineral Waters Using the IonPac AS19 Column

Mineral water	Analyte	Amount found (µg/L)	Amount added (µg/L)	Recovery (%)
A	Chlorite	<MDL	10	87.7
	Bromate	<MDL	5.0	96.0
	Chlorate	4.4	10	91.1
B	Chlorite	<MDL	10	86.4
	Bromate	<MDL	5.0	97.4
	Chlorate	<MDL	10	90.7
C	Chlorite	<MDL	10	87.6
	Bromate	<MDL	5.0	94.7
	Chlorate	<MDL	10	92.8

Table 4. Recoveries of Disinfection Byproduct Anions in Natural Mineral Waters Using the IonPac AS23 Column

Mineral water	Analyte	Amount found (µg/L)	Amount added (µg/L)	Recovery (%)
A	Chlorite	<MDL	10	107.6
	Bromate	<MDL	5.0	91.2
	Chlorate	4.6	10	99.3
B	Chlorite	<MDL	10	110.6
	Bromate	<MDL	5.0	93.5
	Chlorate	<MDL	10	92.9
C	Chlorite	<MDL	10	104.3
	Bromate	<MDL	5.0	83.9
	Chlorate	<MDL	10	102.6

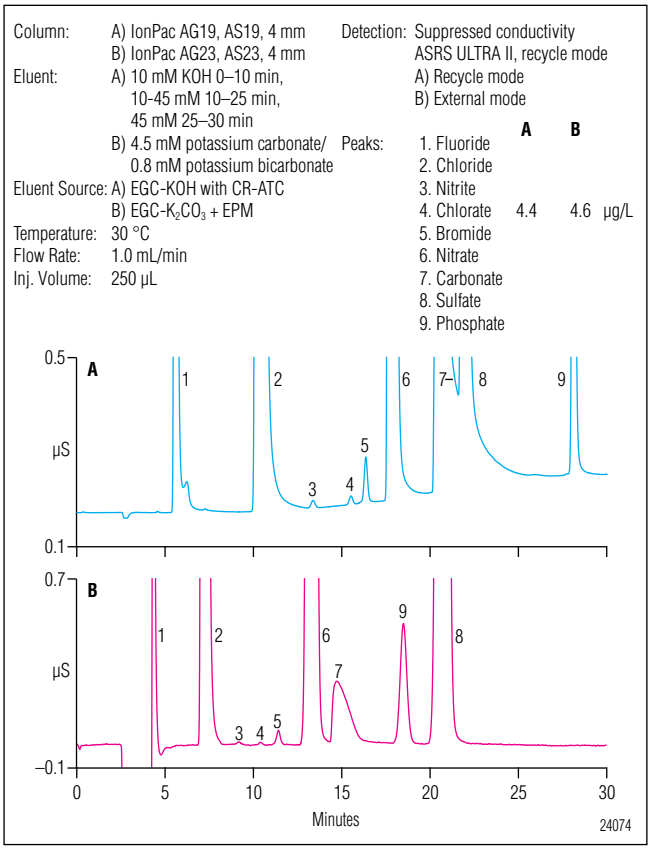

Figure 3. Comparison of the A) IonPac AS19 and B) IonPac AS23 columns for the separation of DPB anions in mineral water A.

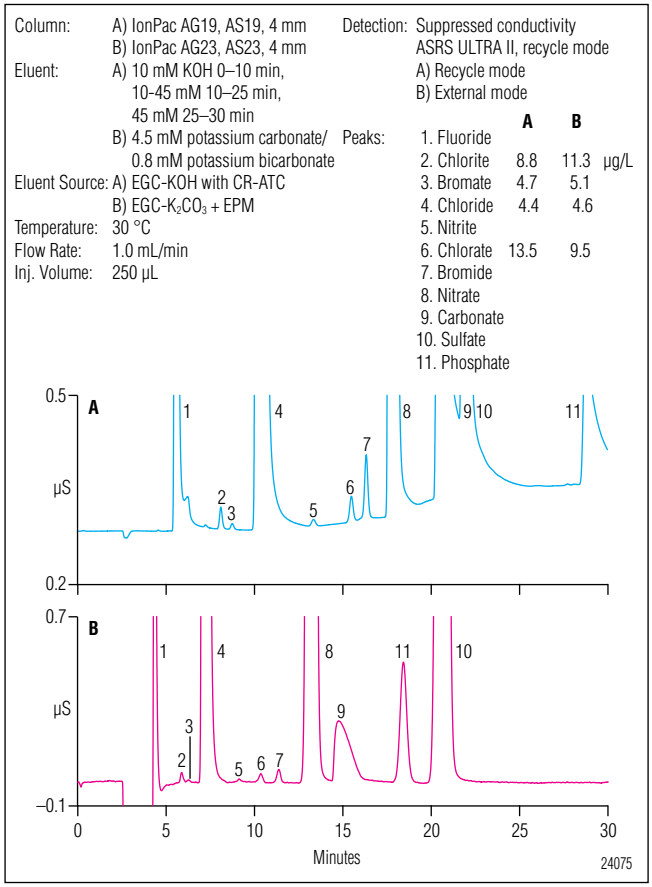

Figure 4. Comparison of the A) IonPac AS19 and B) IonPac AS23 columns for the separation of trace concentrations of common anions and DPB anions spiked in mineral water A.

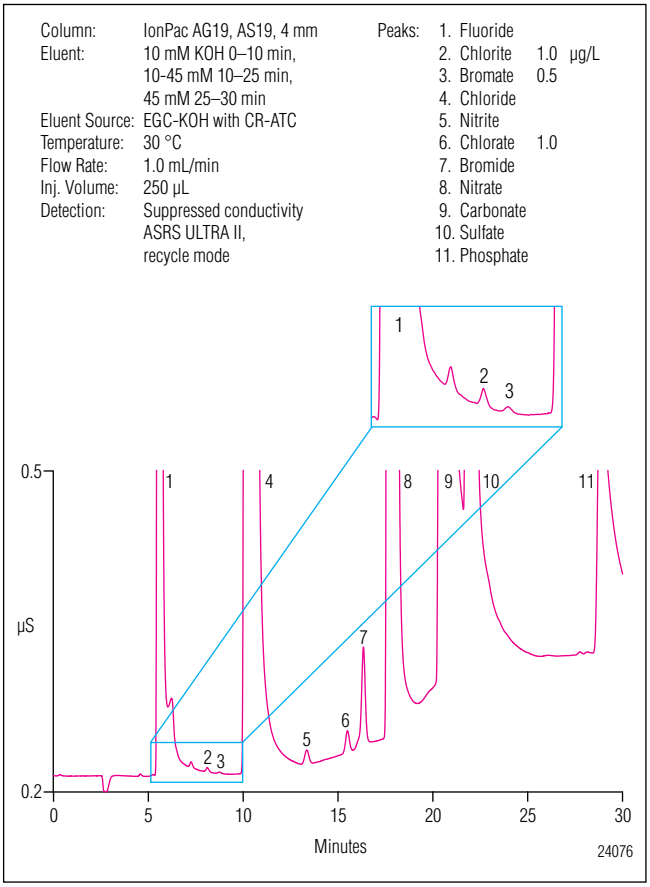

Figure 5. Chromatogram of mineral water A spiked with 1 µg/L each chlorite and chlorate and 0.5 µg/L bromate.

CONCLUSION

The IonPac AS19 column using an electrolytically generated hydroxide eluent was compared to the AS23 column using an electrolytically generated carbonate/bicarbonate eluent for the determination of trace concentrations of DBP anions in natural mineral waters. The improved sensitivity using a hydroxide eluent allowed the detection of lower concentrations of bromate, a potential human carcinogen, in drinking waters. Therefore, the IonPac AS19 with an electrolytically generated hydroxide eluent is recommended for laboratories that must comply with EU Directive 2003/40/EC, which permits a maximum of 3 µg/L bromate in mineral waters treated with ozone. The use of either the IonPac AS19 column with a hydroxide eluent or IonPac AS23 column with a carbonate/bicarbonate eluent provides the required sensitivity to meet the maximum permissible limit of 10 µg/L bromate currently required by most regulatory agencies. Both columns demonstrated good resolution between bromate and chloride and comparable recovery for mineral water samples spiked with known concentrations of chlorite, bromate, and chlorate. In addition, hydroxide or carbonate/bicarbonate eluents can be generated on-line from deionized water, freeing the operator from manually preparing eluents. This increases the automation, ease-of-use, and reproducibility between analysts and laboratories.

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Determination of Phenols in Drinking and Bottled Mineral Waters Using Online Solid-Phase Extraction Followed by HPLC with UV Detection

INTRODUCTION

Phenolic compounds are subject to regulation as water pollutants due to their toxicity. The European Community (EC) Directive specifies a legal tolerance level of 0.5 µg/L for each phenol in water intended for human consumption[1] and Japan's Ministry of Health, Labour, and Welfare specifies a maximum contaminant level (MCL) of 5 µg/L for phenols in drinking water.[2] The U.S. EPA specifies a MCL of 1 µg/L for pentachlorophenol,[3] and eleven common phenols are on the U.S. EPA priority pollutants list.[4] The structures for these common phenols are shown in Figure 1. The method typically used for determining phenols is gas chromatography (GC) combined with flame ionization detection (FID)[5,6] or mass spectrometric detection (GC–MS).[7-9] However, liquid chromatography (LC) methods combined with UV/DAD,[10] electrochemical,[11] and fluorescence[12] detections are finding increased application, particularly due to nonvolatiles in many samples that can poison GC columns.

Method detection limits (MDLs) of LC techniques employing direct injection of samples are too high for the detection of the low levels allowed in natural waters. Therefore, water samples require preconcentration before analysis. Solid-phase extraction (SPE) is one of the most important techniques for sample enrichment, because it overcomes many of the disadvantages of liquid-liquid extraction. Unfortunately, preparing individual samples is time consuming, and a new SPE cartridge must be used for each sample.

The expense of using multiple SPE cartridges and the associated manual labor can be eliminated with online SPE combined with HPLC. This technique delivers a simple, rapid, and accurate means for determining phenols at low concentrations in real samples.[13,14] The UltiMate® 3000 was designed to easily execute more advanced HPLC methods, such as parallel LC, 2-D LC, and online SPE/HPLC. An UltiMate 3000 together with an autosampler capable of injecting large volumes can be used to execute an online SPE method to determine phenols in drinking and bottled waters. A method using one pump channel of a dual pump system instead of the large volume injector can also be used to achieve online SPE, as described in the Appendix.

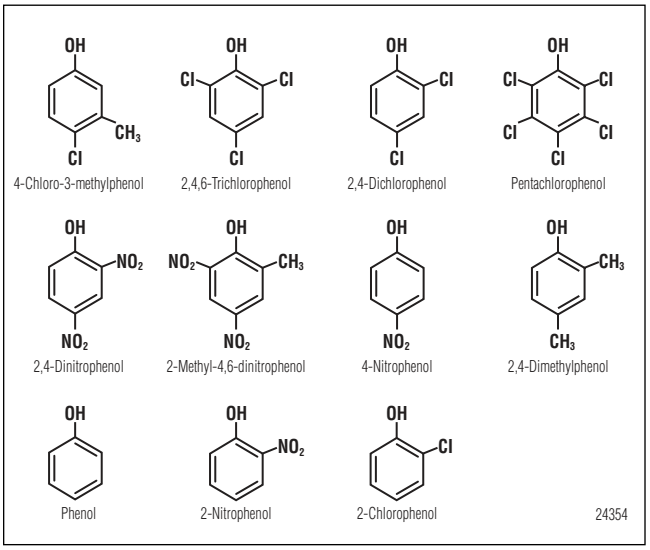

Figure 1. Structures of the 11 phenols specified in the U.S. EPA priority pollutants list.

This application note details an online SPE method followed by HPLC with UV detection for determining the 11 phenols specified in U.S. EPA Priority Pollutants List at the concentrations required by world regulatory agencies. Phenols from drinking and bottled waters are trapped on an IonPac® NG1, a small polymeric reversed-phase column, then separated on a polar-embedded reversed-phase column, the Acclaim® PA. This automated method is a cost-effective way to determine phenols in drinking and bottled water samples.

EQUIPMENT

Dionex UltiMate 3000 HPLC system consisting of:

- DGP 3600M dual gradient pump
- SRD 3600 solvent rack with integrated vacuum degasser
- TCC-3200 Thermostatted Column Compartment with two two-port, six-position (2P-6P) valves
- VWD-3400 Variable Wavelength Detector

AS-HV High-Volume Autosampler*

Chromeleon® Chromatography Management Software, version 6.80

*See Precautions.

REAGENTS AND STANDARDS

Use only ACS reagent grade chemicals for all reagents and standards.

Deionized (DI) water from a Milli-Q® Gradient A10 water purification system

Methanol (CH_3OH), HPLC grade (Fisher)

Acetonitrile (CH_3CN), HPLC grade (Fisher)

Glacial acetic acid (HAc), analytical reagent-grade (Shanghai Chemical Reagent Company)

Ammonium acetate (NH_4Ac), analytical reagent-grade (Shanghai Chemical Reagent Company)

Methanesulfonic acid (MSA), > 99.5% (Aldrich)

Trifluoroacetic acid (TFA), > 99% (Aldrich)

604 Phenols Calibration Mix (Restec) 2000 µg/mL in methanol, consisting of:

4-chloro-3-methylphenol, 2-chlorophenol, 2,4-dichlorophenol, 2,4-dimethylphenol, 2,4-dinitrophenol, 2-methyl-4,6-dinitrophenol, 2-nitrophenol, 4-nitrophenol, pentachlorophenol, phenol, and 2,4,6-trichlorophenol

CONDITIONS

Solid-Phase Extraction

Column:	IonPac NG1, 5 µm, 4 × 35 mm (P/N 039567)
Mobile Phases for SPE (Left Pump):	A. 0.2 mM MSA B. CH_3CN
Flow Rates:	Rinse: 1 mL/min with 100% B Loading: 2 mL/min with 100% A Phenol Elution: 1 mL/min with 15% B
Inj. Volume:	10 mL
Column Temperature:	40 °C

The total time for on-line SPE is 14 min. For the detailed program see Table 1A.

Analytical

Column:	Acclaim PA, 5 µm, 4.6 × 150 mm (P/N 061320)
Mobile Phases for Analysis (Right Pump):	A. 25 mM HAc / 25 mM NH_4Ac (1.45 : 1, v/v) B. CH_3CN
Gradient:	25 to 70% B in 17.5 min
Flow Rate:	1 mL/min
Inj. Volume:	10 mL
Temperature:	40 °C
Detection:	UV, 280 nm

Total analysis time is 18 min. During SPE, the column is equilibrated for the next separation prior to injection while online SPE is occurring. For the detailed program see Table 1B.

Table 1A. Left Pump Program (Loading Pump Used for SPE) A = 0.2 mM MSA, B = Acetonitrile		
Time (min)	**Commands**	**Comments**
Preparation	ValveLeft = 6_1, ValveRight = 6_1	
–14.0	Flow = 1000 [µL/min] %B = 100.0, %C = 0.0, Curve = 5	Rinse the SPE column (NG1) using 100% CH_3CN, about 3 min.
–11.5	Flow = 1000 [µL/min] %B = 100.0, %C = 0.0, Curve = 5	
–11.0	Flow = 1000 [µL/min] %B = 1.0, %C = 0.0, Curve = 5	Equilibrate the SPE column.
–8.5	Flow = 2000 [µL/min] %B = 1.0, %C = 0.0, Curve = 5	Load sample from the loop to SPE column at 2 mL/min, about 5 min.
–3.5	Flow = 2000 [µL/min] %B = 1.0, %C = 0.0, Curve = 5	
–3.0	Flow = 1000 [µL/min] %B = 15.0, %C = 0.0, Curve = 5	Wash the SPE column.
0.2	Flow = 0 [µL/min] %B = 0.0, %C = 0.0, Curve = 5	
3.5	Flow = 200 [µL/min] %B = 100.0, %C = 0.0, Curve = 5	SPE column switches back to the system. Begin to wash the SPE column to prepare for loading the next sample.

Table 1B. Right Pump Program (Analytical Pump) A = 25 mM HAc/NH_4Ac, B = Acetonitrile		
Time (min)	**Commands**	**Comments**
Preparation	ValveLeft = 6_1, ValveRight = 6_1	
–14.0	Flow = 200 [µL/min] %B = 100.0, %C = 0.0, Curve = 5	Wash the analytical column.
–13.0	Flow = 200 [µL/min] %B = 25.0, %C = 0.0, Curve = 5	
–7.0	Flow = 200 [µL/min] %B = 25.0, %C = 0.0, Curve = 5	
–5.0	Flow = 1000 [µL/min] %B = 25.0, %C = 0.0, Curve = 5	Begin to equilbrate the analytical column using initial conditions for 5 min. Injections at 0 min.
17.5	Flow = 1000 [µL/min] %B = 70.0, %C = 0.0, Curve = 5	17.5 min gradient
18.0	Flow = 1000 [µL/min] %B = 100.0, %C = 0.0, Curve = 5	Begin the column wash.

PREPARATION OF STANDARDS

The preparation of standards for calibration is based on the requirements of EPA Method 604.[6]

Stock Standard Solution 1

Add 9.95 mL methanol using a graduated 5-mL pipette (two times) to a 10-mL vial, and add 50 µL of the 604 Phenols Calibration Mix (2000 µg/mL) using a 250-µL syringe. The concentration of stock standard solution 1 is 10 µg/mL.

Stock Standard Solution 2

Add 900 µL methanol to a 10-mL vial using a 5-mL graduated pipette, and add 100 µL of stock standard solution 1 using a 250-µL syringe. The concentration of stock standard solution 2 is 1 µg/mL.

Working Standard Solutions

Add 50, 100 and 200 µL of stock standard solution 2 into three separate 100-mL volumetric flasks, using a 250-µL syringe. Bring each to volume with a 0.2 mM MSA solution containing 1% methanol. The concentrations of these solutions are 0.5, 1.0 and 2.0 µg/L.

Add 50, 100 and 200 µL of stock standard solution 1 into three separate 100-mL volumetric flasks, using a 250-µL syringe. Bring each to volume with a 0.2 mM MSA solution containing 1% methanol. The concentrations of these solutions are 5, 10 and 20 µg/L.

SYSTEM SETUP

Figure 2A is a schematic of the devices used for the determination of phenols using online solid-phase extraction (SPE) followed by HPLC with UV detection. The AS-HV has a peristaltic pump that can draw samples from sample bottles through a movable needle. This needle can sample from 15 different 100 mL sample bottles in the sample tray. The movement of the AS-HV is controlled by Chromeleon software. The AS-HV uses the left valve of the TCC-3200 as a sample valve and the right valve as an online SPE switching valve. Figure 2B shows the diagram for programming the large volume injection using the AS-HV. The program for the AS-HV is listed in Table 2. Tables 1A and 1B list the programs for the left (SPE) and right (analytical) UltiMate pumps.

SAMPLE PREPARATION

For the present analysis, tap water was collected at the Dionex Shanghai Applications Lab located in the Pudong District, Shanghai, China. One bottle of pure distilled drinking water and two brands of bottled mineral drinking water (named mineral drinking water 1 and 2, respectively) were purchased from a local supermarket.

Bottled pure distilled drinking water, bottled mineral drinking waters 1 and 2, and tap water samples were prepared by filtering 495 mL of each through 0.45 µm filters into four 500-mL bottles and adding 5 mL methanol and 56 µL MSA to each. The final concentration of MSA in the samples was approximately 2 mM.

Spiked samples were prepared from the above solutions. The procedures for preparation of spiked water samples are shown in Table 3.

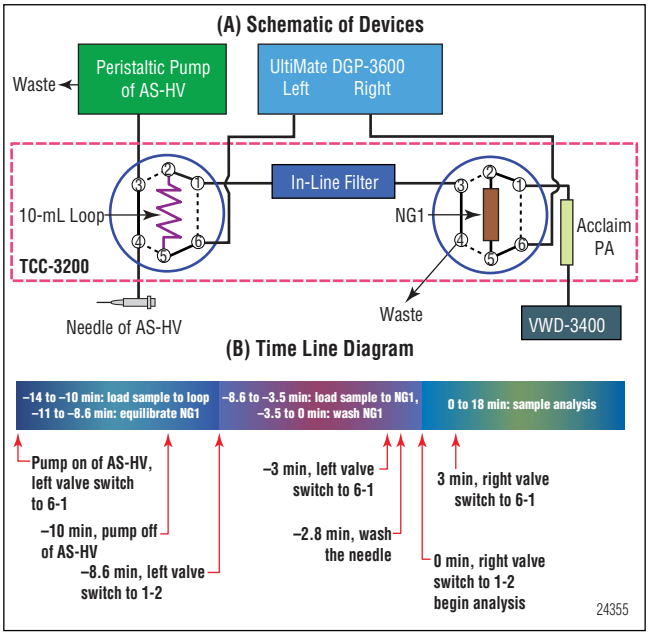

Figure 2. A) Schematic of devices for determination of phenols using online solid-phase extraction (SPE) followed by HPLC with UV detection. B) Time line diagram for programming the high-volume injection using the AS-HV.

Table 2. AS-HV Program

Time (min)	Commands	Comments
Preparation	Y_Axis = AIM_sampler.position X_Axis = AIM_sampler.position Needle = 157, Go To Position	Find position from CM sequence. Set the needle's height and enter the sample bottle.
–14.0	Pump On	Begin to load sample from the bottle. The flow rate of the peristaltic pump is about 3.3 mL/min.
–10.0	Pump Off Needle Home	End sample loading. After sample loading, sample loop switches inline with the SPE column.
–2.8	AIM Sampler, Wash = On, Pump On	Wash the sampling needle and the sample loop in preparation for the next injection.
3.0	Pump Off, Needle Home	End of AS-HV wash.

Table 3. Preparation of Spiked Water Samples		
Samples prepared with 1% methanol and 2 mM MSA	**Amount of added stock standard solution 1 (µL)**	**Phenol concentration (µg/L)**
Distilled drinking water	50	5
Mineral drinking water 1	100	10
Mineral drinking water 2	100	10
Tap water	150	15

RESULTS AND DISCUSSION

Optimization of the Online SPE Method

Different concentrations of acids (HAc or MSA) mixed with methanol or acetonitrile were investigated as wash solutions to elute phenols concentrated on the SPE column. Experiments demonstrated that compared to the acid/methanol solutions, acid/acetonitrile solutions yielded higher peak efficiency, and 0.2 mM MSA/acetonitrile yielded the lowest background.

Figure 3 shows an overlay of chromatograms of phenols spiked into tap water samples, eluted from the SPE column using acetonitrile solutions with different concentrations, and then separated on an Acclaim PA column. More impurities and a high background (poor baseline) were obtained when using acidified water only (Chromatogram A). Although fewer impurities and a lower background were found when using a 20% acetonitrile solution, the recovery of early eluting phenols was reduced (Chromatogram D). Therefore, a 15% acetonitrile solution was selected to ensure recovery of all phenols (Chromatogram C).

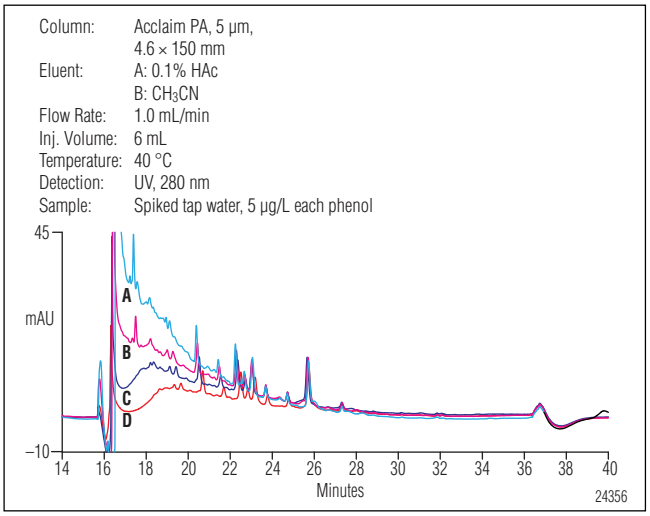

Figure 3. Overlay of chromatograms of tap water samples spiked with 5 µg/L of each phenol, and washed from the IonPac NG1 SPE column using acetonitrile solutions with different concentrations: A) 0% CH_3CN, B) 10% CH_3CN, C) 15% CH_3CN, D) 20% CH_3CN.

Effect of Acidic Solution and Its Concentration in the Mobile Phase on Retention of Phenols

Several acid solutions[15-17] can be used as mobile phases to separate phenols. As shown in Figure 4, good separation of the phenols can be obtained when using methanesulfonic acid (MSA), trifluoroacetic acid (TFA), acetic acid (HAc), or an acetic acid-ammonium acetate buffer (HAc-NH_4Ac).

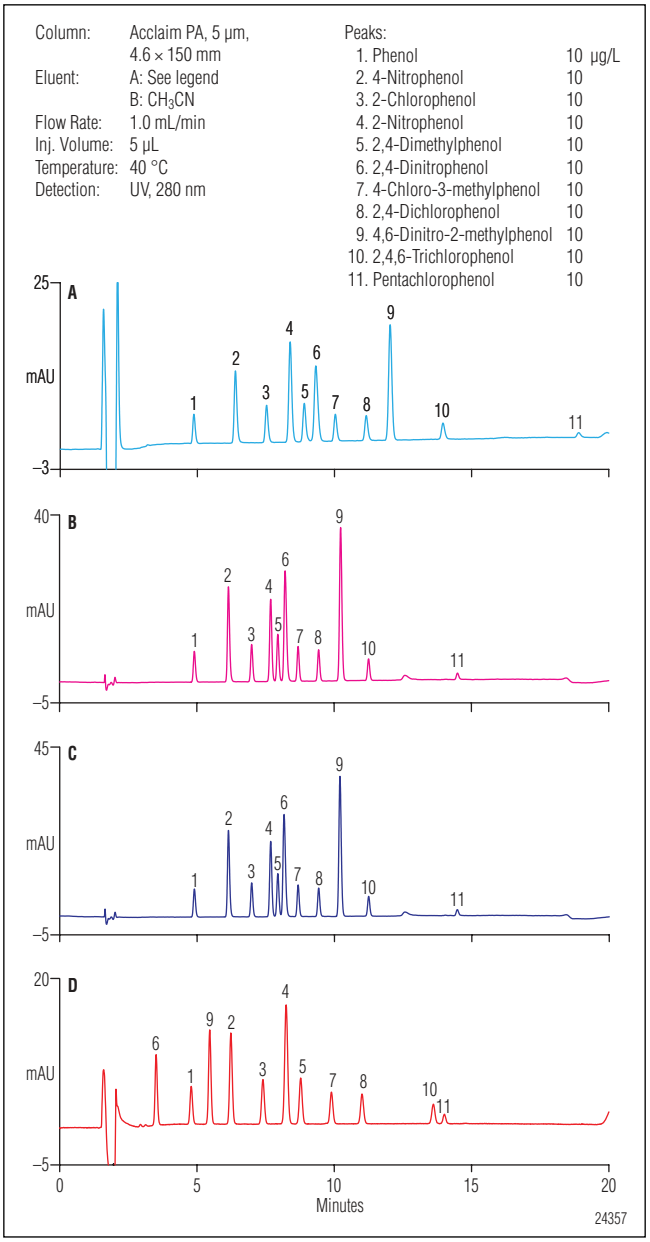

Figure 4. Chromatograms of 10 µg/L phenol working standard separated using acetonitrile as mobile phase B and different acid solutions as mobile phase A: A) 0.1 mM MSA, B) 0.1% TFA, C) 0.1% HAc, D) 25 mM HAc/NH_4Ac.

The effect of changing the mobile phase acid concentration on retention of phenols was investigated. As shown in Figure 5, the retention time of most phenols changed slightly, but that of a few phenols changed significantly with mobile phases and concentrations. When MSA concentration was increased from 0.1 mM to 3.0 mM, the retention time of 2,4-dinitrophenol shifted considerably. The retention time of 4,6-dinitro-2-methylphenol also decreased slightly (Figure 5A). When HAc concentration was increased from 0.03% to 2.0%, the same pattern of retention change was observed (Figure 5B). Substituting TFA for HAc yielded similar results, therefore those data have been omitted.

Changing the proportions of the 25 mM HAc/NH_4Ac buffer had a stronger effect on the retention times of 2,4-dinitrophenol and 4,6-dinitro-2-methylphenol than changing the concentrations of the acid solutions. The retention times of 2,4,6-trichlorophenol and pentachlorophenol also shifted more with changes in the acid concentration (Figure 5C).

Selection of Mobile Phase

HAc, MSA, and TFA solutions all yielded good separation of the eleven phenols specified in U.S. EPA Method 604. When the concentration of acid in the mobile phase was lower, the separation was much better, but the retention times of a few phenols were sensitive to small changes in acid concentration, resulting in unsatisfactory method reproducibility. Therefore, HAc/NH_4Ac buffer was selected as the mobile phase for separating phenols, because it delivered good separation and reproducibility. From Figure 5C, we can predict all eleven phenols will be well resolved using the buffer at about a 1.5:1 (v/v) ratio of the two 25 mM components.

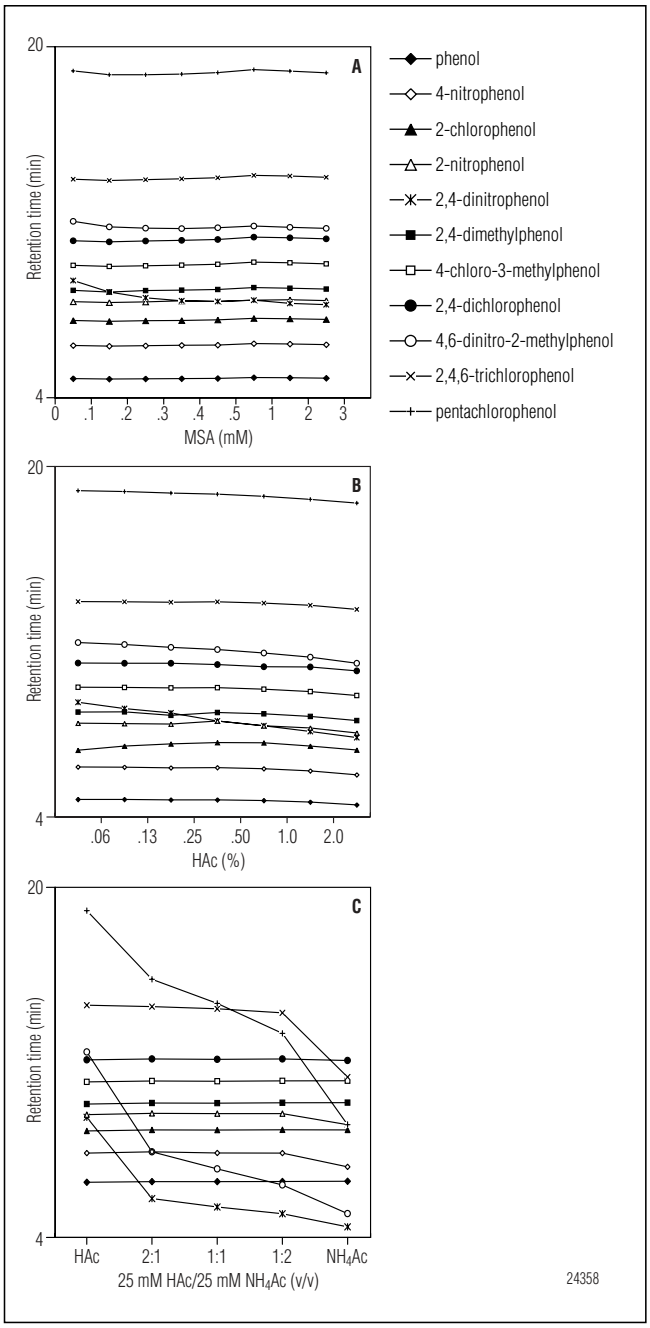

Figure 5. Effect of changing acid concentration in the mobile phase on retention time. A) MSA from 0.1 to 3.0 mM, B) HAc from 0.03 to 2.0%, C) 25 mM HAc-NH_4Ac buffer from 100% HAc to 100% NH_4Ac (v/v).

Table 4. Retention Time Reproducibility, Peak Area Reproducibility, and Comparison of Detection Limits for the 11 Phenols on the U. S. EPA Priority Pollutants List					
Phenol	**RT RSD[a] (%)**	**Area RSD[a] (%)**	**MDL[b] (µg/L)**	**MDL (µg/L) obtained by GC-FID in EPA 604**	**MDL (µg/L) obtained by GC-ECD in EPA 604**
2,4-Dinitrophenol	0.292	1.358	0.46	13.0	0.63
Phenol	0.240	5.584	0.87	0.14	2.2
4,6-Dinitro-2-methylphenol	0.164	0.647	0.40	16.0	not detected
4-Nitrophenol	0.155	0.432	0.42	2.8	0.70
2-Chlorophenol	0.122	1.659	0.41	0.31	0.58
2-Nitrophenol	0.092	1.487	0.41	0.45	0.77
2,4-Dimethylphenol	0.089	0.462	0.30	0.32	0.68
4-Chloro-3-methylphenol	0.085	0.477	0.31	0.36	1.8
2,4-Dichlorophenol	0.072	0.731	0.08	0.39	not detected
2,4,6-Trichlorophenol	0.056	0.717	0.20	0.64	0.58
Pentachlorophenol	0.064	8.599	0.93	7.40	0.59

[a]Seven injections of the 2 µg/L working standard solution.

[b]The single-sided Student's *t* test method (at the 99% confidence limit) was used for estimating MDL, where the standard deviation (SD) of the peak area of seven injections is multiplied by 3.14 (at n = 7) to yield the MDL.

Reproducibility, Detection Limits, and Linearity

The reproducibility was estimated by making seven replicate injections of the 2 µg/L calibration standard. Table 4 summarizes the retention time and peak area precision data. The method detection limits (MDLs) of the phenols are also listed in Table 4, as are the MDLs reported for the GC method in U.S. EPA Method 604. The MDLs of the on-line SPE-HPLC method are similar to and in most cases better than those achieved using GC, without the labor and cost of liquid/liquid extraction or manual SPE.

Calibration linearity for the determination of phenols was investigated by making replicate injections of a mixed standard of phenols prepared at six different concentrations. The external standard method is used in EPA Method 604. Therefore, we used it to calculate the calibration curve and for sample analysis. Table 5 lists the data from the calibration as reported by Chromeleon.

Table 5. Calibration Data and Linearity of the 11 Phenols		
Phenol	**r**	**RSD (%)**
2,4-Dinitrophenol	0.9998	1.73
Phenol	0.9984	4.29
4,6-Dinitro-2-methylphenol	0.9998	1.69
4-Nitrophenol	0.9997	1.79
2-Chlorophenol	0.9996	2.22
2-Nitrophenol	0.9992	3.03
2,4-Dimethylphenol	0.9999	1.33
4-Chloro-3-methylphenol	0.9998	1.42
2,4-Dichlorophenol	0.9998	1.33
2,4,6-Trichlorophenol	0.9999	1.28
Pentachlorophenol	0.9965	6.07

Sample Analysis

To achieve satisfactory chromatography of phenols in the tap and mineral water samples, these samples should be acidified to approximately pH 3.5 prior to analysis. Figure 6 shows the chromatograms of spiked mineral water sample acidified to pH 7 and pH 3 with MSA, respectively. The peak shapes of 2,4-dinitrophenol, 4,6-dinitro-2-methylphenol, and 4-nitrophenol are superior at pH 3.

For different water samples, the amount of acid required to achieve a pH < 4.5 varies. For example, 6 µL MSA (about 0.2 mM final concentration) was added to the 500 mL pure distilled water sample solution (495 mL distilled water + 5 mL methanol) to yield a pH of approximately 3.9. For the tap water and mineral water samples, much more MSA was needed because these samples contain ions that are capable of buffering the MSA, most notably bicarbonate (Table 6). Therefore, approximately 56 µL MSA (about 2 mM final concentration) was added to the tap and mineral water samples to achieve pH values ranging from 2.5 to 4.5.

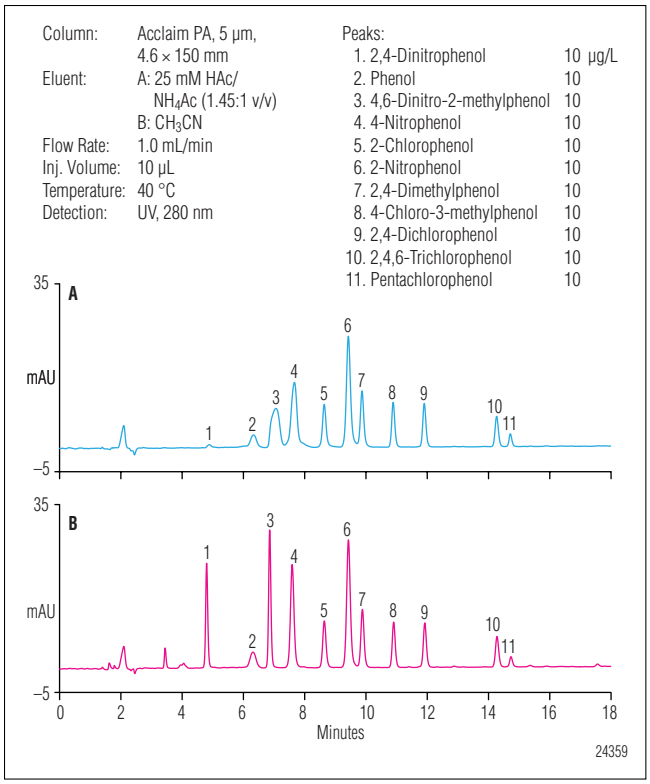

Figure 6. Chromatograms of bottled mineral drinking water 1 spiked with 10 µg/L phenols and acidified with MSA to A) pH 7, and B) pH 3.

Table 6. Listed Amounts of Ions in Bottled Mineral Drinking Waters

Labeled contents	Bottled mineral drinking water 1 (mg/L)	Bottled mineral drinking water 2 (mg/L)
Na^+	≥0.8	4–12
K^+	≥0.35	0.3–1.0
Ca^{2+}	≥4	not reported
Mg^{2+}	≥0.5	0.3–0.5
Zn^{2+}	not reported	0.25
Sr^{2+}	not reported	0.14
$HSiO_2$	≥1.8	71.6
HCO_3^-	not reported	14
pH (25 °C)	7.35 ± 0.5	7.0–8.0

Table 7. Bottled Mineral Drinking Water Analytical Results								
Phenol	**Bottled mineral drinking water 1[a]**				**Bottled mineral drinking water 2[b]**			
	Unspiked (µM)	**Added (µM)**	**Found (µM)**	**Recovery (%)**	**Unspiked (µM)**	**Added (µM)**	**Found (µM)**	**Recovery (%)**
2,4-Dinitrophenol	ND[c]	10	9.44	94.4	ND	10	9.57	95.7
Phenol	ND	10	11.9	119	0.37	10	10.0	100
4,6-Dinitro-2-methylphenol	ND	10	9.56	95.6	ND	10	9.57	95.7
4-Nitrophenol	ND	10	10.2	102	ND	10	10.0	100
2-Chlorophenol	ND	10	10.4	104	ND	10	9.02	90.2
2-Nitrophenol	ND	10	11.9	119	ND	10	10.9	109
2,4-Dimethylphenol	ND	10	10.5	105	ND	10	9.97	99.7
4-Chloro-3-methylphenol	ND	10	9.56	95.6	ND	10	9.40	94.0
2,4-Dichlorophenol	ND	10	9.75	97.5	ND	10	9.05	90.5
2,4,6-Trichlorophenol	ND	10	10.1	101	0.75	10	9.55	95.5
Pentachlorophenol	0.73	10	9.67	96.7	ND	10	9.60	96.0

[a]One unspiked sample of mineral drinking water 1 was prepared and two injections were made. One spiked sample was prepared and four injections were made.
[b]One unspiked sample of mineral drinking water 2 was prepared and three injections were made. One spiked sample was prepared and five injections were made.
[c]ND = not detected.

Bottled Mineral Drinking Water

Two brands of bottled mineral drinking water were analyzed. Table 6 shows the contents listed on the labels of each. Figures 7 and 8 show chromatograms of the bottled mineral water samples and the same samples spiked with phenols. The results are summarized in Table 7. Low concentrations of two phenols were detected in the unspiked mineral water 2 sample and a low concentration of one phenol in the unspiked mineral water 1. Good recoveries were obtained for all eleven phenols.

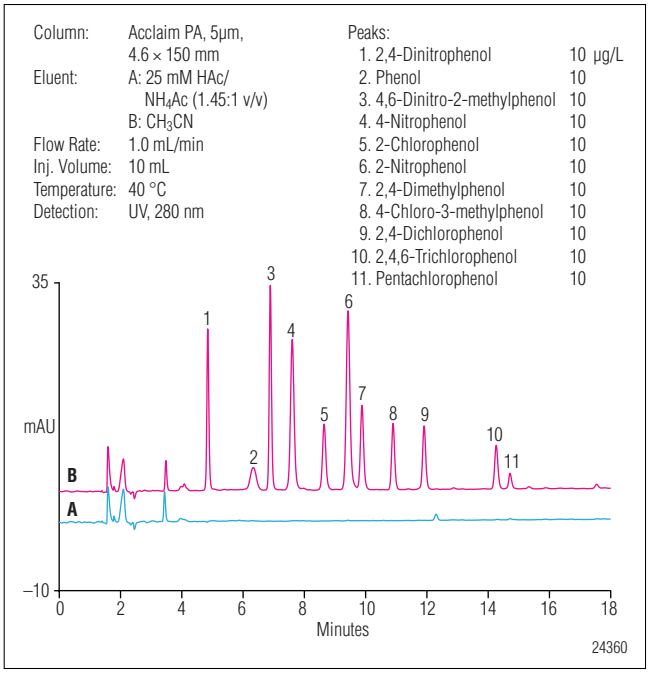

Figure 7. Overlay of chromatograms of bottled mineral drinking water 1, A) unspiked, and B) spiked with 10 µg/L phenols.

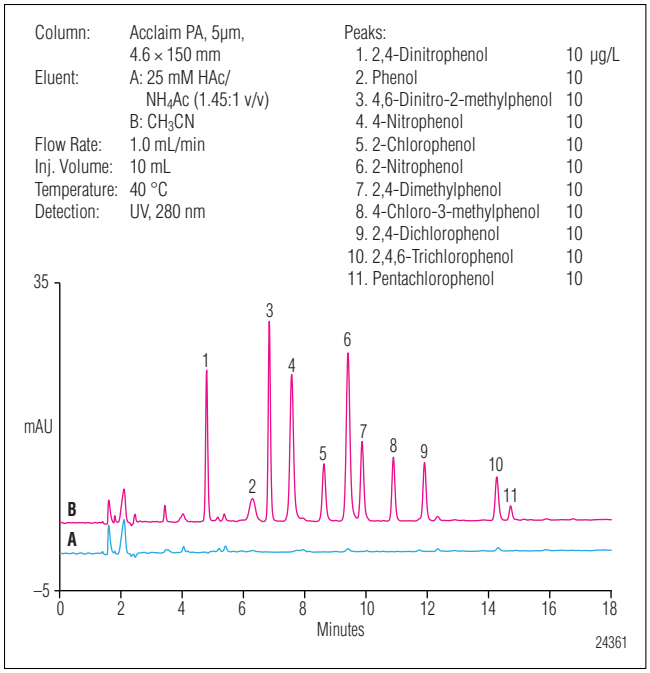

Figure 8. Overlay of chromatograms of bottled mineral drinking water 2, A) unspiked, and B) spiked with 10 µg/L phenols.

Table 8. Bottled Pure Distilled Drinking Water and Tap Water Analytical Results								
Phenol	**Pure distilled water[a]**				**Tap water[b]**			
	Unspiked (µM)	**Added (µM)**	**Found (µM)**	**Recovery (%)**	**Unspiked (µM)**	**Added (µM)**	**Found (µM)**	**Recovery (%)**
2,4-Dinitrophenol	ND[c]	5	4.95	99.0	2.11	15	10.4	70.0
Phenol	ND	5	4.84	96.8	0.41	15	14.2	94.7
4,6-Dinitro-2-methylphenol	ND	5	5.02	100	ND	15	15.1	101
4-Nitrophenol	ND	5	5.09	102	0.80	15	15.2	101
2-Chlorophenol	ND	5	5.22	104	<MDL[d]	15	11.50	76.7
2-Nitrophenol	ND	5	5.30	106	ND	15	14.0	93.3
2,4-Dimethylphenol	ND	5	5.19	104	1.63	15	15.0	100
4-Chloro-3-methylphenol	ND	5	5.07	101	<MDL	15	14.5	96.4
2,4-Dichlorophenol	ND	5	4.98	99.6	ND	15	14.1	94.0
2,4,6-Trichlorophenol	ND	5	5.20	104	0.65	15	14.6	97.0
Pentachlorophenol	ND	5	4.99	99.8	1.13	15	14.2	94.5

[a]One unspiked sample of pure distilled drinking water was prepared and five injections were made. One spiked sample was prepared and four injections were made.

[b]One unspiked sample of tap water was perpared and two injections were made. One spiked sample was prepared and five injections were made.

[c]ND = not detected..

[d]<MDL = lower than method detection limit.

Bottled Pure Distilled Drinking Water

Figure 9 shows chromatograms of pure distilled drinking water and the same water spiked with phenols. The results are summarized in Table 8. No phenols were found in the unspiked sample, and recovery of all phenols in the spiked sample was excellent.

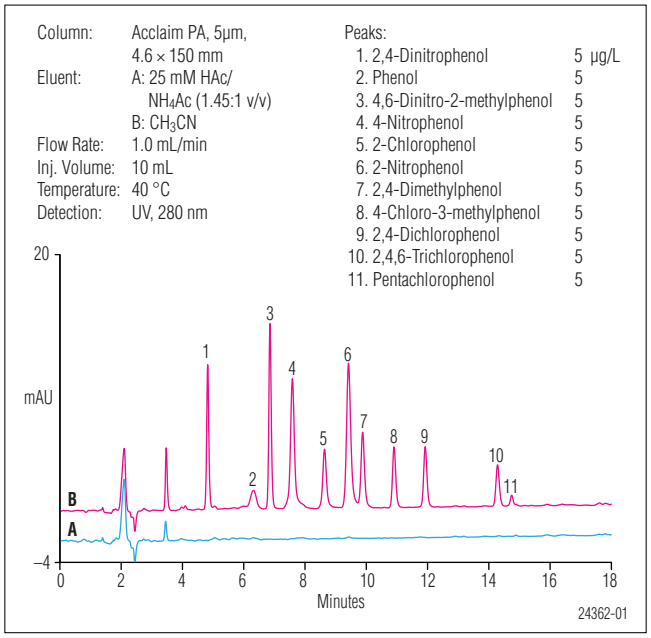

Figure 9. Overlay of chromatograms of pure distilled drinking water, A) unspiked, and B) spiked with 5 µg/L phenols.

Tap Water

Figure 10 shows chromatograms of tap water and the tap water spiked with phenols. The results are summarized in Table 8. Low concentrations of several phenols were detected and some peaks were detected with peak areas that yielded concentrations below the estimated MDL.

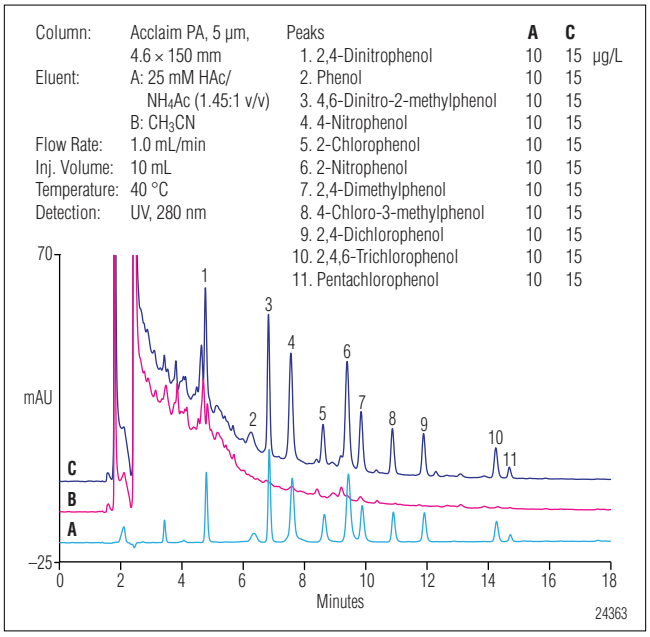

Figure 10. Overlay of chromatograms of A) the 10 µg/L phenol standard, B) unspiked tap water, and C) tap water spiked with 15 µg/L phenols.

CONCLUSION

The successful analysis of all the water samples above demonstrates that online SPE with a dual UltiMate system can determine the 11 phenols designated on the EPA Priority Pollutants List without laborious offline sample preparation. The online SPE method with UV detection has very good reproducibility, with detection limits similar to and in many cases superior to the GC methods described in EPA Method 604.

PRECAUTIONS

Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware. Clean all glassware scrupulously and use high purity reagents and solvents to minimize interference problems.

Samples must be acidified to about pH 3.5 with MSA before large volume injections, especially for the mineral drinking water and tap water samples. If not, the determination of 2,4-dinitrophenol, 4,6-dinitro-2-methylphenol and 4-nitrophenol can be affected.

The tubing and sample loop of the AS-HV are not compatible with high concentration organic solvents. Change the sample loop and the tubing used to connect the loop to the sample valve to either stainless steel or PEEK™.

APPENDIX

Using One Pump Channel of a Dual Pump System Instead of the High-Volume Autosampler

If only a few samples need to be analyzed for phenols, it is possible to use one pump channel of a dual pump system instead of the AS-HV autosampler for sample injection. This configuration is shown in Figure 11. Figure 11A shows the system schematic and Figure 11B shows the program.

Place the sample in an eluent bottle and use one pump of the dual pump system to deliver the sample to the SPE column at a defined flow rate for a set amount of time. Bypass the degasser with the eluent lines used to deliver sample to minimize carryover between injections. Clean eluent lines thoroughly with 100% organic solvent and pure water prior to using this pump channel for other applications.

Use the left pump as the SPE pump and channel C of the left pump as an injector. Pump the sample for 6 min at 1 mL/min to deliver 6 mL of sample to the SPE column. Use channels A (0.2mM MSA) and B (acetonitrile) of the left pump to rinse the SPE column and elute the captured phenols. Use the second (right) pump to deliver the gradient to separate the phenols on the Acclaim PA column. Figure 12 shows a chromatogram of the separation of phenols in a spiked tap water sample using this setup.

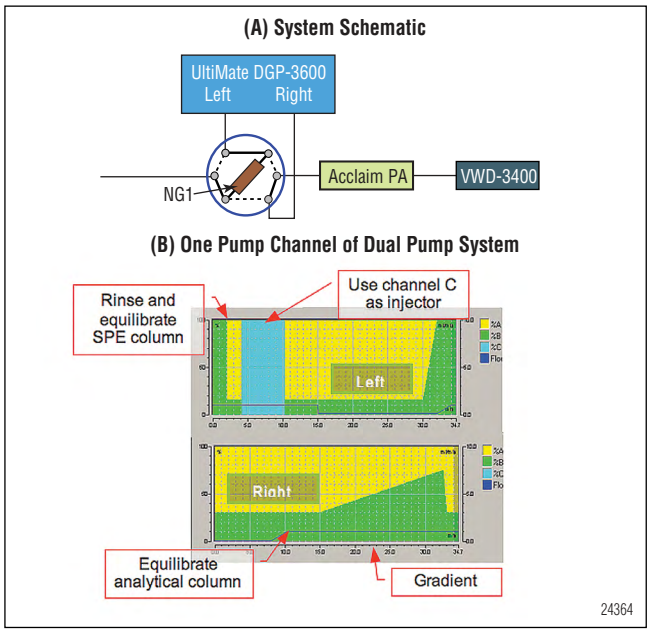

Figure 11. A) System schematic and B) program for using one pump channel of a dual pump system in place of the AS-HV Autosampler.

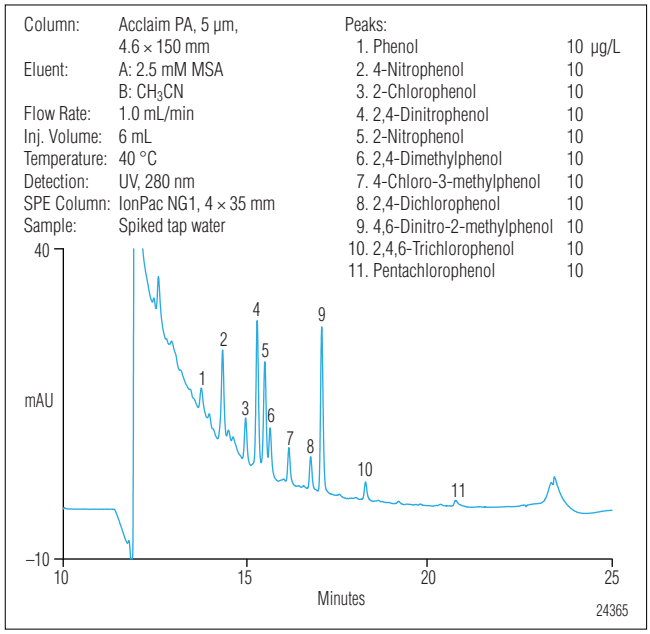

Figure 12. Chromatogram of a tap water sample spiked with 10 µg/L phenols, using one pump channel of a dual pump system instead of the AS-HV Autosampler.

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Determination of Bromate in Bottled Mineral Water Using the CRD 300 Carbonate Removal Device

INTRODUCTION

Drinking and bottled waters are commonly disinfected with ozone. Ozone is highly effective and, unlike many other disinfectants, does not remain in the water or change its taste. Unfortunately, when bromide is present in water, it is converted to bromate by the ozone treatment. Bromate is recognized as a potential human carcinogen, which has led to the regulation of its concentration in drinking and bottled water. Major regulatory bodies worldwide (e.g., U.S. EPA and the European Commission) have set a maximum allowable bromate concentration in drinking water of 10 µg/L.[1] In Europe, the limit was lowered to 3 µg/L for bottled natural mineral and spring waters disinfected by ozonation.[2]

Over the past two decades, Dionex has led the effort in developing sensitive and robust ion chromatography (IC) methods for determining bromate and other oxyhalides (e.g., chlorite and chlorate). U.S. EPA Method 300.0 (B) and 300.1 (B) used the IonPac® AS9-SC and IonPac AS9-HC columns, respectively, along with suppressed conductivity detection for bromate, chlorite, and chlorate determinations in drinking water. In 1997, Dionex introduced the AS9-HC column to allow the direct injection of 250 µL of drinking water to easily meet the 10 µg/L regulatory requirement. This method was documented in Dionex Application Note 81 (AN 81).[3] Since then, Dionex has developed a number of products and techniques, and worked with regulatory agencies and international standards organizations to improve the sensitivity and ruggedness of bromate determinations as well as the types of samples that can be directly injected.

Dionex products were instrumental in the development of the postcolumn derivatization techniques in U.S. EPA methods 317.0 and 326.0. These methods used the AS9-HC and Dionex suppression technology for conductivity detection of oxyhalides combined with postcolumn addition and absorbance detection for enhanced determination of bromate. EPA Methods 317.0 and 326.0 are documented in AN 136 and AN 149.[4,5] To improve the sensitivity for bromate using direct injection, Dionex developed the IonPac AS19 column. This column was designed for use with hydroxide eluents rather than the carbonate eluents used with the AS9-HC. Hydroxide eluents offer improved sensitivity for suppressed conductivity detection as compared to carbonate eluents. This improved sensitivity was documented in AN 167.[6] Hydroxide eluents are also advantageous because they can be generated easily using an eluent generator as part of a Reagent-Free™ IC (RFIC™) system. RFIC systems improve reproducibility and simplify analysis. The AS19 separation can also replace the AS9-HC separation in EPA Methods 317.0 and 326.0, which is documented in AN 168 and AN 171.[7,8] The AS19 was also used with an isocratic hydroxide eluent rather than the typical gradient for analysis of drinking water for bromate.[9] This method, presented in Application Update 154 (AU 154), cannot determine all the common inorganic anions in a single injection like the gradient method in AN 167. For determination of sub-µg/L concentrations of bromate in drinking water and higher ionic strength matrices without postcolumn derivatization, Dionex developed a two-dimensional

IC technique (AN 187) that uses an AS19 column in the first dimension, and an AS24 column, developed specifically for determining haloacetic acids and bromate by IC-MS and IC-MS/MS, in the second dimension.[10]

Dionex AN 184 showed that the AS19 method in AN 167 could be used to meet the 3 µg/L European limit for bromate in natural mineral and spring waters disinfected by ozonation.11 The same application note compared the AS19 chromatography to chromatography with the AS23, a column that uses carbonate eluents and was designed to replace the AS9-HC. The AS23 has a higher capacity than the AS9-HC, and a different selectivity for the carbonate ion so that it is less likely to interfere with bromate determinations. AN 184 showed that poorer sensitivity associated with using carbonate eluents when compared to hydroxide eluents made the AS23 performance inferior to that of the AS19.

The present application note describes the use of a carbonate removal device, the CRD 300, to remove the majority of carbonate from the eluent and allow hydroxide-like performance and detection sensitivity. This device was used with the IonPac AS23 to determine bromate in a bottled mineral water samples. Detection sensitivity when using the CRD 300 was improved compared to chromatography without the CRD 300. Scientists responsible for water analysis can choose the column and eluent chemistry that best meets their needs to reliably determine bromate at concentrations below the common 10 µg/L regulatory limit.

EQUIPMENT

Dionex ICS-2000 Reagent-Free Ion Chromatography System* equipped with the following for carbonate/bicarbonate eluent generation:

EluGen® EGC II K2CO3 cartridge (P/N 058904)

EPM Electrolytic pH Modifier (P/N 063175)

EGC Carbonate Mixer (P/N 079943)

CRD 300 Carbonate Removal Device (4 mm) with VC Vacuum Pump (P/N 068474)

Chromeleon® 6.8 Chromatography Management Software

*This application can be run on any Dionex system equipped for carbonate/bicarbonate eluent generation.
Alternately, this application can be run with a manually prepared carbonate/bicarbonate eluent.

REAGENTS AND STANDARDS

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

Sodium chlorite, 80% ($NaClO_2$, Fluka)

Potassium bromate ($KBrO_3$, Fluka)

Sodium chlorate ($NaClO_3$, Fluka)

Individual stock standards of fluoride, chloride, and sulfate, 1000 mg/L each (Merck)

PREPARATION OF SOLUTIONS AND REAGENTS

Carbonate Eluent Generation

The Eluent Generator (EG) produces the eluent using the EluGen EGC II K2CO3 cartridge, Electrolytic pH Modifier, EGC Carbonate Mixer, and deionized water supplied by the pump. The eluent concentration is controlled by the Chromeleon software. Backpressure tubing must be added to achieve 2300–2500 psi backpressure that will allow the EG degasser to function properly. See the ICS-2000 Operator's Manual Section 2.4.4, "Eluent Generator" for instructions on adding backpressure.

To set up the EGC II K2CO3, see the EGC II K_2CO_3 cartridge, Electrolytic pH Modifier, and EGC Carbonate Mixer Product Manual (Doc. No. 065075) for more information.

Manual Eluent Preparation

From Eluent Concentrate

Prepare 1 L of eluent by adding 10 mL of the Dionex IonPac AS23 Eluent Concentrate (P/N 064161) to a 1 L volumetric flask. Bring to volume with DI water and mix thoroughly.

From Manually Prepared Stock Solutions

Stock Carbonate/Bicarbonate Eluent Preparation 1.0 M Na_2CO_3 and 1.0 M $NaHCO_3$

Weigh 10.596 g sodium carbonate and 8.400 g sodium bicarbonate into separate 100 mL volumetric flasks. Bring each to volume with DI water.

IonPac AS23 Eluent (4.5 mM Na_2CO_3/0.8 mM $NaHCO_3$)

For 1L, prepare by adding 4.5 mL of 1.0 M Na_2CO_3 and 0.8 mL of 1.0 M $NaHCO_3$ to a 1L volumetric flask, bring to volume with DI water, and mix thoroughly.

Stock Standard Solutions

Prepare 1000 mg/L stock standard solutions of fluoride, chloride, sulfate, chlorite, bromate, and chlorate by weighing 0.221 g, 0.165 g, 0.148 g, 0.168 g, 0.131 g, and 0.128 g, respectively, into separate 100 mL volumetric flasks. Bring each to volume with DI water.

Secondary Standards

The stock standards are used to prepare the 1000 µg/L secondary standards of chlorite, bromate, and chlorate. Take a defined volume of the stock standard and dilute it 1 to 1000 with DI water (e.g., dilute 100 µL to 100 mL in a 100 mL volumetric flask). Use these standards to prepare the working standards and to spike the bottled mineral water sample.

Working Standards

Prepare the standards for calibration and MDL studies by mixing defined volumes of the 1000 mg/L stock standard solutions of fluoride, chloride, and sulfate and the 1000 µg/L secondary standards of chlorite, bromate, and chlorate. For example, to prepare the working standard containing 0.5 mg/L fluoride, 50 mg/L chloride, 100 mg/L sulfate, and 40 µg/L of each of the oxyhalides, add 0.05 mL of the fluoride stock standard, 5 mL of the chloride stock standard, 10 mL of the sulfate stock standard, and 4 mL of each oxyhalide secondary standard to a 100 mL volumetric flask and bring to volume.

Sample

The bottled mineral water sample was purchased from a local market in Bangkok, Thailand and was bottled at its source in the mountains of Thailand. The label reported the presence of fluoride, chloride, sulfate, and bicarbonate, but not their concentrations.

CRD 300 IN VACUUM MODE SETUP

The CRD 300 in vacuum mode uses a vacuum pump to evacuate the regenerant chamber of the CRD 300 so that CO2 gas is literally sucked out of the eluent. A bleed tube feeds a trickle of fresh air into the regenerant chamber to constantly sweep out the CO_2 gas. To operate the CRD 300 in vacuum mode, mount the CRD 300 directly on top of the suppressor and plumb the eluent from the Eluent Out of the suppressor to the Eluent In of the CRD 300. The Eluent Out of the CRD 300 is connected to the conductivity cell In and conductivity cell Out goes to waste if the system is running in external water mode. If the system is operated in recycle mode, connect conductivity cell Out to the suppressor Regen In. Connect the vacuum tubing to the vacuum port of the vacuum pump and to the ballast bottle. Connect a length of 1/8" Teflon® tubing from the ballast bottle to the Regen Out of the CRD 300. Make sure the third port on the ballast bottle is closed and air tight. Connect 15 cm of red (0.005" i.d.) PEEK™ tubing to the Regen In of the CRD 300; this is the air bleed assembly. Begin eluent flow before beginning vacuum operation. When eluent flow is established, turn on the vacuum pump. The background conductivity should drop almost immediately. When the eluent pump is turned off, immediately turn off the vacuum pump. Avoid operating the vacuum pump while eluent flow is stopped. A TTL can be wired to automate stopping the vacuum pump.

CONDITIONS

Condition A (Eluent Generation and CRD 300)

Column:	IonPac AS23 (4 × 250 mm) (P/N 064149)
	IonPac AG23 (4 × 50 mm) (P/N 064147)
Eluent:	EGC II K_2CO_3 (P/N 058904)
	EPM (P/N 063175)
	4.5 mM K_2CO_3/0.8 mM $KHCO_3$
Flow Rate:	1.0 mL/min
Inj. Volume:	250 µL
Temperature:	30 °C
Suppressor:	Suppressed conductivity, ASRS® 300, 4 mm (P/N 064554), external water mode, 25 mA
	CRD 300, 4 mm, (P/N 064637) vacuum mode
Background:	< 1.5 µS
Noise:	~ 0.3 nS
Back Pressure:	~2200 psi

Condition B (Manual Eluent Preparation and no CRD 300)

Column:	IonPac AS23 (4 × 250 mm) (P/N 064149)
	IonPac AG23 (4 × 50 mm) (P/N 064147)
Eluent:	4.5 mM Na_2CO_3/0.8 mM $NaHCO_3$
Flow Rate:	1.0 mL/min
Inj. Volume:	250 µL
Column Temp:	30 °C
Suppressor:	Suppressed conductivity, ASRS 300, 4 mm (P/N 064554), external water mode, 25 mA
Background:	17-19 µS
Noise:	~ 3.0 nS
Back Pressure:	~1800 psi

RESULTS AND DISCUSSION

Chromatography

Bromate, chlorite, and chlorate were resolved from seven common inorganic anions using an IonPac AS23 column under its recommended eluent conditions (4.5 mM Na_2CO_3/0.8 mM $NaHCO_3$). Chromatogram B in Figure 1 shows this separation. The background conductivity after suppression using the carbonate eluent is between 18 and 19 µS. The higher the background, the higher the noise, and this results in a lower signal-to-noise ratio (i.e., lower sensitivity). The background of the suppressed hydroxide eluent used for the IonPac AS19 column is < 1 µS. In order for the carbonate eluent system of the AS23 to approach the detection limits delivered by the hydroxide eluent system of the AS19, the background must be reduced. The CRD 300 was designed to remove carbonate from the eluent (after suppression) and thereby reduce the background to improve detection limits. Chromatogram A shows the same AS23 separation as B using a CRD 300. Note that the background has been reduced to about 1 µS, the injection dip at about 2 min is greatly reduced in size, and there is a noticeable improvement in analyte sensitivity. Throughout this application note, we compare the determination of bromate, chlorite, and chlorate with the AS23 and suppressed conductivity, both with and without the CRD 300.

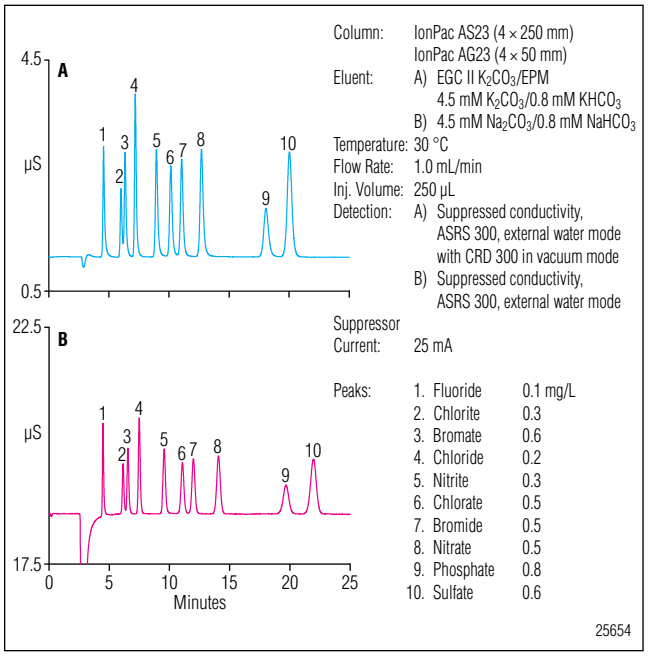

Figure 1. Chromatography of a mixed anion standard A) with a CRD 300 and electrolytically prepared eluent, and B) without a CRD 300 and with manually prepared eluent.

Figure 2 shows single injections from the MDL determinations of bromate, chlorite, and chlorate with and without the CRD 300. Fluoride, (0.5 mg/L), chloride (50 mg/L), and sulfate (100 mg/L) were added to the MDL standards to simulate the ionic strength of bottled water samples. Due to the higher background and noise of the system without the CRD 300 (Chromatogram B, Figure 2), higher analyte concentrations were used for the MDL test compared to the system with the CRD 300. Table 1 shows the results of the MDL determination. For all three oxyhalide analytes, the MDL is lower for the system with the CRD 300. The MDL values without the CRD 300 are similar to those determined with the AS23 in AN 184. The values when using the CRD 300, though lower than without, are not as low as those determined with the AS19 and hydroxide eluent in AN 184.

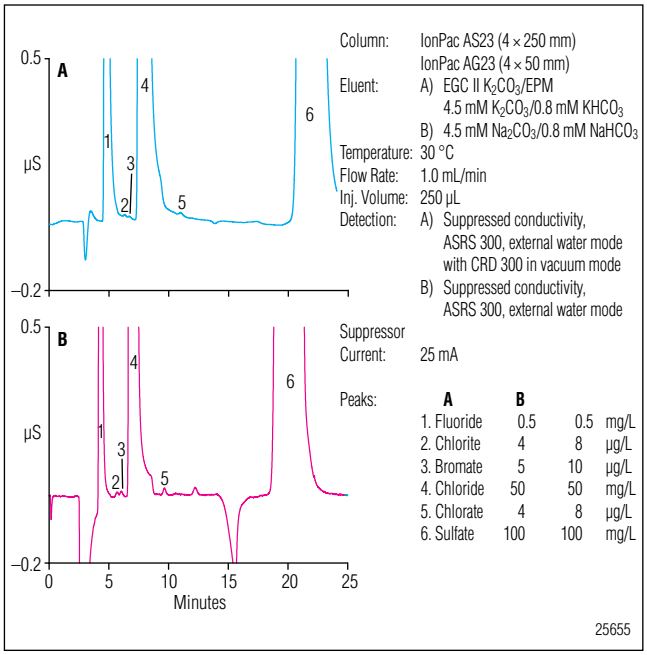

Figure 2. Example chromatograms from the MDL determination A) with a CRD 300, and B) without a CRD 300.

Table 1. MDL Determinations of Chlorite, Bromate, and Chlorate with and without a CRD 300

Injection No.	Height (µS)					
	With CRD 300			Without CRD 300		
	Chlorite	Bromate	Chlorate	Chlorite	Bromate	Chlorate
	4 µg/L	5 µg/L	4 µg/L	8 µg/L	10 µg/L	8 µg/L
1	0.0057	0.0041	0.0076	0.0099	0.0121	0.0189
2	0.0051	0.0042	0.0071	0.0114	0.0128	0.0199
3	0.0053	0.0042	0.0065	0.0093	0.0115	0.0204
4	0.056	0.0043	0.0074	0.0105	0.0132	0.0215
5	0.059	0.0047	0.0074	0.0111	0.0133	0.0205
6	0.0061	0.0045	0.0077	0.0103	0.0125	0.0201
7	0.0057	0.0042	0.0076	0.0114	0.0111	0.0199
Average	**0.0056**	**0.0043**	**0.0073**	**0.0105**	**0.0124**	**0.0202**
RSD	**5.97**	**5.04**	**5.42**	**7.41**	**6.67**	**3.94**
MDL (µg/L)	**0.75**	**0.79**	**0.68**	**1.86**	**2.10**	**0.99**

Another calibration was performed for both systems using consistent concentrations of fluoride, chloride, and sulfate (0.5 mg/L, 2 mg/L, and 10 mg/L, respectively) in standards with three levels of chlorite, bromate, and chlorate concentrations; 10, 20, and 40 µg/L. Overlays of three calibration standards are shown in Figure 3 and the results are in Table 2. The calibration data are equivalent.

Both systems were used to analyze a bottled mineral water sample from the mountains of Thailand. Figure 4 shows the analysis of this sample and Table 3 reports the results of the analysis. The sample had just over 10 µg/L bromate and 1–2 µg/L chlorate, suggesting a second disinfection process besides ozonation was used. Due to the noise of the system without the CRD 300, the chlorate peak could not be identified with confidence. To evaluate accuracy, known amounts of bromate, chlorite, and chlorate were spiked into the bottled mineral water sample. Figure 5 shows the chromatography from this study and Table 4 shows that all analytes were recovered at >85%. In this experiment, the recovery was better for the system with the CRD 300.

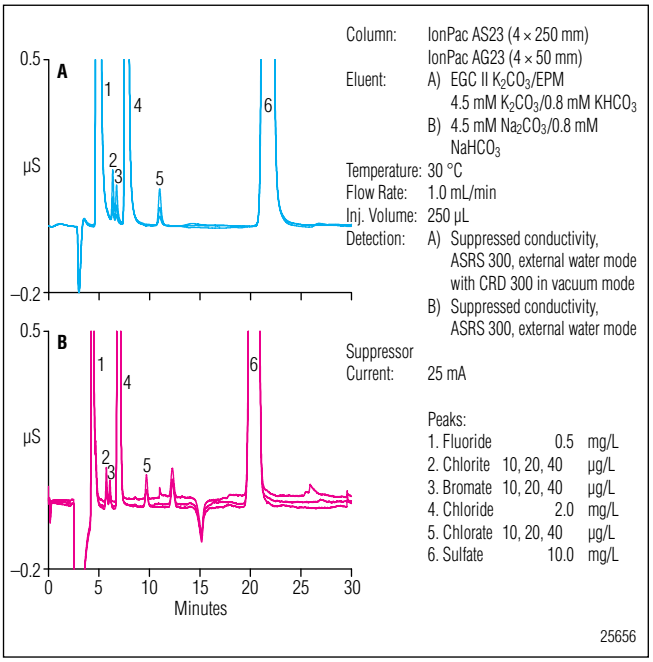

Figure 3. Overlay of chromatograms of three concentration levels of chlorite, bromate, and chlorate in a mixed anion standard A) with a CRD 300, and B) without a CRD 300.

Table 2. Chromeleon Calibration Report for Chlorite, Bromate, and Chlorate with and without a CRD 300

Peak Name	Points	R-Square (%)	
		With CRD 300	Without CRD 300
Chlorite	3	99.9961	99.9748
Bromate	3	100.0000	99.9986
Chlorate	3	99.9995	99.9637

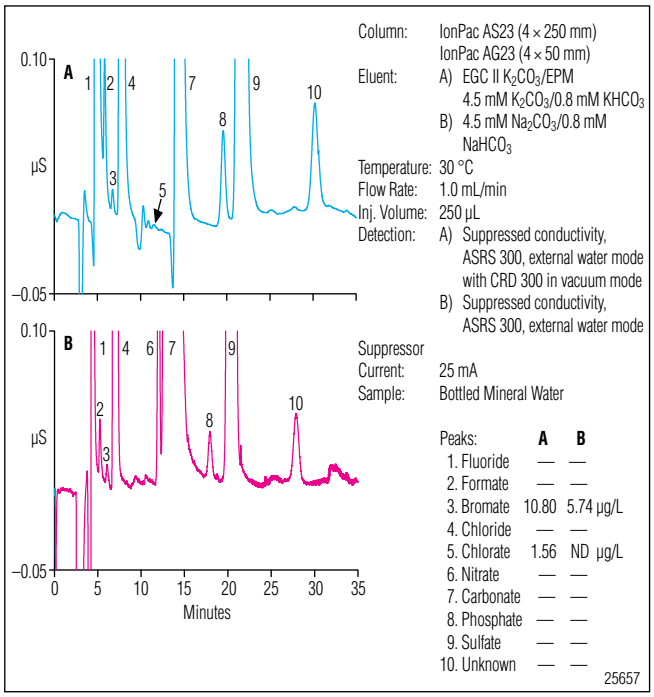

Figure 4. Chromatography of a bottled mineral water sample A) with a CRD 300, and B) without a CRD 300.

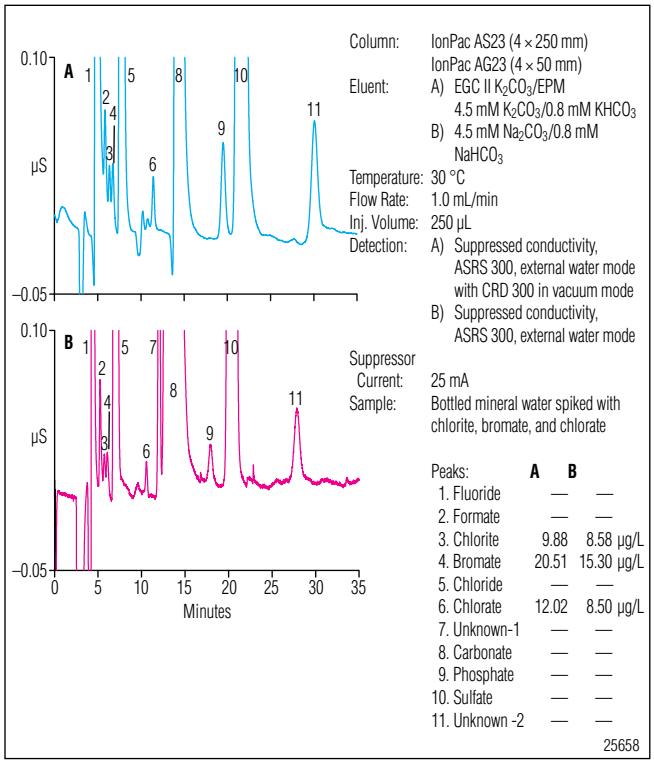

Figure 5. Chromatography of a bottled mineral water sample spiked with chlorite, bromate, and chlorate (10 µg/L each) A) with a CRD 300, and B) without a CRD 300.

Table 3. Determination of Bromate and Chlorate in a Bottled Mineral Water Sample with and without a CRD 300

Injection No.	With CRD 300 (µg/L)		Without CRD 300 (µg/L)	
	Bromate	Chlorate	Bromate	Chlorate
1	11.0	1.52	5.33	ND
2	10.9	1.55	6.23	ND
3	10.9	1.35	5.02	ND
4	10.1	1.91	6.25	ND
5	11.3	1.48	5.89	ND
Average	10.8	1.56	5.74	—
RSD	4.34	13.42	9.61	—

Table 4. Spike Recovery of Chlorite, Bromate, and Chlorate with and without a CRD 300

	With CRD 300			Without CRD 300		
	Chlorite	Bromate	Chlorate	Chlorite	Bromate	Chlorate
Sample	ND[a]	10.83	1.56	ND[a]	5.74	ND[a]
Spike	10	10	10	10	10	10
Measured[b] Amount	9.88	20.51	12.02	8.58	15.30	8.50
RSD	2.39	1.60	2.45	2.39	1.60	2.45
Recovery(%)	98.8	98.5	104	85.8	97.2	85.0

[a] ND = Not Detected

[b] The average of five injections

SUMMARY

This application note shows that using the CRD 300 with the IonPac AS23, bromate can be determined in bottled mineral water at concentrations < 5 µg/L. The method sensitivity for bromate and other oxyhalides approaches that of the hydroxide eluent system featured in Dionex Application Note 184.

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4. Dionex Corporation. *Determination of Inorganic Oxyhalide Disinfection Byproduct Anions and Bromide in Drinking Water Using Ion Chromatography with the Addition of a Postcolumn Reagent for Trace Bromate Analysis,* Application Note 136, LPN 1229-01. Sunnyvale, CA, 2004.
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6. Dionex Corporation. Determination of Trace Concentrations of Oxyhalides and Bromide in Municipal and Bottled Waters Using a Hydroxide-Selective Column with a Reagent-Free Ion Chromatography System, Application Note 167, LPN 1662. Sunnyvale, CA 2004.
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9. Dionex Corporation. *Determination of Bromate in Drinking and Natural Mineral Water by Isocratic Ion chromatography with a Hydroxide Eluent,* Application Update 154, LPN 1793-01. Sunnyvale, CA, 2006.
10. Dionex Corporation. *Determination of Sub-µg/L Bromate in Municipal and Natural Mineral Waters Using Preconcentration with Two-Dimensional Ion Chromatography and Suppressed Conductivity Detection,* Application Note 187, LPN 1943-02. Sunnyvale, CA, 2007.
11. Dionex Corporation. *Determination of Chlorite, Bromate, and Chlorate in Bottled Natural Mineral Waters,* Application Note 184, LPN 1890. Sunnyvale, CA, 2007.

Determination of Bromate in Drinking and Mineral Water by Isocratic Ion Chromatography with a Hydroxide Eluent

INTRODUCTION

To ensure that the water we drink is safe, it is disinfected. Unfortunately some of the by-products of disinfection are potentially harmful. Therefore many countries have established concentration limits for certain disinfection by-products. Ozonation is an effective disinfection process that is used worldwide, but will produce bromate if the source water contains bromide. Bromate is a potential human carcinogen and its concentration in drinking water is regulated in many countries with the upper limit often set at 10 µg/L — or 3 µg/L in Europe. The introduction to Dionex Application Note 167 discusses bromate risk and regulations.[1]

Ion chromatography (IC) is an established technique for determining bromate and the disinfection by-products chlorite and chlorate. Bromate has been determined by IC using either a hydroxide or carbonate eluent and suppressed conductivity detection[1,2] according to U.S. EPA Method 300.1, Part B.[3] The method using a hydroxide eluent is more sensitive than the method using a carbonate eluent, a result of the known advantages of hydroxide eluents for suppressed conductivity detection. Bromate has also been determined using either a hydroxide or carbonate eluent, suppressed conductivity detection, and absorbance detection after either a postcolumn addition of *o*-dianisidine[4,5] according to U.S. EPA Method 317.0,[6] or postcolumn reaction to produce the triiodide ion[7,8] according to U.S. EPA Method 326.0.[9] Methods 317.0 and 326.0 are used for determining bromate concentrations <1 µg/L. All the above IC methods for determining bromate using a hydroxide eluent use gradient elution.

This application update shows that bromate, chlorate, and chlorite can be determined with an isocratic hydroxide eluent to easily meet current bromate regulations. The method was tested with mineral water, a sample that has a higher ionic strength than most drinking water samples and is, therefore, a good test of the method. This method can use either a Reagent-Free™ IC (RFIC™) system or a standard IC system. Unlike the gradient elution method in Application Note 167, this method cannot determine all standard inorganic anions (e.g., phosphate).

Equipment

ICS-1000 Ion Chromatography System

To run this as an RFIC application:

ICS-2000 Ion Chromatography System

Chromeleon® Chromatography Management Software

*This application can also be executed on other RFIC systems including the ICS-2500 and ICS-3000.

Reagents and Standards

Deionized water (DI H_2O), 18.2 MΩ-cm resistance or better

Sodium hydroxide solution, 400 g/L (Cica-reagent grade, Kantor Chemical) or 50% NaOH (Fisher Scientific)

Stock individual standards of fluoride, chloride, nitrite, bromide, nitrate, and sulfate

1000 mg/L each (Merck)

Sodium chlorite, 80% ($NaClO_2$, Fluka)

Potassium bromate ($KBrO_3$, Fluka)

Sodium chlorate ($NaClO_3$, Fluka)

PREPARATION OF SOLUTIONS AND REAGENTS

Stock Standard Solutions

Prepare 1000 mg/L standards of chlorite, bromate, and chlorate by dissolving 0.1676, 0.1308, and 0.1275 g, respectively, in 100 mL DI H_2O.

Mixed Standard Solutions

Appropriate mixed standards are prepared from the 1000 mg/L stock standards. The standard concentration ranges should span the expected analyte concentrations. The concentrations used in this application are shown in Table 1.

Table 1. Concentrations of Calibration Standards

Peak Name	Standard 1 (µg/L)	Standard 2 (µg/L)	Standard 3 (µg/L)
Fluoride	500	1,000	2,000
Chlorite	5	10	20
Bromate	5	10	20
Chloride	25,000	50,000	100,000
Nitrite	5	10	20
Chlorate	5	10	20
Bromide	250	500	1,000
Nitrate	250	500	1,000
Sulfate	25,000	50,000	100,000

ELUENT SOLUTION

For an RFIC system, the eluent generator produces the eluent using the EluGen® EGC-KOH cartridge and DI water supplied by the pump. The concentration of eluent is controlled by Chromeleon.

To prepare a 20 mM sodium hydroxide solution, dilute 4 mL of 400 g/L (10 M) NaOH to 2 L with DI H_2O. When using 50% NaOH, dilute 3.2 g to 2 L with DI H_2O. For more information on preparing hydroxide eluents, please see section 4.5 of the IonPac® AS19 manual (document #065003).

CONDITIONS

Column:	IonPac AS19 Analytical, 4 × 250 mm (P/N 062885) IonPac AG19 Guard, 4 × 50 mm (P/N 062887)
Eluent:	20 mM KOH (RFIC systems), 20 mM NaOH
Eluent Source:	EluGen II EGC-KOH (for RFIC systems) (P/N 058900)
Temperature:	25 ºC
Flow Rate:	1.0 mL/min
Inj. Volume:	200 µL
Detection:	ASRS® ULTRA II, 4 mm, recycle mode
Suppressor Current:	60 mA
Background:	0.9–1.1 µS (RFIC system), 1.5–2.5 µS (prepared eluent)

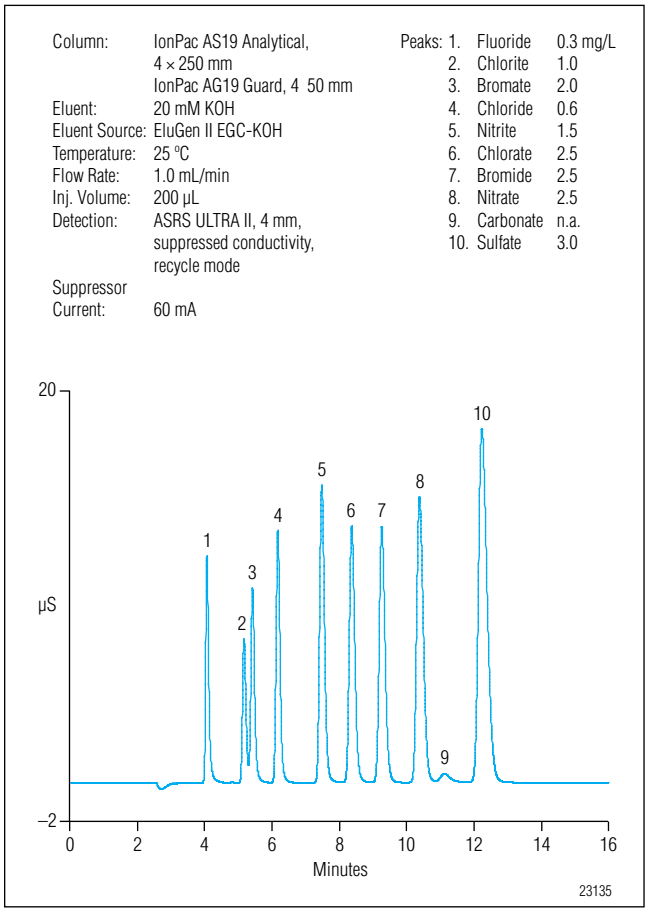

Figure 1. Separation of a mixed anion standard.

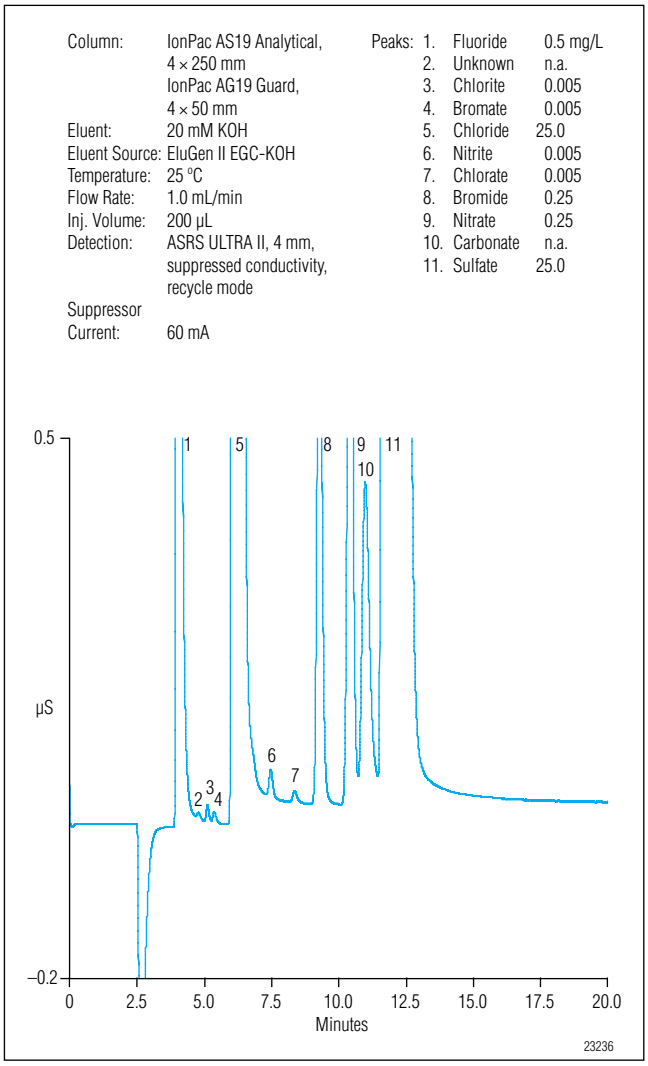

Figure 2. Separation of a mixed anion standard, containing 5 µg/L of chlorite, bromate, and chlorate.

Results and Discussion

An IonPac AS19 column set with an isocratic 20 mM hydroxide eluent separates fluoride, chlorite, bromate, chloride, nitrite, chlorate, bromide, nitrate, and sulfate in under 15 min (Figure 1). This separation is possible with either 20 mM KOH prepared by an RFIC system or manually prepared 20 mM NaOH. Chromatograms of the same sample separated with either a prepared eluent or an RFIC eluent differ in total conductivity (not shown). The total conductivity of the 20 mM manually prepared hydroxide eluent is higher than the 20 mM hydroxide eluent generated by the RFIC system. The higher purity of the RFIC eluent yields a lower background. To determine if this isocratic method is suitable for determining bromate at <10 µg/L together with chlorite and chlorate in a drinking water sample, a standard containing 5 µg/L chlorite, bromate, and chlorate, 25 mg/L chloride and sulfate, and five other anions was prepared. Figure 2 shows a separation of this standard and that the low concentrations of chlorite, bromate, and chlorate are easily detected and resolved from other anions.

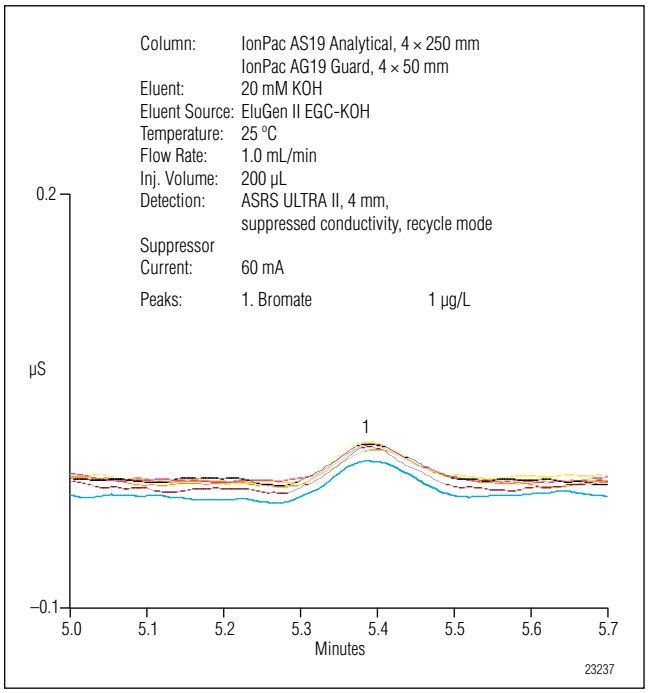

Figure 3. Overlay of seven injections of a 1 µg/L bromate standard with the RFIC method.

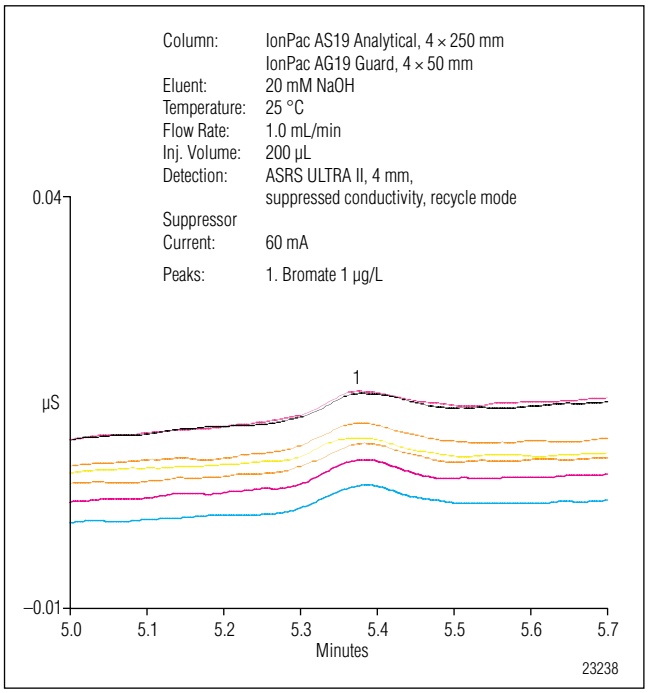

Figure 4. Overlay of seven injections of a 1 µg/L bromate standard with a manually prepared 20 mM NaOH eluent.

Minimum Detection Limit (MDL)

The MDL for bromate was determined using both manually prepared hydroxide eluent and RFIC eluent by making seven injections of 1-µg/L bromate standard. Figures 3 and 4 show overlays of seven injections for each of the eluent systems, and Tables 2 and 3 show the data from these injections. Using the single-sided Student's *t* test with a 99% confidence limit, the calculated MDL of bromate with the RFIC system was 0.14 ppb. The calculated MDL for bromate using the IC system with a manually prepared hydroxide eluent was 0.16 ppb. The calculated MDLs are similar, but the baseline of the RFIC system was more stable than the baseline with the manually prepared hydroxide eluent. Consequently, proper peak integration—important for MDL determinations—is easier (i.e., requires less postanalysis manipulation of the data to obtain proper integration). A comparison of Figures 3 and 4 reveals the stability of the RFIC system. Both figures were created by overlaying the seven injections with no offset. The injections with the manually prepared hydroxide exhibited variations in the background and baseline, while the injections with the RFIC eluent showed little variation.

Calibration

Standards were prepared at three different concentrations that should be appropriate for mineral and drinking water samples. Figure 2 shows a chromatogram of one of the three standards. The calibration results for both the RFIC eluent and the manually prepared hydroxide eluent are shown in Tables 4 and 5. Each anion exhibited a linear response in its chosen concentration range using either eluent system ($r^2 \times 100 > 99.9$ for all anions). The peaks for the lower analyte concentrations were easier to integrate in the chromatograms run on the RFIC system.

Table 2. Data from the MDL Determination of Bromate Using the RFIC Method

Sample Name	Ret. Time (min)	Area (µS * min x 10^{-4})
Bromate 1 ppb	5.387	3.21
Bromate 1 ppb	5.397	2.96
Bromate 1 ppb	5.390	3.19
Bromate 1 ppb	5.390	3.40
Bromate 1 ppb	5.393	3.21
Bromate 1 ppb	5.383	3.37
Bromate 1 ppb	5.400	3.22
RSD	0.11%	4.49%

Table 3. Data from the MDL Determination of Bromate Using a Manually Prepared 20 mM NaOH Eluent

Sample Name	Ret. Time (min)	Area (µS * min x 10^{-4})
Bromate 1 ppb	5.380	2.83
Bromate 1 ppb	5.383	2.91
Bromate 1 ppb	5.383	3.07
Bromate 1 ppb	5.387	2.83
Bromate 1 ppb	5.367	2.90
Bromate 1 ppb	5.377	2.82
Bromate 1 ppb	5.377	3.23
RSD	0.12%	5.22%

Table 4. Calibration Data for the RFIC Eluent

No	Ret. Time (min)	Peak	Coeff.Det. (%)	Offset	Slope
1	4.00	Fluoride	99.9913	0.2107	0.0035
2	5.11	Chlorite	99.9963	0.0003	0.0004
3	5.36	Bromate	99.9906	0.0003	0.0003
4	6.19	Chloride	99.9974	1.1322	0.0023
5	7.46	Nitrite	99.9987	–0.0001	0.0011
6	8.35	Chlorate	99.9823	0.0000	0.0006
7	9.27	Bromide	99.9176	–0.0547	0.0010
8	10.41	Nitrate	99.9535	–0.0568	0.0011
9	11.71	Sulfate	99.9988	1.0156	0.0017

Table 5. Calibration Data Using Manually Prepared Hydroxide Eluent

No	Ret. Time (min)	Peak	Coeff.Det. (%)	Offset	Slope
1	3.96	Fluoride	99.9710	0.0609	0.0031
2	5.08	Chlorite	99.9937	0.0002	0.0004
3	5.37	Bromate	99.9989	0.0002	0.0003
4	6.17	Chloride	99.9998	0.0314	0.0022
5	7.48	Nitrite	99.9920	-0.0003	0.0010
6	8.46	Chlorate	100.0000	0.0001	0.0005
7	9.34	Bromide	99.9198	-0.0422	0.0008
8	10.55	Nitrate	99.9941	0.0593	0.0011
9	11.98	Sulfate	99.9993	-0.3359	0.0016

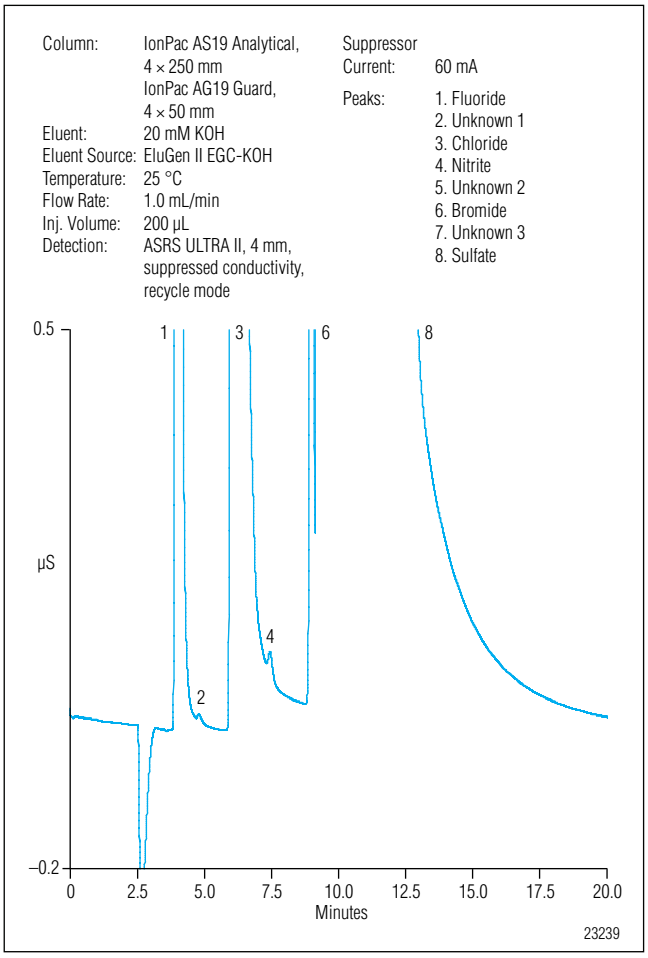

Figure 5. Determination of bromate in a mineral water sample using an RFIC system.

Table 6. Summary of Chlorite, Bromate, and Chlorate Recovery (10 µg/L Spike of Each) from Mineral Water with RFIC Eluent

Sample No.	Sample	Amount Chlorite (µg/L)	Amount Bromate (µg/L)	Amount Chlorate (µg/L)
1	Spiked mineral water	10.0338	9.7644	10.5122
2	Spiked mineral water	9.8631	9.5171	10.3528
3	Spiked mineral water	9.9147	9.6518	10.3823
4	Spiked mineral water	9.9843	9.6292	10.4107
5	Spiked mineral water	9.7719	9.6821	10.3929
	Average Amount:	9.9140	9.6490	10.4100
	Recovery (%):	**99.14**	**96.49**	**104.10**

Table 7. Summary of Chlorite, Bromate, and Chlorate Recovery (10 µg/L Spike of Each) from Mineral Water with Manually Prepared Hydroxide Eluent

Sample No.	Sample	Amount Chlorite (µg/L)	Amount Bromate (µg/L)	Amount Chlorate (µg/L)
1	Spiked mineral water	9.7310	8.9411	11.3125
2	Spiked mineral water	9.8688	8.8031	11.1004
3	Spiked mineral water	9.9669	8.7507	11.1460
4	Spiked mineral water	9.7876	8.7352	11.1813
5	Spiked mineral water	9.7764	8.7353	11.1806
	Average Amount:	9.8260	8.7930	11.1840
	Recovery (%):	**98.26**	**87.93**	**111.84**

Sample Analysis and Recovery

A bottled mineral water sample was analyzed using either manually prepared hydroxide eluent or hydroxide prepared by eluent generation. Figure 5 shows the separation of the mineral water sample and that no chlorite, bromate, or chlorate were detected. To ensure that the 200 µL of mineral water was not overloading the column, we spiked 10 µg/L of chlorite, bromate, and chlorate into the mineral water (Figure 6) and evaluated the recovery from five injections of this sample. Tables 6 and 7 show that we observed good analyte recovery using either eluent system with better results using the RFIC system. These results show that the isocratic hydroxide method is suitable for chlorite, bromate, and chlorate determinations in typical drinking and mineral water samples. Using 20 mM hydroxide, phosphate does not elute within 15 min and is probably retained on the column because no broad baseline disturbances were observed in subsequent injections of mineral water. Wash the column with 100 mM hydroxide to prevent the low concentrations of phosphate from lowering column capacity and eventually shortening retention times. Performing the column wash once a week should be adequate because no loss of retention time was observed in two weeks of analysis.

SUMMARY

Bromate was determined in a mineral water sample using the IonPac AS19 and isocratic elution. The results of using two sources of eluent, manually prepared hydroxide and hydroxide eluent prepared by an eluent generator, were compared. The results of the MDL, cali-

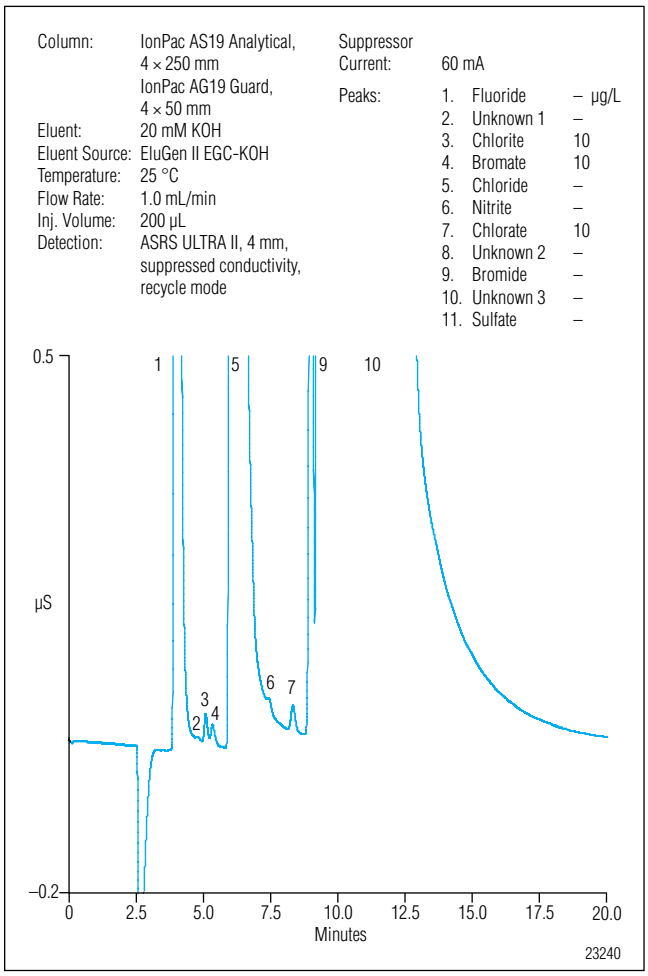

Figure 6. Determination of chlorite, bromate, and chlorate in a mineral water sample using an RFIC system after a 10 µg/L spike of each.

bration, sample analysis, and percent recovery were used to compare the two eluent sources. The RFIC results were better, but the manually prepared eluents could also determine low µg/L (<10) levels of bromate in mineral and drinking waters.

REFERENCES

1. *Determination of Trace Concentrations of Oxyhalides and Bromide in Municipal and Bottled Waters Using a Hydroxide-Selective Column with a Reagent-Free Ion Chromatography System.* Application Note 167, LPN 1662. Dionex Corporation, Sunnyvale, CA, **2006**.
2. *Ion Chromatographic Determination of Oxyhanlides and Bromide at Trace Level Concentrations in Drinking Water Using Direct Injection*. Application Note 81, LPN 0965. Dionex Corporation, Sunnyvale, CA, **1997**.
3. U.S. EPA Method 300.1, U.S. Environmental Protection Agency. Cincinnati, OH, **1997**.
4. *Determination of Inorganic Oxyhalide Disinfection By-Product Anions and Bromide in Drinking Water Using Ion Chromatography with the Addition of a Postcolumn Reagent for Trace Bromate Analysis.* Application Note 136, LPN 1229-01. Dionex Corporation, Sunnyvale, CA, **2002**.
5. *Determination of Trace Concentrations of Disinfection By-Product Anions and Bromide in Drinking Water Using Reagent-Free Ion Chromatography Followed by Postcolumn Addition of* o*-Dianisidine for Trace Bromate Analysis.* Application Note 168, LPN 1706. Dionex Corporation, Sunnyvale, CA, **2005**.
6. U.S. EPA Method 317.0, U.S. Environmental Protection Agency. Cincinnati, OH, **2000**.
7. *Determination of Chlorite, Bromate, Bromide, and Chlorate in Drinking Water by Ion Chromatography with an On-Line Generated Postcolumn Reagent for Sub-µg/L Bromate Analysis.* Application Note 149, LPN 1523. Dionex Corporation, Sunnyvale, CA, **2003**.
8. *Determination of Disinfection By-Product 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.* Application Note 171, LPN 1767. Dionex Corporation, Sunnyvale, CA, **2006**.
9. U.S. EPA Method 326.0, U.S. Environmental Protection Agency. Cincinnati, OH, **2002**.

SUPPLIERS

Merck & Co., Inc., One Merck Drive, P.O. Box 100, Whitehouse Station, NJ, 08889-0100, USA. Tel: 908-423-1000, www.merck.com.

Fluka Chemika-BioChemika, Fluka Chemie AG, Industriestrasse 25, CH-9471, Buchs, Switzerland, Tel: +81 755 25 11, www.sigma-aldrich.com.

Kanto Corporation, 13424 North Woodrush Way, Portland, OR, 97203, USA, Tel: 866-609-5571, kantocorp.com.

Thermo
SCIENTIFIC

Column Selection Guide

Silica Columns

			Reversed-Phase (RP)						Mixed-Mode			HILIC		Application-Specific					Example Applications
			Acclaim 120 C18	Acclaim 120 C8	Acclaim 300 C18	Acclaim Polar Advantage (PA)	Acclaim Polar Advantage II (PA2)	Acclaim Phenyl-1	Acclaim Trinity P1	Acclaim Mixed-Mode WAX-1	Acclaim Mixed-Mode WCX-1	Acclaim Mixed-Mode HILIC-1	Acclaim HILIC-10	Acclaim Organic Acid	Acclaim Surfactant	Acclaim Explosives E1	Acclaim Explosives E2	Acclaim Carbamate	
General Applications	Neutral Molecules	High hydrophobicity	√	√	√	√	√	√	√	√	√	√	√						Fat-soluble vitamins, PAHs, glycerides
		Intermediate hydrophobicity	√	√	√	√	√	√	√	√	√	√							Steroids, phthalates, phenolics
		Low hydrophobicity	√			√	√					√	√						Acetaminophen, urea, polyethylene glycols
	Anionic Molecules	High hydrophobicity	√	√	√	√	√	√	√	√	√	√							NSAIDs, phospholipids
		Intermediate hydrophobicity	√	√	√	√	√	√	√	√		√							Asprin, alkyl acids, aromatic acids
		Low hydrophobicity				√			√	√		√	√						Small organic acids, e.g. acetic acids
	Cationic Molecules	High hydrophobicity	√	√	√	√	√	√		√	√	√							Antidepressants
		Intermediate hydrophobicity	√	√	√	√	√	√	√		√	√							Beta blockers, benzidines, alkaloids
		Low hydrophobicity	√			√			√		√	√	√						Antacids, pseudoephedrine, amino sugars
	Amphoteric/ Zwitterionic Molecules	High hydrophobicity	√	√	√	√	√	√	√	√	√	√							Phospholipids
		Intermediate hydrophobicity	√	√	√	√	√	√			√								Amphoteric surfactants, peptides
		Low hydrophobicity				√	√		√	√	√	√	√						Amino acids, aspartame, small peptides
	Mixtures of Neutral, Anionic, Cationic Molecules	Neutrals and acids	√			√	√		√	√									Artificial sweeteners
		Neutrals and bases	√			√	√		√		√								Cough syrup
		Acids and bases				√			√										Drug active ingredient with counterion
		Neutrals, acids, and bases				√			√										Combination pain relievers
Specific Applications	Surfactants	Anionic	√	√	√	√	√								√				SDS, LAS, laureth sulfates
		Cationic													√				Quats, benzylalkonium in medicines
		Nonionic	√	√	√	√	√					√			√				Triton X-100 in washing tank
		Amphoteric	√	√	√	√	√								√				Cocoamidopropyl betaine
		Hydrotropes													√				Xylenesulfonates in handsoap
		Surfactant blends													√				Noionic and anionic surfactants
	Organic Acids	Hydrophobic							√	√				√					Aromatic acids, fatty acids
		Hydrophilic							√	√				√					Organic acids in soft drinks, pharmaceuticals
	Environmental Contaminants	Explosives														√	√		U.S. EPA Method 8330, 8330B
		Carbonyl compounds															√		U.S. EPA 1667, 555, OT-11; CA CARB 1004
		Phenols	√			√													Compounds regulated by U.S. EPA 604
		Chlorinated/Phenoxy acids				√													U.S. EPA Method 555
		Triazines	√			√													Compounds regulated by U.S. EPA 619
		Nitrosamines				√													Compounds regulated by U.S. EPA 8270
		Benzidines	√			√													U.S. EPA Method 605
		Perfluorinated acids				√													Dionex TN73
		Microcystins	√																ISO 20179
		Isocyanates					√					√							U.S. OSHA Methods 42, 47
		Carbamate insecticides																√	U.S. EPA Method 531.2
	Vitamins	Water-soluble vitamins				√	√		√										Vitamins in dietary supplements
		Fat-soluble vitamins	√	√	√	√	√	√		√									Vitamin pills
	Pharmaceutical Counterions	Anions							√	√									Inorgaic anions and organic acids in drugs
		Cations							√		√								Inorgaic cations and organic bases in drugs
		Mixture of Anions and Cations							√										Screening of pharmaceutical counterions
		API and counterions							√										Naproxen Na^+ salt, metformin Cl^- salt, etc.

Polymer Columns

		IonPac AS23	IonPac AS22	IonPac AS22-Fast	IonPac AS14/A	IonPac AS12A	IonPac AS9/HC/SC	IonPac AS4A/SC	IonSwift MAX-100	IonPac AS24	IonPac AS21	IonPac AS20	IonPac AS19	IonPac AS18	IonPac AS18-Fast	IonPac AS17-C	IonPac AS16	IonPac AS15	IonPac AS11(-HC)	IonPac AS10	IonPac AS7	IonPac AS5	IonPac Fast Anion IIIA	OmniPac PAX-100	OmniPac PAX-500
ANIONS	Inorganic Anions	√	√	√	√	√	√	√	√	√		√	√	√	√	√		√	√	√					
	Oxyhalides	√				√	√			√			√												
	Bromate	√					√			√			√												
	Perchlorate										√	√					√								
	Organic Acids								√							√		√	√	√					
	Phosphoric/Citric Acids																						√		
	Poly/High-Valence Anions								√			√					√		√		√	√			
	Hydrophobic Anions								√			√					√		√						
	Hydrophobic/Halogenated Anions								√			√							√					√	
	Anionic Neutral Molecules									√	√	√	√												√
CATIONS	Inorganic Cations																								
	Sodium/Ammonium																								
	Amines/Polyvalent Amines																								
	Aliphatic/Aromatic Amines																								
	Alkanol/Ethhanolamines																								
	Biogenic Amines																								
	Transition/Lanthanide Metals																								
	Hydrophobic Cations																								
	Cationic Neutral Molecules																								
BIO-MOLECULES	Amino Acids																								
	Phosphorylated Amino Acids																								
	Amino Sugars																								
	Oligoscharides																								
	Mono-/Di-Saccharides																								
	Glycoproteins																								
	Alditols/Aldoses mono/di Saccharides																								
	ds Nucleic Acids																								
	Single-Stranded Oligonucleotides																								
	Peptides																								
	Proteins																								
	Metal-binding Proteins																								
	Monoclonal antibodies																								
ORGANIC MOLECULES	Aliphatic Organic Acids																								
	Alcohols																								
	Borate																								
	Large Molecules, Anions																								
	Small Molecules																								
	Small Molecules/LC-MS																								
	Polar/Non-Polar Small Molecules																								
	Hydrophobic/Aliphatic Organic Acids																								
	Surfactant Formulations																								
	Explosives/EPA 8330																								
MODE	Anion Exchange / Carbonate	√	√	√	√	√	√	√																	
	Anion Exchange / Hydroxide								√	√	√	√	√	√	√	√	√	√	√	√	√	√			
	Cation Exchange																								
	Multi-Mode																							√	√
	Affinity																								
	Ion Exclusion																								
	Reversed Phase																								
	Anion Exchange/Other																								

		IonPac CS18	IonPac CS17	IonPac CS16	IonPac CS15	IonPac CS14	IonPac CS12A	IonPac CS11	IonPac CS10	IonPac CS5A	OmniPac PCX-100	OmniPac PCX-500	AminoPac PA10	AminoPac PA1	CarboPac PA200	CarboPac PA100	CarboPac PA20	CarboPac PA10	CarboPac PA1	CarboPac MA1	DNAPac PA200	DNAPac PA100	ProPac WAX/SAX	ProPac WCX/SCX	ProPac IMAC	ProPac HIC	ProPac PA1	ProSwift	IonPac ICE-AS6	IonPac ICE-AS1	IonPac ICE-Borate	IonPac NS1
ANIONS	Inorganic Anions	√	√	√	√	√	√	√	√																						
	Oxyhalides			√	√		√																								
	Bromate																														
	Perchlorate																														
	Organic Acids																														
	Phosphoric/Citric Acids																														
	Poly/High-Valence Anions																														
	Hydrophobic Anions																														
	Hydrophobic/Halogenated Anions																														
	Anionic Neutral Molecules																														
CATIONS	Inorganic Cations	√	√	√	√	√	√	√	√																						
	Sodium/Ammonium			√	√		√																								
	Amines/Polyvalent Amines	√	√																												
	Aliphatic/Aromatic Amines		√			√	√																								
	Alkanol/Ethhanolamines	√	√		√																										
	Biogenic Amines	√	√																												
	Transition/Lanthanide Metals									√																					
	Hydrophobic Cations	√	√			√					√																				
	Cationic Neutral Molecules											√																			
BIO-MOLECULES	Amino Acids												√	√																	
	Phosphorylated Amino Acids												√																		
	Amino Sugars												√		√	√	√	√													
	Oligoscharides														√	√			√	√											
	Mono-/Di-Saccharides															√	√	√	√												
	Glycoproteins																							√	√			√			
	Alditols/Aldoses mono/di Saccharides															√	√	√	√												
	ds Nucleic Acids																			√	√										
	Single-Stranded Oligonucleotides																			√	√							√			
	Peptides																									√	√	√	√		
	Proteins																							√	√	√	√	√	√		
	Metal-binding Proteins																									√					
	Monoclonal antibodies														√	√			√					√	√	√	√	√	√		
ORGANIC MOLECULES	Aliphatic Organic Acids																													√	√
	Alcohols																													√	√
	Borate																														√
	Large Molecules, Anions																														√
	Small Molecules																														
	Small Molecules/LC-MS																														
	Polar/Non-Polar Small Molecules																														
	Hydrophobic/Aliphatic Organic Acids																														
	Surfactant Formulations																														√
	Explosives/EPA 8330																														
MODE	Anion Exchange / Carbonate																														
	Anion Exchange / Hydroxide														√	√	√	√	√	√											
	Cation Exchange	√	√	√	√	√	√	√	√	√														√			√	√			
	Multi-Mode										√	√																			
	Affinity																								√						
	Ion Exclusion																												√	√	√
	Reversed Phase																										√	√	√		√
	Anion Exchange/Other												√	√						√	√			√				√	√		

Column Specifications

IC Anion Columns

Column	Format	Primary Eluent	Application	Particle Diameter	Substrate Crosslinking	Latex Diameter	Latex Crosslinking	Capacity (per column)	Functional Group	Hydrophobicity
IonPac AS24	2 × 250 mm	Hydroxide	Recommended column for haloacetic acids prior to MS or MS/MS detection	7 µm	55%	-	-	140 µeq	Alkanol quaternary ammonium	Ultralow
IonPac AS23	2 × 250 mm 4 × 250 mm	Carbonate	Recommended column for inorganic anions and oxyhalides. Trace bromate in drinking water.	6 µm	55%	-	-	80 µeq 320 µeq	Alkyl quaternary ammonium	Ultralow
IonPac AS22	2 × 250 mm 4 × 250 mm	Carbonate	Recommended column for fast analysis of common inorganic anions.	6.5 µm	55%	-	-	52.5 µeq 210 µeq	Alkyl quaternary ammonium	Ultralow
IonPac AS21	2 × 250 mm	Hydroxide	Recommended column for trace perchlorate prior to MS or MS/MS detection	7.0 µm	55%	-	-	45 µeq	Alkanol quaternary ammonium	Ultralow
IonPac AS20	2 × 250 mm 4 × 250 mm	Hydroxide	Recommended column for trace perchlorate prior to suppressed conductivity detection.	7.5 µm	55%	-	-	77.5 µeq 310 µeq	Alkanol quaternary ammonium	Ultralow
IonPac AS19	2 × 250 mm 4 × 250 mm	Hydroxide	Recommended column for inorganic anions and oxyhalides. Trace bromate in drinking water.	7.5 µm	55%	-	-	60 µeq 350 µeq	Alkanol quaternary ammonium	Low
IonPac AS18	2 × 250 mm 4 × 250 mm	Hydroxide	Recommended column for the analysis of common inorganic anions.	7.5 µm	55%	65 nm	8%	75 µeq 285 µeq	Alkanol quaternary ammonium	Low
IonPac AS17-C	2 × 250 mm 4 × 250 mm	Hydroxide	Trace anions in HPW matrices. Carboxylated resin, no sulfate blank. Low capacity for fast analysis of common inorganic anions using gradient elution with the Eluent Generator.	10.5 µm	55%	75 nm	6%	7.5 µeq 30 µeq	Alkanol quaternary ammonium	Low
IonPac AS16	2 × 250 mm 4 × 250 mm	Hydroxide	High capacity for hydrophobic anions including iodide, thiocyanate, thiosulfate, and perchlorate. Polyvalent anions including: polyphosphates and polycarboxylates	9 µm	55%	80 nm	1%	42.5 µeq 170 µeq	Alkanol quaternary ammonium	Ultralow
IonPac AS15	2 × 250 mm 4 × 250 mm	Hydroxide	High capacity for trace analysis of inorganic anions and low molecular weight organic acids in high purity water matrices.	9 µm	55%	-	-	56.25 µeq 225 µeq	Alkanol quaternary ammonium	Medium-High
IonPac AS15-5mm	3 × 150 mm	Hydroxide	Fast run, high capacity for trace analysis of inorganic anions and low molecular weight organic acids in high purity water matrices.	5 µm	55%	-	-	70 µeq	Alkanol quaternary ammonium	Medium-High
IonPac AS14A- 5 µm	3 × 150 mm	Carbonate	Recommended column for fast analysis of common inorganic anions.	5 µm	55%	-	-	40 ueq	Alkyl quaternary ammonium	Medium
IonPac AS14A	4 × 250 mm	Carbonate	For analysis of common inorganic anions.	7 µm	55%	-	-	120 µeq	Alkyl quaternary ammonium	Medium
IonPac AS14	2 × 250 mm 4 × 250 mm	Carbonate	Moderate capacity for fast analysis of common inorganic anions.	9 µm	55%	-	-	16 µeq 65 µeq	Alkyl quaternary ammonium	Medium-High

Column	Format	Primary Eluent	Application	Particle Diameter	Substrate Crosslinking	Latex Diameter	Latex Crosslinking	Capacity (per column)	Functional Group	Hydrophobicity
IonPac AS12A	2 × 200 mm 4 × 200 mm	Carbonate	Moderate capacity for analysis of inorganic anions and oxyhalides. Trace chloride and sulfate in high carbonate matrices.	9 µm	55%	140 nm	0.20%	13 µeq 52 µeq	Alkyl quaternary ammonium	Medium
IonPac AS11-HC	2 × 250 mm 4 × 250 mm	Hydroxide	High capacity for the determination of organic acids and inorganic anions in uncharacterized samples.	9 µm	55%	70 nm	6%	72.5 µeq 290 µeq	Alkanol quaternary ammonium	Medium-Low
IonPac AS11	2 × 250 mm 4 × 250 mm	Hydroxide	Low capacity for fast profiling of organic acids and inorganic anions in well-characterized samples.	13 µm	55%	85 nm	6%	11 µeq 45 µeq	Alkanol quaternary ammonium	Very Low
IonPac AS10	2 × 250 mm 4 × 250 mm	Hydroxide	High capacity for the analysis of inorganic anions and organic acids in high nitrate samples.	8.5 µm	55%	65 nm	5%	42.5 µeq 170 µeq	Alkyl quaternary ammonium	Low
IonPac AS9-HC	2 × 250 mm 4 × 250 mm	Carbonate	High-capacity column for inorganic anions and oxyhalides. Trace bromate in drinking water.	9 µm	55%	90 nm	18%	48 µeq 190 µeq	Alkyl quaternary ammonium	Medium-Low
IonPac AS9-SC	4 × 250 mm	Carbonate	Low capacity for fast analysis of inorganic anions and oxyhalides. Specified column in US EPA Method 300.0 (B).	13 µm	55%	110 nm	20%	30-35 µeq	Alkyl quaternary ammonium	Medium-Low
IonPac AS4A-SC	2 × 250 mm 4 × 250 mm	Carbonate	Low capacity for fast analysis of common inorganic anions. Specified column in U.S. EPA Method 300.0 (A).	13 µm	55%	160 nm	0.50%	5 µeq 20 µeq	Alkanol quaternary ammonium	Medium-Low
IonPac Fast Anion IIIA	3 × 250 mm	Hydroxide	Recommended column for phosphoric and citric acids in cola soft drinks.	7.5 µm	55%	-	-	55 µeq	Alkanol quaternary ammonium	Ultralow
IonPac AS7	4 × 250 mm	Specialty Eluents	Polyvalent anions including chelating agents, polyphosphates and polyphosphonates. Cyanide, sulfide, hexavalent chromium, and arsenic speciation.	10 µm	2%	530 nm	5%	100 µeq	Alkyl quaternary ammonium	Medium-High
IonPac AS5A	4 × 150 mm	Hydroxide	Low capacity for fast profiling of organic acids and inorganic anions in well-characterized samples.	5 µm	2%	60 nm	4%	35 µeq	Alkanol quaternary ammonium	Low
IonPac AS5	4 × 250 mm	Hydroxide	Metal-EDTA complexes, metal-cyanide complexes, and oxyanions.	15 µm	2%	120 nm	1%	20 µeq	Alkanol quaternary ammonium	Low

IC Cation Columns

Column	Format	Primary Eluent	Application	Particle Diameter	Substrate Crosslinking	Latex Diameter	Latex Crosslinking	Capacity (per column)	Functional Group	Hydrophobicity
IonPac CS18	2 × 250 mm	MSA	Recommended column for polar amines (alkanolamines and methylamines) and moderately hydrophobic and polyvalent amines (biogenic and diamines). Nonsuppressed mode when extended calibration linearity for ammonium and weak bases is required	6 µm	55%	-	-	0.29 µeq	Carboxylic acid	Medium
IonPac CS17	2 × 250 mm 4 × 250 mm	MSA	Recommended column for hydrophobic and polyvalent amines (biogenic amines and diamines)	7 µm	55%	-	-	0.363 µeq 1.45 µeq	Carboxylic acid	Very Low
IonPac CS16	3 × 250 mm 5 × 250 mm	MSA	Recommended column for disparate concentration ratios of adjacent-eluting cations such as sodium and ammonium. Can be used for alkylamines and alkanolamines.	5 µm	55%	-	-	3.0 µeq 8.4 µeq	Carboxylic acid	Medium
IonPac CS15	2 × 250 mm 4 × 250 mm	MSA	Disparate concentration ratios of ammonium and sodium. Trace ethanolamine in high-ammonium or high- potassium concentrations. Alkanolamines.	8.5 µm	55%	-	-	0.7 µeq 2.8 µeq	Carboxylic acid/ phosphonic acid/ crown ether	Medium
IonPac CS14	2 × 250 mm 4 × 250 mm	MSA	Aliphatic amines, aromatic amines, and polyamines plus mono- and divalent cations.	8.5 µm	55%	-	-	0.325 µeq 1.3 µeq	Carboxylic acid	Low
IonPac CS12A-MS	2 × 100 mm	MSA	IC-MS screening column for fast elution and low flow rates required for interfacing with IC-MS	8.5 µm	55%	-	-	0.28 µeq	Carboxylic acid/ phosphonic acid	Medium
IonPac CS12A-5 µm	3 × 150 mm	MSA	Recommended column for high efficiency and fast analysis (3 min) of mono- and divalent cations.	5 µm	55%	-	-	0.94 µeq	Carboxylic acid/ phosphonic acid	Medium
IonPac CS12A	2 × 250 mm 4 × 250 mm	MSA	Recommended column for the separation of mono- and divalent cations. Manganese morpholine, alkylamines, and aromatic amines.	8.5 µm	55%	-	-	0.7 µeq 2.8 µeq	Carboxylic acid/ phosphonic acid	Medium
IonPac CS11	2 × 250 mm	HCl + DAP	Separation of mono- and divalent cations. Ethanolamines if divalent cations are not present.	8 µm	55%	200 nm	5%	0.035 µeq	Sulfonic acid	Medium
IonPac CS10	4 × 250 mm	HCl + DAP	Separation of mono- and divalent cations.	8.5 µm	55%	200 nm	5%	0.08 µeq	Sulfonic acid	Medium
IonPac CS5A	2 × 250 mm 4 × 250 mm	Pyridine dicarboxylic acid	Recommended column for transition and lanthanide metals analysis. Aluminum analysis.	9 µm	55%	140 nm 75 nm	10% 20%	0.02 µeq/ 0.005 µeq 0.04 µeq/ 0.01 µeq	Sulfonic acid/ alkanol quaternary ammonium	-

Ion-Exclusion Columns

Column	Format	Primary Eluent	Application	Particle Diameter	Substrate Crosslinking	Latex Diameter	Latex Crosslinking	Capacity (per column)	Functional Group	Hydrophobicity
IonPac ICE-AS1	4 × 250 mm 9 × 250 mm	Heptafluorobutyric acid	Organic acids in high ionic strength matrices. Fast separation of organic acids.	7.5 µm	8%	-	-	5.3 µeq 27 µeq	Sulfonic acid	Ultra Low
IonPac ICE-AS6	9 × 250 mm	Heptafluorobutyric acid	Organic acids in complex or high ionic strength matrices.	8 µm	8%	-	-	27 µeq	Sulfonic and carboxylic acid	Moderate
IonPac ICE-Borate	9 × 250 mm	MSA/ Mannitol	Trace concentrations of borate	7.5 µm	8%	-	-	27 µeq	Sulfonic acid	Ultra Low

Acclaim General and Specialty Columns

Column	Bonded Phase	USP Type	Endcapped	Substrate	Particle Shape	Particle Size	Metal Impurity (ppm) Na, Fe, AL	Average Pore Diameter	Surface Area (m^2/g)	Total Carbon Content
Mixed-Mode WAX	Proprietary alkyl amine	na	Proprietary	Ultrapure silica	Spherical	5 µm	<10 ppm	120 Å	300	na
Mixed-Mode HILIC	Proprietary alkyl diol	na	Proprietary			5 µm		120 Å	300	na
Mixed-Mode WCX	Proprietary alkyl carboxyl	na	Proprietary			5 µm		120 Å	300	na
Organic Acid (OA)	Proprietary	na	Yes			5 µm		120 Å	300	17%
Surfactant and Explosives E1/2	Proprietary	na	Yes			5 µm		120 Å	300	na
120 C18	C18	L1	Yes			2, 3 and 5 µm		120 Å	300	18%
120 C8	C8	L7	Yes			3 and 5 µm		120 Å	300	11%
300 C18	C18	L1	Yes			3 µm		300 Å	100	7%
Polar Advantage	Sulfamido C16	na	Yes			3 and 5 µm		120 Å	300	17%
Polar Advantage II	Amide C18	na	Yes			2, 3 and 5 µm		120 Å	300	17%
HILIC	Proprietary hydrophilic		Yes			3 µm		120 Å	300	
Phenyl-1	Proprietary alkyl phenyl		Yes			3 µm		120 Å	300	
Carbamate	Proprietary alkyl group		Yes			3 and 5 µm		120 Å	300	
Trinity			Yes					120 Å	300	

Bio Columns

Protein

Column	Phase	Target Applications	Base Matrix Material	Substrate Crosslinking	Capacity	Recommended Flow Rate	Solvent Compatibility	Maximum Backpressure	pH Range
MAbPac SEC-1									
MAbPac SCX-10									
ProPac WCX-10	Weak Cation Exchange	High resolution and high efficiency separations of proteins and glycoproteins, pI =3-10, MW>10,000 units	10-µm diameter nonporous substrate to which is grafted a polymer chain bearing carboxylate groups.	55%	6 mg/ mL lysozyme	0.2–2 mL/min	80% ACN, acetone. Incompatable with alcohols and MeOH	3000 psi (21 MPa)	2–12.0
ProPac SCX-10	Strong Cation Exchange	High resolution and high efficiency separations of proteins and glycoproteins, pI =3-10, MW>10,000 units	10 µm diameter nonporous substrate to which is grafted a polymer chain bearing sulfonate groups.	55%	3 mg/ mL lysozyme	0.2–2.0 mL/min	80% ACN, acetone, MeOH	3000 psi (21 MPa)	2–12.0
ProPac SCX-20									
ProPac WAX-10	Weak Anion Exchange	High resolution and high efficiency separations of proteins and glycoproteins, pI =3-10, MW>10,000 units	10 µm diameter non-porous substrate to which is grafted a polymer chain bearing tertiary amine groups.	55%	5 mg/ mL BSA/ mL	0.2–2.0 mL/min	80% ACN, acetone, MeOH,	3000 psi (21 MPa)	2–12.0
ProPac SAX-10	Strong Anion Exchange	High resolution and high efficiency separations of proteins and glycoproteins, pI =3-10, MW>10,000 units	10 µm diameter non-porous substrate with grafted polymer chain bearing quaternary ammonium groups.	55%	15 mg/ mL BSA	0.2–2.0 mL/min	80% ACN, acetone, MeOH	3000 psi (21 MPa)	2–12.0
ProSwift RP-1S	Reversed-Phase	Fast protein separation with high capacity using Reversed Phase	Monolith; polystyrene-divinylbenzene with phenyl functional group	Monolith Standard permeability	5.5 mg/mL Insulin	2–4 mL/min	Most common organic solvents	2800 psi (19.2 Mpa)	1–14
ProSwift RP-2H	Reversed-Phase	Fast protein separation with high capacity using Reversed Phase	Monolith; polystyrene-divinylbenzene with phenyl functional group	Monolith High permeability	1.0 mg/mL Lysozyme	1–10 mL/min	Most common organic solvents	2800 psi (19.3 Mpa)	1–14
ProSwift RP-4H									
ProSwift RP-3U	Reversed-Phase	Fast protein separation with high capacity using Reversed Phase	Monolith; polystyrene-divinylbenzene with phenyl functional group	Monolith Ultrahigh permeability	0.5 mg/mL Lysozyme	1– 16 mL/min	Most common organic solvents	2800 psi (19.3 Mpa)	1–14
ProSwift SAX-1S	Strong Anion Exchange	Fast protein separation with good resolution using Anion Exchange	Monolith; polymethac-rylate with quaternary amine functional group	Monolith Standard permeability	18 mg/mL BSA	0.5–1.5 (4.6 mm), 0.05–.25 (1.0 mm)	Most common organic solvents	1000 psi (4.6 mm) 2000 psi (1.0 mm)	2–12.0
ProSwift SCX-1S	Strong Cation Exchange	Fast protein separation with good resolution using Cation Exchange	Monolith; polymethac-rylate with sulfonic acid fuctional group	Monolith Standard permeability	30 mg/mL Lysozyme	0.5–1.5 mL/min (4.6 mm)	Most common organic solvents	1000 psi (4.6 mm)	2–12.0
ProSwift WAX-1S	Weak Anion Exchange	Fast protein separation with good resolution using Anion Exchange	Monolith; polymethacrylate with tertiary amine (DEAE) functional group	Monolith Standard permeability	18 mg/mL BSA	0.5–1.5 mL/min (4.6 mm), 0.05–.25 (1.0 mm)	Most common organic solvents	1000 psi (4.6 mm) 2000 psi (1.0 mm)	2–12.0
ProSwift WCX-1S	Weak Cation Exchange	Fast protein separation with good resolution using Cation Exchange	Monolith; polymethacrylate with carboxylic acid (CM) functional group	Monolith Standard permeability	23 mg/mL Lysozyme	0.5–1.5 mL/min (4.6 mm), 0.05–.20 (1.0 mm)	Most common organic solvents	1000 psi (4.6 mm) 2000 psi (1.0 mm)	2–12.0
ProPac IMAC-10	Immobilized Metal Affinity	High resolution separation of certain metal-binding proteins and peptides	10 µm diameter non-porous polystyrene divinylbenzene substrate with poly (IDA) grafts.	55%	>60 mg lysozyme/ mL gel (4 x 250 mm)	1.0 mL/min	EtOH, urea, NaCl, non- ionic detergents, glycerol, acetic acid, guanidine HCl	3000 psi (21MPa)	2–12
ProSwift ConA-1S									
ProPac HIC-10	Reversed-Phase	Protein separation using hydrophobic interaction with salt gradient elution	Spherical 5 µm, ultrapure silica, 300 A, surface area 100 m^2/ g,	n/a	340 mg lysozyme per 7.8 x 75 mm column	1.0 mL/ min	2M Ammonium sulfate/ phosphate salts, organic solvent for cleanup	4,000 psi	2.5–7.5

Carbohydrate

Column	Target Applications	Base Matrix Material	Substrate Crosslinking	Latex Crosslinking	Capacity	Recommended Eluents	Recommended Flow Rate	Solvent Compatibility	Maximum Backpressure	pH Range
CarboPac MA1	Reduced mono- and disaccharide analysis.	7.5 µm diameter macroporous substrate fully functionalized with an alkyl quaternary ammonium group	15%	No latex	1450 µeq (4 × 250 mm)	Hydroxide	0.4 mL/min	0%	2000 psi (14 MPa)	0–14
CarboPac PA1	General purpose mono-, di-, and oligosaccharide analysis	10 µm diameter nonporous substrate agglomerted with a 500 nm MicroBead quaternary ammonium functionalized latex	2%	5%	100 µeq (4 × 250 mm)	Hydroxide, acetate/ hydroxide	1.0 mL/min	0–5%	4000 psi (28 MPa)	0–14
CarboPac PA10	Monosaccharide compositonal anaylysis	10 µm diameter nonporous substrate agglomerated with a 460 nm MicroBead di-functionalized latex	55%	5%	100 µeq (4 × 250 mm)	Hydroxide, acetate/ hydroxide	1.0 mL/min	0–90%	3500 psi (24.5 MPa)	0–14
CarboPac PA20	Fast mono-, and disaccharide analysis	6.5 µm diameter nonporous substrate agglomerated with a 130 nm MicroBead quaternary ammonium functionalized latex	55%	5%	65 µeq (3 × 150 mm)	Hydroxide, acetate/ hydroxide	0.5 mL/min	0–100%	3000 psi (21 MPa)	0–14
CarboPac PA100	Oligosaccharide mapping and analysis	8.5 µm diameter nonporous substrate agglomerated with a 275 nm MicroBead di-functionalized latex	55%	6%	90 µeq (4 × 250 mm)	Hydroxide, acetate/ hydroxide	1.0 mL/min	0–90%	4000 psi (28 MPa)	0–14
CarboPac PA200	High resolution oligosaccharide mapping and analysis	5.5 µm diameter nonporous substrate agglomerated with a 43 nm MicroBead quaternary ammonium functionalized latex	55%	6%	35 µeq (3 × 250 mm)	Hydroxide, acetate/ hydroxide	0.5 mL/min	0–100%	4000 psi (28 MPa)	0–14

DNA

Column	Target Applications	Base Matrix Material	Substrate Crosslinking	Latex Crosslinking	Capacity	Recommended Eluents	Recommended Flow Rate	Solvent Compatibility	Max. Backpressure	pH Range
DNAPac PA100	Single stranded DNA or RNA oligonucleotides, restriction fragments, glycoprotein isoforms.	13-µm diameter nonporous substrate agglomerated with a 100-nm MicroBead alkyl quaternary ammonium functionalized latex.	55%	5%	40 µeq	Chloride, acetate, bromide, perchlorate: in lithium sodium or ammonium forms	1.5 mL/min	0–100%	4000psi (28MPa)	2–12.5
DNAPac PA200	High resolution single stranded DNA or RNA oligonucleotides, restriction fragments, glycoprotein isoforms.	8-µm diameter nonporous substrate agglomerated with a 130-nm MicroBead alkyl quaternary ammonium functionalized latex.	55%	5%	40 µeq	Chloride, acetate, bromide, perchlorate: in lithium sodium or ammonium forms	1.2 mL/min	0–100%	4000psi (28MPa)	2–12.5
DNASwift										

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