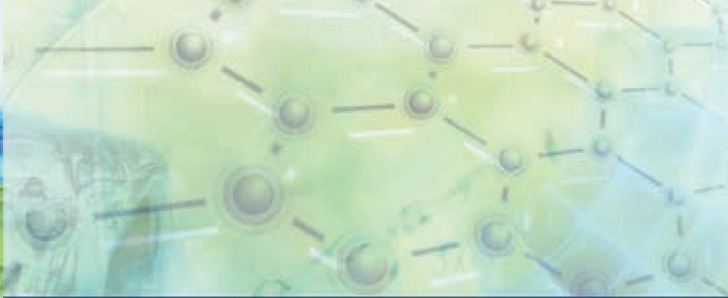


Thermo Scientific Dionex
Ion Chromatography Solutions

Global water safety

bromate analysis in drinking water

Thermo
SCIENTIFIC

Safe drinking water
public health assurance

As a vital limited resource required for survival, water fit for human consumption must be produced from natural sources such as ground and surface reservoirs. Since a clean water supply is the single most important determinant of public health, these ground and surface water reservoirs must undergo a purification process to ensure that all undesirable chemicals, biological organisms, and suspended solids are removed. As part of the purification process, water is often treated with ozone. Due to its high degree of oxidative reactivity, ozone effectively kills all microbial organisms that may be present and also serves to decolorize and deodorize the treated water. However, ozone reacts with bromide to form the carcinogenic compound bromate. The World Health Organization, European Commission, U.S. EPA, and Japanese Ministry of Health, Labor, and Welfare have established a regulatory maximum contaminant level (MCL) of 10 µg/L for bromate in municipal drinking waters treated with ozone for disinfection. Furthermore, the European Commission has an MCL of 3 µg/L in ozonated natural mineral waters and spring waters.

As the innovator in ion chromatography (IC), Dionex (now part of Thermo Scientific) **developed a variety of methods for bromate analysis in ozone-treated drinking water. These methods utilize different column chemistries, detectors, and system capabilities to provide drinking water suppliers with choices customizable for their analytical requirements.**

Dionex ICS-900 Dionex ICS-1100 Dionex ICS-1600 Dionex ICS-2100 Dionex ICS-4000 Dionex ICS-5000+

Regulatory leaders
ion chromatography

IC plays an important role in the analysis of ozone-treated drinking water. Over the past two decades, we've led the effort to develop sensitive and robust IC methods that help water treatment facilities ensure that bromate levels remain below the regulatory limit before water is released for consumption.

Bromate can be separated using different column chemistries and detected using a variety of detection techniques. Which one to use primarily depends on the sample and the detection limits required. When matrix conditions allow, suppressed conductivity detection is the easiest method to use. Otherwise, several strategies can be used to increase signal and deal with interfering anions by a combination of eluent, column, and detection methods.

Thermo Scientific IC applications have been validated by the U.S. EPA and the International Standards Organization (ISO) **for bromate determination of both low- and high-salt conditions. Our IC product line offers the flexibility, improved performance, and low overall cost-of-ownership to meet your laboratory's analysis needs.**

Technique	U.S. EPA Method	ISO Method	Application Note	Drinking Water
IC Suppressed Conductivity	300.0 B	15061	167, 184	Low salt conditions
IC Suppressed Conductivity	300.1	15061	167, 184	Low salt conditions
IC Suppressed Conductivity with Postcolumn ODA	317.0	11206	168	Tolerates higher salt conditions
IC Suppressed Conductivity with Postcolumn Acidified KI	326.1	11206	171	Tolerates higher salt conditions
2D-IC Suppressed Conductivity	302.0		187	Tolerates higher salt conditions
IC-ICP-MS	321.8			Tolerates higher salt conditions

EPA Methods 300.0 B/300.1 & ISO Method 15061

IC with suppressed conductivity detection

Since EPA Methods 300.0 and 300.1 were written over ten years ago, bromate determination using suppressed conductivity detection has been the preferred application. While carbonate/bicarbonate eluents have commonly been used for these methods, our columns are designed to work with both carbonate and hydroxide eluents.

The Thermo Scientific Dionex IonPac AS23 is a high-capacity anion-exchange column designed to work with carbonate eluents for the determination of trace bromate together with the common inorganic anions specified in EPA Method 300.0 B and 300.1. Figure 1 shows the determination of bromate at 5 µg/L along with the detection of bromide at 10 µg/L.

The high-capacity Dionex IonPac™ AS19 column is designed to work with hydroxide eluent. Since the suppression product of hydroxide is water, this eluent enables greater sensitivity than carbonate eluents. Hydroxide eluents also allow the use of gradients, which expand separation possibilities. Figure 2 compares the selectivities of the two columns for the separation of disinfection byproducts.
The use of a hydroxide eluent is also approved for EPA Methods 300.0 and 300.1 for anions and bromate determination.

Column: Dionex IonPac AG23, AS23, 4mm
Eluent: 4.5 mM Sodium carbonate/ 0.8 mM sodium bicarbonate
Flow Rate: 1.0 mL/min
Inj. Volume: 200 µL
Temperature: 30 °C
Detection: Suppressed conductivity, Thermo Scientific Dionex ASRS ULTRA II, 4 mm, AutoSuppression™ external water mode

Peaks:

1. Fluoride	1.0	mg/L (ppm)
2. Chlorite	0.01	
3. Bromate	0.005	
4. Chloride	50	
5. Nitrite	0.1	
6. Chlorate	0.01	
7. Bromide	0.01	
8. Nitrate	10	
9. Carbonate	50	
10. Phosphate	0.1	
11. Sulfate	50	

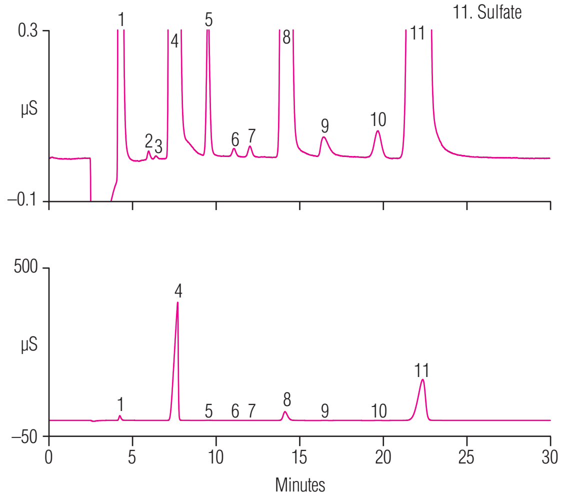


Figure 1. Determination of trace concentrations of bromate using the Dionex IonPac AG23 and AS23 columns with a large-loop injection.

Column: A) Dionex IonPac AG19, AS19, 4 mm
B) Dionex IonPac AG23, AS23, 4 mm
Eluent: A) 10 mM KOH 0-10 min, 10-45 mM 10-25 min, 45 mM 25-30 min
B) 4.5 mM potassium carbonate/0.8 mM potassium bicarbonate
Eluent Source: A) Thermo Scientific Dionex EGC II KOH with Dionex CR-ATC
B) Dionex EGC III K_2CO_3 + Dionex EPM
Flow Rate: 1.0 mL/min
Inj. Volume: 250 µL
Temperature: 30 °C
Detection: Suppressed conductivity Dionex ASRS™ ULTRA II, 4 mm, A) Recycle mode B) External water mode

Peaks:

1. Chlorite	10	µg/L
2. Bromate	5	
3. Chlorate	10	

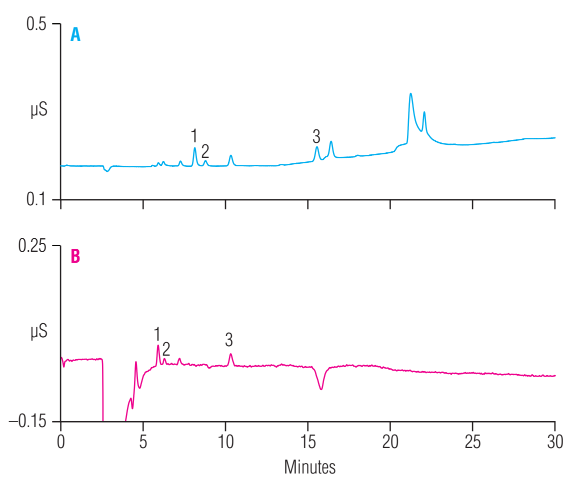


Figure 2. Different column selectivities in the separation of disinfection byproducts: A) Dionex IonPac AG19/AS19 columns; B) Dionex IonPac AG23/AS23 columns.

Bromate analysis using
Reagent-Free IC systems

While EPA Methods 300.0 B and 300.1 have traditionally used a manually prepared eluent, Thermo Scientific has improved sensitivity and reproducibility with the introduction of Reagent-Free™ IC (RFIC™) systems. Our RFIC systems eliminate the need to manually prepare eluents, combining electrolytic eluent generation with self-regenerating suppression. By electrolytically producing high quality eluents from deionized water, RFIC systems save time and improve method performance for bromate detection.

As shown in Figure 3, electrolytically generated hydroxide eluents facilitate both an improved separation of bromate from chloride (the major component) and an improved limit of detection. This application provides greater sensitivity than conventional IC with manually prepared eluents, and can determine bromate at sub-ppb levels.

Electrolytically generated eluents are approved for use with EPA Methods 300.0 B and 300.1 to determine bromate and the seven inorganic anions required for regulation. Electrolytically generated KOH is available for use with the Dionex IonPac AS19 column. Precise control of current allows repeatable concentrations and gradients for improved reproducibility over manually prepared eluents and standard proportioning valves. The Dionex IonPac AS23 column can be used with electrolytically generated potassium carbonate to automatically and reproducibly generate carbonate/bicarbonate eluent at the desired concentration.

Column:	Dionex IonPac AG19, AS19, 4 mm
Eluent:	10 mM KOH 0-10 min, 10-45 mM 10-25 min, 45 mM 25-30 min
Eluent Source:	Dionex EGC II KOH with Dionex CR-ATC
Flow Rate:	1.0 mL/min
Inj. Volume:	250 µL
Temperature:	30 °C
Detection:	Suppressed conductivity Dionex ASRS ULTRA II, 4 mm, recycle mode

Peaks:		
1.	Fluoride	
2.	Chlorite	1.0 µg/L
3.	Bromate	0.5
4.	Chloride	
5.	Nitrite	
6.	Chlorate	1.0
7.	Bromide	
8.	Nitrate	
9.	Carbonate	
10.	Sulfate	
11.	Phosphate	

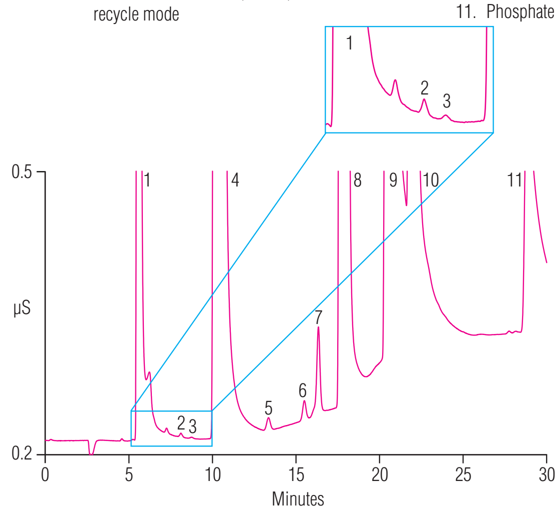


Figure 3. Chromatogram of mineral water spiked with 1 µg/L each chlorite and chlorate and 0.5 µg/L bromate.

EPA Methods 317.0/326.0 & ISO Method 11206

postcolumn reaction & visible detection

While suppressed conductivity is the most popular detection technique, bromate recovery will be reduced in the presence of high-salt concentrations. Since surface and ground waters can contain chloride and sulfate in excess of 50 ppm, the resolution of bromate diminish due to interference from these two salts. In order to achieve good chromatographic resolution in these circumstances, the use of postcolumn reagent with absorbance detection may be required.

Thermo Scientific's postcolumn derivatization techniques combined with UV detection have been validated by the EPA for Methods 317.0 and 326.1. These methods increase the specificity of bromate detection while yielding very low detection limits, and can also be used to quantify bromate at sub-µg/L concentrations. Our applications meet the requirements of U.S. EPA Method 317.0 and 326.0 by achieving a method detection limit (MDL) of 0.1 µg/L.

Figure 4 compares the results of the analysis of drinking water using suppressed conductivity and postcolumn derivatization with UV detection after separation on a Dionex IonPac AS9-HC column with a carbonate/bicarbonate eluent. The postcolumn technique reduces the calculated bromate MDL to 0.06 µg/L, which exceeds even the European Commission's low detection limits specified for bottled mineral waters. By using the Dionex IonPac AS19 column, applying an electrolytically generated hydroxide eluent combined with the postcolumn KI reaction, the MDL is further reduced to 0.04 µg/L. Figure 5 demonstrates the sensitivity of postcolumn derivatization and UV detection of disinfection byproducts (DBPs) compared to suppressed conductivity on a Dionex IonPac AS19 column.

Column: Dionex IonPac AG9-HC, AS9-HC
Eluent: 9.0 mM Sodium carbonate
Flow Rate: 1.30 mL/min
Inj. Volume: 225 µL
Temperature: 30 °C
Detection: A) Suppressed conductivity, Dionex Anion Atlas™ external water mode
B) Absorbance, 352 nm
Postcolumn Reagent: Acidified KI
PCR Flow Rate: 0.4 mL/min
Postcolumn Temperature: 80 °C

Peaks (A): (Conductivity)
1. Chlorite 1.85 µg/L (ppb)
2. Bromate 0.33
3. DCA*
4. Bromide 20.3
5. Chlorate 82.9

Peaks (B): (UV)
2. Bromate 0.21 µg/L (ppb)

* DCA = Dichloroacetate Quality control surrogate

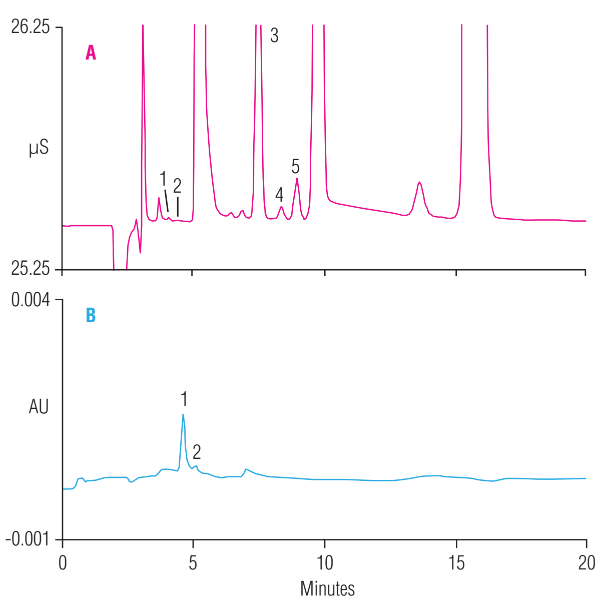


Figure 4. Determination of DBP anions in drinking water using: A) suppressed conductivity detection; and B) UV absorbance detection after postcolumn reaction with acidified KI.

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

Postcolumn Reagent: Acidified potassium iodide (KI)
PCR Flow Rate: 0.3 mL/min
Postcolumn Heater: 80 °C

Peaks (A):
1. Bromate 2.4 µg/L (ppb)
2. Chlorate 62.4
3. Bromide 17.5

Peaks (B):
1. Bromate 2.8

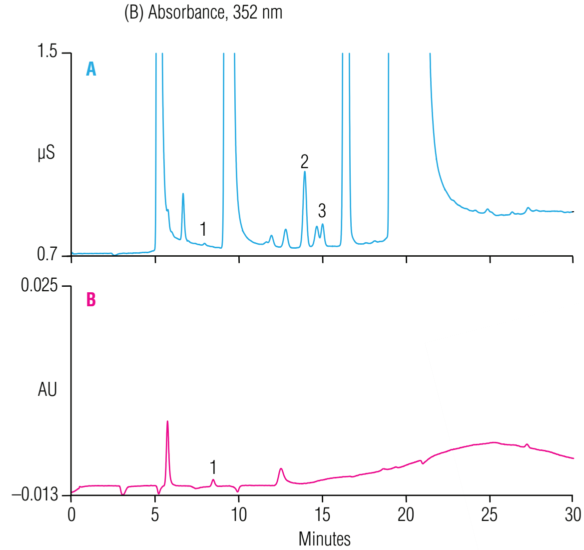


Figure 5. Determination of trace DBP anions and bromide in tap water using: A) suppressed conductivity detection; and B) UV absorbance after postcolumn reaction with acidified KI.

EPA Method 302.0—bromate analysis
with 2D-IC and suppressed conductivity

EPA Method 302.0 provides another strategy for bromate determination in high salt matrices—two-dimensional IC (2D-IC). 2D-IC allows the use of an RFIC system for both dimensions with conductivity detection to yield sub-ppb detection limits. Automated column switching, facilitated by the Thermo Scientific Dionex ICS-5000 system and Thermo Scientific Chromeleon Chromatography Data System software, makes it possible to remove matrix ions before analysis. A high-volume water sample is injected onto a high-capacity 4 mm Dionex IonPac AS19 column using a KOH gradient. Bromate is partially resolved from matrix ions, a cut volume containing the bromate is transferred to the second dimension, and the matrix ions are flushed to waste. In the second dimension, the sample is collected on a concentrator column and resolved on a Dionex IonPac AS24, 2 mm column.

Figure 7 shows the results of a 2D-IC separation of bromate in a high-salt matrix. The upper chromatogram shows that the bromate is not resolved from the chloride in this sample by the Dionex IonPac AS19, 4 mm column. The lower chromatogram shows the results after separation on a Dionex IonPac AS19 column, reinjection of a cut sample onto a concentrator column, and separation on a Dionex IonPac AS24, 2 mm column. The bromate that was undetectable in the first dimension is fully resolved in the second. Using this 2D-IC technique, an MDL of 0.036 µg/L can be achieved in high-salt matrices.

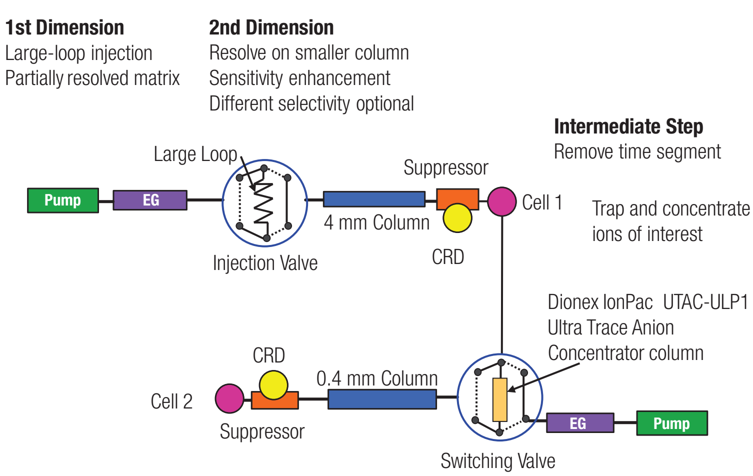
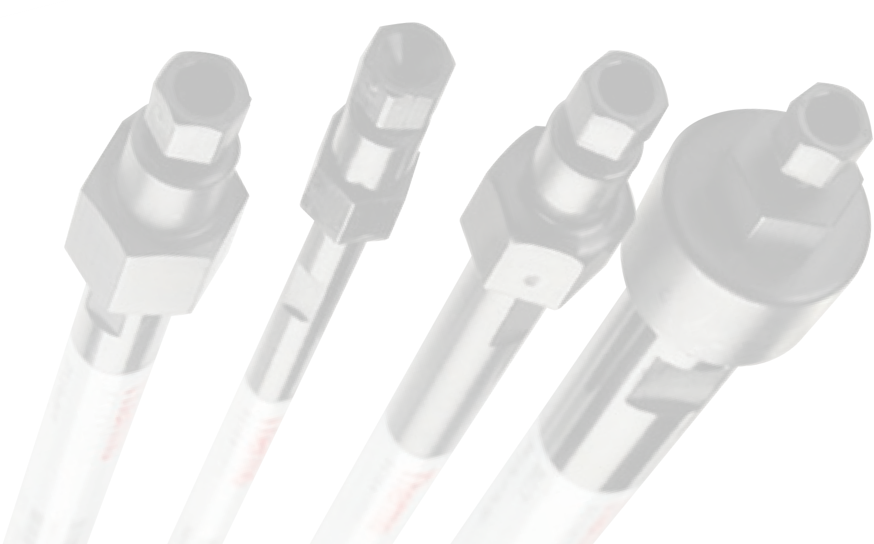


Figure 6. 2D-IC configuration.



Column A:	Dionex IonPac AS19, 4 mm	Column B:	Dionex IonPac AS24, 2 mm
Eluent:	10 mM KOH 0–12 min, 65 mM 12.1–35 min	Eluent:	10 mM KOH 0–24 min, 65 mM 24.1–35 min
Flow Rate:	1.0 mL/min	Flow Rate:	0.25 mL/min
Inj. Volume:	1000 µL	Cut Volume:	2000 µL
Temperature:	30 °C	Temperature:	30 °C
Detection:	Suppressed conductivity, Dionex ASRS ULTRA II, 4 mm, external water mode, 161 mA	Detection:	Suppressed conductivity, Dionex ASRS ULTRA II, 2 mm, external water mode, 41 mA
		Concentrator:	Thermo Scientific Dionex TAC-ULP1 (5 × 23 mm)
		Peak:	1. Bromate 0.5 µg/L

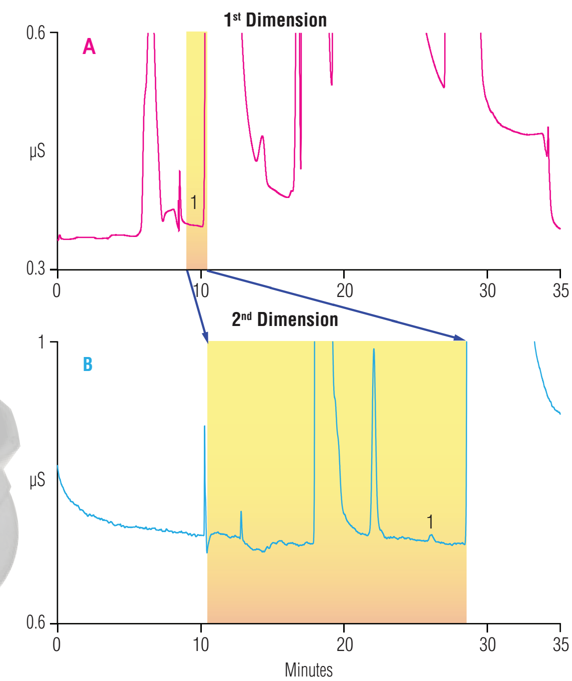


Figure 7. Two-dimensional bromate analysis using: A) a 4 mm Dionex IonPac AS19 column in the first dimension; and B) a 2 mm Dionex IonPac AS24 column in the second dimension.

Applications for Bromate in Water Using IC

AN 208: *Determination of Bromate in Bottled Mineral Water Using the CRD 300 Carbonate Removal Device* uses a Dionex IonPac AS23 along with the Thermo Scientific Dionex CRD-300 Carbonate Removal Device to reduce background noise with a carbonate eluent to achieve less than 1 ppb MDL.

AN 167: *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* uses a Dionex IonPac AS19 and RFIC hydroxide to improve sensitivity compared to carbonate eluents with conductivity detection.

AN 171: *Determination of Disinfection Byproduct Anions and Bromide in Drinking Water Using a Reagent-Free Ion Chromatography System Followed by Postcolumn Addition of an Acidified On-Line Generated Reagent for Trace Bromate Analysis* uses the Dionex IonPac AS19 and RFIC hydroxide to replace the Dionex IonPac AS9-HC and carbonate eluent with postcolumn KI and visible detection.

AN 168: *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* uses a Dionex IonPac AS19 and RFIC hydroxide to replace a Dionex IonPac AS9-HC and carbonate eluent with postcolumn ODA and visible detection.

AN 187: *Determination of Sub-μg/L Bromate in Municipal and Natural Mineral Waters Using Preconcentration with Two-Dimensional Ion Chromatography and Suppressed Conductivity Detection* is a two dimensional IC method using the Dionex IonPac AS19 (4 mm), Dionex IonPac AS24 (2 mm), and RFIC hydroxide with conductivity detection that is comparable and lower than ODA and KI visible detection methods for bromate detection in high ionic strength matrices.

AN 184: *Determination of Trace Concentrations of Chlorite, Bromate, and Chlorate in Bottled Natural Mineral Waters* demonstrates that the Dionex IonPac AS19 and RFIC hydroxide eluent provides lower detection limits than the Dionex IonPac AS23 carbonate column, and can be used to meet new EU 3 μg/L detection limits for natural mineral and spring waters, as previously shown in AN 167.

AN 81: *Ion Chromatographic Determination of Oxyhalides and Bromide at Trace Level Concentrations in Drinking Water Using Direct Injection* uses direct Injection with a 250 μl loop and the Dionex IonPac AS9-HC to meet the 10 μg/L regulatory requirement and conductivity detection.

AN 136: *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* demonstrates the Dionex IonPac AS9-HC and carbonate eluent with postcolumn ODA and absorbance detection.

AN 149: *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* uses a Dionex IonPac AS9-HC and carbonate eluent using postcolumn KI and absorbance detection.

AU 154: *Determination of Bromate in Drinking and Mineral Water by Isocratic Ion Chromatography with a Hydroxide Eluent* demonstrates that the Dionex IonPac AS19 with RFIC hydroxide in isocratic mode cannot determine all the inorganic anions like the gradient method in AN 167.

TN 116: *Determination of Bromate by ISO Method 11206* uses a Dionex CarboPac PA1 and MSA eluent with postcolumn KI and visible detection.

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ISO 9001 REGISTERED

Thermo Scientific Dionex products are designed, developed, and manufactured under an ISO 9001 Quality System.

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