

New EPA Method for Disinfection Byproducts Co-Developed by Thermo Scientific: EPA 302 Bromate Determination Using Two-Dimensional IC

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Abstract

Bromate is commonly formed from the ozonation of bromide in drinking water, and has been determined to be a human carcinogen. Currently, bromate is regulated in drinking water at 10 µg/L; methods 300.1 B, 317.0, and 326.0 are approved by the US EPA for compliance monitoring. High concentrations of common anions such as chloride, sulfate, and carbonate can produce poor bromate peak shapes and lower recoveries.



Figure 1.Thermo Scientific™ Dionex™ ICS-3000 ion chromatography system.

Instrumentation Details and Configurations

Dionex ICS-3000 Automation Manager Specifications

- High-pressure valves—6- or 10-port, 2-way, PEEK™
- Low-pressure valves—2- or 3-port, PEEK
- Reaction coil heater
 - Reaction coil capacity = 2
 - Temperature range 5 °C above DC set temperature to 80 °C
 - Temperature accuracy ± 1 °C
 - Temperature stability ± 0.2 °C
 - Temperature adjustable in 1 °C increments



Figure 2. The Automation Manager allows implementation of a variety of applications requiring switching valves and reaction coil heaters.

Analysis of Trace Ions in the Presence of Matrix Ions

- Trace analysis in a sample stream with low levels of matrix ions typically requires:
 - Preconcentration
 - Large loop injections
 - Example applications: analysis of ultrapure water (UPW)
- High concentrations of matrix ions can overload the column
 - Matrix ions may elute or coelute with species of interest
 - Leading to recovery and integration issues due to band broadening
 - Example applications: Analysis of drinking water, wastewater
- These applications require an automated means of diverting the matrix prior to analyzing the trace ions

Bromate Analysis: Current Methods

Analysis performed using Thermo Scientific™ Dionex™ IonPac™ AS9-HC chemistry with various detection modes

- US EPA Method 300.1 Part B using conductivity detection
 - Chloride removal required for some samples leading to added cost and time
- EPA Method 317 postcolumn addition of o-dianisidine (ODA) followed by visible detection:
 - Requires hardware to implement the (PCR) postcolumn reaction and detector
 - Requires frequent optimization of PCR reagent flow rate
 - Has reagent purity issues
 - Requires handling of ODA, a potential human carcinogen
- EPA Method 326 postcolumn generation of hydroiodic acid in situ by addition of potassium iodide to the eluent; this combines with bromate to form the triiodide anion which is detected by absorbance at 352 nm:
 - Requires the hardware to implement the PCR and absorbance detector
 - Requires frequent optimization of PCR reagent flow rate

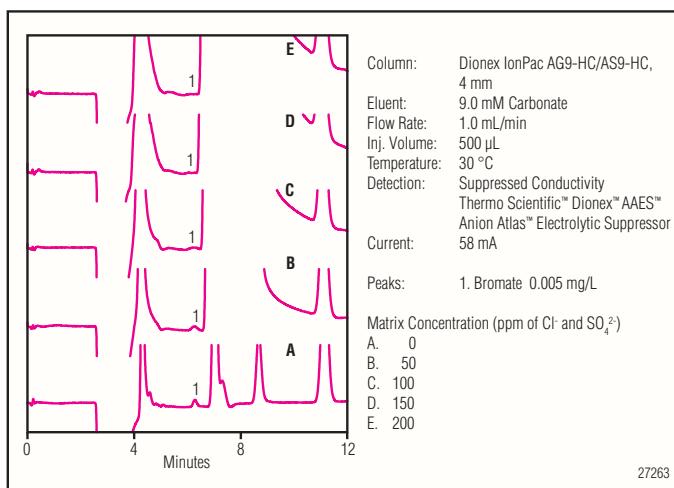


Figure 3. The effect of matrix concentration on the bromate peak is shown using Dionex IonPac AS9-HC chemistry. For low levels of matrix ions, this method provided good peak area recovery and peak shapes. However, as the matrix concentration increased, the bromate peak width increased, making integration difficult. To address the issue, a new matrix diversion method was developed.

New Two-Dimensional Diversion Method

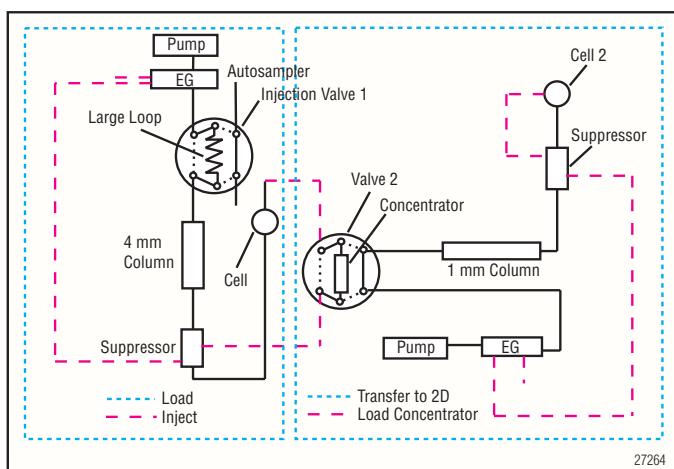


Figure 4. The experimental configuration for a new two-dimensional analysis method is shown above. The analysis in the first dimension is performed using 4 mm column chemistry and in the second dimension using 1 mm or 2 mm column chemistry leading to improved sensitivity proportional to the flow rate ratio of the 1st dimension to the 2nd dimension.

New Two-Dimensional Method: Features

- Allows for large-loop injection in the first dimension (4 mm column)—It is possible to inject a larger loop volume than with the standard approach because the capacity and selectivity of the analytical column in the 1st dimension dictates the recovery, and the analyte of interest is analysed in the 2nd dimension.
- Focuses the ions of interest in a concentrator column after suppression in the first dimension
 - Hydroxide eluent is suppressed to DI water, providing an ideal environment for focusing or concentrating the ions of interest.
- Allows analysis in the second dimension using a smaller column format operated at a lower flow rate, providing sensitivity enhancement that is proportional to the flow-rate ratio of the 1st dimension to the 2nd dimension.
 - For a 4 mm column operated in the first dimension at 1 mL/min and a 1 mm column operated in the second dimension at 0.05 mL/min, the enhancement factor is 20.
- Easy implementation using the Dionex ICS-3000 system

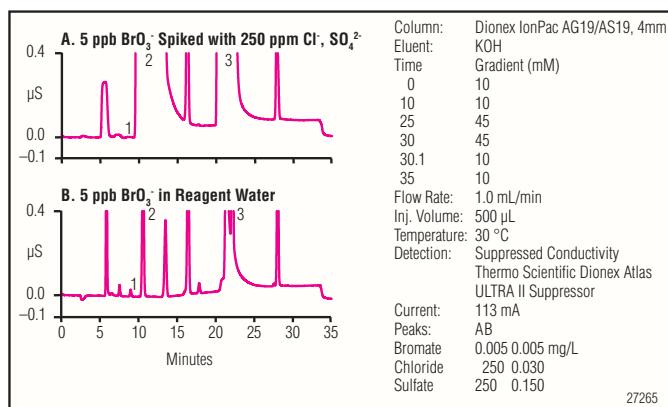


Figure 5. The bromate peak is completely lost using one-dimensional IC with a total concentration of 250 ppm matrix ions (top chromatogram) compared to a bromate standard in DI water (bottom chromatogram).

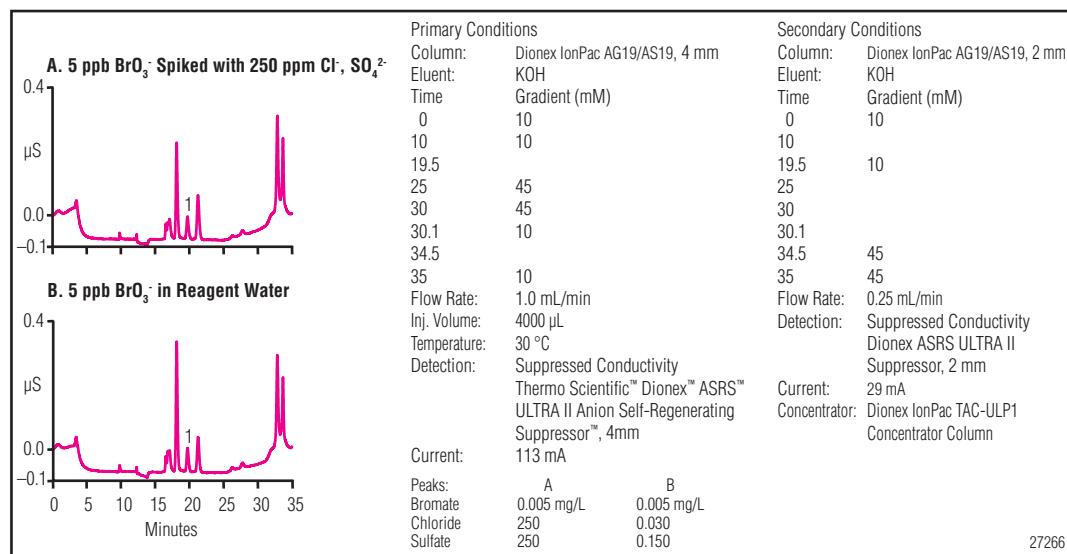


Figure 6. Using the two-dimensional analysis approach, the bromate peak shape is retained even in the presence of high levels of matrix ions.

Table 1. The table above summarizes recovery results for bromate in the presence of matrix ions with the two-dimensional analysis method.

Matrix Concentration* (ppm)	Bromate Peak Area	Recovery
0	0.0248	100%
50	0.0245	98.8%
100	0.0250	100.8%
150	0.0244	98.4%
200	0.0249	100.4%
250	0.0249	100.4%

*Matrix concentrations are for individual ions (chloride and sulfate)

Table 2. The table above shows the observed sensitivity enhancement using the two-dimensional method.

Dimension	Peak Area Response	Flow Rate (mL/min)	Sensitivity
First (4 mm)	0.0063	1	1
Second (2 mm)	0.0248	0.25	3.936

*MDL based on n = 7 runs (Students t test) 0.2 ppb for a 500 μ L Injection with 200 ppm chloride and sulfate using suppressed conductivity detection.

Table 3. Conditions for perchlorate analysis as described in US EPA Methods 314.0 and 314.1.

	EPA Method 314.0	EPA Method 314.1
Columns	Dionex IonPac AG16/AS16 (4 mm)	Dionex IonPac AG16/AS16 (2 mm), (primary method) Dionex IonPac AG20/AS20 (2 mm), (confirmatory method)
Eluent	50 mM NaOH	0.5 mM NaOH; 0–12 min, 65 mM; 12.1–28 min, 100 mM; 28.1–30 min
Temperature	30 °C	35 °C
Flow Rate	1.5 mL/min	0.25 mL/min
Sample Volume	1000 μ L	2 mL
Rinse Volume	—	1 mL (10 mM NaOH)
Concentrator	—	Dionex IonPac Cryptand C1 (4 \times 35 mm)
Detection	Suppressed conductivity, Dionex ASRS ULTRA II Suppressor (4 mm), Thermo Scientific™ Dionex™ AutoSuppression device; external water mode	Suppressed conductivity, Dionex ASRS ULTRA II Suppressor (4 mm), Dionex AutoSuppression device; external water mode

Table 4. The table above summarizes recovery results for perchlorate under a variety of matrix concentrations with the new two-dimensional method.

Matrix* (ppm)	Perchlorate Peak Area	Recovery
0	0.3522	100%
50	0.3560	101.1%
100	0.3567	101.3%
200	0.3509	99.6%
500	0.3505	99.5%
800	0.3468	98.5%
1000	0.3438	97.6%

*Matrix concentrations are for individual ions (chloride, bicarbonate, and sulfate)

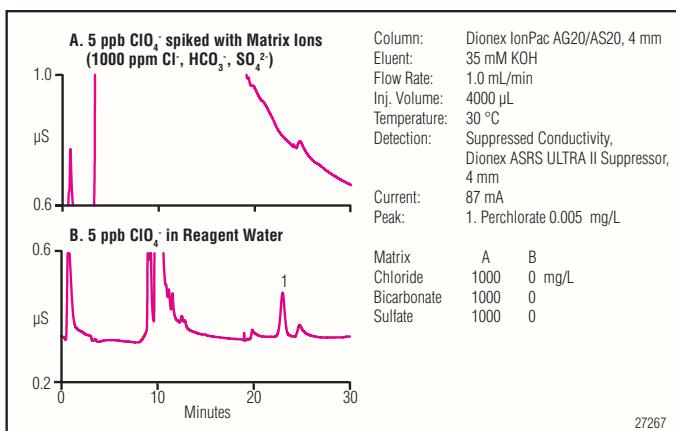


Figure 7. The perchlorate peak shape and response is poor in the presence of matrix ions compared to analysis performed with perchlorate standard in DI water.

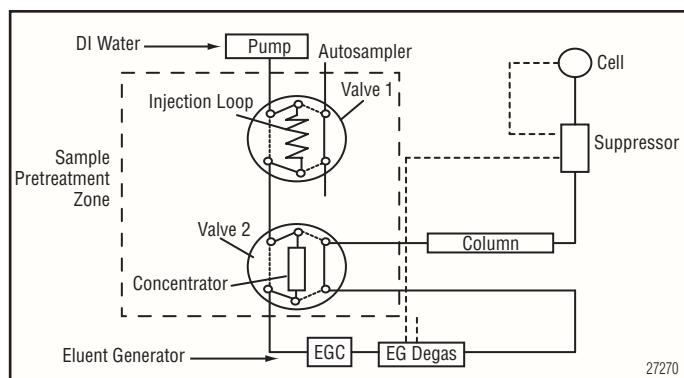


Figure 10. The experimental configuration for implementing the new sample pretreatment approach in conjunction with Reagent-Free™ (RFIC™) instrumentation is shown above. Trace enrichment of ions is possible using this configuration.

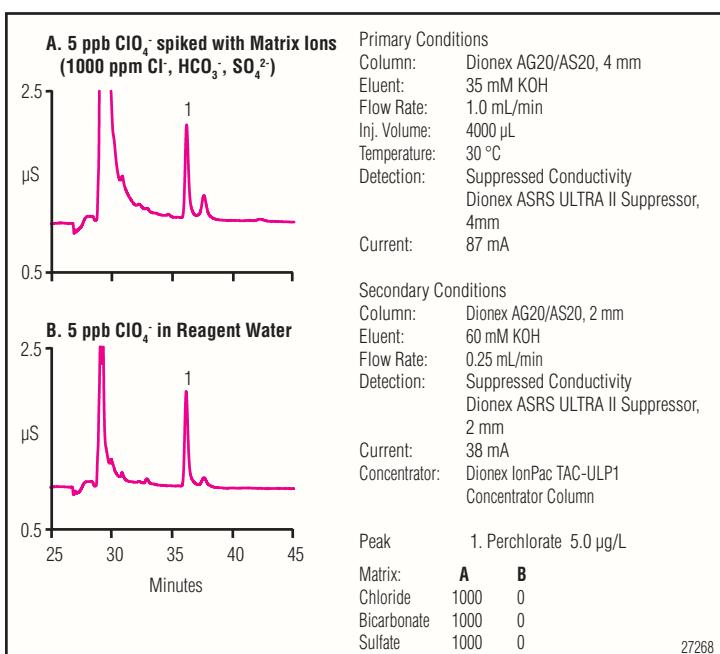


Figure 8. The perchlorate peak shape and response is preserved in the presence of matrix ions using the two-dimensional analysis method.

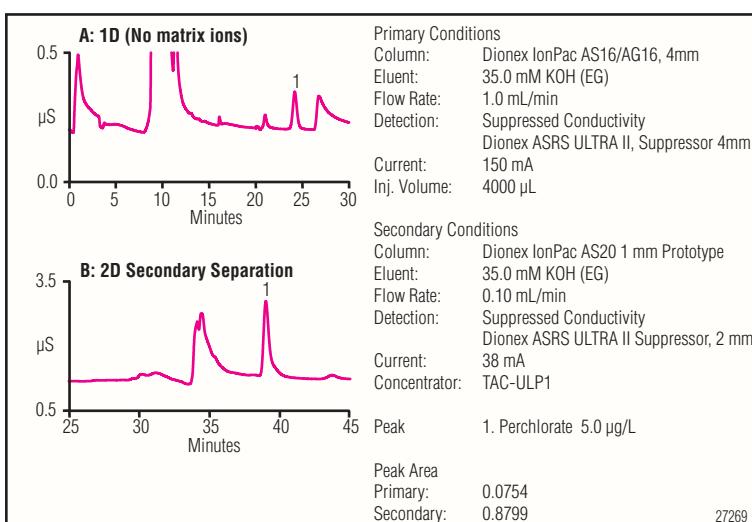


Figure 9. This figure shows the benefit of performing the analysis using a 1 mm column operated at 0.1 mL/min flow rate. The sensitivity gain for the two-dimensional analysis method from the observed peak response is roughly 10× greater than the one-dimensional approach as predicted from theory.

New Sample Pretreatment Using an RFIC System

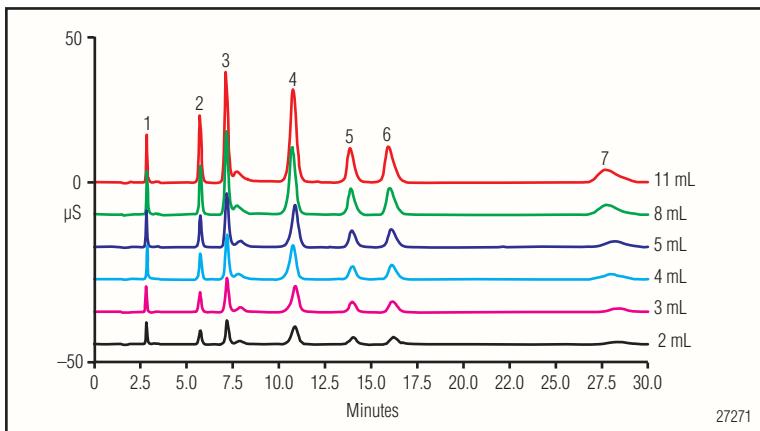


Figure 11. The analysis of trace (ppb) levels of a standard anion mixture is shown at different enrichment volumes using Dionex IonPac AS15 chemistry and Dionex IonPac TAC-LP1 concentrator column.

Conclusions

- The Dionex ICS-3000 system equipped with an Automation Manager allows implementation of applications with multiple valving schemes
- The new two-dimensional method demonstrates:
 - Enhanced sensitivity for selected analytes (bromate, perchlorate) using suppressed conductivity detection
 - Minimal interference from matrix ions
 - A simpler analytical method compared to systems using postcolumn reaction
- Operating the new two-dimensional methods using an RFIC system:
 - Provides automation and ease of use
 - Requires only DI water
 - Eliminates reagent preparation
 - Reduces chemical exposure
 - Eliminates stability, shelf life, and reagent purity issues
 - Eliminates the requirement to optimize postcolumn reagent flow rate or mixing
- The new sample pretreatment with the RFIC system:
 - Eliminates the need for an extra pump
 - Provides improved preconcentration and sensitive detection of trace components
 - Is suitable for other applications such as neutralization and matrix removal

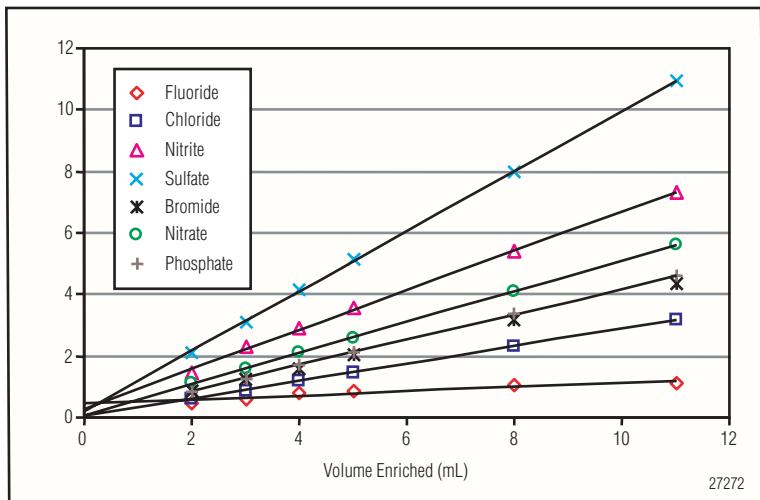


Figure 12. The response versus the volume-enriched plot shows the excellent linearity of the enrichment method, with correlation coefficients in the 0.9999 regime.

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