

Determination of Trace Concentrations of Bromate in Natural Mineral Waters Using Ion Chromatography with Suppressed Conductivity Detection

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ABSTRACT

The consumption of bottled water has increased significantly over the last five to ten years, with a total global consumption of 157 billion liters (43 billion gallons) in 2005, according to the Earth Policy Institute. Bottled water manufacturers that use ozonation as a disinfection treatment can produce trace concentrations of bromate, a potential human carcinogen. The U.S. FDA established a maximum permissible limit of 10 µg/L bromate in bottled water, whereas the European Commission permits up to 3 µg/L bromate in natural mineral waters and spring waters treated by ozonation. Ion chromatography (IC) with suppressed conductivity detection, as described in EPA Method 300.1 (B), is the most common method used to determine bromate in drinking waters. However, mineral waters contain high concentrations of common anions, such as chloride, sulfate, and carbonate. Determining low parts-per-billion (ppb) concentrations by Method 300.1 is challenging in the presence of these high concentration matrices, which can produce poor bromate peak shapes and low recoveries. In this poster, we compare the determination of trace concentrations of bromate in natural mineral waters by Method 300.1 (B), using direct injection with a hydroxide-selective anion-exchange column, to a two-dimensional (2-D) IC system. The system diverts most of the interfering matrix anions after separation in the first dimension; bromate is trapped on a concentrator column and determined in the second dimension. The 2-D method permits a bromate detection limit of 0.036 µg/L, significantly lower than the detection limit of 0.31 µg/L achieved using a direct injection approach. The linearity, detection limits, and recoveries of bromate spiked in natural mineral waters are compared between the two system configurations.

EXPERIMENTAL

Method A: Direct Injection IC

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

Method B: 2-D IC

First Dimension

Columns:	IonPac AG19, AS19, 4-mm
Eluent:	10 mM KOH from 0–12 min, 65 mM from 12.1–35 min
Eluent Source:	EGC II KOH with CR-ATC
Flow rate:	1.0 mL/min
Inj. Volume:	1000 µL
Temperature:	30 °C
Detection:	Suppressed Conductivity, ASRS ULTRA II, 4-mm, AutoSuppression® external water mode

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Second Dimension

Columns:	IonPac AG24, AS24, 2-mm
Eluent:	10 mM KOH 0–24 min, 65 mM 24.1–35 min
Eluent Source:	EGC II KOH with CR-ATC
Flow Rate:	0.25 mL/min
Cut Volume:	2 mL
Temperature:	30 °C
Detection:	Suppressed Conductivity, ASRS ULTRA II, 2-mm, AutoSuppression external water mode

SAMPLES

Five different European mineral waters were analyzed for bromate in this study. Table 1 summarizes the ionic properties of the investigated samples according to the manufacturers' specifications. None of the bottled mineral waters indicated that ozonation was used as a disinfection treatment method; therefore, the detection of bromate was not anticipated.

Table 1. Concentrations (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
D	5.5	0.7	9.5	50.8	— ^a	5.9	<3	190	5.8
E	9.0	0.6	3.4	147.3	0.12	21.5	18	390	33

^aNot specified.

SAMPLE PREPARATION

Method A

Mineral waters B and C were degassed for 10–15 min under vacuum to reduce the excess bicarbonate concentrations of 133 and 278 mg/L, respectively, in the samples. Increased amounts of bicarbonate can produce shifts in retention times and lower analyte recoveries. Mineral water C was also diluted 1:5 with deionized water to reduce the 1445 mg/L sulfate in the sample.

Method B

The mineral water samples were injected directly without further preparation.

RESULTS AND DISCUSSION

Figure 1 illustrates the 2-D IC system configuration used for determining trace concentrations of bromate in natural mineral waters. The first dimension consists of a conventional IC system configuration similar to that used for determining bromate using a 250- μ L direct injection (Method A). However, Method B requires the use of the first and second dimensions for determining bromate by 2-D IC. The use of 2-D IC provides several advantages over conventional IC, such as:

- Allowing large loop injections on the first dimension (4-mm column) - 2-D IC for bromate determinations permits up to a 1000- μ L sample injection relative to a 250- μ L injection for conventional IC, increasing the sensitivity four fold.
- Eliminating or reducing the need for sample preparation - Most of the interfering matrix anions are diverted to waste in the first dimension while a 2-mL plug (cut volume) containing the bromate is transferred to the second dimension. This process eliminates most of the complications encountered with a conventional IC system when analyzing high ionic strength matrices. Therefore, 2-D IC saves time and expense by eliminating many sample preparation procedures.
- Enhancing the bromate sensitivity by injecting a large sample volume on a 4-mm column followed by transferring a pre-set cut volume to 2-mm column - A signal improvement of four times is observed due to the difference in cross-sectional area between the two columns.
- Easy implementation using an ICS-3000 Reagent-Free™ IC (RFIC™) system

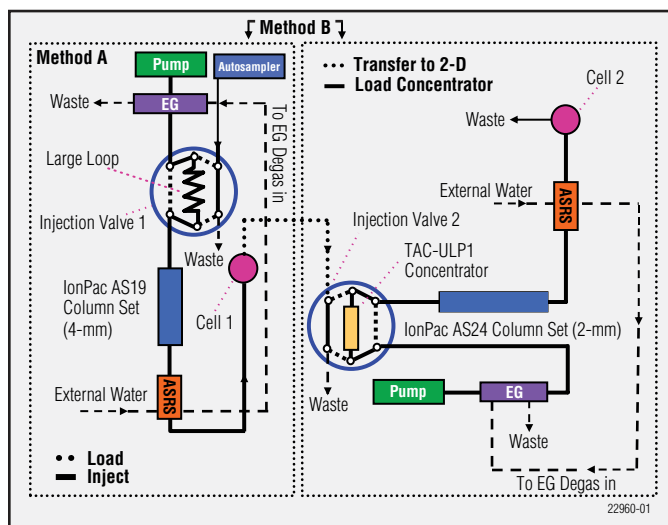


Figure 1. Schematic diagram for the determination of trace concentrations of bromate using Method A (left side of diagram) or Method B (both sides of diagram).

LINEARITY AND METHOD DETECTION LIMITS

As shown in Table 2, Method B (2-D IC) demonstrates a significantly lower quantitation limit and detection limit relative to Method A (direct injection IC).

Table 2. Comparison of Linearity and Method Detection Limits for Methods A and B						
Method	Analyte	Range (µg/L)	Linearity (r ²)	MDL Standard (µg/L)	SD	Calculated MDL ^c (µg/L)
A	Bromate	1–25	0.9995 ^a	1.5	0.08	0.34
B	Bromate	0.15–15	0.9995 ^b	0.20	0.12	0.036

^aLinear fit.

^bQuadratic fit.

^cMDL = $t_{s,99}$ where $t_{s,99} = 3.14$ for $n = 7$

Figures 2 and 3 compare the separation of 5 µg/L bromate in reagent water using Methods A and B, respectively. As shown in Figure 3B, the peak area response for bromate is improved by a factor of 16 relative to the response shown in Figure 2. The improved sensitivity for the 2-D method is achieved by injecting 1000 µL on a 4-mm column in the first dimension (250 µL × 4 = 1000 µL) followed by selectively transferring bromate to a concentrator column and determining bromate on a 2-mm column in the second dimension. The four-times larger injection volume and four-times difference in cross sectional area yields a factor of 16 improvement. However, Method A also permits the determination of bromide and oxyhalides such as chlorite and chlorate, whereas Method B is specific for trace concentrations of bromate.

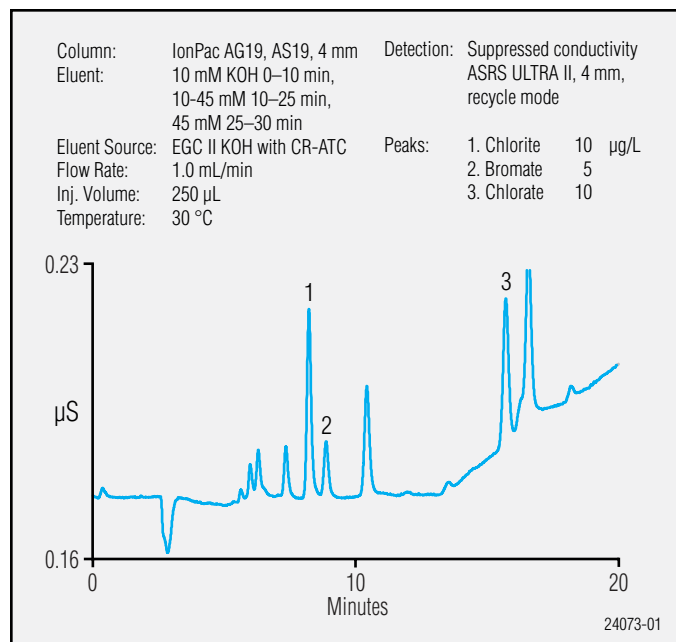


Figure 2. Method A: Separation of chlorite, bromate, and chlorate on the IonPac AS19 column.

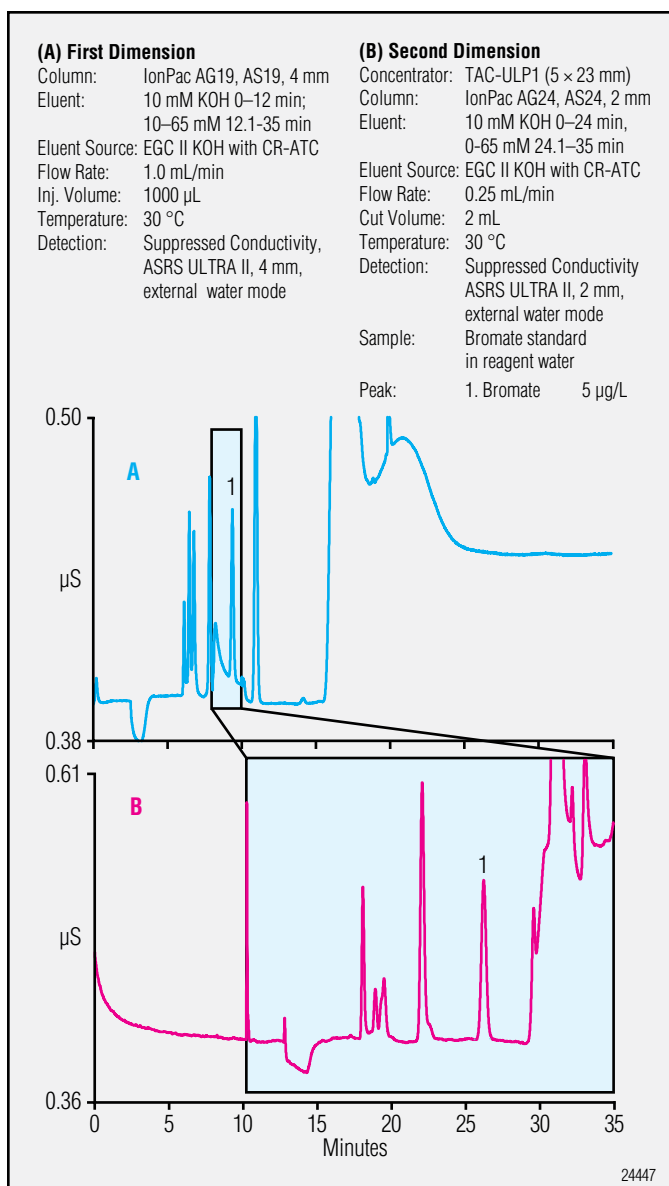


Figure 3. Method B: Determination of 5 ppb bromate in reagent water using 2-D IC with the IonPac AS19/AS24 columns.

PRECISION AND ACCURACY

Tables 3 and 4 summarize the performance for single-operator data using Methods A and B, respectively, for trace concentrations of bromate spiked in natural mineral water samples. Due to the improved sensitivity of the 2-D configuration, bromate can be determined at a concentration that is well below the European regulated value of 3 µg/L for ozonated natural mineral waters and spring waters.

Matrix	Amount Found (µg/L)	Amount Added (µg/L)	Average Recovery ^a (%)
Mineral Water A	<MDL	5.0	91.2
Mineral Water B ^b	<MDL	5.0	93.5
Mineral Water C ^{b,c}	<MDL	5.0	104.3

^aDuplicate injections.

^bSample degassed for 10-15 min prior to analysis.

^cSamples diluted 1:5 prior to analysis.

Matrix	Amount Found (µg/L)	Amount Added (µg/L)	# Reps	Average Recovery (%)	Peak Area Precision (RSD)
Mineral Water C	<MDL	0.5	7	95.6	7.23
		5.0	7	103.8	1.22
Mineral Water D	<MDL	0.5	7	95.2	3.37
		5.0	7	103.9	1.22
Mineral Water E	<MDL	0.5	7	95.2	5.85
		5.0	7	105.5	0.62

The determination of trace concentrations of bromate in high ionic strength matrices using current EPA Methods is a challenging analytical problem because of column overloading. Therefore, sample dilution is often required, which increases the minimum reporting level in proportion to the dilution factor. Alternatively, sample pretreatment cartridges can be used, requiring additional time and expense.

Figure 4 demonstrates the use of Method A for determining bromate in mineral water C, which contains nearly 300 mg/L bicarbonate and >1400 mg/L sulfate. Due to the high ionic strength of the sample, additional sample preparation steps were required before analysis using a 250 µL direct injection. However, Figure 5 illustrates the analysis of the same sample injected directly using Method B without any sample pretreatment. This is possible because only a small volume (2 mL) containing the bromate is selectively transferred to a concentrator while most of the interfering matrix anions are diverted to waste. Bromate is then determined in the second dimension while the potential for column overloading that is typically observed in a conventional IC system is significantly reduced.

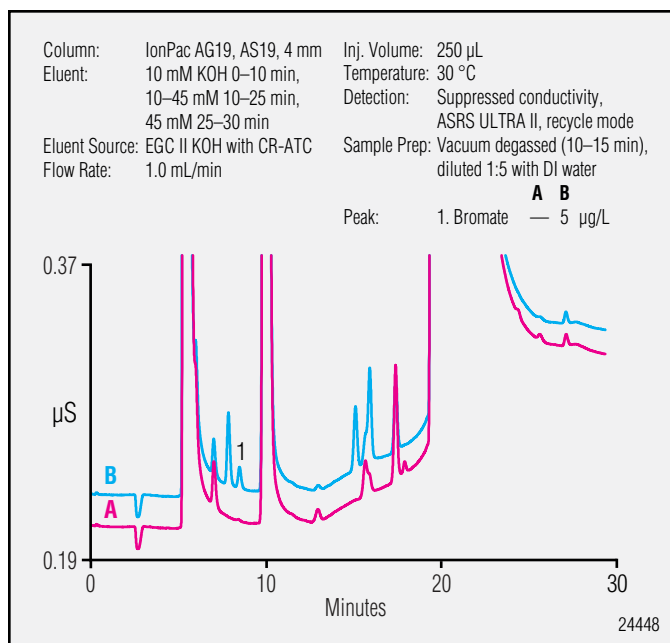


Figure 4. Determination of bromate in A) mineral water C and B) spiked mineral water C using Method A.

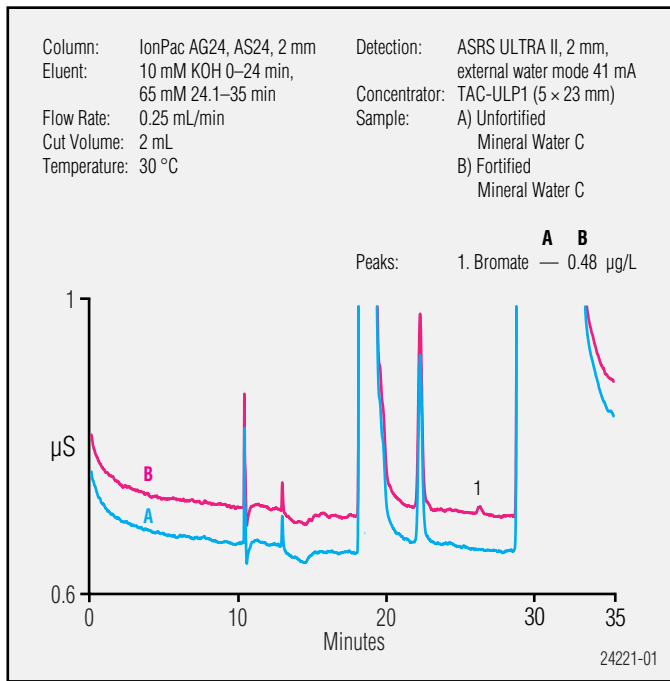


Figure 5. Determination of bromate in A) mineral water C and B) spiked mineral water C using Method B.

CONCLUSIONS

This poster demonstrates the following:

- Method A (direct injection IC)
 - Enables the determination of ≥ 1 $\mu\text{g/L}$ bromate, which is well below the current U.S. FDA and European regulations for natural mineral waters
 - Enables the determination of chlorite, bromate, chlorate, and bromide
 - High ionic strength waters may require sample pretreatment to reduce excess bicarbonate or excess concentrations of other common anions present in natural mineral waters
- Method B (2-D IC)
 - Enables the determination of ≥ 0.5 $\mu\text{g/L}$ bromate, which is six times less than the European regulated concentration of 3 $\mu\text{g/L}$ bromate in ozonated natural mineral and spring waters
 - Enables the determination of sub- $\mu\text{g/L}$ bromate in a wide range of samples with varying ionic strengths
 - Sample pretreatment is not required for high ionic strength waters, such as mineral water C, improving the method's ease-of-use and reducing the time and cost of each analysis

REFERENCES

1. Application Note 184; LPN 1890. Dionex Corporation, Sunnyvale, CA, 2007.
2. Application Note 187; LPN 1943-02. Dionex Corporation, Sunnyvale, CA, 2007.

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