

The Determination of 10 Anions in EPA Method 300.1 using Shimadzu High-Resolution Ion Chromatography

■ Introduction

Ion chromatography (IC) continues to be the most commonly used chromatographic technique to determine the concentration of inorganic ions in waters. A considerable number of regulatory IC methods exist around the world. EPA Methods 300.0 and 300.1^[1,2] are two of them. They are validated for the determination of inorganic anions in reagent water, surface water, ground water and finished drinking water.

The anions in EPA method 300.1 are divided into common anions and inorganic disinfection by-products (DBPs). Seven common anions listed in Part A include Fluoride (F⁻), Chloride (Cl⁻), Nitrite (NO₂⁻), Bromide (Br⁻), Chloride (Cl⁻), Nitrate (NO₃⁻), Phosphate (PO₄³⁻) and Sulfate (SO₄²⁻). DBPs listed in Part B include Chlorite (ClO₂⁻), Bromate (BrO₃⁻), Bromide (Br⁻) and Chlorate (ClO₃⁻).

To protect public health, potable waters are usually treated with disinfectants such as chlorine dioxide and ozone. Disinfectants will destroy microorganisms that can cause disease in humans. However, the disinfection treatment process produces byproducts such as chlorite and bromate, which are potentially harmful to humans. For example, bromate will increase the risk of cancer and chlorite can potentially affect nervous system. Therefore, EPA National Drinking Water Regulations has proposed that the Maximum Contaminant Level (MCL) of bromate and chlorite be 10 ppb and 1 ppm, respectively.

This application note provides two high-resolution IC methods to quantify 10 anions listed in EPA Method 300.1 simultaneously using a Shimadzu modular IC system coupled with a new Shimadzu electrolytically

regenerated suppressor, a continuation of work from a previous application note: *HPLC-021, The Determination of EPA 300 Anions using Shimadzu Ion Chromatography*. The previous application note uses a method optimized for the analysis of the seven common anions (EPA 300 Part A). Provided herein are methods suitable to extend the analysis to include the DBPs.

■ Experimental

Equipment

Experiments were performed using a modular Shimadzu LC system, consisting of:

- CBM-40 lite system controller
- DGU-403 degassing unit
- LC-20Ai pump with automatic rinsing kit
- SIL-20AC autosampler with inert kit
- CTO-40S column oven
- Suppressor installation kit for CTO-40S
- CDD-10Avp conductivity detector
- ICDS-40A electrochemical suppressor starter kit
- LabSolutions chromatography software

Columns

- Shodex IC SI-52 4E, 4 x 250 mm (Part number: 220-91524-04)
- Guard column, Shodex SI-90G, 4.6 x 10 mm (Part number: 220-91524-05)

Materials

Sodium carbonate and sodium bicarbonate were obtained from Sigma-Aldrich. Standards including Fluoride (F⁻) 1000 ppm, Chloride (Cl⁻) 1000 ppm, Nitrite (NO₂⁻) 1000 ppm, were obtained from RICCA Chemical Company. Bromide (Br⁻) 1000 ppm, Bromate (BrO₃⁻) 1000 ppm, Chlorite (ClO₂⁻) 1000 ppm, Chlorate (ClO₃⁻) 1000 ppm, Nitrate (NO₃⁻) 1000 ppm, Phosphate (PO₄³⁻) 1000 ppm and Sulfate (SO₄²⁻) 1000 ppm, were purchased from Sigma. Working standards at different concentration were prepared by diluting from the commercial stock standards using degassed deionized water with resistivity equal or greater than 18.0 MΩ-cm.

Eluent preparation

Preparation of 1 L of 0.18 M stock sodium carbonate; dissolve 19.08 g sodium carbonate (Na₂CO₃) in deionized water and dilute to 1 L. Preparation of 1 L of 0.17 M stock sodium bicarbonate; dissolve 14.28 g of sodium bicarbonate (NaHCO₃) in deionized water and dilute to 1 L. Preparation of 1 L of eluent (2.7 mM sodium carbonate/5.1 mM sodium bicarbonate); pipet 15 mL of stock sodium carbonate and 30 mL of stock sodium bicarbonate into a 1 L volumetric flask, then dilute to the mark with deionized water. Preparation of 1 L of eluent (5.4 mM sodium carbonate); pipet 30 mL of stock sodium carbonate then dilute to the mark with deionized water.

Method Conditions-1

Column: Shodex IC SI-52 4E, 4 x 250 mm (220-91524-04)
Eluent: 2.7 mM sodium carbonate/5.1 mM sodium bicarbonate
Flow rate: 0.8 mL/min
Oven: 50 °C
Inj. Vol.: 50 µL
System
Backpressure: ~ 1450 psi
Detection: Suppressed conductivity; 180 mA in recycle mode
Background
Conductance: ~ 35 µS/cm
Noise: < 3 nS/cm peak to peak

Method Conditions-2

Column: Shodex IC SI-52 4E, 4 x 250 mm (220-91524-04)
Eluent: 5.4 mM sodium carbonate
Flow rate: 0.8 mL/min
Oven: 50 °C
Inj. Vol.: 10 µL
System
Backpressure: ~ 1450 psi
Detection: Suppressed conductivity; 180 mA in recycle mode
Background
Conductance: ~ 29 µS/cm
Noise: < 3 nS/cm peak to peak

■ Results and Discussion

Figures 1 and 2 show the separation results of 10 anions using two different eluents listed in method condition 1 and method condition 2, respectively. As shown in the figures, both methods can be used to separate 10 anions.

All anions are eluted in less than 20 minutes using eluent listed in the second method condition. Although the elution time is longer when using the eluent listed in the first method condition, the advantage of this method is the resolution of bromide and chlorate is higher even with larger injection volume. This method will be useful for trace chlorate and bromide analysis.

Linearity and Method Detection Limit

In order to evaluate the method and overall system performance, linearity, method detection limits (MDL) and reproducibility were also determined using method condition 1. Method detection limit (MDL) investigation was performed following the procedure described in EPA Method 300.1 by making seven replicate injections of MDL standards. MDL standards were prepared by fortifying the blank with anion standards to a concentration 3 to 5 times that of the instrument detection limit. MDL was calculated as $(t) \times (S)$, where t is student's t value for 99% confidence level ($t=3.14$ for seven replicates) and S is standard deviation from seven injections.

The linear calibration range, linearity (or coefficient of determination), MDL standard concentration and calculated MDL are shown in table 1. The results show that the system produces linear response with coefficient of determination greater than 0.999 for all 10 anions in a broader concentration range.

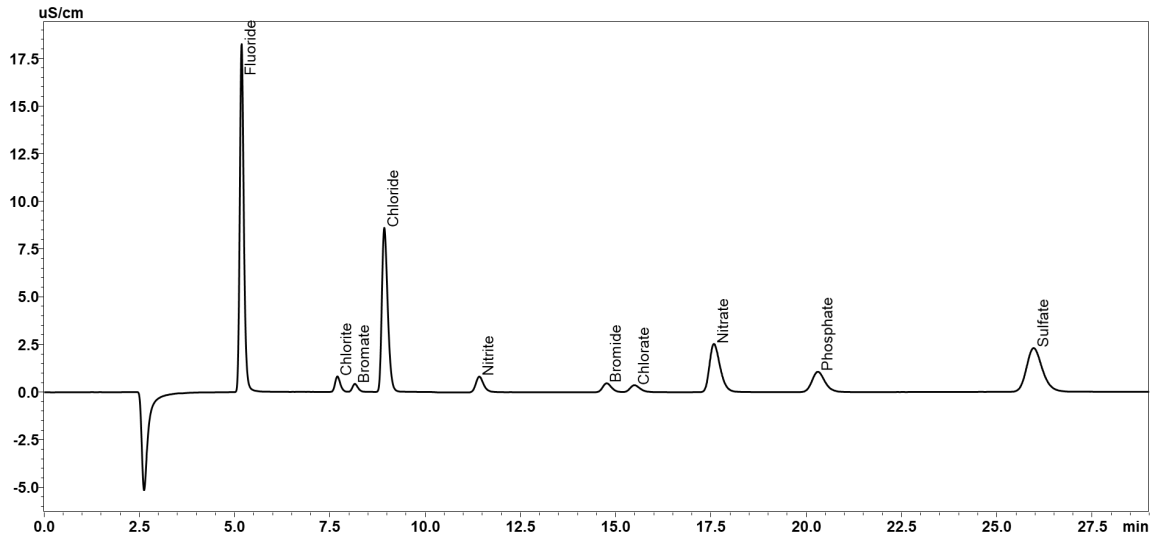


Figure 1: Separation of 10 anions from Shodex IC SI-52 4E column using method condition 1.

Inj. Vol.: 50 μ L

Peaks: 1. Fluoride (5 ppm), 2. Chlorite (1 ppm), 3. Bromate (1 ppm), 4. Chloride (5 ppm), 5. Nitrite (1 ppm), 6. Bromide (1 ppm), 7. Chlorate (1 ppm), 8. Nitrate (5 ppm), 9. Phosphate (5 ppm), 10. Sulfate (5 ppm)

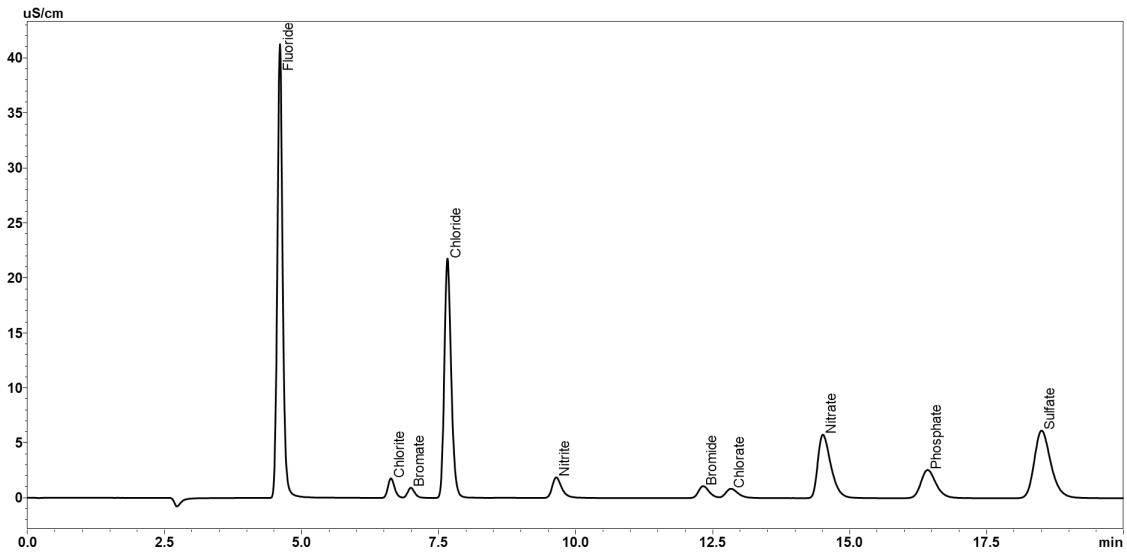


Figure 2: Separation of 10 anions from Shodex IC SI-52 4E column using method condition 2.

Inj. Vol.: 10 μ L

Peaks: 1. Fluoride (25 ppm), 2. Chlorite (5 ppm), 3. Bromate (5 ppm), 4. Chloride (25 ppm), 5. Nitrite (5 ppm), 6. Bromide (5 ppm), 7. Chlorate (5 ppm), 8. Nitrate (25 ppm), 9. Phosphate 2(5 ppm), 10. Sulfate (25 ppm)

Table 1: Linear calibration range, linearity (coefficient of determination), MDL standards and MDL

Anions	Calibration range (ppm)	Linearity (r ²)	MDL Standard (ppb)	Calculated MDL (ppb)
Fluoride (F ⁻)	0.005-50	0.9999	5	1.26
Chlorite (ClO ₂ ⁻)	0.005-5	0.9999	5	1.82
Bromate (BrO ₃ ⁻)	0.005-5	0.9999	5	3.36
Chloride (Cl ⁻)	0.05-25	0.9991	5	12.56
Nitrite (NO ₂ ⁻)	0.01-20	0.9996	10	1.44
Bromide (Br ⁻)	0.005-20	0.9992	5	2.98
Chlorate (ClO ₃ ⁻)	0.005-20	0.9992	5	2.39
Nitrate (NO ₃ ⁻)	0.005-25	0.9996	5	2.51
Phosphate (PO ₄ ³⁻)	0.025-25	0.9997	25	4.05
Sulfate (SO ₄ ²⁻)	0.025-25	0.9997	5	4.74

Reproducibility and Accuracy

Method reproducibility was performed using a mixed standard with concentration of 25 ppm for fluoride, chloride, nitrate, phosphate and sulfate, and concentration of 5 ppm for chlorite, bromate, nitrite, bromide and chlorate.

Table 2 shows retention time precision and peak area precision of 10 anions from 8 injections of the mixed standard. As shown in the table, excellent reproducibility was achieved using method 1 for both retention time and peak area. Retention time RSDs of 10 anions are from 0.02 to 0.08% and peak area RSDs are from 0.23 to 0.42% for all the anions.

Table 2: Retention time and peak area reproducibility

Anions	T _r precision (RSD)	Area precision (RSD)
Fluoride (F ⁻)	0.03%	0.3%
Chlorite (ClO ₂ ⁻)	0.03%	0.26%
Bromate (BrO ₃ ⁻)	0.02%	0.27%
Chloride (Cl ⁻)	0.02%	0.25%
Nitrite (NO ₂ ⁻)	0.04%	0.36%
Bromide (Br ⁻)	0.07%	0.32%
Chlorate (ClO ₃ ⁻)	0.06%	0.42%
Nitrate (NO ₃ ⁻)	0.08%	0.3%
Phosphate (PO ₄ ³⁻)	0.04%	0.37%
Sulfate (SO ₄ ²⁻)	0.03%	0.23%

The performance and accuracy of the methods are investigated by spiking standards into different water matrices.

Table 3 and Table 4 show the acceptable recoveries were obtained for all inorganic ions in three water matrices from using both methods respectively. Figure 3 shows the chromatogram of three water samples obtained using method 1.

Table 3: Recoveries in different waters using method 1

Anions	Added concentration (ppm)	Bottle water Recovery (%)	Tap water Recovery (%)	Dispenser water Recovery (%)
Fluoride (F ⁻)	1	99.8	102.7	103.6
Chlorite (ClO ₂ ⁻)	0.2	107	106	107
Bromate (BrO ₃ ⁻)	0.2	105	99.7	107
Chloride (Cl ⁻)	1	110	86.4	83.4
Nitrite (NO ₂ ⁻)	0.2	97	98.5	92
Bromide (Br ⁻)	0.2	100	100	101
Chlorate (ClO ₃ ⁻)	0.2	106	101.5	104
Nitrate (NO ₃ ⁻)	1	98.5	97.9	97
Phosphate (PO ₄ ³⁻)	1	91.7	109.6	110.4
Sulfate (SO ₄ ²⁻)	1	120	99.8	98.1

Table 4: Recoveries in different waters using method 2

Anions	Added concentration (ppm)	Bottle water Recovery (%)	Tap water Recovery (%)	Dispenser water Recovery (%)
Fluoride (F ⁻)	1	92.6	104.1	99.1
Chlorite (ClO ₂ ⁻)	0.2	103	103	102
Bromate (BrO ₃ ⁻)	0.2	105	107	106
Chloride (Cl ⁻)	1	82.3	80	87.5
Nitrite (NO ₂ ⁻)	0.2	102	102	107
Bromide (Br ⁻)	0.2	101	100.5	100.2
Chlorate (ClO ₃ ⁻)	0.2	105	104.5	100.5
Nitrate (NO ₃ ⁻)	1	84.8	90	83.4
Phosphate (PO ₄ ³⁻)	1	93.4	111.7	110
Sulfate (SO ₄ ²⁻)	1	83.3	98.9	103.4

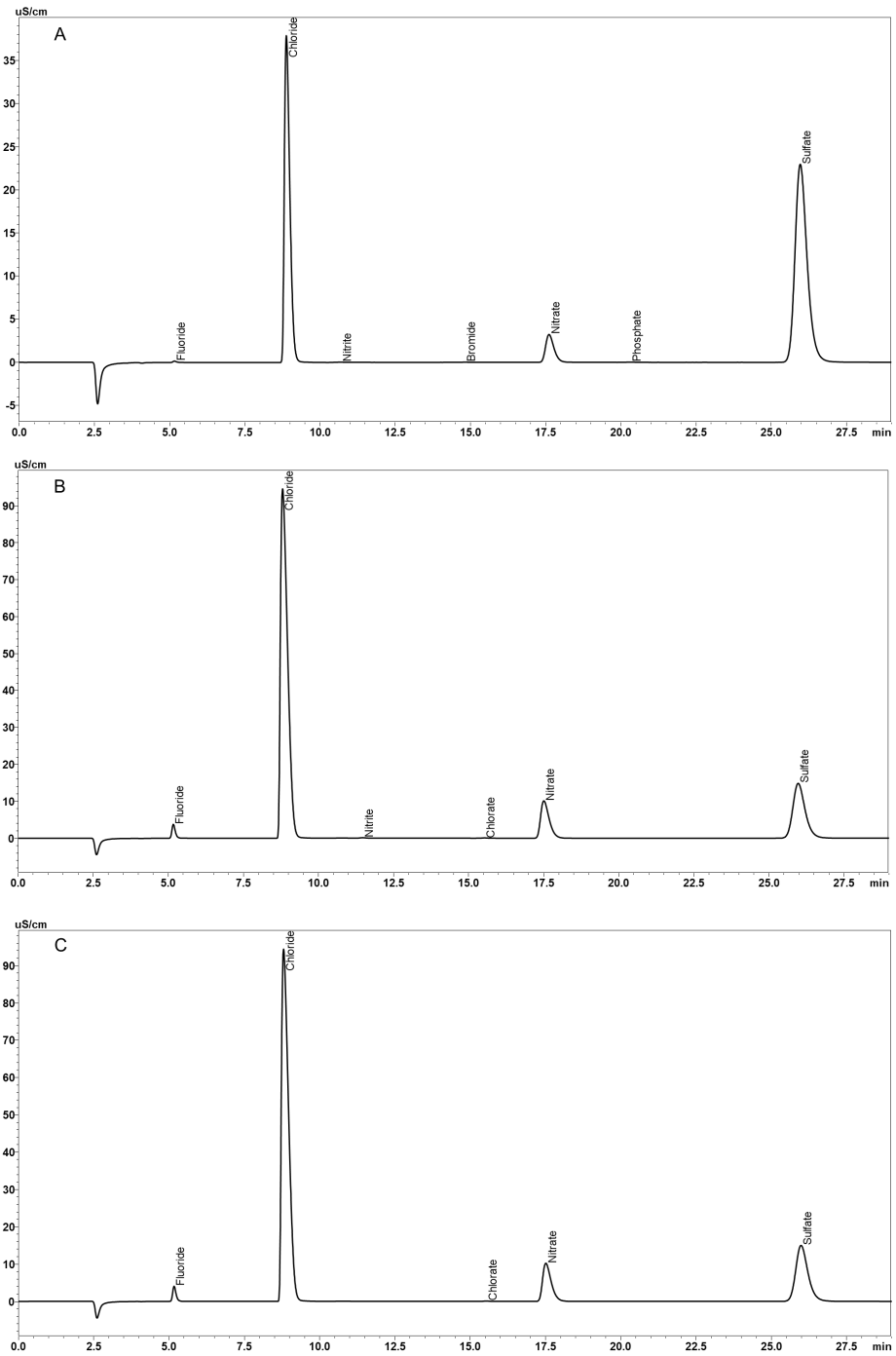


Figure 3: Inorganic anions analysis of water samples using method 1.
Panels: A. bottle water, B. dispenser water, C. tap water.

■ Conclusion

This study demonstrates that the robust and reliable performance of the Shimadzu high-resolution IC system with electrolytically regenerated suppression is achieved for the determination of common inorganic anions and DBPs listed in EPA Method 300.1.

Two high-resolution methods are described in this study, either of which can be used to analyze 10 anions simultaneously. More specifically, method 1 provides improved resolution of bromide and chlorate, even with a larger sample injection, making it more applicable to trace-level analysis of DBPs in more complex water matrices. Method 2 can be used for rapid analysis.

■ References

1. EPA Method 300.0 Determination of inorganic anions by ion chromatography
2. EPA Method 300.1 Determination of inorganic anions in drinking water by ion chromatography Revision 1.0

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