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Application News

Suppressor Ion Chromatograph Prominence IC

Analysis of inorganic anions in tap water according to EPA Method 300.1 using Ion Chromatography

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User Benefits

- Suppressed ion chromatography can be used for analysis of tap water according to EPA Method 300.1.
- It can measure 10 anions such as chloride and sulfate with high sensitivity in about 22 minutes.
- The ICDS™-40 reuses the waste liquid from the detector into reclaimed liquid, allowing environmentally conscious analysis.

■ Introduction

Many countries have standards for environmental and drinking water. In the United States, the Environmental Protection Agency (EPA) provides methods for the analysis of inorganic anions in water by ion chromatography in Method 300.1[1] (EPA Method 300.1).

The suppressor ion chromatograph is designed to improve sensitivity by replacing sodium ions in the eluent with hydrogen ions before detection. Fig. 1 shows the flow chart of the Shimadzu Prominence IC, an ion chromatography system for anion analysis equipped with an electrodialysis suppressor.

In this report, we introduce examples of analysis of 10 inorganic anions in accordance with EPA Method 300.1 using the Prominence IC.

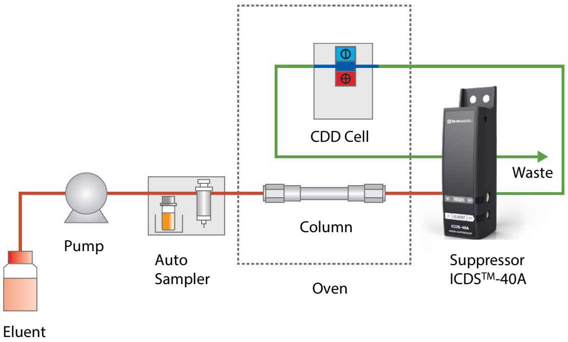

Fig. 1 The Prominence IC Suppressor Ion Chromatograph Flow Chart for Anion Analysis

■ EPA Method 300.1

In EPA Method 300.1, a total of 10 anions are subject to measurement, which are divided into common anions (Part A) and inorganic disinfection by-products (DBP) (Part B) according to the difference in designated injection amounts.

Seven common anions listed in Part A include Fluoride (F^-), Chloride (Cl^-), Nitrite (NO_2^-), Bromide (Br^-), Chloride (Cl^-), Nitrate (NO_3^-), Phosphate (PO_4^{3-}) and Sulfate (SO_4^{2-}). DBPs listed in Part B include Chlorite (ClO_2^-), Bromate (BrO_3^-), Bromide (Br^-) and Chlorate (ClO_3^-). Among them, Br^- is included in both Part A because of its importance as a common anion and Part B because of its important role as a disinfection by-product precursor.

For the surrogate solution, 0.50 mg/mL dichloroacetic acid (DCA) was used. All samples were added DCA to achieve a final concentration of 1 mg/L. And the preservation solution used was 100 mg/mL of ethylenediamine (EDA). It was measured with the addition of EDA to achieve a final concentration of 50 mg/L during Part B analysis.

■ Analytical Conditions

Table 1 shows the analysis conditions.

Table 1 Analytical Conditions

Column	Shodex SI-52 4E (250 mm × 4.0 mm I.D., 5 µm)
Guard column	Shodex SI-92G (10 mm × 4.6 mm I.D., 9 µm)
Mobile phase	5.4 mmol/L sodium carbonate
Flow rate	0.8 mL/min
Column temp.	45 °C
Injection volume	50 µL (Part A)
	200 µL (Part B)
Vial	Shimadzu Vial, LC, 4 mL, Polypropylene*1
Detection	Conductivity

*1 P/N：228-31537-91

■ Analysis of Standard Solutions and Method Detection Limit

EPA Method 300.1 requires prior confirmation of method detection limit (MDL), linearity, recovery and reproducibility to evaluate analytical methods and system performance.

All the standard solutions were prepared by diluting from commercial standard solution. DCA was used as the surrogate in all standard solutions with a final concentration of 1 mg/L. And EDA was added with a final concentration of 50 mg/L during Part B analysis.

Fig. 2 shows the results of injecting 50 µL of a mixed standard solution of Part A. Fig. 3 shows the results of injecting 200 µL of a mixed standard solution of Part B.

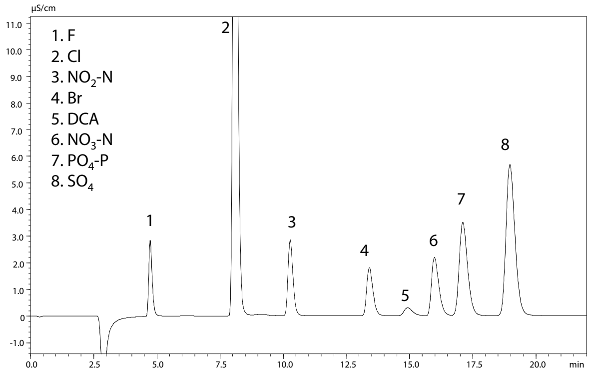

Fig. 2 Chromatogram of Standard Solution (Part A)
(1: 0.5 mg/L 2: 10 mg/L 3: 0.5 mg/L 4: 2 mg/L 5: 1 mg/L 6: 0.5 mg/L 7: 2.5 mg/L 8: 5 mg/L)

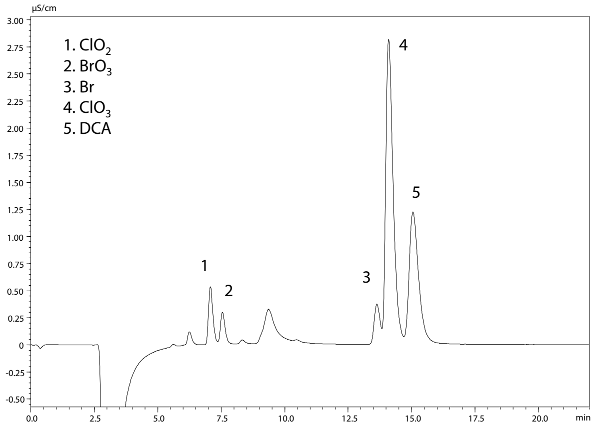

Fig. 3 Chromatogram of Standard Solution (Part B)
(1, 2, 3: 100 μg/L 4, 5: 1000 μg/L)

The MDL was calculated as (t) x (S) after preparing the MDL standard solution according to the procedure described in EPA Method 300.1 and performing 7 consecutive analyses. The formula is shown in Table 2., 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.

Table 2 Formula of MDL

$$\mathrm{MDL}=(t)\times(s)$$

t=Student's t value for n-1 degrees of freedom at the 99% confidence level;
t = 3.143 for six degrees of freedom
s = standard deviation of the replicate analyses

The results of MDL Standard Solution are shown in Fig. 4 (Part A) and Fig. 5 (Part B). The calibration curve ranges, RRF (Relative Response Factor: Calculated from the ratio of the slope of the calibration curve representing the relationship between the concentration of a standard solution and the peak area.), MDL standard concentrations as described in EPA Method 300.1 and the calculated MDL are shown in Table 3 (Part A) and Table 4 (Part B).

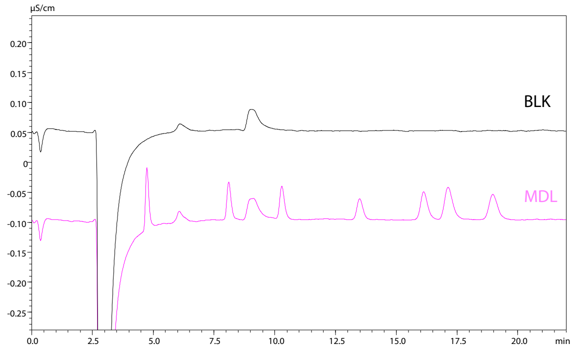

Fig. 4 Analysis Result of MDL Standard Solution and Blank (Part A)

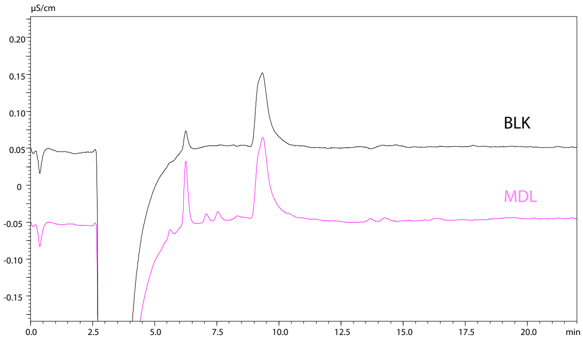

Fig. 5 Analysis Result of MDL Standard Solution and Blank (Part B)

Table 3 Linear calibration range, RRF, MDL standards and MDL (Part A)

Anions	Retention time (min)	Calibration curve		MDL Calculation	
		Calibration range (mg/L)	RRF (%)	MDL Standard (mg/L)	Calculated MDL (mg/L)
F	4.72	0.01 – 1	1.22	0.02	0.0008
Cl	8.11	0.2 – 20	6.10	0.02	0.0025
NO$_2$-N	10.29	0.01 – 1	5.02	0.01	0.0012
Br	13.49	0.04 – 4	1.25	0.04	0.0009
DCA	14.97	---	---	---	---
NO$_3$-N	16.11	0.01 – 1	2.73	0.01	0.0018
PO$_4$-P	17.13	0.05 – 5	2.34	0.04	0.0048
SO$_4$	18.98	0.1 – 10	2.04	0.04	0.0041

Table 4 Linear calibration range, RRF, MDL standards and MDL (Part B)

Anions	Retention time (min)	Calibration curve		MDL Calculation	
		Calibration range (μg/L)	RRF (%)	MDL Standard (μg/L)	Calculated MDL (μg/L)
ClO$_2$	7.07	2 – 200	2.18	2	0.530
BrO$_3$	7.54	2 – 200	9.15	2	0.643
Br	13.67	2 – 200	8.03	2	0.980
ClO$_3$	14.27	20 - 2000	7.61	2	1.33
DCA	15.05	---	---	---	---

■ Sample Analysis of Tap Water

We analyzed tap water using procedures according to EPA Method 300.1. As tap water pre-treatment, 0.2 mL of DCA was added to 100 mL of sample along with Part A and Part B. Part B was further supplemented with 0.05 mL of EDA. The chromatograms are shown in Fig. 6 (Part A) and Fig. 7 (Part B). And the results of tap water determination are summarized in Table 5.

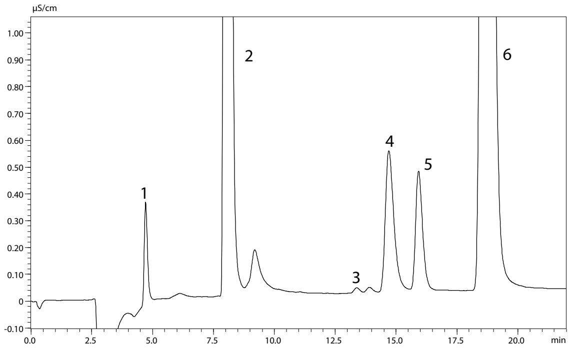

Fig. 6 Chromatogram of Tap Water (Part A)
(Peak: 1. F, 2. Cl, 3. Br, 4. DCA, 5. NO$_3$-N, 6. SO$_4$)

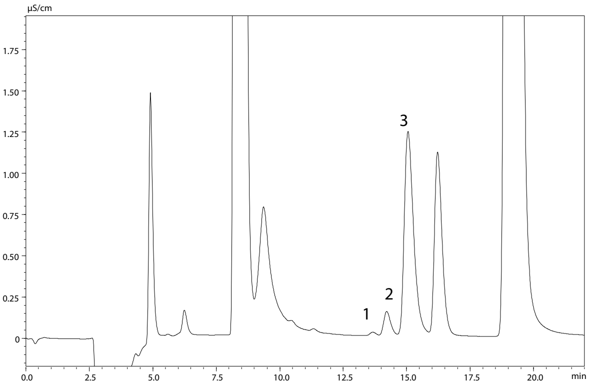

Fig. 7 Chromatogram of Tap Water (Part B)
(Peak: 1. Br, 2. ClO$_3$, 3. DCA)

Table 5 Analysis Results and Recoveries of Tap Water

Anions (Part A)	Measurement concentration (mg/L)	Number of replicates	%RSD	Fortified concentration (mg/L)	Number of replicates	Mean concentration (mg/L)	Mean recoveries (%)	%RSD
F	0.0074	7	1.69	0.07	7	0.143	99.0	1.10
Cl	16.6	7	1.57	6.0	7	23.0	107.5	1.06
NO_2-N	<MDL	7	---	0.03	7	0.033	109.6	1.28
Br	0.027	7	2.02	0.05	7	0.078	101.6	1.63
NO_3-N	0.108	7	1.89	0.1	7	0.205	96.4	1.52
PO_4-P	<MDL	7	---	0.15	7	0.150	99.7	2.56
SO_4	11.6	7	1.28	4.0	7	15.3	91.2	0.90
DCA				1.0	7	1.06	106.1	1.58
Anions (Part B)	Measurement concentration (µg/L)	Number of replicates	%RSD	Fortified concentration (µg/L)	Number of replicates	Mean concentration (µg/L)	Mean recoveries (%)	%RSD
ClO_2	<MDL	7	---	6	7	5.61	93.5	0.17
BrO_3	<MDL	7	---	2	7	2.05	102.7	0.11
Br	26.1	7	1.53	6	7	31.6	92.2	0.23
ClO_3	38.0	7	1.41	60	7	92.7	91.1	0.71
DCA				1000	7	999.6	99.7	1.44

■ Recoveries and Accuracy

The performance and accuracy of EPA Method 300.1 were confirmed by recovery tests. In the recovery tests, tap water was evaluated by adding a standard solution to each ion.

Recoveries were calculated according to EPA Method 300.1. The formula is shown in Table 6. The recoveries obtained from the analysis of the fortified samples are summarized in Table 5. Good recoveries were obtained for all components.

Table 6 Formula of Samples' Recovery

$$R=\frac{C_F-C}{F}\times 100$$

R = percent recovery
CF = fortified sample concentration
C = sample background concentration
F = concentration equivalent added to sample

■ Conclusion

This application news introduced inorganic anion analysis in accordance with EPA Method 300.1 using the Shimadzu Prominence IC with suppressed ion chromatography .

The MDL and method performance criteria were well within the requirements of the method. In addition, the shorter analysis time also promises to increase productivity and reduce the amount of solvent used compared to conventional methods.

<References>

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

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