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Application News

No. L553

Ion Chromatography

US EPA 300 Method-Compliant Environmental and Water Analysis

Many countries and regions specify standard values for general inorganic anions such as fluoride, chloride, nitrate, nitrite, and sulfate ions in order to minimize the potential health effects of environmental water and drinking water.

A suppressor-type ion chromatograph is generally used in quantitation of these inorganic anions. In the United States, Environmental Protection Agency (EPA) Methods 300.0 and 300.1 specify the analysis method for inorganic anions in water by ion chromatography (IC).

In anion analysis, conductivity suppressor-type IC enhances sensitivity by replacing the sodium ions in the eluent, which are necessary and indispensable for separation, with hydrogen ion before detections of the target anions.

In this article, an EPA 300-compliant quantitative analysis of 7 general inorganic anions in various types of water samples was conducted using an HIC-ESP, which is a new Shimadzu ion chromatograph system equipped with an electrodialysis-type suppressor.

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Analytical Conditions

Fig. 1 shows the results when a 50 µL mixed standard sample of the 7 anions prescribed in EPA 300 was injected. Table 1 shows the analytical conditions.

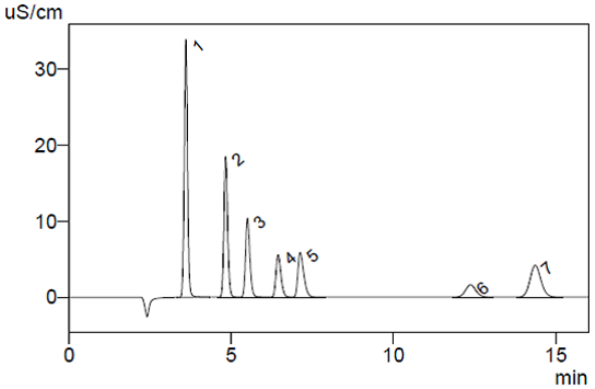

Fig. 1 Chromatogram of Mixed Standard Sample of Anions
Peaks: 1. F (5 mg/L), 2. Cl (5 mg/L), 3. NO_2 (5 mg/L), 4. Br (5 mg/L), 5. NO_3 (5 mg/L), 6. PO_4 (5 mg/L), 7. SO_4 (5 mg/L)

Table 1 Analytical Conditions

Column	: Shim-pack™ IC-SA2 (250 mmL. × 4.0 mmI.D.)
Mobile phase	: 1.8 mmol/L Sodium Carbonate 1.7 mmol/L Sodium Hydrogen Carbonate
Flow rate	: 1.0 mL/min
Column temp.	: 40 °C
Injection volume	: 50 µL
Detection	: Electro conductivity detector

Linearity and Detection Limit

Under EPA Method 300, advanced confirmation of linearity, the detection limit, the recovery rate, and repeatability is necessary for evaluation of the analysis method and system performance.

For the detection limit, in accordance with the procedure described in Method 300, an MDL (Method Detection Limit) standard sample was prepared, 7 continuous analyses were carried out, and MDL was calculated as (t) × (S). Here, t means the t value for the 99% confidence level (Student's t-value in t-test; in 7 continuous analyses, t = 3.14), and S means the standard deviation of 7 continuous analyses.

Table 2 shows the calibration curve range, linearity, MDL standard concentration, and calculated MDL. Fig. 2 shows the calibration curves of all of the anions.

Table 2 Linear Calibration Region, Linearity, MDL Standard, and MDL

Component	Calibration curve range (mg/L)	Coefficient of correlation (r^2)	MDL standard concentration (µg/L)	MDL (µg/L)
F	0.05-20	0.9999	10	3.31
Cl	0.1-100	0.9992	5	2.05
NO_2	0.05-20	0.9995	20	1.49
Br	0.05-20	0.9989	20	3.3
NO_3	0.05-20	0.9991	20	2.69
PO_4	0.05-20	0.9995	50	14.38
SO_4	0.05-20	0.9992	20	3.63

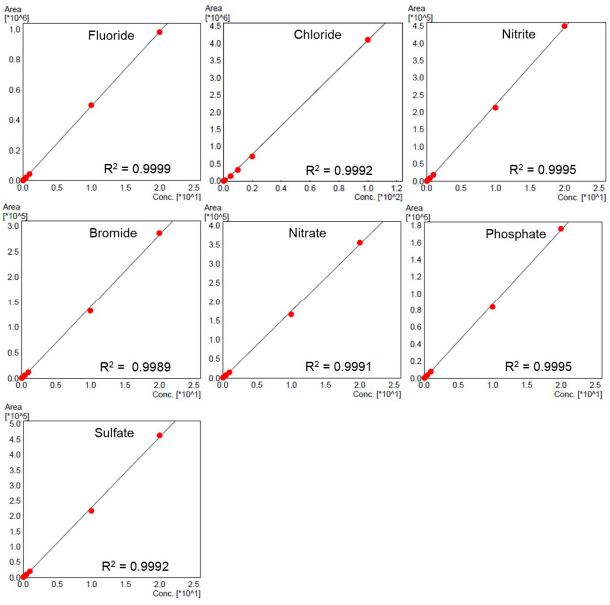

Fig. 2 Calibration Curves of 7 Anions in EPA Method 300

Repeatability and Accuracy

The repeatability of the retention time and peak area was verified by using a mixed standard sample with a 10 mg/L of each ion. To also verify day-to-day repeatability at the same time, the test was conducted for a period of 4 days.

The repeatability of the retention time and peak area was verified from the results of 5 continuous analyses each day. Table 3 shows the results for the 1st and 4th days. The results showed excellent repeatability of the retentions times and peak areas of all components during the test period.

Table 3 Repeatability of Retention Time and Peak Area (One Day, Day-to-Day Repeatability)

Component	1st day		4th day	
	Retention time (%RSD)	Peak area (%RSD)	Retention time (%RSD)	Peak area (%RSD)
F	0.06	0.07	0.12	0.72
Cl	0.06	0.07	0.15	0.78
NO_2	0.06	0.14	0.18	0.70
Br	0.07	0.24	0.20	0.75
NO_3	0.08	0.20	0.22	0.97
PO_4	0.15	0.25	0.24	0.64
SO_4	0.13	0.18	0.30	0.63

To determine accuracy, blank ultrapure water (DI) and tap water were evaluated after standard spiking with a 2 mg/L concentration of each anion. Table 4 shows the results. Satisfactory recovery rates were obtained from the various water samples.

Table 4 Recovery Rates of Blank and Tap Water

Component	Spiked concentration (mg/L)	Recovery rate (%)	
		Ultrapure water	Tap water
F	2.0	93.9	99.4
Cl	2.0	94.0	96.2
NO_2	2.0	96.1	95.2
Br	2.0	97.1	91.2
NO_3	2.0	98.0	106.0
PO_4	2.0	98.4	103.0
SO_4	2.0	98.3	92.6

Analysis of Actual Samples

Fig. 3 shows the chromatograms of three types of water samples, and Table 5 shows the quantitation results.

Table 5 Results of Quantitation of Anions in Water Samples

Component	Concentration (mg/L)		
	PET bottle water	Water server water	Tap water
F	0.08	0.50	0.64
Cl	12.99	41.06	39.69
NO_2	N.D.	0.25	N.D.
Br	0.27	0.39	0.36
NO_3	2.66	8.93	8.87
PO_4	N.D.	N.D.	N.D.
SO_4	25.88	15.95	15.37

The negative peaks detected at around 2.5 min in the chromatograms are called water dip and originate from the water in the injected sample. Satisfactory separation between this peak and the fluoride peak, which has a short retention time, was obtained under these conditions, demonstrating that high quantitation accuracy is possible.

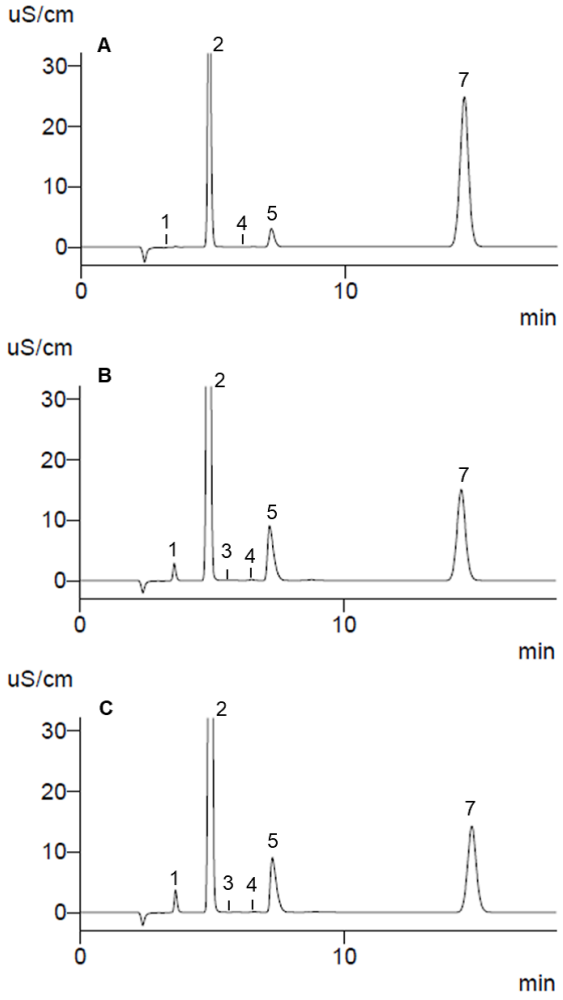

Fig. 3 Chromatograms of Water Samples
A: PET Bottle Water, B: Water Server Water, C: Tap Water
(Peaks: 1. F, 2. Cl, 3. NO_2, 4. Br, 5. NO_3, 6. PO_4, 7. SO_4)

* The samples were obtained and the analysis was conducted in the United States.

Conclusion

EPA 300-compliant analysis of inorganic anions with high sensitivity and high reliability is possible by using the Shimadzu HIC-ESP ion chromatograph system.

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