

Analysis of Cations in Drinking Water and Wastewater, Conforming to ASTM D6919-03

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User Benefits

- ◆ Data with good linearity and repeatability can be obtained in analysis conforming to ASTM D6919-03.
- ◆ Cations in drinking water and wastewater can be quantified.
- ◆ Separation of sodium and ammonium ions can be improved by adding 18-crown-6 ether to the mobile phase.

Introduction

Ion chromatography can be widely employed for the detection and quantification of ionic components in aqueous solutions. ASTM D6919-03⁽¹⁾, published by ASTM International, USA, specifies an ion chromatographic method for analyzing the six cations (lithium, sodium, ammonium, potassium, magnesium, and calcium ions) in drinking water and wastewater.

This article introduces analysis of the six cations in drinking water and wastewater using non-suppressor ion chromatograph that conforms to ASTM D6919-03.

Analysis of Standard Solutions

Fig. 1 shows the chromatogram of the six listed in ASTM D6919-03, and Table 1 shows the analytical conditions.

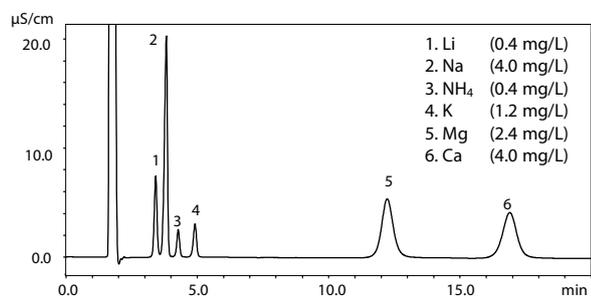


Fig. 1 Chromatogram of 6 Cations

Table 1 Analytical Conditions

Column	: Shim-pack™ IC-C4 ^{*1} (150 mm × 4.6 mm I.D., 7 μm)
Guard Column	: Shim-pack IC-GC4 ^{*2} (8 mm × 3 mm I.D., 7 μm)
Mobile phase	: 2.5 mmol/L Methanesulfonic Acid
Flow rate	: 1.0 mL/min
Column temp.	: 40 °C
Injection volume	: 50 μL
Vial	: Shimadzu Vial, LC, 4mL, Polypropylene ^{*3}
Detection	: Conductivity

*1 P/N: 228-41616-91

*2 P/N: 228-59900-91

*3 P/N: 228-31537-91

Linearity and Repeatability

Five level calibration curves were created for the respective the six cations in the concentration range specified in ASTM D6919-03. Although a quadratic curve is recommended for the calibration curve of ammonium ions when using a suppressor method, a linear calibration curve can be employed when using a non-suppressor method.

Table 2 shows the coefficients of determination(r^2) of the calibration curves. While the ASTM D6919-03 suggests a minimum value of 0.995, the results of this analysis showed a value of 0.999 or greater for all the cations.

Table 2 Calibration Curve Ranges and Coefficients of Determinations of 6 Cations

	Li	Na	NH_4	K	Mg	Ca
Calibration curve range (mg/L)	0.4-10	4.0-40	0.4-10	1.2-20	2.4-40	4.0-40
Coefficients of Determination (%)	≥ 0.999	≥ 0.999	≥ 0.999	≥ 0.999	≥ 0.999	≥ 0.999

The repeatabilities were also evaluated based on the relative standard deviations (%RSD) of the retention times and the peak areas obtained at the concentrations of the lowest calibrants through seven times consecutive analyses. Table 3 shows the concentration, the repeatability, and peak area repeatability of respective cations. Good repeatabilities were confirmed in both the retention times and the peak areas.

Table 3 Concentrations and Relative Standard Deviations of 6 Cations

	Li	Na	NH_4	K	Mg	Ca
Concentration (mg/L)	0.4	4.0	0.4	1.2	2.4	4.0
Retention time %RSD	0.02	0.02	0.02	0.02	0.02	0.02
Area value %RSD	0.16	0.17	0.94	0.69	0.47	0.52

Analysis of Drinking Water and Tap Water

Two types of commercial drinking water and a tap water were filtered through 0.2 μm filters and subjected to the analyses. Fig. 2-1 to 2-3 show the results of respective analyses, and Table 4 shows the concentrations of respective cations in drinking water and tap water.

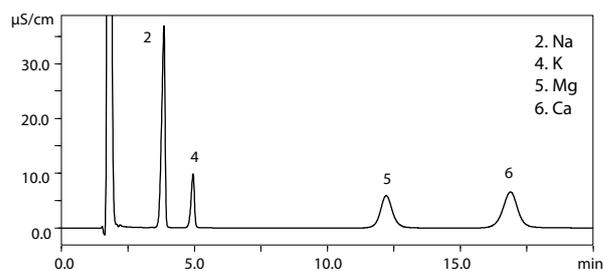


Fig. 2-1 Chromatogram of Commercial Drinking Water A

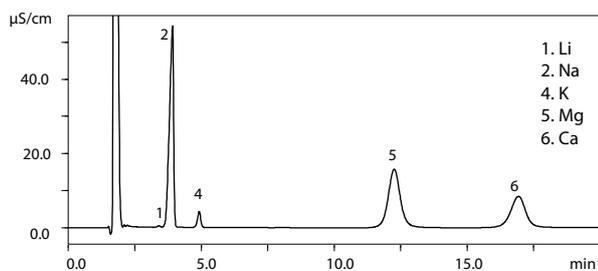


Fig. 2-2 Chromatogram of Commercial Drinking Water B

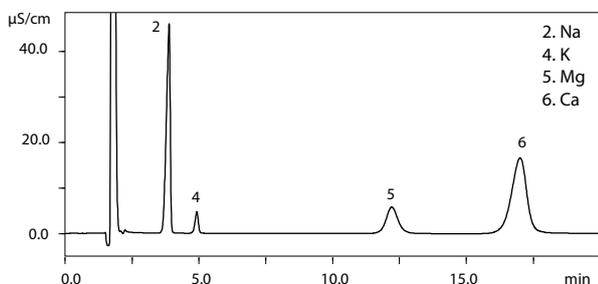


Fig. 2-3 Chromatogram of Tap Water

Table 4 Concentrations of the 6 cations in Drinking Water and Tap Water

	Li	Na	NH ₄	K	Mg	Ca
Drinking water A	N.D.	6.61	N.D.	3.16	2.11	5.10
Drinking water B	0.01	11.70	N.D.	1.37	5.63	6.44
Tap water	N.D.	9.12	0.05	1.51	2.06	12.79

Unit: mg/L (N.D.=Not Detected)

■ Analysis of Factory Wastewater

Factory wastewater was filtered through a 0.2 μm filter, diluted twice with ultrapure water, and subjected to analysis. Fig. 3 shows the result of the analysis. Table 5 shows the concentrations of respective cations in the factory wastewater.

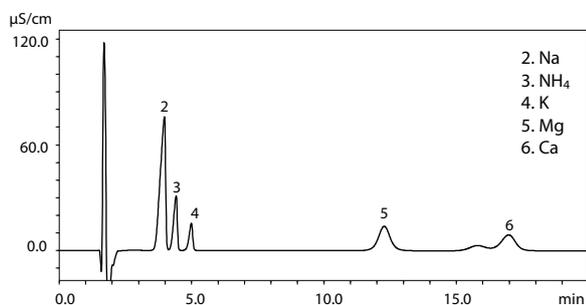


Fig. 3 Chromatogram of Factory Wastewater

Table 5 Concentrations of Factory Wastewater (after Undiluted Solution Conversion)

Li	Na	NH ₄	K	Mg	Ca
N.D.	42.27	9.91	10.61	9.98	14.18

Unit: mg/L (N.D.=Not Detected)

■ Spike-and-Recovery Test

Spike-and-recovery tests were conducted on tap water confirming to ASTM D6919-03. Table 6 shows the concentration of the spiked standard solutions and the recovery rates calculated using the formula described later.

Table 6 Spike Concentrations and Recovery Rates in Spike-and-Recovery Test

	Li	Na	NH ₄	K	Mg	Ca
Spike concentration (mg/L)	0.40	9.00	0.01	1.50	2.00	13.00
Recovery rate* (%)	96.5	100.1	105.6	99.3	100.8	101.2

*: Recovery rate (%) =

$$\frac{\text{Quantitative value after spike (mg/L)}}{\text{Quantitative value (mg/L) + Spike concentration (mg/L)}} \times 100$$

■ Separation of Sodium Ions and Ammonium Ions

ASTM D6919-03 states that a quantitation of the ammonium ion may drastically be affected by a presence of high concentration of sodium ion. As a countermeasure, however, 18-crown-6 ether can be added to the mobile phase to delay the elution of ammonium ion, and thus improve the separation of the two components.

Fig. 4 shows the chromatogram of a standard solution containing 20 mg/L sodium ion and 0.02 mg/L ammonium ion when 18-crown-6 ether was added to the mobile phase, and Table 7 shows the analytical conditions. The result showed that the sufficient separation and the detection were able to be done even under the concentration ratio of 1000 : 1.

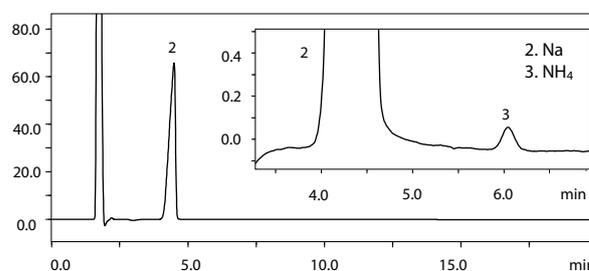


Fig.4 Chromatogram when 18-crown-6 ether is Spiked and its Enlarged View

Table 7 Analytical Conditions when 18-crown-6 ether is Spiked

Column	: Shim-pack IC-C4 ^{†1} (150 mm × 4.6 mm I.D., 7 μm)
Guard Column	: Shim-pack IC-GC4 ^{†2} (8 mm × 3 mm I.D., 7 μm)
Mobile phase	: 2.5 mmol/L Methanesulfonic Acid 5.0 mmol/L 18-Crown 6-ether
Flow rate	: 1.0 mL/min
Column temp.	: 40 °C
Injection volume	: 50 μL
Vial	: Shimadzu Vial, LC, 4mL, Polypropylene ^{†3}
Detection	: Conductivity Detector

■ Conclusion

This article introduced the cation analysis of drinking water and wastewater using non-suppressor ion chromatograph conforming to ASTM D6919-03.

Using this method, we obtained the specified linearities and good repeatabilities for all six cations listed in ASTM D6919-03.

In the analyses of drinking water and wastewater, we also obtained good results in terms of the separation from the contaminants as well as spike recovery rates.

<Reference>

- (1) ASTM D6919-03, Standard Test Method for Determination of Dissolved Alkali and Alkaline Earth Cations and Ammonium in Water and Wastewater by Ion Chromatography, ASTM International, West Conshohocken, PA, 2003, www.astm.org

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