

## Suppressed Cation Analysis of Wastewater Using Ion Chromatograph Nexera™ IC, Conforming to ASTM D6919-17

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### User Benefits

- ◆ Analysis in accordance with ASTM D6919-17 can be performed.
- ◆ Reliable linearity, repeatability, and related data can be obtained in cation analysis using suppressor.
- ◆ Simultaneous analysis of six target cations can be completed within 20 minutes.

### Introduction

Ion chromatography is widely used for the detection and quantification of ionic components in aqueous solutions. ASTM D6919-17<sup>1)</sup>, published by ASTM International in the United States, specifies a test method for the six cations in drinking water and wastewater using ion chromatograph.

In this article, the analysis of the six cations in industrial wastewater using suppressor-ion chromatograph in accordance with ASTM D6919-17 is introduced.

### Analysis of mixed standard solution

A standard solution containing the six cations designated in ASTM D6919-17 (lithium ion (Li), sodium ion (Na), ammonium ion (NH<sub>4</sub>), potassium ion (K), magnesium ion (Mg), and calcium ion (Ca)) at the concentrations indicated in Fig. 1 and Table 2 was used as the Initial Demonstration of Performance (IDP) solution and analyzed. Obtained chromatogram is shown in Fig. 1, and the analytical conditions are listed in Table 1.

Table 2 shows the relative standard deviations of retention times and peak areas of respective ions obtained from seven consecutive analyses of the IDP solution.

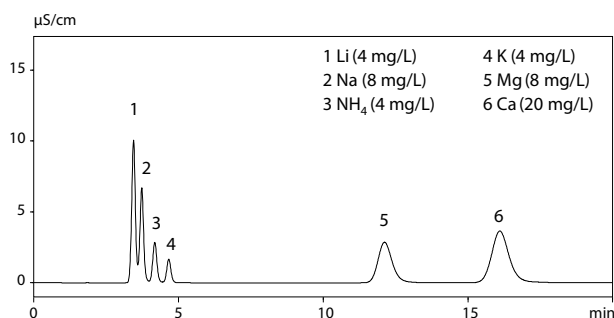


Fig. 1 Chromatogram of IDP solution

Table 1 Analytical conditions

System	Nexera IC
Column	Shim-pack IC-C4 <sup>*1</sup> (150 mm × 4.6 mm I.D., 7 µm)
Guard Column	Shim-pack IC-GC4 <sup>*2</sup> (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	10 µL
Vial	Shim-vial PP-U for 1.5 mL <sup>*3</sup>
Detection	Conductivity Detector

\*1 P/N : 228-41616-91 \*2 P/N : 228-59900-91 \*3 P/N : 228-59584-41

Table 2 Repeatability using IDP solution

Target cation	Concentration (mg/L)	Retention time	
		%RSD	%RSD
Li	4	< 0.1	0.18
Na	8	< 0.1	0.12
NH <sub>4</sub>	4	< 0.1	0.10
K	4	< 0.1	0.13
Mg	8	< 0.1	0.18
Ca	20	< 0.1	0.18

### Coefficient of determination for calibration curve

Five-level calibration curves, a quadratic curve for NH<sub>4</sub> and linear curves for the other cations, were created using five different concentrations, each containing six cations, as shown in Table 3. Table 3 also shows the coefficients of determination (r<sup>2</sup>) for respective calibration curves. Coefficients of determination for all the ions were 0.999 or higher, which satisfy the requirement of 0.995 or higher specified by ASTM D6919-17.

Table 3 Concentration and coefficient of determination of mixed standard solution

Target cation	Concentration(mg/L)	r <sup>2</sup>
Li	0.8/1/2/4/8	≥ 0.999
Na	4/8/16/20/25	≥ 0.999
NH <sub>4</sub>	0.8/1/2/4/8	≥ 0.999
K	0.8/1/2/4/8	≥ 0.999
Mg	4/8/16/20/25	≥ 0.999
Ca	8/16/20/25/50	≥ 0.999

### Method detection limit

A mixed standard solution prepared to make respective concentrations of 100 µg/L was used as the method detection limit (MDL) solution. The MDL solution was subjected to consecutive seven analyses, and the MDL was calculated from the standard deviations of obtained concentrations.

The concentrations of respective cations were calculated from the calibration curves passing through the origin. The calculated MDLs are shown in Table 4. The chromatogram of the MDL solution is shown in Fig. 2.

Table 4 Calculated MDL for respective ions

Target cation	Concentration (µg/L)	Standard deviation (µg/L)	MDL (µg/L)
Li	100	0.05	0.2
Na	100	0.16	0.5
NH <sub>4</sub>	100	0.16	0.5
K	100	0.19	0.6
Mg	100	0.29	0.9
Ca	100	0.52	1.6

MDL=t×s

t: Student's t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom [t =3.143]

s: Standard deviation of MDL sample

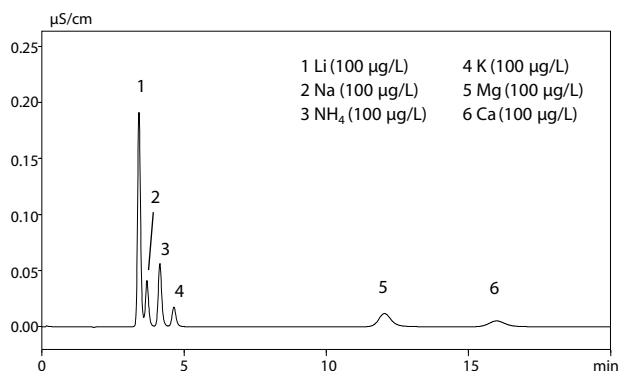


Fig. 2 Chromatogram of MDL solution

### Sample Analysis

Factory wastewater was analyzed as a test sample. The factory wastewater was filtered using a 0.2 µm syringe filter (for ion chromatography, P/N: 227-33306-03) prior to analysis. Fig. 3 shows the chromatogram of the factory wastewater. Table 5 shows obtained concentrations of respective ions.

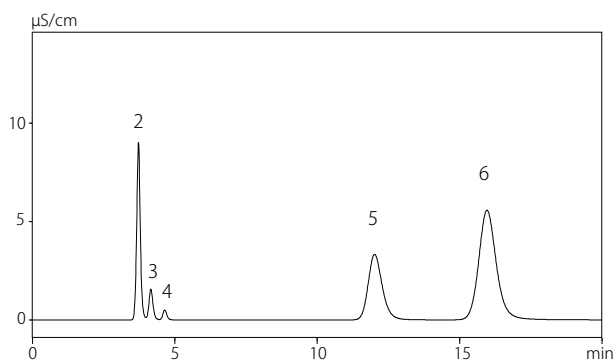


Fig. 3 Chromatogram of factory wastewater

Table 5 Ion concentration in factory wastewater

Target cation	Concentration (mg/L)
Li	N.D.*
Na	9.7
NH <sub>4</sub>	2.0
K	1.3
Mg	8.8
Ca	27.0

\*N.D.=Not Detected

### Spike and Recovery test

Spike and recovery test was conducted to confirm that impurities in the sample did not affect quantitative determination. Individual ion chromatography standard solutions (1000 mg/L, manufactured by Fujifilm Wako Pure Chemical Industries, Ltd.) were mixed as the volumes shown in Table 6 to prepare the spike and recovery test solution. 48.5 µL of the spiking recovery test solution was added to 1 mL of factory wastewater, then subjected to analysis to calculate respective recovery rates. Fig. 4 shows overlaid chromatograms of the unspiked and spiked samples, and Table 7 lists the concentrations of the spiked standard ions and calculated recovery rates.

Table 6 Composition of spike and recovery test solution

Target cation	Volume (µL)
Li	20
Na	100
NH <sub>4</sub>	20
K	20
Mg	100
Ca	200

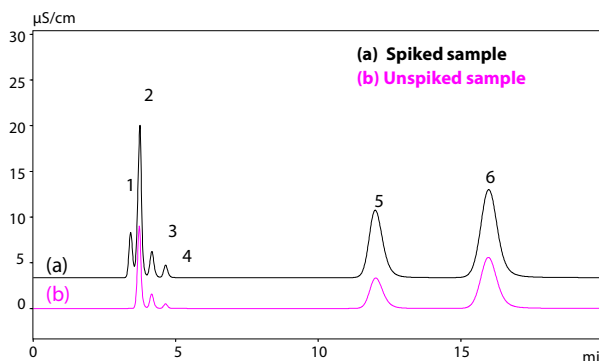


Fig. 4 Chromatogram of factory wastewater in spike and recovery test

Table 7 Spiked concentration and recovery rate from spike and recovery test

Target cation	Spiked concentration (mg/L)	Recovery(%)
Li	2	97.0
Na	10	94.4
NH <sub>4</sub>	2	102.1
K	2	97.9
Mg	10	101.1
Ca	20	99.8

$$\text{Recovery (\%)} = \frac{a-b}{c} \times 100$$

a: Spiked sample concentration

b\*: Unspiked sample concentration

c: Spiked concentration

\*: Concentrations in table 5 were corrected to meet actual concentrations in added sample

### Conclusion

In this article, suppressor cation analysis conducted in accordance with ASTM D6919-17 using Nexera IC was introduced. Coefficients of determination meeting specified limitations and good repeatabilities were obtained for all six cations designated in ASTM D6919-17.

Additionally, excellent recovery rates were obtained in the spike and recovery test.

### <References>

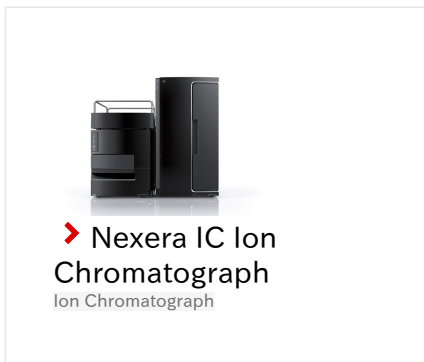
- 1) ASTM D6919-17, Standard Test Method for Determination of Dissolved Alkali and Alkaline Earth Cations and Ammonium in Water and Wastewater by Ion Chromatography, ASTM International, West Conshohocken, PA, 2017

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