

# Application News

## No. L521

### High Performance Liquid Chromatography

## Quantifying NH<sub>4</sub><sup>+</sup> in Industrial Wastewater Using Ion Chromatography (Non-Suppressor System)

Plating solution and wastewater from plating plants contain multiple ions including those of sodium and ammonium. Ion chromatography is used to quantify these types of ions.

Ion chromatography employs a conductivity detector to selectively detect only ions. However, since the eluent contains ions that cause increased background level, a suppressor which is located between the column and detector is sometimes used to convert the eluent into pure water by means of ion exchange.

When using a suppressor, a minimum of six calibration points are required because the responsiveness to conductivity decreases as the concentration of ammonium ions increases, causing poor linearity of the calibration curve.

On the other hand, the non-suppressor system in which a suppressor is not used provides a linear calibration curve. Consequently, an accurate quantitation even with only a few calibration points are possible due to poor linearity of conductivity for ammonium ions at high concentration.

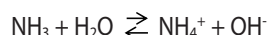
This article compares calibration curves created using the suppressor and non-suppressor systems and introduces an example of measuring cations contained in industrial wastewater using the non-suppressor system.

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### ■ Suppressor and Non-Suppressor Systems

Fig. 1 shows the ammonium ion calibration curve with the suppressor system and Fig. 2 shows the ammonium ion calibration curve with the non-suppressor system, each over the same concentration range of 0.5 to 20 mg/L. Even though both calibration curves were created using the analytical conditions listed in Table 1, the non-suppressor system in Fig. 2 provided favorable linearity when compared to that of the calibration curve of the suppressor method in Fig. 1.

The curvature occurs due to the use of the suppressor system in which the eluent is converted into water which have no pH buffering capacity. Consequently, the dissociations of target ions are suppressed due to the increasing pH value of the eluent flowing into the conductivity detectors along with the increase of ammonium ions. In other words, the equilibrium relationship expressed by the following formula shifts to the left-hand side.

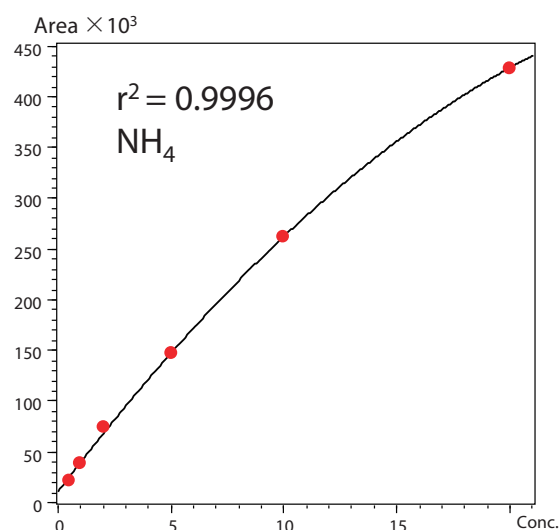


This leads to a reduction in responsiveness to conductivity as the concentration of ammonium ions increases, and a curved line is obtained for the calibration curve.

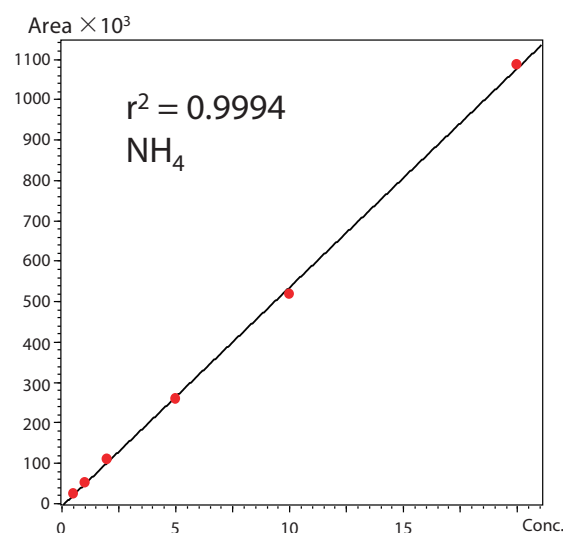
Conversely, the non-suppressor system in which a suppressor is not used always obtains a linear calibration curve because the ion concentration in the eluent does not change.

Although quantitative values of the same level can be obtained with or without a suppressor as long as the calibration curve is created accurately, the non-suppressor system provides accurate quantitation with less calibration points due to the linear calibration curve which allows reliable linear approximation.

Moreover, suppressors require periodic replacement because their performance gradually deteriorates with use. However, such replacement is not required for the non-suppressor system, making it also advantageous in terms of running cost.



**Fig. 1** NH<sub>4</sub> Calibration Curve Obtained Using the Suppressor System (Second-order approximation)



**Fig. 2** NH<sub>4</sub> Calibration Curve Obtained Using the Non-Suppressor System (First-order approximation)

**Table 1** Analytical Conditions

Column	: Shim-pack IC-C4 (150 mmL. × 4.6 mm I.D.)
Mobile phase	: 3 mmol/L methanesulfonic acid
Flow rate	: 1.0 mL/min
Column temp.	: 40 °C
Detection	: Conductivity detector (CDD-10Avp)
Injection vol.	: 50 µL

### ■ Analysis of Industrial Wastewater

Industrial wastewater was filtered through a membrane filter with a pore size of 0.2 μm dedicated to ion chromatography, and then analyzed using the non-suppressor system of ion chromatography.

Table 2 lists the analytical conditions. 2 mmol/L of 18-Crown-6 was added to the eluent to ensure adequate separation of sodium ions and ammonium ions.

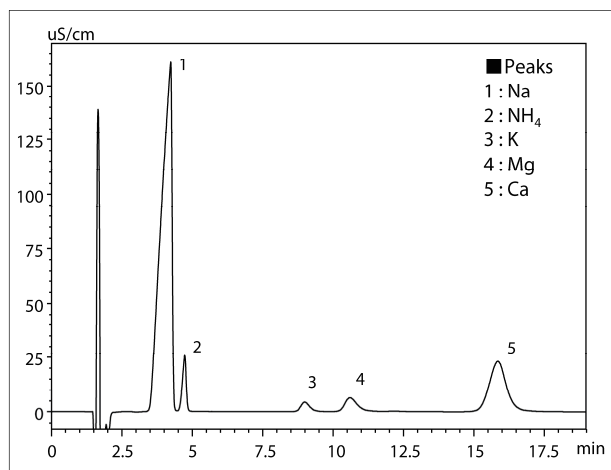
Table 3 lists the quantitative results of the cation types and Fig. 3 shows the corresponding chromatogram. Favorable separation is achieved even for samples that contain significantly more sodium ions than ammonium ions and the high linearity of the calibration curve enables accurate quantitation.

**Table 2 Analytical Conditions**

Column	: Shim-pack IC-C4 (150 mmL. × 4.6 mm I.D.)
Mobile phase	: 3 mmol/L methanesulfonic acid 2 mmol/L 18-crown-6
Flow rate	: 1.0 mL/min
Column temp.	: 40 °C
Detection	: Conductivity detector (CDD-10Avp)
Injection vol.	: 50 μL

**Table 3 Quantitative Results**

No.	Ion	Quantitative value (mg/L)
1	Na	85.9
2	NH <sub>4</sub>	4.2
3	K	3.8
4	Mg	2.5
5	Ca	18.9



**Fig. 3 Chromatogram of Industrial Wastewater**

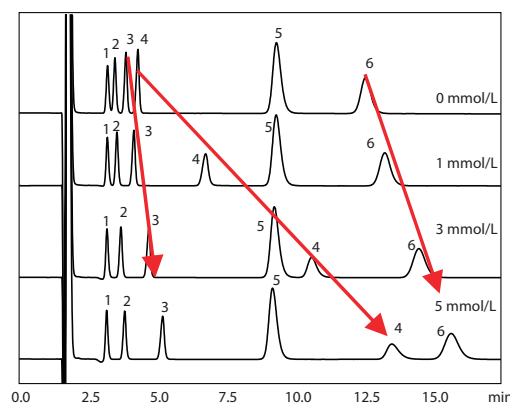
### ■ Separation of Ammonium Ions

In the analysis of industrial wastewater, a point of concern is the interference in the quantitation of ammonium ions due to the high concentration of sodium ions compared to only trace amounts of ammonium ions and the proximity of their elution times.

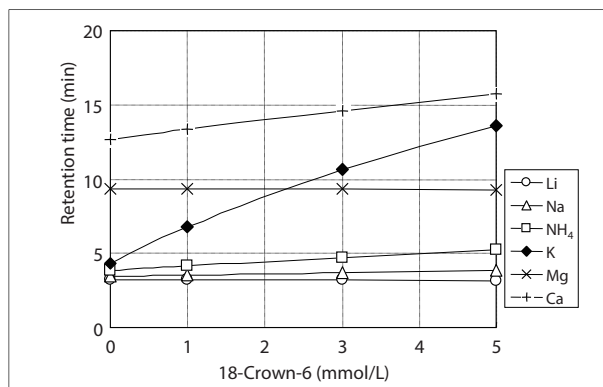
To alleviate this problem, a method for improving separation is used in which 18-Crown-6, which has an inclusive effect on ammonium ions and potassium ions, is added to the eluent.

Crown ethers are hollow ring-shaped compounds comprised of C, H, and O, and have an inclusive effect on certain cations caused by the oxygen atoms located on their interior. They are able to selectively increase the retention of certain cations due to strong interaction with the stationary phase.

However, since the retention time of potassium ions changes even more drastically than ammonium ions when 18-Crown-6 is added, separation must be adjusted according to the amount of the crown ether to be added and temperature. Fig. 4 shows a conceptual graph of changes in elution behavior depending on the amount of added 18-Crown-6, and Fig. 5 shows a graph that plots the amount of added 18-Crown-6 against retention time.



**Fig. 4 Amount of Added 18-Crown-6 and Changes in Elution Behavior**  
(1: Li, 2: Na, 3: NH<sub>4</sub>, 4: K, 5: Mg, 6: Ca)  
Eluent: 3 mmol/L oxalic acid 0 to 5 mmol/L 18-Crown-6



**Fig. 5 Amount of Added 18-Crown-6 and Changes in Retention Time**  
(Eluent: 3 mmol/L oxalic acid 0 to 5 mmol/L 18-Crown-6)

References: Ion Chromatography Q&A, pp. 60, 74, Shimadzu Corporation, 2014

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