QUANTIFICATION OF AMMONIUM CATIONS IN INDUSTRIAL WASTEWATER USING ION CHROMATOGRAPHY

Ion monitoring in wastewater using a non-suppressed IC system for cation analysis

Introduction

Ammonia, as present in industrial wastewater, poses a toxic threat to aquatic life and ultimately to humans, when converted to nitrate. The National Pollutant Discharge Elimination System (NPDES) permit program, as authorized by the Clean Water Act (US), requires information on the amount of ammonia dissolved in water by monitoring of ammonium cations.

Ion chromatography with conductivity detection is the ideal tool for the selective and sensitive determination of inorganic ions. However, since the eluent also contains ions that generate an increased background noise level, an ion suppressor located between the column and detector can be used to neutralize the eluent by means of ion exchange.

When using a suppressor, a minimum of six calibration points are required, as the responsiveness to conductivity decreases with increasing concentration of ammonium ions, causing poor linearity of the calibration curve. An IC system without cation suppression does not show this effect, resulting in accurate quantitation even with only a few calibration points. This article compares calibration curves created using a suppressor versus a non-suppressor system and introduces an example of measuring cations contained in industrial wastewater using no cation suppression.

Calibration curve with and without ion suppression

Figures 1 and 2 show calibration curves for quantification of ammonium ions over the concentration range of 0.5 to 20 mg/L by ion chromatography with and without ion suppression respectively.
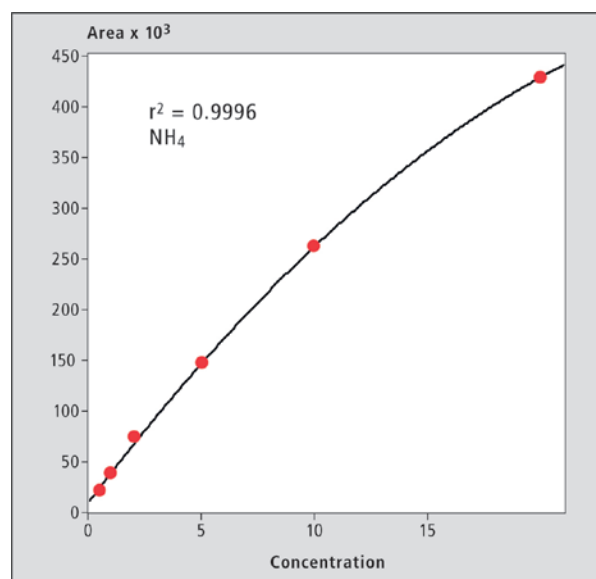

Figure 1: NH4 calibration curve obtained using an IC system with eluent suppression (Second-order approximation).
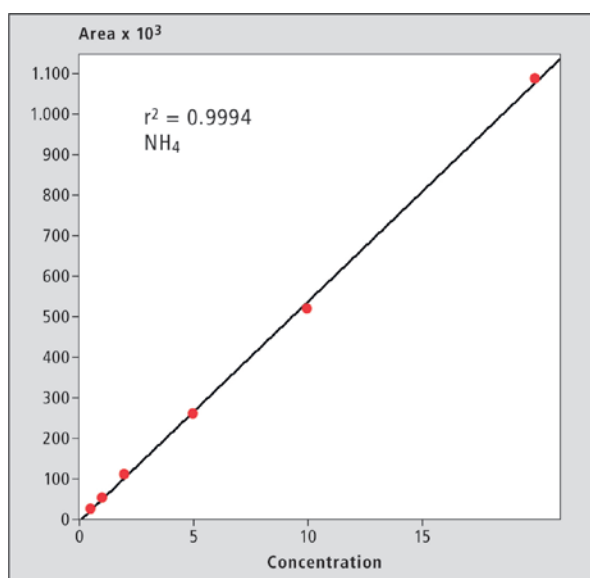

Figure 2: NH4 calibration curve obtained using an IC system without eluent suppression (First-order approximation).

Both graphs were created using the same analytical conditions as listed in table 1.

Table 1: Analytical conditions for NH4 standard determination.

Column	Shim-pack IC-C4 (150 x 4.6 mm)
Mobile phase	3 mmol/L methanesulfonic acid
Flow rate	1.0 mL/min
Column temperature	40 °C
Detection	Conductivity detector (CDD-10Avp)
Injection volume	50 µL

As can be seen from the two figures, the non-suppressor system (fig. 2) provided good linearity over the calibration range, while the curve obtained using ion suppression was non-linear (fig. 1).

When using the ion exchange suppressor, the eluent is converted into water with no pH buffering capacity, resulting in suppressed dissociation of target ions with increasing pH of the eluent flowing into the conductivity detector, along with an increase of ammonium ions. In other words, the equilibrium relationship expressed in equation 1 shifts to the left [1].

$$NH_3 + H_2O \rightleftharpoons NH_4 + OH^-$$

Hence, while the concentration of ammonium ions in the sample solution is increasing, the response of the conductivity detector is reduced, resulting in a non-linear calibration curve. This effect cannot be seen in the system without eluent suppression.

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 for reliable linear approximation.

Table 2: Analytical conditions for IC analysis of industrial wastewater.

Column	Shim-pack IC-C4 (150 x 4.6 mm)
Mobile phase	3 mmol/L methanesulfonic acid; 2 mmol/L 18-crown-6
Flow rate	1.0 mL/min
Column temperature	40 °C
Detection	Conductivity detector (CDD-10Avp)
Injection volume	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 an ion chromatography system without ion suppressor. As can be seen from the analytical conditions described in table 2, 2 mmol/L of 18-Crown-6 was added to the eluent to ensure adequate separation of sodium and ammonium ions. Quantitative results for cations found in the sample are listed in table 3; figure 3 shows the corresponding chromatogram. Good separation and accurate quantification were achieved even for samples containing significantly more sodium than ammonium ions.

Table 3: Quantitative results of cation analysis in industrial wastewater.

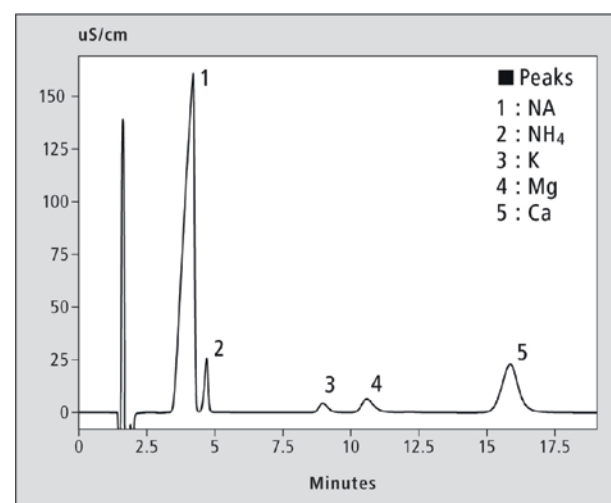| Peak ID	Ion ID	Concentration (mg/L)
1	Na	85.9
2	NH4	4.2
3	K	3.8
4	Mg	2.5
5	Ca	18.9

Figure 3: Typical chromatogram of IC analysis of industrial wastewater.

Method optimization for separation of ammonium ions

In the analysis of industrial wastewater, a point of concern is the interference of high concentrations of sodium ions compared to only trace amounts of ammonium ions and the proximity of their elution times. To optimize the method with regard to this separation, 18-Crown-6 was added to the eluent. Crown ethers are hollow, ring-shaped compounds comprising of carbon, hydrogen and oxygen and have an inclusive effect on certain cations such as ammonium and potassium ions due to the oxygen atoms located on their interior. They can selectively increase the retention of these cations due to strong interaction with the stationary phase.

However, since the retention time of potassium ions is more strongly affected than ammonium ions, a series of experiments was carried out, gradually increasing the quantity of 18-Crown-6 in the eluent, to determine optimum conditions for both analytes. Fig. 4 shows a conceptual graph of changes in elution behavior depending on the amount of crown ether added, and the diagram in fig. 5 plots concentration of 18-Crown-6 against retention time of the 6 cations in the mixture.

Conclusion

This article compared the usefulness of eluent suppression in the determination of NH_4 cations in industrial wastewater by ion chromatography. It also discussed method optimization by addition of 18-Crown-6 ether to the eluent to improve separation of NH_4^+ in the presence of interference by sodium ions. Good separation and accurate quantification were achieved, even for samples containing significantly more sodium than ammonium ions.

References

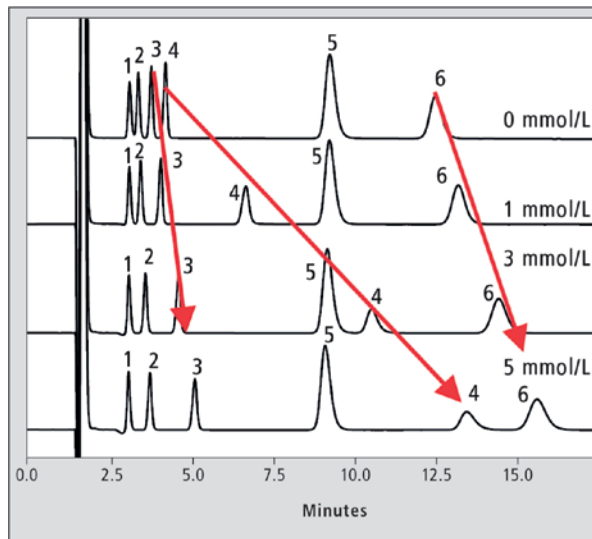[1] Application News No. L521, Shimadzu Corporation, 2017

Figure 4: Chromatograms showing the effect of 18-Crown-6 addition on retention of 1: Li, 2: Na, 3: NH4, 4: K, 5: Mg and 6: Ca ions.

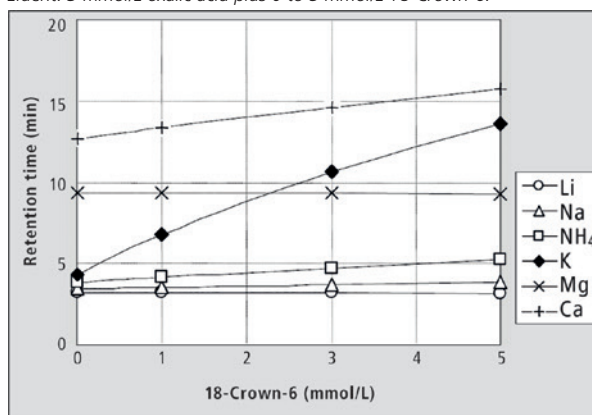Eluent: 3 mmol/L oxalic acid plus 0 to 5 mmol/L 18-Crown-6.

Figure 5: Graph visualizing the effect of 18-Crown-6 addition on retention of 1: Li, 2: Na, 3: NH4, 4: K, 5: Mg and 6: Ca ions.

Eluent: 3 mmol/L oxalic acid plus 0 to 5 mmol/L 18-Crown-6.

Biography

Dr. Gesa Johanna Schad graduated with a diploma in chemical engineering from the Technical University NTA in Isny, Germany in 2004 and an MSc in pharmaceutical analysis from the University of Strathclyde in Glasgow, UK in 2005. She worked until 2006 as a consultant in HPLC method development and validation in an analytical laboratory of the FAO/IAEA in Vienna, Austria. She gained her doctorate for research in pharmaceutical sciences at the University of Strathclyde in 2010 and was employed as a HPLC specialist in the R&D department at Hichrom Ltd. in Reading, UK from 2009. Since 2013, she has worked as a HPLC product specialist and since 2015 as HPLC Product Manager in the analytical business unit of Shimadzu Europa in Duisburg, Germany.

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