Application Note AN-S-403

Anions in lithium-ion battery solvents

Determination of anions in N-methylpyrrolidone (NMP) by ion chromatography (IC)

N-Methylpyrrolidone (also known as *N*-methyl-2-pyrrolidone or NMP) is an organic solvent used to make slurry in battery manufacturing and is a key raw material for the lithium-ion battery (LIB) industry. It serves as an effective solvent for electrode binders, such as polyvinylidene fluoride, which are essential for maintaining electrode stability [1,2]. NMP is completely removed during the manufacturing process and can be recycled efficiently [3]. Global demand for NMP is high and it accounts for a substantial percentage of lithium-ion battery manufacturing costs [4].

NMP impurity analysis is crucial to assess the

quality of both newly fabricated and recycled NMP. Ion chromatography (IC) with matrix elimination is a robust and reliable technique to quantify impurities in NMP in the µg/L range. Using this method, battery manufacturers can ensure the proper composition and electrochemical behavior of the electrolyte and evaluate Li-ion battery stability and safety.

Metrohm's intelligent Preconcentration Technique with Matrix Elimination (MiPCT-ME) quantifies **anions in *N*-methyl pyrrolidone** down to the **µg/L range** without sample treatment or dilution steps

SAMPLE AND SAMPLE PREPARATION

A volume of 500 L NMP was directly injected into the preconcentration column (PCC) of the IC without any treatment using an 800 Dosino (807 Dosing Unit 5 mL). The PCC, which is installed in place of a sample loop, captures the target ions and enables matrix removal. This allows trace analysis of anions even in complex matrices.

The application was carried out using a 930 Compact IC Flex with MiPCT-ME and a fixed injection volume of 500 L (preconcentration volume). A volume of 1.5 mL ultrapure water (UPW) was used for rinsing the PCC to remove the matrix. For further experimental details, see **Table 1**.

The IC system setup is schematically shown in **Figure 1**. Calibration ranged from 5 to 100 g/L, prepared as mixed standards containing fluoride, chloride, nitrite, bromide, nitrate, phosphate, and sulfate. To guarantee comparability, standards were injected via the PCC as well.

Table 1. IC parameters used for the determination of anion impurities in N-methylpyrrolidone.

Parameter	Setting
Detection	Conductivity
Column	Metrosep A Supp 7 - 250/4.0
Preconcentration column	Metrosep A PCC 2 HC/4.0
Injection volume	500 L
Temperature	45 °C
Eluent	3.2 mmol/L Na_2CO_3 + 1.0 mmol/L $NaHCO_3$
Suppression	Sequential suppression
Regenerant	100 mmol/L H_2SO_4
Flow	0.7 mL/min

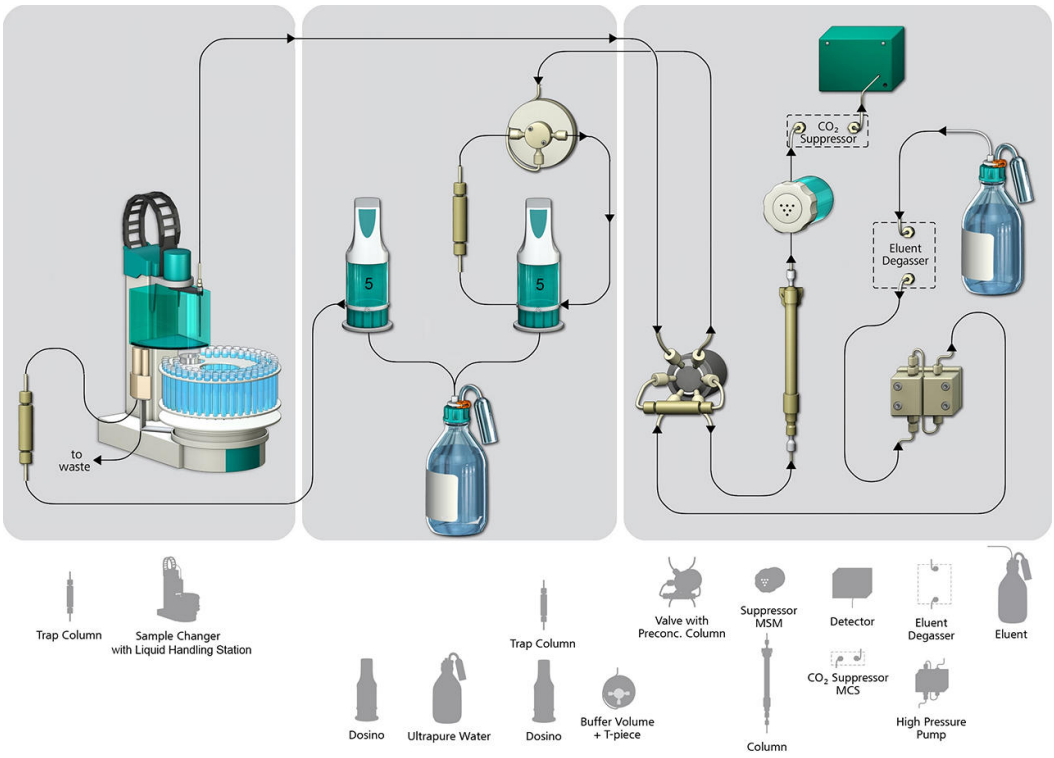

Figure 1. Flow path of the 930 Compact IC Flex system with MiPCT-ME. The preconcentration column Metrosep A PCC 2 HC/4.0 is used at the loop position of the injection valve to bind the analytes and eliminate the matrix. One Dosino is responsible for sample handling (i.e., sample transport to the PCC). The other Dosino fills the rinsing station with fresh ultrapure water that is used to rinse the PCC, thereby removing the matrix. Trap columns are installed to ensure ultrapure water purity. The system can also be set up with only one Dosino for both tasks. After matrix removal, the preconcentrated sample is injected onto the analytical column and subsequently analyzed by sequentially suppressed conductivity detection.

RESULTS

Anions were separated and eluted from the Metrosep A Supp 7 column in less than 34 minutes under isocratic conditions. Concentrations ranged from 1176 g/L.

The undiluted NMP sample was measured both unspiked and spiked with 30 g/L standard ions, reaching a recovery of 90120 % even for the very low concentrated ions (**Table 2**).

Figure 2 shows the separation of anions in NMP. Baseline separation is achieved for the indicated anions. The chromatogram shows two early eluting peaks which were not identified. Most likely these peaks account for acetate and formate showing the **enormous potential** for further development and thereby allowing **quantification of other relevant anions**.

Table 2. Results for anion determination in NMP. The samples were measured in both spiked and unspiked forms and the recovery was calculated from the determined concentrations.

Analyte	NMP unspiked (g/L)	Spike (g/L)	NMP spiked (g/L)	Recovery (%)
Fluoride	48.94	30	80.23	104.3
Chloride	74.5	30	102.83	94.3
Nitrite	76.31	30	103.35	90.1
Bromide	<1	30	27.89	93.0
Nitrate	28.99	30	58.87	99.6
Phosphate	11.21	30	47.04	119.4
Sulfate	15.55	30	43.65	93.7

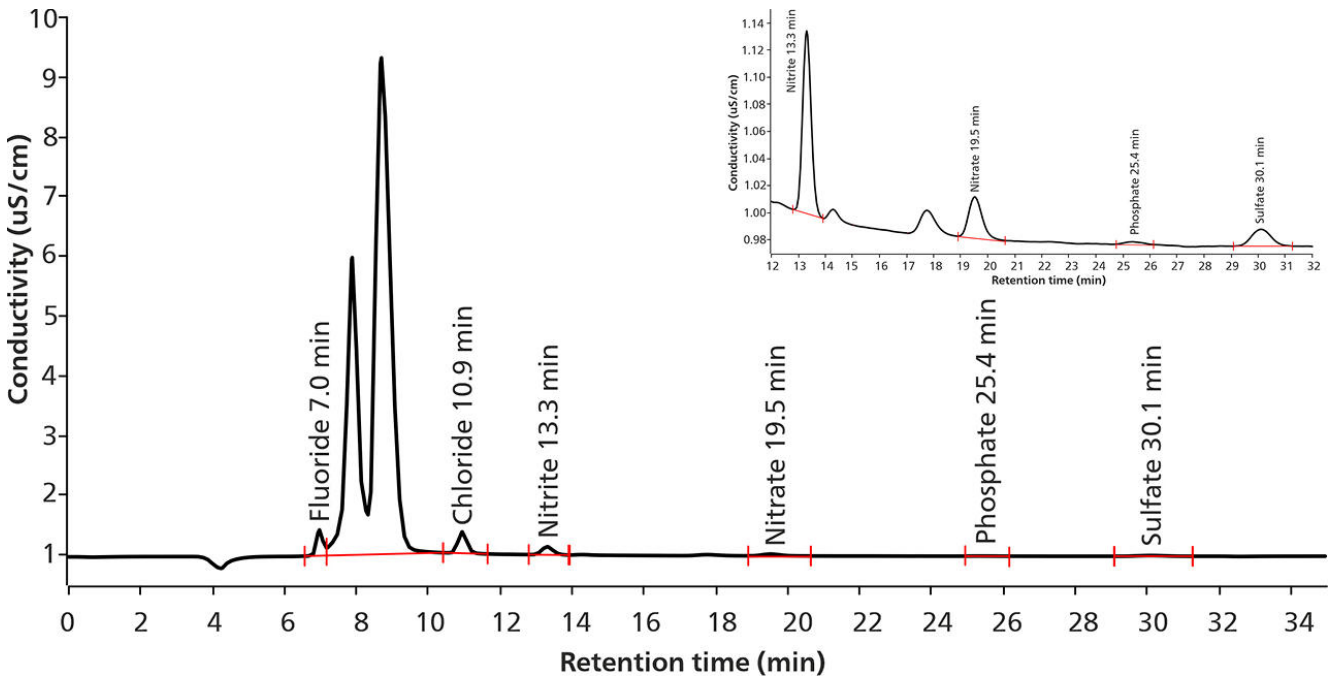

Figure 2. Chromatogram of major anions in an NMP sample separated with the Metrosep A Supp 7 - 250/4.0 (carbonate eluent) using MiPCT-ME for preconcentration and matrix elimination purposes. Detection was performed using sequentially suppressed conductivity.

The concentrations of the measured anions in **NMP** range from 11 to 76 g/L. Such low analyte concentrations in combination with an interfering matrix can be challenging for chromatography. **Metrohm MiPCT-ME** is capable of **measuring trace anions** in a widely used solvent of the **lithium battery manufacturing process**. This analytical technique can make a major contribution to **guarantee the quality, lifetime, and safety of lithium batteries**.

The method can easily be transferred to other relevant solvents like methanol, ethanol, acetone, and 2propanol.

REFERENCES

1. Yue, M.; Azam, S.; Zhang, N.; et al. Residual NMP and Its Impacts on Performance of Lithium-Ion Cells. *J. Electrochem. Soc.* **2024**, *171* (5), 050515. DOI:10.1149/1945-7111/ad4396
2. *The role of NMP in the production process of lithium batteries - Shenyang East Chemical Science-Tech Co., Ltd.(ES CHEM Co.,Ltd)*. https://www.eschemy.com/news/the-role-of-nmp-in-the-production-process-of-lithium-batteries (accessed 2024-08-16).
3. Darcel, C. *What is NMP Solvent?*. https://www.maratek.com/blog/what-is-nmp-solvent (accessed 2024-08-16).
4. The Advanced Rechargeable & Lithium Batteries Association. Recommendation about N-Methyl-Pyrrolidone (NMP; CAS No. 872-50-4) Proposal for Inclusion in Annex XIV for Authorization, 2017.

CONTACT

143-0006 6-1-1
null 9
metrohm.jp@metrohm.jp

CONFIGURATION

930 Compact IC Flex Oven/SeS/PP/Deg

930 IC Flex Oven/SeS/PP/Deg IC

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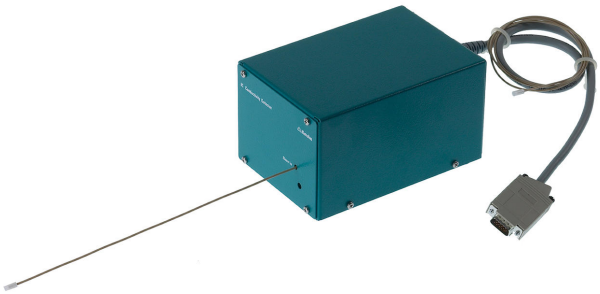

IC Conductivity Detector

IC DSP (Digital Signal Processing) ()

858 Professional Sample Processor

858 500 L500 mL850 IC 800

Metrosep A Supp 7 - 250/4.0

() (EPA 300.1 Part BEPA 317.0EPA 326.0)

Metrosep A Supp 7 - 250/4.0 g/L 5-m

Metrosep A PCC 2 HC/4.0

PEEK

800 Dosino

800 Dosino (150 cm)