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 µL 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.

EXPERIMENTAL

The application was carried out using a 930 Compact IC Flex with MiPCT-ME and a fixed injection volume of 500 µL (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 µg/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 µL
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

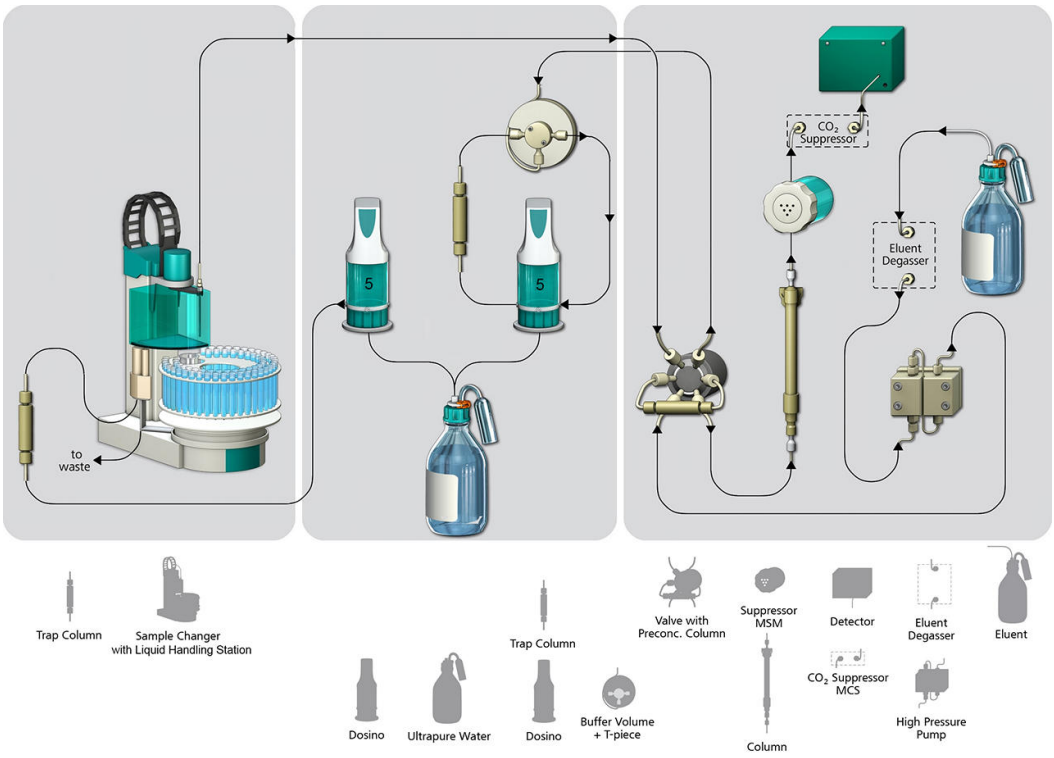

Figure 1. Flow path of the 930 Compact IC Flex system with MiPCT-ME. The preconcentration column Metrosep A PCC 2 HC/4.0 is used at the loop position of the injection valve to bind the analytes and eliminate the matrix. One Dosino is responsible for sample handling (i.e., sample transport to the PCC). 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 11–76 µg/L.

The undiluted NMP sample was measured both unspiked and spiked with 30 µg/L standard ions, reaching a recovery of 90–120 % 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 (µg/L)	Spike (µg/L)	NMP spiked (µg/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

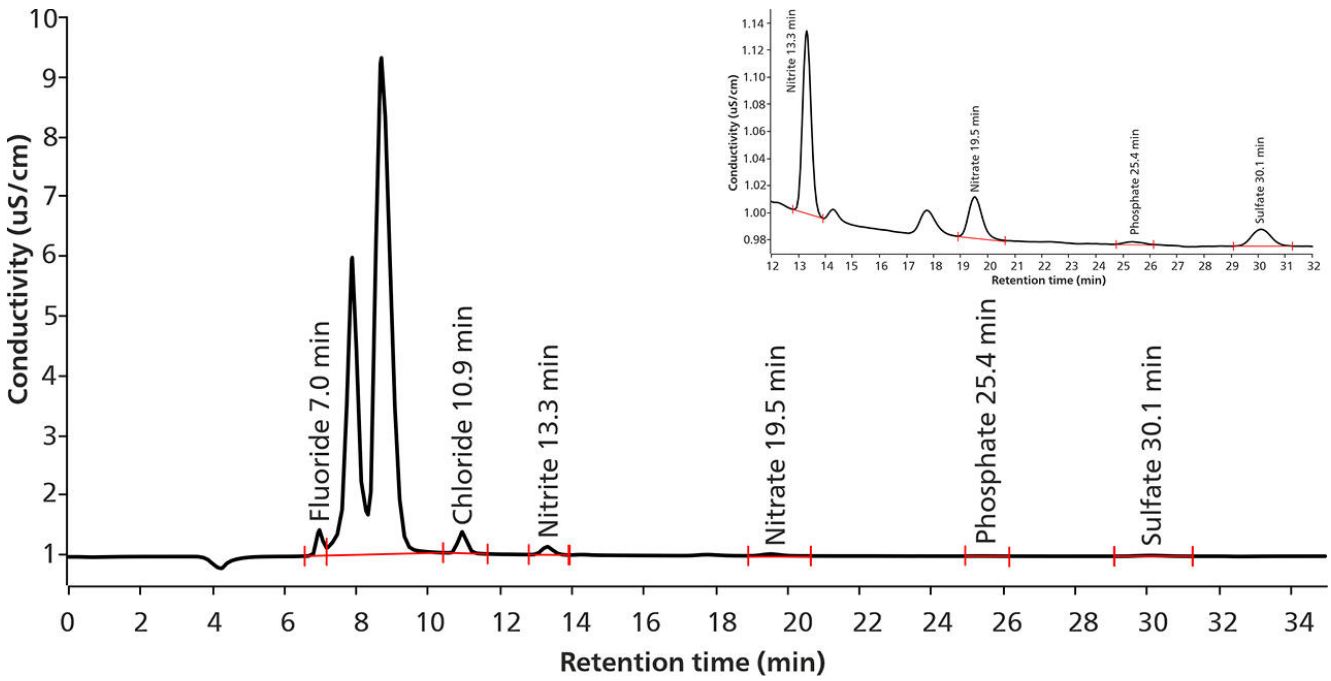

Figure 2. Chromatogram of major anions in an NMP sample separated with the Metrosep A Supp 7 - 250/4.0 (carbonate eluent) using MiPCT-ME for preconcentration and matrix elimination purposes. Detection was performed using sequentially suppressed conductivity.

CONCLUSION

The concentrations of the measured anions in NMP range from 11 to 76 µg/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 2-propanol.

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.

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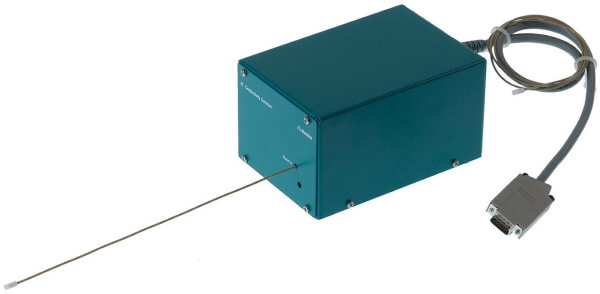
CONFIGURATION

930 Compact IC Flex Oven/SeS/PP/Deg

The 930 Compact IC Flex Oven/SeS/PP/Deg is the intelligent Compact IC instrument with **column oven**, **sequential suppression**, **peristaltic pump** for suppressor regeneration and built-in **degasser**. The instrument can be used with any separation and detection methods.

Typical areas of application:

- Anion or cation determinations with sequential suppression and conductivity detection



IC Conductivity Detector

Compact and intelligent high performance conductivity detector for intelligent IC instruments. Outstanding temperature stability, the complete signal processing within the protected detector block and the latest generation of DSP – Digital Signal Processing – guarantee the highest precision of the measurement. No change of measuring ranges (not even automatic ones) is required, due to the dynamic working range.

858 Professional Sample Processor

The 858 Professional Sample Processor processes samples from 500 µL to 500 mL. The sample transfer takes place either by means of a peristaltic pump on the 850 Professional IC system or with an 800 Dosino.

Metrosep A Supp 7 - 250/4.0

Disinfection byproducts from water treatment are suspected not only of being health hazards but even of being carcinogenic. Oxyhalides have therefore become the subject of many investigations and standards (e.g., EPA 300.1 Part B, EPA 317.0, EPA 326.0). Of primary concern is bromate, which forms from bromide during the ozonization of drinking water. The Metrosep A Supp 7 - 250/4.0 is a high-performance separation column for the parallel determination of standard anions, oxohalides and dichloroacetic acid. With this column, these ions are determined with certainty and precision down to the lower µg/L range. The high detection sensitivity is achieved through the use of the 5 µm polyvinyl alcohol polymer, with which extremely high plate numbers and thus outstanding separation and detection properties are achieved. In addition, the separation can be adapted to the specific requirements of the application by modifying the temperature.

Metrosep A PCC 2 HC/4.0

For anion preconcentration and matrix elimination. The enlargement of the packing bed increases the capacity of the two preconcentration columns completely made of PEEK. The high capacity is required primarily when matrix effects might cause an overloading of the preconcentration column or when samples with high ionic strength are to be analyzed.

800 Dosino (cable: 1.5 m)

The 800 Dosino is a drive with write/read hardware for intelligent dosing units. With permanently attached cable (length 1.5 m).