



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 ₂ CO ₃ + 1.0 mmol/L NaHCO ₃
Suppression	Sequential suppression
Regenerant	100 mmol/L H ₂ SO ₄
Flow	0.7 mL/min

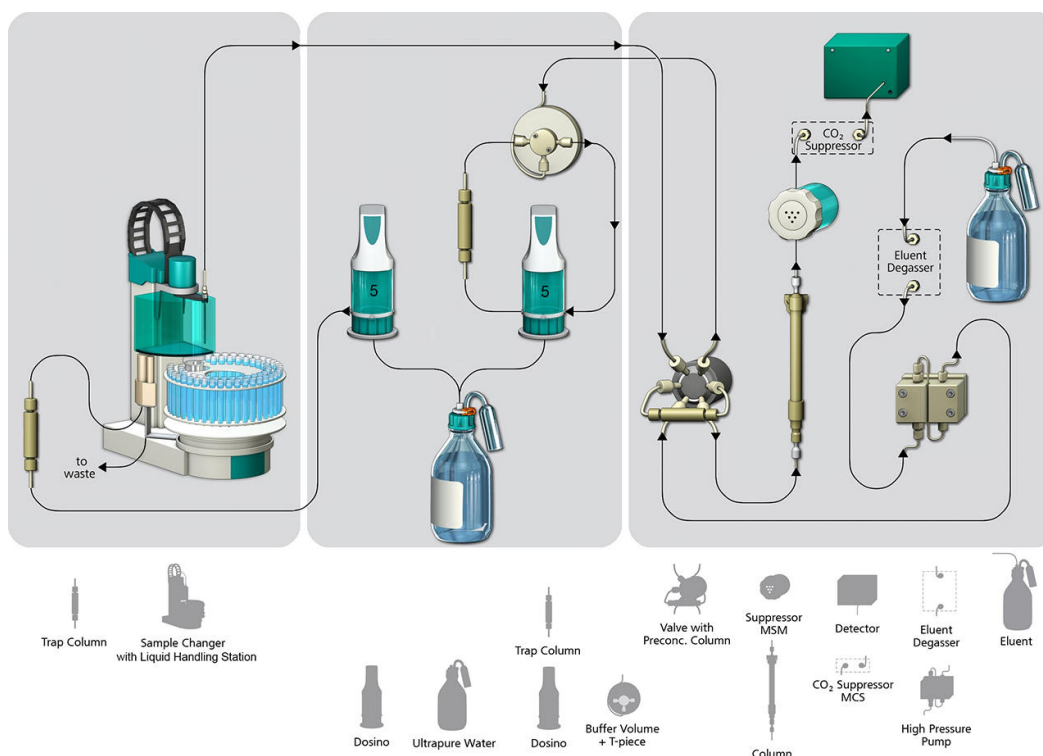


Figure 1. Flow path of the 930 Compact IC Flex system with MiPCT-ME. The preconcentration column Metrosep A PCC 2 HC/4.0 is used at the loop position of the injection valve to bind the analytes and eliminate the matrix. One Dosino is responsible for sample handling (i.e., sample transport to the PCC).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

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

RESULTS

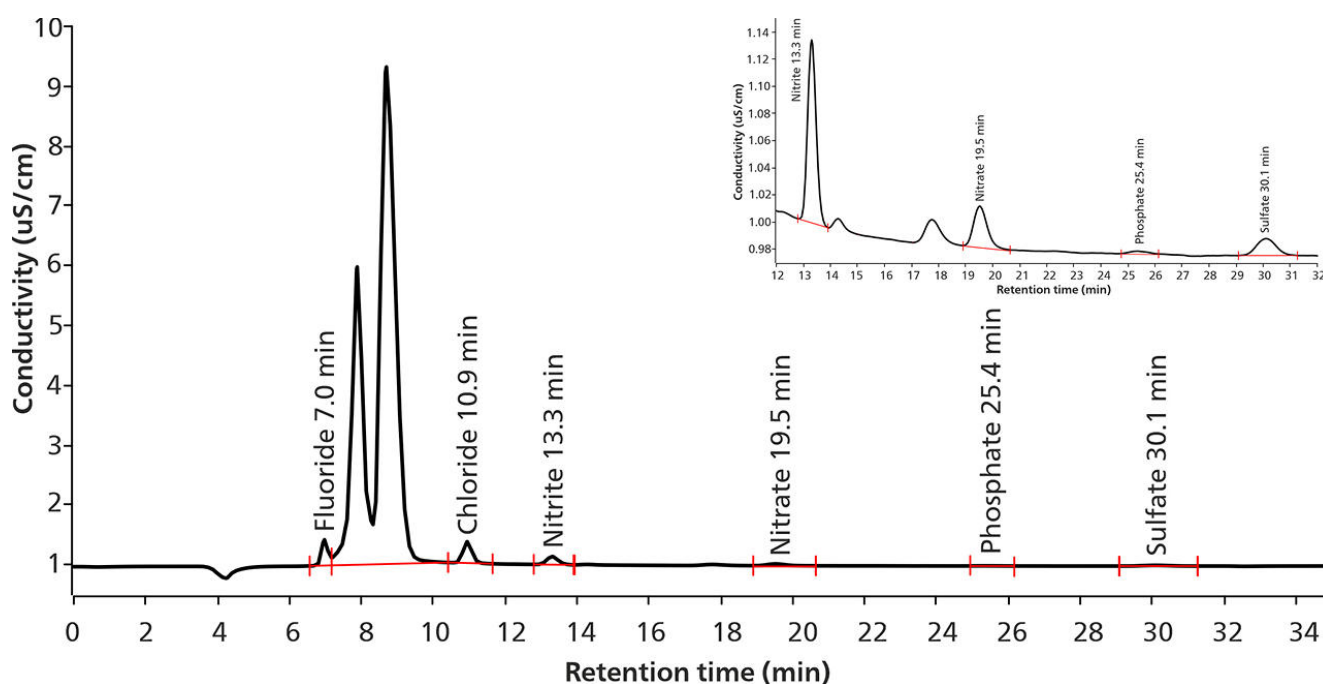


Figure 2. Chromatogram of major anions in an NMP sample separated with the Metrosep A Supp 7 - 250/4.0 (carbonate eluent) using MiPCT-ME for preconcentration and matrix elimination purposes. Detection was performed using sequentially suppressed conductivity.

The concentrations of the measured anions in NMP range from 11 to 76 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

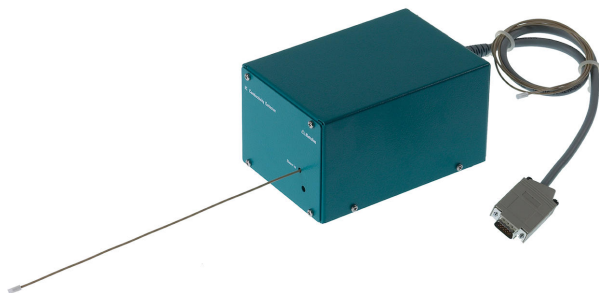


930 Compact IC Flex Oven/SeS/PP/Deg

Le 930 Compact IC Flex Oven/SeS/PP/Deg est un appareil CI compact intelligent avec un **four à colonne**, **suppression séquentielle**, une **pompe péristaltique** pour la régénération du supprimeur et un **dégazeur** intégré. L'appareil peut être utilisé avec n'importe quelles méthodes de séparation et de détection.

Domaines d'application typiques :

- Déterminations d'anions ou de cations avec suppression séquentielle et détection de conductivité



IC Conductivity Detector

Détecteur de conductivité haute performance compact et intelligent destiné aux appareils CI intelligents. Excellente constance de la température, tout le traitement du signal au sein du bloc de détecteur protégé et DSP – Digital Signal Processing – de la dernière génération garantissent une précision de mesure optimale. Grâce à la plage de travail dynamique, aucun changement de plage n'est nécessaire (même automatique).



858 Professional Sample Processor

Le 858 Professional Sample Processor traite des échantillons de 500 µL à 500 mL. Le transfert des échantillons s'opère soit au moyen de la pompe péristaltique au 850 Professional IC System soit par un 800 Dosino.



Metrosep A Supp 7 - 250/4.0

Les produits secondaires du traitement de l'eau (disinfection by-products) sont soupçonnés d'être non seulement nocifs pour la santé, mais aussi cancérigènes. C'est la raison pour laquelle les oxohalogénures sont devenus l'objet de nombreuses recherches et de normes (p. ex. EPA 300.1 partie B, EPA 317.0, EPA 326.0). Il s'agit en premier lieu du bromate, produit du bromure lors de l'ozonisation de l'eau potable. La colonne Metrosep A Supp 7 - 250/4.0 est une colonne de séparation haute performance pour la détermination en parallèle des anions standard, des oxyhalogénures et de l'acide dichloracétique. Avec cette colonne, ces ions peuvent être déterminés jusque dans la gamme inférieure des µg/L de manière sûre et précise. La sensibilité de détection élevée est atteinte par l'utilisation d'un polymère à base d'alcool polyvinylique de 5 µm, permettant d'obtenir un nombre de plateaux très élevé et, par conséquent, d'excellentes propriétés de séparation et de détection. En plus, par modification de la température, il est possible d'adapter la séparation aux exigences spécifiques de l'application.



Metrosep A PCC 2 HC/4.0

Pour la préconcentration des anions et l'élimination de la matrice. L'agrandissement du lit de matériau permet d'augmenter la capacité des deux colonnes de préconcentration totalement fabriquées en PEEK. Cette haute capacité est surtout requise lorsque les effets de matrice pourraient provoquer une surcharge de la colonne de préconcentration ou que des échantillons de force ionique élevée doivent être analysés.



800 Dosino

Le Dosino 800 est un moteur de burette avec système de lecture/écriture pour les Unités de distribution intelligentes. Avec câble attenant (150 cm).