Application Note AN-S-403

锂离子电池溶剂中的阴离子

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

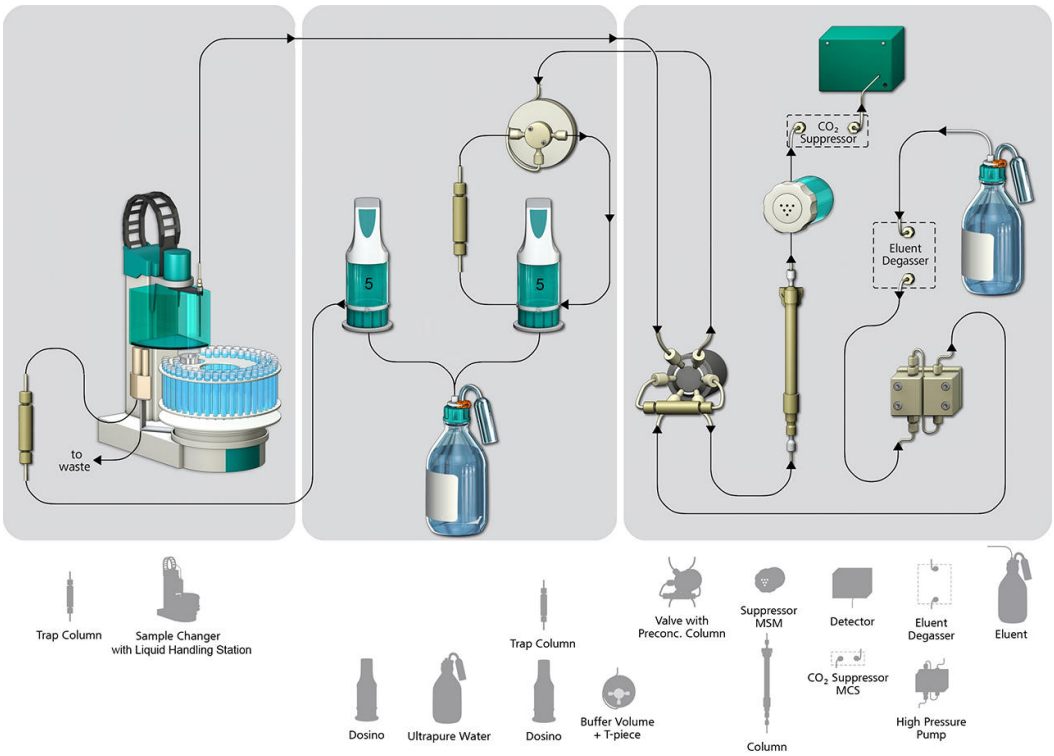

Figure 1. Flow path of the 930 Compact IC Flex system with MiPCT-ME. The preconcentration column Metrosep A PCC 2 HC/4.0 is used at the loop position of the injection valve to bind the analytes and eliminate the matrix. One Dosino is responsible for sample handling (i.e., sample transport to the PCC). 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 1176 µg/L.

The undiluted NMP sample was measured both unspiked and spiked with 30 µg/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 (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

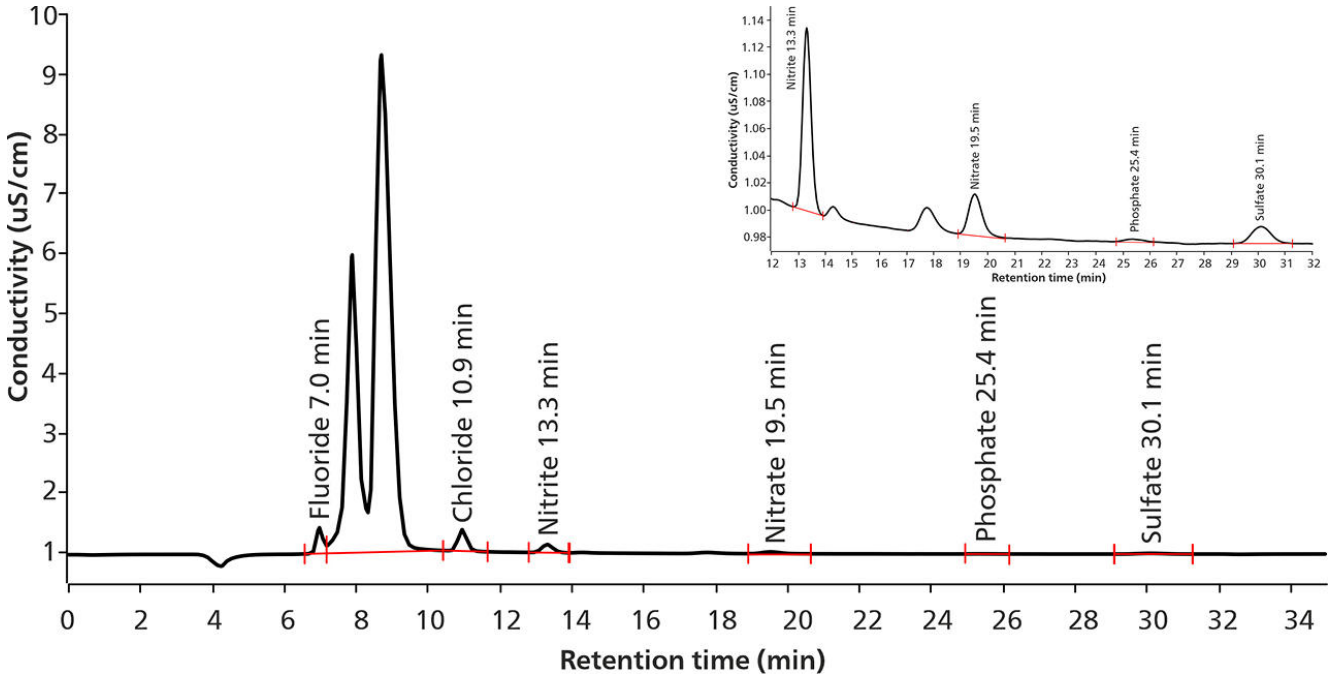

Figure 2. Chromatogram of major anions in an NMP sample separated with the Metrosep A Supp 7 - 250/4.0 (carbonate eluent) using MiPCT-ME for preconcentration and matrix elimination purposes. Detection was performed using sequentially suppressed conductivity.

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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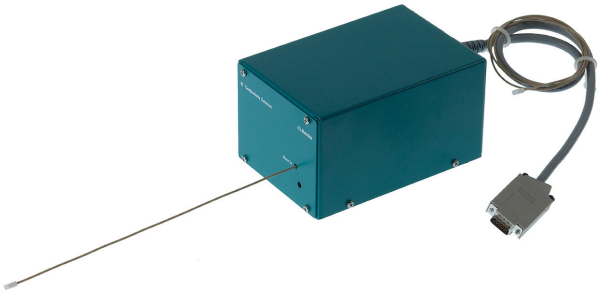
CONFIGURATION

930 Compact IC Flex Oven/SeS/PP/Deg

930 Compact IC Flex Oven/SeS/PP/Deg 是智能型 Compact 离子色谱仪器,带有**柱加热炉**、**序列抑制**和**蠕动泵**用于抑制器再生,以及内置的**脱气装置**。该仪器可使用各种分离和检测方法。

典型的应用范围:

- 阴离子或阳离子测定,序列抑制法及电导检测



IC Conductivity Detector

用于智能型离子色谱仪的紧凑智能型高性能电导检测器。不凡的温度稳定性,受保护的检测器端子板内的整个信号处理过程以及新一代的 DSP(数字式信号处理)均能确保测量的准确性。归功于动态工作范围,无需进行范围变更(也不是自动进行)。

858 Professional Sample Processor

858 Professional Sample Processor 可处理体积在 500 µL 至 500 mL 之间的样品。进行样品转移时,既可以使用 850 Professional IC System 上的蠕动泵、也可通过 800 Dosino 来进行。

Metrosep A Supp 7 - 250/4.0

水处理中的副产物(消毒副产物)不仅可能危害健康,甚至可能致癌。因此羰基卤化物成为许多检测方法及标准的目标(例如 EPA 300.1 方法 B 部分、EPA 方法 317.0、EPA 方法 326.0)。首先针对那些饮用水臭氧化过程中由溴化物中产生的溴酸盐。Metrosep A Supp 7 - 250/4.0 是可以同时测定标准阴离子、羰基卤化物和二氯乙酸的高效分离柱。借助此柱甚至在低 µg/L 范围内也可准确可靠地测定这些离子。使用 5 µm 的聚乙烯醇聚合物使其达到高度指示灵敏度,其分离度高,由此实现优秀的分离性能和指示灵敏度。此外,还可通过更改温度来针对特殊应用要求调整分离工作。

Metrosep A PCC 2 HC/4.0

用于阴离子富集和基质消除。 加大型填充床可提高两根富集柱(由 PEEK 制成)的容量。 其高容量主要用于基体效应会导致预富集柱过载或需要对高离子强度的样品进行分析的情况。

800 Dosino (1.5 m)

800 Dosino 是一种带有智能型配液单元读写硬件的驱动装置。配有固定安装的电缆(长度 1.5 m)。