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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.

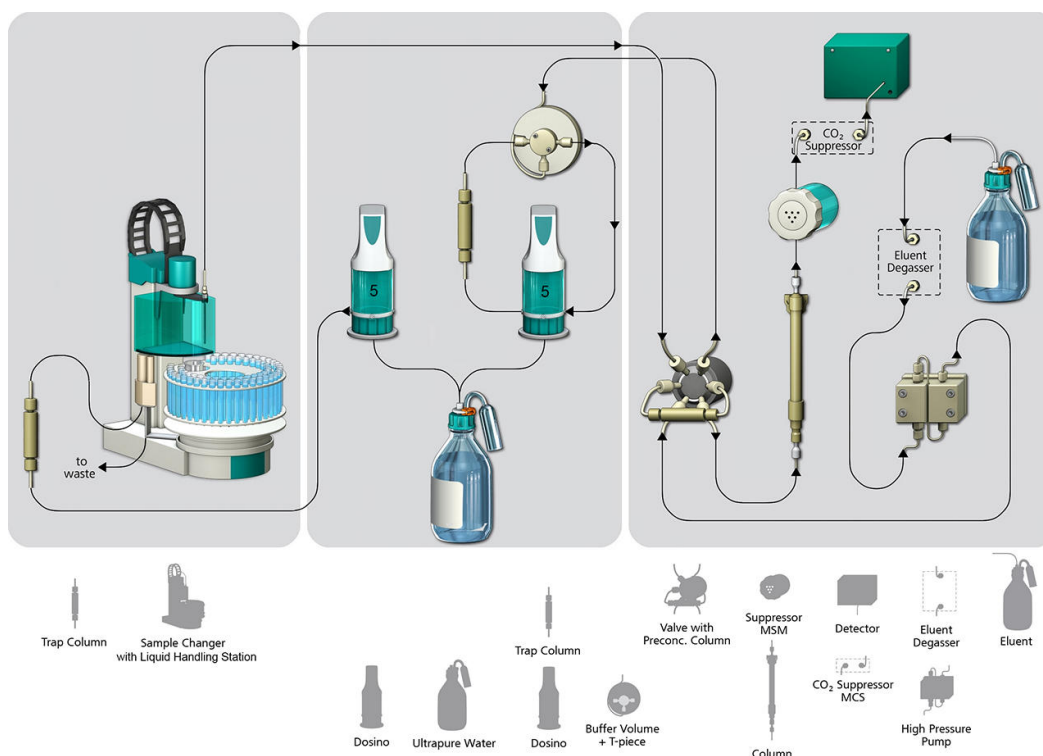| Parameter	Setting
Detection	Conductivity
Column	Metrosep A Supp 7 - 250/4.0
Preconcentration column	Metrosep A PCC 2 HC/4.0
Injection volume	500 µL
Temperature	45 °C
Eluent	3.2 mmol/L Na_2CO_3 + 1.0 mmol/L $NaHCO_3$
Suppression	Sequential suppression
Regenerant	100 mmol/L H_2SO_4
Flow	0.7 mL/min

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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**.

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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.

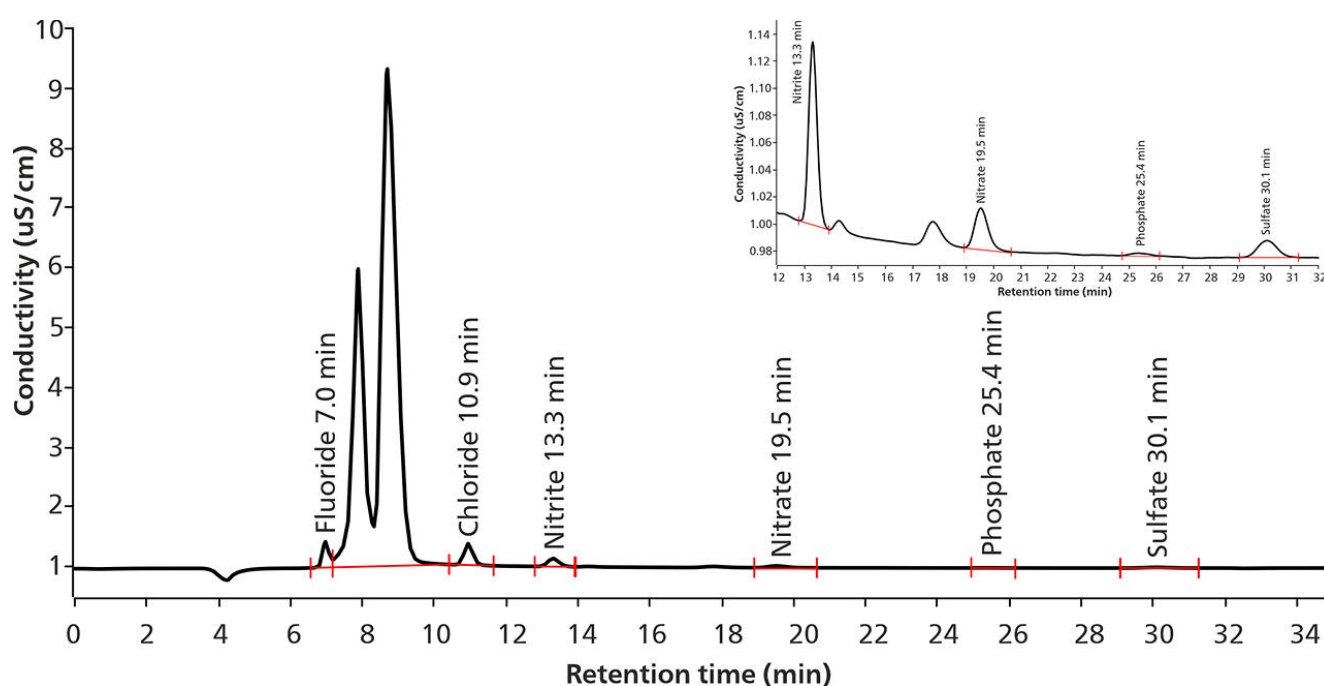| Analyte	NMP unspiked (µg/L)	Spike (µg/L)	NMP spiked (µg/L)	Recovery (%)
Fluoride	48.94	30	80.23	104.3
Chloride	74.5	30	102.83	94.3
Nitrite	76.31	30	103.35	90.1
Bromide	<1	30	27.89	93.0
Nitrate	28.99	30	58.87	99.6
Phosphate	11.21	30	47.04	119.4
Sulfate	15.55	30	43.65	93.7

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.

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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

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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).

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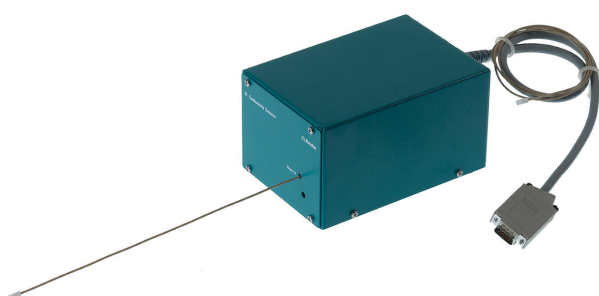1号楼7702
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CONFIGURATION

930 Compact IC Flex Oven/SeS/PP/Deg

930 Compact IC Flex Oven/SeS/PP/Deg 是智能型 Compact 子色器,有**柱加炉**、**序列抑制**和**蠕**用于抑制器再生,以及内置的**脱气装置**。器可使用各分和方法。典型的用范:

- 子或子定,序列抑制法及

IC Conductivity Detector

用于智能型子色的智能型高性能器。不凡的温度定性,受保的器端子板内的整个信号理程以及新一代的 DSP(数字式信号理)均能保量的准性。功于工作范,无需行范更(也不是自行)。

858 Professional Sample Processor

858 Professional Sample Processor 可理体在500 μL 至 500 mL 之的品。行品移,既可以使用 850 Professional IC System 上的蠕、也可通 800 Dosino 来行。

Metrosep A Supp 7 - 250/4.0

水理中的副物(消毒副物)不可能危害健康,甚至可能致癌。因此基化物成多方法及准的目(例如 EPA 300.1 方法 B 部分、EPA 方法 317.0、EPA 方法 326.0)。首先那些用水臭化程中由化物中生的酸。Metrosep A Supp 7 - 250/4.0 是可以同定准子、基化物和二乙酸的高效分柱。借助此柱甚至在低 μg/L 范内也可准可靠地定些子。使用 5 μm 的聚乙醇聚合物使其到高度指示敏度,其分度高,由此秀的分性能和指示敏度。此外,可通更改温度来特殊用要求整分工作。

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Metrosep A PCC 2 HC/4.0

用于子富集和基消除。 加大型填充床可提高根富集柱
(由 PEEK 制成)的容量。 其高容量主要用于基体效会
致富集柱或需要高子度的品行分析的情况。

800 Dosino

800 Dosino ,有可用于智能型加液元的/写硬件。 固
定。

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