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

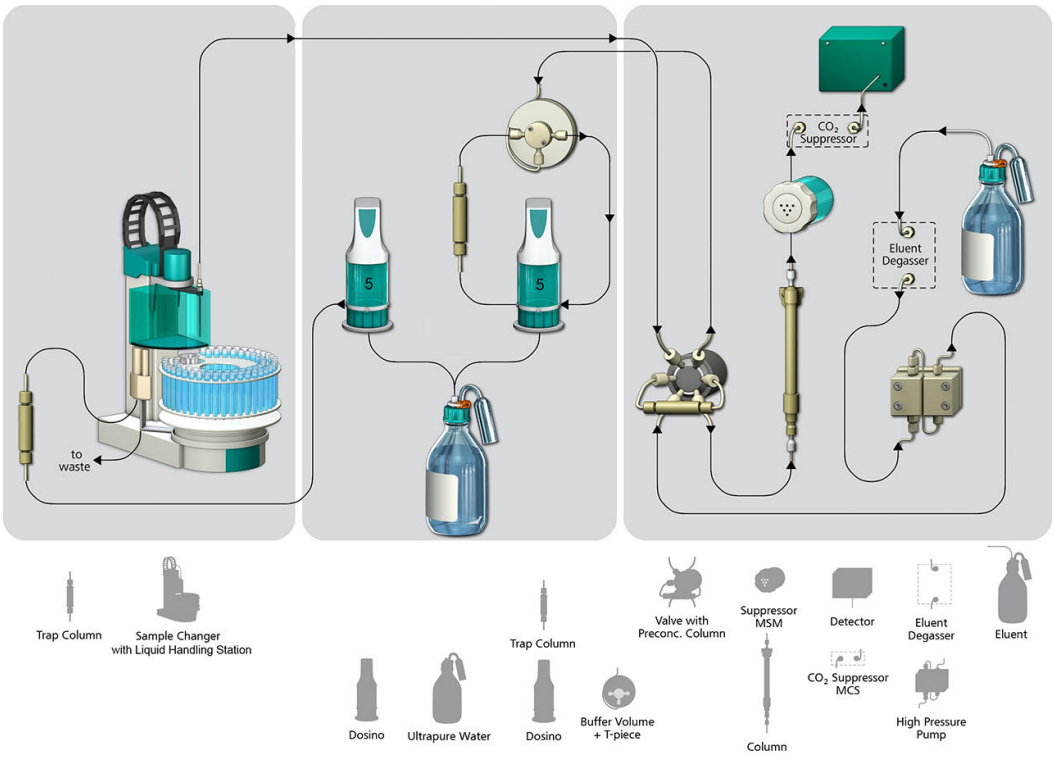

Figure 1. Flow path of the 930 Compact IC Flex system with MiPCT-ME. The preconcentration column Metrosep A PCC 2 HC/4.0 is used at the loop position of the injection valve to bind the analytes and eliminate the matrix. One Dosino is responsible for sample handling (i.e., sample transport to the PCC).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

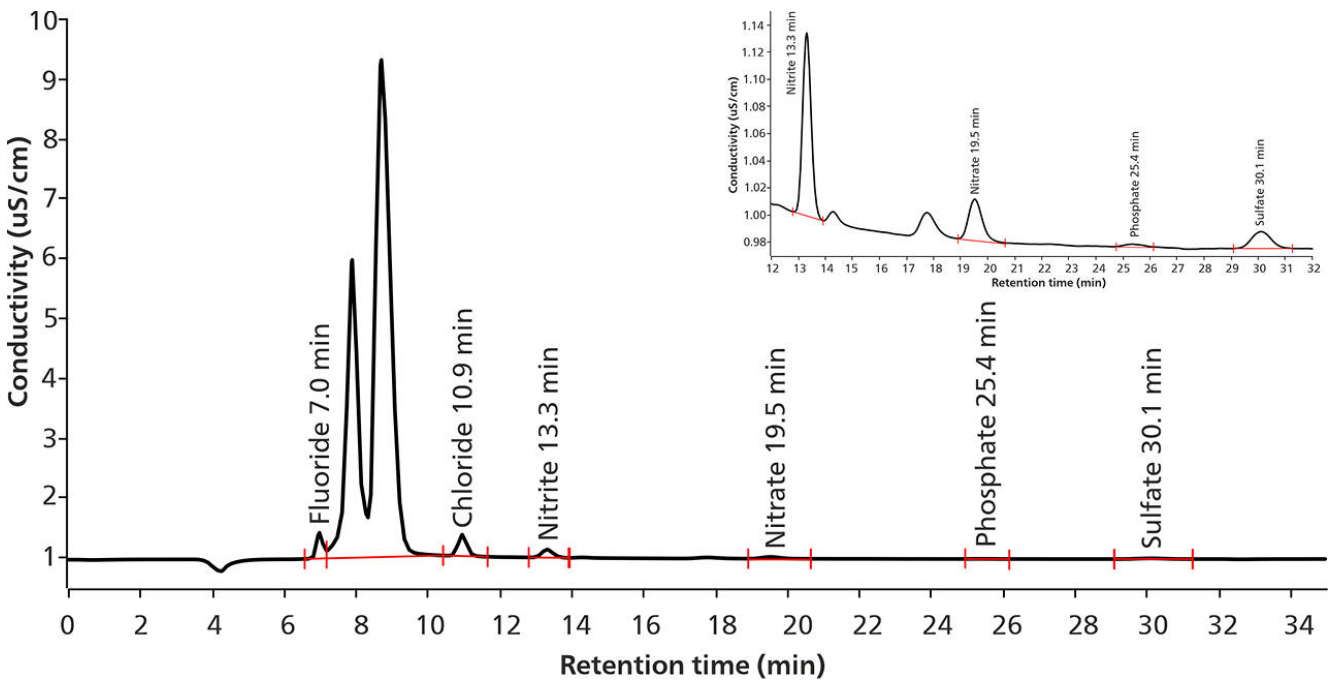

Figure 2. Chromatogram of major anions in an NMP sample separated with the Metrosep A Supp 7 - 250/4.0 (carbonate eluent) using MiPCT-ME for preconcentration and matrix elimination purposes. Detection was performed using sequentially suppressed conductivity.

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.

CONTACT

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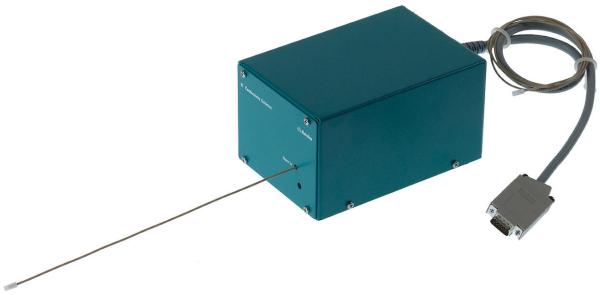
CONFIGURATION

930 Compact IC Flex Oven/SeS/PP/Deg

930 コンパクト IC Flex Oven/SeS/PP/Deg は**カラムオーブン**、**連続サプレッション**、サプレッサー再生のための**ペリスタリックポンプ**、内蔵式**脱気装置**を備えたインテリジェントコンパクトIC装置です。この装置は任意の分離メソッドおよび検出メソッドによって使用することができます。

典型的な使用領域:

- 連続サプレッションおよび電気伝導度検出器による陰イオンの測定



IC Conductivity Detector

インテリジェントIC装置のためのコンパクトかつインテリジェントな高出力電気伝導度検出器。 優れた温度安定性、保護された検出器ブロック内の総合的な信号処理、最新版のDSP (Digital Signal Processing) が高精度の測定を保証します。稼動範囲がダイナミックなので測定範囲の変更は(自動のものも含めて)必要ありません。

858 Professional Sample Processor

858 プロフェッショナルサンプルプロセッサは、500 µLから500 mLまでのサンプルを処理します。サンプルは850 プロフェッショナル IC システム のペリスタリックポンプまたは800 ドジーノ電動ビュレットを使用することによって転送されます。

Metrosep A Supp 7 - 250/4.0

水処理における副産物 (消毒副産物) は、健康を害するだけではなく発がん性も疑われています。そのため、オキシハライドは、多くの調査や規格の対象となっています (例えば EPA 300.1 Part B、EPA 317.0、EPA 326.0 など) 。その際、何よりも問題となっているのは、飲料水をオゾン処理する際に臭化物から生成される臭素酸塩です。Metrosep A Supp 7 - 250/4.0は、標準陰イオン、オキシハライドおよびジクロロ酢酸の並行測定に高性能を発揮する分離カラムです。このカラムを用いることで、これらのイオンを µg/L の低い範囲まで、確実かつ精密に測定できます。5-µm ポリビニルアルコール・ポリマーを使用することで、検出感度が高まり、極端に高い理論段数を示し、その結果傑出した分離特性および検出特性を実現することができます。さらに、温度変化によって、アプリケーション特有の条件に分離を順応させることができます。

Metrosep A PCC 2 HC/4.0

陰イオン濃縮ならびにマトリックス除去用です。 充填ベッドの拡大は、PEEK 製両濃縮カラムの容量を増大します。 特にマトリックス効果が濃縮カラムの過負荷となる場合、あるいはサンプルを高度のイオン強度で解析するべき場合に、大きな容量が必要となります。

800 Dosino

800 Dosino 高機能電動ビュレットのドージングユニット用書き込み・読み取り用ハードウェア付き駆動部。固定されたケーブル付き (長さ150 cm)。