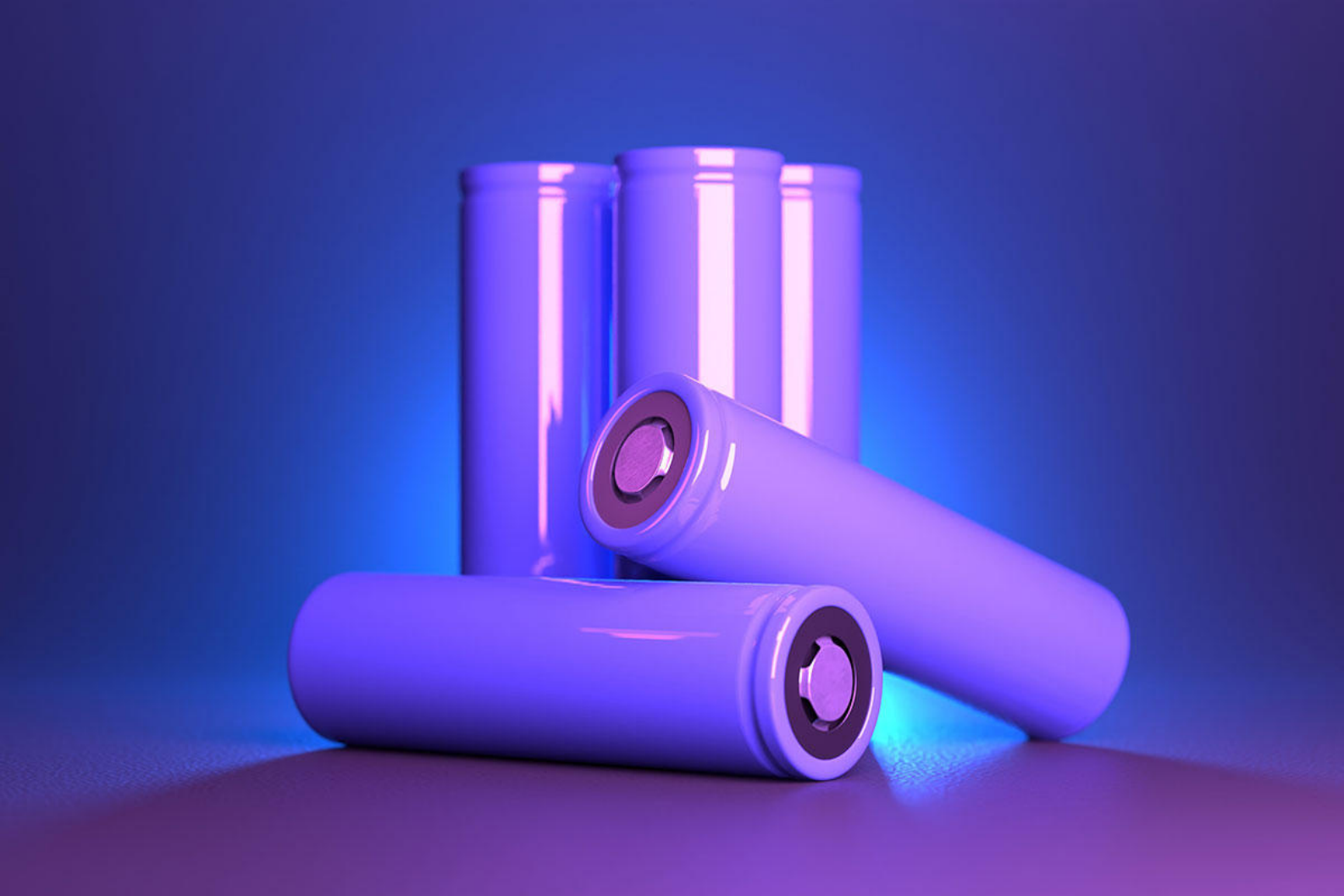




Application Note AN-S-372

Analysis of Li-ion battery electrolytes with ion chromatography

SUMMARY

In the next decade, our reliance on batteries is predicted to increase five-fold [1]. Lithium-ion (Li-ion) batteries (LIBs) dominate the current market. LIBs operate by moving electrons from an anode to a cathode (discharging) and back (charging). The Li ions from the liquid electrolyte balance this flow [2].

Consequently, the lithium battery electrolyte composition is crucial for the performance and lifetime of the battery [3,4]. Li electrolytes are mostly

composed of lithium hexafluorophosphate (LiPF_6) or lithium difluorophosphate (LiPO_2F_2) dissolved in organic carbonates. The content of LiPF_6 or LiPO_2F_2 significantly influences the ionic conductivity, electrolyte stability, and battery safety. Therefore, it is crucial to determine the LiPF_6 or LiPO_2F_2 content to ensure that Li-ion batteries meet performance, safety, and aging criteria [5,6].

Analysis is challenging for certain techniques due to

solvent or salt effects. Ion chromatography provides an accurate, economic solution for battery electrolyte analysis. The **Metrohm intelligent Partial-Loop Technique (MiPT)** simplifies the analysis, improves reproducibility and accuracy, and decreases costs. This Application Note details an ion chromatographic

SAMPLE AND SAMPLE PREPARATION

Three different samples of Li-ion battery electrolytes were used for this study (Sample 1, Sample 2, and Sample 3, as noted in the Results section). A 500 mg portion of the respective sample material was weighed into a 50 mL volumetric flask and brought up to the correct volume with acetone (HPLC grade, 99.8%).

EXPERIMENTAL

Sample handling was performed with the 858 Professional Sample Processor and MiPT. MiPT enables the precise generation of a calibration curve out of a single standard. Therefore, the 800 Dosino accurately aspirates a specific volume of the given standard into the injection loop. Samples were injected with a volume of 4 μL .

After injection, the target analytes (ODFB^- , PO_2F_2^- , PF_6^-

approach to determine lithium-ion battery electrolyte composition, i.e., the concentration of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), lithium difluoro(oxalato)borate (LiODFB), LiPF_6 , and LiPO_2F_2 .

A mixed standard with a concentration of 40 mg/L LiODFB (lithium difluoro(oxalato)borate), LiPO_2F_2 (lithium difluorophosphate), LiPF_6 (lithium hexafluorophosphate), and LiTFSI (lithium bis(trifluoromethanesulfonyl)imide) was used for the automatic system calibration with MiPT.

and TFSI^-) were separated using the high-capacity Metrosep A Supp 7 - 250/4.0 column and a mixture of 14.4 mmol/L Na_2CO_3 and 40 vol% acetone as eluent. For accurate conductivity measurement, the background conductivity is reduced via sequential suppression, followed by conductivity detection. The example flow path for this analysis is shown in **Figure 1**.

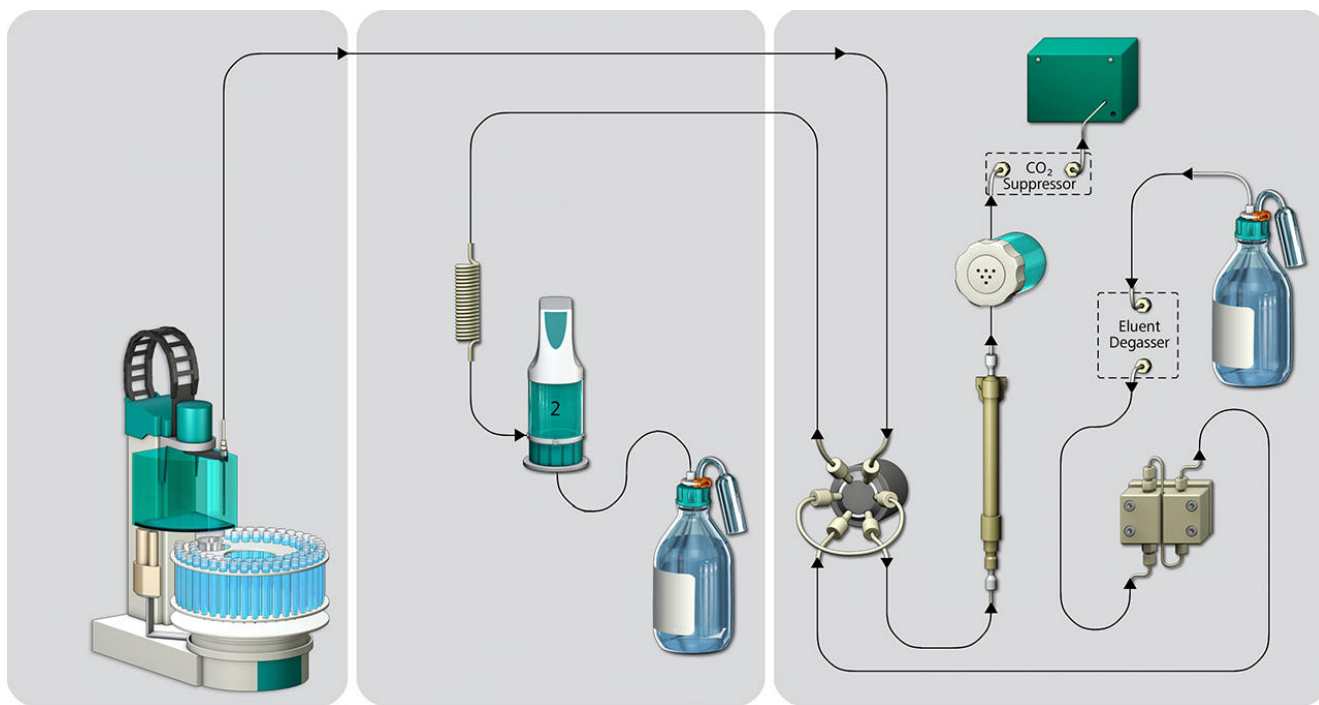


Figure 1. Schematic of an ion chromatographic setup with MiPT.

SAMPLE ANALYSIS

Five standards each of LiODFB, LiPO_2F_2 , LiPF_6 , and LiTFSI were automatically prepared (at concentrations of 40, 80, 200, 400, and 800 mg/L) via MiPT. Due to the precise liquid handling offered by MiPT, the

resulting calibration curve for LiODFB, LiPO_2F_2 , and LiPF_6 had RSD values <2%, and LiTFSI achieved an RSD value of 2.61%.

RESULTS

The target analytes, i.e., LIB electrolyte components (LiODFB, LiPO_2F_2 , LiPF_6 and LiTFSI), are effectively separated in their anionic forms (i.e., ODFB^- , PO_2F_2^- , PF_6^- , and TFSI^-) within 29 minutes (**Figure 2**). The recovery from two-level spike experiments (**Table 1**) ranged from 90–100% and reveals the robustness of the analysis. The sample concentration ranges

covered 0.52–1.1 mg/L for ODFB^- (**Table 2**), 0.28–0.76 mg/L for PO_2F_2^- (**Table 3**), 11.05–14.07 mg/L for PF_6^- (**Table 4**), and 0.45–1.05 mg/L for TFSI^- (**Table 5**). The samples were determined in triplicate and showed average RSD values of 2.8% for ODFB^- , 2.8% for PO_2F_2^- , 1.8% for PF_6^- , and 0.8% for TFSI^- .

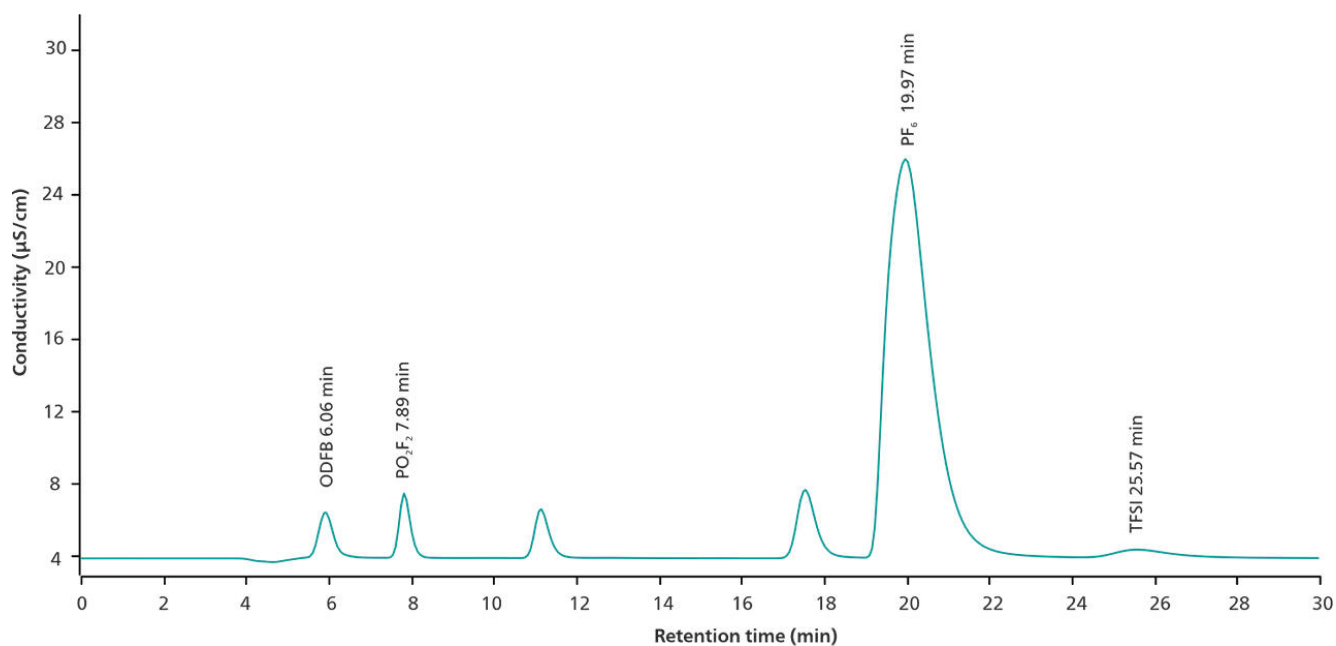


Figure 2. Chromatogram for the determination of lithium difluoro(oxalato)borate, lithium difluorophosphate, lithium hexafluorophosphate, and lithium bis(trifluoromethanesulfonyl)imide with a 930 Compact IC Flex and MiPT. The LiB electrolyte components are determined in their anionic forms and separated on a Metrosep A Supp 17 column.

Table 1. Results for the recovery of the spiked samples. The spike experiments were performed in two levels (added concentration) and the recovery was determined from the target and final concentrations.

Sample, [conc.] (mg/L)	Added conc. (mg/L)	Target conc. (mg/L)	Final conc. (mg/L)	Recovery(%)
ODFB ⁻ , [0.52]	0.20	0.72	0.72	100
	0.40	0.92	0.94	100
PO ₂ F ₂ ⁻ , [0.42]	0.20	0.62	0.60	90
	0.40	0.82	0.79	95
PF ₆ ⁻ , [12.64]	5.58	18.22	18.37	100
	11.42	24.06	23.99	99
TFSI ⁻ , [1.05]	0.79	1.84	1.83	99
	1.58	3.42	2.61	99

Table 2. Results of concentration and %RSD for the analyte ODFB⁻.

Analyte		Sample 1	Sample 2	Sample 3
ODFB ⁻ (mg/L)	1	0.52	0.68	1.08
	2	0.54	0.68	1.12
	3	0.49	0.66	1.09
	Average	0.52	0.67	1.10
	%RSD	4.9	1.7	1.9

Table 3. Results of concentration and %RSD for the analyte PO₂F₂⁻.

Analyte		Sample 1	Sample 2	Sample 3
PO ₂ F ₂ ⁻ (mg/L)	1	0.43	0.75	0.29
	2	0.43	0.76	0.28
	3	0.40	0.76	0.27
	Average	0.42	0.76	0.28
	%RSD	4.1	0.8	3.6

Table 4. Results of concentration and %RSD for the analyte PF₆⁻.

Analyte		Sample 1	Sample 2	Sample 3
PF ₆ ⁻ (mg/L)	1	12.63	14.23	11.15
	2	12.33	13.95	11.18
	3	12.95	14.03	10.81
	Average	12.64	14.07	11.05
	%RSD	2.4	1.0	1.9

Table 5. Results of concentration and %RSD for the analyte TFSI⁻. N.D: Not detectable.

Analyte		Sample 1	Sample 2	Sample 3
TFSI ⁻ (mg/L)	1	1.07	N.D.	0.44
	2	1.09	N.D.	0.46
	3	0.99	N.D.	0.45
	Average	1.05	N.D.	0.45
	%RSD	1.1	—	0.5

CONCLUSION

Ion chromatography with the Metrohm intelligent Partial-Loop Injection technique is an accurate and efficient method to determine the concentration of LIB electrolytes such as LiODFB, LiPO₂F₂, LiPF₆, and LiTFSI.

An advantage of ion chromatography over other analytical methods is that the salts and organic

solvents that are present in LIB samples do not interfere with the analysis, and therefore results are more accurate and reproducible. With the help of spike experiments and replicate measurements, this application example shows that ion chromatography is a reliable method to determine the LIB electrolyte composition.

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CONFIGURATION

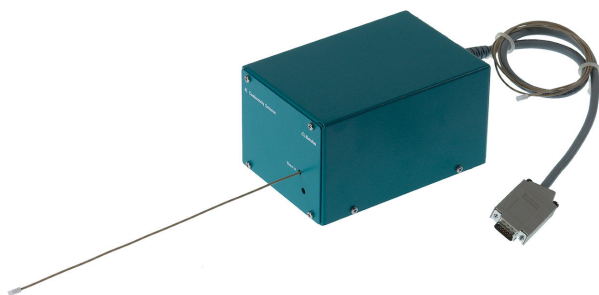


930 Compact IC Flex Oven/SeS/PP/Deg

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).



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 cancérogènes. 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 Supp 5 Guard/4,0

La Metrosep A Supp 5 Guard/4,0 protège la colonne CI pour anions Metrosep A Supp 5 et 7 de manière fiable contre les contaminations provenant des échantillons et de l'éluant.

Cette précolonne contient le même matériau de séparation que la Metrosep A Supp 5, est comme elle fabriquée en PEEK et directement vissée sur la colonne de séparation correspondante, pratiquement sans volume mort, selon le système « On Column Guard ». La précolonne prolonge la durée de vie de la colonne analytique sans altérer pour ainsi dire sa performance de séparation chromatographique. Son prix avantageux et sa facilité de manipulation font que l'utilisation de la A Supp 5 Guard/4,0 est souvent recommandée.



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.



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).



Équipement CI : MiPT

Jeu d'accessoires pour le montage d'un Dosino pour Partial-Loop-Injection.