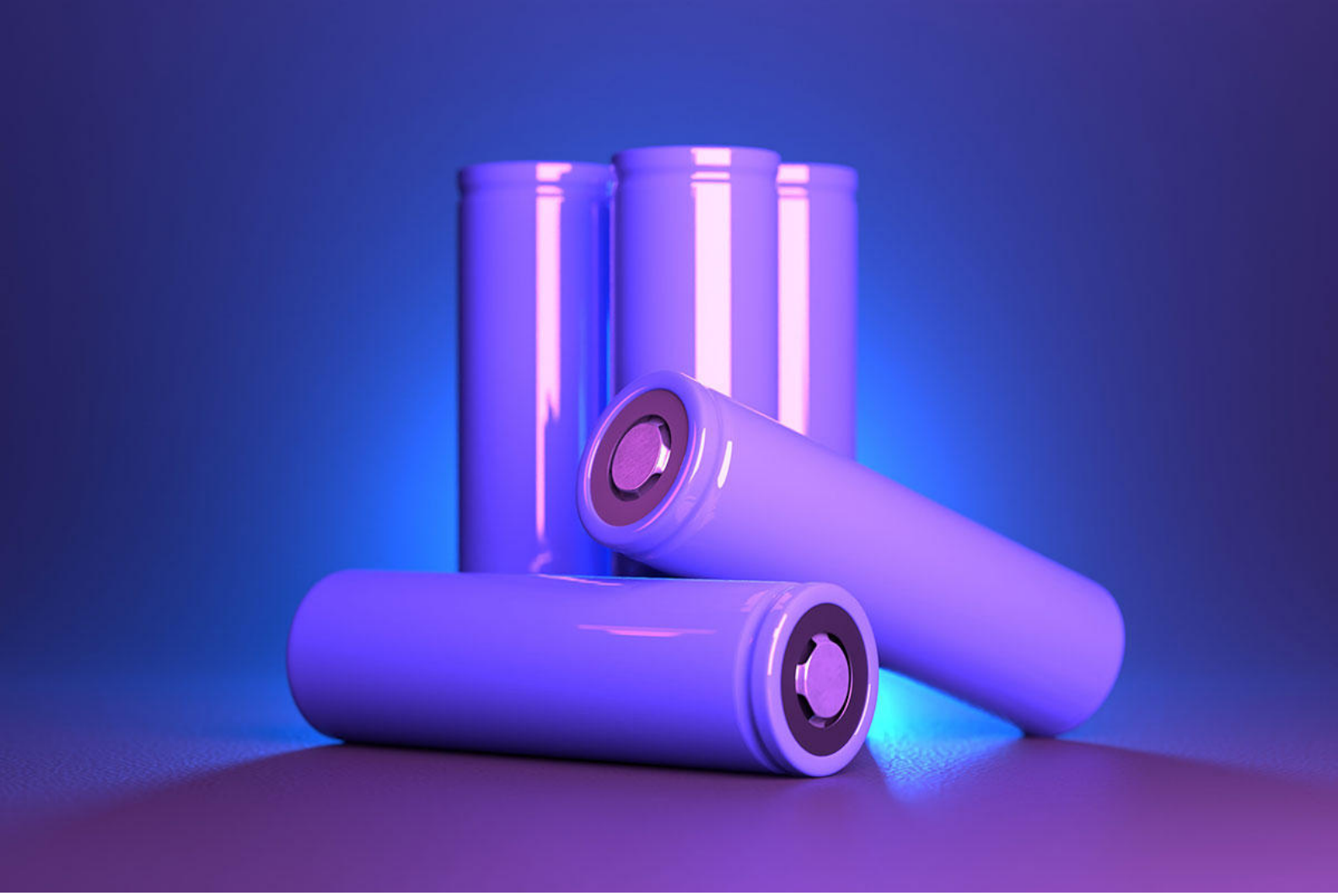

Application Note AN-S-372

Analysis of Li-ion battery electrolytes with ion chromatography

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 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 $LiPO_2F_2$.

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%).

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.

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^- 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.

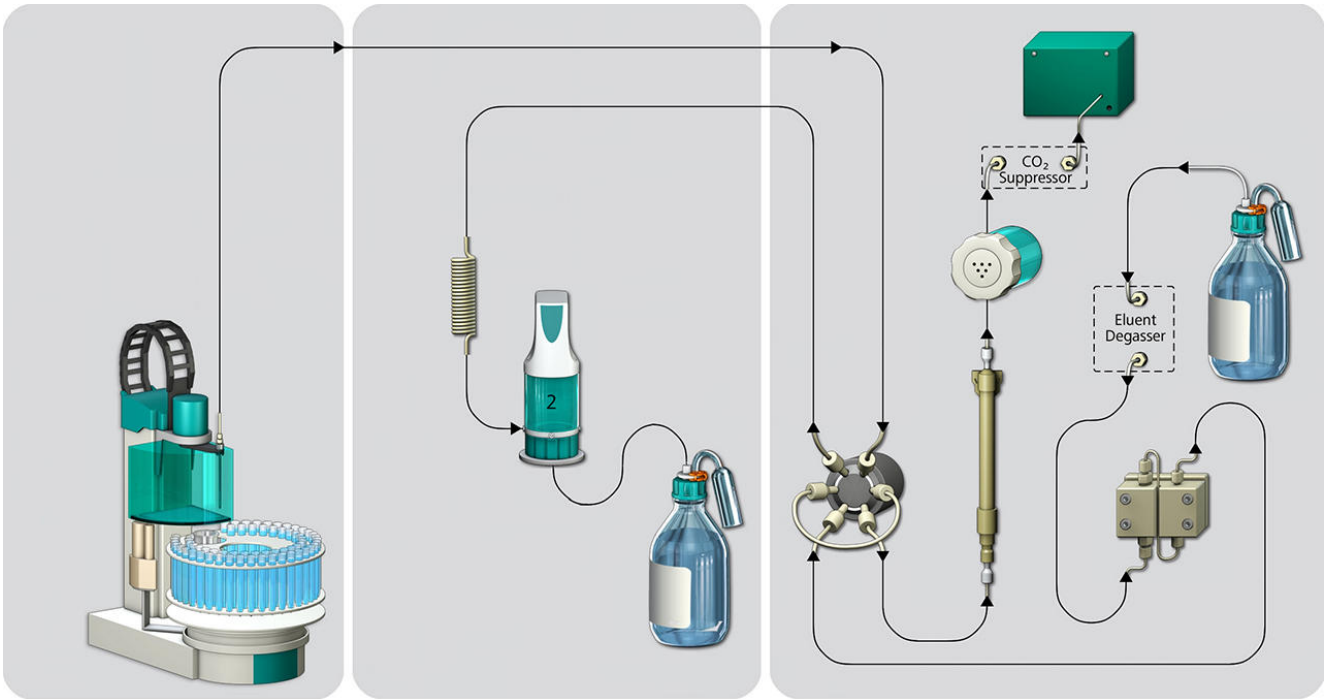

Figure 1. Schematic of an ion chromatographic setup with MiPT.

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 $TFSI^-$.

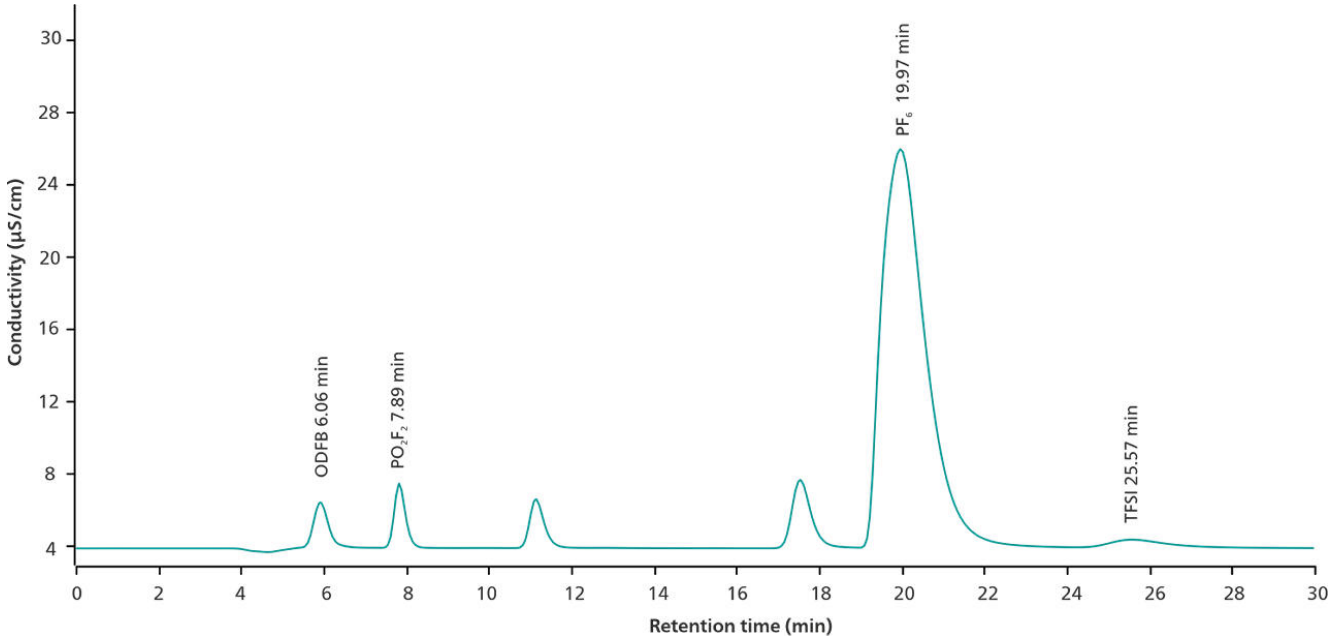

Figure 2. Chromatogram for the determination of lithium difluoro(oxalato)borate, lithium difluorophosphate, lithium hexafluorophosphate, and lithium bis(trifluoromethanesulfonyl)imide with a 930 Compact IC Flex and MiPT. The LiB electrolyte components are determined in their anionic forms and separated 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
$PO_2F_2^-$, [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
$PO_2F_2^-$ (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, $LiPO_2F_2$, $LiPF_6$, 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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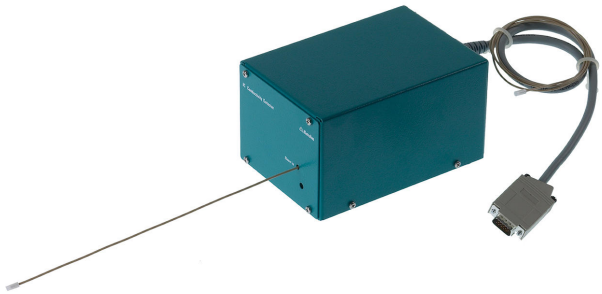
CONFIGURATION

930 Compact IC Flex Oven/SeS/PP/Deg

The 930 Compact IC Flex Oven/SeS/PP/Deg is the intelligent Compact IC instrument with **column oven**, **sequential suppression**, **peristaltic pump** for suppressor regeneration and built-in **degasser**. The instrument can be used with any separation and detection methods.

Typical areas of application:

- Anion or cation determinations with sequential suppression and conductivity detection



IC Conductivity Detector

Compact and intelligent high performance conductivity detector for intelligent IC instruments. Outstanding temperature stability, the complete signal processing within the protected detector block and the latest generation of DSP – Digital Signal Processing – guarantee the highest precision of the measurement. No change of measuring ranges (not even automatic ones) is required, due to the dynamic working range.

Metrosep A Supp 7 - 250/4.0

Disinfection byproducts from water treatment are suspected not only of being health hazards but even of being carcinogenic. Oxyhalides have therefore become the subject of many investigations and standards (e.g., EPA 300.1 Part B, EPA 317.0, EPA 326.0). Of primary concern is bromate, which forms from bromide during the ozonization of drinking water. The Metrosep A Supp 7 - 250/4.0 is a high-performance separation column for the parallel determination of standard anions, oxohalides and dichloroacetic acid. With this column, these ions are determined with certainty and precision down to the lower µg/L range. The high detection sensitivity is achieved through the use of the 5 µm polyvinyl alcohol polymer, with which extremely high plate numbers and thus outstanding separation and detection properties are achieved. In addition, the separation can be adapted to the specific requirements of the application by modifying the temperature.

Metrosep A Supp 5 Guard/4.0

The Metrosep A Supp 5 Guard/4.0 reliably protects the Metrosep A Supp 5 and 7 IC anion columns against contamination from the sample or the eluent. It contains the same separation material as the Metrosep A Supp 5, is also made of PEEK, and is screwed directly onto the respective separation column with virtually no dead volume ("On Column Guard System"). The guard column prolongs the service life of the analytical column, with practically no influence on its chromatographic separating efficiency. The economical price and simple handling make using the A Supp 5 Guard/4.0 highly recommended.

858 Professional Sample Processor

The 858 Professional Sample Processor processes samples from 500 µL to 500 mL. The sample transfer takes place either by means of a peristaltic pump on the 850 Professional IC system or with an 800 Dosino.

800 Dosino

The 800 Dosino is a drive with write/read hardware for intelligent Dosing Units. With fixed cable (length 150 cm).

IC equipment: MiPT

Accessory set for assembling a Dosino for Partial-Loop-Injection.