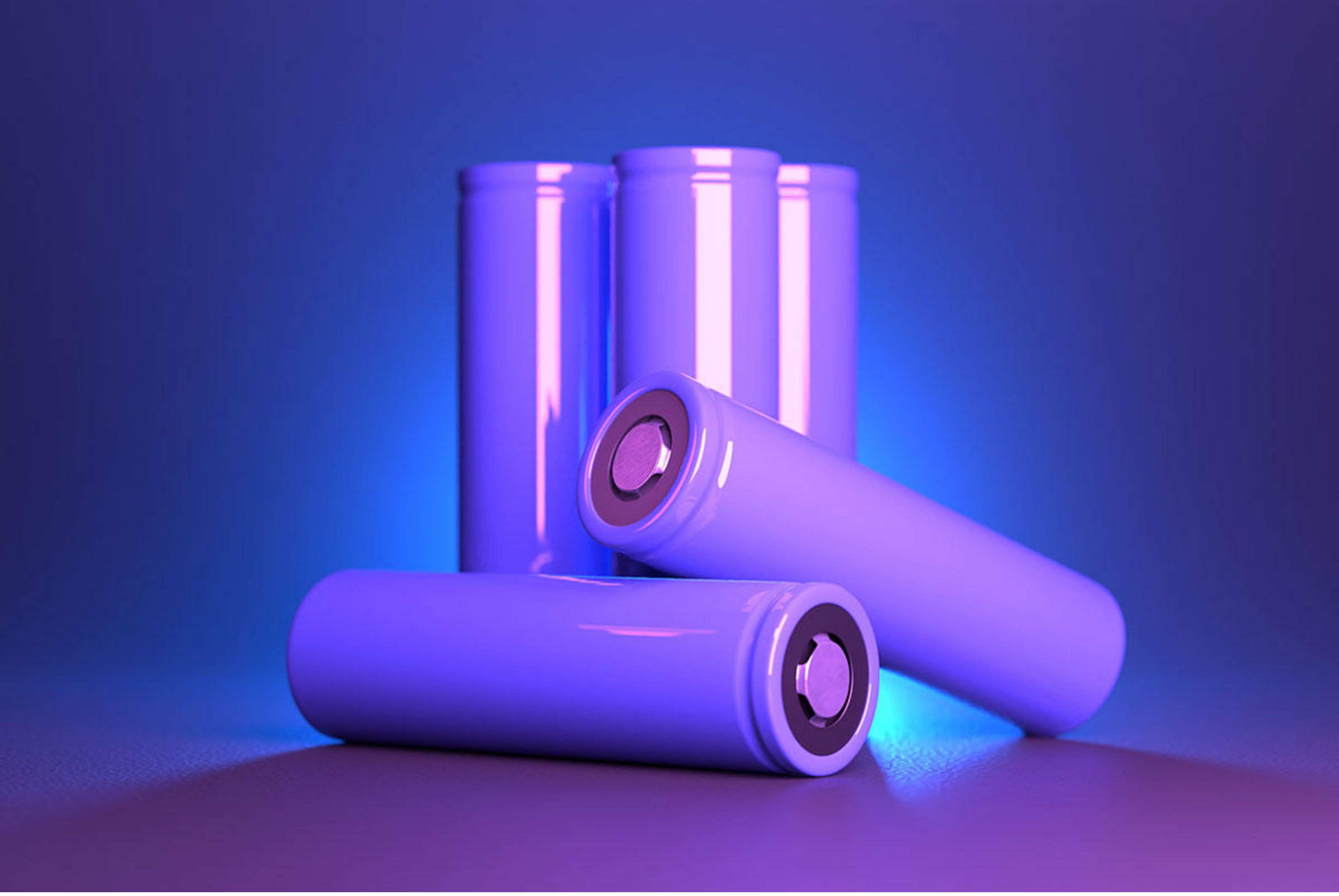

Application Note AN-S-372

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**.

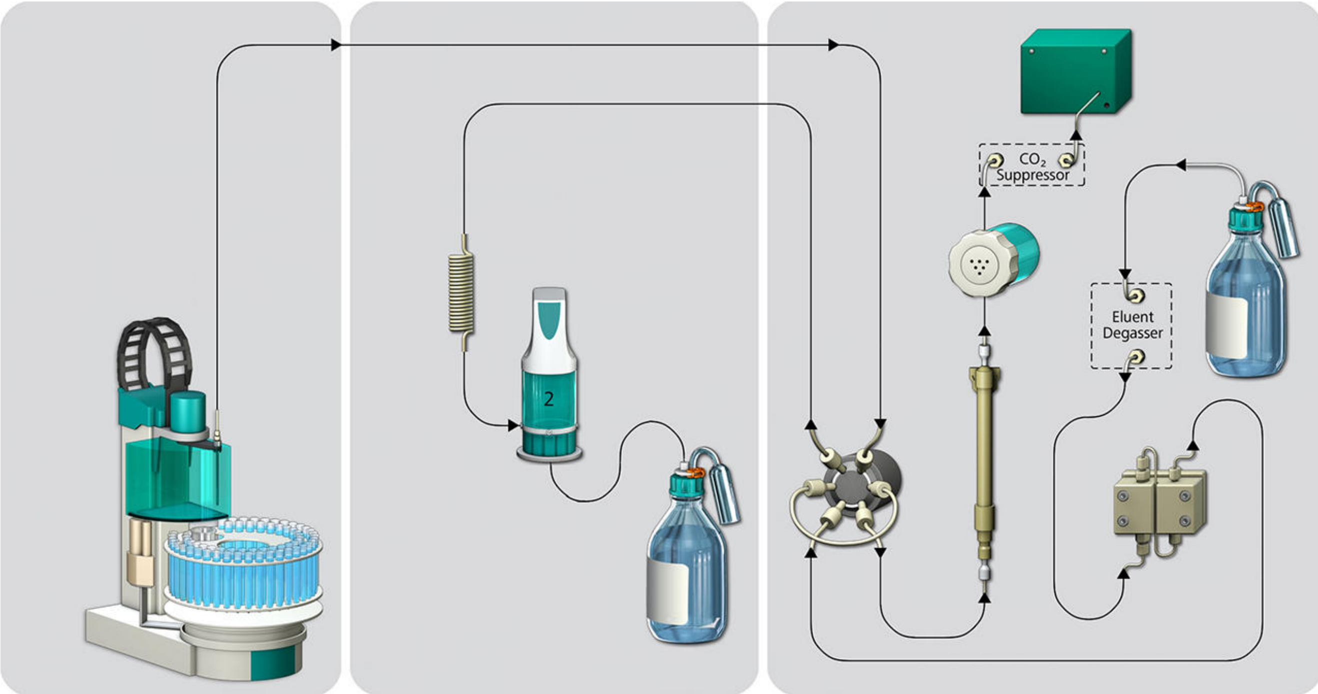

Figure 1. Schematic of an ion chromatographic setup with MiPT.

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 $TFSI^-$.

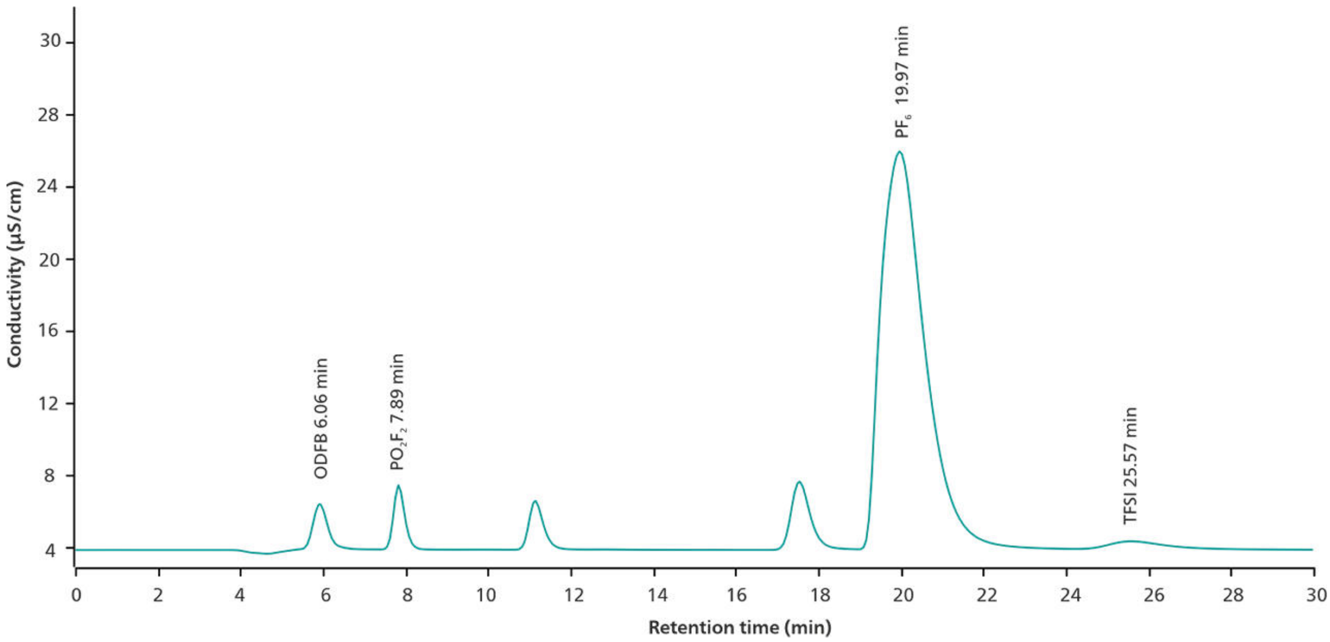

Figure 2. Chromatogram for the determination of lithium difluoro(oxalato)borate, lithium difluorophosphate, lithium hexafluorophosphate, and lithium bis(trifluoromethanesulfonyl)imide with a 930 Compact IC Flex and MiPT. The LiB electrolyte components are determined in their anionic forms and separated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

REFERENCES

1. Zhao, Y.; Pohl, O.; Bhatt, A. I.; et al. A Review on Battery Market Trends, Second-Life Reuse, and Recycling. *Sustainable Chemistry* **2021**, *2* (1), 167–205. DOI:10.3390/suschem2010011
2. Fathi, R. A Guide to Li-Ion Battery Research and Development.
3. Treptow, R. S. Lithium Batteries: A Practical Application of Chemical Principles. *J. Chem. Educ.* **2003**, *80* (9), 1015. DOI:10.1021/ed080p1015
4. Liu, Y.-K.; Zhao, C.-Z.; Du, J.; et al. Research Progresses of Liquid Electrolytes in Lithium-Ion Batteries. *Small* **2023**, *19* (8), 2205315. DOI:10.1002/smll.202205315
5. Palacín, M. R. Understanding Ageing in Li-Ion Batteries: A Chemical Issue. *Chem. Soc. Rev.* **2018**, *47* (13), 4924–4933. DOI:10.1039/C7CS00889A
6. Wang, Q.; Jiang, L.; Yu, Y.; et al. Progress of Enhancing the Safety of Lithium Ion Battery from the Electrolyte Aspect. *Nano Energy* **2019**, *55*, 93–114. DOI:10.1016/j.nanoen.2018.10.035

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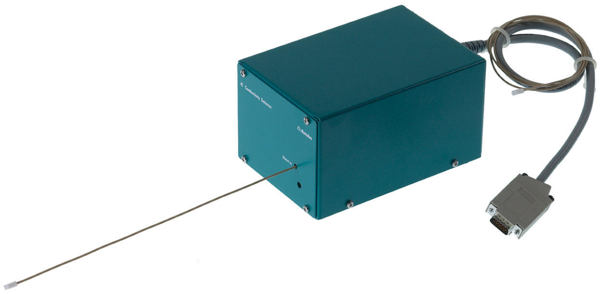
CONFIGURATION

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)。

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 Supp 5 Guard/4.0

Metrosep A Supp 5 Guard/4.0 对 IC 阴离子柱 Metrosep A Supp 5 和 7 进行可靠保护,使其不受样品或淋洗液的污染。

它含有与 Metrosep A Supp 5 相同的分离材料,也同样由 PEEK(聚醚醚酮)制成,并直接以几乎无死点容积的方式拧到相应分离柱上(«On Column Guard System»)。保护柱将延长分析用柱的使用寿命,且不会影响其色谱分离效率。建议使用 A Supp 5 Guard/4.0,其价格优惠且操作简单。

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。

800 Dosino

800 Dosino 驱动头,带有可用于智能型加液单元的读/写硬件设备。带固定电缆。

MiPT

用于安装 Dosino 以进行局部循环进样的附件组。