



Author: Derrick Quarles Jr., Patrick Sullivan, Brianna Dufek

Automated and Fast Determination of Li Salt Species in Electrolyte Solutions

Brief

Electrolyte solutions used in lithium-ion batteries are analyzed utilizing an automated system (prepFAST IC) in combination with an ICPMS to determine accurate and precise amounts of Li salts and stabilizing agents.

Highlights

- Separation of up to 8 different lithium species (e.g., LiPF_6) in under 4 minutes
- Autocalibration and autodilution of standards and samples eliminates tedious sample preparation
- Detection limits range from low ppt to ppb levels
- Excellent linearity, accuracy, and precision demonstrated in this report

Introduction

Liquid electrolytes are one of the main components that are used in lithium-ion batteries. The electrolyte allows positively charged ions (typically Li ions) to move between the cathode and anode, and plays a crucial role in battery performance and lifespan. There are three components that make up the electrolyte: Li salt (e.g., LiPF_6), organic solvent (ethylene carbonate), and a stabilizing additive (e.g., LiPO_2F_2). Some of the

common Li salts are LiPF_6 , LiBF_4 , and LiClO_4 . This work will focus on a quick and easy analytical method for determining which Li salts (or Li species) and additives are present in each electrolyte. To conduct this work, an automated total metals and elemental speciation sample introduction system, prepFAST IC, was coupled to an ICPMS for accurate determination of Li species in electrolyte solutions.



Experimental

prepFAST IC – automated total metals and elemental speciation system. The prepFAST IC (Figure 1) autocalibrates standards so that the analyst is only required to prepare a single stock standard rather than a series of standards. The system will also autodilute samples and adds internal standard as prescribed in the method. The hardware automatically switches from total metals mode to speciation (chromatography) mode which eliminates the need for a separate HPLC to perform chromatographic separations into the



Figure 1. Elemental Scientific's prepFAST IC.

ICPMS. The ICPMS was used to monitor the masses for ^{11}B , ^{31}P , ^{32}S , and ^{35}Cl . Lithium hexafluorophosphate (LiPF_6), lithium tetrafluoroborate (LiBF_4), lithium perchlorate (LiClO_4), lithium difluoro(oxalate)borate (LiDFOB), lithium difluorophosphate (LiPO_2F_2), lithium bis(fluorosulfonyl)amide (LiFSI), and sulfate (SO_4) were commercially purchased and used in this work. Figure 2 displays the chemical structures of these compounds. The chromatographic separation was performed using ESI's lithium battery speciation kit (ICX-LiF-1), which utilizes an anion exchange column with a gradient separation (0 to 50 mM KOH) at 1 mL/min. An injection volume of 50 μL was used to introduce the standards and samples onto the column.

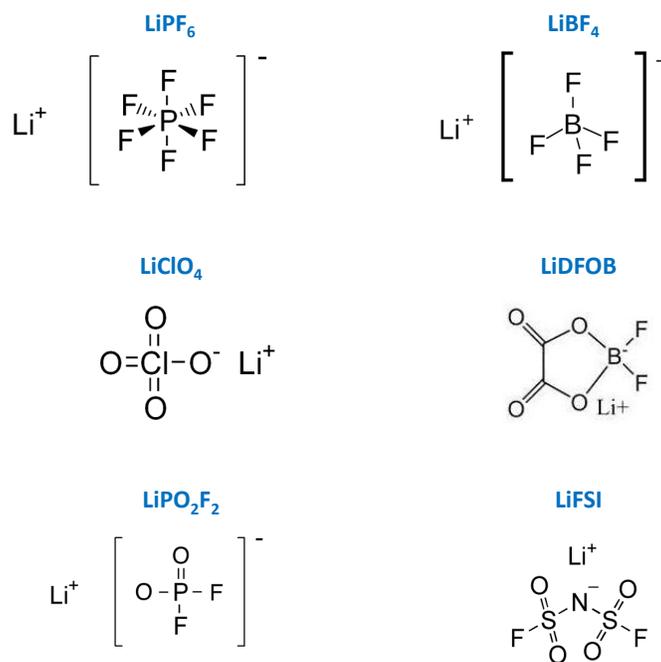


Figure 2. Chemical structures for the Li salt compounds studied in this work.

Results

A comprehensive method was developed that separates LiDFOB, LiBF_4 , LiPO_2F_2 , LiPF_6 , LiFSI, and LiClO_4 in under 4 minutes using a gradient elution of 0 to 50 mM

KOH (Figure 3). In addition, SO_4 was included in the method to monitor potential breakdown products that occur from cycling FSI (or other S based Li salts).

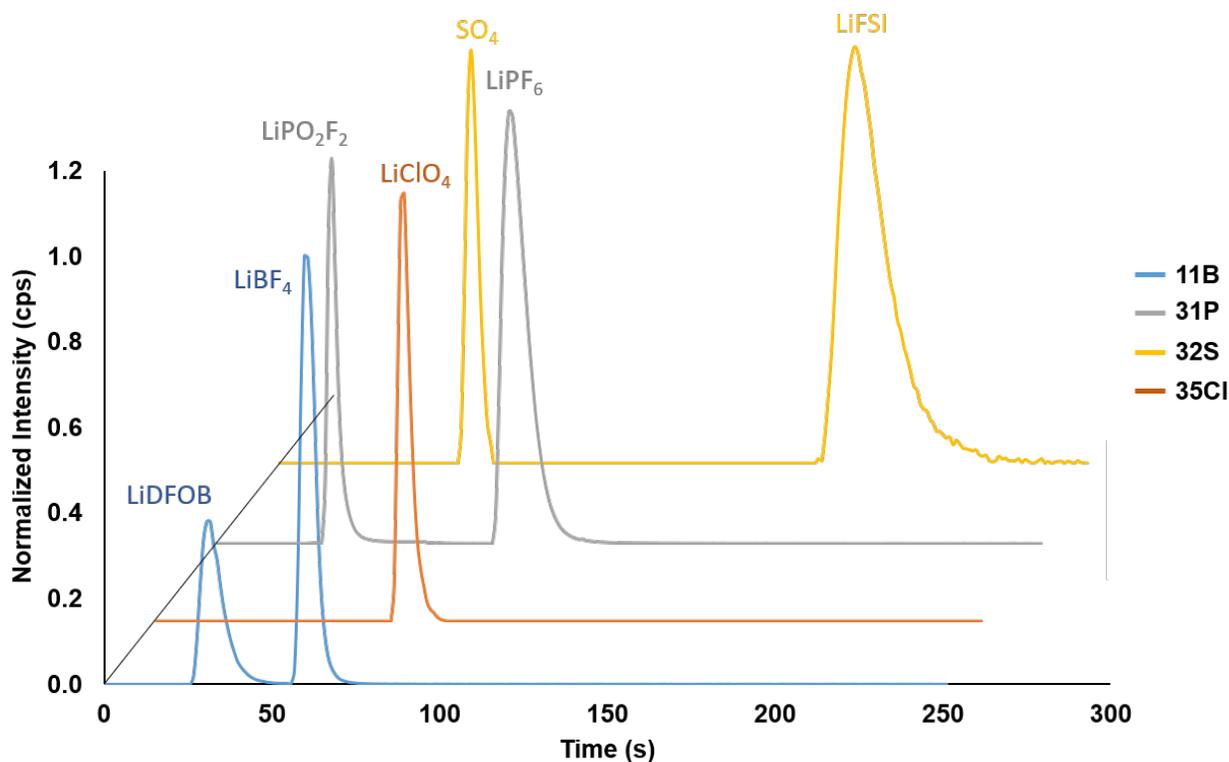


Figure 3. Optimized chromatographic separation for Li compounds typically used in lithium-ion battery electrolytes. Isotopes of ^{11}B , ^{31}P , ^{32}S , and ^{35}Cl were monitored by ICPMS.

These Li salt compounds can be utilized as the main electrolyte solution, an additive, or can be a breakdown product from cycling over time. Therefore, a large dynamic range was tested to account for the various concentrations that could be encountered with different sample types. The optimized method showed excellent linearity ($R^2 \geq 0.9997$) from 1 ppb to 100 ppm. Figure 4 displays the calibration curve for

PF_6 ranging from 0.01-100 ppm and 10-200 ppb. Since the prepFAST IC can easily autodilute any sample, if the concentration found in the sample is over the 100 ppm range it can easily be diluted inline by the system eliminating the need for user interaction or additional calibration preparation. Figure 5 displays the calibration curves for all the other Li salt compounds.

Results (Continued)

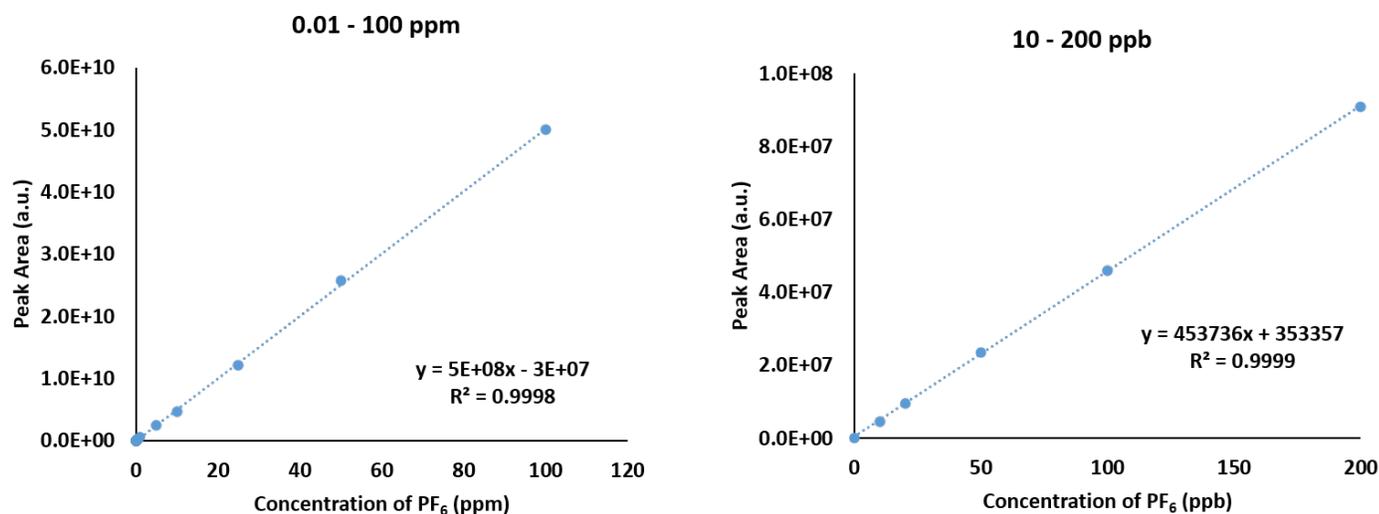


Figure 4. PF₆ calibration curves ranging from 0.01-100 ppm and 10-200 ppb.

Table 1. Linearity for each Li salt compound calibration curve for both the low and high calibration ranges.

	DFOB	PF ₆	PO ₂ F ₂	FSI	BF ₄	ClO ₄	SO ₄
Calibration Range (ppm)	0.001-20	0.01-100	0.001-20	0.001-20	0.001-20	0.001-20	0.001-20
Linearity (R ²)	0.9998	0.9997	0.9997	0.9998	0.9998	0.9997	0.9997
Low Cal Range (ppb)	1-20	10-200	1-20	1-20	1-20	1-20	1-20
Linearity (R ²)	0.9999	0.9999	0.9997	0.9999	0.9998	0.9998	0.9999
High Cal Range (ppm)	1-20	5-100	1-20	1-20	1-20	1-20	1-20
Linearity (R ²)	0.9998	0.9997	0.9997	0.9999	0.9998	0.9997	0.9998

Results (Continued)

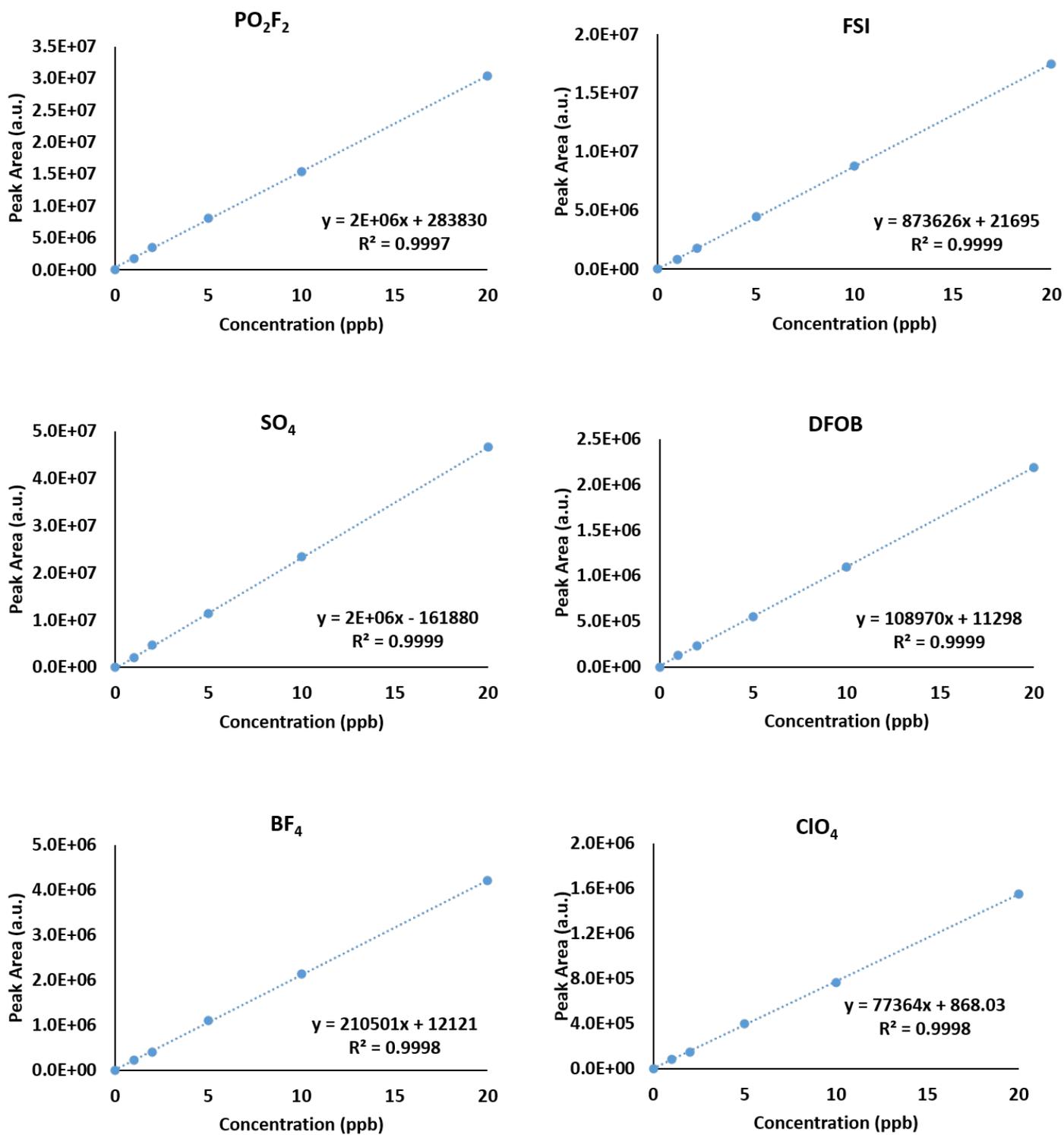


Figure 5. Calibration curves for the Li salts ranging from 1-20 ppb.

Results (Continued)

Detection limits were determined for each compound of interest, which ranged from 17 ppt to 2.12 ppb (Table 2). The injection volume was set to 50 μL to not overload the column and handle both the low and high concentrations. If the desired application is to only monitor the additives or breakdown compounds, then the injection volume could be increased which would lead to lower detection limits. To determine the accuracy and precision for this method, samples were

prepared at two different levels (low ppm and 100's of ppm) and analyzed in triplicate. Table 3 displays the results which highlight the measured value \pm standard deviation and the % recovery (based on the targeted concentration prepared in-house). The recovery for all compounds was within $\pm 10\%$. The precision was 0.3 to 3.9 %RSD (except for SO_4 which was 8.2 %RSD) for the low concentration samples and was 0.8 to 3.1 %RSD for the high concentration samples.

Table 2. Method detection limits for each Li salt compound. MDL based on 10 blank measurements ($n = 10$).

	DFOB	PF_6	PO_2F_2	FSI	BF_4	ClO_4	SO_4
MDL (ppb)	0.030 ppb	0.165 ppb	0.267 ppb	0.842 ppb	0.017 ppb	1.35 ppb	2.12 ppb

Table 3. Precision and accuracy for in-house prepared samples. Standard deviations were determined from 3 replicate measurements ($n = 3$). % recovery = (measured value / targeted value) $\times 100$.

	DFOB	PF_6	PO_2F_2	FSI	BF_4	ClO_4	SO_4
Target (ppm)	1	15	1	10	10	10	1
Measured (ppm)	0.960 ± 0.011	14.7 ± 0.2	0.972 ± 0.010	9.91 ± 0.03	9.97 ± 0.25	10.4 ± 0.4	1.10 ± 0.09
% Recovery	96	98	97	99	100	104	110
Target (ppm)	100	500	100	100	500	500	100
Measured (ppm)	101 ± 2	463 ± 5	95 ± 1	93 ± 1	485 ± 7	487 ± 4	98 ± 3
% Recovery	101	93	95	93	97	97	98

During the development, there were two additional findings that were of significance. The first was that after preparing the DFOB standard it started to degrade over time. Figure 6 shows the comparison of the fresh DFOB standard vs. the older standard. The second finding was that the only standard initially purchased

that was not pure was the FSI. Figure 7 displays the comparison of two different commercially available FSI sources. Source 1 was found to have 10% SO_4 and 90% FSI, whereas, source 2 was found to only contain FSI with no sulfate.

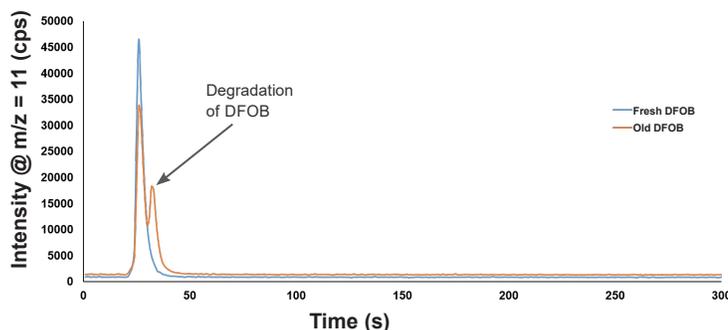


Figure 6. Chromatogram showing the comparison of a freshly made DFOB standard vs an older standard. The appearance of a 2nd peak in the old DFOB standard represents the degradation of the compound.

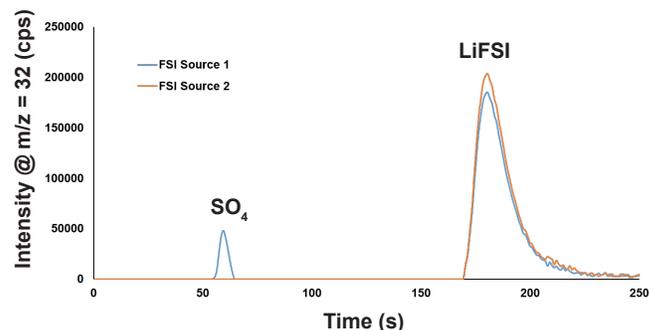


Figure 7. Chromatogram showing the comparison of two different commercially available FSI sources. Source 1 = 10% SO_4 , 90% FSI and source 2 = 100% FSI.

Results (Continued)

The last experiment measured samples with varying ratios of the different Li salts. Eight samples were prepared, the first 4 had different ratios of DFOB, PF₆, PO₂F₂, and FSI ranging from 2 to 100 ppm per each compound. The second 4 samples had varying ratios

of DFOB, PF₆, PO₂F₂, FSI, BF₄, ClO₄, and SO₄. Table 4 shows the targeted amount, measured amount (value ± SD), and the % recovery for each of the 8 samples. All the samples were found to be within ± 10 % recovery.

Table 4. In-house prepared samples varying in Li salt concentrations to act as surrogates for complex electrolytes that would contain a main Li salt in addition to one or more additives. The measured value ± SD is based on the average of 5 repeat measurements (n = 5).

		DFOB	PF ₆	PO ₂ F ₂	FSI	BF ₄	ClO ₄	SO ₄
Sample 1	Target (ppm)	2.5	100	3	2	0	0	0
	Measured (ppm)	2.33 ± 0.07	92.3 ± 1.0	3.20 ± 0.02	1.90 ± 0.11	-	-	-
	%Recovery	93	92	107	95	-	-	-
Sample 2	Target (ppm)	2.5	100	3	40	0	0	0
	Measured (ppm)	2.24 ± 0.22	95.6 ± 0.1	3.21 ± 0.01	41.2 ± 0.3	-	-	-
	%Recovery	90	96	107	103	-	-	-
Sample 3	Target (ppm)	2.5	100	40	2	0	0	0
	Measured (ppm)	2.40 ± 0.05	95.7 ± 1.3	39.2 ± 0.6	1.83 ± 0.12	-	-	-
	%Recovery	96	96	98	92	-	-	-
Sample 4	Target (ppm)	20	50	20	40	0	0	0
	Measured (ppm)	18.1 ± 0.4	48.1 ± 0.2	18.6 ± 0.2	41.7 ± 0.1	-	-	-
	%Recovery	90	96	93	104	-	-	-
Sample 5	Target (ppm)	0	60	20	0	20	20	0
	Measured (ppm)	0	62.2 ± 1.1	20.6 ± 0.4	0	18.2 ± 0.5	21.5 ± 0.2	0
	%Recovery	-	104	103	-	91	108	-
Sample 6	Target (ppm)	20	70	20	20	3	0	2
	Measured (ppm)	18.7 ± 0.5	67.5 ± 0.8	20.7 ± 0.2	18.5 ± 0.2	2.7 ± 0.2	0	2.1 ± 0.1
	%Recovery	94	96	103	93	90	-	103
Sample 7	Target (ppm)	0	70	20	20	20	20	2
	Measured (ppm)	0	68.2 ± 0.9	20.9 ± 0.2	18.6 ± 0.1	18.1 ± 0.4	21.6 ± 0.5	2.1 ± 0.1
	%Recovery	-	97	104	93	90	108	103
Sample 8	Target (ppm)	20	60	0	20	20	20	2
	Measured (ppm)	19.8 ± 0.6	59.9 ± 1.0	0	18.6 ± 0.2	20.1 ± 0.5	20.9 ± 0.4	2.1 ± 0.1
	%Recovery	99	100	-	93	101	105	103

Results (Continued)

LiFSI was measured after cycling and it was determined that the FSI compound had begun to breakdown to LiNSO₂F (Figure 8). This was confirmed by accurate mass determination by prepFAST CARBON, which is

a fully automated sample preparation station that utilizes an electrospray ionization-quadrupole time of flight-mass spectrometer.

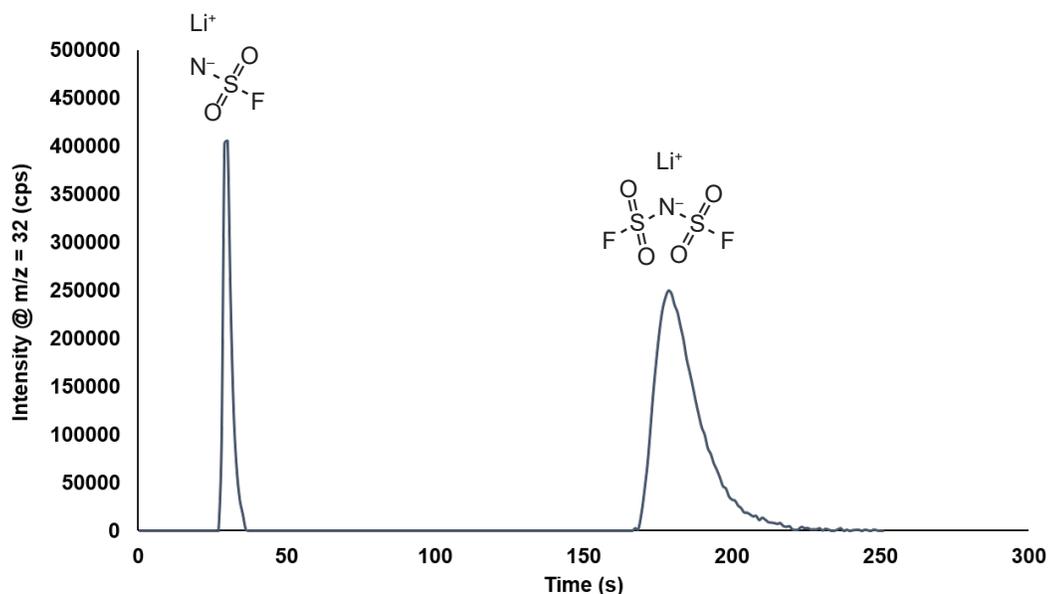


Figure 8. The determination of breakdown products in cycled LiFSI. Compound structures verified by prepFAST CARBON.

Conclusion

These results show that this method can take a complex electrolyte solution and determine the compounds. This method could be used as a quality control check for freshly prepared electrolyte solutions to ensure the correct ratio of Li salt to additive is achieved. An additional use would be to analyze electrolyte solutions before and after cycling

to determine if the compounds remained stable and in the desired ratio. Combining the prepFAST IC with an ICPMS, the determination of Li compounds can be achieved in less than 4 minutes. In addition, this system can be used to do routine analysis (total or trace metals analysis) in addition to the Li speciation method presented in this work.

Appendix

LiPF₆ – Lithium hexafluorophosphate

LiBF₄ – Lithium tetrafluoroborate

LiClO₄ – Lithium perchlorate

LiDFOB – Lithium difluoro(oxalate)borate

LiPO₂F₂ – Lithium difluorophosphate

LiFSI – Lithium bis(fluorosulfonyl)amide



© Elemental Scientific | 7277 World Communications Drive | Omaha, NE 68122
Tel: 1-402-991-7800 | sales@icpms.com | www.icpms.com

A-23123