Application note | 003262

Industrial

Analysis of common lithium salts, trace additives, and contaminants in lithium-ion battery electrolytes by ion chromatography-mass spectrometry

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Keywords

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Introduction

Understanding the electrolyte composition of batteries is pivotal in achieving enhanced battery performance, safety, and longevity at every stage of product evolution, including research, manufacturing, and recycling. By analyzing the electrolyte, valuable insights can be gained to further improve performance, efficiency, and safety.

In the early stages of lithium-ion battery (LIB) development, common electrolytes consisted of a simple lithium salt, such as lithium hexafluorophosphate ($LiPF_6$), dissolved in organic solvents like ethylene carbonate (EC), also known as organic carbonates. However, as researchers and manufacturers have strived to improve battery performance, alternative salts and various additives have been incorporated in different combinations, increasing the complexity of LIB electrolytes.

This application note describes an ion chromatography-mass spectrometry (IC-MS) method that was developed with sequential detection using a conductivity detector followed by mass spectrometry detection to meet the analytical need of understanding the sample composition and degradation byproducts. This method utilizes a Thermo Scientific™ Dionex™ ICS-6000 HPIC System with a conductivity detector and Thermo Scientific™ ISQ™ EC Single Quadrupole Mass Spectrometer. This advanced analytical approach allows common lithium salts and trace contaminants to be analyzed accurately in simulated battery electrolytes.

This study used a carbonate eluent instead of hydroxide, which was used in prior work to analyze PF_6^-.[1] The carbonate eluent's lower pH prevented the hydrolysis of lithium difluorophosphate, which was added to the components of interest after the conclusion of the previous work; however, it is widely used today for its ability to improve the battery's low temperature performance[2,3].

The column temperature was elevated to 40 °C, and an acetonitrile-gradient was applied to reduce the analysis time, increase efficiency, and streamline the analytical process. With this newly developed method, key components of LIB electrolytes were successfully analyzed in less than 40 minutes.

Experimental

Equipment

- Dionex ICS-6000 HPIC system including:
    - DP gradient dual pump module with degas option, or SP gradient pump module with degas option and AXP-MS pump (P/N 060684)
    - DC detector/chromatography module with CD conductivity detector
    - Thermo Scientific™ Dionex™ AS-AP Autosampler (P/N 074921)
    - VP vacuum pump kit (P/N 066463)

* In this experiment, the second injection valve on the DC module was used as a diverter valve. Optional AM Automation Manager (P/N 079833) and 6-port valve (P/N 075917) can also be used.

- ISQ EC single quadrupole mass spectrometer

Software

Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) Software 7.3.2 or higher

Consumables

- Thermo Scientific™ Dionex™ IonPac™ AG23 Guard Column 2 mm (P/N 064143)
- Thermo Scientific™ Dionex™ IonPac™ AS23 Analytical Column 2 mm (P/N 064145)
- Thermo Scientific™ Dionex™ ADRS 600 Dynamically Regenerated Suppressor 2 mm (P/N 088667)
- Thermo Scientific™ Dionex™ CRD 300 Carbonate Removal Device 2 mm (P/N 064638)

Reagents and standard

- Deionized water (DI), Type 1 reagent grade, 18 MΩ·cm resistivity or better
- Sodium carbonate monohydrate, Fisher Chemical (P/N S262-3)
- Sodium bicarbonate, MilliporeSigma (P/N MSX0320-1)
- Acetonitrile, Fisher Chemical (P/N A955)
- Ethylene carbonate (EC), Thermo Scientific Chemicals (P/N AAA1573536)
- Dimethyl carbonate (DMC), Thermo Scientific Chemicals (P/N AAA1310436)
- Diethyl carbonate (DEC), Thermo Scientific Chemicals (P/N AAA12477AP)
- Sodium fluorophosphate (Na_2PO_3F), MilliporeSigma (P/N 34443-500G)
- Sodium fluoride, Sigma (P/N S1504)
- Sodium acetate, anhydrous: Thermo Scientific Chemicals (P/N 01155430)
- Sodium formate, Fisher Chemical (P/N S648)
- Potassium chloride, Fisher Chemical (P/N P330)
- Sodium nitrate, Sigma-Aldrich (P/N 221341)
- Sodium phosphate monobasic anhydrous, Fisher Chemical (P/N S397)
- Sodium sulfate, Sigma-Aldrich (P/N 239313)
- Lithium oxalate, Thermo Scientific Chemicals (P/N 013426A1)
- Lithium perchlorate, Sigma-Aldrich (P/N 634565)
- Lithium hexafluorophosphate ($LiPF_6$), Thermo Scientific Chemicals (P/N AC191260250)
- Phosphorodifluoridic acid lithium salt ($LiPO_2F_2$), AstaTech (P/N 50-244-0179)
- Lithium bis(trifluoromethanesulfonimide) (LiTFSI), Thermo Scientific Chemicals (P/N AC381030100)
- Lithium bis(fluorosulfonyl)imide (LiFSI), TCI America (P/N L02815G)
- Lithium bis(oxalato)borate (LiBOB), AmBreed (P/N A304321)
- Lithium difluoro(oxalato)borate (LiODFB), AmBreed (P/N A548767)
- Lithium tetrafluoroborate ($LiBF_4$), Sigma-Aldrich (P/N 451622)

Instrument method

System	Dionex ICS-6000	
Columns	Dionex IonPac AS23, Analytical, 2 × 250 mm Dionex IonPac AG23, Guard, 2 × 50 mm	
Eluent source	A: 45 mM sodium carbonate, 25 mM sodium bicarbonate B: DI water C: acetonitrile	
Gradient	See “Eluent gradient program” below	
Flow rate	0.25 mL/min	
Column temp.	40 ˚C	
Injection vol.	5 µL full loop	
Detection	CD	Suppressed conductivity with a Dionex ADRS 600 suppressor in constant current mode at 10 mA, recycling/external water mode using the diverter valve, and Dionex CRD 300 Carbonate Removal Device in vacuum mode
	MS	ISQ EC electrospray ionization (ESI), Negative Mode
	Ion transfer tube	350 °C
	Vaporizer	500 °C
	Aux gas	6.0 psig*
	Sheath gas	65.8 psig
	Sweep gas	2.0 psig
	Eluent flow is diverted to waste until 4.2 minutes	

Component	*m/z*	CID** (V)	Component	*m/z*	CID (V)
Fluoride (HF_2^-)	39.2	10	Sulfate	97.0	20
Acetate	59.2	10	BF_4^-	87.1	20
Formate	45.2	20	Oxalate	89.1	10
Chloride	35.2	20	Perchlorate	99.1	20
$PO_2F_2^-$	101.1	20	PF_6^-	145.1	20
Nitrate	62.2	20	TFSI$^-$	280.0	10
Phosphate	97.0	20	FSI$^-$	180.1	20
HPO_3F^-	99.0	10			

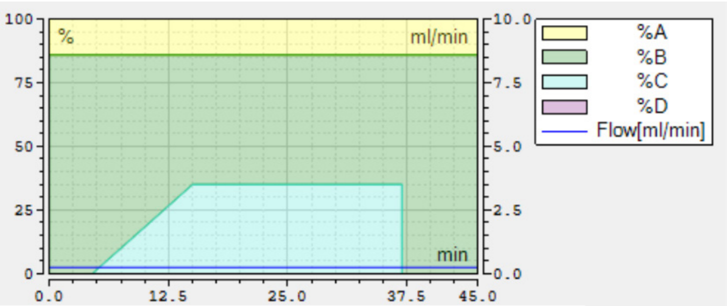
Run time	45 min

*Measurement of pressure relative to atmospheric pressure

**Collision-induced dissociation (CID)

Eluent gradient program

Time (min)	%A 45mM Na_2CO_3 25 mM $NaHCO_3$	%B DI water	%C acetonitrile
0.0	14.0	86.0	0.0
4.5	14.0	86.0	0.0
15.0	14.0	51.0	35.0
37.0	14.0	51.0	35.0
37.0	14.0	86.0	0.0
45.0	14.0	86.0	0.0



Dionex CRD 300 carbonate removal device in vacuum mode

The CRD 300 carbonate removal device was used in vacuum mode to mitigate baseline shift and improve sensitivity. Carbon dioxide is continuously removed from the system so that less bicarbonate can be formed, and the background conductivity drops lower. A small amount of air is introduced via a bleed tube to aid in the removal process (Figure 1).

It is crucial to exercise caution and avoid subjecting the device to high pressure, especially when using a second detector like a mass spectrometer. Switching off the vacuum pump when the eluent flow is stopped is recommended to ensure proper long-term function.

System setup with a diverter valve

Excessive amounts of salts entering the MS system lead to frequent detector cleaning or instrument downtime through corrosion. The continuously regenerated suppressor enables the use of MS by removing the counter ions from the eluent and the sample matrices.[6] An effective measure to reduce the MS-interface exposure is to divert the eluent flow away from the MS. A diverter valve manages the eluent flow directions, bypassing the MS when no data is collected.

Figures 2A and 2B illustrate the IC-MS system at two stages. When the system runs idle or a high ionic strength matrix is eluted, the diverter valve is in the "DIVERT" position (Figure 2A). After passing through the conductivity detector, the eluent is used as the suppressor regenerant in the Recycling Mode.

During data acquisition, the diverter valve is switched to the "MS" position (Figure 2B). The suppressed eluent is directed toward the mass spectrometer for analysis, and the suppressor operates in the External Water Mode.

Employing this diverter valve mechanism minimizes the potential for excessive salt to enter the MS system, ensuring the detector's integrity and longevity.

The diverter valve installed on the Dionex ICS-6000 HPIC system can be controlled and programmed in Chromeleon CDS, as shown in Figure 2C. Depending on the diverter valve's configuration, the valve position may appear different (e.g., INJECT/LOAD or A/B).

An optional Emergency Instrument Method safeguards the MS system in case of an abort error mid-analysis. This method should be programmed to stop the pump and/or switch the diverter valve before terminating the sequence.

These preventive measures protect the MS system from excessive exposure to the non-suppressed caustic eluent or the sample.

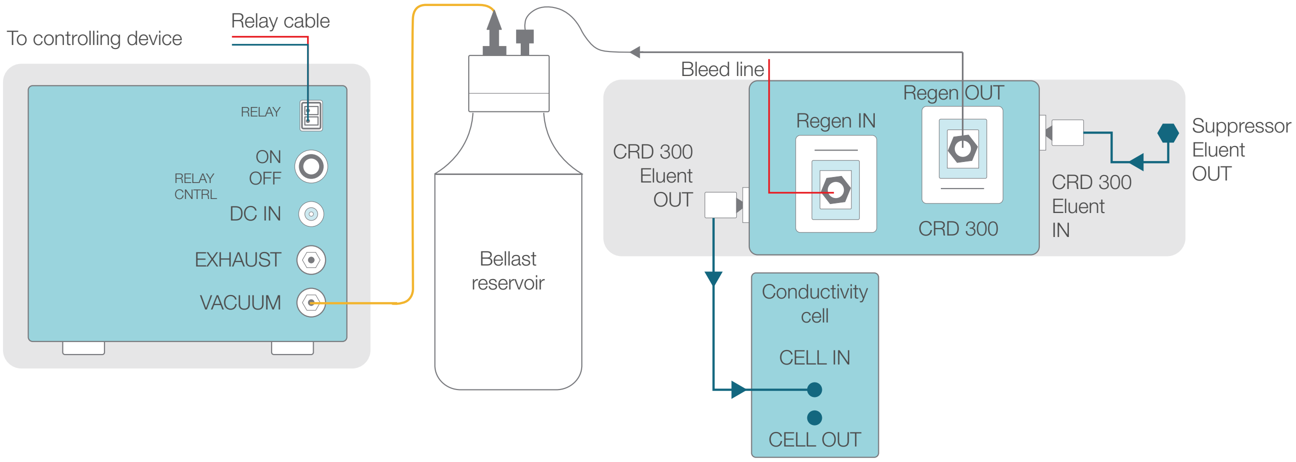


Figure 1. Flow diagram of Dionex CRD 300 carbonate removal device in vacuum mode.

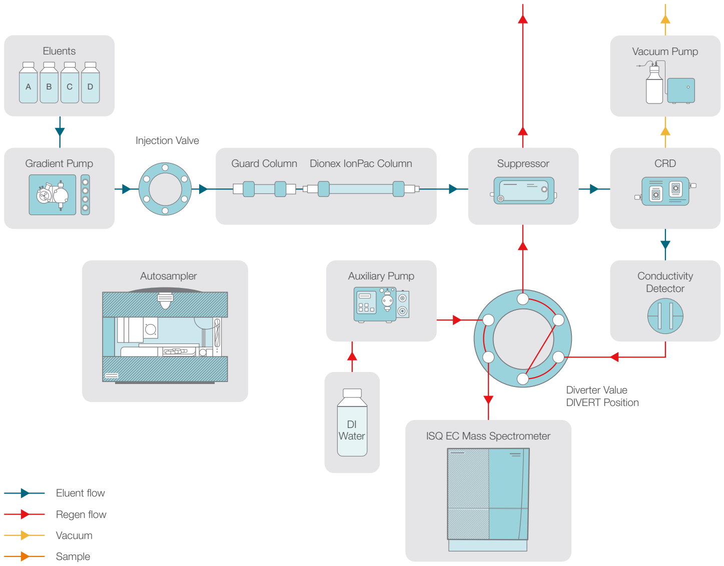


Figure 2A. Diverter valve in DIVERT position. While the system runs idle or a high ionic strength matrix elutes, the eluent is diverted from the MS, and the suppressor operates in the Recycling Mode.

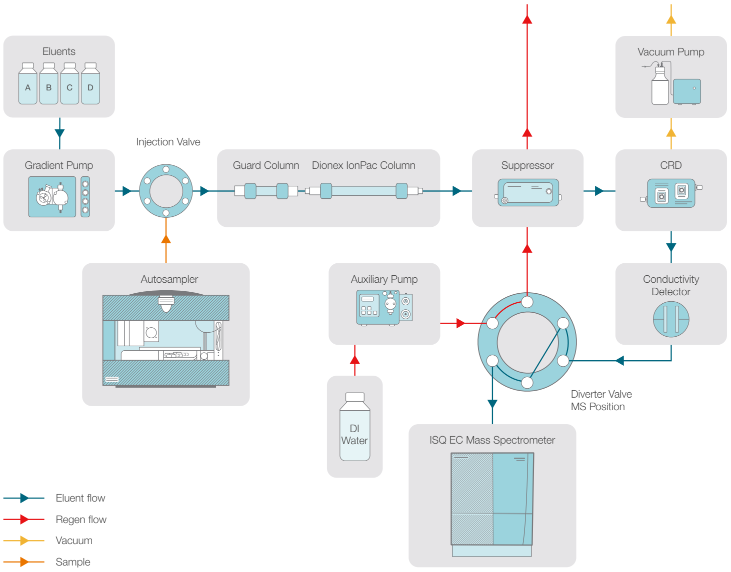
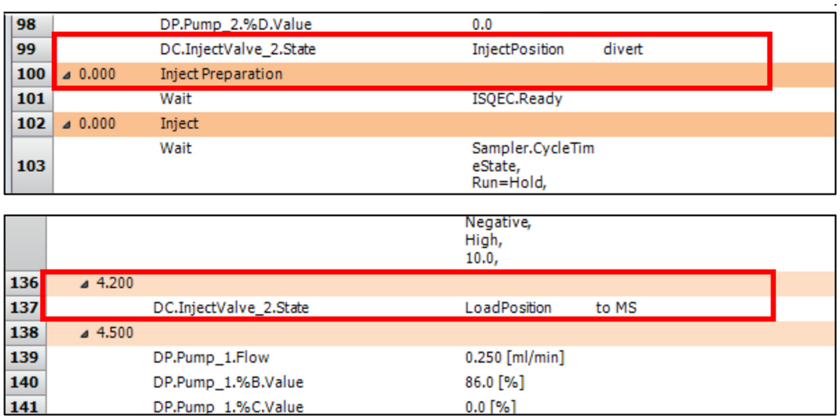


Figure 2B. Diverter valve in MS position. The eluent flow is directed to the mass spectrometer for analysis, and the suppressor operates in the External Water Mode.



98		DP.Pump_2.%D.Value	0.0	
99		DC.InjectValve_2.State	InjectPosition	divert
100	◢ 0.000	Inject Preparation		
101		Wait	ISQEC.Ready	
102	◢ 0.000	Inject		
103		Wait	Sampler.CycleTim eState, Run=Hold,	

			Negative, High, 10.0,	
136	◢ 4.200			
137		DC.InjectValve_2.State	LoadPosition	to MS
138	◢ 4.500			
139		DP.Pump_1.Flow	0.250 [ml/min]	
140		DP.Pump_1.%B.Value	86.0 [%]	
141		DP.Pump_1.%C.Value	0.0 [%]	

Figure 2C. Example of diverter valve control in the Chromeleon CDS Instrument Method Script Editor.

Standard preparation

Stock standard solutions

Stock standard solutions were prepared by dissolving the appropriate amount of each analyte in DI water, except for PF_6^-, to which the matrix mixture of "organic carbonates" was added to help with dissolution. The specific formulations for each stock standard solution are provided in Table 1.

Table 1. Preparation of individual stock solutions.

Analyte	Compound	Amount (mg)
Masses of compounds to prepare 1,000 mg/L anion standards in 20 mL DI water		
Fluoride	Sodium fluoride	44.2
Acetate	Sodium acetate	27.8
Formate	Sodium formate	30.2
Chloride	Potassium chloride	42.6
Nitrate	Sodium nitrate	27.4
Phosphate	Sodium phosphate	25.3
Sulfate	Sodium sulfate	29.6
Oxalate	Lithium oxalate	23.2
Perchlorate	Lithium perchlorate	21.5
PO_3F^{2-}	Sodium fluorophosphate	29.4
Masses of lithium salts to prepare 20,000 mg/L standards in 5 mL DI water		
$PO_2F_2^-$	Lithium difluorophosphate	106.9
$TFSI^-$	Lithium bis(trifluoromethanesulfonimide)	102.5
FSI^-	Lithium bis(fluorosulfonyl)imide	103.9
BF_4^-	Lithium tetrafluoroborate	108.0
Mass of $LiPF_6$ to prepare 50,000 mg/L PF_6^- standard in 9 mL DI water + 1 mL carbonate matrix mixture		
PF_6^-	Lithium hexafluorophosphate	523.9

Working standard solutions

Working standard solutions were prepared using stock standards (Table 2). Three distinct standard groups: anion calibration standard, lithium salt calibration standard, and fluorophosphate calibration standard, were created to address potential interferences caused by hydrolysis of certain lithium salts. For each of these three groups, six concentration levels were produced to generate calibration curves.

Table 2. Preparation of calibration standards.

Analyte	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6
Anion calibration standard (mg/L)						
Fluoride	1.00	2.00	5.00	9.99	33.30	49.95
Acetate	0.50	1.00	2.00	5.01	10.02	33.39
Formate	0.50	1.00	2.00	5.00	10.01	33.35
Chloride	0.50	1.00	2.00	5.00	10.00	33.33
Nitrate	0.50	1.00	2.00	5.01	10.01	33.38
Phosphate	0.95	1.90	4.76	9.51	31.70	47.55
Sulfate	0.50	0.99	1.98	4.95	9.90	33.00
Oxalate	0.99	1.98	4.95	9.90	32.99	49.49
Perchlorate	0.50	1.00	2.00	5.00	9.99	33.31
Lithium salt calibration standard (mg/L)						
$PO_2F_2^-$	8.80	35.19	87.98	175.97	586.56	879.85
BF_4^-	8.87	35.48	88.71	177.42	591.38	887.08
PF_6^-	92.99	371.94	929.85	1859.69	6198.97	9298.45
$TFSI^-$	10.67	42.70	106.74	213.48	711.58	1067.38
FSI^-	10.34	41.37	103.43	206.85	689.51	1034.26
Fluorophosphate calibration standard (mg/L)						
PO_3F^{2-}	1.02	2.04	5.09	10.18	33.93	50.89

Sample preparation

Sample matrix

Ethylene carbonate (EC), dimethyl carbonate (DMC), and diethyl carbonate (DEC) are esters of carbonic acid and solvents typically used for LIB electrolyte matrices. These three "organic carbonates" were mixed in equal parts by weight and used as a simulated sample matrix.

Simulated battery electrolyte samples

Two samples were prepared by weighing lithium salts and dissolving them in the sample matrix mixture, as shown in Table 3.

Table 3. Preparation of simulated LIB electrolyte.

	Sample 1 (*w*)	Sample 2 (*w*)
$LiPO_2F_2$	0.7%	0.6%
$LiBF_4$	1.0%	0.0%
LiBOB	0.9%	0.0%
LiODFB	0.0%	0.9%
$LiPF_6$	11.4%	12.0%
LiTFSI	0.7%	0.8%
LiFSI	1.0%	1.1%

Except for oxalate and fluorophosphate, anion standards were added to these samples to simulate contaminations with typical non-electrolyte components.

The simulated electrolyte was vigorously vortexed after preparation and before dilution to achieve an even distribution. The sample was then carefully pipetted and diluted 100-fold with DI water, resulting in no visible solid particles at this point. Subsequently, the sample was filtered through a syringe filter (pore size: 0.45 µm) and injected for analysis.

Results and discussion

Separation

Figure 3 shows the separation of 15 components. The chromatogram obtained with suppressed conductivity is at the top, and Selected Ion Monitoring (SIM) MS traces are in the middle. The bottom SIM chromatograms show the minor components at larger magnifications. Due to their different *m/z* values, MS detection can resolve fluorophosphate and sulfate, which are indistinguishable in conductivity detection.

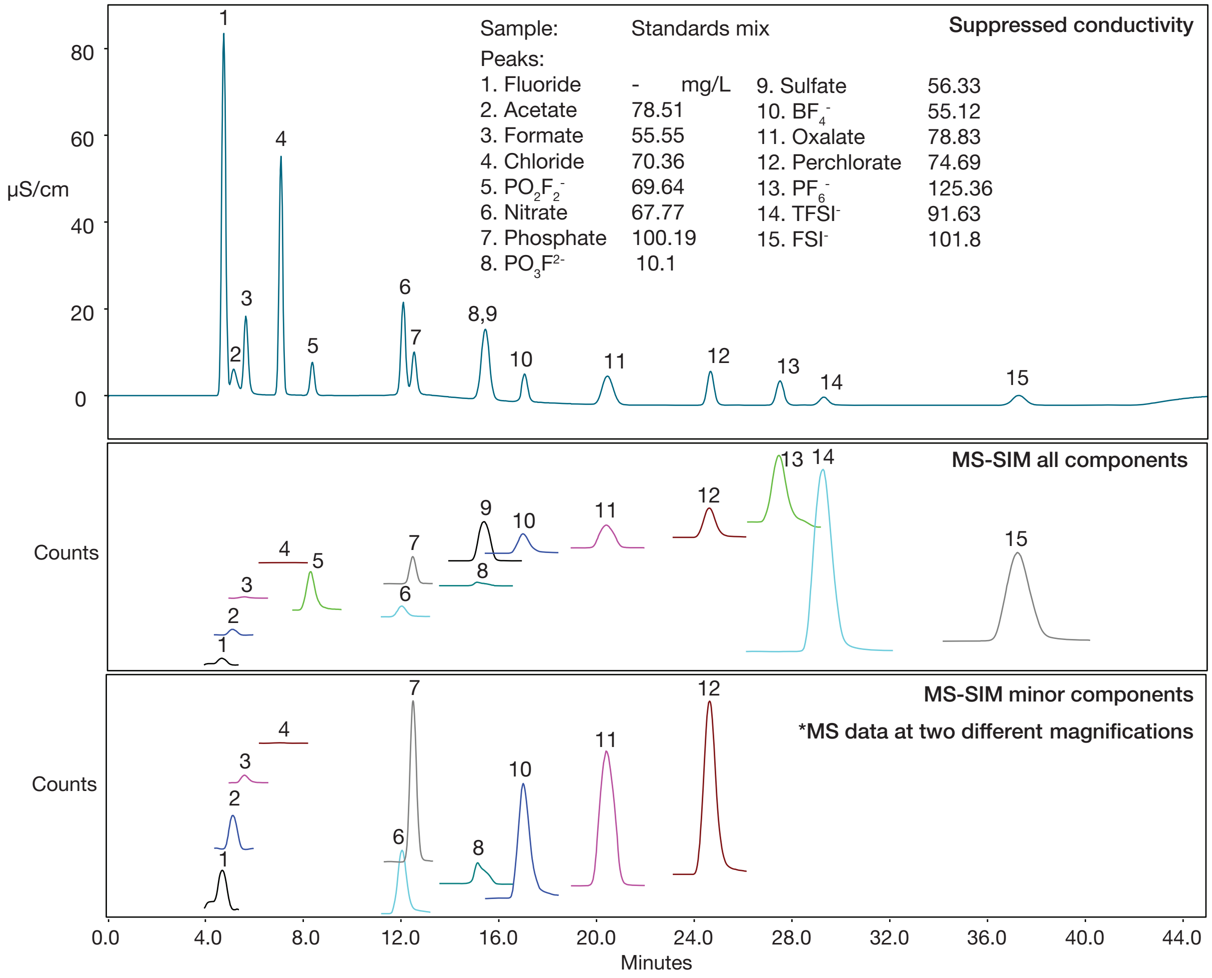


Figure 3. Separation and detection of 15 standard components by IC-MS. Top trace: suppressed conductivity detection. Middle trace: MS-SIM of all components at the same scale. Bottom trace: MS-SIM of minor components at larger magnification.

Calibration and estimated detection and quantitation limits

Calibration curves were generated (Table 4) for CD or MS detection. The detector choice depends on factors such as the analyte response, sample complexity, and potential chromatographic interference. Due to its higher sensitivity, smaller anions (e.g., fluoride and acetate) were quantified by CD. However, the degradation of individual electrolyte components can create a prominent fluoride peak, making integration of closely eluting peaks in the CD trace challenging. In such cases, more specific MS-SIM is advantageous.

High concentrations of polarizable ions (e.g., PF_6^-, $TFSI^-$, FSI^-) can cause ion suppression in the MS, resulting in reduced linear range and sensitivity. CD is recommended for quantitation in such cases, and MS data can be applied for analyte confirmation. On the other hand, PO_3F^{2-} and sulfate are better quantified and confirmed by MS due to almost identical retention times observed from conductivity detection.

The limit of detection (LOD) and limit of quantitation (LOQ) were calculated following the International Council for Harmonisation (ICH) guidelines.[7] The templates to perform these calculations directly in Chromeleon CDS are part of the Chromeleon CDS ICH-Extension Pack.

$$LOD = \frac{3.3\,\sigma}{S} \qquad LOQ = \frac{10\,\sigma}{S}$$

where σ = the standard deviation of the response
S = the slope of the calibration curve

Sample analysis

Figure 4 and Table 5 summarize the results for LIB electrolytes from suppressed conductivity and IC-MS detection. Recovery ranged from 60 to 142%. Values of 200% or more were observed for fluoride and fluorophosphate, suggesting hydrolysis of other sample constituents resulting in the above-mentioned anions.

Table 4. Calibration information, LOD, and LOQ for 15 standard components on IC-MS.

Compound	Retention time (min)	Number of points	Range (mg/L)	Detector used for calibration	Calibration type	Coefficient of determination (r^2)	LOD (mg/L)	LOQ (mg/L)
Fluoride	4.65	6	1.00–49.95	CD	Linear, With Offset	0.999	0.10	0.31
Acetate	5.06	6	0.50–33.39	CD	Linear, With Offset	1.000	0.02	0.07
Formate	5.55	6	0.50–33.35	CD	Quadratic, With Offset	1.000	0.10	0.29
Chloride	6.95	6	0.50–33.33	CD	Quadratic, With Offset	1.000	0.05	0.14
$PO_2F_2^-$	8.23	6	8.80–879.85	CD	Linear, With Offset	0.999	13.40	42.13
Nitrate	11.85	6	0.50–33.38	MS	Quadratic, With Offset	0.996	0.32	0.97
Phosphate	12.17	6	0.95–47.55	MS	Quadratic, With Offset	1.000	0.18	0.53
PO_3F^{2-}	15.03	6	1.02–50.89	MS	Quadratic, With Offset	0.998	0.22	0.66
Sulfate	15.18	6	0.50–33.00	MS	Quadratic, With Offset	1.000	0.14	0.44
BF_4^-	16.87	6	8.87–887.08	CD	Linear, With Offset	1.000	4.72	14.31
Oxalate	20.01	6	1.00–49.49	CD	Linear, With Offset	1.000	0.26	0.80
Perchlorate	24.49	6	0.50–33.31	CD	Quadratic, With Offset	1.000	0.05	0.16
PF_6^-	27.22	6	92.99–9298.45	CD	Linear, With Offset	1.000	72.88	220.80
$TFSI^-$	29.25	6	10.67–1067.38	CD	Linear, With Offset	0.999	7.81	23.66
FSI^-	37.14	6	10.34–1034.26	CD	Linear, With Offset	0.999	6.58	19.94

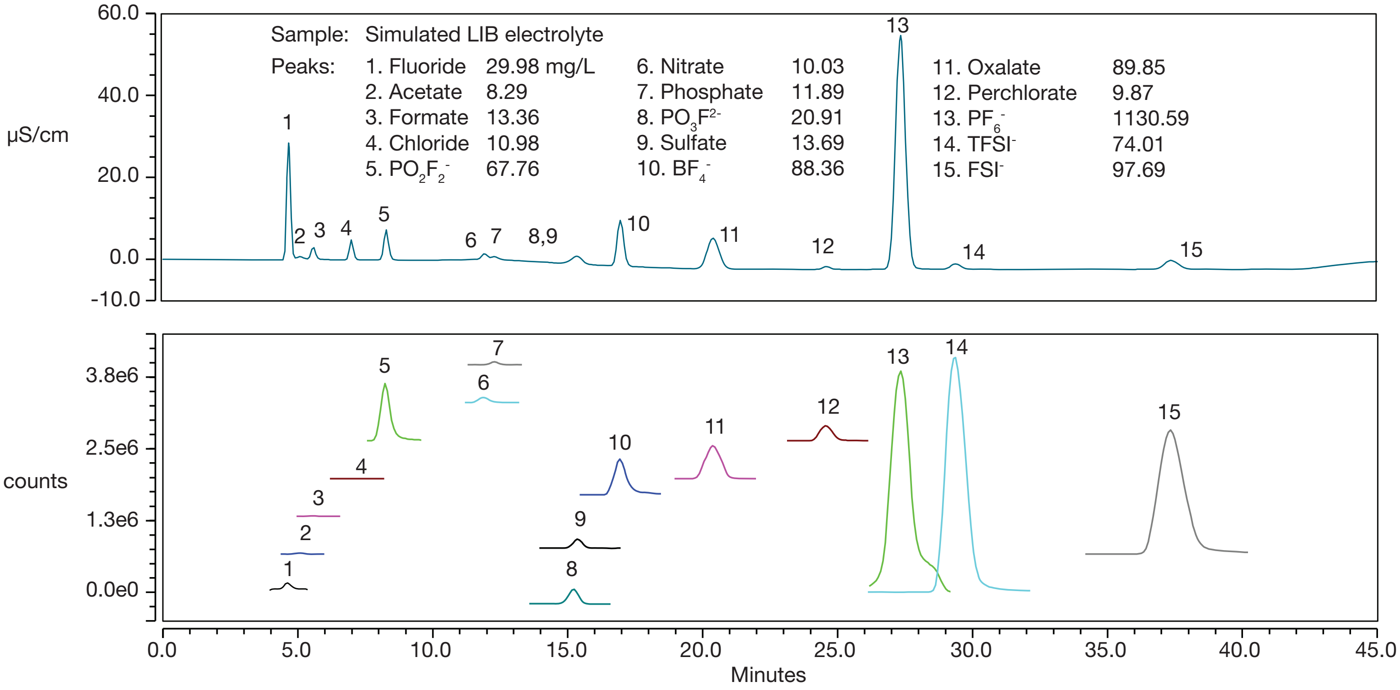


Figure 4. Analysis of simulated LIB electrolyte on IC-MS.

Table 5. Quantitation and recovery of simulated LIB electrolyte samples.

		Sample 1			Sample 2		
		Added amount (mg/L)	Detected amount (mg/L)	Recovery (%)	Added amount (mg/L)	Detected amount (mg/L)	Recovery (%)
1	Fluoride	9.99	29.98	300	9.99	56.26	563
2	Acetate	10.02	8.29	83	10.02	6.02	60
3	Formate	10.01	13.36	133	10.01	14.23	142
4	Chloride	10.00	10.98	110	10.00	11.62	116
5	$PO_2F_2^-$	64.46	67.76	105	58.14	76.03	131
6	Nitrate	10.01	10.03	100	10.01	10.26	102
7	Phosphate	9.51	11.89	125	9.51	12.00	126
8	PO_3F^{2-}	10.18	20.91	205	10.18	24.10	237
9	Sulfate	9.90	12.69	128	9.90	13.19	133
10	BF_4^-	90.34	88.32	98	-	17.91	-
As Oxalate	BOB^-	89.07	84.92	95	-	-	-
As Oxalate	$ODFB^-$	-	-	-	81.37	76.90	95
12	Perchlorate	9.99	9.89	99	9.99	10.25	103
13	PF_6^-	1091.76	1130.59	104	1145.01	1166.08	102
14	$TFSI^-$	71.89	74.02	103	78.54	75.16	96
15	FSI^-	98.92	97.67	99	108.02	104.30	97

BOB and ODFB amounts were calculated using oxalate using the following equations:

BOB^- (mg/L) = oxalate (mg/L) · 186.85 (g/mol BOB^-) / (2·88.00 (g/mol oxalate))

$ODFB^-$ (mg/L) = oxalate (mg/L) · 136.83 (g/mol $ODFB^-$) / 88.00 (g/mol oxalate)

Hydrolysis of lithium salts

Hydrolysis of some lithium salts imposed some limitations for this work. We found that $PO_2F_2^-$ decomposes at high pH. Although KOH eluents have previously been used in LIB applications, we wondered whether lower pH eluents would help. As Figure 5A shows, 1 g/L $LiPO_2F_2$ injected in KOH eluent exhibits significant tailing on fluoride and fronting on the PO_3F^{2-}, further decomposing into hydrolysis products as more NaOH is added to the sample. The changes in peak size for each component are plotted in Figure 5B.

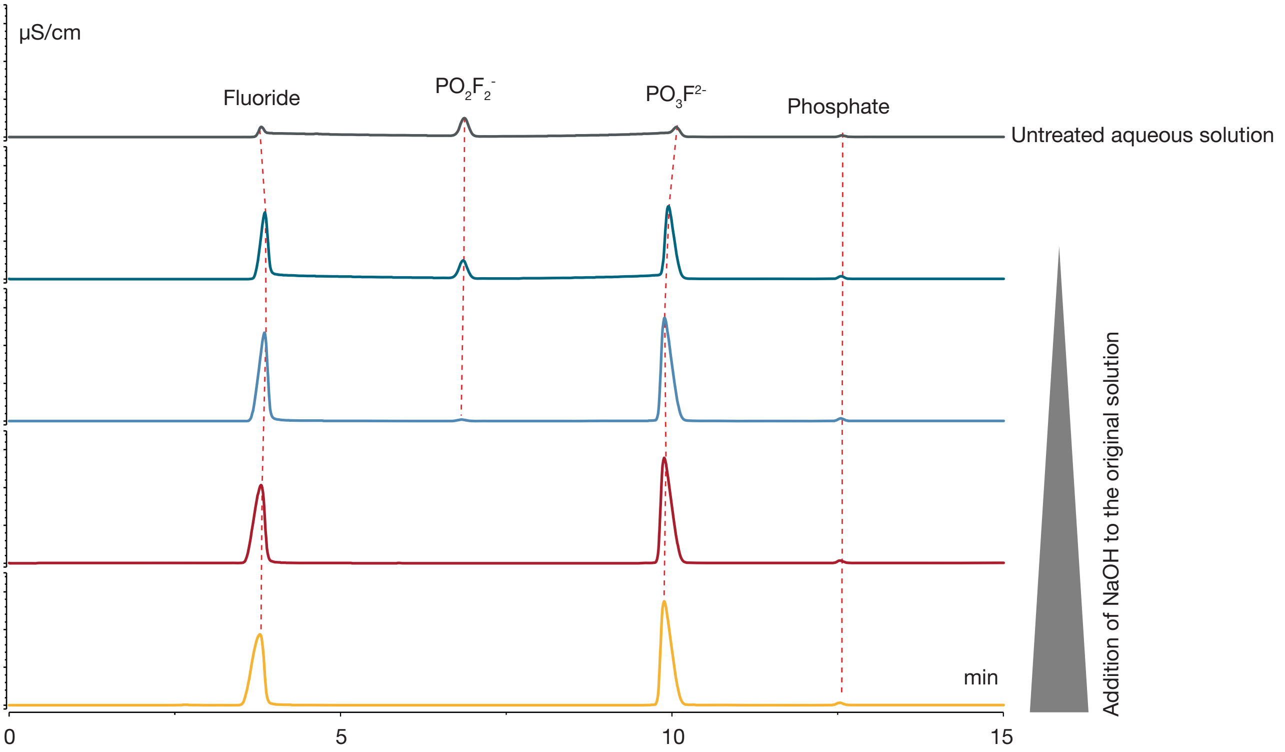
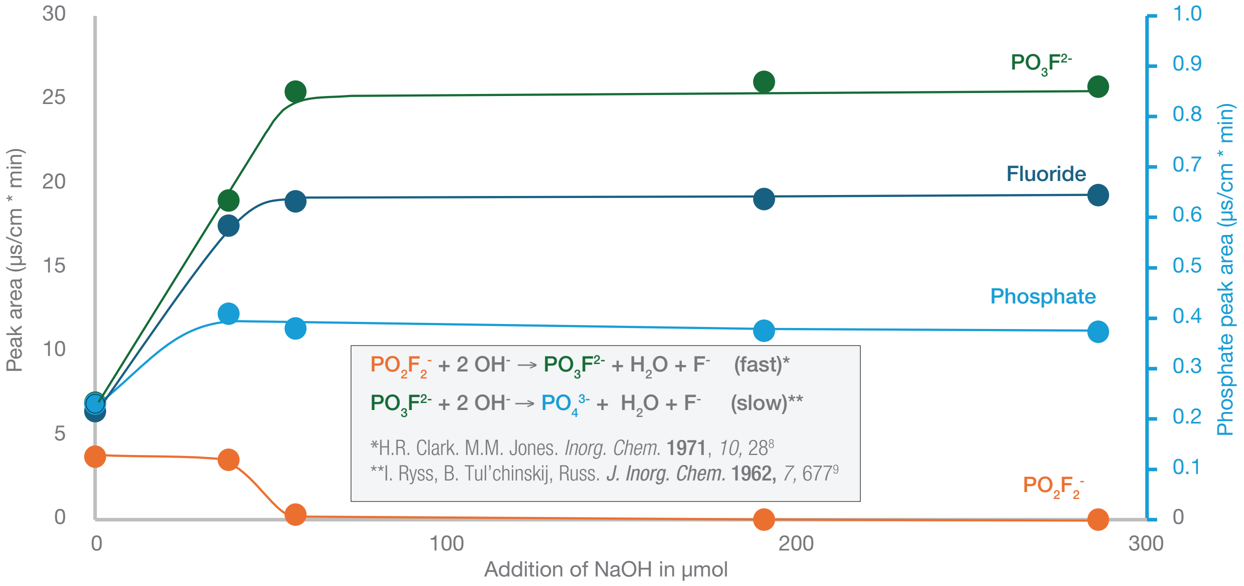


Figure 5A. Chromatograms of $LiPO_2F_2$ in KOH eluent. Untreated 1g/L $LiPO_2F_2$ in DI water (top chromatogram) shows hydrolysis products with significant tailing and fronting. The same sample was treated with increasing amounts of NaOH, showing a progressively greater degree of hydrolysis.



$PO_2F_2^- + 2\,OH^- \rightarrow PO_3F^{2-} + H_2O + F^-$ (fast)*

$PO_3F^{2-} + 2\,OH^- \rightarrow PO_4^{3-} + H_2O + F^-$ (slow)**

*H.R. Clark. M.M. Jones. *Inorg. Chem.* **1971**, *10*, 28[8]

I. Ryss, B. Tul'chinskij, Russ. *J. Inorg. Chem.* **1962, *7*, 677[9]

Figure 5B. Hydrolysis of $LiPO_2F_2$ in high pH environment. Changes in peak areas are observed with increasing amount of NaOH additions.

Though KOH eluent had previously been used in LIB applications work, we questioned whether alternative eluents with lower pH could be used to avoid degradation of the lithium salt during analysis of LIB samples. To address this, we switched to a carbonate/bicarbonate-based eluent and found that untreated $PO_2F_2^-$ remained intact, while degradation products appeared in the NaOH-treated sample (Figure 6). At high pH, PO_3F^{2-} and two new yet unidentified degradation products were formed.

Despite using carbonate eluents, hydrolysis was still observed to varying extents for certain lithium salts, as depicted in Figure 7. LiODFB and LiBOB underwent degradation and were quantified as oxalate. Additionally, LiODFB formed BF_4^- and oxalate (trace D of Figure 7). This suggests that the quantification of LiODFB is only feasible in the absence of both BF_4^- and BOB^-, while the quantification of LiBOB is only possible in the absence of $ODFB^-$.

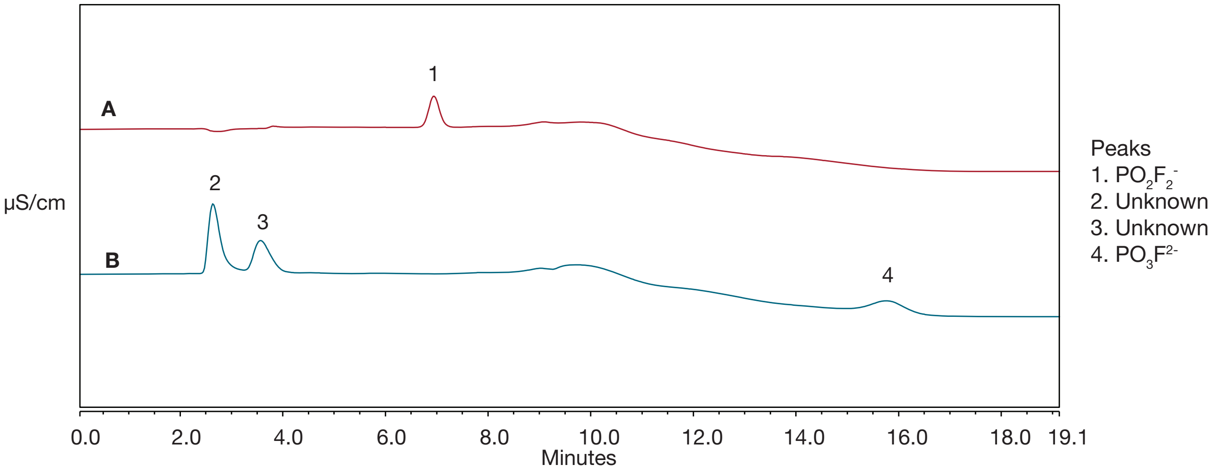


Figure 6. Effect of high pH environment on $PO_2F_2^-$. Eluent: See instrument method. A: $LiPO_2F_2$ standard. $PO_2F_2^-$ remains intact. B: $LiPO_2F_2$ standard with the addition of NaOH simulating the degradation of $PO_2F_2^-$ in higher-pH environments.

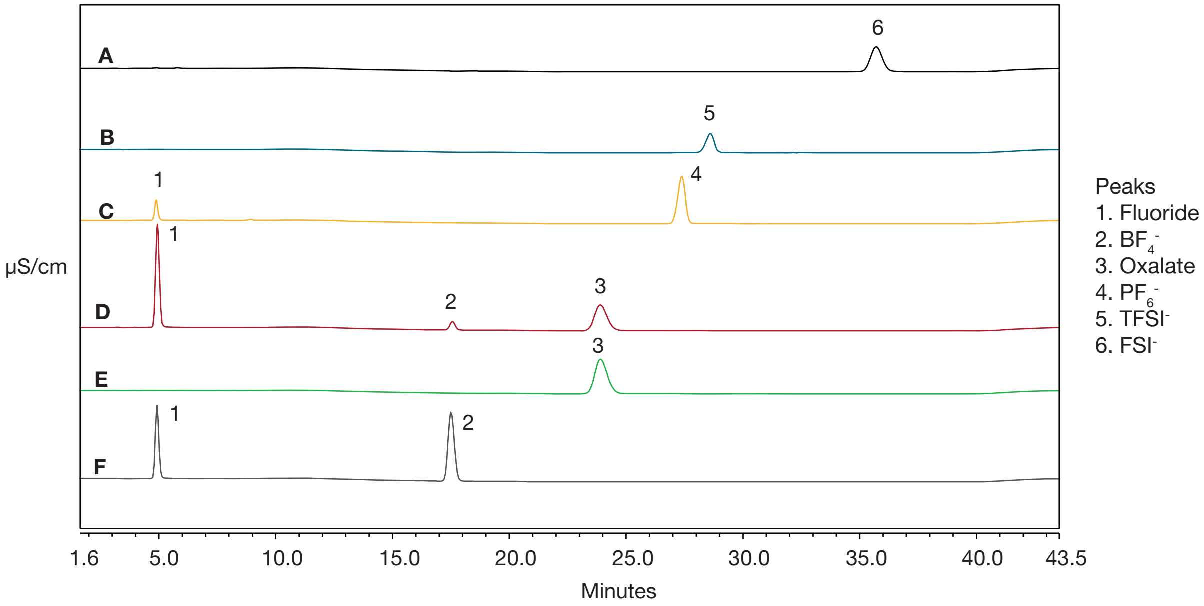


Figure 7. Hydrolysis products of lithium salt standards. A: LiFSI; B: LiTFSI; C: $LiPF_6$; D: LiODFB; E: LiBOB; F: $LiBF_4$.

Fifty-five injections were conducted over two days to assess degradation and method robustness. Each component's retention times (RT) and peak areas were recorded. The resulting relative standard deviations (RSD), mainly in the low-to-mid single digits, indicate that the sample composition remains stable after initial partial hydrolysis. The detailed RSD calculations are provided in Table 6.

Table 6. RT and area counts RSD for each peak over 55 consecutive injections.

	CD		MS	
Compound	**RT**	**Area**	**RT**	**Area**
Fluoride	0.09%	4.21%	0.12%	8.15%
Acetate	0.12%	5.42%	0.16%	13.08%
Formate	0.12%	5.94%	0.15%	6.29%
Chloride	0.16%	5.58%	0.18%	5.79%
$PO_2F_2^-$	0.18%	5.42%	0.21%	4.45%
Nitrate	0.22%	6.60%	0.24%	3.29%
Phosphate	0.50%	9.19%	0.45%	15.67%
PO_3F^{2-}	-	-	1.02%	19.66%
Sulfate	-	-	1.08%	22.24%
BF_4^-	0.33%	2.99%	0.35%	14.10 %
Oxalate	1.01%	1.58%	1.02%	6.85%
Perchlorate	0.24%	4.27%	0.25%	6.54%
PF_6^-	0.28%	0.84%	0.29%	3.47%
TFSI$^-$	0.34%	5.77%	0.35%	5.73%
FSI$^-$	0.35%	2.50%	0.36%	5.87%

Adjusting instrument method for alternate selectivity

The resolution of nitrate/phosphate and BF_4^-/oxalate/perchlorate proved challenging during method development. However, if the resolution of all 15 components is unnecessary, the instrument method can be adjusted to change the chromatographic selectivity. One practical approach is to alter the eluent's carbonate/bicarbonate concentration, which influences the RT of multivalent anions like phosphate, sulfate, PO_3F^{2-}, and oxalate.

To demonstrate this, a sample of simulated LIB electrolytes was analyzed using an adjusted bicarbonate concentration and a modified acetonitrile gradient (Figure 8). Notably, the nitrate and phosphate peaks were well resolved, while the PO_3F^{2-}/sulfate and BF_4^- eluted in reversed order. These effects can be attributed to a different ionic strength and eluent pH. This modified separation may be more desirable if enhanced resolution is needed for nitrate and sulfate with BF_4^- absent from the sample.

Eluent: A: 45 mM Sodium carbonate, 30 mM Sodium bicarbonate
B: DI water
C: Acetonitrile
Gradient: See right

Peaks:
1. Fluoride
2. Acetate
3. Formate
4. Chloride
5. $PO_2F_2^-$
6. Nitrate
7. Phosphate
8. PO_3F^{2-}
9. Sulfate
10. BF_4^-
11. Oxalate
12. Perchlorate
13. PF_6^-
14. TFSI$^-$
15. FSI$^-$

Gradient:

Time (min)	%A	%B	%C
0.0	12.0	88.0	0.0
3.0	12.0	88.0	0.0
12.0	12.0	61.0	27.0
14.5	12.0	61.0	27.0
15.0	12.0	51.0	37.0
35.0	12.0	88.0	0.0
45.0	12.0	88.0	0.0

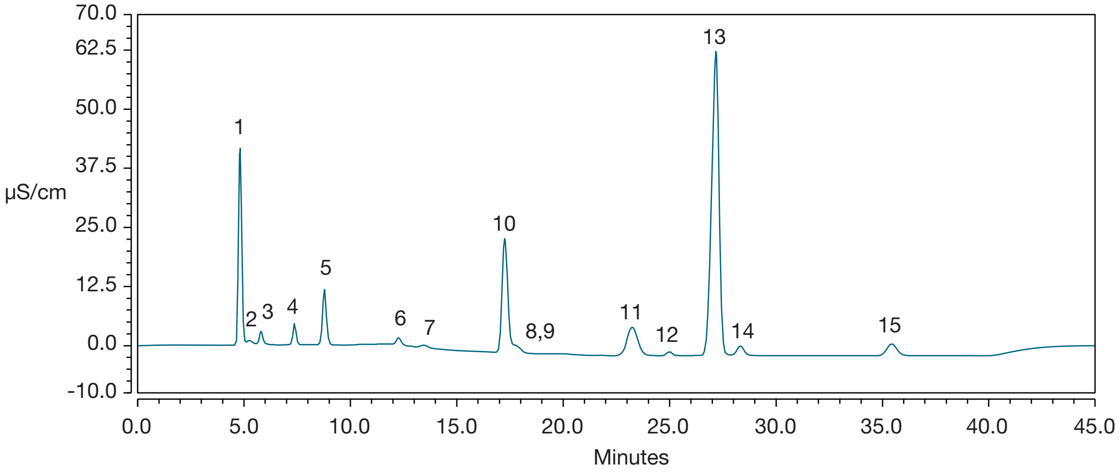


Figure 8. Example of the alternate separation of components in a simulated LIB electrolyte as a result of modifying the method gradient and eluent concentration. The chromatographic resolution of nitrate and phosphate improved, while BF_4^- and PO_3F^{2-}/sulfate peaks eluted in reversed order.

Conclusion

We developed an IC-MS method using a Dionex IonPac AS23 column with a Dionex ADRS 600 suppressor and a Dionex CRD 300 carbonate removal device in vacuum mode for the determination of common lithium salts, additives, and contaminants in under 40 minutes. One notable aspect of this study is the integration of an organic solvent to enhance chromatographic resolution. Introducing acetonitrile, we achieved excellent separation of many analytes in simulated LIB electrolyte samples.

Furthermore, our approach showcases the role of a CRD in minimizing the baseline effect caused by adding the non-protic organic solvent and of the suppressor in enabling sensitive anion detection with CD and MS. This dual-detection capability enhances the robustness and versatility of the approach, allowing for comprehensive characterization of the analytes of interest.

This method provides in-depth understanding of electrolyte composition, allowing LIB manufacturers and researchers to conduct further research, leading to advancements in future LIBs such as increased charging capacity and improved battery safety. Moreover, the knowledge gained from this method can be utilized for quality assurance, quality control, and failure analysis purposes to ensure the battery's performance. In essence, this method provides valuable information for a wide range of applications in the field of LIB research and manufacturing.

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