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Anions Analysis from Lithium-Ion Battery Electrolyte on Inuvion Ion Chromatography System

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Executive Summary

Lithium-ion, lead-acid, and alkaline batteries are frequently utilized in industrial and portable utility applications. Lithium-ion batteries have a longer lifespan, are more environmentally friendly, and have a higher power density than other batteries. The electrolyte plays a crucial function in lithium-ion batteries. Lithium salts and organic solvents make up its composition. The most common lithium salts used as electrolytes in lithium-ion batteries are lithium hexafluorophosphate (LiPF6), lithium bis(oxalate)borate (LiBOB), and lithium bis(fluorosulfonyl)imide (LiFSI). The kind and amount of lithium salts present in the electrolyte control the conduction current and ion transport efficiency. Higher concentrations permitted large load discharge, for instance, when the lithium salt concentration was between 0.9 and 1.5 mol/L; nevertheless, the rate of discharge at moderate voltages dropped above ion concentrations of 1.4 mol/L. Certain lithium salts, such LiPF6, are susceptible to heat instability and moisture, which makes them easily broken down into other compounds during battery operation. Consequently, it's critical to examine the types and amounts of lithium salts present in lithium ion battery electrolytes.

Ion chromatography (IC) is thought to be a highly helpful analytical method that has the major advantages of convenience and sensitivity when employed for complex ion analysis. Currently, there are little to none published reports on the simultaneous determination of these three lithium salts described above. In this work, a unique approach for the simultaneous measurement of these mentioned anions in a lithium-ion electrolyte by simple, rugged and cost effective Ion Chromatography system was proposed.

Equipment Required

- Thermo Scientific™ Dionex™ Inuvion™ IC system
- Thermo Scientific™ AS-AP Autosampler
- Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) Software

Reagents and Chemicals

- Deionized (DI) water, Type 1 reagent grade, 18 MΩ·cm resistivity or better
- Sodium Carbonate, AR grade
- Sodium Bicarbonate, AR grade
- Acetonitrile, LCMS grade
- Sulfuric Acid (H2SO4), AR grade
- Lithium hexafluorophosphate (LiPF6), battery grade
- Lithium bis(oxalate)borate (LiBOB), battery grade
- Lithium bis(fluorosulfonyl)imide (LiFSI), battery grade

Chromatographic Conditions

LC System	Inuvion Ion Chromatography system
Columns	IonPac™ AS23, 4mm PN 064149 and IonPac™ AG23, 4mm PN 064147
Eluent	25mM Na2CO3 + 5mM NaHCO3 in 30% Acetonitrile
Flow Rate	1.0mL/min
Suppressor	ACRS 500, 4mm PN 085090 or ASRS300, 4mm PN SP6949
Suppressor Regenerant	50mN H2SO4
Suppressor Peristaltic Pump Flow Rate	3.0mL/min
Injection Volume	25µL
Detection	Conductivity
Run Time	50 minutes

Flow chart:

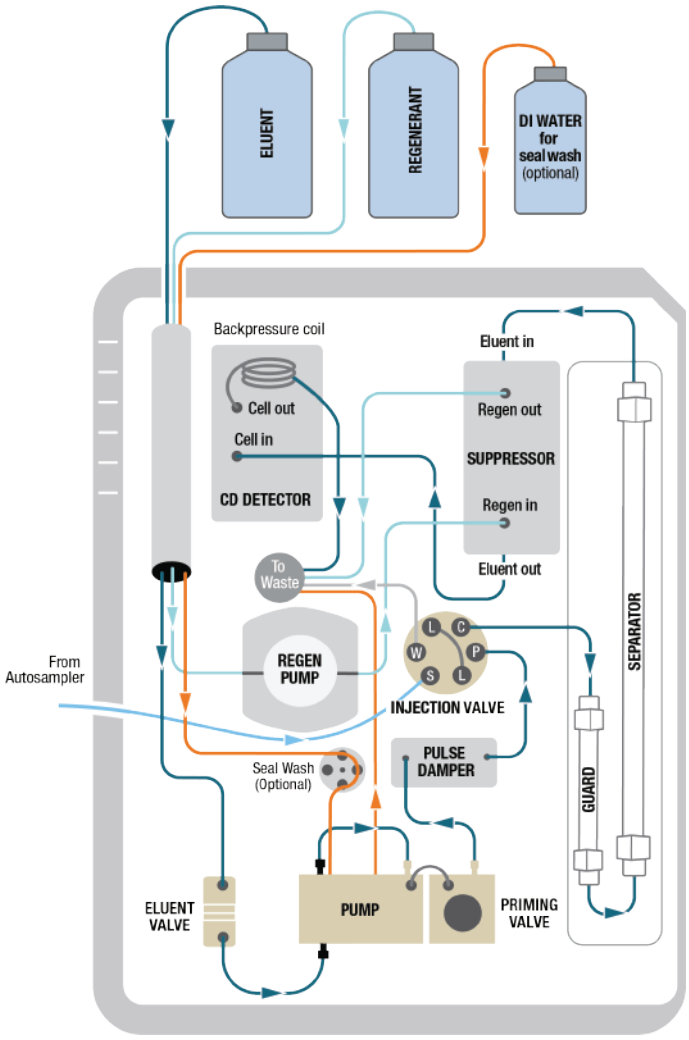

Figure 1 : Thermo Scientific™ Dionex™ Inuvion™ Core Ion Chromatography Schematic Diagram

Preparation of Diluent, Standard and Sample Solution

Diluent : Deionized Water

Standard Stock Solution: 1000mg/L (ppm) separate stock standards were prepared in glove box taking utmost precautions.

Standard Solution: Standard mixture for linearity study was prepared for its stock in following table.

Analyte	Level 1 (in mg/L)	Level 2 (in mg/L)	Level 3 (in mg/L)	Level 4 (in mg/L)	Level 5 (in mg/L)
BOB	2.50	5.00	10.00	15.00	20.00
PF6	5.00	10.00	15.00	20.00	30.00
FSI	5.00	10.00	15.00	20.00	30.00

Sample Solution: Electrolyte solution from discharged and consumed battery was recovered (in glove box) using centrifuge technique. About 0.1mL of this solution was diluted to 10mL with diluent. It was further diluted according to sample anionic content and analyte response.

Example Chromatograms

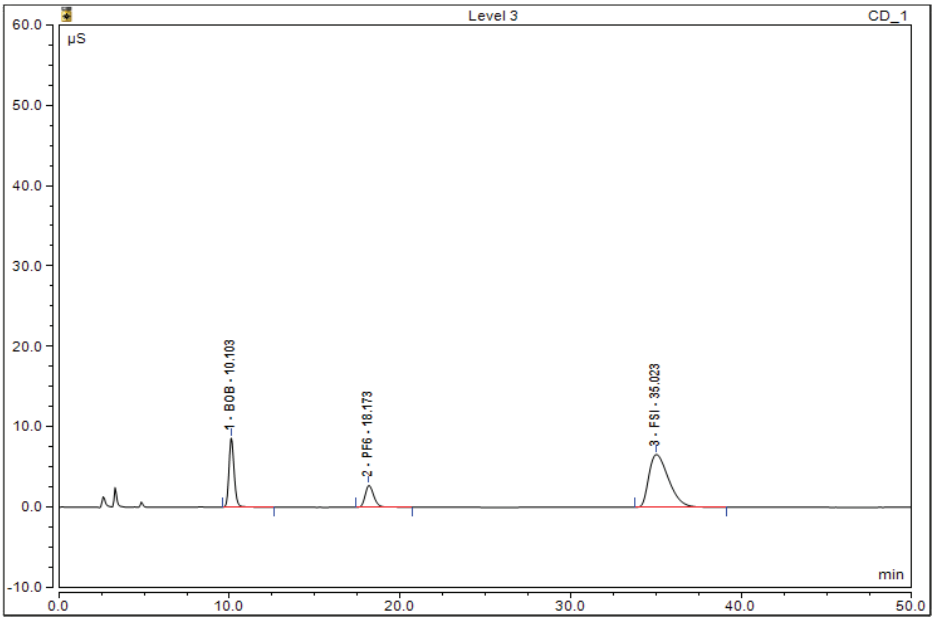

Figure 2 : Standard Mixture Chromatogram of 10.0mg/L BOB, 15.0mg/L PF6 and 15.0mg/L FSI.

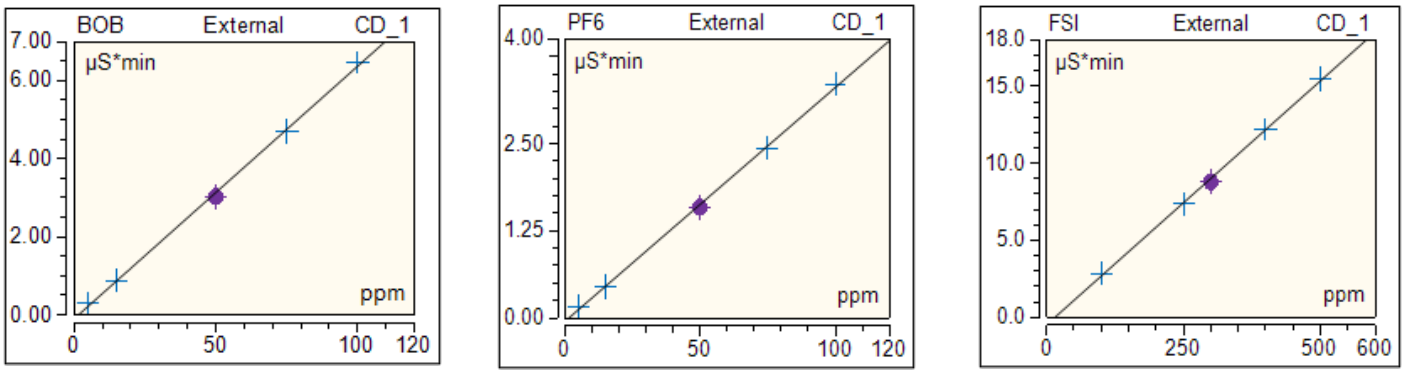

Figure 3 : Standard Mixture linearity plot for 2.50, 5.00, 10.0, 15.0 and 20.0 mg/L of BOB, 5.00, 10.0, 15.0, 20.0 and 30.0 mg/L of PF6, 5.00, 10.0, 15.0, 20.0 and 30.0 mg/L of FSI. Observed correlation coefficient for BOB = 0.9998, PF6 = 0.9995, FSI = 0.9993.

Sample Chromatogram

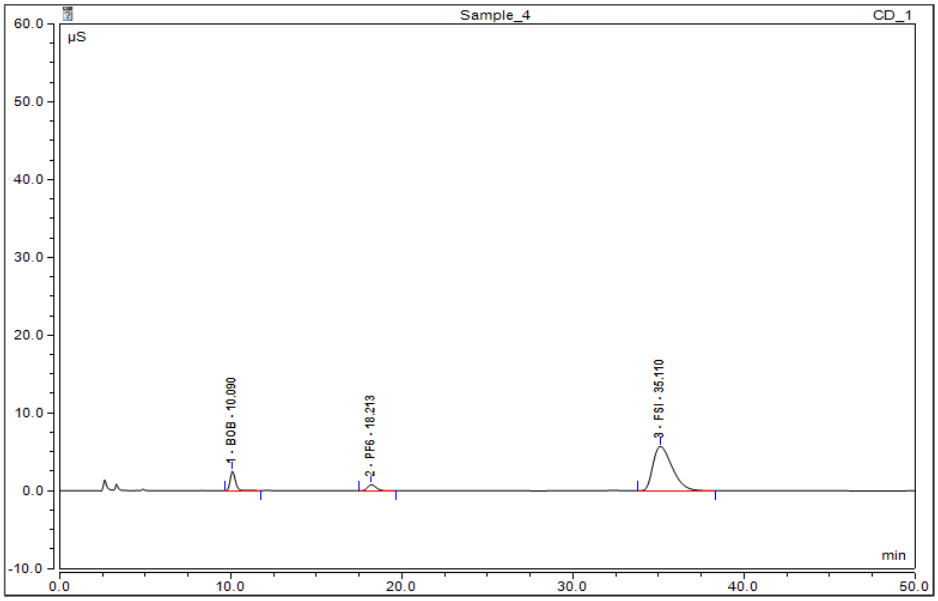

Figure 4 : Sample Chromatogram of consumed and discharged battery electrolyte

Method Accuracy

Method accuracy was evaluated through spike recovery studies. Mixture of BOB, PF6 and FSI standards were spiked into sample (n=3). The recovery results were provided in following table.

Analyte	Expected Amount, mg/L	Observed Amount, mg/L	% Recovery
BOB	2.50	2.52	100.80
PF6	5.00	5.08	101.60
FSI	5.00	4.93	98.60

Inuvion IC System

The Thermo Scientific™ Dionex™ Inuvion™ Core ion chromatography system provides the benefits of continuous chemical suppression through integrated pump which is controlled through Chromeleon™ 7.3.2 Software and higher-pressure operation to deliver consistently excellent results. The robust Dionex Inuvion platform is easily configurable and economically upgradeable to full-featured capabilities as budget allows.

Conclusion

Compounds like LiPF6, LiBOB and LiFSI retains very strongly on anionic exchange resins. In order to elute them from column and having good resolution, addition of organic solvents in eluent is mandatory. Dionex™ Inuvion™ Core IC with chemical suppression mode facility make it very easy for end users to develop method for anions analysis from battery electrolyte samples and use it during routine analysis for attaining best sensitivity, consistency and accuracy.

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