Application Note 258

Determination of Tetrafluoroborate, Perchlorate, and Hexafluorophosphate in a Simulated Electrolyte Sample from Lithium Ion Battery Production

INTRODUCTION

Lithium ion batteries are commonly used in portable consumer electronic devices. The electrolyte solution in these batteries consists of a lithium salt in an organic solvent. Commonly used salts are lithium hexafluorophosphate ($LiPF_6$), lithium perchlorate ($LiClO_4$), lithium tetrafluoroborate ($LiBF_4$), lithium hexafluoroarsenate ($LiAsF_6$), lithium hexafluorosilicate ($LiSiF_6$), and lithium tetraphenylborate ($LiB(C_6H_5)_4$). Some organic solvents used in the electrolyte solution are ethylene carbonate, diethyl carbonate, dimethyl carbonate, ethyl methyl carbonate, propylene carbonate, methyl formate, methyl acrylate, methyl butylate, and ethyl acetate. The electrolyte in lithium batteries may have a mixture of these lithium salts and organic solvents. The electrolyte's concentration in the solvent ranges from 0.1 to 2 mol/L, with an optimal range of 0.8–1.2 mol/L. The anions of the added lithium salts can be determined by ion chromatography (IC) to ensure that the solutions have been prepared at the proper concentrations.

Here, the authors prepare simulated samples that contain either lithium tetrafluoroborate, lithium perchlorate, or lithium hexafluorophosphate in an equal mixture of ethylene carbonate, diethyl carbonate, and propylene carbonate, and demonstrate that the anionic content can be determined accurately using a Reagent-Free™ IC system (RFIC™). The RFIC system allows the analyst to avoid the problems encountered in eluent preparation. The RFIC system also delivers excellent retention time reproducibility for easy and reproducible quantification in the analysis of lithium ion battery electrolyte solutions.

EQUIPMENT

Dionex ICS-3000* system including:
- DP Dual Pump
- DC Detector/Chromatography module with dual-temperature zone equipped with 6-port valve

EG Eluent Generator module

Chromeleon® Chromatography Data System (CDS) software Version 6.80 SR7

*This application can be conducted with any Dionex RFIC system.

REAGENTS AND STANDARDS

Deionized water (DI), Type I reagent-grade, 18 MΩ-cm resistivity or better

Lithium tetrafluoroborate, ($LiBF_4$, Sigma-Aldrich)

Lithium perchlorate, ($LiClO_4$, Sigma-Aldrich)

Lithium hexafluorophosphate, ($LiPF_6$, Sigma-Aldrich)

Ethylene carbonate, 98% ($C_3H_4O_3$, Sigma-Aldrich)

Diethyl carbonate, 99% ($C_5H_{10}O_3$, Sigma-Aldrich)

Propylene carbonate, ($C_4H_6O_3$, Sigma-Aldrich)

CHROMATOGRAPHIC CONDITIONS

Column:	IonPac® AS20 (4 × 250 mm) (P/N 063148)
Guard:	IonPac AG20 (4 × 50 mm) (P/N 063154)
Eluent Source:	EGC II KOH (P/N 058900) with CR-ATC (P/N 060477)
Gradient Steps:	Potassium hydroxide; 15 mM from –7 to 10 min 15 to 80 mM (Curve 4) from 10 to 13 min and 80 mM from 13 to 26 min
Flow Rate:	1.2 mL/min
Sample Volume:	10 µL
Column Oven:	35 °C
Pressure:	~2200 psi
Detection:	Suppressed conductivity ASRS® 300, 4 mm (P/N 060554) CRD 200, 4 mm (P/N 062983), Recycle mode
Suppressor Current:	238 mA

PREPARATION OF SOLUTIONS AND REAGENTS

Stock Standard Solutions

Dissolve 0.093, 0.112, and 0.105 g of lithium tetrafluoroborate, lithium perchlorate, and lithium hexafluorophosphate respectively in DI water in separate 100 mL volumetric flasks. Dilute to volume with DI water.

Calibration Standard Solutions

Prepare mixed calibration standard solutions by diluting a mixture of defined volumes of 1000 mg/L stock standard solutions with DI water in a 10 mL volumetric flask. The volumes of each 1000 mg/L stock standard solution and the prepared calibration standard concentrations are shown in Table 1.

Table 1. Volumes of 1000 mg/L Stock Standard Solutions Used to Prepare Calibration Standards at the Listed Concentrations

Concentration of each Anion (mg/L)	Volume of each 1000 mg/L Stock Standard Solution (µL)	Final Volume (mL)
5	50	10
10	100	10
20	200	10

Eluent

The eluent generator (EG) produces the eluent using the EluGen EGC II KOH cartridge and deionized water (18 MΩ-cm resistivity or better) supplied by the pump. The eluent concentration is controlled by Chromeleon CDS software. The EluGen cartridge requires at least 14 MPa (2000 psi) of system backpressure, which ensures optimal removal of electrolysis gas from the eluent produced by the generator. See the *ICS-3000 Operator's Manual* (Document No. 065031-04) for instructions on adding backpressure.

Mixture of Three Carbonate Solvents (1:1:1)

Thoroughly mix 10 g each of ethylene carbonate, diethyl carbonate, and propylene carbonate.

Simulated Electrolyte Sample

To simulate samples from lithium ion batteries, prepare three samples. Two samples are 1 M solutions of lithium tetrafluoroborate and lithium perchlorate prepared in the mixture of three carbonate solvents. The third sample is a 1 M solution of lithium hexafluorophosphate prepared in DI water. Later, this sample will be diluted 1:1 with the mixture of three carbonate solvents. This preparation is necessary because lithium hexafluorophosphate does not dissolve in the mixture of three carbonate solvents. Table 2 shows details of the sample preparation for these three samples.

Table 2. Preparation of Simulated Samples

Simulated Sample	Weight of Lithium Salt (g)	Solvent	Final Volume (mL)
1 M Lithium tetrafluoroborate	0.938	Mixture of three carbonate solvents	10
1 M Lithium perchlorate	1.068	Mixture of three carbonate solvents	10
1 M Lithium hexafluorophosphate	1.519	DI water	10

Sample Preparation

Tetrafluoroborate and Perchlorate Sample

Dilute 1 M lithium tetrafluoroborate and lithium perchlorate solutions 10,000 times with DI water.

Hexafluorophosphate Sample

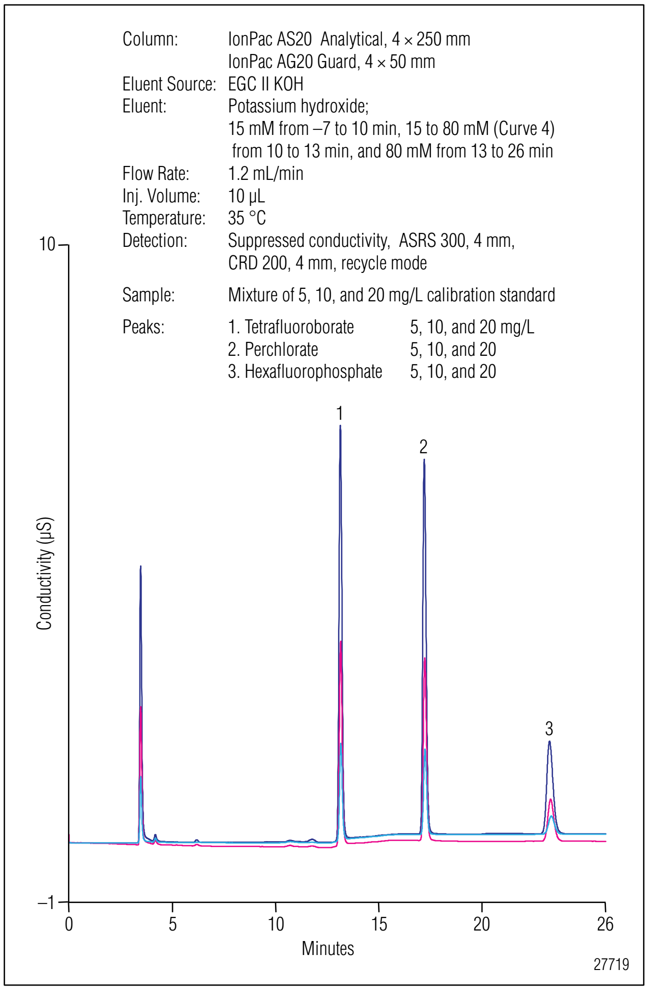
Mix 1 M lithium hexafluorophosphate with the mixture of three carbonate solvents in a 1:1 ratio. Dilute this solution 5,000 times with DI water.

RESULTS AND DISCUSSION

Chromatography

The analyte anions in this application—perchlorate, tetrafluoroborate, and hexafluorophosphate—are classified as polarizable anions. These anions tend to be strongly retained and have poor peak shapes with typical anion-exchange columns. With anion-exchange columns, analysts often include organic additives in the eluent (e.g. *p*-cyanophenol) to improve the peak shapes of polarizable anions. This is undesirable as it increases eluent costs, eluent complexity, waste disposal costs, and decreases detection sensitivity. To address this problem, Dionex designed the IonPac AS16 column and later, the IonPac AS20 column. These are high-capacity, hydroxide-selective, anion-exchange columns designed for polarizable anions. The stationary phases in these columns allow easy elution of polarizable anions with good peak shapes while requiring no organic solvent in the eluent. The high capacity allows the determination of polarizable anions in the presence of high concentrations of other anions.

In the analysis presented here, the authors used the AS20 column because it has higher column capacity than the AS16 column (310 µeq/column compared to 160); however, the AS16 column can also be used with different hydroxide eluent concentrations. Because both columns can be used with hydroxide eluents, they can be paired with an eluent generator (EG). An EG, the key component of an RFIC system, produces error-free pure hydroxide eluent. This translates to highly reproducible analyte retention times for reproducible determination without the labor involved in manually preparing hydroxide eluents. Figure 1 shows the separation of three mixed standard solutions (used for method calibration) of the three analytes of interest, perchlorate, tetrafluoroborate, and hexafluorophosphate. The three anions were well separated in about 25 min, with the first analyte, tetrafluoroborate, eluting at about 13 min. The first 12 min of the separation were included to allow most common inorganic anions to elute so that they did not interfere with the determination of the three analytes. Tetrafluoroborate eluted between sulfate and phosphate, while perchlorate and hexafluorophosphate eluted after phosphate. Table 3 shows the calibration information for each analyte.



Column:	IonPac AS20 Analytical, 4 × 250 mm IonPac AG20 Guard, 4 × 50 mm
Eluent Source:	EGC II KOH
Eluent:	Potassium hydroxide; 15 mM from –7 to 10 min, 15 to 80 mM (Curve 4) from 10 to 13 min, and 80 mM from 13 to 26 min
Flow Rate:	1.2 mL/min
Inj. Volume:	10 µL
Temperature:	35 °C
Detection:	Suppressed conductivity, ASRS 300, 4 mm, CRD 200, 4 mm, recycle mode
Sample:	Mixture of 5, 10, and 20 mg/L calibration standard
Peaks:	1. Tetrafluoroborate 5, 10, and 20 mg/L 2. Perchlorate 5, 10, and 20 3. Hexafluorophosphate 5, 10, and 20

Figure 1. Overlay of chromatograms of the calibration standards.

Table 3. Concentrations of Calibration Standards and the Calibration Results Reported by Chromeleon Software

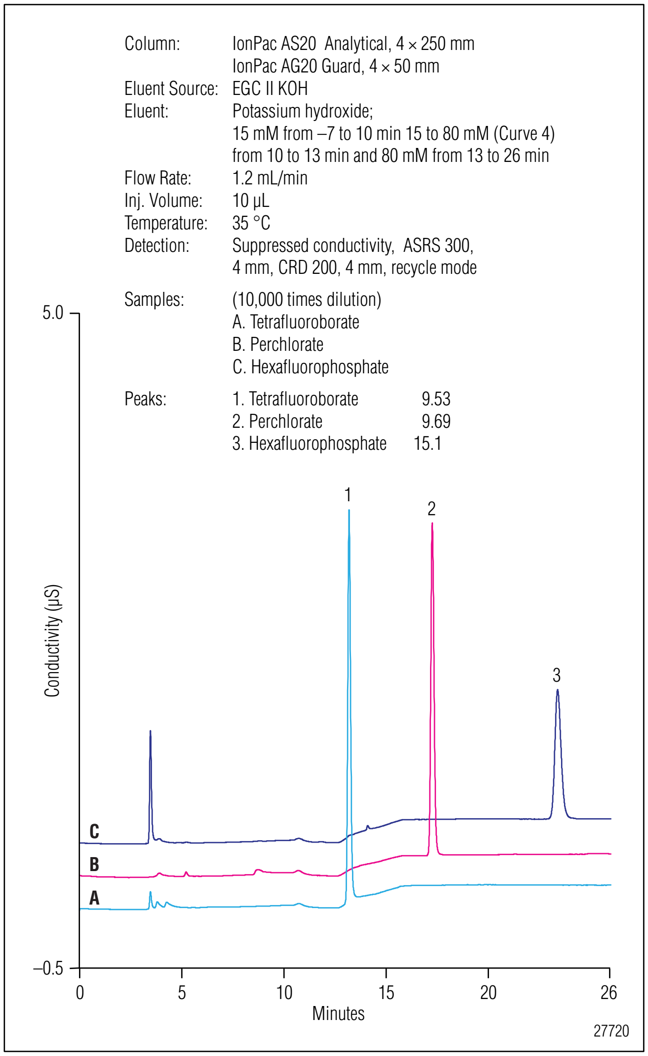
Analyte	**Concentration (mg/L)**			**Result**		
	Level 1	**Level 2**	**Level 3**	**% Coeff.Det.**	**Offset (µS*min)**	**Slope (µS*min)/mg/L**
Tetrafluoroborate	5	10	20	100.00	–0.0485	0.0606
Perchlorate	5	10	20	99.99	–0.0597	0.0623
Hexafluorophosphate	5	10	20	99.91	–0.0449	0.0296

Sample Analysis

Here, three simulated lithium ion battery electrolyte samples were prepared. One molar solution each of lithium tetrafluoroborate and lithium perchlorate was prepared in a mixture of three carbonate solvents. One molar lithium hexafluorophosphate was prepared in DI water and then diluted 1:1 with the mixture of three carbonate solvents. The first two samples were diluted 1 to 10,000 and the third sample was diluted 1:5,000 with DI water prior to analysis by IC. Figure 2 shows the chromatography of each of the three samples. The CRD-200 was used to eliminate any possible interference from sample carbonate. Short-term reproducibility was measured by making five injections of each sample. The data in Table 4 show good reproducibility for the amount measured in each sample. To judge accuracy, the authors compared measured concentration to the calculated concentration (Table 5) and found that the measured concentration was between 97.4, 104, and 109% of the calculated concentration for perchlorate, hexafluorphosphate, and tetrafluoroborate, respectively. As a second test of accuracy, the simulated samples were spiked with 2 mg/L of the same anion prior to dilution. The data in Table 5 also show good recoveries for each anion, suggesting method accuracy.

CONCLUSION

This application demonstrates an IC method that uses an RFIC system to easily assay the anions in the simulated lithium ion battery electrolyte samples. The results show that this method is both accurate and reproducible.



Column: IonPac AS20 Analytical, 4 × 250 mm
IonPac AG20 Guard, 4 × 50 mm
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Eluent: Potassium hydroxide;
15 mM from –7 to 10 min 15 to 80 mM (Curve 4)
from 10 to 13 min and 80 mM from 13 to 26 min
Flow Rate: 1.2 mL/min
Inj. Volume: 10 µL
Temperature: 35 °C
Detection: Suppressed conductivity, ASRS 300,
4 mm, CRD 200, 4 mm, recycle mode

Samples: (10,000 times dilution)
A. Tetrafluoroborate
B. Perchlorate
C. Hexafluorophosphate

Peaks:
1. Tetrafluoroborate 9.53
2. Perchlorate 9.69
3. Hexafluorophosphate 15.1

Figure 2. Chromatograms of samples (10,000 times dilution).

Table 4. Assay Results for the Samples and Spiked Samples

Injection No.	Amount (mg/L)					
	Tetrafluoroborate		Perchlorate		Hexafluorophosphate	
	Sample	Spiked Sample	Sample	Spiked Sample	Sample	Spiked Sample
1	9.57	11.3	9.74	11.9	15.1	16.7
2	9.45	11.3	9.68	11.9	15.1	16.8
3	9.58	11.1	9.75	11.7	15.1	16.7
4	9.55	11.3	9.69	11.8	15.1	16.8
5	9.48	11.2	9.57	11.8	15.2	16.8
Average	**9.53**	**11.3**	**9.69**	**11.8**	**15.1**	**16.8**
RSD	**0.62**	**0.55**	**0.74**	**0.64**	**0.30**	**0.26**

Table 5. Recovery Results

Ion	Calculated Concentration after 10,000 Times Dilution (mg/L)	Average Found Concentration (mg/L)	Recovery (%)	Spiked Concentration (mg/L)	Average Found Concentration in Spiked Sample (mg/L)	Recovery (%)
Tetrafluoroborate	8.70	9.53	109	2	11.3	88.5
Perchlorate	9.95	9.69	97.4	2	11.8	106
Hexafluorophosphate	14.5	15.1	104	2	16.8	85.0

Dionex Corporation
1228 Titan Way
P.O. Box 3603
Sunnyvale, CA
94088-3603
(408) 737-0700

North America
U.S./Canada (847) 295-7500

South America
Brazil (55) 11 3731 5140

Europe
Austria (43) 1 616 51 25 Benelux (31) 20 683 9768 (32) 3 353 4294
Denmark (45) 36 36 90 90 France (33) 1 39 30 01 10 Germany (49) 6126 991 0
Ireland (353) 1 644 0064 Italy (39) 02 51 62 1267 Sweden (46) 8 473 3380
Switzerland (41) 62 205 9966 United Kingdom (44) 1276 691722

Asia Pacific
Australia (61) 2 9420 5233 China (852) 2428 3282 India (91) 22 2764 2735
Japan (81) 6 6885 1213 Korea (82) 2 2653 2580 Singapore (65) 6289 1190
Taiwan (886) 2 8751 6655

www.dionex.com

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