Application note | 002666

Industrial

Determination of impurities in lithium salts used in battery manufacturing by ion chromatography and ICP-MS

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Keywords

Dionex IonPac AS11-HC column, Dionex IonPac CS16 column, suppressed conductivity, anions, cations, elemental impurities, iCAP RQ ICP-MS

Goal

Quantification of ionic impurities present in lithium-based raw materials used in batteries by Thermo Scientific™ ion chromatography and ICP-MS systems

Introduction

Lithium-ion batteries (LIBs) have revolutionized the modern electronic industry by providing high energy density, longer lifespan, and a more environmentally friendly alternative to traditional lead-acid and nickel-cadmium batteries. These rechargeable batteries are widely used in portable electronic devices, electric vehicles, and energy storage systems.[1]

The key advantages of LIBs over other battery chemistries are their high energy density, which allows them to store more energy in a smaller size and weight, and their low self-discharge rate, which means that they can hold their charge for a longer time when not in use. Additionally, LIBs have a longer lifespan compared to other rechargeable batteries, which makes them more cost-effective.[1,2]

However, despite their numerous advantages, there are still challenges associated with the production and use of LIBs. These challenges include the high cost of raw materials, concerns regarding their safety and stability, and the environmental impact of battery disposal. To overcome these challenges, there is ongoing research to improve the performance and sustainability of LIBs.

Lithium-ion batteries are now ubiquitous in modern-day technology, powering everything from smartphones and laptops to electric vehicles and grid-scale energy storage. Central to the performance of LIBs are the salts that make up their electrolytes which facilitate the movement of lithium ions between the battery's electrodes. As such, the choice of electrolyte salt plays a critical role in determining the battery's overall performance, including its energy density, power output, safety, and lifespan. For instance, impurities can interfere with the electrochemical process, leading to reduced battery capacity, and certain elements can react with battery components causing instability or potential hazards, such as overheating or even battery failure. In recent years, there has been considerable research aimed at developing new electrolyte salts and improving existing ones to enhance the performance of LIBs and enable their broader adoption.[6]

In this Application Note, various electrolyte salts (raw materials) such as lithium carbonate, lithium fluoride, lithium hydroxide, and phosphorus pentachloride were tested for their ionic and elemental impurities content using ion chromatography (IC) and ICP-MS separately. The percentage assay of these salts was also checked using an IC system.

Experimental

Equipment

Thermo Scientific™ Dionex™ ICS-6000 HPIC system including*:

- Dionex ICS-6000 SP Pump module
- Dionex ICS-6000 EG Eluent Generator module with high-pressure degasser module
- Dionex ICS-6000 DC Detector/Chromatography module with conductivity detector
- Thermo Scientific™ Dionex™ AS-AP Autosampler with 250 µL sample syringe (P/N 074306) and 1,200 µL buffer line (P/N 074989), and 10 mL vial trays

* Equivalent results can be achieved using a Thermo Scientific™ Dionex™ Integrion™ HPIC system.

- Thermo Scientific™ iCAP™ RQ ICP-MS

Software

- Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS), version 7.2.10 SR
- Thermo Scientific™ Qtegra™ ISDS software

Chemicals and reagents

- Deionized (D.I.) water, Type I reagent grade, 18.2 MΩ·cm resistivity or better
- Thermo Scientific™ Dionex™ EGC 500 KOH Potassium Hydroxide Eluent Generator Cartridge (P/N 075778).
- Methane sulfonic acid (MSA) with 99% purity or Thermo Scientific™ Dionex™ EGC 500 MSA Methane Sulfonic Acid Eluent Generator Cartridge (P/N 075779)
- Nitric acid (65–69%), TraceMetal™ grade, Fisher Scientific (ICP-MS).
- Individual elemental standard solutions (for all elements under study, each at 1,000 mg/L, Thermo Scientific™)

Products assessed

Lithium carbonate ($LiCO_3$), lithium fluoride (LiF), lithium hydroxide monohydrate ($LiOH.H_2O$), and phosphorous pentachloride (PCl_5) were tested for their anionic and elemental impurities content.

Analysis

The analysis was carried out using IC (Dionex ICS-6000 HPIC system) coupled with a suppressed conductivity detector (CD) for anion impurities determination and ICP-MS for elemental impurities. The optimized IC conditions are listed in Table 1 and the ICP-MS method parameters in Table 2. For the cation assay of lithium salts, analytical conditions are provided in Table 3.

Table 1. Ion chromatography conditions: anion impurities

Parameter	Value
Columns	Thermo Scientific™ Dionex™ IonPac™ AS11-HC (2 × 250 mm, P/N 052961) and IonPac AG11-HC (2 × 50 mm, P/N 052963)
Eluent	Potassium hydroxide (gradient) Time (min) KOH (mM) 0.0 2.0 2.0 2.0 25.0 25.0 32.0 25.0 33.0 2.0 40.0 2.0
Eluent source	KOH RFIC*
Flow rate	0.38 mL/min
Column oven temperature	30 °C
Injection volume	10 µL
Detection	Suppressed conductivity, Thermo Scientific™ Dionex™ ADRS 600 suppressor (2 mm), recycle mode, 24 mA current
Detection temperature	35 °C
Suppressor compartment	20 °C
Runtime	40 min

*RFIC: Reagent free ion chromatography

Table 2. ICP-MS method parameters

Parameter	Value
RF power	1,550 W
Nebulizer gas flow	1.12 L/min
Auxiliary gas flow	0.8 L/min
Cool gas flow	14 L/min
Sample uptake/wash	60 s
Pump speed flush	100 RPM
Pump speed analysis	40 RPM
Number of replicates	3
Helium flow (KED)	4.9 mL/min

Table 3. Chromatographic conditions for the cation assay of 10 ppm lithium standards. Precision study done with six injections.

Parameter	Value
Columns	Thermo Scientific™ Dionex™ IonPac™ CS16 (5 × 250 mm P/N 079805) + CG16 (5 × 50 mm P/N 057574)
Eluent	30 mM Methane sulfonic acid (MSA)
Flow rate	1.0 mL/min
Detector	Suppressed conductivity
Suppressor	Thermo Scientific™ Dionex™ CDRS 600 (4 mm), recycle mode
Suppressor current	88 mA
Column oven temperature	40 °C
Injection volume	10 µL
Runtime	40 min

Sample preparation for impurities

Diluent: D.I. water

- Lithium carbonate: Around 0.5 g of sample was placed in a 50 mL volumetric flask and diluted to the mark with diluent. The solution was sonicated to aid dissolution and then filtered through a 0.2 µm nylon membrane filter and with a Thermo Scientific™ Dionex™ OnGuard™ II H (1 cc, P/N 057085) syringe filter, to remove alkali and alkaline earth metals, and the resultant solution was used for analysis.

- Phosphorus pentachloride: Around 0.1 g of sample was placed in a 50 mL volumetric flask and diluted to the mark with diluent. The solution was sonicated to aid dissolution and then filtered through a 0.2 µm nylon membrane filter. A further 0.25 mL of aliquot was diluted to 50 mL, then used for phosphate analysis.

- Lithium fluoride and lithium hydroxide monohydrate: Around 0.1 g of sample was placed in a 50 mL volumetric flask and diluted to the mark with diluent. The solution was sonicated to aid dissolution and then filtered through a 0.2 µm nylon membrane filter and used for analysis.

Sample preparation for assay

- Lithium carbonate: Around 0.187 g of sample was placed in a 50 mL polypropylene (PP) volumetric flask and diluted to the mark with 1 M HCl. This solution was sonicated to aid dissolution and filtered through a 0.2 µm membrane filter. 0.1 mL of this sample was diluted to 10 mL for analysis.

- Lithium fluoride: Around 0.302 g of sample was placed in a 50 mL polypropylene (PP) volumetric flask and diluted to the mark with 1 M HCl. This solution was sonicated to aid dissolution and filtered through a 0.2 µm nylon membrane filter. 0.1 mL of this sample was diluted to 10 mL and used for analysis.

- Lithium hydroxide monohydrate: Around 0.532 g of sample was placed in a 50 mL polypropylene (PP) volumetric flask and diluted to the mark with 1M HCl. This solution was sonicated to aid dissolution and filtered through a 0.2 µm membrane filter. 0.1 mL of this sample was diluted to 10 mL for analysis.

Standards preparation for anionic impurities

Diluent: D.I. water

Preparation of standards: Prepared from respective 1,000 ppm standards

Table 4. Standards concentrations

Analyte	Concentrations (mg/L)
Fluoride (F)	1.0, 2.5, 5.0, 10.0, 15.0
Chloride (Cl)	0.5, 1.0, 2.5, 5.0, 10.0
Nitrate (NO_3)	0.1, 0.5, 1.0, 2.5, 5.0
Sulfate (SO_4)	1.0, 2.5, 5.0, 10.0, 15.0
Phosphate (PO_4)	0.1, 0.5, 1.0, 2.5, 5.0

Sample preparation for elemental impurities by ICP-MS

- Lithium fluoride, lithium hydroxide, lithium carbonate, phosphorous pentachloride: Approx. 0.1 g of sample was dissolved using 2% (v/v) nitric acid and vortexing. A clear solution was obtained and then diluted to 50 mL. The solutions were analyzed using ICP-MS. Scandium (Sc), yttrium (Y), terbium (Tb) and germanium (Ge) were used as internal standards. Eight-point calibration curves were generated using certified standards from 1 ppb to 500 ppb. The blank was 2% (v/v) nitric acid containing internal standards.

Standards preparation for elemental impurities

Diluent: 2% (v/v) nitric acid

Preparation of standards: Prepared from respective 1,000 ppm standards

For analyte concentrations see Table 5.

Table 5. Analyte concentrations

Analyte	Concentrations (µg/L)
Boron (B)	1, 5, 10, 50, 100, 500
Sodium (Na)	1, 5, 10, 50, 100, 500
Aluminum (Al)	1, 5, 10, 50, 100, 500
Magnesium (Mg)	1, 5, 10, 50, 100, 500
Potassium (K)	1, 5, 10, 50, 100, 500
Calcium (Ca)	10, 50, 100, 500, 1,000, 5,000
Iron (Fe)	1, 5, 10, 50, 100, 500
Silicon (Si)	1, 5, 10, 50, 100, 500
Zinc (Zn)	1, 5, 10, 50, 100, 500
Lead (Pb)	1, 5, 10, 50, 100, 500
Copper (Cu)	1, 5, 10, 50, 100, 500
Chromium (Cr)	1, 5, 10, 50, 100, 500
Nickel (Ni)	1, 5, 10, 50, 100, 500

Results and discussion

Separation

The Dionex IonPac AS11-HC column (for anionic impurities) and the Dionex IonPac CS16 column (for the lithium cation assay) were used for the determination of anions and cations using a KOH gradient and MSA, respectively. The system features electrolytic eluent generation, which simplifies the method, avoids manual eluent preparation, improves reproducibility, and provides a high degree of automation.

Method linearity (anions)

Linearity for anions (Figure 1) was determined using five different concentrations as mentioned previously (sample preparation section). Correlation coefficients of >0.9996 were obtained for all the anions.

Example chromatograms

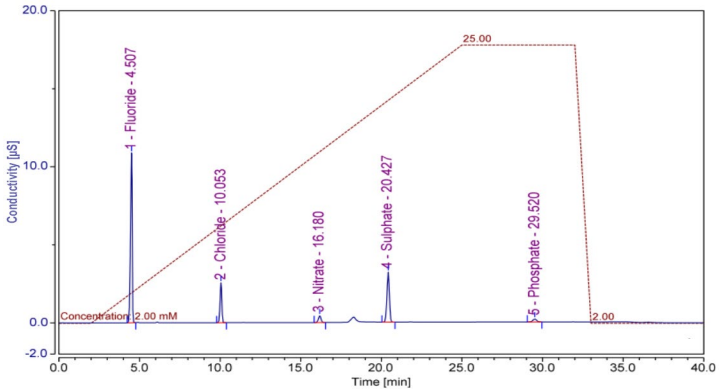

Figure 2. An example chromatogram for anionic impurities standard-3, showing excellent separation and resolution for all anions, with no interference from other compounds

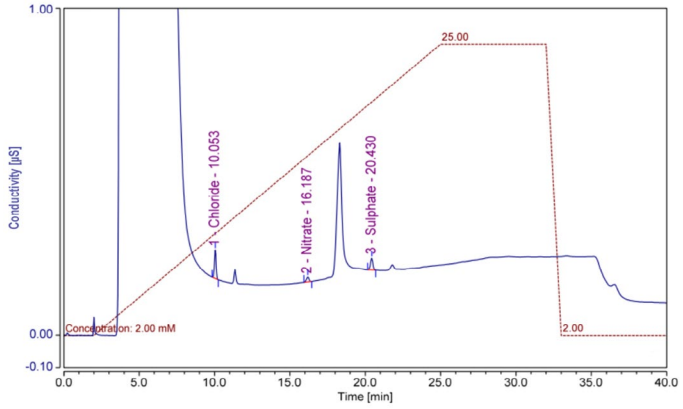

Figure 3. Chromatogram for lithium fluoride (B1)

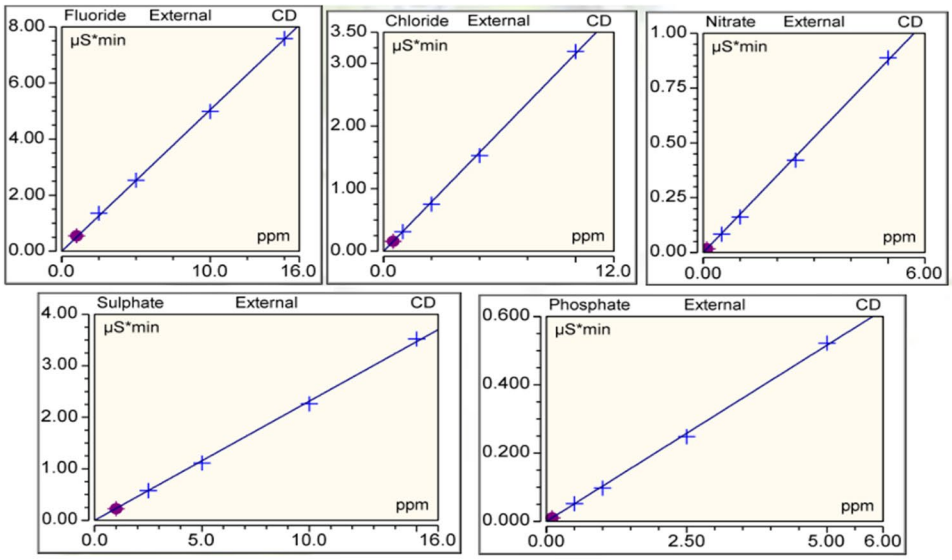

Figure 1. Linearity for anionic impurities

Sample no.	Retention time min	Peak name	Points	Correlation coefficient
1	4.45	Fluoride	5	0.9997
2	10.03	Chloride	5	0.9999
3	16.17	Nitrate	5	0.9999
4	20.42	Sulfate	5	0.9999
5	29.52	Phosphate	5	0.9999
Average:				0.9999

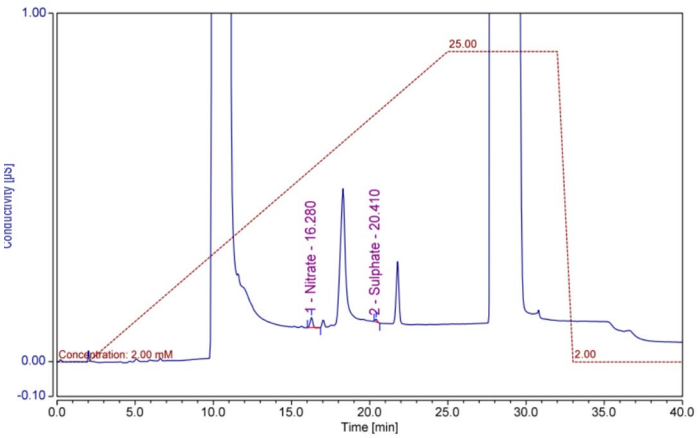

Figure 4. Chromatogram of phosphorous pentachloride (PCl_5)

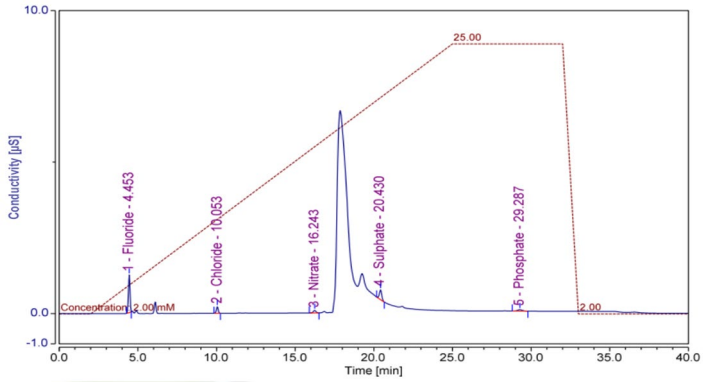

Figure 5. Chromatogram of lithium carbonate (B1)

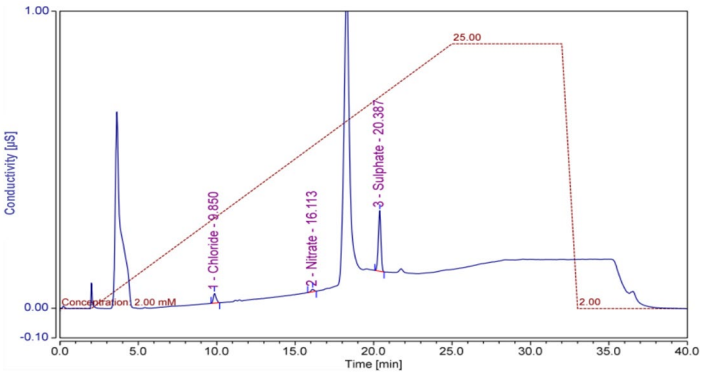

Figure 6. Chromatogram of lithium hydroxide monohydrate

Sample results (anion impurities)

Table 6 describes the concentration of anionic impurities present in various samples. Samples were diluted 10 times with diluent, to bring the concentration of chloride, sulfate, and phosphate into the linearity range, and injected. For phosphate content from phosphorus pentachloride, the sample was diluted 10,000 times with diluent and injected.

Table 6. Sample results (anion impurities) in mg/kg, dilution corrected

Sample name	Fluoride	Chloride	Nitrate	Sulfate	Phosphate
Lithium carbonate (B1)	27.9	8.6	9.1	24.5	15.7
Lithium carbonate (B2)	10.2	86.7	56.2	156.0	39.4
Phosphorous pentachloride	ND**	ND**	14.5	2.5	336,000
Lithium fluoride (B1)	NA*	16.2	8.1	13.9	ND*
Lithium fluoride (B2)	NA*	33.9	8.7	23.0	ND*
Lithium hydroxide (B1)	NA*	10.1	5.0	79.9	ND*
Lithium hydroxide(B2)	NA*	14.0	3.2	92.4	ND*
Lithium hydroxide(B3)	NA*	15.6	N. D	97.6	ND*

*NA: Not Applicable **ND: Not Detected

Cation assay for lithium content

The relative standard deviation (RSD) for the lithium assay (n = 6) displayed good reproducibility with RSD of 0.31 (area) and 0.05 (RT).

Table 7. % RSD for lithium (n=6) for assay

Sample name	Retention time (min)	Area (µS·s)
Standard_Injection 1	5.43	199.7
Standard_Injection 2	5.43	201.09
Standard_Injection 3	5.44	200.94
Standard_Injection 4	5.44	200.85
Standard_Injection 5	5.43	200.13
Standard_Injection 6	5.44	201.28
Average	**5.436**	**200.663**
RSD	**0.05%**	**0.31%**

The method performance was further demonstrated with the overlay of chromatograms for 10 ppm lithium (Figure 7).

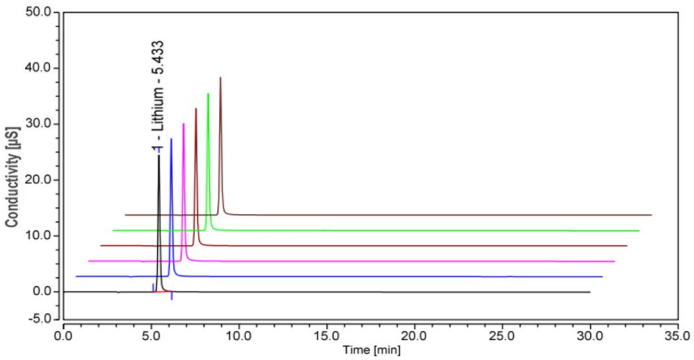

Figure 7. Chromatogram overlay (offset for conductivity and time, for clarity) for repeated injections of the 10 ppm lithium standard

Sample results (cation assay)

For the cation assay, all samples showed assay results as given in Table 8 with good recoveries of between 98% and 102%. Example chromatograms are shown in Figures 8–10.

Table 8. Sample results (cation assay)

Sample	Details	Results in %
Sample-1	Lithium fluoride(B1)	98.2
Sample-2	Lithium fluoride(B2)	98.8
Sample-3	Lithium hydroxide (B1)	98.3
Sample-4	Lithium hydroxide (B2)	98.6
Sample-5	Lithium hydroxide (B3)	98.1
Sample-6	Lithium carbonate(B1)	99.4
Sample-7	Lithium carbonate(B2)	98.8

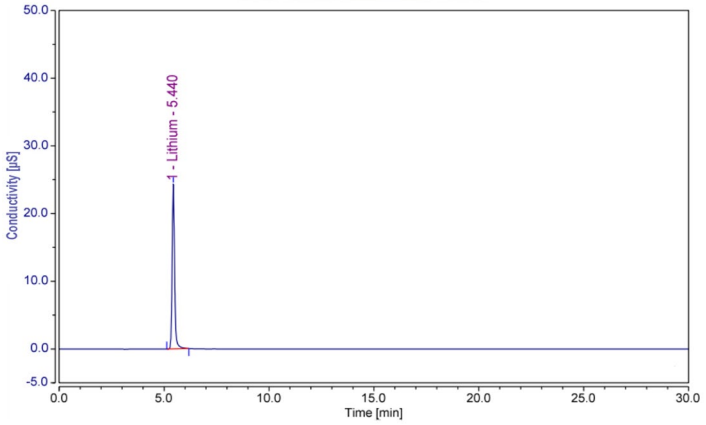

Figure 8. Chromatogram of lithium fluoride sample

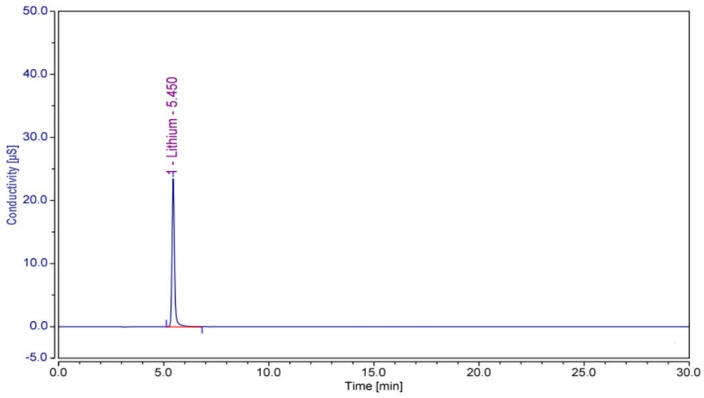

Figure 9. Chromatogram of lithium hydroxide monohydrate sample

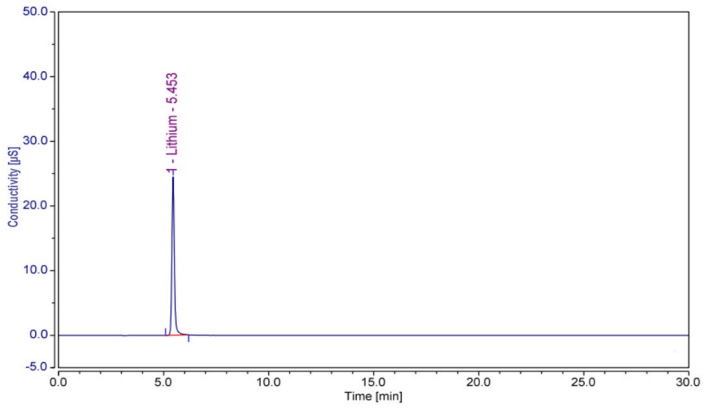

Figure 10. Chromatogram of lithium carbonate sample

Linearity for elemental impurities by ICP-MS

Linearity analysis was performed for elemental impurities by using six concentrations, as mentioned previously, and excellent correlation coefficients were found for all the elements (>0.999), as shown in Figure 11. Measured impurity concentrations and spike recovery test results are given in Tables 9 and 10, respectively. Good analytical robustness was obtained, as shown by the signal response of the yttrium and terbium internal standards throughout the analysis (Figure 12).

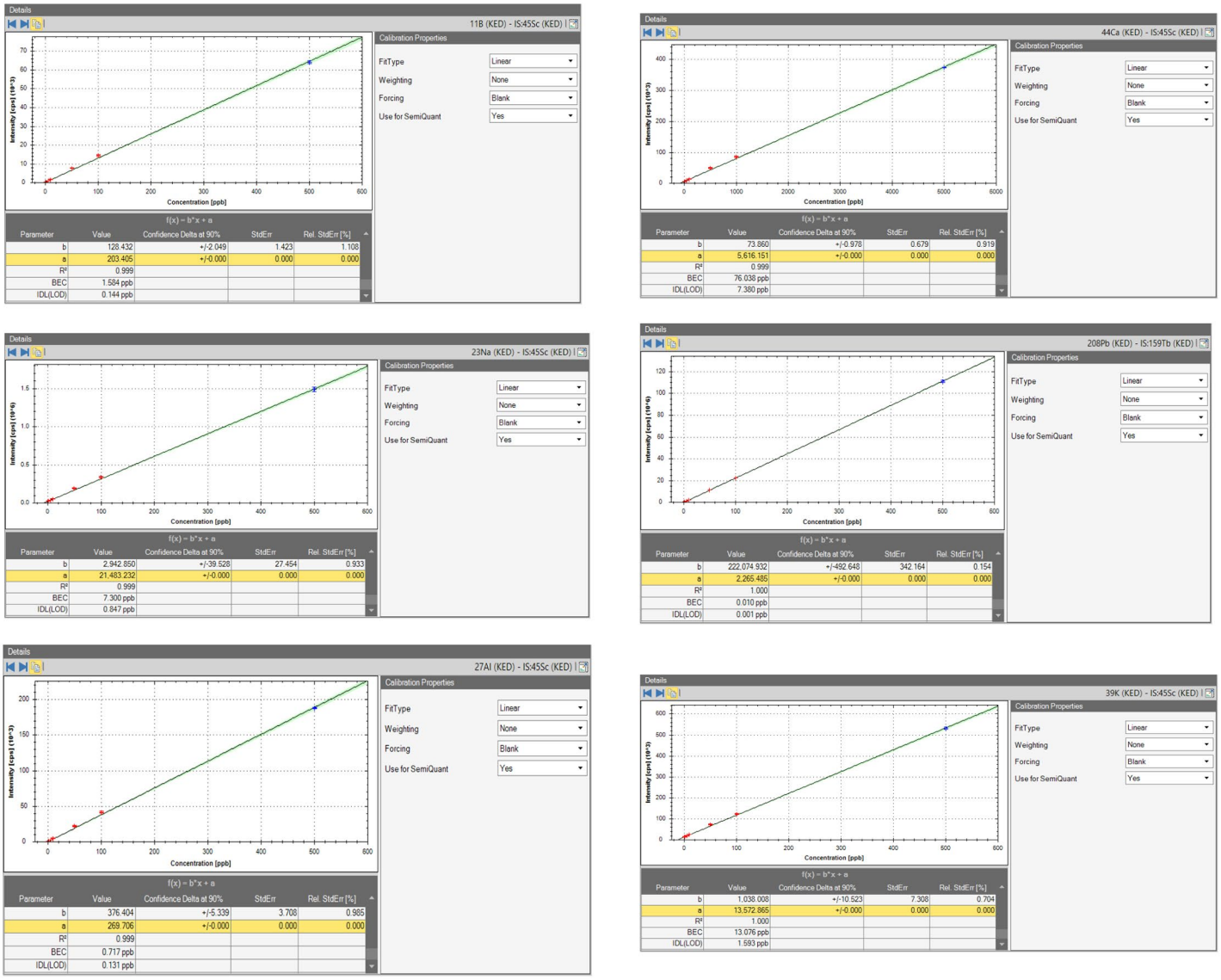

Figure 11. Linearity analysis for elemental impurities

Table 9. Concentration of elements (mg/kg)

Sr. no.	Element	Lithium hydroxide batch 1	Lithium hydroxide batch 2	Lithium hydroxide batch 3	Lithium fluoride batch 1	Lithium fluoride batch 2	Lithium carbonate batch 1	Lithium carbonate batch 2	Phosphorus pentachloride
1	Boron	1.82	0.29	0.11	NA	NA	0.18	1.32	0.39
2	Sodium	49.28	70.24	63.91	15.20	16.28	1.91	243.75	3.70
3	Aluminum	5.85	1.39	1.30	5.19	5.75	0.45	31.03	3.70
4	Magnesium	0.34	0.11	0.22	0.65	0.86	0.45	4.09	1.99
5	Potassium	19.99	16.51	14.51	<0.05	<0.05	0.82	9.18	1.07
6	Calcium	17.75	6.75	7.98	0.80	1.67	0.20	15.99	2.62
7	Iron	0.22	0.05	0.36	1.41	2.05	0.95	5.83	9.78
8	Silicon	189.77	117.18	110.90	65.98	88.64	NA	NA	NA
9	Zinc	0.16	0.13	0.15	<0.05	<0.05	NA	NA	0.15
10	Lead	< 0.05	0.17	0.18	<0.05	<0.05	<0.05	<0.05	<0.05
11	Copper	NA	NA	NA	0.06	0.08	NA	NA	<0.05
12	Chromium	NA	NA	NA	0.10	0.13	NA	NA	0.41
13	Nickel	NA	NA	NA	0.08	0.09	NA	NA	0.38

*NA: Not requested to be analyzed

Table 10. Spike recovery performed at 25 ppb (25% of linearity level)

Sr. no.	Element	Lithium hydroxide batch 1	Lithium hydroxide batch 2	Lithium hydroxide batch 3	Lithium fluoride batch 1	Lithium fluoride batch 2	Lithium carbonate batch 1	Lithium carbonate batch 2	Phosphorus pentachloride
1	Boron	90.5	106.4	110.7	----	----	93.8	96.5	119.2
2	Sodium	----	----	----	122.7	123.3	106.9	----	108.7
3	Aluminum	121.3	115.9	119.6	108.4	102.3	95.5	100.2	113.9
4	Magnesium	119.8	121.8	120.9	121.7	120.6	97.7	95.7	119.1
5	Potassium	81.3	118.4	120.7	92.7	98.5	95.9	93.1	118.4
6	Calcium	102.6	116.2	101.9	108.9	105.6	87.5	93.1	118.2
7	Iron	102.0	109.7	100.3	107.8	105.8	103.2	111.7	94.1
8	Silicon	----	----	----	----	----	NA	NA	NA
9	Zinc	81.2	82.4	82.3	86.6	85.5	NA	NA	101.8
10	Lead	82.7	83.9	82.4	84.4	82.5	89.5	91.6	112.8
11	Copper	NA	NA	NA	89.9	87.5	NA	NA	90.4
12	Chromium	NA	NA	NA	95.4	93.5	NA	NA	89.3
13	Nickel	NA	NA	NA	98.3	96.5	NA	NA	88.8

*NA: Not requested to be analyzed
----: Sodium and silicon in particular samples were observed in higher concentrations, so that testing spike recovery at a concentration of 25 µg/L was not performed.

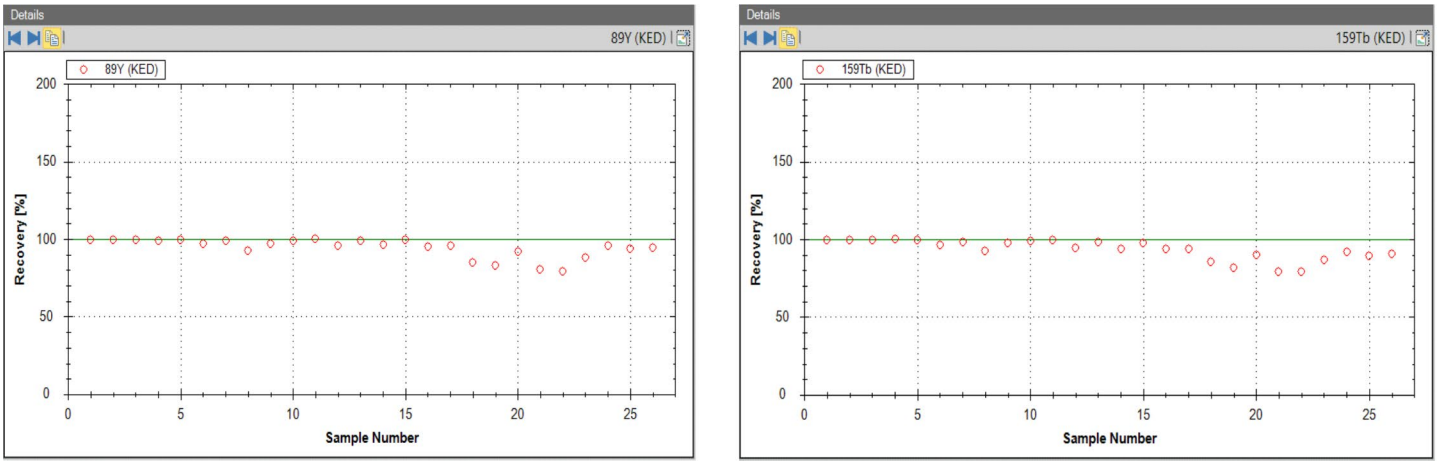

Figure 12. Internal standard recovery for both yttrium and terbium

Conclusion

This study demonstrated the accurate quantification of anionic impurities and cations in lithium salts by IC. This method uses a Dionex IonPac AS11-HC column with a hydroxide eluent, which is ideal for separating a wide range of inorganic anions with high sensitivity. The high capacity Dionex IonPac CS16 column is ideal for the analysis of a wide range of cations with high sensitivity and resolution. Eluent generation technology is used for both anionic and cationic methods and provides uniform, highly stable eluent concentrations, which helps to achieve highly reproducible results.

One of the main advantages of using ICP-MS for elemental impurities determinations is its ability to detect low concentration levels (sub-ppb) routinely and with ease. The fast scanning speed, robustness, and selectivity of ICP-MS allow for rapid, accurate, and efficient analysis of elemental content in salts.

Since regulations are becoming tougher, fast and accurate techniques are the solution for the present and future. In this regard, IC and ICP-MS have proven to be the best solutions in terms of productivity and performance for the analysis of ions and elements in lithium-ion battery electrolyte salts.

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