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Accurate ICP-MS Analysis of Elemental Impurities in Electrolyte Used for Lithium-Ion Batteries

Determination of 68 elements in lithium salts $LiPF_6$, $LiBF_4$, $LiClO_4$, and LiFSI

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Introduction

The lithium-ion (Li-ion) battery industry is thriving due to demand for portable electronic devices and a surge in the use of battery electric vehicles (EVs). There is also a growing need for battery storage associated with renewable electricity generation. Li-ion batteries (LIBs) currently provide the best combination of cost, capacity, charging speed, and lifetime, and electrolyte composition is a key factor in the overall performance of the battery. The salts used in LIB electrolytes include lithium hexafluorophosphate ($LiPF_6$), lithium tetrafluoroborate ($LiBF_4$), and lithium perchlorate ($LiClO_4$). Imide-based Li salts such as lithium bis(fluorosulfonyl)imide (LiFSI) are also used as electrolyte additives to increase battery lifetime at high temperatures (1).

Electrolyte performance is strongly affected by the presence of elemental impurities, which must be monitored in the lithium salts to ensure consistency and quality of the electrolyte and the final battery product (2). Electrolyte producers and battery manufacturers therefore require accurate analytical methods to determine a wide range of elements in lithium salts. ICP-OES is often used to determine contaminant elements in battery electrolyte salts and other raw materials. But ICP-OES does not provide low enough detection limits for labs that are interested in quantifying trace elements at sub-µg/kg (ppb) levels in the solid Li salts (3). ICP-MS is the preferred technique for trace element analysis across multiple industries and applications, because of its high speed, low detection limits, wide elemental coverage, and good selectivity. These characteristics make ICP-MS the ideal technique to meet the increasingly stringent requirements for quality control of components used in LIBs. For routine analysis of raw materials and battery components such as electrodes and electrolytes, a single quadrupole ICP-MS provides the low detection limits and wide elemental coverage that the industry requires. For more advanced manufacturing and for research into new materials and processes, a triple quadrupole ICP-MS provides even lower detection limits, especially for analytes that are affected by spectral overlaps.

In this study, a single quadrupole ICP-MS method was developed that uses standard addition calibration to quantify 68 elements in the lithium salts, $LiPF_6$, $LiBF_4$, $LiClO_4$, and LiFSI. The analyte list included the metals listed in ISO/WD 10655, which is the draft ICP-OES method for the analysis of metals in $LiPF_6$ (4). The analytes specified in ISO/WD 10655 are Al, Ca, Cd, Cr, Cu, Fe, K, Mg, Na, Ni, Pd, and Zn, and these elements were included in the ICP-MS method together with a further 56 elements.

Standard addition calibration is a useful approach when high matrix samples are being analyzed, as it eliminates errors due to variations in sample transport, nebulization, and matrix suppression. Also, using standard addition reduces reliance on internal standards (ISTDs) to correct the signal for different matrix levels. When the analyte list is very long, as in this analysis, it can be difficult to identify suitable ISTDs that are not required analytes.

The analysis was performed using an Agilent 7900 ICP-MS with an HF resistant PFA sample introduction system. Method performance, in terms of linearity, method detection limit (MDL), spike recovery, and robustness, was evaluated for all target elements in the four lithium salts.

Experimental

Reagents and standards

Ultrapure water prepared by a Milli-Q water purification system was used in this study. High purity nitric acid (HNO_3) (≥99.999% trace metal basis) was bought from Sigma-Aldrich. Agilent multi-element and single element calibration standards were used, as detailed in Table 1. An intermediate standard mix containing 67 analytes (excluding sulfur) was prepared freshly from the separate standards to give a mixed stock standard at a concentration of 50 µg/L for Hg and 1,000 µg/L for other elements. The mixed stock standard was prepared in 2% HNO_3 (v/v) and the source standards contained the acids (HCl and trace HF) to stabilize chemically incompatible elements such as Hg, Ag, Sb, Sn, PGEs, etc. The mixed multi-element intermediate standard was used as the standard addition spiking solution. No intermediate standard was used for the 1000 ppm sulfur stock solution, which was directly spiked into the standard addition calibration solutions.

Table 1. Agilent multi-element and single element standards used to prepare standard addition calibrations.

Standard Description	Analyte	Concentration µg/mL	Part Number
Multi-element calibration standard-1	Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sc, Sm, Tb, Th, Tm, Y, Yb	10	8500-6944
Multi-element calibration standard-2A	Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, K, Li, Mg, Mn, Na, Ni, Pb, Rb, Se, Sr, Tl, U, V, Zn	10	8500-6940
Multi-element calibration standard-3	Sb, Au, Hf, Ir, Pd, Pt, Rh, Ru, Te, Sn	10	8500-6948
Multi-element calibration standard-4	B, Ge, Mo, Nb, P, Re, S, Si, Ta, Ti, W, Zr	10	8500-6942
Single element standard	Mercury (Hg)	10	5190-8575
Single element standard	Indium (In)	10	8500-6946
Single element standard	Bismuth (Bi)	10	8500-6936
Single element standard	Sulfur (S)	1000	5190-8529

Samples and standard preparation

Four commercially available, battery grade (≥ 99.9% purity on a trace metals basis) lithium salts – $LiPF_6$, $LiBF_4$, $LiClO_4$, and LiFSI – were analyzed in this study. To prepare the solid Li salts for analysis, a 5 ± 0.01 g sample of each salt was weighed into a 50 mL PFA bottle. Ultrapure water was then added to give a final sample weight of 50 ± 0.01 g (10x dilution). The bottles were tightly capped and placed in an ultrasonic bath for 5 mins to aid dissolution.

The concentrated Li salt solutions were further diluted two times (giving a 20x total dilution, so 5% TDS solutions). These sample solutions were then spiked with the multi-element intermediate standard and separate sulfur standard to give standard addition calibrations for each salt. For the final dilution and spiking of each Li salt solution, 2.5 ± 0.001 g of sample solution was weighed into a 15 mL conical polypropylene tube and topped up to 5 ± 0.01 g with 2% HNO_3. These unspiked solutions were used as the standard addition sample blank (SB) for each salt. Following the same approach used for the SB, up to nine standard addition calibration levels were prepared by weight for each Li salt solution. Higher level spikes were used for the analytes present at higher concentrations in the salts. Each calibration level was prepared by spiking an appropriate volume of the intermediate standard mix and sulfur stock solution into the sample tubes, before final dilution to 5 g. In this way, a series of standard addition solutions was created for each Li salt matrix, at analyte concentrations from 0.05 to 5 µg/kg (ppb) for Hg, 0.5 to 10 µg/g (ppm) for sulfur, and 1 to 500 µg/kg for all other elements. To avoid significant dilution of the sample matrix for the standard addition method, the maximum spike volume of standard solution added to the samples was 500 µL. Note that if a series of samples of the same Li salt are being analyzed in a routine batch, only one standard addition calibration is needed for each salt. The standard addition calibration can be automatically converted to an external calibration during the run, and the other (matrix-matched) samples are then quantified by external calibration.

Instrumentation

A 7900 ICP-MS fitted with optional H_2 cell gas line was used for this work. As some of the samples were Li salts that contain fluoride, the 7900 was fitted with a PFA inert sample introduction kit (p/n G4912-68000). The inert kit comprises an HF resistant PFA spray chamber, demountable quartz torch with 2.5 mm id sapphire injector, and PFA tubing compatible with aqueous samples containing HF. An inert PFA nebulizer (p/n G3285-80000) was also used. The standard nickel (Ni) interface cones were replaced with a platinum (Pt) tipped copper sampling cone (p/n G3280-67036) and Pt-tipped Ni skimmer cone (p/n G8400-67202). An Agilent I-AS integrated autosampler was used for sample delivery.

The 7900 ICP-MS features a fourth-generation collision/reaction cell (CRC), the ORS[4], which supports helium (He) collision mode using either standard gas flow and KED settings, or enhanced (high flow, high collision energy, HE) conditions. H_2 cell gas mode was also used to give the most effective removal of plasma-based spectral overlaps on Si (main overlap from N_2), Ca (Ar), Fe (ArO), and Se (Ar_2). Instrument operating conditions are given in Table 2.

Table 2. Agilent 7900 ICP-MS operating conditions.

Cell Mode	No Gas	He	HEHe	H_2
RF Power (W)	1550			
Sampling Depth (mm)	10			
Nebulizer Gas Flow (L/min)	1.09			
Ext 1 (V)	0			
Ext 2 (V)	−250	−245	−250	
Omega Bias (V)	−100	−120		
Omega Lens (V)	11.3	10.4	12.3	10.3
ORS Gas (mL/min)	–	4.3	9	5
Energy Discrimination (V)	5		7	3

Results and discussion

Optimization

The 7900 ICP-MS operating conditions given in Table 2 were optimized automatically using the Agilent ICP-MS MassHunter autotune function for all tune modes. The autotuning algorithm provides conditions that are optimum for the current instrument hardware and sample type and ensures consistent operating conditions regardless of operator expertise.

To ensure that the best performance was achieved for the large number and variety of analytes, different cell gas modes were used. He mode was used as the default mode for most elements, as usual for Agilent single quadrupole ICP-MS systems. For a few elements with intense matrix- or plasma-based spectral overlaps, enhanced (HE) He mode or H_2 reaction mode was used. Table 3 lists the cell mode used for each analyte in this study.

In a lithium matrix, sodium (Na) is among the most challenging impurity elements to measure by ICP-MS, because of the lithium oxide ($^7Li^{16}O^+$) polyatomic interference that appears at the same mass as the only isotope of Na (m/z 23). Agilent ICP-MS systems use the ORS^4 cell, which is optimized for effective removal of polyatomic ions using helium mode with kinetic energy discrimination (KED). Helium KED is the standard CRC mode for effective and reliable removal of multiple polyatomic interferences and was used for the determination of Na, together with most other elements, in this work.

Table 3. Analyte masses, cell modes, and MDLs.

Analyte	Gas Mode	LiPF$_6$	LiBF$_4$	LiClO$_4$	LiFSI
		MDL in Solid Salt (µg/kg)	MDL in Solid Salt (µg/kg)	MDL in Solid Salt (µg/kg)	MDL in Solid Salt (µg/kg)
9 Be	No Gas	0.35	0.81	0.07	0.07
11 B	He	ND*	ND**	180.00	109.50
23 Na	He	129.07	229.32	404.06	117.58
24 Mg	He	9.73	25.78	516.72	2.79
27 Al	He	13.61	27.48	21.14	3.09
28 Si	H$_2$	ND*	1098.92	247.30	98.78
31 P	HEHe	ND**	135.50	36.80	78.06
34 S	HEHe	1142.32	917.34	3359.14	ND**
39 K	He	137.59	158.20	396.31	84.19
40 Ca	H$_2$	29.10	43.81	82.17	14.36
45 Sc	He	0.21	1.38	0.12	0.09
47 Ti	He	66.74	2.31	1.71	1.61
51 V	He	0.23	0.45	0.52	0.18
52 Cr	He	2.19	19.95	1.05	0.83
55 Mn	He	0.47	2.98	0.57	0.26
56 Fe	H$_2$	15.00	119.04	31.04	2.12
59 Co	He	0.10	0.34	0.04	0.12
60 Ni	He	2.91	10.03	1.93	3.40
63 Cu	He	0.45	2.22	3.00	0.32
66 Zn	He	8.04	3.89	2.90	5.68
71 Ga	He	0.17	0.20	0.09	0.04
74 Ge	He	0.08	0.08	0.05	0.07
75 As	He	0.40	4.41	0.11	0.33
78 Se	H$_2$	0.17	0.14	0.10	0.08
85 Rb	He	0.10	0.14	0.07	0.04
88 Sr	He	0.16	0.24	0.33	0.14
89 Y	He	0.03	0.02	0.37	0.01

Table 3 continues on next page

Table 3 continued...

90 Zr	He	0.23	0.96	0.03	0.02
93 Nb	He	0.79	0.04	0.05	0.25
98 Mo	He	0.45	2.32	0.24	0.28
101 Ru	He	0.07	0.03	0.01	0.01
103 Rh	He	0.27	0.07	0.05	0.03
105 Pd	He	0.02	0.03	0.02	0.03
107 Ag	He	0.60	0.31	0.10	0.28
111 Cd	He	0.03	0.08	0.03	0.02
115 In	He	0.20	0.01	0.84	0.02
118 Sn	He	1.32	0.80	0.36	0.67
123 Sb	He	2.20	0.15	0.06	0.03
125 Te	He	0.15	0.15	0.17	0.18
133 Cs	He	0.09	0.10	10.13	0.02
135 Ba	He	1.10	12.30	9.88	0.94
139 La	He	0.01	0.01	0.08	0.02
140 Ce	He	0.02	0.02	0.63	0.01
141 Pr	He	0.01	0.01	0.01	0.01
146 Nd	He	0.02	0.03	0.04	0.01
147 Sm	He	0.01	0.03	0.04	0.01
153 Eu	He	0.09	0.01	4.81	0.01
157 Gd	He	0.07	0.03	0.08	0.01
159 Tb	He	0.01	0.01	0.03	0.01
163 Dy	He	0.01	0.02	0.06	0.01
165 Ho	He	0.01	0.01	0.01	0.01
166 Er	He	0.01	0.01	0.01	0.01
169 Tm	He	0.01	0.01	0.01	0.01
172 Yb	He	0.01	0.01	0.04	0.01
175 Lu	He	0.01	0.01	0.02	0.01
178 Hf	He	0.06	0.06	0.04	0.01
181 Ta	He	0.16	0.01	0.05	0.16
182 W	He	0.13	0.10	0.15	0.47
185 Re	He	0.01	0.02	0.01	0.01
193 Ir	He	0.08	0.02	0.08	0.15
195 Pt	He	0.19	1.93	0.02	0.04
197 Au	He	0.38	0.55	0.50	0.13
202 Hg	He	0.10	0.14	0.07	0.12
205 Tl	He	0.05	0.04	0.02	0.03
Pb***	He	0.22	0.15	0.14	0.03
209 Bi	He	0.02	0.02	0.03	0.03
232 Th	He	0.01	0.03	0.01	0.01
238 U	He	0.01	0.01	0.01	0.01

*Not determined as the measured concentration was above the top calibration level. **Not determined in that matrix, as the analyte was a major component in the salt. ***Pb was measured as the sum of the three most abundant isotopes, 206, 207, and 208.

Some elements, including P and S, are traditionally considered difficult to determine by ICP-MS. Both elements are affected by spectral overlaps from polyatomic ions, such as NO^+, NOH^+, O_2^+, O_2H^+, and $O_2H_2^+$, which are formed from the surrounding air and the aqueous solvent. These polyatomic ions are very intense and may not be adequately resolved using conventional He collision mode (5). The ORS⁴ cell can operate in enhanced, high energy (HE) He mode, which provides better removal of the interfering polyatomic ions, while also increasing the sensitivity for ^{31}P and ^{34}S.

H_2 reaction cell mode was used for improved interference removal on certain elements that suffer intense plasma-based polyatomic overlaps, notably ^{28}Si, ^{40}Ca, ^{56}Fe, and ^{78}Se (6, 7). ^{28}Si suffers an intense interference from $^{14}N_2^+$ and $^{12}C^{16}O^+$ polyatomic ions that form from components of the plasma gas, aqueous solvent, and lithium salt solution. While He mode can reduce the contribution from these polyatomic ions, H_2 reaction gas provides more efficient removal of the interferences by utilizing reaction mode instead of He KED. $^{14}N_2^+$ and $^{12}C^{16}O^+$ react quickly with H_2, while Si^+ does not react, so the interferences are effectively removed, and Si can be measured successfully.

Standard addition calibration

In ICP-MS analysis, a sample matrix that contains a high concentration of an easily ionized element, such as Li, will cause ionization suppression of other, less easily ionized analytes (6). Because ionization suppression varies depending on the element's ionization potential (IP), it can be difficult to find suitable, IP-matched ISTDs for all analytes, particularly when nearly every element is a required analyte. An external calibration approach using simple, synthetic – non-matrix matched – calibration standards is therefore unlikely to give accurate results for all analytes. One possible solution is to apply very high dilution factors to the high salt sample matrix to reduce the effect of ionization suppression. But this approach makes it more difficult to meet the required detection limits and increases the potential for errors due to contamination from the diluent.

An alternative approach to deal with ionization suppression caused by the sample matrix is to use matrix-matched standards, where the sample matrix is replicated in the standard. The ultimate form of matrix matching is a calibration strategy called standard addition, also known as method of standard additions, or MSA. In a standard addition calibration, the calibration standards are spiked directly into the sample solution, so the calibration standards are perfectly matched to the matrix of each sample. Because of this perfect matrix matching, the errors caused by ionization suppression are eliminated and the need for ISTD correction is greatly reduced. One reason many labs prefer not to use standard addition routinely is the perception that every sample must be spiked, which would make the standardization much more time consuming and labor intensive. But the standard addition functionality in ICP-MS MassHunter software allows a standard addition calibration to be automatically converted to an external calibration. This conversion means that subsequent samples of the same matrix type do not need to be spiked individually and so can be run in the same way as for normal, external calibration.

In this study, a standard addition calibration approach was used for the quantitative analysis of 68 elements in four lithium salts. Good linearity with calibration coefficients ≥0.999 (minimum 3 points) was achieved for all target analytes. Representative calibration curves for Si, Ca, Fe, Cr, Ni, and Cu in LiFSI, respectively, are shown in Figure 1. The calibrations illustrate the good linearity obtained for the standard addition calibrations in the analyses of multiple elements in the complex Li salt samples.
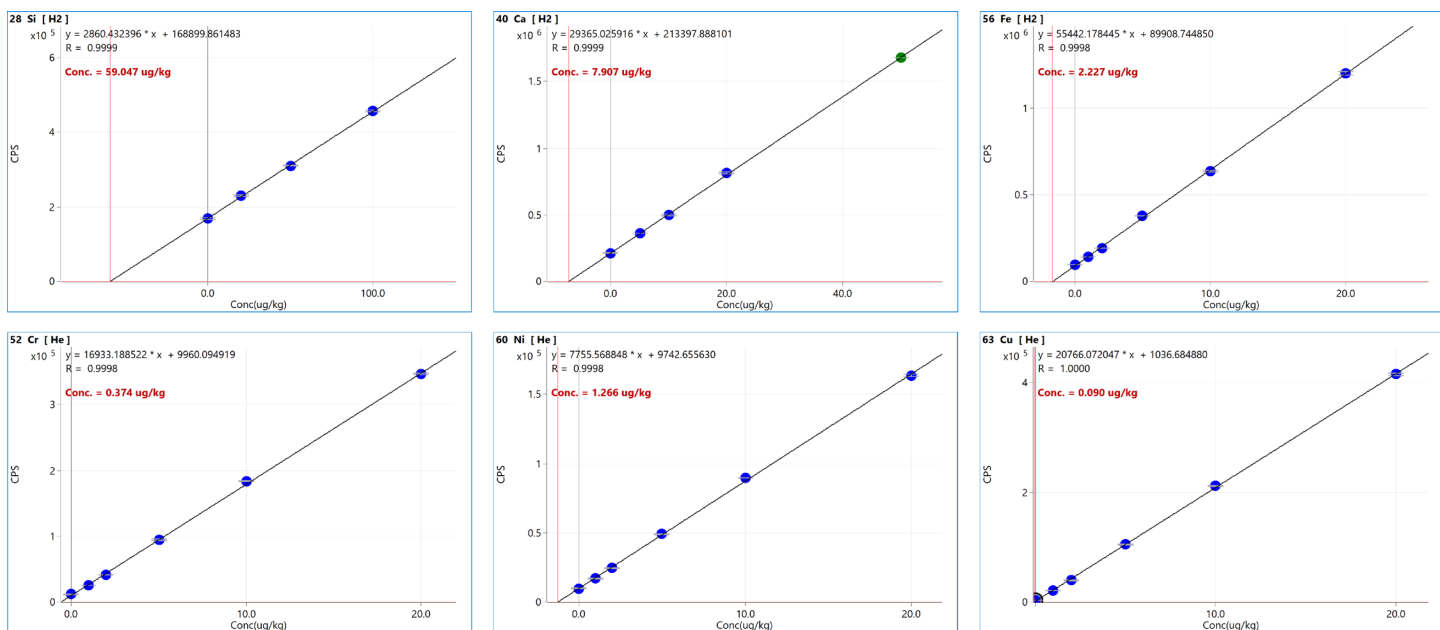
Figure 1. Representative calibration curves for Si, Ca, Fe, Cr, Ni, and Cu in LiFSI salt matrix.

Method detection limits

Method detection limits (MDLs) were calculated for all analytes in each of the Li salts measured in this study. The MDLs were determined from 3 x the standard deviation (SD) of 11 replicate measurements of the unspiked sample blank for each salt matrix. The MDLs calculated for the diluted electrolyte solution were then multiplied by the total dilution factor of 20 to give the analyte MDLs in the original solid Li salt. MDLs for all target analytes across four lithium salts are given in Table 3. Sub-µg/kg detection limits were achieved for most of the trace elements, which illustrated the excellent selectivity and sensitivity of the 7900 ICP-MS for the determination of multiple elements in the high Li salt matrices. The relatively high matrix blank contribution to standard deviation was observed for some elements, which resulted in the higher MDLs.

Sample analysis and spike recovery result

Table 4 summarizes the quantitative results for all 68 analytes in each Li salt, calibrated using standard addition and dilution corrected to give the concentrations in the original solid salts. For each Li salt matrix, three separate aliquots were prepared and spiked to evaluate the method accuracy and precision of the standard addition procedure. Spike recovery values and precision (%RSD of recovery) for all analytes are listed in Table 4.

Recoveries between 80 to 120% with RSD <12% (n=3) were obtained for all analytes except B, Si, P, and S. These elements were not determined either because they were a main component of the salt matrix (P in $LiPF_6$, for example), or because the native concentration in the salt matrix was too high relative to the standard addition spike levels.

Long-term stability study

To evaluate the long-term stability of the 7900 ICP-MS for the high matrix Li salt analysis, a six-hour analytical run was carried out. A QC sample with the same concentration as the midpoint of the standard addition calibration solutions was run after every 10 samples. Figure 2 shows normalized QC recoveries (%) for all the analytes over six hours analysis of $LiPF_6$ sample matrix, using initial Cal 6 as the QC reference values. QC recoveries for P are excluded, as this element is a major component of this sample. Good recoveries with precision less than ±15% were obtained for all analytes, demonstrating the long-term robustness and high matrix tolerance of the 7900 ICP-MS.

To assess the tolerance of the 7900 to matrix deposition, the surface condition of the platinum tipped sampling cone was investigated after six hours' salt matrix analysis. Figure 3A shows minimal matrix deposition on the surface of the sampling cone, while Figure 3B shows the sampling cone condition after being cleaned in 0.5% citric acid for 5 mins in an ultrasonic bath. The simple cleaning procedure illustrates how the Pt-tipped sampling cone resists salt matrix deposition and provides excellent corrosion resistance suitable for routine, long-term analysis of corrosive, HF-containing solutions.
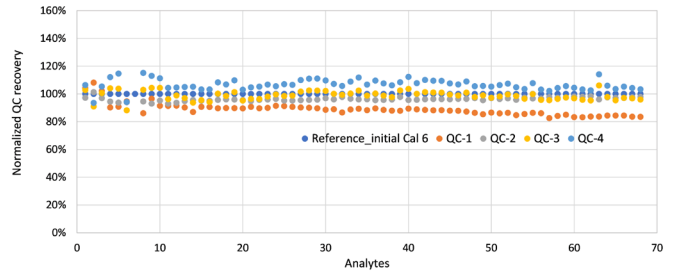

Figure 2. Normalized QC recoveries over six hours run in LiPF$_6$ sample matrix.

Table 4. Measured concentrations in the original solid Li salt samples (after correction for the dilution factor) and spike recoveries.

Analyte	LiPF$_6$			LiBF$_4$			LiClO$_4$			LiFSI		
	Measured Concentration in LiPF$_6$ (µg/kg)	Spike Recovery (%)	%RSD of Recovery (n=3)	Measured Concentration in LiBF$_4$ (µg/kg)	Spike Recovery (%)	%RSD of Recovery (n=3)	Measured Concentration in LiClO$_4$ (µg/kg)	Spike Recovery (%)	%RSD of Recovery (n=3)	Measured Concentration in LiFSI (µg/kg)	Spike Recovery (%)	%RSD of Recovery (n=3)
9 Be	< MDL	100	5	< MDL	112	4	< MDL	103	7	< MDL	115	5
11 B	ND*			ND**			556.01	113	4	300.77	108	6
23 Na	2347.32	103	2	4267.21	90	3	3084.86	114	1	1518.33	107	1
24 Mg	185.14	93	6	293.43	99	3	2585.25	114	3	81.59	114	3
27 Al	94.92	104	6	269.32	101	3	38.63	106	3	47.82	107	1
28 Si	ND*			5810.56	109	5	636.93	109	4	1180.94	107	3
31 P	ND**			1802.42	103	1	228.22	83	5	441.98	83	5
34 S	5033.49	117	3	5990.05	101	6	10079.49	101	3	ND**		
39 K	1764.23	82	4	993.26	98	6	1375.92	82	3	1023.11	112	1
40 Ca	177.41	104	2	290.54	86	5	208.05	114	5	158.14	107	5
45 Sc	1.23	105	4	3.50	102	5	0.33	102	3	0.38	106	2
47 Ti	478.35	83	5	16.36	103	4	5.43	100	2	3.81	106	2
51 V	0.43	105	4	2.73	104	4	2.28	99	3	0.62	103	2
52 Cr	36.80	108	4	339.27	103	3	29.20	103	4	7.48	112	2
55 Mn	5.34	106	4	33.27	108	5	3.98	104	3	1.75	107	2
56 Fe	113.61	115	2	1583.58	84	4	93.78	114	3	44.54	114	3
59 Co	0.37	102	4	3.40	97	4	0.20	102	3	0.79	108	2
60 Ni	25.90	103	4	139.66	108	4	13.48	102	3	25.32	108	2
63 Cu	3.14	101	4	12.71	107	3	21.87	101	3	1.80	109	2
66 Zn	22.65	107	5	18.14	112	4	14.19	102	3	32.22	108	2
71 Ga	0.24	105	4	< MDL	110	5	0.18	104	3	0.06	108	2
74 Ge	<MDL	105	4	< MDL	109	5	< MDL	104	3	< MDL	109	2
75 As	2.18	103	4	55.61	105	5	0.23	104	3	2.47	107	2
78 Se	<MDL	108	1	< MDL	105	3	< MDL	91	4	0.18	110	4
85 Rb	0.10	102	4	< MDL	104	7	0.13	104	3	0.12	107	2
88 Sr	0.67	103	4	1.16	107	6	1.54	104	3	0.71	108	3
89 Y	0.06	100	4	0.03	108	6	2.79	103	3	0.03	108	2

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Table 4 continued...

90 Zr	1.30	100	4	3.60	107	5	0.07	102	3	0.05	107	2
93 Nb	6.13	100	3	0.15	93	5	< MDL	103	2	< MDL	107	3
98 Mo	2.44	101	3	34.98	112	4	1.46	103	3	0.39	110	3
101 Ru	0.21	104	3	< MDL	111	3	< MDL	104	3	< MDL	111	2
103 Rh	1.03	107	3	0.83	112	4	0.76	106	3	0.24	114	3
105 Pd	<MDL	101	4	< MDL	104	3	< MDL	102	3	< MDL	108	3
107 Ag	<MDL	99	4	< MDL	106	6	< MDL	101	2	< MDL	107	3
111 Cd	<MDL	105	4	< MDL	108	7	0.03	104	3	< MDL	112	3
115 In	1.30	102	4	0.01	103	5	4.74	106	3	< MDL	112	3
118 Sn	9.47	105	4	1.65	111	4	2.16	105	3	2.24	112	2
123 Sb	16.31	106	4	0.35	99	4	< MDL	106	3	0.03	113	3
125 Te	0.19	102	2	< MDL	106	6	0.25	105	4	< MDL	111	3
133 Cs	0.61	98	3	< MDL	102	6	63.68	113	3	0.02	111	3
135 Ba	2.42	103	3	162.50	109	6	53.14	105	3	< MDL	112	2
139 La	0.02	102	3	0.02	97	5	0.36	105	3	0.06	113	3
140 Ce	0.03	104	4	0.09	101	7	3.17	106	3	< MDL	115	4
141 Pr	<MDL	103	4	< MDL	100	4	0.01	105	3	< MDL	113	3
146 Nd	<MDL	105	3	0.03	111	4	< MDL	114	3	< MDL	114	3
147 Sm	<MDL	105	3	< MDL	109	5	< MDL	114	3	< MDL	114	3
153 Eu	0.62	103	3	< MDL	99	8	25.90	114	3	< MDL	110	3
157 Gd	0.20	108	3	< MDL	108	4	0.15	115	3	< MDL	111	3
159 Tb	<MDL	109	4	< MDL	108	4	0.12	106	4	< MDL	112	3
163 Dy	<MDL	108	3	< MDL	107	6	< MDL	115	4	< MDL	114	4
165 Ho	<MDL	111	3	< MDL	101	1	< MDL	115	3	< MDL	112	3
166 Er	<MDL	106	3	< MDL	93	3	< MDL	114	2	< MDL	112	6
169 Tm	<MDL	111	4	< MDL	94	7	0.01	115	4	< MDL	110	6
172 Yb	<MDL	109	3	< MDL	95	3	0.06	115	6	< MDL	109	5
175 Lu	<MDL	104	4	< MDL	108	3	0.03	115	6	< MDL	114	6
178 Hf	0.23	110	3	0.11	98	2	0.05	115	3	< MDL	108	7
181 Ta	1.00	115	3	0.18	94	2	< MDL	112	7	< MDL	111	5
182 W	0.32	111	3	0.39	101	1	0.23	114	5	< MDL	108	7
185 Re	<MDL	108	3	< MDL	99	2	< MDL	113	2	< MDL	103	11
193 Ir	<MDL	111	3	< MDL	96	1	< MDL	115	1	< MDL	114	5
195 Pt	0.88	113	3	20.63	106	1	0.07	114	1	0.34	113	5
197 Au	<MDL	85	11	< MDL	106	7	< MDL	97	8	< MDL	82	4
202 Hg	<MDL	111	3	< MDL	99	10	< MDL	87	5	< MDL	98	5
205 Tl	<MDL	108	3	< MDL	111	7	0.04	114	3	< MDL	99	7
Pb***	1.13	111	3	0.67	103	2	0.73	113	3	0.17	108	7
209 Bi	0.04	109	3	< MDL	101	5	0.10	114	4	< MDL	106	7
232 Th	0.01	110	3	0.04	100	1	< MDL	109	9	< MDL	113	7
238 U	<MDL	111	3	< MDL	101	2	< MDL	113	5	< MDL	105	7

*Not determined as the unspiked concentration was higher than the top spike level. **Not determined in that matrix, as the analyte was a major component in the salt. ***Pb was measured as the sum of the three most abundant isotopes, 206, 207, and 208.
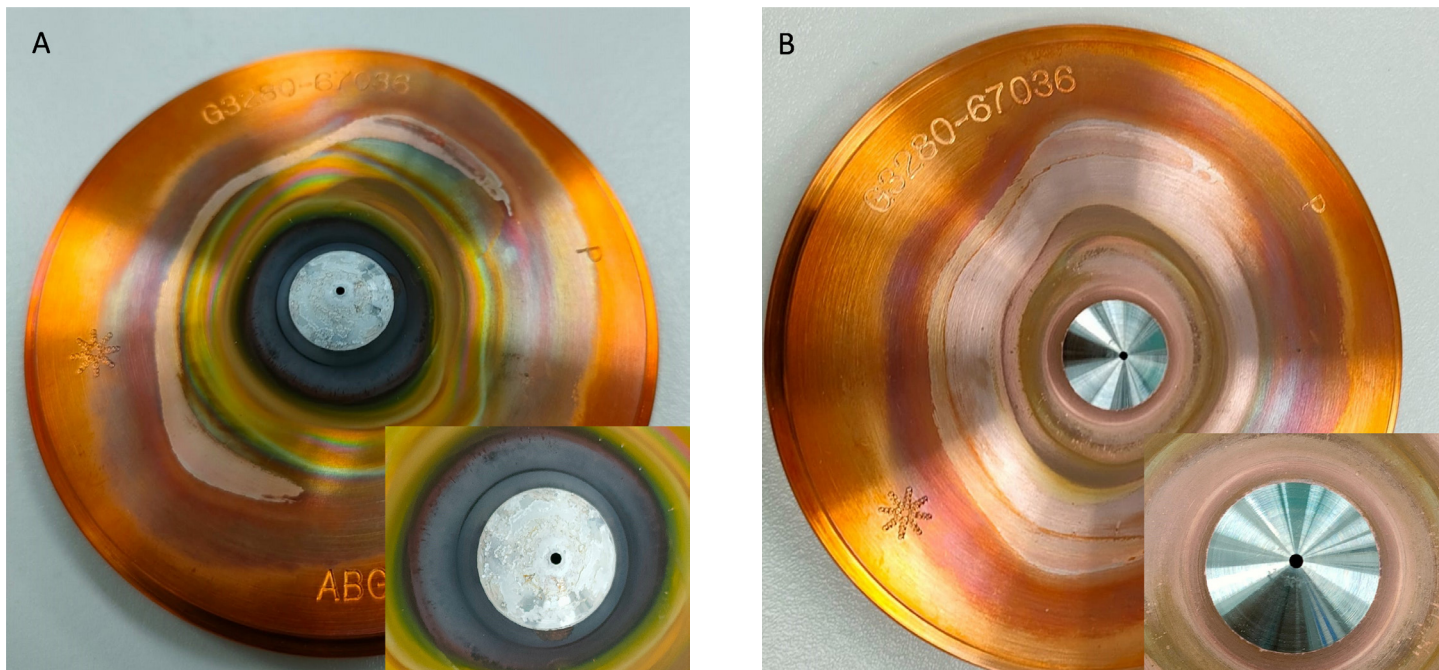
Figure 3. A: Agilent 7900 Pt-tipped sampling cone showing minimal matrix deposition after six hours analysis of 5% TDS Li salt matrices. B: Same sampling cone after ultrasonic cleaning with 0.5% citric acid.

Conclusion

This newly developed ICP-MS method uses a standard addition calibration approach to provide good accuracy, low detection limits, and excellent control of ionization suppression effects from the easily ionized Li matrix. The ICP-MS method is suitable for the routine multi-element analysis of common electrolyte salts including $LiPF_6$, $LiBF_4$, $LiClO_4$, and LiFSI.

An Agilent 7900 ICP-MS configured with HF resistant sample introduction system, PFA inert nebulizer, and Pt-tipped sampling and skimmer cones was used for the analysis of high matrix Li salt samples. A simple sample preparation procedure was used, giving Li salt solutions with nominally 5% TDS. These solutions were spiked to give standard addition calibrations for the quantification of 68 analytes in each of the four Li salts. The use of a standard addition calibration approach eliminated the effects of ionization suppression caused by the Li matrix and avoided the need for internal standard correction. The 7900 ICP-MS provided excellent matrix tolerance and good long-term stability, as required for routine battery electrolyte analysis.

The 7900 utilized the ORS[4] collision/reaction cell, operated in standard He collision mode to remove polyatomic interferences on most analytes. Enhanced (HE) He mode and optional H_2 reaction mode were used to resolve intense interferences on selected elements, enabling accurate low-level determination of all the target elements in the high Li salt matrices. Sub-µg/kg MDLs in the original solid salt were achieved for the trace elements, demonstrating the high sensitivity and good control of spectral overlaps provided by the 7900 ICP-MS. Good linearity and spike recoveries were obtained, demonstrating the accuracy achieved using the quantitative analytical protocol developed in this study.

The 7900 ICP-MS method addresses the need for stricter quality control of low-level contaminant elements in Li-ion battery materials, as required by electrolyte producers and battery manufacturers. For manufacturers and raw material suppliers that need even lower levels of quantification, an Agilent 8900 Triple Quadrupole ICP-MS would provide higher sensitivity, lower DLs, and even better control of interferences.

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