APPLICATION NOTE

ICP - Mass Spectrometry

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Determination of Impurities in Lithium Materials with the NexION 5000 ICP-MS

Introduction

Lithium (Li) plays an important role in everyday life and can be found around us in nearly every aspect of modern living. One of the most common uses of lithium is in batteries. Lithium batteries can be found in cell phones, computers, electric vehicles, and every portable electronic device. For decades, consumers have been valuing longer battery lives and faster-charging capabilities, and the advancements in lithium battery technology are a reflection of this. In addition, global trends in electrification, renewable energy, and the adoption of electric vehicles are creating a demand for more lithium-based materials with higher quality control (QC) requirements.

With the demand for higher-capacity batteries, current battery production technology must improve, requiring better control of the raw materials used and their physical properties. For example, lithium salts are commonly refined from brine, a highly concentrated solution of NaCl. Sodium must be removed from the final product during the extraction process since excess sodium can lead to overheating in the battery end products. Therefore, the capability to identify the presence of impurities in lithium battery materials is critical for manufacturers and suppliers to ensure that the final battery performance is not compromised.

Most Li salt compounds are currently analyzed by ICP-OES for purity, with only a handful of elements being measured due to sensitivity limitations of ICP-OES. Because the industry requires better-performing batteries with a longer lifetime, higher-purity raw materials are required. Although there is no industry standard yet for the purity of Li salts required in battery production, the purity requirements from many manufacturers have risen from 99% to 99.9% in the space of just a few years. It is predicted that this trend will continue in the future, with the manufacturers of high-grade batteries needing to progress even further to 99.95-99.99% purity in the next few years as demand for lithium batteries continues to grow. This surge will alter the analysis of raw materials with an increase in the number of elements needing to be analyzed and the ability to measure lower levels accurately. These requirements will necessitate the analysis of impurities moving from ICP-OES to ICP-MS or multi-quadrupole ICP-MS.

This application note describes the analysis of four lithium salts using PerkinElmer's NexION® 5000 multi-quadruple ICP-MS.

Experimental

Samples and Sample Preparation

A total of four lithium salts were analyzed: 98% LiOH, 99.95% LiOH, 99% Li_2CO_3, and 99.998% Li_2CO_3 (VWR International, Radnor, Pennsylvania, USA) – see Table 1.

Table 1: Lithium salts analyzed.

Sample	Purity %
LiOH	98
	99.95
Li_2CO_3	99
	99.998

Sample preparation involved weighing 250 mg of each salt and combining it with 50 mL 1% nitric acid (v/v). The samples were allowed to degas for an hour and then were diluted 100x with 1% nitric acid for analysis. Each sample was prepared in triplicate to assess both robustness and reproducibility. It should be noted that caution was taken to minimize static charge when handling the samples by remaining grounded and discharging to a conductive material beforehand. All measurements were made against external calibration curves, with standards prepared in 1% nitric acid.

Instrumental Conditions

Analyses were performed on the NexION 5000 ICP-MS, a multi-quadrupole based system. The NexION 5000 includes the following features which were utilized in this study:

- Universal Cell technology[1], which offers the option of using Reaction, Collision, and Standard modes;
- All Matrix Solution (AMS) on-line Ar dilution system[2];
- Extended Dynamic Range (EDR), a unique capability of the NexION's Universal Cell which allows for electronic dilution of target elements without increasing analysis time or affecting the sensitivity of other elements;
- OmniRing technology, part of the second-generation Triple Cone Interface (TCI), optimized to increase sensitivity and give the lowest BECs for both MS/MS and Mass Shift modes of operation.

The NexION 5000 ICP-MS was configured with a High Throughput System (HTS). This valve-and-loop system minimizes both sample uptake and washout times, coupled with an S23 autosampler for automated sample introduction. The conditions of the NexION 5000 ICP-MS and HTS system are shown in Table 2, while Table 3 shows the modes of operation for each element.

Table 2: NexION 5000 ICP-MS instrumental conditions.

	Parameter	Value
NexION 5000 ICP-MS	Plasma Flow	16 L/min
	Auxiliary Flow	1.2 L/min
	RF Power	1600 W
	Nebulizer	PFA
	Nebulizer Gas Flow	0.84 L/min
	AMS Gas Flow	0.2 L/min
	Spray Chamber	SilQ cyclonic
	Injector/Torch	SilQ one-piece torch with 2 mm injector
	Pump Tubing - Carrier	Green/orange
	Pump Tubing - IS	Orange/blue
	Cones	Pt (sampler & skimmer), Hyper-skimmer with OmniRing used in focusing mode
	Analysis Modes	Standard, Reaction, MS/MS, Mass Shift
High Throughput System	Loop Size	2 mL
	Loop Fill Time	8 s
	Wash Time	15 s
	Carrier Flow Rate	0.164 mL/min

Table 3: Elements, analytical masses, and modes of operation.

Analyte	Scan Type	Cell Mode	Q1 (amu)	Q3 (amu)
Li	MS/MS	Standard	6	6
B	MS/MS	Standard	11	11
Na	MS/MS	Reaction NH_3	23	23
Mg	MS/MS	Reaction NH_3	24	24
Al	MS/MS	Reaction NH_3	27	27
Si	MS/MS	Reaction NH_3	28	28
P	Mass Shift	Reaction O_2	31	47
S	Mass Shift	Reaction O_2	32	48
K	MS/MS	Reaction NH_3	39	39
Ca	MS/MS	Reaction NH_3	40	40
Sc	Mass Shift	Reaction O_2	45	61
Ti	Mass Shift	Reaction O_2	48	64
V	MS/MS	Reaction NH_3	51	51
Cr	MS/MS	Reaction NH_3	52	52
Mn	MS/MS	Reaction NH_3	55	55
Fe	MS/MS	Reaction NH_3	56	56
Co	MS/MS	Reaction NH_3	59	59
Ni	MS/MS	Reaction NH_3	60	60
Cu	MS/MS	Reaction NH_3	63	63
Zn	MS/MS	Reaction NH_3	66	66
As	Mass Shift	Reaction O_2	75	91
Se	Mass Shift	Reaction O_2	80	96
Rb	MS/MS	Reaction NH_3	85	85
Sr	MS/MS	Reaction NH_3	88	88
Y	Mass Shift	Reaction O_2	89	105
Zr	Mass Shift	Reaction O_2	90	106
Mo	MS/MS	Standard	95	95
Ag	MS/MS	Standard	107	107
Cd	MS/MS	Standard	111	111
Sn	MS/MS	Standard	118	118
Sb	MS/MS	Standard	121	121
Cs	MS/MS	Standard	133	133
Ba	MS/MS	Standard	137	137
La	Mass Shift	Reaction O_2	139	155
Ce	Mass Shift	Reaction O_2	140	156
Pr	Mass Shift	Reaction O_2	141	157
Nd	Mass Shift	Reaction O_2	146	162
Sm	Mass Shift	Reaction O_2	147	163
Eu	MS/MS	Standard	153	153
Gd	Mass Shift	Reaction O_2	157	173
Tb	Mass Shift	Reaction O_2	159	175
Dy	Mass Shift	Reaction O_2	163	179

Table 3: Elements, analytical masses, and modes of operation (continued).

Analyte	Scan Type	Cell Mode	Q1 (amu)	Q3 (amu)
Ho	Mass Shift	Reaction O_2	165	181
Er	Mass Shift	Reaction O_2	166	182
Tm	Mass Shift	Reaction O_2	169	185
Yb	MS/MS	Reaction NH_3	174	174
Lu	Mass Shift	Reaction O_2	175	191
Au	MS/MS	Standard	197	197
Pb	MS/MS	Standard	208	208
Bi	MS/MS	Standard	209	209
U	MS/MS	Standard	238	238

Results and Discussion

During the analysis of high-purity materials, both the major/matrix elements and impurities may need to be measured, as was done in this work. However, there are analytical challenges associated with the measurements of both major and minor elements which must be overcome.

Analyzing a major element within a solution (Li in this work) can be challenging. Since the concentration is very high compared to the trace elements, analysis without dilution will cause either saturation or a heavy load on the detector. This can necessitate analyzing the sample twice at two different concentrations in most systems: one for trace elements and the other for major components. However, in the NexION series ICP-MS instruments, the signal of user-selected masses can be selectively attenuated in the Universal Cell with RPa (rejection parameter a). Using RPa does not require any extra time in the analysis. It can be applied to a single mass without affecting the other masses in the method or requiring an additional internal standard. In this work, RPa was optimized for both ^{6}Li and ^{7}Li, at 0.015 and 0.1 respectively, to ensure that all analytes in all standards and samples were measured on the same stage of the detector.

Table 4 shows the lithium results from three separate sample preparations of lithium carbonate. The mean results from the three samples are within 0.1% for ^{6}Li and ^{7}Li, confirming the accuracy of the methodology. However, it should be noted that a difference of 0.1% corresponds to 1 mg out of a 250 mg sample size.

Table 4: Results from analysis of three separate preparations of lithium carbonate (99.998%).

Sample Number	^{6}Li Lithium Carbonate (%)	^{7}Li Lithium Carbonate (%)
1	19.00	18.64
2	18.31	18.88
3	18.53	18.61
Mean	18.61	18.71
STD	0.35	0.15
RSD	1.89	0.80

Therefore, to attain accurate, reproducible results, great care must be taken with weighing the samples, as was done in this work, to minimize static electricity during sample weighing and transfer.

With the accuracy of Li analysis established, the impurity measurements in the four different samples will now be discussed. Traditionally, the industry only required a Li salt to be about 99% pure with impurity levels being measured by ICP-OES and with the required elemental analysis limited to a small handful of elements: Al, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Pb and Zn. However, purity requirements are changing with battery manufacturers preferring compounds with 99.9-99.95% purity and a more thorough list of elements.

Table 5 (pages 5 - 6) shows the concentrations of impurities in four different Li salts. The total impurity level can be seen at the end of the table along with the corresponding impurity concentrations. Both the lower-grade LiOH and Li_2CO_3 samples are seen to be within limit. Although the LiOH 99.995% compound was found to be 99.992% pure, the Li_2CO_3 99.998% compound is 99.995% pure, in which case both of these compounds would fail a QC check. However, suppose only those traditionally analyzed elements in the salts mentioned earlier are considered. In that case, both of these samples are 99.998% and 99.999% pure respectively, in which case they would be considered within limits.

When measuring impurities in lithium compounds, sodium (Na) and sulfur (S) are challenging, but these challenges can be overcome with the NexION 5000 ICP-MS. It is critical to accurately measure Na since its presence leads to reduced battery life and explosive events. Because most lithium compounds originate from brine, they all have very high levels of Na, which must be removed or significantly reduced to be feasible for battery productions. The challenge when analyzing trace Na in a Li matrix using ICP-MS is the lithium oxide (LiO) interference which occurs at the same mass of Na: m/z 23. Since Na is monoisotopic, there are no alternative masses which can be used.

There are two options for removing the LiO^+ interference on Na:

1. A correction equation applied using the ^6Li isotope, which requires measuring a known Li standard with each sample set to ensure an accurate correction.
2. Removing the LiO^+ interference by reacting it with 100% ammonia in the Universal Cell. LiO^+ reacts with ammonia via charge exchange, resulting in neutral LiO, which is no longer visible at mass 23; Na does not react with ammonia and remains at mass 23 for analysis.

For this work, the second option was used for the determination of Na since it is simpler, faster, and more reliable.

Sulfur is another difficult element to measure with ICP-MS as all isotopes occur at the same masses as O_2^+. However, S^+ reacts with O_2 to form SO^+ at m/z 48. Therefore, by adding O_2 to the Universal Cell, S^+ is readily converted to SO^+. Unfortunately, titanium (Ti) and calcium (Ca) isotopes also exist at mass 48. Because Ti^+ reacts rapidly with O_2 to create TiO^+, it does not interfere with SO^+.[3] However, Ca^+ does not react with O_2 and will interfere with SO^+.

In single quadrupole instruments, a correction equation is applied to account for the Ca interferences at 48. However, this can be overcome with the NexION 5000 multi-quadrupole ICP-MS: the first resolving quad (Q1) is set to mass 32, allowing only O_2^+ and S^+ to pass into the Universal Cell, removing Ca. The sulfur then reacts with oxygen to form SO^+, and the second resolving quad (Q3) is set to mass 48, so that only SO^+ reaches the detector. There is no need for correction equations with the NexION 5000 ICP-MS as neither Ti nor Ca make it past Q1.

Table 5: Impurities in Li salts.

		Impurity (µg/g)			
Analyte	**MDL**	**LiOH 98%**	**LiOH 99.995%**	**Li_2CO_3 99%**	**Li_2CO_3 99.998%**
B	0.03038	< MDL	< MDL	4.0205	1.0651
Na	0.07752	524.9767	8.4421	182.8105	1.5979
Mg	0.00158	0.7179	< MDL	78.1201	< MDL
Al	0.00236	2.5975	3.6484	2.2142	2.0035
Si	0.48837	30.0055	43.3769	94.4323	< MDL
P	0.00862	< MDL	< MDL	22.2056	< MDL
S	0.03108	14.5817	9.8760	103.0854	41.5285
K	0.01264	1054.2141	6.9061	5.6879	1.3957
Ca	0.00150	16.3423	1.5160	60.8525	2.6508
Sc	0.00003	< MDL	< MDL	0.0340	< MDL
Ti	0.00039	< MDL	< MDL	0.0389	< MDL
V	0.00007	0.2013	0.6033	0.0034	0.0795
Cr	0.00028	0.0822	< MDL	< MDL	0.1482
Mn	0.00033	< MDL	0.0058	0.0139	0.0908
Fe	0.00480	4.9218	2.0979	0.9086	0.3413
Co	0.00032	0.0282	0.0155	0.0152	0.0165
Ni	0.00410	0.3795	0.2135	0.2620	0.2096
Cu	0.00057	0.0809	0.0298	0.1300	0.0481
Zn	0.00259	4.2295	< MDL	< MDL	< MDL
As	0.00026	0.0271	0.2187	36.2235	0.0022
Se	0.00076	0.0215	0.0231	0.0023	0.0316
Rb	0.00007	0.2276	0.0215	0.0211	0.0051
Sr	0.00012	0.1407	< MDL	2.1795	< MDL
Y	0.00002	< MDL	0.0002	0.0333	0.0004
Zr	0.00027	< MDL	< MDL	< MDL	< MDL
Mo	0.00019	0.0602	0.0092	0.0126	0.0217
Ag	0.00015	0.0039	< MDL	0.0003	0.0066
Cd	0.00025	0.0045	0.0029	0.0078	< MDL

Table 5: Impurities in Li salts (continued).

		Impurity (µg/g)			
Analyte	**MDL**	**LiOH 98%**	**LiOH 99.995%**	**Li_2CO_3 99%**	**Li_2CO_3 99.998%**
Sn	0.00822	< MDL	< MDL	< MDL	< MDL
Sb	0.00071	< MDL	< MDL	< MDL	< MDL
Cs	0.00004	0.0010	0.0006	0.0077	0.0004
Ba	0.00094	< MDL	< MDL	2.0767	< MDL
La	0.00002	< MDL	0.0002	0.0015	0.0070
Ce	0.00005	< MDL	< MDL	0.0301	0.0010
Pr	0.00002	< MDL	< MDL	0.0001	< MDL
Nd	0.00016	< MDL	0.0025	0.0029	< MDL
Sm	0.00009	0.0044	0.0035	0.0061	0.0028
Eu	0.00006	0.0007	< MDL	< MDL	< MDL
Gd	0.00010	< MDL	< MDL	0.0382	< MDL
Tb	0.00002	0.0018	0.0004	0.0012	0.0003
Dy	0.00008	0.0020	0.0006	0.0065	0.0005
Ho	0.00002	0.0001	< MDL	0.0018	0.0016
Er	0.00003	< MDL	< MDL	0.0034	0.0023
Tm	0.00002	< MDL	0.0003	0.0013	< MDL
Yb	0.00018	0.0019	0.0035	0.0120	0.0026
Lu	0.00002	0.0005	0.0005	0.0029	0.0004
Au	0.00062	0.0283	0.0084	0.0094	< MDL
Pb	0.00025	0.0105	0.0011	0.1738	< MDL
Bi	0.00016	0.0064	0.0087	0.0027	0.0750
U	0.00004	0.0021	0.0168	0.0007	0.0001
Impurity (µg/g)		1653.904	77.054	595.694	51.337
% Impurity		0.1654%	0.0077%	0.0596%	0.0051%
% Purity		99.8346%	99.9923%	99.9404%	99.9949%

Figure 1 shows plots of impurities of the four compounds measured in this study. The shades of blue represent the impurities traditionally measured in lithium salts, while the “other” represents the additional impurities measured in this work. As shown in Figure 1, the majority of the impurities in 98% LiOH and 99% Li_2CO_3 are the traditionally measured elements. However, in 99.995% LiOH and 99.998% Li_2CO_3, the majority of impurities are “others” – elements measured in this work which have not been traditionally measured. These plots demonstrate the importance of measuring additional elements when assessing the purity of lithium salts used to produce lithium-ion batteries.

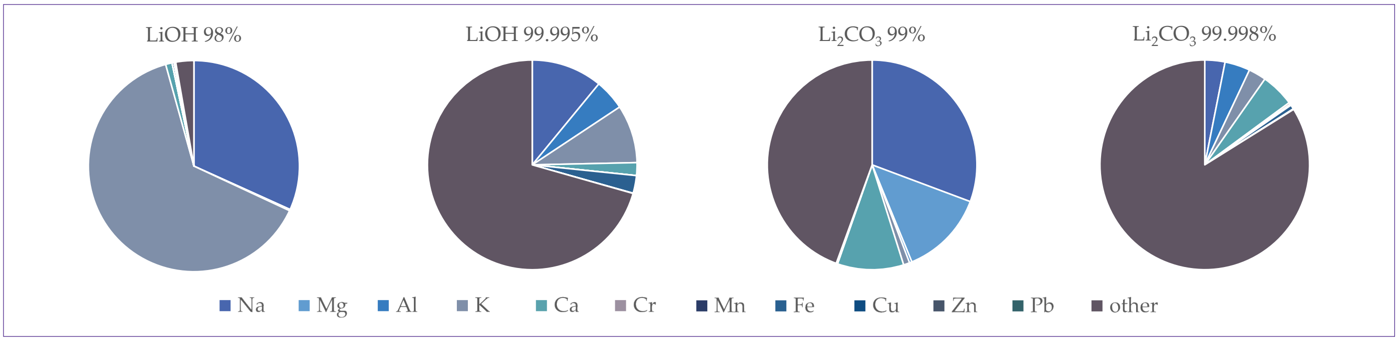

Figure 1: Graphic depictions showing the distribution of impurities. The impurities that are currently measured are listed, while the other section includes all other impurities.

Conclusion

Lithium batteries are an important commodity in today's society, and the demand for longer life and more efficient batteries will only increase as the world turns away from fossil fuels. Li salts used in the production of batteries are, for the most part, extracted from brines and, subsequently, have high impurity levels. The purity of these salts can impact battery lifetime, stability and efficiency, pushing the need for higher purity in these raw materials. Current elemental analysis techniques are becoming inadequate for these higher-purity materials. In this study, we have shown that as the purity of Li salts increases, it becomes necessary to analyze more than just the traditional impurity elements. The results indicate that the majority of impurities result from elements which have not been traditionally measured. For the analysis of Li salts, the NexION 5000 ICP-MS offers outstanding detection limits and interference correction thanks to the combination of its multi-quadrupole technology, quadrupole Universal Cell, and other proprietary features.

References

1. NexION 5000 Multi-Quadrupole ICP Mass Spectrometer, Product Note, PerkinElmer, 2020.
2. All Matrix Solution System for NexION ICP-MS, Technical Note, PerkinElmer, 2020.
3. Bandura, D.R.; Baranov, V.I.; Tanner, S.D. "Detection of Ultratrace Phosphorus and Sulfur by Quadrupole ICPMS with Dynamic Reaction Cell", Analytical Chemistry 2002 74(7), 1497-1502.

Consumables Used

Component	Part Number
PFA ST3 Nebulizer with Integrated Gas Line	N8152378
Fixed 2.0 mm Injector UHP Quartz Torch	N8152428
SilQ Spray Chamber with AMS Gas Port	N8152539
Grey/Grey 1.30 mm I.D. Santoprene Peristatic Pump Tubing	N8152415
Orange/Green Flared 2-Stop PVC Pump Tubing	N8145197
Gas Line-Matrix	N8152374

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