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Industrial analysis

Elemental analysis of lithium salts using ICP-MS combined with argon gas dilution (AGD)

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Keywords

Li salts analysis, AGD, high matrix, Li battery, total dissolved solids (TDS)

Goal

This application note describes the performance of the Thermo Scientific™ iCAP™ RQ ICP-MS system combined with argon gas dilution (AGD) for the analysis of impurities in lithium salts used for the manufacturing of lithium-ion batteries.

Introduction

Lithium batteries are one of the most important electrochemical energy storage systems in use today. Their superior energy density and high storage capacity has led to their rapid adoption in portable electronic devices and other industrial applications, and more recently they have become the current standard technology for electric vehicle battery packs. With the ongoing rapid growth of the electric vehicle market, the requirement for large quantities of high performance, robust, and safe lithium-ion batteries with long lifetimes has arisen. This in turn has led to intensified global research on enhancing battery technology, together with an unparalleled ramp up in manufacturing capacity and an increase in the need for accurate, precise, and reliable battery material analysis.

In the up- and mid-stream of the lithium-ion battery industry value chain, quality control of raw materials and finished products requires the use of instrumental analysis methods to test for impurities and physical properties to ensure that the finished products comply with performance and safety specifications. This includes in particular lithium salts, such as lithium carbonate (Li_2CO_3) and lithium hydroxide (LiOH).

Currently, most lithium salts are analyzed for purity by inductively coupled plasma optical emission spectroscopy (ICP-OES), a very robust analytical technique that enables detection of impurities in concentration ranges between sub μg·L^{-1} and % levels. Since in the future, batteries with better performance and longer life are required, higher purity raw materials will be needed. In just a few years, many manufacturer's lithium salt purity requirements are likely to increase to 99.99% (or even higher), and this trend will probably continue for some time. This level of purity will challenge the current methods used for analysis, as not only the concentration levels to be detected will decrease, but also the number of elements to be analyzed will likely increase to include elements typically present at trace and ultra-trace levels. Combining these requirements, analysis of some key lithium battery raw materials is likely to gradually transfer from ICP-OES to ICP-MS.

This application note describes the analysis of three different lithium salts using the iCAP RQ ICP-MS. The method developed includes common impurities, such as alkali and alkaline earth elements, transition elements, heavy metals, and the lanthanide series elements. In total, more than 60 analytes are included in the purity assessment.

Instrumentation

An iCAP RQ ICP-MS with argon gas dilution was used to analyze three samples, including two samples of Li_2CO_3 and one of LiOH. Raw materials for battery production usually represent a complex matrix. However, dilution during sample preparation is not always desired, as it increases the workload and leads to elevated method detection limits (MDLs) that may render the detection of low concentration impurities impossible. ICP-MS systems have usually limited matrix tolerance, thus often requiring significant sample dilution prior to the sample entering the plasma. The iCAP RQ ICP-MS offers argon gas dilution (AGD) as a solution specifically designed to overcome this challenge. The use of argon gas, provided directly from the instrument, is an attractive way to dilute the sample online at no additional cost. Samples can be placed as received onto the autosampler and analyzed directly, with the dilution carried out inside the instrument.[1]

The instrument parameters used for this application work are shown in Table 1.

Table 1. Instrument parameters

Instrument parameter	Setting
Measurement mode	KED
Insert	High matrix 3.5 mm
Pump tubing	Sample: PVC tubing orange/green (0.381 mm i.d.) for uptake Internal standard: PVC tubing orange/green (0.381 mm i.d.) Drain: Santoprene™ tubing gray/gray (1.295 mm i.d.)
Pump speed	40 rpm
Spray chamber	Quartz cyclonic
Torch	Ceramic torch (PLUS torch)
Nebulizer	Glass concentric, MicroMist™
Nebulizer gas flow	0.26 L·min^{-1}
Argon gas dilution flow	62.6% (1,000 mL·min^{-1} MFC)
Injector	2.5 mm i.d., quartz
RF power	1,550 W
Replicates	3
Autosampler	ESI SC-4DX
Dwell time	0.05 s/isotope
Uptake/wash time	35/10 s

The instrument was equipped with a PLUS torch, a direct replacement for the standard quartz torch, which is made from high purity and high-performance ceramic material. The sampling process was automated using an autosampler (SC-4DX, Elemental Scientific, Omaha, NE, USA). To overcome common interferences, all analyses were performed using helium as an inert collision gas and applying kinetic energy discrimination (KED). The use of KED in combination with the automatically configured low mass cut off, a unique feature of the QCell collision/reaction cell (CRC), enables complete removal of common polyatomic interferences and ensures high ion transmission (also for elements with low mass), so that additional measurement modes within the method can be omitted. The use of a single measurement mode across all analytes significantly simplifies method development and enables a decrease in sample turnaround times, as cell gas switching within the measurement of a sample is avoided. The setup of the instrumental parameters was accomplished using the autotune routines provided with the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software.

Samples and sample preparation

Three Li salt samples were analyzed, including Li_2CO_3 (99%, Thermo Scientific™ and 99.998%, Puratronic™, Thermo Scientific™) and $LiOH{\cdot}H_2O$ (98%, Puratronic™, Thermo Scientific™).

An aliquot of 250 mg of each salt was weighed accurately and dissolved in 50 mL 2% nitric acid (v/v). The samples were left to react in a fume hood for one hour and then analyzed directly using the iCAP RQ ICP-MS without any further manual dilution. This means that about 0.5% (m/v) total dissolved solids (TDS) are directly introduced to the system.

Calibration standards

Calibration standards were prepared in 2% (v/v) nitric acid, with analyte concentrations covering the range expected in the samples.

An internal standard solution, containing 20 $\mu g{\cdot}L^{-1}$ scandium, 10 $\mu g{\cdot}L^{-1}$ yttrium, indium and iridium in 2% (v/v) nitric acid, was added to all samples via a T-piece (the mixing rate between internal standard and samples was 1:1) before entering the spray chamber.

Data acquisition and data processing

The Qtegra ISDS Software was used to create LabBooks for sample analysis, data acquisition, processing, and reporting. For the development of a complex method, including more than 60 analytes, Qtegra ISDS Software includes an automatic isotope selection based on the user's choice of element. With this approach, a combination of highest abundance, lowest relative level of polyatomic ion interference, and freedom from isobaric overlaps is used to select the optimum isotope for the analysis.

Results and discussion

Method performance

The linearity of the instrument was demonstrated using a six-point calibration curve. All calibration curves from trace elements to major elements were established in the same run, and excellent correlation coefficients (>0.9999 or even higher) were achieved.

Detection limits (DLs) in solution were established by measuring a reagent blank solution, which was prepared in parallel to the samples. This solution was analyzed 10 times, and based on the standard deviation of the repeats, the instrumental detection limit was automatically calculated and reported by the Qtegra ISDS Software. As all samples were analyzed without any further dilution, the IDL can be converted to the method detection limit simply by multiplication with the dilution factor (200 in this case).

In comparison to ICP-OES, the detection limits are typically lower by at least 3–4 orders of magnitude when using ICP-MS. The increase in detection power is especially important for the analysis of the lanthanides, a group of metals with very specific chemical properties that are often found only in $\mu g{\cdot}kg^{-1}$ amounts (or below) in geological samples. Here, the exceptional sensitivity of ICP-MS, together with the (often non-existent lanthanide element backgrounds) facilitate instrumental detection limits in the $ng{\cdot}L^{-1}$ concentration range. Table 2 provides an overview of the calibration correlation coefficients and detection limits for all the target elements.

Table 2. Overview of the correlation coefficients of the calibration plots and achieved detection limits

Element	R^2	DLs (µg·L^{-1})	Element	R^2	DLs (µg·L^{-1})	Element	R^2	DLs (µg·L^{-1})
^{6}Li	>0.9999	0.306	**^{77}Se**	>0.9999	0.532	**^{159}Tb**	>0.9999	0.189*
^{9}Be	>0.9999	0.097	**^{85}Rb**	>0.9999	0.005	**^{163}Dy**	>0.9999	0.001
^{11}B	0.9993	0.767	**^{88}Sr**	>0.9999	0.005	**^{165}Ho**	>0.9999	0.001
^{23}Na	0.9996	3.164	**^{90}Zr**	>0.9999	0.007	**^{166}Er**	0.9998	0.001
^{24}Mg	0.9997	0.228	**^{93}Nb**	0.9998	0.060*	**^{169}Tm**	>0.9999	0.278*
^{27}Al	0.9999	0.405	**^{95}Mo**	0.9997	0.009	**^{172}Yb**	>0.9999	0.001
^{31}P	0.9967	13.22	**^{101}Ru**	>0.9999	0.002	**^{175}Lu**	>0.9999	0.152*
^{39}K	0.9966	8.575	**^{105}Pd**	0.9999	0.011	**^{178}Hf**	>0.9999	0.001
^{44}Ca	0.9998	0.629	**^{107}Ag**	>0.9999	0.003	**^{181}Ta**	>0.9999	0.258*
^{48}Ti	>0.9999	0.019	**^{111}Cd**	>0.9999	0.003	**^{182}W**	0.9998	0.001
^{51}V	0.9999	0.010	**^{118}Sn**	>0.9999	0.011	**^{185}Re**	>0.9999	0.494*
^{52}Cr	0.9999	0.001	**^{121}Sb**	>0.9999	0.003	**^{195}Pt**	>0.9999	0.001
^{55}Mn	>0.9999	0.004	**^{133}Cs**	>0.9999	0.001	**^{197}Au**	0.9996	0.004
^{57}Fe	0.9998	0.124	**^{137}Ba**	>0.9999	0.002	**^{202}Hg**	>0.9999	0.301*
^{59}Co	0.9999	0.022*	**^{139}La**	>0.9999	0.002	**^{205}Tl**	>0.9999	0.088*
^{60}Ni	0.9998	0.005	**^{140}Ce**	>0.9999	0.001	**^{208}Pb**	>0.9999	0.001
^{63}Cu	0.9998	0.001	**^{141}Pr**	>0.9999	0.444*	**^{209}Bi**	0.9998	0.001
^{66}Zn	>0.9999	0.033	**^{146}Nd**	>0.9999	0.001	**^{232}Th**	>0.9999	0.486*
^{71}Ga	0.9999	0.002	**^{147}Sm**	>0.9999	0.001	**^{238}U**	>0.9999	0.280*
^{73}Ge	0.9999	0.079	**^{153}Eu**	>0.9999	0.365*			
^{75}As	>0.9999	0.043	**^{157}Gd**	>0.9999	0.002			

DLs with * in ng·L^{-1}

Raw material results

When analyzing high-purity materials, in many cases, simultaneous measurement of both major / matrix elements and impurities is required, as described in this application note. In this case, a total of 60 elements were measured to assess the purity of the lithium salts under investigation. In addition to the impurities, the lithium content was also determined, using ^{6}Li as a less abundant (7.50%) isotope to avoid excessively large signals on the detector as a result of measuring the high Li concentration in the samples. Three lithium salts were analyzed, and each salt sample was prepared in duplicate for comparison. Table 3 shows the concentrations of all elements in the three different Li salt samples. The total impurity level can be seen in Table 4, together with the corresponding purity.

Table 3. Element content in the three different lithium salts

Element	Li_2CO_3 99%		Li_2CO_3 99.998%		$LiOH·H_2O$ 98%	
	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
^{6}Li	18.2%	18.4%	18.6%	18.9%	16.2%	16.6%
^{11}B*	4.25	3.83	4.75	4.00	2.54	2.37
^{23}Na*	166	174	ND	ND	112	114
^{24}Mg*	6.53	7.03	0.28	0.28	0.41	0.45
^{27}Al*	0.79	0.62	0.64	0.81	32.1	31.9
^{39}K*	0.80	0.84	0.22	0.19	33.9	35.8
^{44}Ca*	15.2	15.9	0.66	0.44	1.18	1.30
^{48}Ti	308	580	10	8	24	24
^{51}V	4	4	6	8	600	638
^{52}Cr	356	394	76	72	370	374
^{55}Mn	94	96	12	12	18	16
^{57}Fe*	1.68	1.60	ND	ND	0.48	0.43
^{59}Co	6	4	ND	ND	ND	ND
^{60}Ni	162	164	10	14	36	28
^{63}Cu	12	12	ND	ND	12	10
^{66}Zn	80	62	16	8	208	212
^{71}Ga	ND	ND	ND	ND	30	30
^{75}As	10	12	8	2	16	12
^{77}Se	106	100	ND	ND	ND	ND
^{85}Rb	10	4	14	12	112	106
^{88}Sr	2180	2260	8	10	482	470
^{93}Nb	12	12	4	2	ND	ND
^{95}Mo	64	40	ND	ND	32	26
^{105}Pd	2	2	2	2	ND	ND
^{107}Ag	10	12	ND	ND	ND	ND
^{111}Cd	10	8	ND	ND	ND	ND
^{118}Sn	8	8	ND	ND	8	8
^{121}Sb	2	2	32	32	44	42
^{133}Cs	ND	ND	ND	ND	14	12
^{137}Ba	824	824	34	34	252	268
^{139}La	4	4	2	2	ND	ND
^{140}Ce	2	2	ND	ND	ND	ND
^{146}Nd	2	2	ND	ND	ND	ND
^{182}W	ND	ND	32	40	22	20
^{195}Pt	2	2	2	2	2	2
^{197}Au	6	2	2	4	4	2
^{202}Hg	20	11	14	9	ND	ND
^{205}Tl	ND	ND	ND	ND	2	2
^{208}Pb	170	176	ND	ND	80	74
^{209}Bi	2	2	ND	ND	ND	ND
^{238}U	ND	ND	ND	ND	22	22
Be, Ge, Zr, Ru, Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, Re, Th	Below MDL					

Lithium concentration in %; elements with "*" in $mg·kg^{-1}$; other elements in $μg·kg^{-1}$

Table 4. Determination of the total trace element amount in each sample (in mg·kg^{-1})

Element	Li_2CO_3 99%		Li_2CO 99.998%		$LiOH·H_2O$ 98%	
	Measurement 1	Measurement 2	Measurement 1	Measurement 2	Measurement 1	Measurement 2
Total traces	200	208	6.8	6.0	185	188
%Purity	99.98	99.98	99.9993	99.9994	99.98	99.98

In general, there is good agreement between the individual samples prepared from each of the three lithium salt samples under investigation, which demonstrates the reproducibility and accuracy of the analysis. The overall purity of all the compounds could be verified, but it becomes obvious that a higher purity does not necessarily translate into lower impurity levels for each individual analyte. Although for most elements, the concentrations of impurities are significantly lower for Li_2CO_3 with 99.998% purity, the compound shows similar levels of boron as compared to the same compound with 99% purity. At the same time, the 98% purity LiOH shows significantly lower levels of the same analyte. A similar observation can be made for sodium. Here, in the 99.998% Li_2CO_3, there is no sodium detected at all, and in the 98% pure LiOH, it shows 30% lower results for sodium compared to the 99% pure Li_2CO_3 but significantly higher concentrations of other elements. These differences can likely be explained by the different origin of the raw lithium salts as well as by the different processes used in the refining of the lithium raw materials into the final compounds.

Spike recovery test

To further confirm the potential of the method to provide accurate results for key analytes, and to demonstrate the absence of any drift or other matrix effect as an influencing factor on the results, a spike recovery test with two different spike levels (0.1 µg·L^{-1} and 1 µg·L^{-1}) was performed in duplicate in all three lithium salt samples.

In this work, a focus was made on the lanthanides, as they have specific characteristics relevant to high technology electrotechnical applications. Although generally rare in the environment, the growing purity requirements of high-performance batteries may demand the analysis of uncommon analytes (from today´s perspective) in the future. Due to the typically low concentrations in which lanthanides are found in the environment, the analysis requires a highly sensitive analytical technique. For ICP-OES, the accurate analysis of lanthanides is challenging because there are multiple overlaps between the characteristic emission wavelengths of the target elements and interfering spectral lines from other elements. At the same time, detection limits typically achievable using ICP-OES often do not suffice in practice. Table 5 shows the spike recovery results in the three lithium salt samples. The overall spike recovery observed across all samples was excellent with an average recovery of between 90% and 102%.

Table 5. Rare earth element (REE) spike recovery results for the lithium salt samples

	Li_2CO_3 99%				Li_2CO 99.998%				$LiOH·H_2O$ 98%			
	0.1 µg·L^{-1} (%)		1 µg·L^{-1} (%)		0.1 µg·L^{-1} (%)		1 µg·L^{-1} (%)		0.1 µg·L^{-1} (%)		1 µg·L^{-1} (%)	
	#1	#2	#1	#2	#1	#2	#1	#2	#1	#2	#1	#2
^{139}La	95	88	96	91	94	91	95	94	93	93	95	91
^{140}Ce	94	91	94	89	97	96	96	94	92	92	94	91
^{141}Pr	92	94	95	90	98	96	97	94	91	94	95	91
^{146}Nd	97	96	95	89	97	100	99	92	91	98	96	92
^{147}Sm	95	99	98	91	99	90	98	97	89	97	98	94
^{153}Eu	94	94	97	91	97	95	98	97	94	100	98	93
^{157}Gd	97	93	96	91	97	94	100	97	96	99	97	93
^{159}Tb	97	95	97	92	97	95	98	95	99	97	97	94
^{163}Dy	91	95	98	94	100	96	96	95	97	97	96	92
^{165}Ho	96	96	98	93	97	96	98	96	99	98	97	93
^{166}Er	98	94	98	92	101	100	97	95	98	96	96	94
^{169}Tm	97	96	98	92	99	98	99	97	100	100	98	95
^{172}Yb	94	94	97	90	96	94	97	95	94	98	96	94
^{175}Lu	98	95	100	95	102	98	100	97	102	99	99	96

Quality control procedure and long-term stability

For reliable analysis in an analytical testing laboratory, it is important that the results obtained are accurate and precise in longer batches comprising different sample types as well as in shorter runs. Commonly, quality control (QC) standards containing a known concentration of all analytes are analyzed periodically during a batch to monitor the method performance. Another important indicator that many regulated methods require is the response of the internal standard over the course of the analysis. The internal standard helps to correct for potentially occurring drift of the system during the analysis and also helps to compensate for matrix effects such as signal suppression.

To simulate a high-volume sample analysis, a larger sample batch containing all the lithium salt samples previously analyzed was scheduled for analysis. A QC check (continuing calibration verification, CCV, containing 10 $\mu g \cdot L^{-1}$ of all the elements measured) was analyzed after every 20 unknown samples, so that the accuracy of the analysis was verified at specific points in the batch. In summary, 12 CCVs were analyzed in a batch containing 280 samples in approximately 12 hours. A full overview of all QC samples that were successfully acquired is shown in Figure 1. As can be seen from the data, the average recovery was excellent, being within 98% and 115% throughout the run.

The recovery of the internal standards, using a real time display generated automatically by the Qtegra ISDS Software, is shown in Figure 2. All isotopes used as internal standards showed excellent recoveries between 75% and 120% over the entire duration of the analysis and in different types of sample matrices. This recovery demonstrates stability and accuracy throughout the run, with no adverse effects derived from the sample matrices (e.g., signal suppression or enhancement).

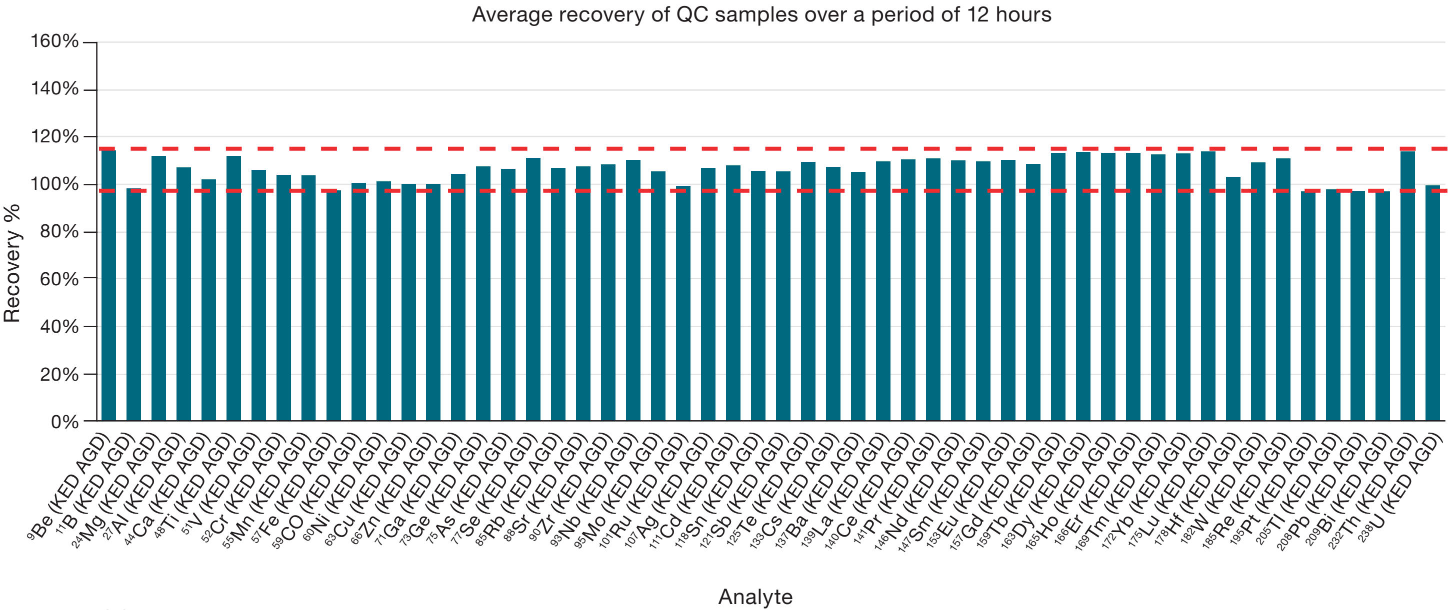

Figure 1. QC sample recoveries during the 12 hour run

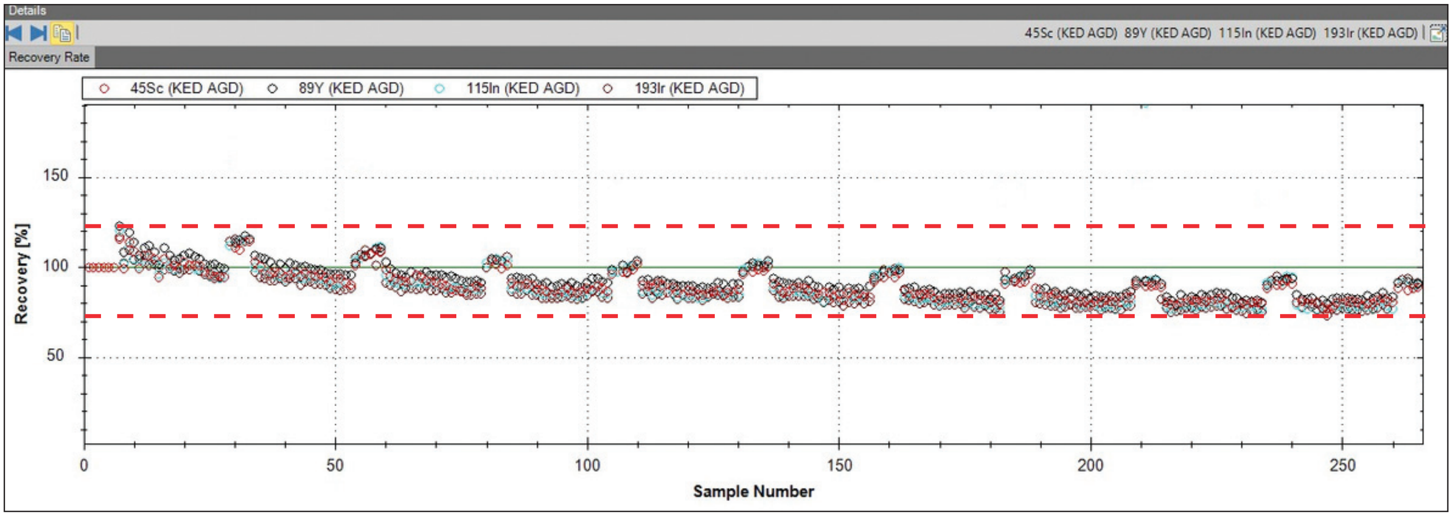

Figure 2. Internal standard performance from the analysis of about 280 samples over 12 hours showing recoveries between 75% and 120%

Conclusions

This application note demonstrates that different lithium salts can be analyzed for impurities with high accuracy and precision using the iCAP RQ ICP-MS. The system was proven to be highly robust, so that sample preparation can be kept to a minimum, and samples can be added for analysis without any further dilution. All instruments of the Thermo Scientific™ iCAP™ Qnova Series ICP-MS are designed to allow robust and reliable analysis while being easy to maintain. The key components that operators handle most, such as the nebulizer, spray chamber, and interface, can be easily accessed and disassembled for effortless maintenance and minimal downtime. This feature is extremely important when analyzing high matrix samples such as lithium salts.

- The simplified workflow of the Qtegra ISDS Software allows simple method development, implementation of quality control protocols, and data evaluation.
- The large linear dynamic range of up to 10 orders of magnitude allows for precise determination of major elements and trace elements in one measurement without further sample dilution, here demonstrated by the analysis of ^{6}Li at the same time as trace level impurities.
- Argon gas dilution (AGD) is a way to overcome the challenges associated with the analysis of samples with matrix content outside the commonly defined limit of around 0.2% (m/v) total dissolved solids. Dilution with argon gas is accomplished automatically inside the instrument with no additional sample handling required. AGD is fully integrated and supported in the Qtegra ISDS Software, so that it is easy to set up and operate.
- Robust and stable analytical performance was demonstrated over 12 hours of continuous acquisition of 280 samples, demonstrating that the system is able to meet the increasing requirements of laboratories supporting growing production lines.

In summary, the iCAP RQ ICP-MS system operated together with the AGD sample aerosol dilution system and controlled by Qtegra ISDS Software allows for accurate, fast, sensitive, and robust elemental determination in different kinds of lithium salt samples. In one analysis process, up to 60 elements, across the full periodic table, can be accurately and precisely analyzed with little sample preparation and short turnaround times. The system delivers outstanding detection limits, effective interference elimination and excellent stability.

Reference

1. Thermo Scientific Technical Note 000387: Resolving the challenges of analyzing samples with high and variable matrix content using argon gas dilution (AGD) with ICP-MS. **https://assets.thermofisher.com/TFS-Assets/CMD/Technical-Notes/tn-000387-tea-icp-ms-argon-gas-dilution-multi-element-analysis-tn000387-na-en.pdf**

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