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Determination of Elemental Impurities in Lithium Hydroxide Using ICP-OES

Quality assurance of lithium-ion battery precursor chemicals by Agilent 5800 VDV ICP-OES

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Introduction

Driven by demand from high tech industries for lithium-ion batteries (LIBs), the global market for lithium (Li) compounds is expected to reach USD 26.7 billion by 2030 (*1*). Commercial production of Li compounds relies on extraction of Li from two naturally occurring sources; brine, principally in South America, and hard rock minerals such as spodumene, from orebodies found mainly in Australia and China. Traditionally, lithium hydroxide (LiOH) was converted from brine-extracted lithium carbonate (Li_2CO_3). However, recent advances in technology (e.g., membrane technology) have enabled the production of LiOH directly from brine. Both Li_2CO_3 and LiOH can be produced directly from hard rock minerals.

Li_2CO_3 is more widely used as the raw material for producing LIB components than LiOH because of its lower cost and availability. Lower energy density cathode materials (e.g., $LiFePO_4$) typically use Li_2CO_3 as a precursor chemical. More recently though, lithium, nickel, manganese, cobalt (NMC) cathode materials, particularly cathodes with a higher Ni content, are preferred in many sectors for their higher energy density and larger storage capacity (*2, 3*). For NMC type cathodes, LiOH rather than Li_2CO_3 is the preferred precursor, as LiOH allows rapid and complete cathode synthesis at a lower temperature, leading to a longer battery life cycle and enhanced safety (*2, 4*). As a result of these advantages, demand for LiOH is growing at a faster rate than for Li_2CO_3 (*4, 5*).

Accurate quality control (QC) methods are needed throughout the supply chain of Li-rich materials like LiOH, including at mining or production sites. Also, any analytical techniques used to quality assure (QA) Li-rich materials must be robust enough to handle the broad range of purities of the samples and the high content of Li in the matrices.

Inductively Coupled Plasma Emission Spectrometry (ICP-OES) is one of the most common analytical methods used for the determination of elemental impurities of chemicals and materials used in the LIB industry. As the leader of global LIB production, China has issued a national standard, GB/T 26008-2020, for the analysis of $LiOH \cdot H_2O$: 'Battery grade lithium hydroxide monohydrate' (*6*). GB/T 26008-2020 refers to GB/T 11064.16-2013 (*7*) for the determination of Ca, Mg, Cu, Pb, Zn, Ni, Mn, Cd, and Al in Li_2CO_3, $LiOH \cdot H_2O$, and lithium chloride (LiCl) using ICP-OES. An ISO method for the quantification of the trace elements, Ca, Mg, Na, K, Al, B, Cd, Cr, Cu, Fe, Ni, Pb, Zn, S, and Si in $LiOH \cdot H_2O$ is under development; ISO/AWI 16423 'Lithium hydroxide monohydrate—Determination of impurities—ICP-OES method' (*8*).

Analyzing high purity Li-rich compounds by ICP-OES is challenging due to the high Li concentration in the sample matrices, which could impact productivity, increase maintenance tasks, and compromise sensitivity and accuracy. The high Li content can also affect the analysis of easily ionized elements (EIEs) such as Na and K, leading to false-positive results (*9*).

To overcome the challenges of the application, the Agilent 5800 Vertical Dual View (VDV) ICP-OES equipped with an Agilent Advanced Valve System (AVS) seven-port switching valve (AVS 7) was used in this study. The AVS 6 or 7 valve system reduces the amount of sample that reaches the sample introduction system, reducing sample load on the nebulizer. Compared to the AVS 6, the 7-port system enables the internal standard to be directly plumbed to the valve (*10*).

The 5800 ICP-OES features a cooled cone interface (CCI) that improves the reliability of the results by overcoming the effects of a cool plasma tail. A cool plasma tail shortens the dynamic range due to analyte self-absorption and increased molecular interferences. The 5800 and Agilent ICP Expert software include smart tools to help with method development, monitor instrument metrics, and check the data set (*11–14*):

– IntelliQuant uses data analytics to automatically identify spectral overlaps that can lead to incorrect results and recommends the emission wavelength that will give the most accurate result.

– Easy-to-use automated algorithms for ICP-OES background correction including default, automated Fitted Background Correction (FBC) and Fast Automated Curve-fitting Technique (FACT).

– Early Maintenance Feedback (EMF) prompts analysts to perform maintenance based on instrument use rather than simple time-based routines.

In this study, the Agilent 5800 Vertical Dual View (VDV) ICP-OES fitted with the AVS 7 was used for the analysis of 27 elemental impurities in a 98% purity LiOH powder. The method was evaluated through sample spiking and long-term stability testing.

Experimental

Materials and standard solutions

A commercial LiOH (98% purity) and a commercial Li_2CO_3 (99% purity) solid samples were used to represent the raw materials used by LIB precursor manufacturers. High purity concentrated nitric acid (HNO_3) (69%) was bought from Merck Pty. Ltd, Australia. Agilent 1,000 or 10,000 mg/L single element standard solutions of Al, As, B, Ba, Be Ca, Cd, Co, Cr, Cu, Fe, Ga, K, Li, Mg, Mn, Mo, Na, Ni, Pb, S, Sb, Si, Sr, Ti, V, Zn, and Zr were used for preparation of the calibration standards. Agilent 1,000 or 10,000 mg/L single element standard solutions of Bi, In, and Rb were used to prepare internal standard (IS) solutions.

Calibration standards and internal standards

A 10 mg/L stock solution containing Al, As, B, Ba, Be Ca, Cd, Co, Cr, Cu, Fe, Ga, K, Mg, Mn, Mo, Na, Ni, Pb, S, Sb, Si, Sr, Ti, V, Zn, and Zr was prepared by diluting each of the 1,000 or 10,000 mg/L single element standard solutions in 5% HNO_3. To prepare calibration standard solutions of all elements, except for Na, in the analytical working range, the stock solution was diluted using 10% HNO_3 to final concentrations of 0, 0.010, 0.050, 0.100, 0.200, and 0.500 mg/L. For Na, the 0.010 mg/L concentration standard was replaced with a 0.020 mg/L standard. To cover the higher concentrations of K, Na, and Si in the samples, extra standards at 5 mg/L for K, 5 mg/L for Na, and 1 mg/L for Si, were added. To obtain sample matrix information, Li was also quantified in the sample. Calibration standard solutions at 100, 1,000, and 3,000 mg/L were prepared from an Agilent 10,000 mg/L Li standard solution.

For quality control purposes, a blank 10% HNO_3 solution was used as the continuing calibration blank (CCB). A standard solution containing 0.1 mg/L of the 27 elements, which was prepared separately from the calibration standards, was used as the continuing calibration verification (CCV) solution. A Li standard solution of 1,000 mg/L was used as an additional CCV, labeled CCV1. The CCB and CCVs were analyzed every 10 to 12 samples. An IS solution containing 20 mg/L Bi and In and 100 mg/L Rb was prepared in 10% HNO_3.

Blank 10% HNO_3 solutions were spiked following the same procedure as the control samples. All solutions were prepared in triplicate.

Sample preparation

The sample preparation method for ICP-OES analysis was based on the method outlined in GB/T 11064.16-2013 (7). About 1 g of LiOH was accurately weighed to ±0.0001 g and slowly dissolved in 10% HNO_3. The solution was allowed to cool to room temperature in the fume hood before being made up to 100 mL. Spike experiments were carried out by spiking an aliquot of the LiOH sample solution at 0.05 and 0.1 mg/L.

To assess the long-term stability of the method for repeated measurements of Li salts, 1% Li_2CO_3 solutions were also included in the test. The 1% Li_2CO_3 solutions were prepared following the same procedures as for the 1% LiOH solution. The solutions were allowed to degas for one hour in the fume hood before being spiked with the 27 elements at 0.1 mg/L.

Instrumentation

The elemental analysis of the samples was carried out using the 5800 VDV ICP-OES fitted with a SeaSpray glass concentric nebulizer, double-pass cyclonic spray chamber, Easy-fit semi-demountable torch with 1.8 mm quartz injector. An argon (Ar) humidifier was also used. The humidifier enables the accurate analysis of challenging sample types that may potentially cause salt to build up on the tip of the nebulizer, and eventually block the nebulizer.

The instrument and method were controlled and optimized using the ICP Expert Pro software, which was also used to process the analytical data. The high level of Li in the LiOH samples (2900–3000 mg/L in 1% LiOH solutions) and the need to analyze trace impurities using axial view of the plasma cause ionization interferences that affect the measurement of EIEs. The instrument operating conditions shown in Table 1 were therefore optimized for the analysis of both trace elements and major group I and II EIEs.

For inline addition of the internal standard to the samples, sample introduction was performed using the AVS 7 with an Agilent SPS 4 autosampler. Control of the AVS 7 and SPS 4 is fully integrated and controlled through the ICP Expert Pro software. The software includes an AVS parameter calculator that facilitates the setup and method development of the AVS. The parameters of the AVS 7 are presented in Table 2.

Table 1. Agilent 5800 VDV ICP-OES operating conditions.

Parameter	Setting	
Viewing Mode	Axial	Radial
Viewing Height (mm)	-	8
RF Power (kW)	1.2	
Nebulizer Flow (L/min)	0.70	
Plasma Flow (L/min)	13.5	
Aux Flow (L/min)	1.2	
Pump Speed (rpm)	12	
Replicates	3	
Rinse Time (s)	10	
Read Time (s)	10	5
Stabilization Time (s)	10	0
Sample Pump Tubing	White/white	
Internal Standard Pump Tubing	Black/black	
Waste Pump Tubing	Blue/blue	

Table 2. Agilent AVS 7 operating parameters.

Parameter	Setting
Sample Loop Size (mL)	1.0
Pump Rate - Uptake (mL/min)	35
Pump Rate - Inject (mL/min)	4
Valve Uptake Delay (s)	6
Bubble Inject Time (s)	2
Pre-emptive Rinse Time (s)	1

IntelliQuant Screening for simplified method development

The IntelliQuant Screening feature in the ICP Expert Pro software allows users to run a quick, semiquantitative screening of unknown samples. It collects data from the entire spectral range from 167 to 785 nm in as little as 15 seconds per sample, providing semiquantitative concentrations of up to 70 elements. Analysts can use IntelliQuant without the need for prior knowledge of the samples or expertise in spectroscopy.

Presenting the data as a color-coded periodic table 'heat map' (Figure 1) is a convenient way to identify the major impurity elements, K and Na, and minor elements, Si, Ca, B, and Fe, in the sample solution.
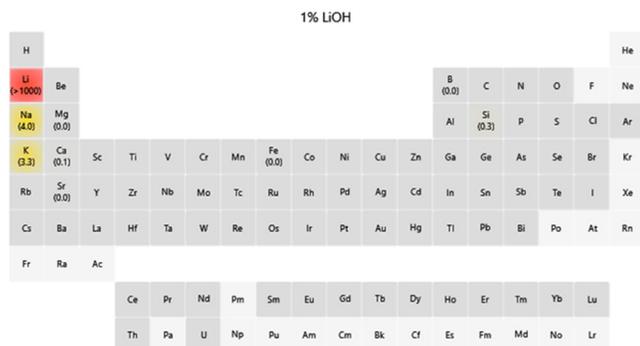
Figure 1. A 'heat map' generated by IntelliQuant showing the concentrations of major and trace elements present in a 1% LiOH solution.

IntelliQuant data can also be used to identify any potential interferences on analyte lines. The software then recommends the best wavelengths to use in the quantitative method using a star ranking based on potential interferences and other factors.

Figure 2 shows an example of the IntelliQuant wavelength star ranking with the recommended wavelengths for Mg, Na, and Si. The red question mark next to Na 588.995 nm gives detailed information on a potential spectral interference from Ar. IntelliQuant helps the analyst create a customized quantitative method more quickly and confidently. IntelliQuant data can also be acquired for every sample as part of the quantitative method by selecting 'Enable IntelliQuant' in the 'Configuration' section.

Figure 2. IntelliQuant star ranking for Mg, Na, and Si helped with selection of analyte wavelengths for the quantitative method.

AVS for reduced maintenance effort and high sample throughput

The use of the AVS is helpful when dealing with complex samples such as compounds that contain high levels of EIEs, such as Li in LiOH. Without the AVS, productivity would be poorer due to the long rinse times required to minimize sample carryover, and maintenance needs would be higher due to Li deposits on the torch. As internal standardization is critical for the analysis of these types of samples, the AVS 7 model with a designated seventh port for IS introduction is advantageous.

The AVS rinses the sample introduction system while the next sample is presented to the instrument, virtually eliminating the delay-times of a conventional ICP-OES analysis. The shorter analysis times with the AVS reduce Ar consumption by as much as 50% per sample, lowering running costs. More efficient analysis and less sample mass passing through the torch minimize the exposure of torches, nebulizers, and pump tubes to complex samples, increasing the lifetime of these sample introduction consumables, and further reducing costs.

The AVS uses Ar bubble injection between the sample and the rinse stream to avoid mixing in the sample loop and dilution of the sample. In this way, the AVS maximizes measurement time and precision for a given sample loop. To increase throughput, a smaller loop can be used which further reduces the uptake delay time and rinse times.

In this study, the average measurement time per sample was reduced from 138 to 84 s using the AVS 7. After almost 400 high concentration Li (>1000 mg/L) samples were measured without any maintenance, and no deterioration of instrument performance was detected. The AVS 7 significantly reduces the total running costs of the analysis and improves productivity.

EMF for proactive maintenance

The 5800 ICP-OES has over 100 sensors that monitor instrument performance. The ICP Expert software includes an EMF function that uses these sensors and other counters to alert the operator when maintenance is required. Traffic light color-coding of the counters (Figure 3) show which maintenance activities should be done immediately (red), which are due (amber), and which can wait (green).

EMF reduces downtime and repair costs by scheduling routine maintenance of components based on actual use (e.g., days elapsed, number of samples run, plasma on hours), rather than at set time intervals (e.g., daily, weekly, or monthly). Analysts can set the counter limits or add new counters to suit their specific needs. For example, in this application the 'Inspect torch outer tube' counter was added and set to 500 solutions. As shown in Figure 3, when the counter limit is approached, the red-colored bar alerts the user to perform the maintenance task.
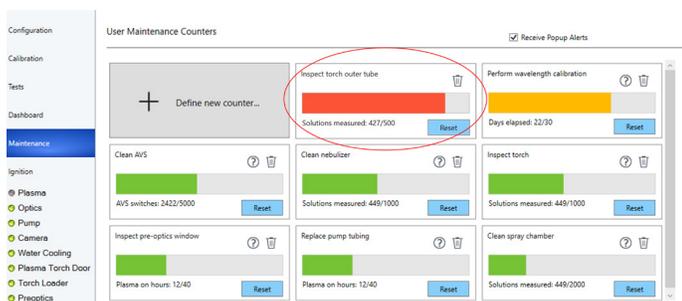
Figure 3. The EMF function in Agilent ICP Exert software uses traffic light color coded counters for proactive maintenance. The analyst is alerted to 'Inspect torch outer tube' once the counter approaches the user-defined limit.

Results and discussion

Calibration linearity

The calibration correlation coefficients (R) of the 27 elements at selected wavelengths are summarized in Table 3. Good linearity (R>0.999) was achieved for all elements in their respective working ranges. Figure 4 shows the linearity of K 766.491 nm (axial) and Na 589.592 nm (radial) from 0.01 or 0.02 to 5 mg/L.
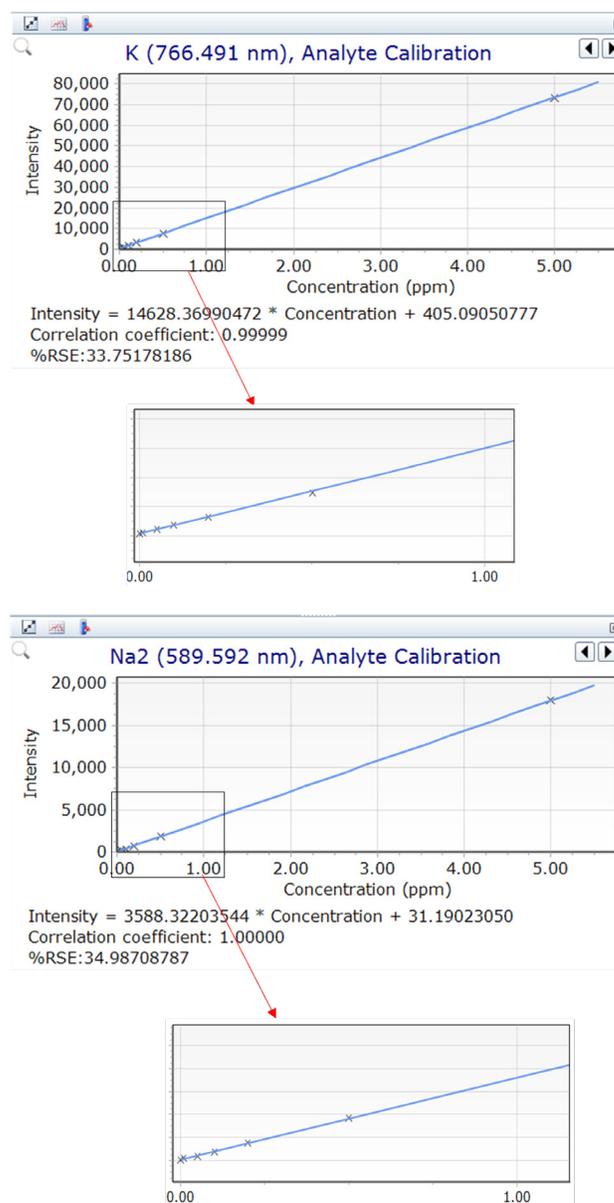
Figure 4. Calibration curves of K 766.491 nm (axial) and Na 589.592 nm (radial).

Table 3. Calibration range, viewing mode, correlation coefficient, background correction mode, and internal standard of 27 elements at selected wavelengths.

Element and Wavelength (nm)	Working Range (mg/L)	Viewing Mode	Correlation Coefficient	Background Correction Mode	IS and Wavelength (nm)
Al 396.152	0.010 – 0.500	Axial	0.9994	FACT	In 325.609
As 193.696	0.010 – 0.500	Axial	0.9997	Fitted	Bi 223.061
B 249.772	0.010 – 0.500	Axial	1.0000	Fitted	Bi 223.061
Ba 455.403	0.010 – 0.500	Axial	1.0000	Fitted	Bi 190.171
Be 234.861	0.010 – 0.500	Axial	1.0000	Fitted	Bi 223.061
Ca 396.847	0.010 – 0.500	Axial	0.9999	Fitted	Bi 190.171
Cd 214.439	0.010 – 0.500	Axial	1.0000	Fitted	Bi 190.171
Co 238.892	0.010 – 0.500	Axial	1.0000	Fitted	Bi 190.171
Cr 267.716	0.010 – 0.500	Axial	1.0000	Fitted	Bi 190.171
Cu 327.395	0.010 – 0.500	Axial	0.9999	Fitted	Bi 306.771
Fe 238.204	0.010 – 0.500	Axial	0.9999	Fitted	Bi 190.171
Ga 294.363	0.010 – 0.500	Axial	0.9998	Fitted	Bi 306.771
K 766.491	0.010 – 5.00	Axial	1.0000	Fitted	Rb 780.026
Mg 279.553	0.010 – 0.500	Axial	0.9995	Fitted	Bi 190.171
Mn 257.610	0.010 – 0.500	Axial	1.0000	Fitted	Bi 190.171
Mo 202.032	0.010 – 0.500	Axial	1.0000	Fitted	Bi 190.171
Na 589.592	0.020 – 5.00	Radial	1.0000	FACT	NA
Ni 231.604	0.010 – 0.500	Axial	1.0000	FACT	Bi 190.171
Pb 220.353	0.010 – 0.500	Axial	1.0000	FACT	Bi 190.171
S 180.669	0.010 – 0.500	Axial	0.9999	Fitted	In 325.609
Sb 206.834	0.010 – 0.500	Axial	0.9999	Fitted	Bi 223.061
Si 251.611	0.010 – 1.00	Axial	1.0000	Fitted	Bi 223.061
Sr 407.771	0.010 – 0.500	Axial	1.0000	Fitted	Bi 190.171
Ti 336.122	0.010 – 0.500	Axial	1.0000	Fitted	Bi 190.171
V 292.401	0.010 – 0.500	Axial	1.0000	Fitted	Bi 190.171
Zn 213.857	0.010 – 0.500	Axial	1.0000	Fitted	Bi 223.061
Zr 343.823	0.010 – 0.500	Axial	1.0000	Fitted	Bi 190.171

NA=not applicable as the Na line was read radially.

Background correction

The presence of a high concentration of Li can impact the accurate detection of trace levels of impurities by ICP-OES. The background would be challenging for any ICP-OES instruments that rely on off-peak-correction. However, ICP Expert software includes default FBC, which identifies off-peak interferences and automatically corrects the interference on the analyte signal.

FBC requires no method development or user input and is applied simultaneously upon measurement of the analyte peak, providing fast and easy background correction that is more accurate than off-peak correction. FBC automatically applies a baseline based on the analyte peak and surrounding background structures. Because the background is automatically calculated by the software, variability from user-to-user is reduced. The lack of required user intervention also reduces the time consuming task of having to verify that each peak has appropriate background mark positioning.

For interference resolution, FACT modeling provides an alternative to Inter-Element Correction (IEC). It is invaluable when the interference must be resolved to gain an accurate result, as required when an alternative wavelength cannot be used. In some instances, FACT modeling can also be used to improve detection limits or data accuracy by subtracting the background, as shown in Figure 5.

Figure 5 shows the FACT spectrum for Ni 231.604 nm. Although there is no significant spectral interference from another element on Ni 231.604 nm, FACT mathematically separates the analyte and blank peaks allowing the accurate measurement of the analyte signal.

FBC was used for background correction of most of the elements, as shown in Table 4, and FACT was used for background correction of Al, Na, Ni, and Pb.
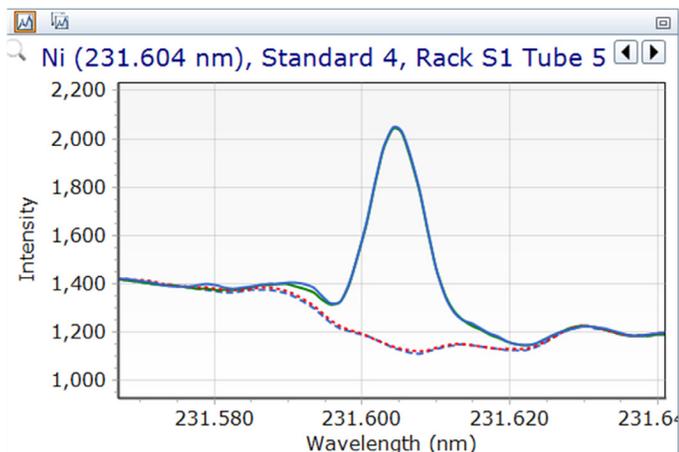
Figure 5. The spectrum of Ni 231.604 nm corrected using FACT. Key for FACT spectra: Raw spectral peak signal (blue solid line), blank (light blue dotted line), interferant peak (red dotted line), corrected analyte peak (green solid line).

Internal standardization

Internal standardization is an important tool for sample matrix correction. In general, the IS element and analyte are matched in terms of atomic or ionic state wavelengths (Table 3). The use of ISs is crucial to this application as the concentration of Li, an EIE, is as high as 3000 mg/L in the sample matrix. EIEs have low ionization energies and are easily ionized in the plasma. When EIEs are present at a very high level, the plasma electron density and the atomization-ionization equilibria are affected. These effects cause either an enhancement or suppression of the emission signals, leading to the reporting of either false high or false low element concentrations. Ionization interferences are especially significant in axial view and when both the analyte (e.g., K or Na) and the coexisting element (e.g., Li) have low ionization potentials (9). In this study, rather than use an IS, radial view was chosen for Na to overcome the very high ionization interferences from Li in axial view mode.

Limit of detection (LOD) and limit of quantitation (LOQ)

The 5800 ICP-OES includes freeform optics to enhance spectral resolution and focus onto the advanced Vista Chip III detector, resulting in lower detection limits (15). The higher resolution optics mean that more analyte lines are separated from neighboring lines, enabling the instrument to achieve lower detection limits for elements in complex matrices.

To determine the LODs and LOQs, 10 solutions of 1% LiOH in 10% HNO_3 were analyzed during the analytical run. The LODs and LOQs were calculated as 3 and 10 times the standard deviation, respectively, of the 10 measurements. As the concentrations of K and Na in 1% LiOH solution are high due to the low purity of the LiOH sample, comparative LODs and LOQs were determined for a 2900 mg/L Li solution in 10% HNO_3, simulating a higher purity LiOH product. The values presented in Table 3 are the average of three LOD and LOQ results from separate tests carried out on three non-consecutive days, calculated as 1 g LiOH in 100 mL solution.

The LODs and LOQs of all elements (except for K and Na) obtained using 1% LiOH are similar to those measured using the 2900 mg/L Li solution, confirming the robustness of the ICP-OES method when handling high Li samples of different purities. The high sensitivity of the 5800 ICP-OES is also demonstrated by the LODs, which were well below 1 mg/kg for most elements. The data also shows that good sensitivity can be achieved for lower purity (e.g. 98%) samples, represented by the 1% LiOH solution, as well as higher purity LiOH, represented by the 2900 mg/L Li solution.

Elemental impurities in LiOH and spike recoveries

The 1% LiOH solution and the solutions spiked at 0.05 and 0.1 mg/L were analyzed using the 5800 VDV ICP-OES. The average measured results and the respective spike recoveries for 27 elements are shown in Table 4. Most elements present in LiOH were below 1 mg/kg. The major elements, Na and K, were around 400 mg/kg, followed by Si, Ca, S, and B, which were between 10 and 100 mg/kg in solid LiOH. Due to the relatively high concentration of Na and K in the 1% LiOH, a 10x matrix matched dilution with 2900 mg/L Li, was performed before the samples were spiked.

Spike recovery tests are an effective way to evaluate the reliability of the sample preparation method and/or the analytical method, especially when no certified reference materials (CRMs) are available. As shown in Table 4, excellent spike recoveries within ±10% of the expected value were achieved for all 27 elements at both 0.05 and 0.1 mg/L spike levels. These results confirm the accuracy of the 5800 ICP-OES method for the analysis of low-level impurities, despite the very high Li concentration in the sample matrix.

Table 4. LOD and LOQ (calculated as 1 g sample in 100 mL solution), concentration of elemental impurities in 98% LiOH and spike recovery data at 5 and 10 mg/kg spike concentrations. Concentration units: mg/kg, n=3.

Element, Wavelength (nm)	1% LiOH		2900 mg/L Li		LiOH	LiOH Spiked at 5 mg/kg*		LiOH Spiked at 10 mg/kg*	
	LOD	LOQ	LOD	LOQ	Measured Concentration	Measured Concentration	Spike Recovery %	Measured Concentration	Spike Recovery %
Al 396.152	0.25	0.83	0.16	0.55	2.02	7.46	109	12.4	104
As 193.696	0.83	2.8	0.74	2.5	0.910	6.20	106	11.5	106
B 249.772	0.18	0.61	0.11	0.35	7.91	13.3	108	18.8	109
Ba 455.403	0.0093	0.031	0.018	0.060	0.0893	5.41	106	10.8	107
Be 234.861	0.0069	0.023	0.0068	0.023	0.0429	5.32	106	10.7	107
Ca 396.847	0.33	1.1	0.18	0.61	26.3	31.4	102	36.0	97
Cd 214.439	0.030	0.099	0.019	0.064	0.0381	5.00	99	9.91	99
Co 238.892	0.058	0.19	0.064	0.21	0.102	4.86	95	9.80	97
Cr 267.716	0.14	0.45	0.074	0.25	0.842	5.69	97	10.6	98
Cu 327.395	0.071	0.24	0.050	0.17	0.270	5.46	104	11.1	108
Fe 238.204	0.34	1.1	0.063	0.21	3.67	8.46	96	13.7	100
Ga 294.363	0.54	1.8	0.43	1.4	0.935	5.92	100	11.6	107
K 766.491**	5.0	17	0.089	0.30	381	435	106	487	106
Mg 279.553	0.033	0.11	0.035	0.12	2.05	6.92	97	11.7	97
Mn 257.610	0.011	0.036	0.019	0.063	0.119	4.92	96	9.74	96
Mo 202.032	0.16	0.54	0.13	0.43	0.174	5.26	102	10.4	102
Na 589.592**	4.3	14	1.1	3.5	413	464	102	509	96
Ni 231.604	0.10	0.35	0.10	0.34	0.730	5.32	92	10.0	93
Pb 220.353	0.62	2.1	0.46	1.5	< LOD	5.41	108	10.4	104
S 180.669	0.80	2.7	0.85	2.8	13.5	18.0	90	22.6	91
Sb 206.834	1.2	4.1	1.0	3.4	< LOD	5.31	106	10.4	104
Si 251.611	0.70	2.3	0.25	0.83	67.3	72.4	102	77.3	100
Sr 407.771	0.0039	0.013	0.056	0.19	0.228	5.29	101	10.4	102
Ti 336.122	0.024	0.081	0.033	0.11	< LOD	5.06	101	10.4	104
V 292.401	0.18	0.60	0.20	0.66	0.217	5.38	103	10.5	103
Zn 213.857	0.035	0.12	0.043	0.14	0.277	5.42	103	10.5	102
Zr 343.823	0.090	0.30	0.098	0.33	< LOD	5.06	101	10.2	102

* Spike concentrations, 5 and 10 mg/kg, are equivalent to 0.05 and 0.1 mg/L, respectively, of 1 g LiOH in 100 mL. ** Spike concentrations of K and Na were 10 times higher than other elements considering the dilution factor.

Long-term stability

To check the stability of the instrument and long-term validity of the calibration, 290 measurements were completed over 6.8 hours at an average rate of 84 s per sample, without recalibration. The sequence included 120 measurements of 1% LiOH and 120 of 1% Li_2CO_3, both spiked at 0.1 mg/L and 25 pairs of CCBs and CCVs (0.1 mg/L). 10 solutions of spiked 1% Li_2CO_3 alternated with 10 solutions of spiked 1% LiOH with a CCB and a CCV in between. More information on the analysis of Li_2CO_3 can be found in reference 16.

The concentrations of the 25 CCV measurements were normalized as percentage recoveries of the expected value (0.1 mg/L) and plotted against time (Figure 6). Accurate measurements within ±10% of the expected value (indicated by the dotted lines) were obtained, with %RSDs for all wavelengths below 3%, except for S 180.669 (3.5%) and Na 589.592 (4.3%). The precision of the 240 measurements of the spiked 1% LiOH and 1% Li_2CO_3 samples was excellent over 6.8 hours, with %RSDs below 5%, as shown in Table 5.
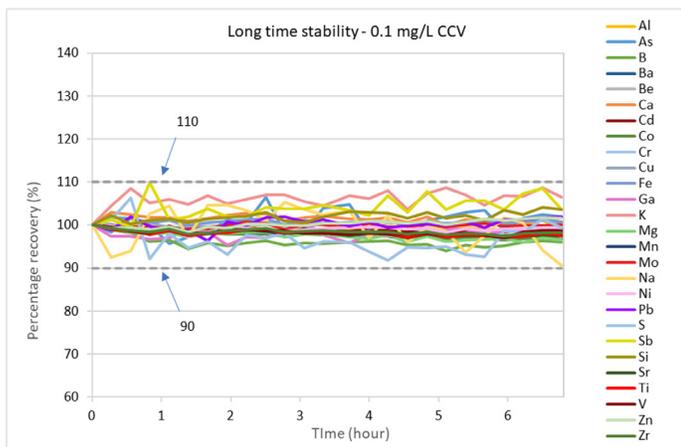
Figure 6. Long-term stability showing percentage recoveries of 0.1 mg/L CCV solution measured over 6.8-hours.

Table 5. Long-term stability of the Agilent 5800 ICP-OES over 6.8 h. %RSD of measurements of 1% LiOH and 1% Li_2CO_3 samples spiked at 0.1 mg/L.

Element and Wavelength (nm)	RSD %	Element and Wavelength (nm)	RSD %
Al 396.152	1.3	Mn 257.610	1.4
As 193.696	4.0	Mo 202.032	0.82
B 249.772	1.9	Na 589.592	4.5
Ba 455.403	1.6	Ni 231.604	1.0
Be 234.861	0.52	Pb 220.353	1.5
Ca 396.847	1.5	S 180.669	4.0
Cd 214.439	1.1	Sb 206.834	3.7
Co 238.892	1.3	Si 251.611	0.65
Cr 267.716	1.3	Sr 407.771	1.5
Cu 327.395	1.2	Ti 336.122	1.6
Fe 238.204	2.2	V 292.401	1.4
Ga 294.363	1.4	Zn 213.857	0.56
K 766.491	0.77	Zr 343.823	1.4
Mg 279.553	1.8		

Conclusion

The Agilent 5800 VDV ICP-OES was used to quantify 27 elemental impurities in a 98% pure LiOH solid, a raw material that is used as a precursor for the production of LIB cathodes. The benefits of the method included:

– The use of the integrated Agilent AVS 7 switching valve, which greatly improved the productivity of the method. It also significantly prolonged the lifetime of the torch, and reduced the maintenance effort, and running costs when analyzing high concentration Li samples.

– The IntelliQuant Screening function enabled quick and easy method development, assisting with selection of the best analyte lines to include in the quantitative method.

– The FBC and FACT background correction modes provided fast, easy, and accurate interference correction to ensure the accuracy of the quantitative measurements.

– The EMF feature enabled proactive maintenance tasks to be performed at the right time.

The high sensitivity of the 5800 ICP-OES method was demonstrated by detection limits of below 1 mg/kg for most elements. Recoveries of all 27 elements spiked at two concentrations in the sample solutions were between 90 and 110%, confirming the accuracy of the ICP-OES method. The instrument was stable over 6.8 h, as shown by %RSDs of <5% for all elements measured in a spiked sample solution and a CCV solution.

This work confirms the suitability of the 5800 VDV ICP-OES for the quality control of complex samples, which are representative of samples found at various stages of the LIB manufacturing process. The results have demonstrated the accuracy, precision, and stability of the method for the analysis of trace elements in LiOH and the low maintenance requirements of the 5800 ICP-OES with AVS 7.

References

1. Lithium compounds market size worth $26.7 billion by 2030: Grand View Research, Inc., accessed May 2023, https://www.prnewswire.com/news-releases/lithium-compounds-market-size-worth-26-7-billion-by-2030-grand-view-research-inc-301524689.html

2. Liu, H., and Azimi, G., Production of battery grade lithium hydroxide monohydrate using barium hydroxide causticizing agent, *Resources, Conservation & Recycling* 179, **2022**, 106115

3. Yudha, C. S., Synthesis of $LiNi_{0.85}Co_{0.14}Al_{0.01}O_2$ cathode material and its performance in an NCA/graphite full-battery. *Energies*, **2019**, 12, 1886

4. Lithium hydroxide demand to overtake carbonate: AABC, 2019, accessed May 2023, https://www.argusmedia.com/en/news/1836977-lithium-hydroxide-demand-to-overtake-carbonate-aabc

5. Barrera, P., Will Lithium Hydroxide Really Overtake Lithium Carbonate? 2019, accessed May 2023, https://investingnews.com/daily/resource-investing/battery-metals-investing/lithium-investing/will-lithium-hydroxide-overtake-lithium-carbonate/

6. GB/T 26008-2020, Battery grade lithium hydroxide monohydrate, 2020, National Standard, China

7. GB/T 11064.16-2013, Methods for chemical analysis of lithium carbonate, lithium hydroxide monohydrate, and lithium chloride. Part 16: Determination of the amounts of calcium, magnesium, copper, lead, zinc, nickel, manganese, cadmium, and aluminum, Inductively coupled plasma atomic emission spectrometry, 2013, National Standard, China

8. ISO/AWI 16423, Lithium hydroxide monohydrate—Determination of impurities—ICP-OES method

9. Morishige, Y., and Kimura, A., Ionization interference in inductively coupled plasma optical emission spectroscopy. *SEI Technical Review*, 66, **2008**, 106–111

10. Reduce Costs and Boost Productivity with the Advanced Valve System (AVS) 6 or 7 Port Switching Valve System, Agilent Publication, 5991-6863EN

11. Agilent ICP Expert Software Powerful software with smart tools for ICP-OES, Agilent publication, 5994-1517EN

12. Agilent IntelliQuant Software: For greater sample insight and simplified method development, Agilent publication, 5994-1516EN

13. Agilent IntelliQuant Screening: Smarter and quicker semiquantitative ICP-OES analysis, Agilent publication, 5994-1518EN

14. ICP-OES Background and Interference Removal Accurate. Easy. Reliable. Agilent publication, 5991-8452EN

15. Innovative Freeform Optical Design Improves ICP-OES Speed and Analytical Performance, Agilent publication, 5994-5891EN

16. Qi, Y., and Drvodelic, N., Determination of Elemental Impurities in Lithium Carbonate Using ICP-OES, Agilent publication, 5994-6112EN

Note: If the AVS 6/7 switching valve is bought for use with the Agilent 5800 VDV ICP-OES, ICP Expert Pro pack software is included. The software is needed to control the AVS 6/7 and to access IntelliQuant Screening—a useful tool for method development. The AVS 6/7 and ICP Expert Pro pack software are standard with the Agilent 5900 SVDV ICP-OES.

Agilent part numbers

Part number	Description
G8020-68005	Easy-fit fully demountable torch with 1.8 mm quartz injector for Agilent 5000 series ICP-OES
G8010-60263	Quartz outer tube set for semi- and fully-demountable torches for Agilent 5000 series VDV/SVDV ICP-OES
G8010-60256	Double-pass spray chamber, glass cyclonic design with ball joint socket and UniFit drain outlet, for Agilent 5000 series ICP-OES
G8010-60255	SeaSpray concentric glass nebulizer for Agilent 5000 series ICP-OES
G8010-60346	Nebulizer gas humidifier for 5000 Series ICP-OES
3710034400	Peristaltic pump tubing, white/white, 12/pk
3710027200	Peristaltic pump tubing, black/black, 12/pk
3710034600	Peristaltic pump tubing, blue/blue, 12/pk.
G8495-60000	Spare valve, 7 port, 2 position, for AVS 7 switching valve
G8495-60003	Stator and rotor, for 7-port valve, for AVS7 switching valve
G8010-60306	Autosampler connection kit for AVS switching valve
G8010-60300	Check valve outlet for AVS switching valve, non-metallic
G8010-60307	Internal standard connection kit, for AVS 7 switching valve
G8010-60304	Nebulizer connection kit for AVS switching valve
G8010-60308	Pump outlet connection kit, for AVS switching valve
G8010-60303	Sample inlet connection kit for AVS switching valve
G8010-60335	Sample/Rinse connection kit, for AVS switching valve, 2/pk
5190-8243	Agilent 1000 ppm single element stock solution for Al
5190-8249	Agilent 1000 ppm single element stock solution for Ba
5190-8328	Agilent 1000 ppm single element stock solution for Cd
5190-8347	Agilent 1000 ppm single element stock solution for Co
5190-8349	Agilent 1000 ppm single element stock solution for Cu
5190-8472	Agilent 1000 ppm single element stock solution for Fe
5190-8468	Agilent 1000 ppm single element stock solution for In
5190-8504	Agilent 1000 ppm single element stock solution for K
5190-8482	Agilent 1000 ppm single element stock solution for Mg
5190-8484	Agilent 1000 ppm single element stock solution for Mn
5190-8487	Agilent 1000 ppm single element stock solution for Mo
5190-8492	Agilent 1000 ppm single element stock solution for Ni
5190-8476	Agilent 1000 ppm single element stock solution for Pb
5190-8527	Agilent 1000 ppm single element stock solution for Sr
5190-8546	Agilent 1000 ppm single element stock solution for Ti
5190-8559	Agilent 1000 ppm single element stock solution for Zr
5190-8356	Agilent 10,000 ppm single element stock solution for As
5190-8365	Agilent 10,000 ppm single element stock solution for B

Part numbers continue on next page

Part numbers continued...

5190-8362	Agilent 10,000 ppm single element stock solution for Bi
5190-8360	Agilent 10,000 ppm single element stock solution for Be
5190-8369	Agilent 10,000 ppm single element stock solution for Ca
5190-8375	Agilent 10,000 ppm single element stock solution for Cr
5190-8389	Agilent 10,000 ppm single element stock solution for Ga
5190-8408	Agilent 10,000 ppm single element stock solution for Li
5190-8206	Agilent 10,000 ppm single element stock solution for Na
5190-8441	Agilent 10,000 ppm single element stock solution for Rb
5190-8210	Agilent 10,000 ppm single element stock solution for S
5190-8354	Agilent 10,000 ppm single element stock solution for Sb
5190-8451	Agilent 10,000 ppm single element stock solution for Si
5190-8229	Agilent 10,000 ppm single element stock solution for V
5190-8235	Agilent 10,000 ppm single element stock solution for Zn

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