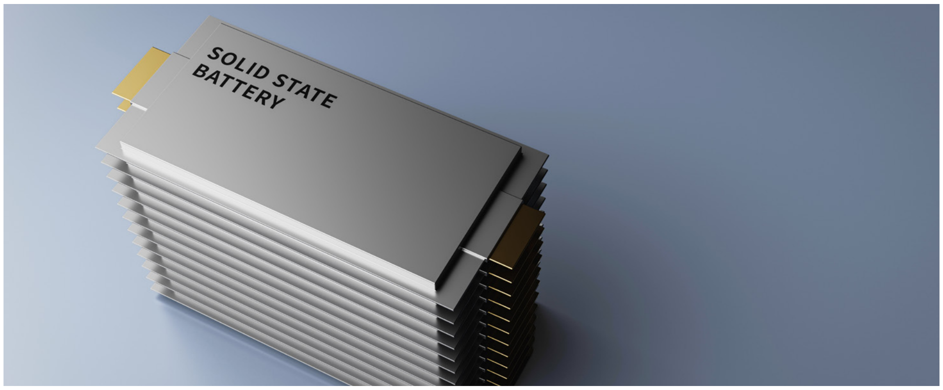
Agilent

Trusted Answers

Elemental Analysis of Solid Electrolyte Lithium Lanthanum Zirconate Tantalum Oxide by ICP-OES

Quantification of Li, La, Zr, and Ta in electrolyte for all-solid-state Li-ion batteries by Agilent 5800 ICP-OES



Author

Ping Zhang,
Agilent Technologies
(China) Co., Ltd

Introduction

The shift towards cleaner electric vehicle (EV) technology, combined with demands for longer driving ranges and faster charging times, is accelerating the need for higher-performance batteries. Likewise, large-scale energy storage systems, which are key components of flexible power grids, are becoming increasingly important for managing power peaks and smoothing fluctuations in renewable energy generation. Meeting the growing demand for clean energy technologies will require greater investment in energy storage batteries that are safe, durable, and cost-effective.

All-solid-state batteries (ASSBs)–which use solid electrolytes instead of conventional liquid ones–offer significant advantages over traditional lithium-ion batteries (LIBs). The stability and compatibility of solid electrolytes with specially developed cathode and anode materials ensure the safe performance of ASSBs. ASSBs are less prone to thermal runaway, which is a significant safety concern of traditional liquid-based LIBs.

They also have the potential to surpass the performance limitations of liquid electrolytes, offering higher energy density, faster charging rates, longer operational lifespans, and improved safety. Given these advantages, the demand for ASSBs in EVs and large-scale energy storage systems is increasing, positioning them as a central area of technological research and market development.

The solid-state electrolyte is a critical component of ASSBs, as it significantly affects the key performance metrics of the battery. So, the functionality and reliability of ASSBs depends on the physical and chemical properties of the solid electrolyte material. However, the presence of impurities, inclusions, or inhomogeneities in the electrolyte can undermine its performance. These structural or compositional inconsistencies may disrupt ionic conductivity, create localized mechanical stress, or even lead to failure pathways like dendrite formation. Therefore, achieving high-purity, homogenous solid electrolytes is necessary for realizing the full potential of ASSB technology.

The ceramic material Lithium Lanthanum Zirconate Tantalum Oxide (LLZTO) is being investigated as a solid electrolyte in LIBs.[1] Properties such as high-ionic conductivity, as well as excellent chemical and thermal stability, make LLZTO a promising candidate for enhancing the performance and safety of solid-state LIBs. Research and development (R&D) scientists are actively exploring dopant strategies to further enhance its formulation. However, challenges such as impurities, inclusions, and inhomogeneities in electrolytes still pose significant risks, potentially degrading performance or inducing failure mechanisms. To verify that the sample composition aligns to theoretical formulas, the matrix elements of LLZTO must be determined using a robust, reproducible, and accurate analytical technique such as inductively coupled plasma-optical emission spectroscopy (ICP-OES). The technique is especially useful for the simultaneous measurement of multiple elements in samples, due to its speed, stability, and tolerance to high total dissolved solids (TDS). Battery scientists also require methods to analyze the elemental composition of spent electrolytes to investigate changes that occur during charge and discharge cycles. These analyses support the production of consistent and reliable materials, helping to develop ASSBs.

Both the Agilent 5800 Vertical Dual View (VDV) and 5900 Synchronous Vertical Dual View (SVDV) ICP-OES instruments have been widely adopted across the LIB value chain to address the varied analytical needs of the industry.[2] The instruments are ideal for labs dealing with novel materials, samples with high lithium matrices, and multi-element analyses where speed, stability, and data accuracy are critical. The capabilities of Agilent ICP-OES instruments are beneficial in overcoming several challenges faced by battery researchers and manufacturers, as follows:

- **High lithium matrix:** Li-rich matrices typically contain high levels of TDS. Instruments such as the 5800 and 5900 that are capable of analyzing such concentrated Li samples over extended periods—without requiring frequent shutdowns and maintenance—offer a significant operational advantage.[3,4]
- **Unknown sample constituents:** Uncharacterized elements in the sample can lead to batch-to-batch variations. However, the screening capabilities of the 5800 or 5900 using IntelliQuant Screening allow visual review of sample composition without the need for exhaustive multi-element calibrations. IntelliQuant Screening enables quick screening and comparative analysis of samples, saving both time and resources.[5,6]
- **Instrumental drift:** Measurement drift over time introduces uncertainty and undermines confidence in temporal data comparisons. The 5800 and 5900 instruments which are engineered without moving optical components—eliminating alignment drift—provide superior long-term stability and reduce maintenance-related interruptions.[7]

In this study, the 5800 VDV ICP-OES was used to measure the four major elements, lithium (Li), lanthanum (La), zirconium (Zr), and tantalum (Ta), in a research sample of a Ta-doped LLZTO powder to verify its molar percentage composition.

Elemental characterization is critical throughout the entire development pipeline, from early R&D to pilot and full-scale manufacturing. Screening precursor materials before their incorporation into solid electrolyte formulations is a key part of process quality control at all production scales, helping to minimize troubleshooting, reduce failure rates, and lower cell-to-cell variability.

Analysts typically evaluate ICP-OES methods using a number of performance criteria to ensure reliability and suitability for their specific application. These include parameters such as linearity of the calibration, detection limits, accuracy, precision, robustness, and matrix tolerance. In this study, precision, short-term stability, molar percentage composition of major elements, and the long-term stability of the method were evaluated.

Experimental

Standard preparation

The following Agilent single element standards were used to create calibration standards across the analytical range: 1000 µg/mL of Li, La, Zr, and Ta. The standards were diluted using a 1% solution of nitric acid (HNO_3).

The Agilent single-element standard solutions were used to prepare five mixed-standard calibration solutions, as described in Table 1.

Table 1. Concentration points of the calibration curve for each element. Concentration units: mg/L.

Elements	Standard 1	Standard 2	Standard 3	Standard 4	Standard 5
Li	1	2	5	10	20
La	5	10	20	50	100
Zr	2	5	10	20	50
Ta	2	5	10	20	50

Sample preparation

The stoichiometric composition of LLZTO often varies between suppliers, as researchers continue to fine-tune elemental ratios to optimize performance. As a result of these compositional differences, multiple or tailored dissolution methods may be required to achieve complete digestion of the material. In this study, the sample was provided as a fine, uniform powder, so we employed a HNO_3 digestion method at ambient temperature for preparation.

To prepare LLZTO, approximately 0.2 g of the fine powder sample was accurately weighed and placed in a 50 mL centrifuge tube. Then, 8 mL of a 1:1 mixture of laboratory-grade HNO_3 and high-purity de-ionized (DI) water prepared by a Millipore Milli-Q ultrapure water system was added. The mixture was left to digest at ambient temperature until a clear, transparent solution without visible particles was obtained. Following digestion, the solution was diluted 10,000-fold with DI water to bring element concentrations into optimal working range of the ICP-OES and to match calibration conditions.

Instrumentation

The elemental analysis of the LLZTO electrolyte samples was performed using an Agilent 5800 VDV ICP-OES, equipped with the following hardware components:

- Proprietary Cool Cone Interface (CCI) technology: designed to minimize interferences, such as recombination and absorption caused by the cooler plasma tail.
- A high-precision thermostatted polychromator with no moving optical components: designed to provide excellent long-term stability and exceptional resolution.
- Vista Chip III detector: capable of processing speeds up to 1 MHz, allowing for simultaneous measurements of all wavelengths in less than half a second.

The 5800 was fitted with a SeaSpray nebulizer, a double-pass cyclonic spray chamber, and an Easy-fit one-piece torch with 1.8 mm id quartz injector torch. The instrument's SSRF system produced a robust plasma suitable for high-matrix samples, such as LLZTO electrolytes.

Agilent ICP Expert Pro software was used to control the 5800 ICP-OES, optimize and run the method, and to process the data. The software includes smart tools such as IntelliQuant Screening that help with the development of robust and reliable methods for analyzing precursor chemicals such as LLZTO. The software also includes easy-to-use automated algorithms for ICP-OES background correction including Fitted Background Correction (FBC). Background correction is commonly used in ICP-OES applications to minimize spectral interferences from other elements in the sample, which could otherwise skew analyte measurements. Analysts can also use the custom columns option within ICP Expert to report the quantitative results for Li, La, Zr, and Ta as molar percentages. The software applies formulas and conversions, providing additional reporting options for materials characterization.

Instrument operating conditions are given in Table 2.

Table 2. Agilent 5800 VDV ICP-OES operating conditions.

Parameter	Setting
Viewing Mode	Radial
Viewing Height (mm)	8
RF Power (kW)	1.30
Nebulizer Flow (L/min)	0.7
Plasma Flow (L/min)	15
Aux Flow (L/min)	1
Replicates	3
Read Time (s)	10
Stabilization Time (s)	15
Pump Speed (rpm)	12
Sample Pump Tubing	Black/black Solvaflex
Waste Pump Tubing	Grey/grey Solvaflex

Results and discussion

Calibration and automatic background correction

The four major elements (Li, La, Zr, and Ta) in LLZTO were quantified using an external standard calibration method, with background correction performed by the instrument's default and automatic FBC method. The FBC software routine corrects simple and complex background peaks automatically, requiring no input from the analyst, saving time and resources. Spectra, standard curves, and results of the linear regression analysis for each target element are shown in Figure 1.

As illustrated in Figure 1, the linear correlation coefficients for the calibration curves of all four elements exceed 0.9999, indicating excellent linearity within the established concentration ranges for each element.

Detection limits

Understanding the detection limits of the ICP-OES method is critical to ensuring that LLZTO samples are prepared at concentrations suitable for accurate measurement. Since the sample preparation involved a 10,000-fold dilution, it was essential to confirm that the concentrations of Li, La, Zr, and Ta in the final solution remained well above the method detection limits (MDLs). Ensuring that analyte concentrations are well above the detection limits supports accurate conversion to molar percentages for reliable formula verification.

Instrument detection limits (IDLs) were determined by measuring a sample preparation blank 11 times and applying the 3σ criterion (three times the standard deviation). The method blank underwent the same digestion and dilution procedure as the actual samples but contained no LLZTO material. MDLs were calculated by applying the 10,000-fold dilution factor to the IDLs. All elements were detected at concentrations well above their respective MDLs, confirming the suitability of the preparation and dilution approach for accurate quantification in LLZTO. The calculated IDLs and MDLs are summarized in Table 3.

The detection limits achieved for all four elements were sufficiently low for the accurate quantification of major elements in solid electrolyte precursor samples using the 5800 ICP-OES method.

Table 3. Analytical wavelengths and detection limits for the four target elements.

Elements and Wavelength (nm)	IDL (µg/L)	MDL (mg/kg)
Li 670.783	1.68	16.83
La 333.749	2.19	21.92
Zr 343.833	1.31	13.12
Ta 268.517	4.85	48.54

Quantitative data and precision

The LLZTO sample solutions were measured 12 times consecutively by the 5800 ICP-OES to assess the precision of the method and to evaluate the short-term stability of the instrument. No internal standard correction was applied.

Molar percentage is the preferred method for reporting the elemental composition of materials with known crystal structures, such as LLZTO. To enable this, the custom column editing window in ICP Expert was used to convert the quantitative data into molar percentages, simplifying data analysis (Figure 2).

Based on solution measurements, the concentrations of Li, La, Zr, and Ta in the solid sample were calculated to be approximately 5.5, 48, 16, and 10.4%, by weight (wt%), respectively. These weight percentages were then automatically converted to molar percentages by the software, as shown in Table 4.

This experimental data enables verification of whether the sample composition aligns with the theoretical formula of $Li_{(7)}La_{(3)}Zr_{(2)}O_{(12)}$. For the Ta-doped sample, represented as $Li_{(7)}La_{(3)}Zr_{(1.6)}Ta_{(0.4)}$, the combined amount of Zr and Ta should equal two.

When normalized to 100%, the molar percentage values reported in Table 4 aligned closely with the theoretical formula for LLZTO. The relative standard deviation (RSD) for the 12 measurements was ≤ 0.16% and the molar percentage range (the difference between the maximum and minimum values) for Li, La, Zr, and Ta was less than 0.06% (Table 4). The excellent precision and short-term stability of the method minimized the molar percentage error for the matrix elements.

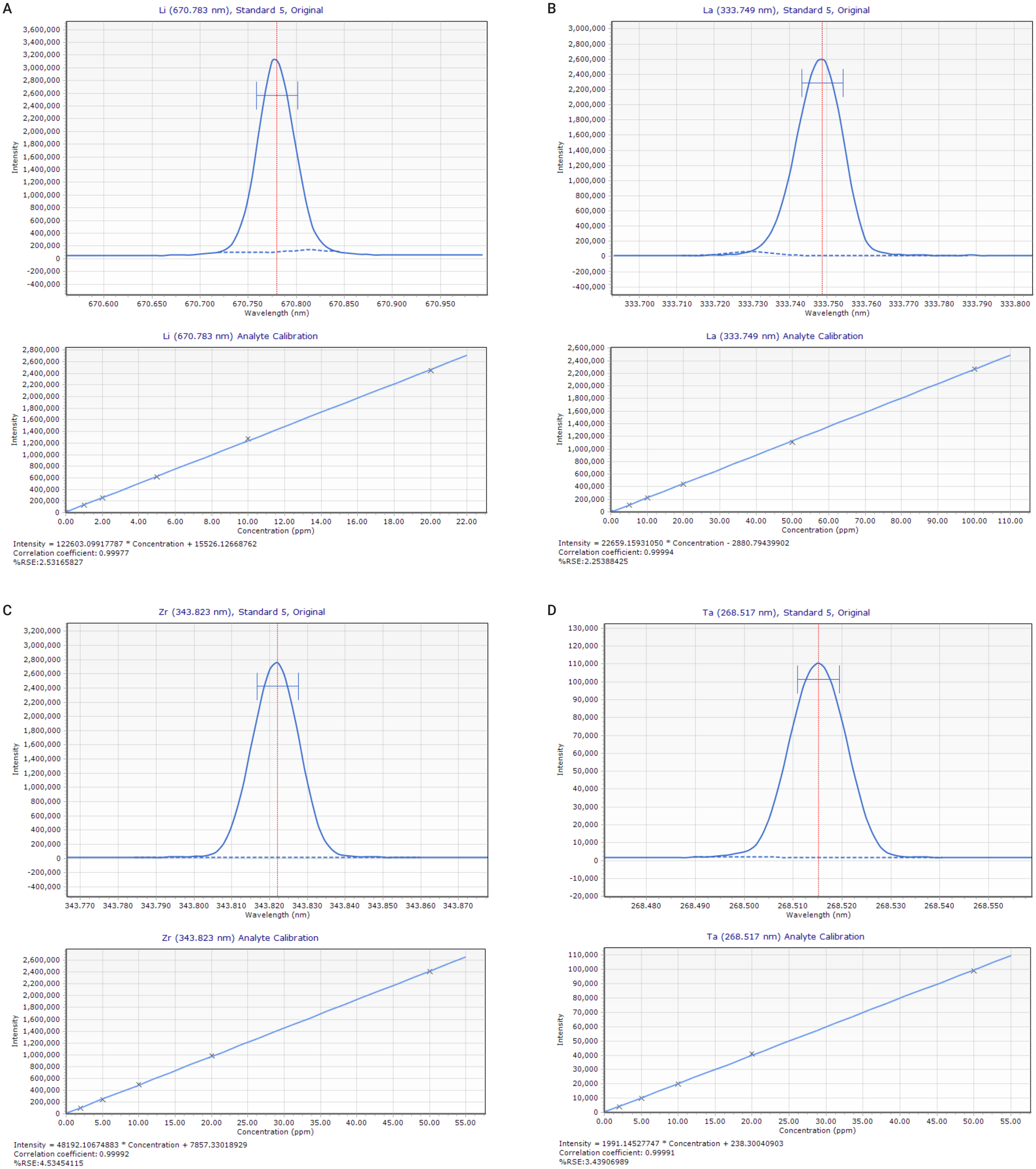
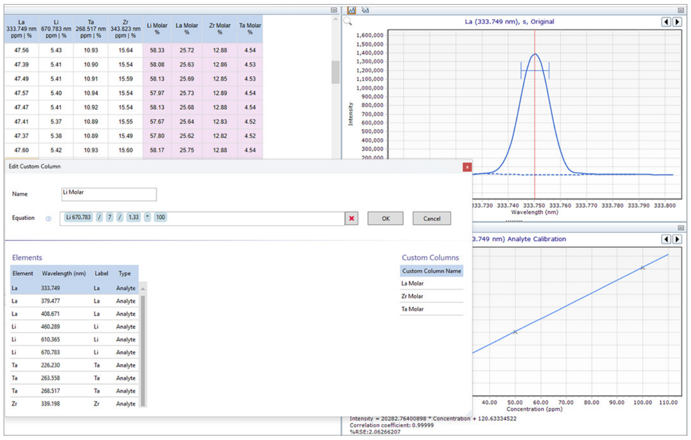


Figure 1. A to D: FBC-corrected spectra and standard curves for Li, La, Zr, and Ta, respectively.



La 333.749 nm ppm | %	Li 670.783 nm ppm | %	Ta 268.517 nm ppm | %	Zr 343.823 nm ppm | %	Li Molar %	La Molar %	Zr Molar %	Ta Molar %
47.56	5.43	10.93	15.64	58.33	25.72	12.88	4.54
47.39	5.41	10.90	15.54	58.08	25.63	12.86	4.53
47.49	5.41	10.91	15.59	58.13	25.69	12.85	4.53
47.57	5.40	10.94	15.54	57.97	25.73	12.89	4.54
47.47	5.41	10.92	15.54	58.13	25.68	12.88	4.54
47.41	5.37	10.89	15.55	57.67	25.64	12.83	4.52
47.37	5.38	10.89	15.49	57.80	25.62	12.82	4.52
47.60	5.42	10.93	15.60	58.17	25.75	12.88	4.54

Edit Custom Column

Name: Li Molar

Equation: Li 670.783 / 7 / 1.33 * 100

Elements

Element	Wavelength (nm)	Label	Type
La	333.749	La	Analyte
La	379.477	La	Analyte
La	408.671	La	Analyte
Li	460.289	Li	Analyte
Li	610.365	Li	Analyte
Li	670.783	Li	Analyte
Ta	226.230	Ta	Analyte
Ta	263.558	Ta	Analyte
Ta	268.517	Ta	Analyte
Zr	339.198	Zr	Analyte

Custom Columns

Custom Column Name
La Molar
Zr Molar
Ta Molar

Intensity = 20282.76400898 * Concentration + 120.63334522
Correlation coefficient: 0.99999
%RSE:2.06266207

Figure 2. Using the custom column editing window in Agilent ICP Expert to convert quantitative results for La, Li, Ta, and Zr into molar percentages. The conversion is useful for reporting purposes.

Table 4. Precision data from 12 analyses of the LLZTO sample by the Agilent 5800 VDV ICP-OES.

Measurement	Li Molar Percentage (%)	La Molar Percentage (%)	Zr Molar Percentage (%)	Ta Molar Percentage (%)
1	57.42	25.39	12.72	4.47
2	57.43	25.40	12.70	4.47
3	57.41	25.42	12.70	4.47
4	57.43	25.39	12.70	4.48
5	57.38	25.43	12.71	4.48
6	57.41	25.42	12.69	4.48
7	57.39	25.41	12.73	4.48
8	57.40	25.41	12.72	4.47
9	57.43	25.39	12.71	4.47
10	57.44	25.40	12.69	4.47
11	57.40	25.41	12.72	4.48
12	57.39	25.41	12.71	4.49
Average	57.41	25.41	12.71	4.48
Standard Deviation	0.0185	0.0125	0.0121	0.0064
RSD (%)	0.032	0.049	0.095	0.143

Long-term stability

The robustness of the 5800 method was evaluated by analyzing the LLZTO sample solutions every 10 minutes over four hours. As seen in Figure 3, in the absence of internal standard correction (in accordance with many Chinese LIB-related standard methods), recoveries of Li, La, Zr, and Ta were all between 98.28 and 101.97%. The average RSD was ≤ 0.97%, indicating excellent precision of the 145 measurements due to the instrument's stability over a four hour period.

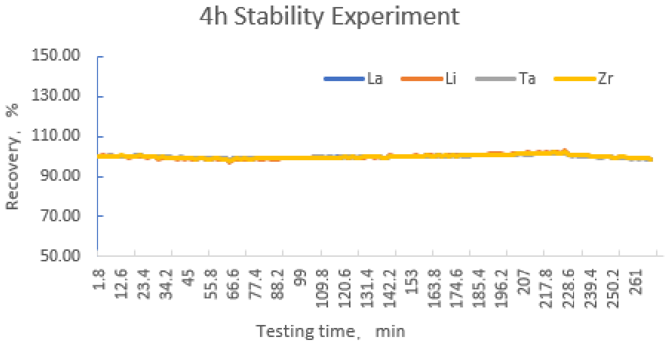


Figure 3. Results of a four-hour stability test for the quantitative measurement of Li, La, Zr, and Ta in LLZTO sample solutions that were measured 145 times during the sequence.

Fast elemental screening for full sample insights

IntelliQuant Screening is a unique and powerful tool that enables rapid full-element scanning of different matrix samples, providing an overview of the sample's elemental composition and their relative abundances. A pie-chart view of the semiquantitative data acquired for an LLZTO sample is presented in Figure 4, showing percentage level concentrations of Li, La, Zr, and Ta in the original sample. While the concentration obtained for Li and Zr appear to be overestimated compared to the quantitative results, the IntelliQuant method provided closer estimates for La and Ta. Despite these differences, the results still offer a useful approximation of the elemental composition, supporting InteliQuant's role as a rapid screening tool to guide further quantitative analysis. IntelliQuant can create and apply a custom calibration tailored to specific sample matrices, based on the standards prepared for the quantitative method, thereby enhancing the accuracy of the semiquantitative results.

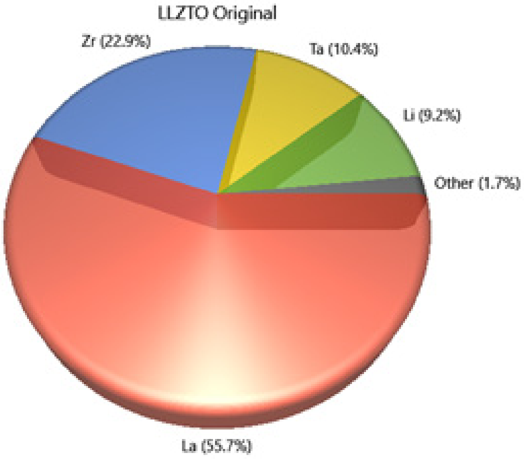


Figure 4. Pie chart presentation of the semiquantitative data of an LLZTO sample acquired using IntelliQuant Screening.

Conclusion

The Agilent 5800 VDV ICP-OES in radial view mode was used for the quantitative analysis of Li, La, Zr, and Ta in an LLZTO sample, an all-solid-state precursor electrolyte material used in next generation lithium-ion batteries. Excellent calibration linearity (R> 0.9999) and method detection limits ranging between 13.12 and 48.54 mg/kg were achieved for the four elements. The Agilent ICP Expert software was used to convert the quantitative results for Li, La, Zr, and Ta from mg/kg to molar percentages, facilitating direct comparison to theoretical stoichiometry.

The 5800 ICP-OES method successfully addressed several analytical challenges presented by the application, making it suitable for both R&D and future-proofing applications in mainstream production, including the production of materials from spent batteries.

- **Complex sample matrices:** The 5800 instrument's robust vertical plasma, SSRF generator, and Cooled Cone Interface effectively handled the high concentration of Li, La, Zr, and Ta in the sample matrix, overcoming concerns regarding high-levels of TDS.
- **Identifying unknown sample constituents:** IntelliQuant Screening provided a comprehensive view of both quantified and non-quantified elements in the samples, complementing the quantitative analysis in establishing the stoichiometric composition of LLZTO. IntelliQuant Screening also facilitated rapid comparative assessment of the elemental profiles of samples based on relative abundances, with user-friendly data visualization options such as pie charts.
- **Instrumental stability:** The 5800 instrument's exceptional stability—enabled by a design that eliminates moving optical components and diffraction gratings—was demonstrated by excellent recoveries of Li, La, Zr, and Ta over four hours during 145 measurements of LLZTO samples.

The 5800 VDV ICP-OES method supports fundamental research and QA/QC by ensuring the consistent and accurate composition of synthesized electrolytes. The consistency of LIB-electrolyte materials is important to meet desired performance targets, enhance safety, and extend the longevity of solid-state batteries.

References

1. Liu, L.; Zhang, D.; Xu, X.; Liu, Z.; Liu, J. Challenges and Development of Composite Solid Electrolytes for All-solid-state Lithium Batteries, *Chem. Res. Chin. Univ.*, 37, **2021**, 210–231
2. A Practical Guide to Elemental Analysis of Lithium-Ion Battery Materials Using ICP-OES, Agilent publication, 5994-5489EN
3. Gagnon, M-A., Elemental Analysis of Brine Samples used for Lithium Extraction, Agilent publication, 5994-5149EN
4. Garcia-Gonzalez, A. ICP-OES Quality Control of Elements in Brines Produced by Direct Lithium Extraction (DLE), Agilent publication, 5994-8041EN
5. Agilent IntelliQuant Screening: Smarter and quicker semiquantitative ICP-OES analysis, Agilent publication, 5994-1518EN
6. Agilent IntelliQuant Software: For greater sample insight and simplified method development, Agilent publication, 5994-1516EN
7. Innovative Freeform Optical Design Improves ICP-OES Speed and Analytical Performance, Agilent publication, 5994-5891EN

Products used in this application

Agilent products

Lithium (Li) standard, 1,000 µg/mL in 5% HNO_3, 100 mL ↗

Lanthanum (La) standard, 1,000 µg/mL in 5% HNO_3, 100 mL ↗

Zirconium (Zr) standard, 1,000 µg/mL in 5% HCl, 100 mL ↗

Tantalum (Ta) standard, 1,000 µg/mL in 2% HF, 100 mL ↗

Easy-fit one piece torch, 1.8 mm id quartz injector ↗

www.agilent.com/chem/5800icpoes

DE-006628

Published in the USA, July 08, 2025
5994-8403EN

Agilent
Trusted Answers