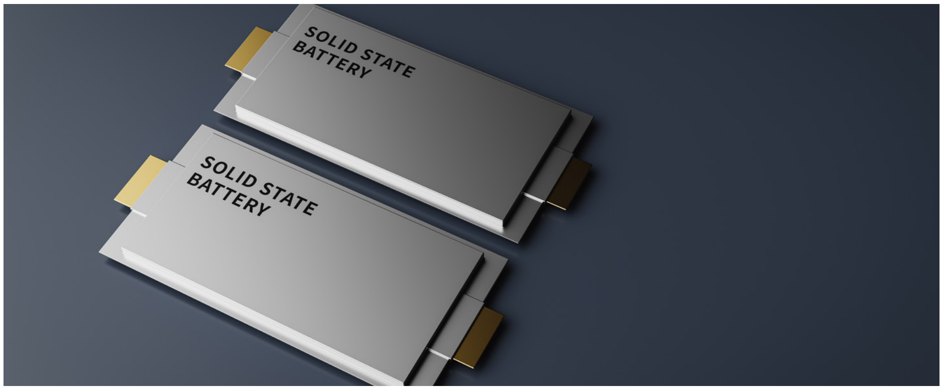
Multi-Elemental Analysis of Lithium Aluminum Titanium Phosphate by Automated ICP-OES

Assay of all-solid-state Li-ion battery electrolytes by Agilent 5800 ICP-OES with ADS 2 autodilutor



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Introduction

Rising global electricity demand and the shift away from fossil fuels are driving developments in the cleaner energy and energy storage sectors. Among the emerging energy storage technologies, all-solid-state batteries (ASSBs) are attracting attention due to their enhanced safety, higher energy density, and improved performance relative to conventional lithium-ion batteries (LIBs). Current research is largely focused on optimizing the electrolyte composition of ASSBs, which use a solid electrolyte in place of the liquid or gel electrolyte found in conventional LIBs.

Various properties of lithium aluminum titanium phosphate (LATP) make it suitable as a solid electrolyte material for use in ASSBs.[1] It has high ionic conductivity (reaching 10^{-4} to 10^{-3} S/cm at room temperature, close to or exceeding some liquid electrolytes), which improves battery charging and discharging efficiency.

Compared to sulfide-based solid electrolytes, LATP is more chemically stable in air and water, minimizing the requirement for an inert atmosphere during processing. This property simplifies manufacturing and reduces costs of storage and transportation. LATP is compatible with high-potential (5 V) cathode materials such as $LiNiCoMnO_2$ (NMC), improving cell energy density. It also offers excellent mechanical strength and ease of processing, allowing it to be shaped into thin films that support miniaturization and robust battery design. The accurate determination of major, doping, and trace elements in materials such as LATP is important at all stages of development, from R&D to pilot-scale production and full-scale manufacturing. The ratio of major elements to doping elements significantly affects the ionic conductivity and stability of lithium (Li) ions, while trace impurities can compromise stability and mechanical strength. Elemental impurities can accumulate during battery charging/discharging cycles, leading to battery performance degradation, such as shortened cycle life, reduced efficiency, or potential safety risks. Multi-elemental analysis of battery precursors like LATP is therefore vital for ensuring the overall quality of ASSBs.[2]

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, promoting technological advancement and enabling the industrial implementation of ASSBs.

Inductively coupled plasma-optical emission spectroscopy (ICP-OES) is widely used for the simultaneous measurement of multiple elements in complex samples, due to its speed, stability, and tolerance to high total dissolved solids (TDS). Samples with elevated concentrations of matrix elements are classified as high TDS. These samples can pose several analytical challenges for ICP-OES, including spectral interferences from overlapping emission lines, plasma instability, signal drift, and increased maintenance. However, these challenges can be managed or avoided using field-proven instrumentation. The Agilent 5800 Vertical Dual View (VDV) and 5900 Synchronous Vertical Dual View (SVDV) ICP-OES instruments have seen widespread adoption throughout the LIB value chain, effectively addressing the diverse analytical requirements of the industry.[3]

In a recent study, the 5800 VDV ICP-OES was used for the quantitative analysis of the matrix elements in a Lithium Lanthanum Zirconate Tantalum sample, another all-solid-state electrolyte material.[4] The 5800, which uses a robust vertical torch, SSRF generator, Cooled Cone Interface, and is engineered without moving optical components, ensured excellent stability and no maintenance-related interruptions during the analysis.[5]

The same instrument was used in this study. However, to improve the productivity of the analysis, the 5800 ICP-OES with integrated Advanced Valve System (AVS 7) was used with the Agilent Advanced Dilution System (ADS 2). This Agilent ICP-OES automated system,[6] which is fully controlled by the Agilent ICP Expert Pro software,[7] significantly improves workflow efficiencies and frees analysts from various manual tasks by performing the following tasks:

- Autocalibration: Fully automated calibration from one or more stock solutions. Autocalibration reduces time spent on standard preparation, mitigates the risk of errors, and minimizes chemical and consumable waste, including single-use plastics.
- Prescriptive dilution up to 400 times: Automatic dilution of solutions or samples by a known (prescribed) dilution factor before analysis. This function is important for high TDS samples like LATP.
- Reactive dilutions up to 400 times: Automatic dilutions are triggered when a sample's concentration exceeds the calibration range (overrange) or when internal standard (IS) recovery falls outside acceptable limits.

To further simplify the analysis and help analysts achieve accurate, reproducible results, analysts can use the following tools that are available in the software:

- IntelliQuant Screening, a fast, full-spectral scan routine that provides semiquantitative results for up to 70 elements, providing a comprehensive overview of the sample's elemental composition.[8]
- Wavelength star rating system, a valuable function within IntelliQuant Screening that helps users identify the best wavelength to use for accurate quantitation by flagging any potential spectral interferences.
- Early Maintenance Feedback (EMF), a series of counters and sensors that prompt analysts to perform maintenance based on instrument usage rather than simple time-based routines. EMF helps prevent instrument downtime caused by unnecessary maintenance.
- Fitted background correction (FBC), a default function that provides automatic correction of simple and complex background structures. FBC simplifies background correction without requiring extensive knowledge—or prior investigation—of the sample matrix.[9]

This application note introduces a method for simultaneously determining four major elements (Li, Al, Ti, P) and 16 trace elements (Ba, Cd, Co, Cr, Cu, Fe, Hf, Mg, Mn, Na, Nb, Ni, Pb, Pt, Sr, Zn) in LATP solid-state electrolyte samples. To ensure the method's suitability for the application, it was evaluated in terms of linearity, detection limits (sensitivity), spike recoveries (accuracy), and stability (temporal precision and robustness).

Experimental

Standard preparation

High-purity deionized water (DI, 18.2 MΩ·cm) was prepared using a Millipore water system. Electronic grade nitric acid (HNO_3), hydrochloric acid (HCl), and hydrofluoric acid (HF) were bought from Anpu Company (China). Agilent standards were used to prepare the calibration standards. Single element standards of Li , Al , Ti , and P at 1000 µg/mL were used for the major elements. Multi-element Quality Control Standard (QC27) including Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sr, V, and Zn at 100 µg/mL, as well as single standards of Hf, Nb, and Pt at 1000 µg/mL were used for the trace elements. The major elements Al and Li were diluted to 100 mg/L, and the trace elements were diluted to 10 mg/L using 2% HNO_3. These two stock solutions were used by the ADS 2 to create calibration standards across the analytical working range.

Sample preparation

Two LATP samples—originating from different production batches—were supplied as white powders by an R&D group located in China.

A 0.1000 g portion of the LATP sample was weighed into a digestion vessel. Then, 6 mL of freshly prepared aqua regia (1:3 v/v of concentrated HNO_3 and HCl) and 4 mL of HF were added. The sample was digested in a microwave digester (Anton Paar) according to the temperature ramping program listed in Table 1. The digested solution was heated on a hot plate at 125 °C to evaporate any residual acid, then transferred to a 50 mL centrifuge tube, diluted to 25 mL with ultrapure water, ready for analysis by ICP-OES. A method blank was prepared using identical reagents and conditions, without the addition of the LATP sample. Spiked samples were prepared by adding a known spike volume before digestion.

Table 1. Microwave digestion temperature ramping program.

Parameter	Setting
Maximum Power (W)	1800
Set Temperature (°C)	220
Ramp Time (min)	10
Hold Time (min)	30

Instrumentation

The Agilent ICP-OES Automation System was used for the analysis of the LATP sample digests (Figure 1). The Agilent 5800 VDV ICP-OES was equipped with a MiraMist nebulizer, inert spray chamber, and a fully demountable torch assembly with a 1.8 mm id injector. The Agilent ADS 2 in-line autodilutor was used for the automatic preparation of calibration standards and autodilution of samples. Details of the operation and capabilities of the ADS 2 can be found elsewhere.[10] Following preparation, the standards and samples were delivered to the ICP-OES by the Agilent SPS 4 autosampler.

Figure 1. Agilent ICP-OES Automation System comprising an Agilent 5800 VDV ICP-OES with AVS 7 high-speed injection valve system, ADS 2 autodilution system, and SPS 4 autosampler—all fully controlled by Agilent ICP Expert Pro software (version 7.7).[6]

The "AVS/ADS Timing Monitor" function in ICP Expert Pro software tracks elemental signal changes in real time across the entire method sequence, as shown in Figure 2. Monitoring the signal at each step can help optimize settings, such as the stabilization time and the AVS 7 parameters, significantly improving the accuracy and reliability of the analysis.[10]

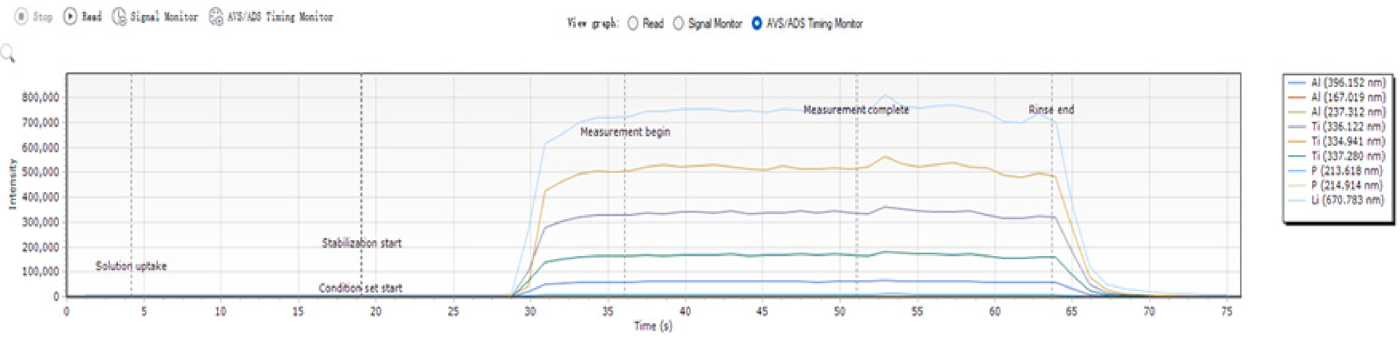


Figure 2. AVS/ADS Timing Monitor function in Agilent ICP Expert Pro software used to check or further optimize method conditions.

The optimized instrument parameters are shown in Table 2.

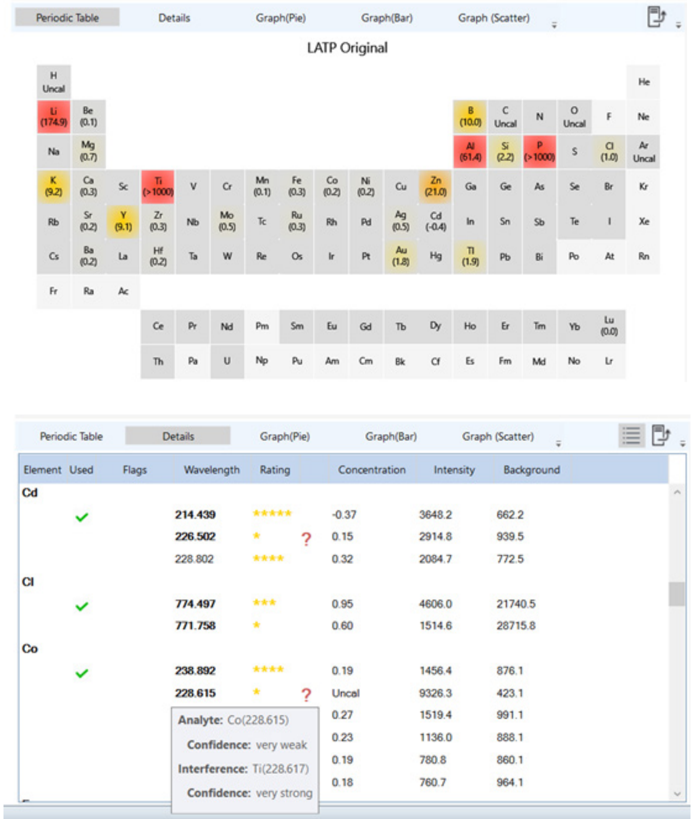
Table 2. Agilent 5800 VDV ICP-OES, AVS 7, and ADS 2 operating parameters.

ICP-OES Parameters	Setting
Viewing Mode	Radial
Viewing Height (mm)	8
RF Power (kW)	1.3
Plasma Gas Flow (L/min)	14
Nebulizer Gas Flow (L/min)	0.85
Auxiliary Gas Flow (L/min)	1.0
Stabilization Time (s)	8
Read Time (s)	8
AVS 7 and ADS 2 Parameters	**Setting**
Sample Loop Size (mL)*	1
Pump Flow - Uptake (mL/min)	33.5
Pump Flow - Inject (mL/min)	6.7
Valve Uptake Delay (s)	10.2
Bubble Injection Time (s)	1.8
Preemptive-Rinse Time (s)	1.4

**Both the AVS 7 and ADS 2 loops are the same size.*

Selection of wavelengths and calibration concentration ranges

IntelliQuant Screening identifies which elements are present in a sample and provides a semiquantiative concentration result for each element—valuable information for determining calibration standard ranges for analytes. The IntelliQuant algorithm also identifies any spectral interferences on analytes, enabling it to recommend interference-free wavelengths using a star rating system. Selecting the best wavelength for the quantitative method improves data accuracy. As shown in Figure 3, the IntelliQuant semiquantitative data for LATP can be displayed using clear graphics. The element wavelengths and calibration concentration points used in the quantitative method are shown in Table 3.



LATP Original

H Uncal																	He
Li (174.9)	Be (0.1)											B (10.0)	C Uncal	N	O Uncal	F	Ne
Na	Mg (0.7)											Al (61.4)	Si (2.2)	P (>1000)	S	Cl (1.0)	Ar Uncal
K (9.2)	Ca (0.3)	Sc	Ti (>1000)	V	Cr	Mn (0.1)	Fe (0.3)	Co (0.2)	Ni (0.2)	Cu	Zn (21.0)	Ga	Ge	As	Se	Br	Kr
Rb	Sr (0.2)	Y (9.1)	Zr (0.3)	Nb	Mo (0.5)	Tc	Ru (0.3)	Rh	Pd	Ag (0.5)	Cd (-0.4)	In	Sn	Sb	Te	I	Xe
Cs	Ba (0.2)	La	Hf (0.2)	Ta	W	Re	Os	Ir	Pt	Au (1.8)	Hg	Tl (1.9)	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu (0.0)	
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

Element	Used	Flags	Wavelength	Rating		Concentration	Intensity	Background
Cd								
	✓		**214.439**	★★★★★		-0.37	3648.2	662.2
			226.502	★	?	0.15	2914.8	939.5
			228.802	★★★★		0.32	2084.7	772.5
Cl								
	✓		**774.497**	★★★		0.95	4606.0	21740.5
			771.758	★		0.60	1514.6	28715.8
Co								
	✓		**238.892**	★★★★		0.19	1456.4	876.1
			228.615	★	?	Uncal	9326.3	423.1
						0.27	1519.4	991.1
						0.23	1136.0	888.1
						0.19	780.8	860.1
						0.18	760.7	964.1

Analyte: Co(228.615)
Confidence: very weak
Interference: Ti(228.617)
Confidence: very strong

Figure 3. IntelliQuant periodic table heat map display of the semiquantitative data (ppm) obtained for LATP (top) and star-rating wavelength recommendations for analytes, using Cd and Co as examples (bottom).

Results and discussion

Calibration curves and linear regression

Calibration curves for the major and trace elements were prepared from two stock solutions using the autocalibration feature of the ADS 2. Under full control of the ICP Expert Pro software, the ADS 2 diluted the stock solutions at specific dilution factors to create the calibration curves. Autocalibration allowed for the preparation of standards and calibration curves in less than four minutes, compared to 12 min using conventional manual methods. This significant streamlining of the calibration process enhanced the overall efficiency of the analytical workflow. The correlation coefficients of the calibration curves for all 20 analytes exceeded 0.999, as shown in Table 3, indicating excellent linearity across the concentration ranges.

Table 3. Recommended wavelengths and linear ranges for target elements.

Element	Recommended Wavelength (nm)	Background Correction	Linear Range (mg/L)	Linear Correlation Coefficient
Al	396.152	Fitted	1–5	0.99988
Ba	455.403	Fitted	0.1–0.5	0.99987
Cd	228.802	Fitted	0.1–0.5	0.99995
Co	238.892	Fitted	0.1–0.5	0.99992
Cr	205.560	Fitted	0.1–0.5	0.99995
Cu	324.754	Fitted	0.1–0.5	0.99988
Fe	238.204	Fitted	0.1–0.5	0.99996
Hf	277.184	Fitted	0.1–0.5	0.99986
Li	670.783	Fitted	1–5	0.99990
Mg	279.553	Fitted	0.1–0.5	0.99989
Mn	257.610	Fitted	0.1–0.5	0.99994
Na	589.592	Fitted	0.1–0.5	0.99983
Nb	309.417	Fitted	0.1–0.5	0.99994
Ni	231.604	Fitted	0.1–0.5	0.99998
P	213.618	Fitted	10–60	0.99998
Pb	220.353	Fitted	0.1–0.5	0.99993
Pt	214.424	Fitted	0.1–0.5	0.99990
Sr	407.771	Fitted	0.1–0.5	0.99997
Ti	336.122	Fitted	10–50	0.99998
Zn	213.857	Fitted	0.1–0.5	0.99994

Detection limits

Method detection limits (MDLs) 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 LATP material. MDLs were calculated by applying the dilution factor to the IDLs (Table 4).

Sample analysis

The LATP sample digests were analyzed by the 5800 ICP-OES. As shown in Table 4, only Fe, Mg, Na, as well as Li, Al, Ti, and P were detected above the MDL. Since the concentration of the three impurity elements exceeded the upper limit of their respective calibration curves, the ADS 2 system automatically determined and applied an appropriate dilution factor. This approach enabled the simultaneous measurement of major and trace elements within a single method.

Spike recoveries

To validate the feasibility of the quantitative method for the determination of trace elements in LATP, spike recovery experiments were conducted at 0.2 mg/L (1.0 mg/L for Mg). As shown in Table 4, the recovery rates of the 16 trace elements ranged from 91.0 to 103.7%, confirming the accuracy of the method.

Method stability

The method's stability was evaluated by analyzing LATP sample digests over two consecutive hours. The matrix elements (Li, Al, Ti, and P) were measured every 10 minutes. As shown in Figure 4, the measured values of the major elements remained consistent over time, with relative standard deviations (RSDs) below 1%. The results demonstrate the robustness of the 5800 VDV ICP-OES for the analysis of LATP.

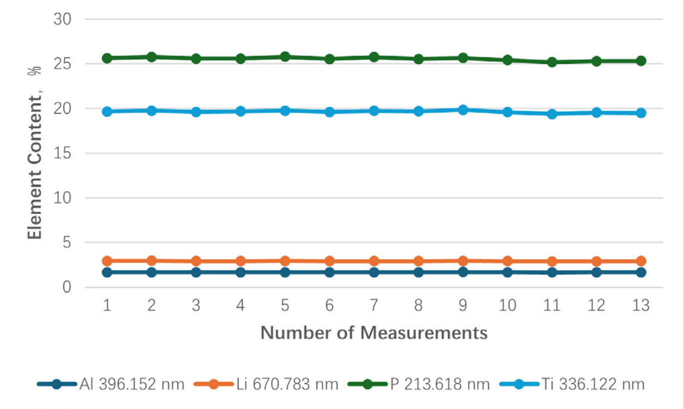


Figure 4. Analytical stability of actual LATP samples over two hours.

Table 4. Detection limits, quantitative data for LATP (average of three measurements and corrected for the dilution factor), and spike recovery rates.

Element	Method Detection Limit (µg/L)	Method Detection Limit (mg/kg)	Quantitative Measurement (mg/kg)	Spike Concentration (mg/L)	Spiked Sample Conc (mg/L)	Spike Recovery (%)
Ba	0.06	0.02	<MDL	0.2	0.191	95.5
Cd	0.5	0.13	<MDL	0.2	0.182	91.0
Co	2.0	0.50	<MDL	0.2	0.197	98.5
Cr	1.1	0.28	<MDL	0.2	0.19	95.0
Cu	1.6	0.40	<MDL	0.2	0.193	96.5
Fe	1.5	0.38	22.50	0.2	0.285	97.5
Hf	3.1	0.78	<MDL	0.2	0.19	95.0
Mg	0.04	0.01	252.5	1.0	2.02	101.5
Mn	0.17	0.04	<MDL	0.2	0.196	98.0
Na	3.8	0.95	42.00	0.2	0.383	107.5
Nb	3.3	0.83	<MDL	0.2	0.182	91.0
Ni	3.2	0.80	<MDL	0.2	0.196	98.0
Pb	8.5	2.13	<MDL	0.2	0.191	95.5
Pt	6.2	1.55	<MDL	0.2	0.191	95.5
Sr	0.06	0.02	<MDL	0.2	0.187	93.5
Zn	0.71	0.18	<MDL	0.2	0.184	92.0
Li	1.0	0.25	2.90%			
Al	2.9	0.72	1.67%			
Ti	0.5	0.12	19.6%			
P	6.3	1.57	25.5%			

Conclusion

A highly automated ICP-OES method was developed for the simultaneous measurement of four major elements and 16 minor and trace elements in lithium aluminum titanium phosphate (LATP) solid electrolyte samples. The samples were acid digested using microwave-assisted digestion and then analyzed using an Agilent ICP-OES Automation System. The automated system comprised an Agilent 5800 VDV ICP-OES with integrated AVS 7 switching valve coupled to an ADS 2 intelligent dilution system, all controlled by Agilent ICP Expert Pro software.

The ADS 2 automatically prepared the calibration standards from two stock solutions, accelerating the preparation process, reducing analyst workload, and minimizing labware usage. Calibration curves with correlation coefficients above 0.999 for all elements were autogenerated.

MDLs below 1 mg/kg were achieved for most of the trace elements in the sample. Recoveries of all 16 trace elements spiked at both 0.2 mg/L (1.0 mg/L for Mg) were between 91 and 107%, confirming the accuracy of the method. The instrument displayed excellent stability during the analysis of the four matrix elements in the actual LATP samples over two hours, with data fluctuation below 1%.

The automated quantitative ICP-OES method supports R&D and QA/QC by detecting impurities like Fe, Mg, and Na, while also measuring Li, Al, Ti, and P in the same run. Ensuring the quality of LIB-electrolyte materials is important to meet desired performance targets, enhance safety, and extend the longevity of solid-state batteries.

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Products used in this application

Agilent products

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

Aluminum (Al) standard, 1,000 µg/mL in 5% HNO_3

Titanium (Ti) standard, 1,000 µg/mL in H_2O

Phosphorus (P) standard, 1,000 µg/mL in 5% HNO_3

Multi-element Quality Control standard (QC27)

Platinum (Pt) standard, 1,000 µg/mL in 20% HCl

Hafnium (Hf) standard, 1,000 µg/mL in 5% HCl

Niobium (Nb) standard, 1,000 µg/mL in 2% HF

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