

Challenge
Sensitive analysis of trace elements and precise determination of major elements in digests of lithium ore samples.

Solution
High-resolution ICP-OES with its DualView PLUS option provides an extended linear dynamic range from sub-ppb level to %-range.

Intended audience
Mining companies or exploration firms that are interested in determining the lithium content of their ore samples for commercial purposes.

Analysis of lithium ore with HR ICP-OES

Introduction

Lithium's economic significance is increasing as it plays a vital role in the creation of green energy storage devices like Li-ion batteries. As a result, the worldwide demand for lithium has risen, and in 2020, lithium was officially added to the list of critical raw materials published by the European Commission for the European Union. Brine deposits from salars or geothermal fields are the primary sources of lithium resources globally, but other essential sources include clays, granites, and granite-related pegmatites. Despite salar deposits containing the largest lithium reserve, lithium-rich mineral concentrates from pegmatites are presently the primary source of lithium production due to their higher grade and lower production costs[1].

To access the lithium and convert it into industrial compounds, these minerals need to be processed. However, before processing, it's crucial to characterize the major and minor components of lithium-containing geological materials. While the lithium content is of most importance, the presence and concentration of other elements determine the grade and processing procedure. Traditional exploration methods rely on identifying geological features that are indicative of mineral deposits. While these methods have been successful in identifying many mineral deposits, they are less effective for lithium deposits because lithium is more widely distributed in the earth's crust and is not associated with specific geological formations. Nowadays, lithium exploration includes the analysis for so called pathfinder elements, which are certain elements in the earth's crust being indicative of lithium deposits. These elements include, for example, beryllium, rubidium, cesium, and tantalum[2,3]. Pathfinder elements provide a more effective exploration tool for lithium deposits because it is based on the distribution of elements that are chemically similar to lithium. This makes it possible to identify areas that are likely to contain lithium deposits even if they do not have the geological features typically associated with mineral deposits. Traditional exploration methods can be expensive and time-consuming, requiring extensive drilling and analysis. On the other hand, the pathfinder element

approach can be conducted more quickly and inexpensively by analyzing soil and rock samples.

Recently, Chinese standard methods summarized in the YS/T 509 series have been established for analyzing lithium ore. These standards mainly cover the different sample preparation procedures (fusion, multi-acid digestion on hot plate) for each targeted element (e.g., Be, Ca, Cs, Fe, Li, Rb, Mn) and recommends three different techniques for the analysis of the samples – flame atomic absorption, photometry, and complexation with ethylenediaminetetraacetic acid (EDTA). If one wants to determine all analytes according to these standards in the lithium ore, this can become very time-consuming and is not very efficient.

The objective of this research is to simplify and speed up the overall analytical procedure for the analysis of major, trace, and pathfinder elements in lithium ore samples by exploring alternative sample preparations than mentioned in the YS/T 509 series and performing analyses with the PlasmaQuant 9200 ICP-OES. This approach takes advantage of the multi-element capability of an ICP-OES, reducing the complexity of the measurement process. Additionally, the speedwave XPERT microwave digestion system was employed, which reduces overall time and acid volumes needed for the sample preparation.

Materials and methods

Sample preparation

All laboratory ware was previously washed with deionized (DI) water from a PURELAB system (18,2 MΩ cm, ELGA LabWater, High Wycombe, England). Chemicals were of analytical reagent grade. In order to verify the applicability and accuracy of the developed method, three certified reference materials (CRMs) were used: OREAS 750 (pegmatide lithium ore), OREAS 753 (pegmatide lithium ore), OREAS 999 (spodumene concentrate). Samples were prepared in two independent replicates per digestion procedure.

Procedure A (without HF complexation): Approximately 0.1 g of each duplicate were accurately weighed (0.0001 mg) into a digestion vessel (DAK100). Afterwards, 4 (± 0.1) mL conc. H_2SO_4, 2 (± 0.1) mL conc. HF, 1 (± 0.1) mL conc. HCl, and 2 (± 0.1) mL conc. HNO_3 were added. The mixture was swirled carefully and left standing for at least 15 minutes before the vessel was closed. Subsequent heating was performed stepwise (210 °C for 10 min (ramping 5 min), 230 °C for 10 min (ramping 2 min), 240 °C for 30 min (ramping 2 min)) in a speedwave XPERT microwave digestion system. Afterwards the vessels were allowed to cool to room temperature (RT) to avoid foaming and splashing. The solutions were transferred to a graduated polypropylene tube, diluted to 50 mL with DI water, and centrifuged (1125xg, 5 min). The resulting clear solutions of the two independent replicates were used for direct analysis.
Procedure B (with HF complexation): After the first digestion step and cooling, the vessels were opened, 10 mL of a saturated H_3BO_3 solution were added, and the complexation of free HF was carried out at 180 °C (10 min, ramping 5 min). Afterwards the vessels were allowed to cool down again to RT, solutions were transferred to a graduated polypropylene tube, diluted to 50 mL with DI water, and centrifuged (1125 xg, 5 min). The supernatants of the duplicates were used for direct analysis.

Long-term stability was investigated by analyzing quality control (QC) standard solutions after each batch of 10 samples. Samples measured in between consisted of a solution mimicking a lithium ore sample. This solution was prepared in 1% (v/v) HNO_3 from single element standard solutions and contained the following analyte concentrations: 5 mg/L (P), 20 mg/L (Ca), 25 mg/L (Fe, K, Li), 50 mg/L (Mg, Mn, Na, Si), 150 mg/L (Al).

Calibration

All quantitative measurements were carried out against external calibration curves. Calibration levels for each element were chosen based on expected concentration range. At least three calibration standards were used for each element, as described in Table 1. Selected calibration curves are shown in Figure 1.

The multi-element stock solutions were prepared using single and multi-element standard solutions (Merck, Sigma-Aldrich), and through serial volume/volume dilution in polypropylene tubes. Blank solution, calibration and QC standards (see Table 1) were prepared in 1% (v/v) HNO_3. QC standards were obtained from a different multi-element stock solution than the source used for calibration standards.

Table 1: Concentration (mg/L) of calibration and quality control (QC) standards

Element	As, Ba, Be, Bi, Co, Cr, Cs, Ga, Nb, Ni, Rb, Sb, Sn, Sr, Ta, Ti, Tl, V, W	Al	Ca, Fe, K, Li, Mn	Mg, Na	P
Blank	0	0	0	0	-
Std. 1	0.01	-	-	-	-
Std. 2	0.10	-	-	-	-
Std. 3	1.0	-	-	-	-
Std. 4	-	-	2.5	2.5	-
Std. 5	-	-	10	10	-
Std. 6	-	50	25	25	-
Std. 7	-	100	50	50	-
Std. 8	-	200	-	100	-
Std. 9	-	-	-	-	1.0
Std. 10	-	-	-	-	2.5
Std. 11		-	-	-	5.0
QC Std. 1	0.25	-	-	-	0.25
QC Std. 2	-	50	25	25	-

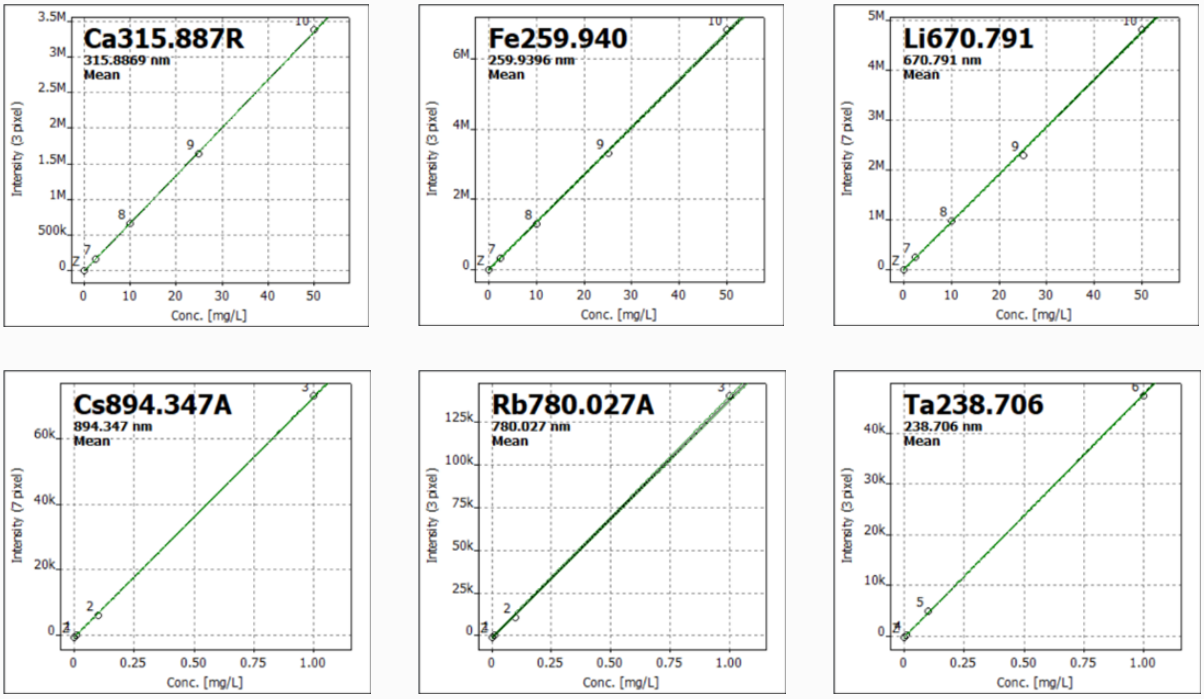


Figure 1: Selected calibration curves

Instrument settings

The analysis was performed on a PlasmaQuant 9100 Elite ICP-OES. Representative test measurements on a PlasmaQuant 9200 Elite confirmed consistent performance under the adjusted plasma conditions. The sample introduction components were selected to achieve a high level of sensitivity for trace elements in high matrix samples while being resistant to hydrofluoric acid. Axial, radial, and radial PLUS plasma viewing mode were selected, thus assuring best performance for traces and minerals. Teledyne CETAC ASX-560 Autosampler was coupled to the instrument. Individual settings and components are summarized in Table 2.

Table 2: Instrument settings

Parameter	Specifications 9100	Specifications 9200
RF power	1250 W	
Plasma gas flow	13 L/min	9 L/min
Auxiliary gas flow	0.5L/min	
Nebulizer gas flow	0.6 L/min	
Nebulizer	Parallel path nebulizer, 1.0 mL/min, PFA	
Spray chamber	Cyclonic spray chamber, 50 mL, PTFE	
Outer tube/inner tube	Syalon/alumina	
Injector	Alumina, ID: 2 mm	
Pump tubing	PVC (black, black)	
Sample pump rate	1.0 mL/min	
Fast pump rate	4.0 mL/min	
Measuring delay/rinse time	60 s/30 s	
Torch position	0 mm	

Method and evaluation parameters

Table 3: Method parameters

Element	Line [nm]	Plasma view	Integration mode	Read time [s]	Evaluation			
					No. of pixels	Baseline fit	Polyn. degree	Correction
Al	396.152	radial	peak	1	3	ABC[1]	auto	-
As	188.979	axial	peak	5	3	ABC[1]	auto	-
Be	313.042	radial	peak	1	3	ABC[1]	auto	-
Bi	223.061	axial	peak	3	3	ABC[1]	auto	-
Ca	315.887	radial	peak	1	3	ABC[1]	auto	-
Co	228.615	axial	peak	3	3	ABC[1]	auto	-
Cr	267.716	axial	peak	3	3	ABC[1]	auto	-
Cs	894.347	axial	peak	3	7	static	auto	-
Fe	259.940	radial	peak	1	3	ABC[1]	auto	-
Ga	294.364	axial	peak	3	3	ABC[1]	auto	-
K	766.491	radial	peak	1	3	ABC[1]	auto	-
Li	670.791	radial PLUS[2]	peak	1	7	ABC[1]	auto	-
Mg	285.213	radial	peak	1	3	ABC[1]	auto	-
Mn	293.931	radial PLUS[2]	peak	1	3	ABC[1]	auto	-
Na	589.592	radial	peak	1	3	ABC[1]	auto	-

Table 3 (continued): Method parameters

Element	Line [nm]	Plasma view	Integration mode	Read time [s]	Evaluation			
					No. of pixels	Baseline fit	Polyn. degree	Correction
Nb	269.706	axial	peak	3	3	ABC[1]	auto	-
Ni	231.604	axial	peak	3	3	ABC[1]	auto	-
P	213.618	axial	peak	1	3	ABC[1]	auto	-
Rb	780.027	axial	peak	5	3	static	auto	-
Sb	217.581	axial	peak	5	3	ABC[1]	auto	-
Sn	189.927	axial	peak	3	3	ABC[1]	auto	-
Sr	407.771	radial	peak	1	3	ABC[1]	auto	-
Ta	238.706	axial	peak	3	3	ABC[1]	auto	-
Ti	334.941	axial	peak	1	3	ABC[1]	auto	-
Tl	190.796	axial	peak	5	3	ABC[1]	auto	-
V	292.401	axial	peak	1	3	ABC[1]	auto	-
W	207.911	axial	peak	3	3	ABC[1]	auto	-

[1] Automated Baseline Correction
[2] Attenuated radial observational view extends linear dynamic range into the percentage range

Results and discussion

According to ISO 11885, the limits of detection (LODs) are calculated following the equation:

$$LOD = 3\ s_0$$

where s_0 is the standard deviation of outlier-free results of at least 3 measurements of a reagent blank. The instrumental and method-specific detection and quantification limits, which consider the dilution factor of the digestion step, are shown in Table 4.

Table 4: Instrumental and method-specific limits of detection (LOD) and quantification (LOQ)

Element	Line [nm]	Plasma view	Instrumental [µg/L]		Method [mg/kg]	
			LOD	LOQ	LOD	LOQ
Al	396.152	radial	4.16	12.50	2.08	6.25
As	188.979	axial	3.06	9.20	1.53	4.60
Be	313.042	radial	0.20	0.60	0.10	0.30
Bi	223.061	axial	3.71	11.10	1.85	5.55
Ca	315.887	radial	2.04	6.10	1.02	3.05
Co	228.615	axial	0.25	0.80	0.13	0.40
Cr	267.716	axial	0.12	0.40	0.06	0.20
Cs	894.347	axial	7.16	21.50	3.58	10.75
Fe	259.940	radial	0.55	1.70	0.28	0.85
Ga	294.364	axial	1.58	4.70	0.79	2.35

Table 4 (continued): Instrumental and method-specific limits of detection (LOD) and quantification (LOQ)

Element	Line [nm]	Plasma view	Instrumental [µg/L]		Method [mg/kg]	
			LOD	LOQ	LOD	LOQ
K	766.491	radial	28.12	84.40	14.06	42.20
Li	670.791	radial PLUS	0.90	2.70	0.45	1.35
Mg	285.213	radial	0.52	1.60	0.26	0.80
Mn	293.931	radial PLUS	2.45	7.30	1.22	3.65
Na	589.592	radial	5.14	15.40	2.57	7.70
Nb	269.706	axial	0.58	1.80	0.29	0.90
Ni	231.604	axial	0.71	2.10	0.36	1.05
P	213.618	axial	7.69	23.10	3.84	11.55
Rb	780.027	axial	0.74	2.20	0.37	1.10
Sb	217.581	axial	6.72	20.10	3.36	10.05
Sn	189.927	axial	1.49	4.50	0.75	2.25
Sr	407.771	radial	0.01	0.02	0.00	0.01
Ta	238.706	axial	4.42	13.30	2.21	6.65
Ti	334.941	axial	0.07	0.20	0.03	0.10
Tl	190.796	axial	2.10	6.30	1.05	3.15
V	292.401	axial	0.19	0.60	0.09	0.30
W	207.911	axial	2.20	6.60	1.10	3.30

The analysis of three CRMs was used to perform method development and validation. Rather, the recoveries in the samples indicate which one of the two digestion procedure is most appropriate for which element. In the YS/T 509 series, the acidic digestion is performed on hot plate be using HF and H_2SO_4. This approach was adapted, scaled down to the microwave system and extended to include additional acids in order to stabilize all analytes appropriately in solution. Since lithium ores contain oxides of silica, aluminum and many of their variations or mixtures, digestion with varying mixtures of sulfuric, hydrofluoric, and hydrochloric acid is a requirement, in many cases with a subsequent complexation step with boric acid. Not surprisingly, this can possibly lead to numerous hardly soluble precipitates. Therefore, it was tested if an additional complexation step is required. Table 5 shows the certified values and recoveries of each element depending on the digestion procedure employing the complexation step of hydrofluoric acid (Proc. B) or leaving it out (Proc. A).

Table 5: Comparison of the reference values with recoveries in samples following sample preparation procedure without (Proc. A) and with (Proc. B) boric acid complexation step

Element	OREAS 750			OREAS 753			OREAS 999		
	Certified [mg/kg]	Recovery Proc. A [%]	Recovery Proc. B [%]	Certified [mg/kg]	Recovery Proc. A [%]	Recovery Proc. B [%]	Certified [mg/kg]	Recovery Proc. A [%]	Recovery Proc. B [%]
Al	54,200	63	93	82,200	28	100	107,700	21	103
As	13.3	102	158*	5.33	99	214*	5.36	111	222*
Be	37.6	106	98	118	93	103	49.8	88	99
Bi	1.00	<MLD	<MLD	2.2	<MLQ	<MLQ	2.11	<MLQ	<MLQ
Ca	8,280	74	95	1,130	22	108	4,500	32	96

Table 5 (continued): Comparison of the reference values with recoveries in samples following sample preparation procedure without (Proc. A) and with (Proc. B) boric acid complexation step

Element	OREAS 750			OREAS 753			OREAS 999		
	Certified [mg/kg]	Recovery Proc. A [%]	Recovery Proc. B [%]	Certified [mg/kg]	Recovery Proc. A [%]	Recovery Proc. B [%]	Certified [mg/kg]	Recovery Proc. A [%]	Recovery Proc. B [%]
Co	3.99	117	103	0.96	92	94	4.95	91	94
Cr	27.6	98	104	20.8	94	109	81	105	104
Cs	22.6	95	108	64	74	102	88	71	117
Fe	16,700	95	92	8,390	89	97	16,200	91	94
Ga	13	110	270*	16.1	102	252*	82	105	135*
K	16,900	94	93	19,300	88	102	5,000	56	99
Li	2320	86	73	9,850	96	95	26,500	94	88
Mg	3150	22	97	110	12	102	4,100	9	98
Mn	380	97	92	740	98	102	1430	99	97
Na	15,300	95	91	21,600	89	90	6,930	83	94
Nb	21.3	101	100	36.3	97	95	75	93	92
Ni	11.4	105	90	10.8	106	89	47.5	103	94
P	700	105	92	1,110	105	95	160	101	93
Rb	254	51	97	612	97	110	n.c.	-	-
Sb	0.42	<MLD	<MLD	0.27	<MLD	<MLD	1.11	<MLD	<MLD
Sn	25.2	90	103	84	97	99	63	93	103
Sr	74	69	99	25.5	11	105	16.9	40	111
Ta	9.78	101	100	20	105	98	49	92	87
Ti	1,580	93	91	40	79	79	340	95	95
Tl	1.45	<MLQ	<MLQ	3.67	<MLQ	<MLQ	4.26	<MLQ	<MLQ
V	26.4	101	111*	1.16	103	315*	14.8	94	110*
W	5.46	92	72	5.62	94	81	6.97	93	72

* overestimation of analyte caused by spectral interferences originating from H_3BO_3 matrix

Basically, it can be stated that for most analytes it is irrelevant which of the two procedures is used for sample preparation. Only for Al, As, Ca, Cs, Ga, Mg, Sr, V, and W there are major deviations in recovery between the two methods. While spectral inferences (caused by the H_3BO_3 matrix) are responsible for the large differences for As, Ga, and V, it can be seen for the elements of the I and II main group as well as Al that the procedure with complexation of the hydrofluoric acid gives significantly better recoveries. This can be partially explained by the fact that the complexation step eliminates formation of insoluble fluoride precipitates (e.g., Al, Ca, and Mg). Additionally, stability in solution of certain elements (e.g., W) strongly depends on the availability of fluoride ions. If the more suitable of the two methods is chosen for the respective element, recovery rates between 86 and 111% are obtained for the majority of the elements.

Since the concentration of some trace elements in the reference materials were below the method-specific limit of quantification, one sample (OREAS 750, without HF complexation) was spiked with a low analyte concentration (0.1 mg/L) to check for accuracy and applicability of the overall method. Additionally, it was tested if possible matrix effects have influences on the signal intensity of pathfinder elements. Standard procedures, such as the EN ISO 11885,

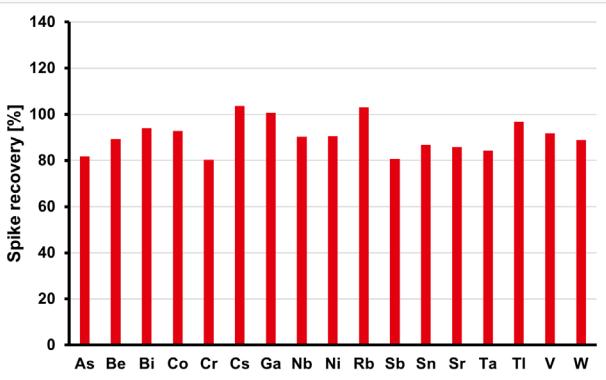


Figure 2: Recovery rates of spiked (0.1 mg/L) analytes in a lithium ore sample (OREAS 750)

indicate that the recovery of the spiked analyte concentration must be within ± 20% of the concentration equivalent added to the sample. Figure 2 shows the analyte recoveries which all were within a ± 20% range proving the applicability of the method for the determination of pathfinder elements in the undiluted ore samples at low concentration levels.

Long term stability was investigated by monitoring the results of QC standard testing for twelve hours, This resulted in recoveries in the range of ± 10% (see Figure 3). Relative standard deviations below 6.2% indicate a highly stable performance of the instrumentation throughout the 12 hours of measurement.

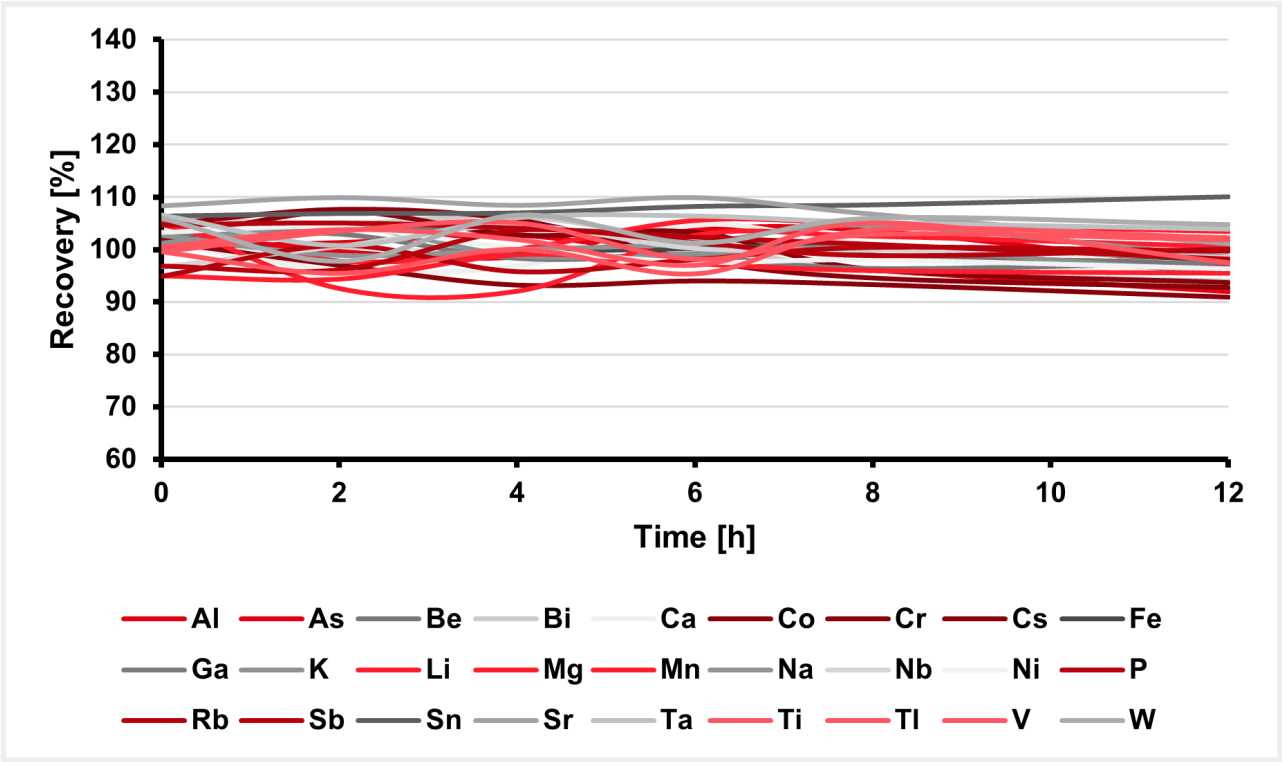


Figure 3: Percentage recoveries of the analytes throughout a 12-hour sequence. RSD values were ≤ 6.2% for all elements

Quantification of traces in geological materials by ICP-OES is one of the most challenging analytical routines. Often containing large amounts of alumina, iron and silica, sulfur and refractory metals, etc., the high matrix contents of digested samples require for exceptional plasma robustness. This is particularly true when attempting to detect trace levels of pathfinder elements, while avoiding sample dilution. The vast number of emission lines arising from matrix elements further adds to the complexity, which can be resolved by high spectral resolution only. Due to the high resolution of the instrument (2pm @ 200 nm), also severe interferences can be spectrally resolved (see Figure 4), resulting in the ability to analyze all targeted elements without any further mathematical correction algorithms.

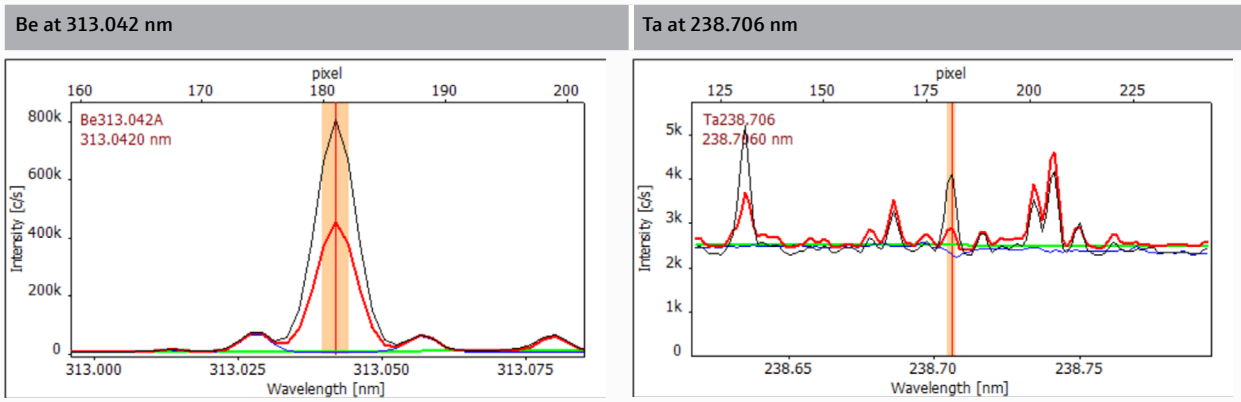


Figure 4: As-recorded spectra (red: sample, blue: blank, black: 0.1 mg/L spike, green: baseline correction (ABC)) of the PlasmaQuant 9200 Elite illustrating the application advantage of high-resolution (2 pm @ 200 nm)

Summary

The presented method describes the use of highly sensitive and robust HR ICP-OES in a standard configuration for the analysis of lithium ore samples. The method validation was performed by analyzing a certified reference material as well as long-term stability analysis demonstrating the suitability of the PlasmaQuant 9200 ICP-OES systems for the elemental analysis of such matrices.

The major challenge comprises the analysis of elements over a wide concentration range (low µg/L to high mg/L) in a single run. Trace elements (e.g., Be, Cs, Rb, and Ta) are analyzed along with major elements (e.g., Al, Fe, Li, and Na). This has been successfully demonstrated by the DualView PLUS feature of the PlasmaQuant 9200 series. Besides the common radial and axial plasma observation modes, the axial PLUS and radial PLUS modes offer further alternatives which attenuates the signal in the respective observational view. The described method uses radial and attenuated radial plasma observation to measure high levels of major elements alongside trace levels of pathfinder and targeted elements in a single measurement run. Herein, the method avoids the running of several dilutions to cover the entire concentration range. This helps especially in the analysis of a high concentration of lithium. The element can be quantified in the undiluted sample without having to dispense with the most sensitive and well-established analytical line at 670 nm.

The results indicate that microwave digestion can be used for all elements, significantly simplifying sample preparation. Depending on the analyte, it may be advantageous to implement an additional step for the complexation of the hydrofluoric acid in the digestion protocol to improve the accuracy of the method.

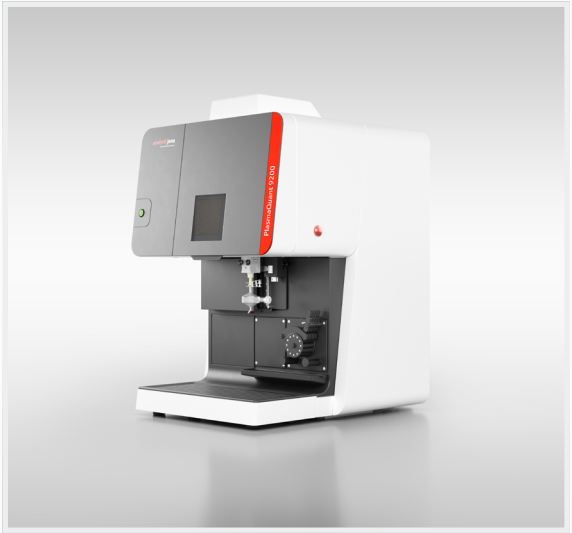


Figure 5: PlasmaQuant 9200

It could be demonstrated that the requirements in terms of sensitivity, stability, and accuracy to perform the analysis of ore samples for pathfinder and targeted elements can be met with this proposed setup. The use of the PlasmaQuant 9200 series for analysis and the speedwave XPERT microwave digestion system for sample preparation is an excellent combination for the routine analysis of lithium ore samples.

Recommended device configuration

Table 6: Overview of devices, accessories, and consumables

Article	Article number	Description
PlasmaQuant 9200 Elite	818-09201-2	High resolution ICP-OES
speedwave XPERT	819-5005000-2	Microwave Pressure Digestion System
HF KIT for PlasmaQuant 9x00 series	810-88007-0	Sample introduction system for HF containing samples
Teledyne Cetac ASX 560	810-88015-0	Autosampler with integrated rinse function

References

[1] Robert J. Bowell et. al.; Classification and Characteristics of Natural Lithium Resources. Elements 2020; 16 (4): 259–264.

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