



## ICP-Optical Emission Spectroscopy

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## Analysis of Lithium Ore with the Avio 550 Max ICP-OES

### Introduction

With the increasing use of lithium (Li) in a wide variety of

products, especially for batteries, there is a growing demand for lithium and its compounds. Li occurs naturally in minerals, clays, and brines; examples of lithium-containing minerals include spodumene ( $\text{LiAlSi}_2\text{O}_6$ ), petalite ( $\text{LiAlSi}_4\text{O}_{10}$ ), and lepidolite ( $\text{K}(\text{Li,Al})_3(\text{Al,Si,Rb})_4\text{O}_{10}(\text{F, OH})_2$ ), among others. These minerals must be processed to access the lithium so that it can be converted into other compounds for industrial use.

Prior to processing, Li-containing geological materials must be characterized for both their major and minor components. While the Li content is most important, the presence and concentration of other elements determines the grade and the processing procedure.

Currently, China has standard methods for the analysis of lithium ore: the YS/T 509 series - "Chemical Analysis of Spodumene and Lepidolite Concentrates", as shown in Table 1. To cover the inorganic components, three different techniques are specified (flame atomic absorption [AA], photometry, and complexation with ethylenediaminetetraacetic acid [EDTA]), along with a variety of different sample preparations, making it cumbersome to measure all the analytes.

The goal of this work is to try to simplify the analysis of components specified in YS/T 509 by exploring alternate sample preparations and performing analyses with the Avio® 550 Max fully simultaneous ICP-OES, taking advantage of the multi-element capability of ICP-OES.

Table 1. YS/T 509 series of methods for the analysis of lithium ore.

Standard ID	Analytes	Technique	Sample Preparation Procedure
YS/T 509.1-2008	Li <sub>2</sub> O, Na <sub>2</sub> O, K <sub>2</sub> O	Flame AA	Hot Plate: 0.1 g + 3 mL H <sub>2</sub> SO <sub>4</sub> + 15 mL HF
YS/T 509.2-2008	Rb <sub>2</sub> O, Cs <sub>2</sub> O	Flame AA	Hot Plate: 0.25 g + 3 mL H <sub>2</sub> SO <sub>4</sub> + 15 mL HF
YS/T 509.8-2008	CaO, MgO	Flame AA	Hot Plate: 0.1 g + 2 mL HClO <sub>4</sub> + 2 mL HCl + 15 mL HF
YS/T 509.3-2008	SiO <sub>2</sub>	Photometric Method	Fusion: 0.5 g + 2 g KOH + 2 g NaOH
YS/T 509.4-2008	Al <sub>2</sub> O <sub>3</sub>	EDTA Complexation Method	Fusion: 0.5 g + 4 g KOH
YS/T 509.5-2008	Fe <sub>2</sub> O <sub>3</sub>	Photometric Method and EDTA Complexation Method	Fusion: 0.5 g + 5 g KOH
YS/T 509.6-2008	P <sub>2</sub> O <sub>5</sub>	Photometric Method	Hot Plate: 0.1 g + 5 mL H <sub>2</sub> SO <sub>4</sub> + 10 mL HF
YS/T 509.7-2008	BeO <sub>2</sub>	Photometric Method	Fusion: 0.1 g + 10 mL HF + 5 g NaOH
YS/T 509.9-2008	F	Ion Selective Electrode Method	Fusion: 0.2 g + 3 g NaOH + 0.5 g Na <sub>2</sub> O <sub>2</sub>
YS/T 509.10-2008	MnO	Photometric Method	Fusion: 0.5 g + 1 mL HNO <sub>3</sub> + 2 mL H <sub>2</sub> SO <sub>4</sub> + 20 mL HF + 7 g K <sub>2</sub> S <sub>2</sub> O <sub>7</sub>

## Experimental

### Samples and Sample Preparation

Samples consisted of two lithium ore certified reference materials (GBW 07152, GBW 07153 - National Research Centre for Certified Reference Materials, China) and one unknown spodumene sample, with the reference materials being used for method development and validation. Table 2 lists the certified values in GBW 07152 and GBW 07153.

Table 2. Certified values in GBW lithium ore reference materials.

Analyte	GBW 07152 (wt %)	GBW 07153 (wt %)
Li <sub>2</sub> O	0.46	2.29
Al <sub>2</sub> O <sub>3</sub>	14.76	19.12
Fe <sub>2</sub> O <sub>3</sub>	0.394	0.301
CaO	0.335	0.076
MgO	0.054	0.036
MnO	0.07	0.252
TiO <sub>2</sub>	0.018	0.028
Na <sub>2</sub> O	4.19	2.33
K <sub>2</sub> O	3.17	4.8
P <sub>2</sub> O <sub>5</sub>	0.173	0.237

Each sample was prepared with two different techniques: digestion on a hot plate and in a microwave digestion system.

With the hot plate digestion, 0.1 g of sample was placed in a PTFE beaker, followed by 9 mL of concentrated hydrofluoric acid (HF) and 2 mL of concentrated perchloric acid (HClO<sub>4</sub>). The beakers were heated to 230 °C until white fumes were observed, and all the acids evaporated to dryness. The residue was dissolved in 2 mL of concentrated nitric acid (HNO<sub>3</sub>) and diluted to 50 mL with 1% nitric acid (v/v) for analysis.

With microwave digestion, 0.1g of sample was combined with 4 mL of concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), 2 mL of concentrated HF, and 1 mL of concentrated HNO<sub>3</sub> in a PTFE microwave digestion vessel. The digestion program consisted of heating at 180 °C for 10 minutes and then raising the temperature to 230 °C for 30 minutes. After the vessels cooled to room temperature, they were diluted to 50 mL with 1% HNO<sub>3</sub> (v/v) for analysis.

Calibration standards were prepared in 1% HNO<sub>3</sub> over different calibration ranges (Table 3) to match the expected concentrations in the ores for greater accuracy,<sup>1</sup> and a linear calculated intercept calibration equation was applied. Scandium (Sc) was added to all calibration standards, blanks, and samples as an internal standard. The quality of the calibration curves was evaluated by examining both the correlation coefficient and the residuals, as shown in Syngistix™ for ICP software's Examine Calibration window in Figure 1.

Table 3. Concentrations of calibration standards.

Analyte	Calibration Standards (ppm)
Li	5, 10, 20, 30
Al	25, 50, 100, 200
Ca, Fe, Mg	0.25, 0.5, 1, 2, 5
Mn	0.1, 0.25, 0.5, 1, 2, 5
Ti	0.25, 0.5, 1
K, Na	10, 25, 50, 100
P	0.5, 1, 2

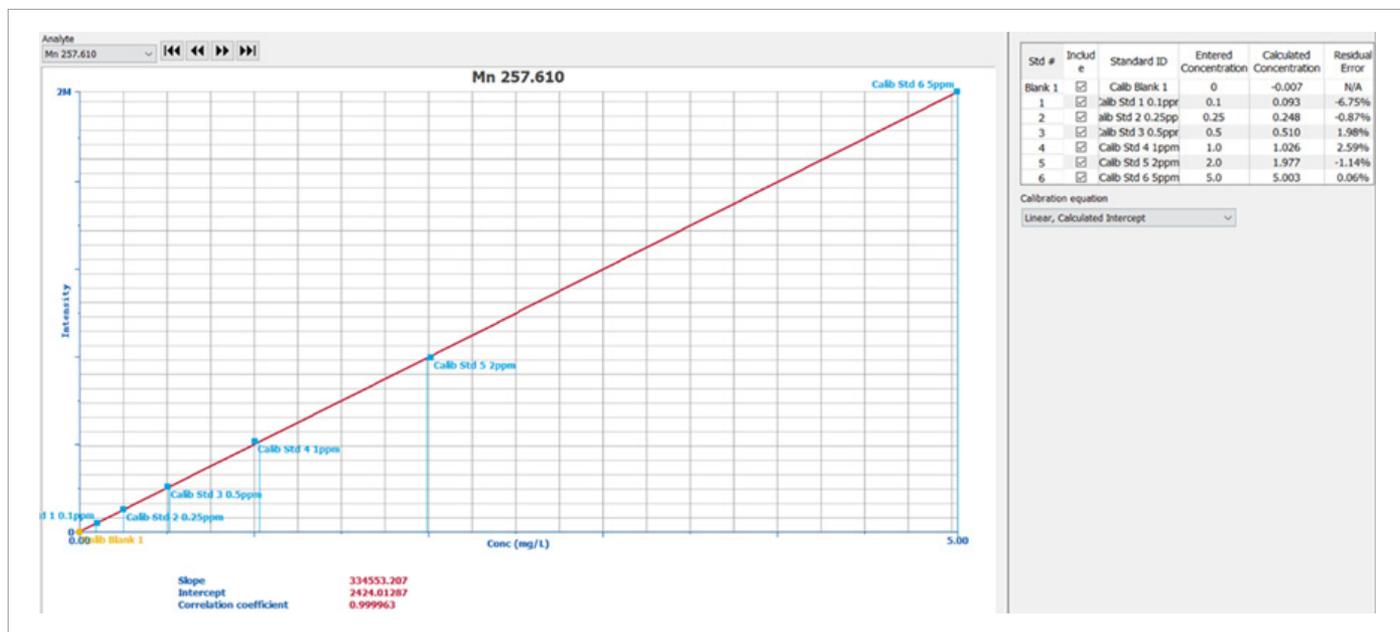


Figure 1. Calibration curve for manganese (Mn), with a correlation coefficient > 0.9999 and residual errors on the standards of less than 7%.

### Instrumental Conditions

All analyses were performed on an Avio 550 Max fully simultaneous ICP-OES using the conditions and parameters in Table 4 with the analytes and wavelengths in Table 5. All analyses were done using radial plasma view.

Table 4. Avio 550 Max ICP-OES operating parameters.

Component / Parameter	Description / Value
Nebulizer	GemTip Cross-Flow
Spray Chamber	Ryton Scott double-pass
Sample Uptake Rate	1.0 mL/min
Injector	2.0 mm id alumina
Torch	Ceramic
RF Power	1500 W
Plasma Gas Flow	10 L/min
Nebulizer Gas Flow	0.65 L/min
Auxiliary Gas Flow	0.4 L/min
Torch Depth	-3
Plasma View	Radial
Integration	Auto
Read Time Range	1-5 sec
Replicates	3
Sample Uptake Tubing	Orange/Yellow (0.51 mm id), PVC
Internal Standard Tubing	Green/Orange (0.38 mm id), PVC
Drain Tubing	Red/Red (1.14 mm id), PVC

Because HF is used for the microwave sample preparation, an HF-resistant nebulizer and spray chamber were utilized. In addition, since Li-containing salts attack quartz torches, a ceramic torch was used.

All data processing was done with Syngistix for ICP software, using auto background correction to simplify data analysis.

Table 5. Elements and wavelengths.

Element	Wavelength (nm)
Al	396.153
Ca	317.933
Fe	238.204
K	766.490
Li	670.784
Mg	285.213
Mn	257.610
Na	589.592
P	213.618
Ti	334.940
Sc (Internal Std)	361.683

## Results and Discussion

When comparing the hot plate and microwave digestion methods, microwave digestion offers two advantages: half the amount of acid is required, and the digestion time is about four times faster. For these reasons, the lithium ore reference materials were first measured after microwave digestion. The recoveries displayed in Figure 2 show that all elements recovered within 10% of their certified values in both reference materials. Equivalent results were obtained with the hot plate digestion, with the exception of  $Al_2O_3$ , which recovered at 80%, indicating that either alkali fusion (as specified in YS/T 509.4-2008) or microwave digestion with  $H_2SO_4/HF$  are required to completely break down the  $Al_2O_3$ . These results demonstrate that either microwave digestion or the proposed hot plate method in combination with fusion (for  $Al_2O_3$ ) can be used as alternatives to the multiple methods specified in the YS/T 509 series of methods. If fusion is used, the Avio 550 Max ICP-OES can easily provide accurate, stable results for fusion samples.<sup>2</sup>

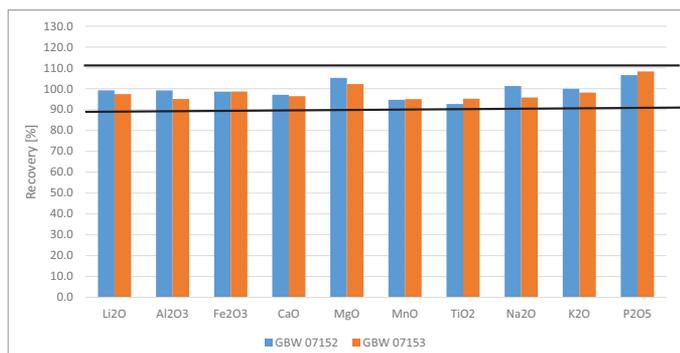


Figure 2. Recoveries in Li ore reference materials.

To evaluate short-term stability, each sample was then measured using 10 replicates; the resulting relative standard deviations (RSDs) of all analytes were all less than 0.5%, demonstrating the excellent stability of the Avio 550 Max ICP-OES. As an example, Figure 3 shows the certified values of Li for each of the 10 replicates.

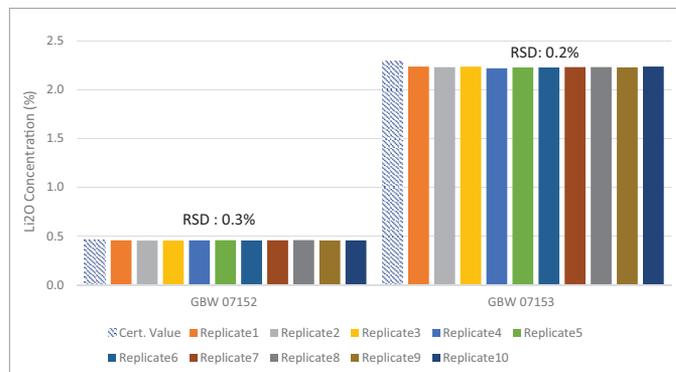


Figure 3. Certified concentrations of Li in CRMs (pattern fill) and measured results from 10 replicates (solid fill).

With Syngistix software, the quality of results for reference materials can quickly be observed: simply enter the certified concentrations in the Method window, along with the desired accuracy. Data Viewer can be set to show when values are out of the sample limits, with a different color being used for high or low results, as shown in Figure 4 for the analysis of the reference materials with the hot plate digestion, where the  $Al_2O_3$  recoveries were below the certified values.

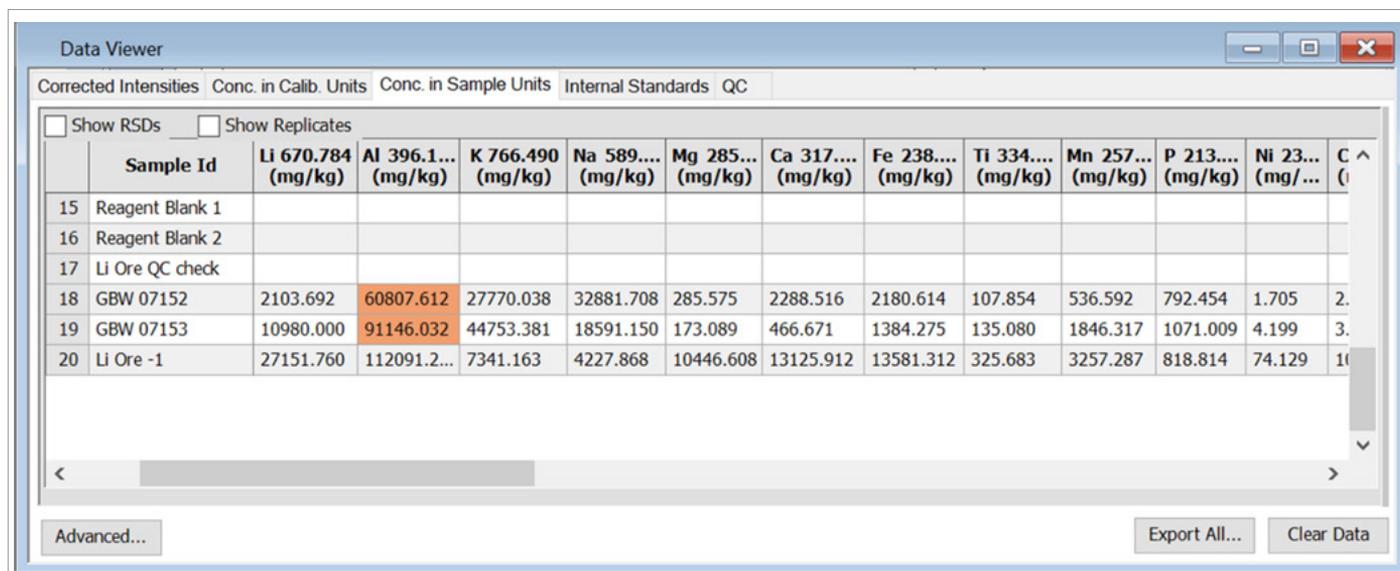


Figure 4. Data Viewer in Syngistix software, automatically highlighting that aluminum (Al) falls below the certified value of the CRMs. Different user-selectable colors are used to identify values which are higher or lower than the user-defined limits.

A direct comparison was made with method YS/T 509.1-2008, which specifies the analysis of Li, Na, and K in ore using flame AA. Samples prepared with the hot plate digestion (as stated in YS/T 509.1-2008) were analyzed by both flame AA and ICP-OES. Figure 5 shows that Li, Na and K recover within 10% of the certified values for both AA and ICP-OES. In addition, the unknown sample was also measured by both flame AA and ICP-OES, with the results shown in Figure 6, along with the relative percent differences between the results from each technique. Since Li is an easily ionizable element, better agreement between AA and ICP-OES results can be achieved by lowering the plasma viewing height when measuring Li, which decreases the relative percent difference to 2.2% in Figure 6. With accurate recoveries in the reference materials and equivalent results in the unknown ore, ICP-OES can be used as an alternative to flame AA for the analysis of major components in Li-ore samples, providing the advantage of multi-element analysis, compared to flame AA.

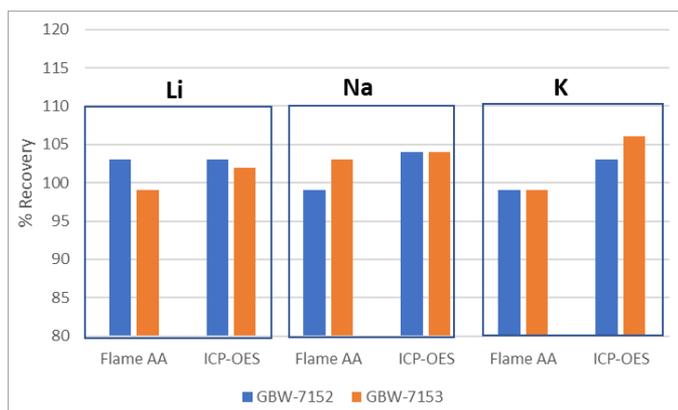


Figure 5. Comparison of flame AA and ICP-OES results for the determination of Li, Na and K in lithium ore reference materials.

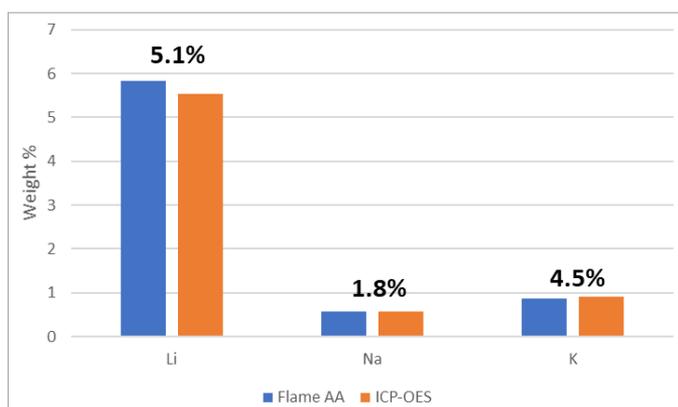


Figure 6. Analysis of an unknown lithium ore by flame AA and ICP-OES for Li, Na and K. The relative percent differences between the results are shown above the bars.

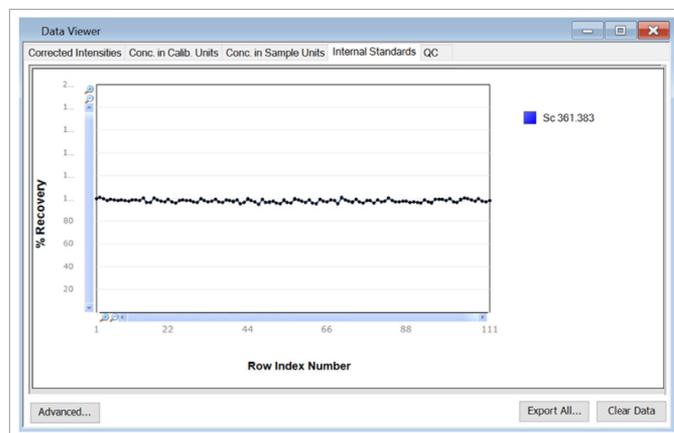


Figure 7. Internal standard stability in radial view during the analysis of major analytes of lithium ore, as plotted by Syngistix software in Data Viewer.

To evaluate the stability of the methodology, the internal standard signals in radial mode were monitored during the whole analysis of the lithium ore samples. As shown in Figure 7, the internal standard signal is plotted in Syngistix software's Data Viewer for easy monitoring both during and after an analytical run. The Avio 550 Max ICP-OES shows excellent stability with a drift of less than 5% over five hours.

## Conclusion

This work explores the ability to measure major elements in lithium ore with the Avio 550 Max ICP-OES, as an alternative to the techniques specified in China's standard methods for the analysis of lithium ore. Sample preparations with both microwave and hot plate digestion were compared, as were the results between flame AA and ICP-OES analyses. The results indicate that either microwave digestion or a modified hot plate method in combination with fusion (for  $\text{Al}_2\text{O}_3$ , as stated in the original method) can be used for all elements, significantly simplifying sample preparation. The analytical results indicate that ICP-OES provides equivalent results to flame AA, with the added advantages of multi-elemental analysis, higher sample throughput, and the ability to measure lower concentrations. The Avio 550 Max fully simultaneous ICP-OES provides accurate, stable, and robust multi-elemental analysis of lithium ore, allowing it to be processed appropriately for its ultimate use in a variety of products, with batteries being the largest and fastest-growing end use product.

## References

1. "Sensitivity, Background, Noise, and Calibration in Atomic Spectroscopy: Effects on Accuracy and Detection Limits", White Paper, PerkinElmer, 2018.
2. "Stable Analysis of Lithium Metaborate Fusion Samples with the Avio 550 Max ICP-OES", Application Note, PerkinElmer, 2021.

## Consumables Used

Avio 550 Max ICP-OES	
Component	Part Number
Orange/Yellow (0.51 mm id), Flared PVC Tubing (Sample)	N0777476
Red/Red (1.14 mm id), Standard PVC Tubing (Drain)	09908585
Orange/Green (0.38 mm id), Standard PVC Tubing (internal standard)	N0777110
Ceramic D-Torch	N0811912
GemTip Cross-Flow Nebulizer	N0780546
Scott Spray Chamber	N0791499
Instrument Calibration Standard 2: 100 mg/L Ag, As, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sn, Sr, Ti, Tl, V, Zn	N9301721 (125 mL)
Al Standard, 1000 mg/L	N9300184 (125 mL)
Li Standard, 1000 mg/L	N9303781 (125 mL)
P Standard, 1000 mg/L	N9303788 (125 mL)
K Standard, 1000 mg/L	N9303779 (125 mL)
Na Standard, 1000 mg/L	N9303785 (125 mL)
Sc Standard, 1000 mg/L	N9303798 (125 mL)
Autosampler Tubes, Conical, Free-Standing	B0193233 (15 mL) B0193234 (50 mL)
Titan MPS Microwave Digestion System	
Component	Part Number
Consumables Kit for Standard 75 mL Digestion Vessels	N3132000
Rupture Disks for Standard 75 mL Digestion Vessels ( 25 pieces)	N3132001
Pressure Seal for Standard 75 mL Digestion Vessels (10 pieces)	N3132002
End Cap Plug for Gas Containment Manifold	N3134004