

# Lithium Content in Pegmatite Ores: Fast and Easy Analysis by Flame AAS

Quick, accurate, robust assay of  $\text{Li}_2\text{O}$  in fused ore samples using Agilent atomic absorption spectroscopy



## Authors

Marc-André Gagnon and Longbo Yang

Agilent Technologies, Inc.

## Introduction

As the lightest and smallest of all metals, lithium (Li) is used widely in the production of high energy density rechargeable batteries. These Li-ion batteries (LIBs) are used in technical products and sectors such as electric vehicles (EVs), power storage systems, consumer electronic goods, and emergency power backup systems. The demand for Li, especially from the EV sector, is projected to increase further over the next 20 to 30 years (1).

Li-bearing minerals (e.g., spodumene, petalite, lepidolite) in pegmatitic orebodies are a major source of Li. The  $\text{Li}_2\text{O}$  content of these orebodies typically ranges from 0.5 to 3% w/w, making it a viable source of Li for the mining industry. The exploration of orebodies, processing of the ore rocks, and production of Li concentrates require information on the chemical composition of the rocks, especially the Li content.

To assess the Li content in ores, onsite measurement of representative samples is often the fastest, most convenient, and the most economical means of analysis. Agilent atomic absorption spectrophotometry (AAS) instruments are ideal when rapid analysis is needed at remote sites due to their robustness and reliability in harsh environments.

In this study, five certified reference materials (CRMs) were prepared using the cost-effective sodium peroxide ( $\text{Na}_2\text{O}_2$ ) fusion procedure followed by analysis by the robust and easy-to-use Agilent AAS. The results show that flame AAS (FAAS) is a simple and efficient technique for the onsite measurement of Li in Li-rich ores.

## Experimental

### Sample preparation

#### Sodium peroxide fusion

Two Li ore standard reference materials (SRMs) from National Institute of Standards and Technology (NIST, Gaithersburg MD, USA) and three CRMs from OREAS (Melbourne, Australia) were prepared and analyzed in this study. The SRMs and CRMs included: NIST 182 (petalite), NIST 183 (lepidolite), OREAS 752 (pegmatite), OREAS 148 (pegmatitic Li-Nb-Sn), and OREAS 999 (concentrate).

Sodium peroxide ( $\text{Na}_2\text{O}_2$ ) fusion is a simple, tried-and-true technique for total digestion of geological samples. The method is versatile, can break down some refractory minerals, and is commonly used at mine sites.

Approximately 0.125 g of fine powdered CRM was weighed directly into a zirconium crucible followed by 1.50 g of  $\text{Na}_2\text{O}_2$  (97%+ purity). The mixture was fused at a temperature just above the  $\text{Na}_2\text{O}_2$  melting point for approximately 30 s. When cool, de-ionized (DI) water was added to solubilize the mixture. The solution was acidified using 10 mL of concentrated HCl and 10 mL of concentrated  $\text{HNO}_3$  and then made up to 100 mL with DI water.

Undissolved silica ( $\text{SiO}_2$ ) was removed using a syringe fitted with a luer-lock filter. All samples were then diluted 10-times in 10% HCl+10%  $\text{HNO}_3$  so that the Li concentration would fit the linear range of the AAS. A separate aliquot of each sample was spiked with 1 mg/L Li and analyzed against the unspiked sample. A fusion blank was obtained by fusing  $\text{Na}_2\text{O}_2$  without adding any sample to the crucible.

### Matrix matched calibration standards

Matrix matched calibration standards were prepared at 0, 0.5, 1, 2.5, and 5 mg/L of Li. For each calibration standard, 5 mL of the fusion blank solution was added to a known amount of Li standard stock solution (1000 mg/L) and made up to 50 mL using the 10% HCl+10%  $\text{HNO}_3$  solution. The effective Na concentration (>800 mg/L) in solution from the flux mixture acted as a suitable ionization buffer.

### Instrumentation

The Agilent 240FS AAS system was used to perform measurements in this study. However, since Fast Sequential (FS) mode was not required, the Agilent 55B AAS, with integrated software, is also ideally suited to this application. Agilent FAAS instruments are robust, user-friendly instruments with exceptional reliability and longevity. Instruments that are controlled using the Agilent SpectrAA software include Precision Optimized Measurement Time (PROMT), which speeds up the analysis without compromising precision. PROMT automatically reduces the measurement time for high-concentration samples while achieving the precision (%RSD) set by the operator. It also reduces sampling volume, improving efficiency while reducing carryover. In this study, manual sample-to-sample measurement time was on average around 20 s, assuming a 10 s rinse time. Instrument operating conditions are outlined in Table 1.

**Table 1.** Agilent AAS operating conditions.

Parameter	Setting
Lamp	Li hollow-cathode (coded)
Lamp current (mA)	5.0
Wavelength (nm)	670.8
Slit width (nm)	1.0
Flame type	Air-acetylene
Spray chamber	Mark-7
Air flow (L/min)	13.5
Acetylene flow (L/min)	1.8
Sampling mode	Manual
Uptake delay (s)	3
Maximum read time (s)	10
Measurement mode	PROMT
Precision (sample and standards)	1%
Calibration curve fitting algorithm	New Rational

Figure 1 shows a representative calibration curve for Li, obtained using New Rational calibration fit. The calibration curve shows excellent linearity up to 5 mg/L.

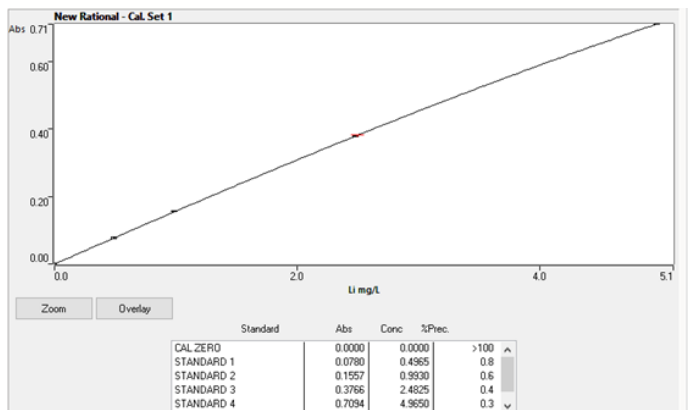


Figure 1. Calibration curve for Li 670.8 nm absorption wavelength.

## Results and discussion

### CRM recoveries and spike recoveries

To evaluate the accuracy of the sample preparation and AAS method, Li was measured in the five CRM samples. Good recoveries (101–106%) were obtained for Li measured in all CRMs (Table 2). The results show that  $\text{Na}_2\text{O}_2$  fusion is efficient for Li extraction from different pegmatite ores, regardless of the presence of undissolved silica particles.

Also, recoveries of the 1 mg/L Li spikes were all within 91–102% (Table 2), further demonstrating the accuracy of the method.

Table 2. Results for the measurement of Li in five different CRMs and recovery data for 1 mg/L Li spike.

SRMs and CRMs	$\text{Li}_2\text{O}$		Recovery	Recovery of 1 ppm Spike
	Certified Value (%)	Measured Value (%)	(%)	(%)
NIST 182 (Petalite)	4.34	4.50	104	101
NIST 183 (Lepidolite)	4.12	4.26	103	94
OREAS 752 (Pegmatite)	1.52	1.62	106	96
OREAS 148 (Pegmatitic Li-Nb-Sn)	1.03	1.06	103	102
OREAS 999 (Concentrate)	5.76	5.79	101	91

### Method Detection Limit (MDL)

The MDL for Li in solution was estimated from three times the standard deviation of 10 successive readings of a 25  $\mu\text{g}/\text{mL}$  Li solution prepared in the fusion blank. The MDL for Li was calculated as 0.005 mg/L. Based on the sample preparation protocol, the MDL corresponds to 0.008% of  $\text{Li}_2\text{O}$  in rock, which is almost two orders of magnitude lower than the industry cut-off grade of around 0.2 to ~0.5%  $\text{Li}_2\text{O}$ .

## Conclusion

The study has demonstrated the accuracy and sensitivity of the robust Agilent AAS system for the measurement of Li in various grades of pegmatite ores. Combining the efficiency of the sodium peroxide fusion and the simplicity of using a cost-effective AAS system, Agilent has provided a fast, easy, and accurate method for the routine, onsite analysis of Li in rocks.

## Reference

- Xu, C., Dai, Q., Gaines, L. *et al.* Future material demand for automotive lithium-based batteries. *Commun Mater*, 1, 99 **2020**. <https://doi.org/10.1038/s43246-020-00095-x>

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