



# Development and Validation of a Method to Quantify Lithium in Mineral Sample Using Atomic Absorption Spectrometry

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## ABSTRACT

A methodology based on flame atomic absorption spectrometry (FAAS) was developed and validated to quantify lithium in spodumene mineral sample. Validation parameters, including linearity and range, precision, accuracy, limit of detection (LOD) and limit of quantification (LOQ), were evaluated. The method is linear over 1.0 – 9.0  $\mu\text{g mL}^{-1}$ , with coefficient of determination ( $R^2$ ) equals to 0.9995. The LOD and LOQ were 0.2  $\mu\text{g mL}^{-1}$  and 0.7  $\mu\text{g mL}^{-1}$ . This method is very precise; intraday precision measurements had a relative standard deviation (RSD) value of 4.0%. This RSD value was lower than that required by Horwitz. The mean recovery percentage was 99.1%, indicating that this method could accurately quantify the lithium in the studied mineral. The percentage of lithium oxide in the spodumene mineral sample was 0.33–0.39%.

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## Introduction

Lithium is found in minerals, clays, and brines in various parts of the world [1]. Brines and hard rock sources such as spodumene and lepidolite (mica), are the most commonly mined lithium sources [2-7]. Mining lithium from hard rock involves one of two processes: the soda ash method or the sulfuric acid method [8-11]. Both methods involve various types of separation, precipitation and purification before the lithium is isolated as a salt.

Lithium minerals are very resistant to chemical attack. Thus the dissolution of lithium minerals includes an initial calcination step, followed by acid digestion with strong mineral acids such as sulfuric acid, hydrochloric acid, and hydrofluoric acid. These acids may be used alone or in combination to completely decompose the mineral samples. In this study, the lithium minerals were dissolved using hydrofluoric acid, according to [12] and sulfuric acid to achieve complete dissolution of the sample. The leach liquor also contains significant amounts of Na, K, Mg, Ca, Al, Fe, and other elements, which affects the quantification of lithium using flame atomic absorption spectrometry (FAAS). Thus, the objective of this study was to develop and validate a method to quantify the lithium in spodumene mineral leachate solutions prior to its separation.

## Experimental

### I. Instrument and Apparatus

A shimadzu AA-6300 atomic absorption spectrophotometer (Shimadzu corporation, Kyoto, Japan) controlled by a computer was used to quantify the amount of lithium after optimizing the working conditions of the instrument; a Siemens D5000 XRD diffractometer (Panalytical, Holland) was used for semi quantitative analysis of the mineral ores; and a platinum crucible was used for the acid dissolution of the samples. Grade B volumetric flasks and glassware were used throughout the study.

### II. Chemicals and reagents

A multi-element standard stock solution containing 1000  $\mu\text{g mL}^{-1}$  of Li, Na, K, Ca, Mg, Al, Fe and other metals (Merck, Germany) was used for calibration. Analytical grade  $\text{H}_2\text{SO}_4$  (95-98%, ACS), and HF (40% v/v, Sigma Aldrich) were used for sample digestion. Ultra-pure water was used for all dilutions. Lithium carbonate, (99.7 % trace metal basis) was used to check the matrix interference on the repeatability of the method. A lithium ore (spodumene) standard reference material (SRM) 181 (NIST, Washington, D.C.) was used to check the accuracy of the method.

### III. Sample origin, preparation and calcination

The spodumene and lepidolite mineral samples were taken from a pegmatite hard rock deposit located at the North Cape of South Africa. Semi-quantitative analyses were performed with a Siemens D5000 XRD diffractometer. The calcination of spodumene was performed in a laboratory muffle furnace at a temperature of 1050 °C for one hour.

The furnace was heated to 1050 °C before the sample was introduced. At the end of the calcination process, the crucible was removed from the furnace, and cooled slowly in air at room temperature. A sub-sample of the calcined spodumene mineral was crushed, ground and sieved through a 53  $\mu\text{m}$  sieve. Aliquots of approximately 0.5 g of the crushed and pulverized sample was accurately weighed to the nearest 0.1 mg and placed into a platinum crucible, and a few drops of  $\text{H}_2\text{SO}_4$  and 1.0 mL of HF were added. The crucible was heated at 250 °C to near dryness.

Then, the crucible was cooled and leached with water at a temperature of 90 °C for 30 minutes. The resulting solution was cooled and filtered into a 100.0 mL volumetric flask and analyzed using flame atomic absorption spectrometry (FAAS). SRM samples of spodumene and lithium carbonate were similarly digested and analyzed using FAAS. Digestion of the samples was carried out in triplicate.

## VI. Method validation

Method validation was performed by assessing a set of validation parameters according to [13] including linearity and range, precision, accuracy, limit of detection (LOD) and limit of quantitation (LOQ).

### Results and Discussion

#### I. X-ray diffraction (XRD) analysis

Figure 1 show the XRD patterns for the mineral samples that were investigated. The composition of the mineral samples were determined by automated searching and matching the more intensive XRD patterns obtained, with the XRD patterns of known minerals. Therefore, the composition of the spodumene mineral sample investigated was primarily composed of lepidolite (81%), plagioclase (8%), K-feldspar (5%), and spodumene (6%). Hence, the amount of spodumene was found to be very low in spodumene mineral sample.

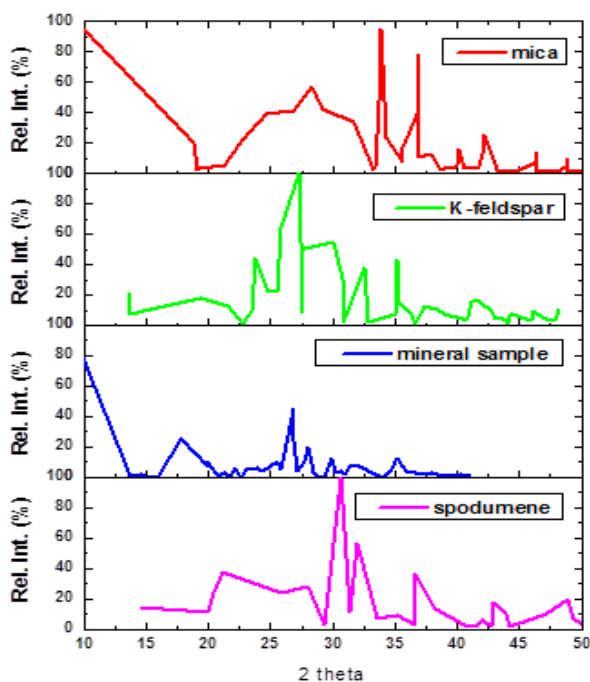


Figure 1. XRD pattern of mica, k-feldspar, spodumene mineral sample and spodumene

#### II. Optimization of instrument working conditions

The optimum working conditions for instrument operation were selected after carrying out a number of trials in which the instrumental parameters were varied in an oxidizing air-acetylene flame. The optimized instrumental parameters are shown in Table 1.

Table 1. Optimized operating conditions and analytical performance for determining lithium

Parameters	Values
Wavelength, nm	670.8
Slit width, nm	0.2
Lamp mode	NON-BGC
Flame type	Air-acetylene
Acetylene flow rate, L min <sup>-1</sup>	13.3
Support gas flow rate, L min <sup>-1</sup>	1.2
Burner height, mm	7
Burner angle, degree	0
Measuring range, g mL <sup>-1</sup>	0.7-10
LOD, g mL <sup>-1</sup>	0.2
Precision, %	4

LOD = (3.3.SD)/slope; Precision is expressed as the mean % RSD of four independent series of measurement (n = 24)

## III. Method Validation

### Linearity and working range

The linearity of the response was studied by aspirating a series of multi-element standard solutions into the flame atomic absorption spectrometry (FAAS) and plotting the corresponding absorbance against concentration.

A linear relationship was obtained with a very high coefficient of determination ( $R^2$ ) equals to 0.9995 as shown in Figure 2.

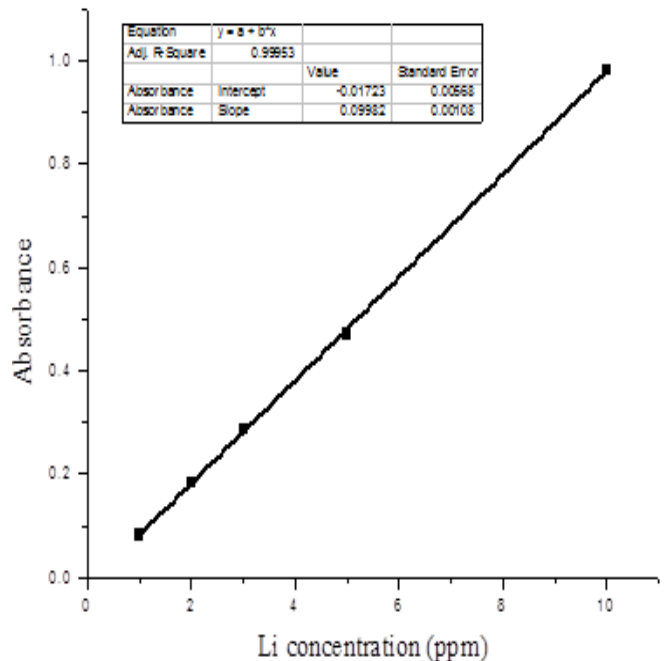


Figure 2. Calibration curve of lithium standards

### Limit of detection (LOD) and limit of quantitation (LOQ)

The LOD and LOQ were calculated based on the standard deviation of the signal (n = 15) and the slope of the calibration curve. The LOD and LOQ were 0.22  $\mu\text{g mL}^{-1}$  and 0.66  $\mu\text{g mL}^{-1}$  respectively. The sensitivity of the method was good with lithium found in concentrations greater than 1.0  $\mu\text{g mL}^{-1}$  in the studied mineral sample.

### Precision

The precision of the method was determined by calculating the repeatability of four independent series of measurements for four standard sample solutions. In each series six repetitions were made as shown in Table 2. The repeatability was calculated as the mean of the %RSD values for the individual series. The repeatability value obtained was 4.0%, which is below the AOAC's maximum acceptable RSD value of 11 %, as cited in [14].

Table 2. Lithium quantification in the standard samples

Li standard sample	Number of results	Standard deviation	%RSD
1	6	0.306	5.29
2	6	0.133	3.38
3	6	0.196	3.99
4	6	0.113	3.35

### Accuracy

The accuracy of the method was checked by comparing the differences between the measured result and the certified result for the SRM 181 with expanded uncertainty (k = 2). The results are shown in Table 3.

The described method quantified the lithium in the mineral sample accurately enough that the measured value was in conformity with the certified value.

**Table 3. Lithium quantification in spodumene SRM sample**

SRM 181(spodumene) sample	% Li <sub>2</sub> O measured value	% Li <sub>2</sub> O certified value	% Recovery
1	6.33	6.39	99.06
2	6.29	6.39	98.44
3	6.37	6.39	99.06
CI for the mean at the 95% CL	(6.33 ± 0.1)	(6.39 ± 0.05)	(99.06 ± 1.6)

**Quantification of Lithium in spodumene mineral sample**

Using the developed and validated method, the amount of lithium in several spodumene samples was quantified. The results are shown in Table 4. The percentage of lithium oxide in the spodumene mineral sample was  $0.36 \pm 0.03\%$ .

**Table 4. Quantification of lithium in spodumene mineral samples**

Spodumene mineral sample	% Li <sub>2</sub> O
1	0.37
2	0.36
3	0.35
Average	0.36
Standard deviation	0.01
%RSD	2.78
CI for the mean at the 95% CL	0.36 ± 0.03

**Conclusions**

A method to quantify lithium in mineral samples using flame atomic absorption spectrometry (FAAS) was successfully developed and verified. However, the use of HF to dissolve spodumene poses both environmental and health hazards. Hence, alternative dissolution techniques should be investigated.

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