Application Note

Lithium Analysis of Spodumene Ore by Quantitative X-Ray Diffraction

by

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AXT Application Note

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Abstract

Spodumene is a lithium-rich mineral. The importance of lithium is growing proportionally to the demand for lithium-ion rechargeable batteries which are used in the ever-increasing number of portable electronic devices that are permeating our lives.

As is the case with assessing other mineral deposits, ensuring high content of the target element (in this case lithium) in the ore deposits is of the utmost importance to the profitability of the mine. For most ores, this is determined by XRF, however, XRF is unsuitable for lithium content determination. Hence we outline a procedure to quantitatively determine lithium content in spodumene-bearing ores using XRD.

XRD is a fast and simple analytical technique that requires little sample preparation and takes only a few minutes to generate results. It can be used to determine the mineralogy of rocks. From quantitative mineralogy, the concentration of elements in the sample can be calculated.

Spodumene

Spodumene is a lithium-bearing mineral with the chemical composition $LiAlSi_2O_6$ and a molecular weight of 186.09 g/mol. The nominal composition of spodumene is given in table 1.

Table 1. Spodumene composition (wt.%) [1,2].

	Elemental		Oxide
Li	3.73	Li_2O	8.03
Al	14.50	Al_2O_3	27.40
Si	30.18	SiO_2	64.58
O	51.59		
Total	100.00		100.00

A number of studies have been carried out looking at variations in the composition of spodumene. The overwhelming consensus from these studies is that regardless of the source and other surrounding minerals, there are only minor deviations from the ideal chemical formula [3,4].

Industrial Significance

Lithium has traditionally found application in ceramics, glass, aluminium alloys and high-temperature grease.

In more recent times, lithium has become increasingly important with the rising use of lithium-based rechargeable batteries in portable electronic devices such as mobile phones, laptop computers, tablets, i-devices etc.

Lithium-ion batteries, first introduced commercially by Sony in 1991, have become the battery technology of choice. Their popularity has grown due to their energy density, high cycle resistance and long life span. For these reasons they are more desirable than other competing technologies such as NiMH and NiCd [5].

The increasing demand for Li-ion batteries is driving the demand for high-purity lithium and hence spodumene. Some other applications do not require high purity lithium sources. In these cases lithium can be derived from brines.

Quantification of Lithium

Lithium content is typically determined by acid digestion followed by ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry) or AAS (Atomic Absorption Spectroscopy).

XRF is a well-accepted analytical technique, commonly used in industry for determination of elemental composition. The sample is presented as either a pressed powder or fused bead. Compared to wet chemical methods (ICP-OES and AAS), XRF is faster and does not require chemical digestion using potent acids such as HF. However, XRF analysis of lithium is not possible (in particular for most EDXRF instruments) due to its low atomic number which produces a fluorescence signal that is too weak to be detected by the XRF technique.

X-Ray Diffraction (XRD)

XRD is a staple tool for phase identification in geology and materials science. It is commonly used to determine the modal composition of crystalline materials. In mining operations, the knowledge of which mineral your target element is present in is crucial to its efficient and successful extraction as different minerals behave differently in minerals processing plants. In the case of lithium, it could be present in minerals such as spodumene, petalite, lepidolite, amblygonite and zinnwaldite.

While XRF can provide elemental data from which the oxide content can be calculated, XRD is able to determine which phases are present and the actual mineral polymorph e.g. Silica (SiO_2) could be (theoretically) present as quartz, cristobalite or tridymite. Similarly, in the analysis of aluminosilicates, XRF can only determine Al_2O_3 and SiO_2 content. It is unable to distinguish between different minerals e.g. Quartz (SiO_2), corundum (Al_2O_3), bauxite ($Al(OH)_3$), silliminate ($Al_2O_3 \cdot SiO_2$), kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$), etc.

For XRD analysis the sample is presented as a finely pulverised powder and is analysed in air. There are no complex and time-consuming sample preparation procedures required such as acid digestions, fused bead preparation or pressing/binding samples. Modern advances in XRD instrumentation and software require only a few keystrokes and few minutes of measurement to generate a complete analysis. This means that the benchtop Rigaku Miniflex XRD instrument is ideally suited for all exploration and mining operations without the need to set up a laboratory with acid extraction systems, hot plates, vacuum pumps nor argon/acetylene gases.

In this application note we provide the methodology to perform a quantitative XRD analysis of lithium in spodumene ore. We demonstrate how this technique can be used in a remote mine site laboratory by operators with minimal training.

Methodology

Spodumene ore samples were pulverised and then analysed using a Rigaku MiniFlex 600 benchtop XRD. The MiniFlex 600 is the most powerful benchtop XRD on the market and is capable of producing publication quality data.

Figure 1. Rigaku MiniFlex 600 benchtop XRD (left) with ASC-6 (6 sample multi-changer) and D/tex Ultra 2 speed silicon strip detector (right).

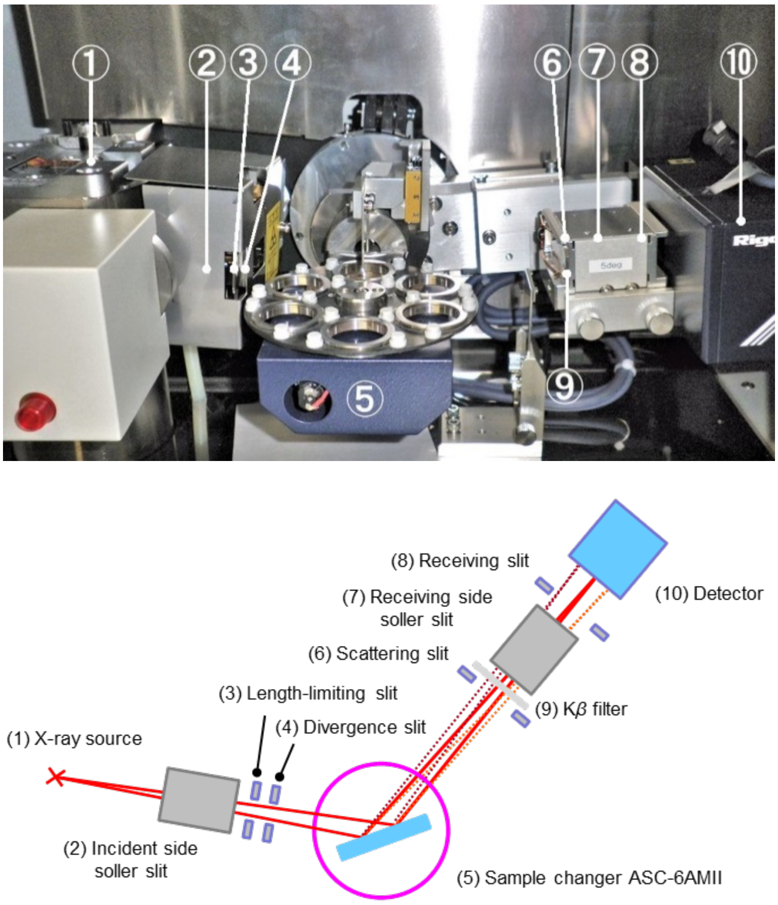

Figure 2. MiniFlex optical configuration.

The system comes with Rigaku Guidance software that controls all operations and configurations of the instrument. The PDXL software in conjunction with the ICDD (International Centre for Diffraction Data) PDF-4+ database of diffraction data was used to identify the phases present in the samples. The WPPF (Whole Pattern Profile Fitting) function was then used to generate quantitative analyses. Apparatus configuration and measurement conditions are provided in tables 2 and 3 respectively.

Table 2. Miniflex configuration.

Apparatus Configuration	
X-Ray source	Cu Kα (1.54186 Å)
Goniometer radius	150mm
Incident optics	
Divergent Slit	1.25°
Incident Soller slit	Soller slit 2.5°
Length-limiting slit	10mm
Attachment	ASC-6 (6 sample autochanger)
Receiving optics	
Scattering slit	8mm
Receiving Soller slit	Soller slit 2.5°
Receiving slit	13mm
Detector	
Detector	D/tex Ultra 250
Monochromator	Kβ filter

Table 3. Experimental measurement conditions.

Measurement Conditions	
Voltage-Current	40kV – 15mA
Scan axis	2θ / θ
Scan mode	Continuous
Scan range	10 – 40°
Scan Speed	8°/min
Step size	0.02°
Sample spinner	On

Experimental Procedure

5 pulverised spodumene ore samples were obtained.

The following procedure was followed to produce and export results including quantitative analysis.

1. Pack samples into round sample holders and load into ASC-6 automatic sample changer
2. Add samples to analysis list in Smartlab guidance software, program measurement conditions and commence measurement
3. Import measured patterns into PDXL software. WPPF analysis is performed automatically using a template with all mineral phases
4. A report can be created or results can be exported to a file in .csv format

The high power output of the Miniflex enabled each sample to be scanned in less than 4 minutes. The auto sample changer provides ultimate efficiency resulting in data for all 5 samples to be collected in less than 20 minutes.

Results

Figure 3 shows the diffraction pattern for sample C. Using PDXL and PDF-4+, all crystalline phases were identified.

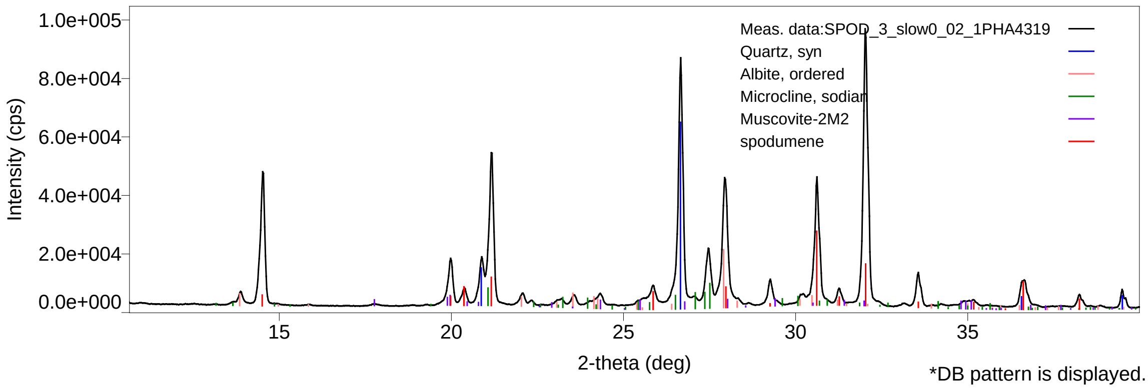

Figure 3. Diffraction pattern for sample C showing all phases present.

As can be seen from the diffraction pattern, there was no evidence to suggest the presence of any other lithium-bearing mineral such as lepidolite or petalite.

Once the phases were identified, an analysis template was created. Using the WPPF method (Rietveld) included in the PDXL software, the percentages of each mineral could be quantified. Table 4 shows the results of this analysis.

The quantitative analysis of the ore samples provides the mineralogical composition. From this, the Li_2O content can be calculated by virtue of the fact that spodumene (theoretically) contains 8.03 wt.% of Li_2O. All Li_2O can be attributed to spodumene as no other lithium-bearing minerals were detected via XRD. Even if other lithium-bearing minerals were detected, they could also be taken into account during the WPPF analysis and their contributions estimated based on their chemical composition.

Table 4. Quantitative analysis of spodumene ores (wt. %).

	Sample				
	A	B	C	D	E
Method	WPPF	WPPF	WPPF	WPPF	WPPF
Quartz, syn	56.3	46.1	26.3	55.6	17.5
Albite, ordered	15.7	9.78	4.77	25.6	6.89
Microcline	21.2	9.38	7.83	7.12	0.52
Muscovite-2M2	4.05	6.71	4.86	4.50	8.71
Spodumene	**2.76**	**28.0**	**56.2**	**7.19**	**66.4**
Li_2O (XRD)	0.22	2.24	4.50	0.58	5.31

The quantitative XRD analysis using the WPPF method is in excellent agreement with the wet chemical analysis data provided by a third party (Li_2O assay) and is represented graphically in figure 4.

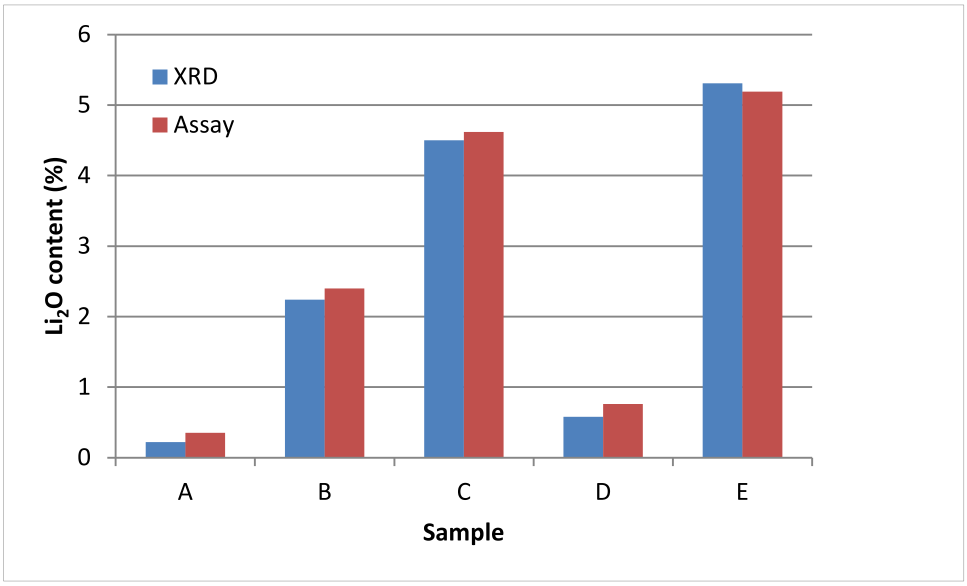

Figure 4. Comparison of Li_2O content determined by quantitative XRD analysis and wet chemical methods.

Summary

Economically important ore samples are typically analysed for elemental composition using XRF spectrometers. XRF is typically unsuitable for determination of the lithium content of ores like spodumene as lithium is beyond its detection limits due to its low atomic number.

Herein, we have outlined a methodology for rapidly determining the lithium content of spodumene ore using XRD. The quantitative analysis determined by XRD is consistent with wet chemical analysis.

XRD has the advantage that sample preparation and measurements can be collected very quickly and involves essentially no consumables. Wet chemical techniques such as ICP-OES and AAS require four acid digestion using HCl, HNO_3, HF and $HClO_4$ as well as costly OH&S compliance. Furthermore, the Rigaku MiniFlex benchtop XRD can be easily installed in a mine site laboratory aiding rapid analysis and improved analytical responsiveness for plant optimisation.

References

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2. Spodumene Mineral Data, accessed August 28, 2016
3. J. Filip, M. Novák, and R. Zbořil, (January 2006) "**Spodumene from granitic pegmatites of various genetic types: crystal chemistry and OH defects concentrations",** Physics and Chemistry of Minerals, 32 (10):733–746
4. Charoy B, Lhote F and Dusausoy Y. (1992) "**The crystal chemistry of spodumene in some granitic aplite pegmatite of northern Portugal",** Canadian Mineralogist 30: 639-651.
5. What is the best battery?, Accessed August 28, 2016

About the Authors

Dr. Stanislav Ulitzka

Stani is a mineralogist with more than 25 years of experience working with XRD, XRF and other complimentary technologies including sample preparation. He is well versed in these analytical technologies and has worked with instruments from all major manufacturers including Rigaku.

He regularly presents papers at AXAA conferences (Australian X-ray Analytical Association) and the Denver conference (2011). Stani is also available to conduct training on both XRD and XRF and can also help you develop analytical methodologies to suit your specific application.

Dr. Cameron Chai

Cameron has a Ph.D in materials science and has hands on experience working with analytical techniques including XRD. He has an extensive list of publications including refereed journal papers and technical articles published in trade magazines and web portals. He has also presented at international conferences.

With over 25 years working in research and industry with numerous manufacturers and technologies, his broad knowledge enables him to understand the client's requirement and the solution required.

Melissa Narbey

Melissa is an analytical chemist who has worked for many years with the mining industry in high throughput laboratories. She appreciates a robust, simple and fast technique that gives a precise and accurate solution.

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