Analysis of lithium raw materials with WDXRF

Introduction

Global demand for lithium extraction is growing, particularly due to increased use of consumer electronics and vehicles that rely on lithium-ion batteries. Lithium is mined from both hard rock and underground brine deposits. This brine is extracted from salars (salt-encrusted depressions in the earth) and pumped into evaporation ponds, where the sun concentrates the brine. Lithium carbonate is then precipitated using soda ash or lime, and can be further processed into lithium hydroxide, which is used in applications such as new high-nickel battery cathodes. The extraction of lithium salts consists of multiple discreet steps, each requiring various materials that must be analyzed and monitored throughout the process, including calcium carbonate, sodium carbonate, and alkaline solutions. Although lithium itself cannot be measured by wavelength-dispersive X-ray fluorescence (WDXRF) spectroscopy, the other elements composing these materials (i.e., calcium, potassium, sodium, etc.) can be analyzed with wide-concentration-range calibration curves.

Generally speaking, WDXRF is one of the most frequently used techniques for the analysis of geological base materials, particularly due to its accuracy, precision, wide dynamic range of concentrations (from ppm to 100%), and simplicity compared to other analytical techniques. Thermo Fisher Scientific has designed a calibration specifically for lithium-salt applications, based on our well known "Soils and Sediments" factory calibration.

Instrument

A 4,200-watt Thermo Scientific™ ARL PERFORM'X™ WDXRF Spectrometer was used for the analyses in this application note. This system is configured with 6 primary beam filters, 4 collimators, up to nine crystals, two detectors, and a helium purge. It is also fitted with a 5GN+ Rh X-ray tube, which offers high-quality performance for a broad range of elements, from ultra-light to heavy, thanks to its 50-µm beryllium window. This novel X-ray tube uses a low-current filament that ensures high analytical stability over an extended period. Designed for demanding laboratories, the ARL PERFORM'X Spectrometer offers dual sample loading to minimize analysis time as well as rapid and precise analysis of up to 84 elements. The system also offers high performance and sample-analysis safety with its unique LoadSafe design, which includes a series of safety features for reliable sample pumping and loading. For instance, liquid cassette recognition prevents any liquid sample from being exposed to vacuum by mistake. An over-exposure safety automatically ejects a liquid sample if X-ray exposure time is too long.

The Thermo Scientific ARL PERFORM'X WDXRF Spectrometer.

The ARL PERFORM'X Spectrometer also features the Secutainer System, which protects the primary chamber by collecting any loose powder in a specially designed container that is easy to remove and clean. Additional spectral chamber protection is offered by a helium shutter that is designed for absolute protection of the goniometer during liquid analysis under a helium environment. In the "LoadSafe Ultra" optional configuration, a special X-ray tube shield provides further protection against sample breakage or liquid cell rupture.

When additional analytical capabilities are needed, the ARL PERFORM'X Spectrometer offers optional small spot analysis and elemental mapping at 1.5 mm or 0.5 mm sizes. These tools enhance the capabilities of the XRF system by providing additional screening, contamination identification, inclusion analysis, and segregation/non-homogeneity mapping.

Sample preparation

Fusion-bead preparation of mineral samples is generally not appropriate for trace-element XRF analysis, largely because of the dilution ratio, which makes determination of very low concentrations (i.e., 1–10 ppm) difficult. For this reason, pressed pellets are a more suitable sample preparation for trace-element XRF analysis. The physical effects of pellet formation, which can at times influence the accuracy of results, were not found to be significant for this analysis. Samples were dried and mixed with 10% by weight Hoechst wax C micropowder (MilliporeSigma) and pressed at 20 tons for 20 seconds, producing 40-mm diameter pellets that were ~5 mm thick (Figure 1).

Figure 1. Pressed mineral sample pellets prepared for XRF analysis.

Calibration and results

The standard "Soils and Sediments" calibration (XR-CAL-SEDI) was fine-tuned using additional samples of materials typically used in the lithium-salt extraction process. Certified reference materials (CRMs) are not easily available for lithium-salt compounds; therefore, raw materials were used instead to extend some of the calibration ranges. Materials such as KCl, $CaCO_3$, Li_2CO_3, $CaSO_4$, and various lithium-salt samples were prepared as pressed pellets. A working curve was established for each element using the multi-variable-regression incorporated in Thermo Scientific™ OXSAS™ Software. Theoretical alpha factors were used for all matrix corrections. Concentrations of elements that cannot be measured with WDXRF were defined using manual input.

The ability to accurately analyze trace elements in geological samples depends on the instrument's sensitivity, resolution, and background/overlap correction functions. Figures 2 and 3 illustrate the accuracy and precision achievable with the ARL PERFORM'X Spectrometer thanks to the background correction of its digital goniometer and its unique optical design. Analysis of most elements in this application note was carried out using background correction. Depending on your specific experimental needs, the total analysis time can be shortened by disregarding elements that are non-essential or that do not occur in some compounds.

Overall, the main elements of the lithium raw materials were quantified in less than six minutes.
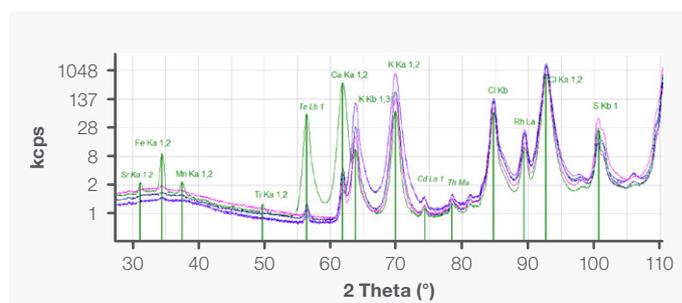
Figure 2. 2θ pack scan from 28 to 108 degrees using a Ge111 crystal and flow-proportional detector.
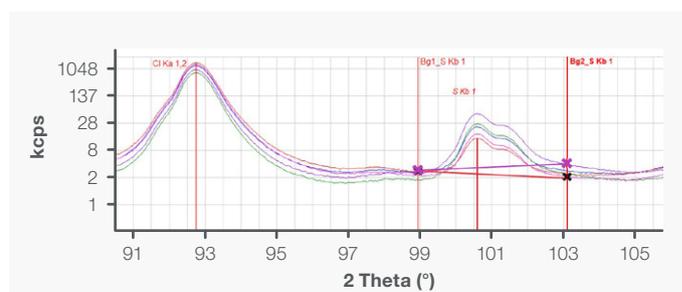
Figure 3. Close up of the 90–105° 2θ region in Figure 2.

Compound	Line	Analytical ranges	SEE	LoD (ppm)	Time (s)
Ag	Ag K_α	LoQ–35 ppm	2.5 ppm	2.5	40
Al_2O_3	Al Ka	LoQ–15.7%	0.47%		20
As	As K_β	LoQ–620 ppm	21 ppm	2	20
Ba	Ba L_β	LoQ–0.12%	48 ppm	2	40
Bi	Bi La	LoQ–90 ppm	1.3 ppm	0.8	40
CaO	Ca K_α	LoQ–31.5%	0.15%		20
Cd	Cd K_α	LoQ–78 ppm	8 ppm	2.5	40
Ce	Ce L_β	LoQ–192 ppm	12 ppm	3.8	40
Cl	Cl K_α	LoQ–58.8%	1.4%		40
Co	Co K_α	LoQ–81 ppm	2.7 ppm	0.6	40
Cr	Cr K_α	LoQ–0.43%	21 ppm	0.6	40
Cu	Cu K_α	LoQ–0.5%	35 ppm	0.5	40
F	F K_α	LoQ–0.19%	120 ppm		40
Fe_2O_3	Fe K_α	LoQ–28.2%	0.48%		20
Ga	Ga K_α	LoQ–27.4 ppm	1.2 ppm		40
Hg	Hg L_α	LoQ–10 ppm	2 ppm	1.4	40
K_2O	K K_α	LoQ–51.7%	44 ppm		20
La	La L_α	LOQ–90 ppm	3 ppm		40
MgO	Mg K_α	LoQ–8.26%	0.44%		20
Mn	Mn K_α	LoQ–1.01%	0.01%	0.7	40
Mo	Mo K_α	LoQ–92 ppm	2 ppm	0.4	40
Na	Na K_α	LoQ–41%	0.12%		30
Nb	Nb K_α	LoQ–95 ppm	1.3 ppm	0.3	40
Ni	Ni K_α	LoQ–280 ppm	3 ppm	0.7	40
P	P K_α	LoQ–0.3%	76 ppm		40
Pb	Pb L_β	LoQ–0.55%	78 ppm	1.2	40
Rb	Rb K_α	LOQ–470 ppm	6 ppm	0.3	40
S	S K_α	LoQ–33.9%	0.21%	1.2	40
Sb	Sb L_β	LoQ–38.4 ppm	0.6 ppm	3.5	40
Si	Si K_α	LOQ–77.3%	1.4%	50	10
Sn	Sn L_α	LoQ–370 ppm	11 ppm	3.5	40
Sr	Sr K_α	LoQ–340 ppm	16 ppm	0.5	40
Th	Th L_β	LoQ–70 ppm	2 ppm	0.6	40
Ti	TiO_2	LoQ–0.86%	0.017%		20
U	U L_α	LoQ–17 ppm	1.3 ppm	1	40
V	V K_α	LoQ–346 ppm	5 ppm	0.5	40
W	W L_α	LoQ–126 ppm	3 ppm		40
Y	Y K_α	LoQ–67 ppm	5 ppm	0.5	40
Zn	Zn K_α	LoQ–0.69%	19 ppm	0.5	40
Zr	Zr K_α	LoQ–460 ppm	11 ppm	0.4	40

Table 1. Results of pressed pellet analysis with working concentration ranges for each compound.

Table 1 shows the elements that were detected in each pressed pellet, along with their working concentration ranges, the standard error of estimate, and the limits of detection. Major compounds found in lithium ores are highlighted in gray. (Note: LoD = limit of detection; LoQ = limit of quantification = 3 x LoD; SEE = standard error of estimate; ppm = parts per million.)

Figures 4–6 are the calibration curves derived from the pressed pellets samples. The Y-axis intensity represents the net peak height (i.e., peak intensity minus background intensity).
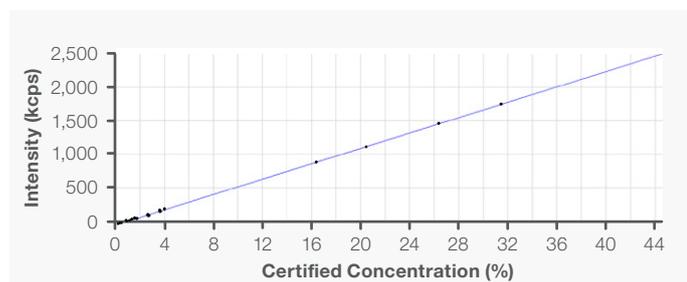
Figure 4. Calibration curve for calcium (Ca K$\alpha_{1,2}$).
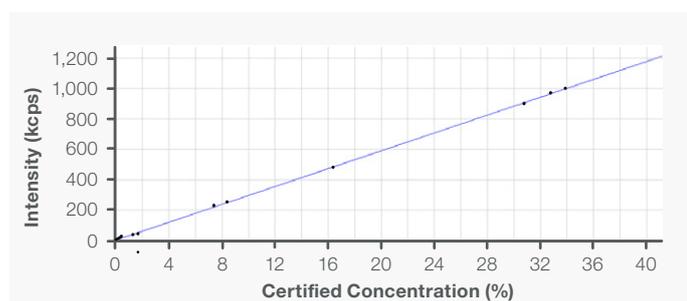
Figure 5. Calibration curve for sulfur (S K$\alpha_{1,2}$).
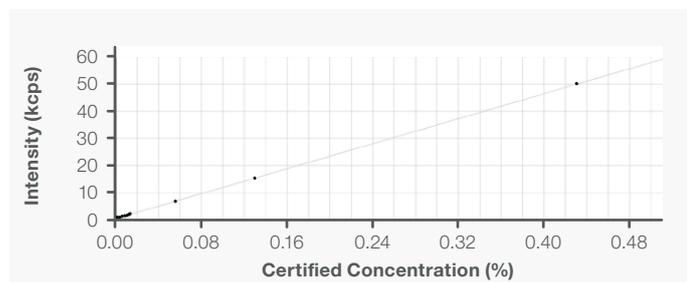
Figure 6. Calibration curve for chromium (Cr K$\alpha_{1,2}$).

Conclusions

Quantitative analysis of lithium ores is enabled by the high-performance ARL PERFORM'X WDXRF Spectrometer along with a unique tailored calibration, which permits the analysis of materials across the lithium-salt extraction process. Data was easily interpreted using state-of-the-art OXSAS Software (compatible with Microsoft Windows 10). Note that all calibration ranges could be extended with the addition of in-process standard samples.

Designed to be broadly applicable, this analysis and calibration method allows for a complete and versatile elemental analysis for many different material types. Additionally, pressed-pellet sample preparation expands the range of workable specimens by being fast, easy, and reliable.

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