



# Trace Element Analysis of Pegmatite Lithium Ores by GDMS

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## Introduction

The lithium-ion battery (LIB) industry sources high purity lithium carbonate and lithium hydroxide from lithium-rich brines and “hard rock” lithium ore. Hard rock lithium is mainly found in spodumene and petalite – lithium-aluminum-silicates found in pegmatite deposits. As the world shifts to more sustainable and equitable mining, it is important to be able to differentiate among ore sources to ensure supply chain integrity. Different deposits have potentially unique ratios of trace element concentrations which can serve as “fingerprints” for source discrimination and traceability of lithium products. Elemental concentration ratios from techniques such as XRF and LA-ICP-MS are widely used in geochemistry and archaeometry for source discrimination studies of geomaterials.<sup>1</sup>

Furthermore, battery manufacturers are demanding increasingly stringent purity requirements for lithium carbonate and lithium hydroxide products manufactured from hard rock lithium. GDMS is positioned to expand the list of measurable trace impurities beyond the limited set traditionally measured by ICP-OES.

## Glow discharge mass spectrometry (GDMS)

GDMS is a solid-state sampling technique able to perform fast, reliable analysis of minor and trace elements down to sub-ppm level. GDMS combines a glow discharge source to a high-resolution magnetic sector mass spectrometer, providing excellent sensitivity and mass resolution. The vast majority of commercially available GDMS instruments utilize a direct current (DC) source. Samples analyzed using DC current are introduced to the cell as the cathode. Nonconductive samples may be analyzed using binders or working electrodes to support the plasma and enhance analysis.

During discharge, the sample is bombarded with positive ions from the argon plasma. Consequently, the cathode releases neutral atoms which diffuse into the plasma and get ionized (figure 1). Ion beam intensities of all analyte elements are then measured using a combination of analog and digital detectors and evaluated in reference to a matrix element or normalized to multiple matrix elements. These ion beam ratios are converted to mass fractions using adjustment factors called relative sensitivity factors (RSFs). RSF values account for the different elemental ion yields in the plasma.

GDMS is a standardless technique and results are biased to within a factor of 2. Recent work at Eurofins EAG Laboratories has developed a generalized mixed oxide RSF set to enable more accurate analysis of nonconductive oxide materials on a tantalum (Ta) holding electrode.<sup>2</sup>

There are 2 geometries samples can be analyzed in: flat and axial. The flat geometry allows for surface analysis, depth profiling, and analyzing thick films. The sampling orifice is ~10mm in diameter. The axial geometry is ideal for conductive pins 20mm long and 2mm wide, powders, and small chunks ~8mm long and ~1.5mm wide. While the axial geometry lacks spatial resolution, it provides higher signal than the flat geometry.

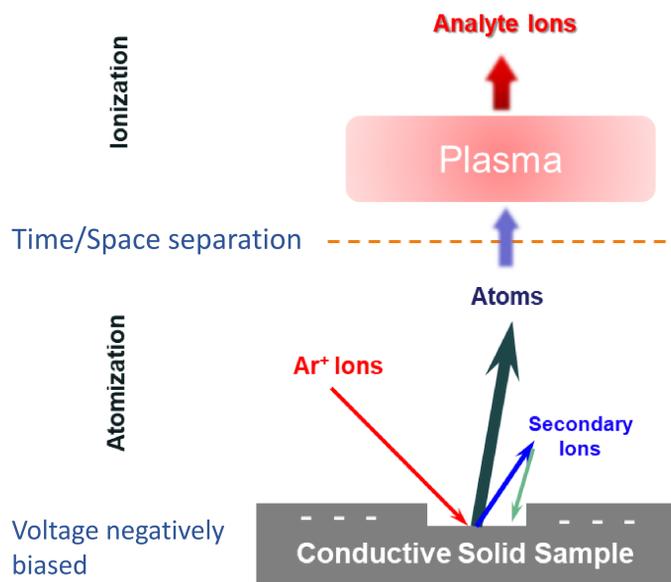


Figure 1. Schematic of glow discharge analysis of a conductive sample.

## Methods

Five commercially available OREAS lithium ore standards (OREAS 750, 751, 752, 753, 999) were processed into nanopowders by myStandards GmbH and were analyzed using an Ametek Nu Instruments Astrum GDMS. Approximately 10 mg of powder were loaded onto a chemically cleaned Ta holding electrode (figure 2). The Ta electrode was cleaned using a 1:1 HNO<sub>3</sub>:HF solution and rinsed with deionized water and lastly with ethanol.

The samples analyzed with a 3.0 mA fixed current and 1000 volts, with argon flow adjusted to achieve the desired voltage. The samples were analyzed in triplicate across multiple days to catch the variability in preparation from day to day.

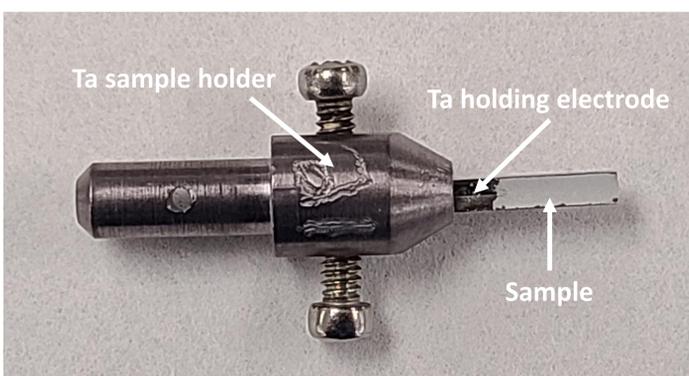


Figure 2. OREAS 753 sample on a Ta holding electrode

## Results & Discussion

Table 1 shows the relative variance between the standards for a given element and the percent recovery relative to the certified OREAS. Out of 54 analyzed elements, including elements with indicative values, 10 were within 10% recovery, 20 were within 25% recovery, and 48 were within a factor of two of the certificates – the expected methodological precision range for GDMS. More importantly, the inter-sample variance of the measured elements across all 5 standards were generally better than 25%, with 45 of the 54 elements exhibiting less than 25% variation between the powders.

## References

- Zipkin, A., et al. Red Earth, Green Glass, and Compositional Data: A New Procedure for Solid-State Elemental Characterization, Source Discrimination, and Provenience Analysis of Ochres. *J Archaeol Method Theory* 27, 930–970 (2020).
- Bartov, G., and Putyera, K. New Oxide-Specific RSFs to Improve Non-Conductive Oxide Materials Analysis by GDMS. *Application Note*. <https://www.eag.com/app-note/rsf-to-improve-analysis-by-gdms/>

Table 1. Inter-sample deviation and percent recovery relative to OREAS certified values.

Element	Inter-sample variance	Percent recovery relative to certified value				
		OREAS 750	OREAS 751	OREAS 752	OREAS 753	OREAS 999
Li	15%	136%	108%	100%	99%	96%
Be	5%	179%	189%	204%	201%	200%
B	60%	-	145%*	33%*	107%*	-
Na	11%	109%	94%	83%	89%	103%
Mg	11%	141%	131%	134%	165%	127%
Al	8%	126%	117%	104%	106%	114%
Si	4%	89%	91%	96%	97%	94%
P	6%	178%	186%	194%	206%	183%
S	12%	180%	202%	223%	241%	191%
Cl	17%	58%*	47%*	63%*	72%*	-
K	14%	146%	125%	121%	104%	146%
Ca	9%	151%	132%	119%	141%	133%
Sc	14%	147%	134%	114%	113%	151%
Ti	9%	144%	134%	126%	113%	140%
V	7%	134%	115%	115%	126%	122%
Cr	34%	127%	199%	71%	172%	146%
Mn	6%	126%	114%	108%	111%	114%
Fe	4%	104%	102%	111%	112%	106%
Co	4%	103%	102%	97%	94%	104%
Ni	7%	113%	101%	100%	105%	95%
Cu	8%	90%	91%	82%	78%	94%
Zn	10%	113%	113%	118%	142%	118%
Ga	20%	131%	106%	90%	80%	92%
Ge	4%	84%	90%	84%	81%	85%
Rb	15%	200%	187%	161%	134%	158%
Sr	19%	181%	164%	122%	121%	128%
Y	8%	218%	205%	180%	183%	194%
Zr	81%	543%	148%	135%	133%	150%
Cd	49%	69%	71%	67%	142%	181%*
Sn	5%	104%	100%	90%	94%	100%
Sb	47%	46%	110%	51%	42%	53%
Te	81%	-	218%*	28%*	44%*	169%*
Cs	21%	189%	169%	151%	104%	144%
Ba	10%	171%	154%	141%	134%	162%
La	9%	218%	199%	196%	186%	233%
Ce	9%	210%	196%	196%	170%	213%
Pr	14%	201%	183%	166%	139%	189%
Nd	15%	200%	192%	175%	134%	183%
Sm	9%	191%	183%	152%	168%	173%
Eu	11%	181%	178%	141%*	-	169%*
Gd	16%	276%	250%	224%	182%	210%
Tb	21%	229%	206%	154%	136%*	189%
Dy	11%	198%	174%	161%	149%	167%
Ho	15%	172%	159%	152%	214%	155%
Er	8%	179%	147%	155%	164%	147%
Tm	29%	184%	169%	87%*	-	175%*
Yb	21%	163%	187%	225%*	-	261%
Lu	28%	206%	254%	123%*	-	198%*
Hf	49%	675%	407%	245%	301%	238%
Tl	11%	83%	74%	84%	96%	76%
Pb	13%	133%	92%	106%	113%	111%
Bi	13%	94%	69%	84%	99%	93%
Th	4%	182%	167%	173%	177%	181%
U	5%	185%	174%	164%	166%	182%

\*Indicative value

## Conclusion

GDMS is able to provide a fast and consistent analytical solution to the increasing demand for traceability and purity requirements from LIB producers. Combined with ICP-MS techniques such as laser ablation, we can provide a full scan of elements; quantifying matrix, major, and minor elements using LA-ICP-MS, and trace elements down to sub-ppm level using GDMS.