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Lithium alloy measurement using B&W Tek's NanoLIBS®-Q Handheld LIBS Elemental Analyzer

Abstract

Lithium alloys, like Li-Al and Li-Mg alloys, are widely used in various industries. For lithium alloy manufacturers, detecting the concentrations of Al in Li-Al alloy and Mg in Li-Mg alloy is a necessary step in daily production and the QC process. B&W Tek's NanoLIBS-Q handheld LIBS elemental analyzer provides a quick and easy solution to lithium alloy manufacturers to make measurements on the production floor.

Introduction of LIBS technology and NanoLIBS-Q

Laser-induced breakdown spectroscopy (LIBS) is a type of atomic emission spectroscopy which uses a highly energetic laser pulse as the excitation source.[1][2] The laser is focused to atomize the sample to form a plasma. The formation of the plasma only begins when the focused laser achieves a certain threshold for optical breakdown, which generally depends on the environment and the target material.[3]

The NanoLIBS-Q is a handheld LIBS elemental analyzer customizable to give quantitative measurements of elements for various material samples. It can detect most elements, especially the light elements Li, Be, B, C. The lightweight NanoLIBS-Q features a high brightness touch screen with an intuitive workflow. The point and shoot operation is used to measure samples directly with results displayed within seconds. The system features a rastering beam to sample an area of 300-400µm diameter.

Lithium alloy

Lithium (Li, atomic number 3) is an extremely light, quite soft, silvery-white metal belonging to the alkali metal group of chemical elements. Like the other metals in the group, it is so chemically active that, in nature, it never occurs as a pure element, but is always bound in stable minerals or salts. Lithium alloy is typically stored in mineral oil to prevent chemical reaction with water, oxygen, carbon dioxide, or even nitrogen.

Lithium is widely used in the industry of atomic energy, aerospace, lithium alloy, lithium battery, controlled nuclear fusion reactor, military, synthetic rubber, and pharmaceuticals. Lithium metal can be categorized by applications into catalyst grade, alloy grade, battery grade. Catalyst grade lithium metal has up to 1% concentration of sodium (Na) and is used as a precursor in the synthesis of various pharmaceuticals and as a catalyst for polymerization.

Alloy grade lithium metal is used in the production of lightweight aluminum lithium alloys, magnesium lithium alloys, and other similar lightweight metal applications. Battery-grade lithium metal is typically composed of >99.8% Li, max. 200 ppm Na, max. 100 ppm K, max. 200 ppm Ca, and max. 300 ppm N.

In factory, the lithium alloys are usually in the form of finished ingots or master alloy batches and are stored in mineral oil and handled in a dry room to prevent furious reaction with water in moist air. Lithium does react with nitrogen or oxygen but the reaction is relatively mild and slow so doesn't affect regular handling processes.

Experiment and results

Lithium ingots must be measured in a dry room or in an argon chamber with low moisture level. In the experiments we used a chamber with the moisture level <2%. The NanoLIBS-Q device can be used in these environments. Gloves are worn to avoid direct skin contact with the lithium alloys to be measured. The lithium ingots were prepared to be clean from oil and with a flat surface for good physical contact with the front nose piece of the NanoLIBS-Q device. Refer to the NanoLIBS-Q user manual for detailed operation procedures.

Comprehensive safety measures for handling lithium metal were followed to prevent hazardous occurrence.

The goal is to effectively detect the concentration of Al in Li-Al alloy and Mg in Li-Mg alloy. The typical concentration values are around 2000 ppm for Al in Li-Al alloy and around 15% - 20% for Mg in Li-Mg alloy. To be more specific, we need to screen Li-Al alloy to three groups based on how close the Al concentration is to 2000 ppm and screen Li-Mg alloy to three groups for High Mg, Medium Mg, and Low Mg. See the tables below, table 1a for Li-Al alloy and table 1b for Li-Mg alloy.

Group	Al concentration
Group A	1500-2500ppm
Group B	1000-1500ppm or 2500-3000ppm
Group C	<1000ppm or >3000ppm

Table 1a: Li-Al alloy

Group	Mg concentration
High Mg	>20%
Medium Mg	15%-20%
Low Mg	<15%

Table 1b: Li-Mg alloy

B&W Tek developed Li-Al and Li-Mg alloy calibrations and put them into NanoLIBS-Q device for the experiments. The calibrations can be further refined by users by measuring standard reference samples following the on-screen instruction. Refer to the NanoLIBS-Q user manual for more details. The quantitative analysis results are displayed on the NanoLIBS-Q display within seconds after measurement, as shown in Figure 1. Five spot averaging was adopted to overcome the unevenness of the concentration distribution in lithium alloy. The detection limit of the instrument is about 200 ppm. A typical LIBS spectrum of Li-Mg measurement is shown in Figure 2.

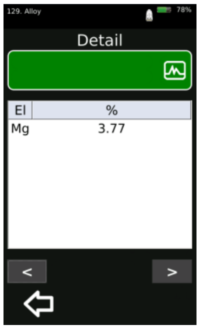

Figure 1: Prediction result on NanoLIBS-Q display

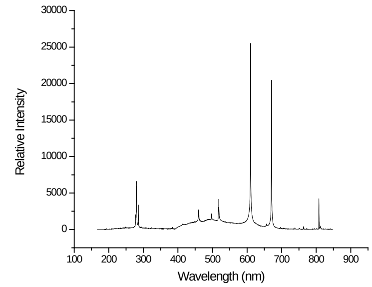

Figure 2: A typical LIBS spectrum of Li-Mg measurement

At beginning of the experiments, we compared the spectra of measurements with the nitride layer on the sample surface removed and with the nitride layer intact. There was no significant difference in the spectra or results. We think it is because the high energy laser pulse easily burns and penetrates the nitride layer. So we shot the samples without removing the nitride layer for the experiments.

The prediction results for Li-Al alloys are shown in Figure 3.

Sample	ICP reading (ppm)	NanoLIBS-Q reading (ppm)						Reading Difference from ICP (ppm)	Accuracy (%)	Standard deviation (ppm)	Precision (%)
		Spot 1	Spot 2	Spot 3	Spot 4	Spot 5	Average				
1	1812	2005	1751	1827	2067	2000	1930	118	6.51%	134	7.40%
2	1903	1834	1948	1996	2010	1999	1957.4	54.4	2.86%	73	3.83%
3	3465	3449	3628	3084	3246	2828	3247	-218	-6.29%	311	8.99%

Figure 3: Al concentration measurement

The samples were measured by ICP-MS in lab before the LIBS experiments to provide the calibration reference values. The five spot averaging results measured by NanoLIBS-Q were very close to the results from ICP-MS, with accuracy within +/-7%. The repeatability of the five-spot measurements was good with precision within 9%.

The prediction results for Li-Mg alloys are shown in Figure 4.

Sample	ICP reading (%)	NanoLIBS-Q reading (%)						Reading Difference from ICP (%)	Accuracy (%)	Standard deviation (%)	Precision (%)
		Spot 1	Spot 2	Spot 3	Spot 4	Spot 5	Average				
1	9.90	10.12	9.28	9.67	9.72	10.72	9.90	0.00	0.02%	0.55	5.51%
2	10.80	11.44	10.70	11.39	11.05	11.69	11.25	0.45	4.20%	0.38	3.56%
3	23.60	20.73	22.72	22.30	23.75	24.57	22.81	-0.79	-3.33%	1.46	6.20%
4	24.60	26.55	24.43	28.57	25.81	24.90	26.05	1.45	5.90%	1.63	6.62%

Figure 4: Mg concentration measurement

As with Li-Al alloys, the Li-Mg alloy samples were measured by ICP-MS in lab before the experiments as references. The five spot averaging results measured by NanoLIBS-Q were very close to the results from ICP-MS, with accuracy within +/-6%. The repeatability of the five spot measurements has precision within 7%.

Conclusion

B&W Tek's handheld LIBS platform provides superior performance when conducting elemental material analysis, especially for light elements. In this work we demonstrated the ability of NanoLIBS-Q for the lithium alloy measurement with accurate and precise quantitative analysis of Al and Mg for daily production and QC process in lithium factory without needing to transport samples to the analytical laboratory.

References

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3. J. P. Singh and S. N. Thakur (2007), Laser-Induced Breakdown Spectroscopy, 1st ed. Elsevier.

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