Aluminium Two Thousand World Congress and
International Conference on Extrusion and Benchmark ICEB 2017

Rapid sorting of aluminum alloys with handheld μLIBS analyzer

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Abstract

The most successful and best suited for rapid identification of alloys in field has been Handheld X-Ray Fluorescence (HHXRF). However, the XRF has inherent difficulty in analysis of many important aluminum alloys as well as other alloys containing low atomic number elements such as lithium, beryllium, boron, silicon or magnesium. The common practice to overcome this deficiency has been use of Optical Emission Spectroscopy (OES) or – most recently – Laser Induced Breakdown Spectroscopy (LIBS). Both these techniques can analyze all alloys the XRF can and especially those the XRF cannot. Recent technological advancements made possible design of handheld analyzers based on LIBS which are especially well suited to analysis of aluminum alloys. In this paper we report on the design features of Rigaku's KT-100, micro-LIBS handheld analyser and discuss its performance in analysis and sorting of aluminum alloys, especially those containing light alloying elements such as Si, Li, Be, Mg.

Keywords: uLIBS; micro-LIBS; alloy analysis; handheld analyzers

1. Introduction

Contemporary industries require reliable and accurate alloy identification. This is especially true for mission critical applications of alloys such as in power generating plants, aviation, refineries and chemical processing installations where the identity (grade) of every metal component must be verified. On the other end of the spectrum the alloy recycling and alloy manufacturing industries also depend on reliable identification of recycled metals used in production of alloys. The most successful and best suited for rapid alloy identification of alloys in field has been Handheld X-Ray Fluorescence (HHXRF). The levels of accuracy and speed of analysis this method provides established it as a benchmark against which other competitive analytical methods are compared. However, the XRF has inherent difficulty in analysis of many important aluminum alloys as well as other alloys containing low atomic number elements such as lithium, beryllium, boron, silicon or magnesium. The common practice to overcome this deficiency has been use of Optical Emission Spectroscopy (OES) or – most recently – Laser Induced Breakdown Spectroscopy (LIBS). Both these techniques can analyze all alloys the XRF can and especially those the XRF cannot. Unfortunately, both these analytical methods were best suited to laboratory environments, until now.

The recent technological advancements such as availability of inexpensive miniature, solid state micro-lasers and small, compact spectrometers, have made the design of handheld LIBS analyzers possible. This development rapidly expanded the use of LIBS especially into field operations such as alloy sorting and analysis. Since LIBS is better suited for analysis of light elements such as lithium (Li), aluminum (Al), magnesium (Mg), and beryllium (Be) than its main rival, handheld x-ray fluorescence (XRF), it quickly gained industry acceptance as a method of choice for sorting alloys, and specifically aluminum scrap. Aluminum recycling is very important economically because using recycled aluminum to make new aluminum alloy requires 5 to 8 % less energy than to make it from

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bauxite ore [1]. Perhaps the best indicator of importance of aluminum scrap recycling is the fact that about 75% of all aluminum ever produced is still in use today [1].

2. The principle of LIBS

Laser Induced Breakdown Spectroscopy, LIBS, in its basic concept is very similar to the well known method of Optical Emission Spectroscopy, OES. Both methods rely on spectral analysis of plasma light generated from the sample. The main difference between them is in the way they generate plasma. In LIBS, unlike in OES, we use laser light rather than an electric arc to break up sampled material and convert it to plasma. The use of laser as excitation source offers many advantages of which the most important is the ability to precisely control the energy delivered by laser pulse to the material.

Many types of lasers can be used as long as they provide in a single pulse energy density in excess of 10^9 W/cm^2, a threshold required for ablation of metals [2, 3]. However, design requirements of the handheld instruments, such as small size, low weight and battery power limit the laser selection to small power, semiconductor types. Typical laser used in HHLIBS instruments is a semiconductor, Q-switched, diode pumped Nd/YAG crystal generating light pulses at wavelength of 1064 nm and energy on the order of 0.1mJ to 1.0 mJ per pulse. The very short (on the order of few nanosecond) pulse of light tightly focused on sample surface generates a burst of high density energy that ablates a small mass of the sample and heats it to tens of thousands of degrees Kelvin, converting it to plasma.

The plume of plasma, made of electrons and ionized atoms, lasts typically about 100 microseconds, long after the initiating laser light pulse is extinguished. In the absence of other sources of energy, the plume of plasma begins to cool, and the electrons freed from the atoms by the initial laser pulse start to recombine with ionized atoms to return to their original atomic states. In the process electrons must shed the surplus energy which is released in the form of light, typically ranging between 200 to 700 nm (UV to red). The emitted light is collected and transmitted to a miniature spectrometer fitted with a high sensitivity CCD detector for spectral analysis. The spectrometer sorts the intensity of light by its wavelength. The resulting histogram of light intensity as function of wavelength, called a wavelength spectrum, is the principle source of data from which quantitative information about sample composition is derived. Finally, the elemental composition of alloy determined from its LIBS spectrum is compared to the table of alloys specifications to identify the grade of the alloy under test.

Figure 1 shows a schematic of the process taking place in the LIBS analyzer. Examples of emission spectra of stainless steel SS316 and aluminum alloy AA7075, obtained with HHLIBS analyzer, are shown in Figure 2.

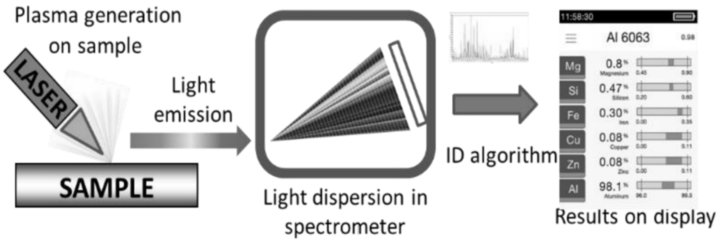


Figure 1. LIBS process in analyser.

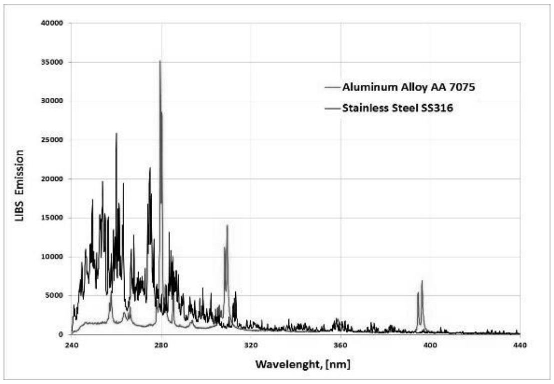


Figure 2. LIBS spectra of aluminum alloy 7075 and that of stainless steel 316. Note the complexity of steel spectrum.

3. Handheld micro-LIBS Analyzer.

3.1. Design and operational characteristics

An example of practical embodiment of a Handheld micro- LIBS analyzer is shown in Figures 3 and 4. The analyzer has been designed primarily for use in harsh environments of scrap recycling yards, metal fabrication and positive material identification (PMI) operations. Therefore, much attention was devoted to making this ergonomically designed instrument dust and shock resistant. Consequently, it is the only handheld LIBS instrument that complies with IP-54 and MIL-STD-810G standards [4]. One of the unique features of the analyzer is its 1064 nm Class 3B laser engine which incorporates fixed excitation and detection optics. The laser generates pulses of 120 uJ energy with frequency that can be selected between 100 to 1000 Hz. A miniature, Czerny-Turner spectrometer with CCD detector complements the analytical module. Its wavelength range covers a band from 200 to 480 nm, at an average wavelength resolution of better than 0.2 nm.

Figure 3. Left - Rigaku Katana KT-100 µLIBS Analyzer; Right - analyzer in use.

To measure composition of an alloy sample operator places the tapered “nose” of the analyzer against the surface of sample and squeezes the trigger to initiate the test. The laser beam focused to diameter of about 30 to 40 µm slides back and forth over sample surface for a period of one second at the end of which chemical composition of tested alloy and its grade are displayed on a color, tiltable LCD screen. All measurement results along with the original spectra are stored in on-board memory which has capacity of several thousands. Optionally, a picture of measured object generated by the build-in camera can be stored with each test result. Full technical details of the analyser may be found in [5].

3.2. Calibration

Handheld LIBS analyzers are calibrated using empirical approach. A set of alloys of well-known composition is measured and from the spectra obtained the intensities of elements are extracted. Next, the intensities are correlated with elemental concentrations to generate calibration curve for each analyte. The mass of material ablated by laser pulse and characteristics of resulting plasma vary considerably from pulse to pulse directly influencing the intensities of analytes. In order to minimize this effect, a ratio of analyte intensity to the intensity of matrix element is used to build calibration curve rather than the analyte intensity itself. The most robust calibration curves are obtained when intensity ratios are correlated with ratios of analyte concentration to that of the matrix element as shown by equation 1.

$$\frac{c_i}{c_{Al}} = \boldsymbol{a_0} + \boldsymbol{a_1}\,\frac{I_i}{I_{Al}} + \boldsymbol{a_2}\left(\frac{I_i}{I_{Al}}\right)^2 + \boldsymbol{a_3}\left(\frac{I_i}{I_{Al}}\right)^3 + \ \dots \qquad (1)$$

where:
- c_i and c_{Al} are concentration of analyte, *I*, and matrix element, *Al*, respectively,
- I_i and I_{Al} are intensities of analyte, *I*, and matrix element, *Al*, respectively,
- a_0, a_1, a_2, a_3 are coefficients of equation

Figures 4 and 5 show examples of calibration curves for magnesium and silicon, the two most important light elements for the most popular aluminum alloys. Typically, an acceptable calibration curve would exhibit correlation coefficient, *R*, greater than 0.95.

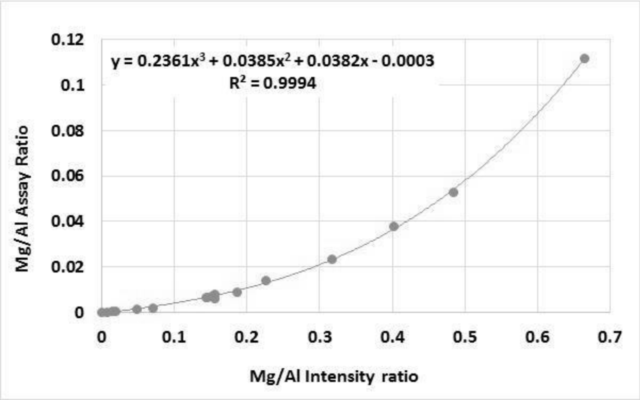


Figure 4. Calibration curve for magnesium in aluminum .

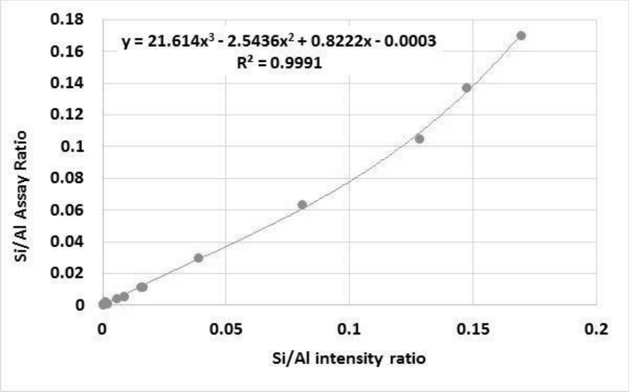


Figure 5. Calibration curve for silicon in aluminum.

Alloys used for calibration must be representative of the unknown material to be tested and cover expected concentration ranges of analytes. If the calibration curve cannot be represented by equation of straight line additional, special composition alloys, must be procured to properly define the shape of calibration curve. In recent years a so called “calibration free” approach (CF-LIBS) has been proposed to alleviate the problem. It is based on application of theoretical, Saha-Boltzmann equation which ties spectral intensities of elements with their concentrations in plasma via plasma temperature [6]. The accuracy of this method in laboratory conditions for metals and alloys may be better than 1% relative but only for the matrix elements while for minor elements inaccuracy may be as much as 10 or even 20% relative. At present time it is impossible to implement it on handheld LIBS devices. Depending on analyte and alloy matrix, typical accuracy offered by empirically calibrated handheld LIBS analyzer varies from 5 to 10 % relative.

3.3. Grade identification

In order to determine grade of an alloy the concentrations of analytes measured in it are compared with composition specifications of alloy grades stored in the device library. The grade of the alloy whose specifications best match the measured composition of unknown sample is then assigned to that unknown. The simplest criterion of match is based on the concept of Euclidean distance as per equation (2) below:

$$d_j = \sqrt[2]{\sum_{i=1}^{n}\left(c_i - c_i^j\right)^2} \qquad (2)$$

where:
- c_i is concentration of element *i* measured in unknown sample,
- c^j_i is nominal/expected concentration of element, *i,* in an alloy grade, *j*, as retrieved from grade

specification,

- d_j is a match number, a measure of similarity of composition of measured alloy to that of the library alloy grade, j.

The smaller the value of d_j, the better the match. In practice, this formula is modified to account for various factors, such as measurement errors or statistical weights of elements critical for the match. Finally, for convenience of interpretation, d_j is normalized in such a way that perfect match is represented by number one and no match by zero.

4. Analytical performance

Figures 6 and 7 illustrate the level of accuracy of analysis achieved by handheld micro-LIBS analyzer for magnesium and silicon measured on certified reference standards of aluminum alloys. All measurements were taken for less than one second each.

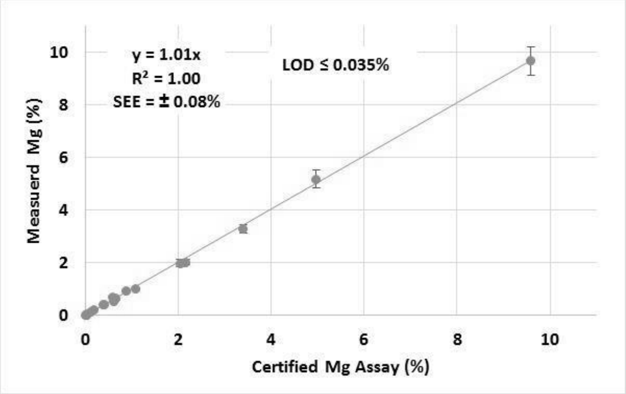


Figure 6. Accuracy of KT-100 Analyzer in Mg analysis

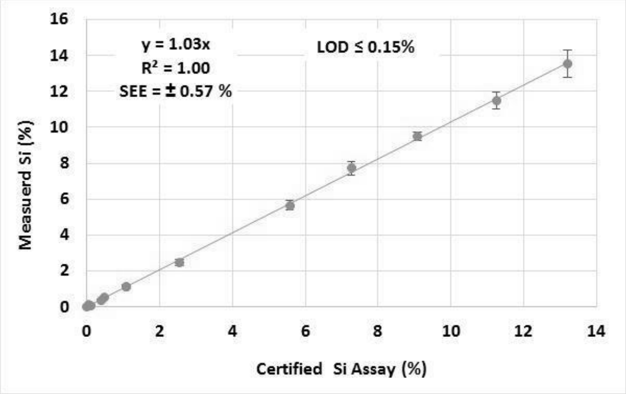


Figure 7. Accuracy of KT-100 Analyzer in Si analysis

A table 1 below shows typical detection limits one may expected when using handheld micro-LIBS analyzer to test aluminum alloys. The data is a snapshot obtained from randomly selected twelve production issue instruments, model KT-100, over the period of three months. Individual instruments may exhibit much better LODs than the values quoted in the table.

Table 1. Typical Limits of Detection (LOD) for aluminum alloys with handheld μLIBS Analyzer

Mg	Si	Mn	Fe	Ni	Cu	Zn
≤ 0.035	≤ 0.15	≤ 0.10	≤ 0.30	≤ 0.30	≤ 0.20	≤ 0.15

Figure 8 demonstrates the level of precision and reproducibility of an analyzer across four different devices. The measurements were repeated ten times per unit. The alloy was of 356 grade aluminum. The red line represents certified weight percent of magnesium (at 0.351%), blue line is an average of all 40 tests (at 0.359%), and gray lines represent a ± 3 standard deviations band around the measured average.

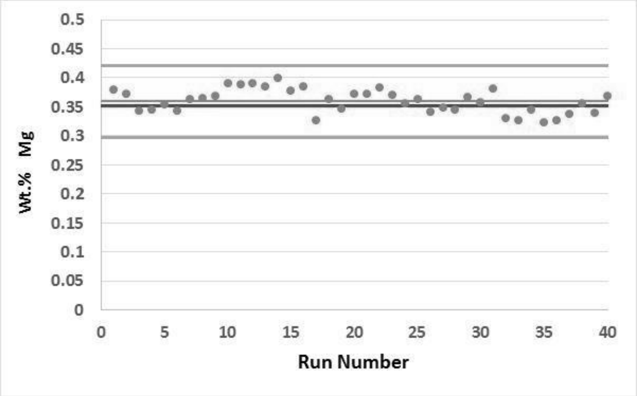
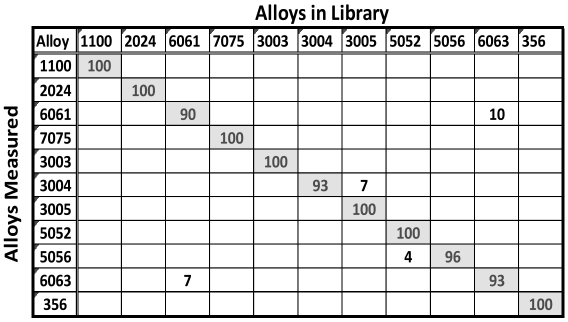


Figure 8. Precision and reproducibility of KT-100 Analyzer



Alloys in Library

Alloys Measured

Alloy	1100	2024	6061	7075	3003	3004	3005	5052	5056	6063	356
1100	100										
2024		100									
6061			90							10	
7075				100							
3003					100						
3004						93	7				
3005							100				
5052								100			
5056								4	96		
6063			7							93	
356											100

Figure 9. Example of identification results.

Figure 9 shows example of results of grade identification. For this test each alloy listed in table was measured at least 3 times on seven different instruments, for a total of 29 tests per alloy. As can be seen, when alloy 6061 was measured, it was identified correctly 90% of the time and misidentified as alloy 6063 10% of the time. Conversely, alloy 6063 was positively identified 93% of the time and mixed with alloy 6061 7% of the time. As it is evidenced by Table 2, the mix-ups are the consequence of very small differences between compositions of these two alloys and unavoidable errors of measurement. Apart from improving the accuracy of measurement the quality of identification will often improve by adjusting composition specifications from the official to "as produced" limits. Results for other alloys listed in Fig. 9 similarly indicate that the potential mix-ups occur within the given alloy series.

Table 2. Composition specifications for aluminium alloy grades 6061 and 6063

Alloy	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti
6061	0.4 – 0.8	< 0.7	0.15 – 0.40	< 0.15	0.8 – 1.2	0.04 – 0.35	< 0.25	< 0.15
6063	0.2 – 0.6	< 0.35	< 0.1	< 0.1	0.45 – 0.9	< 0.1	< 0.1	< 0.1

5. Special considerations

5.1. Sample surface preparation

A micro-LIBS with its 10 to 30 micrometer depth penetration ability is essentially a surface analytical technique. While the analyzer is calibrated with very well characterized, certified alloy standards each having flat, clean surface, the real alloys tested in field do not resemble the ideal of the calibration standard. Their surface is likely to be contaminated, perhaps even painted and not flat. The state of sample surface may negatively affect the results and in order to avoid this one should prepare the surface before analysis.

A short laser "preburn" of the spot before actual LIBS analysis is convenient way of surface preparation. During preburn laser beam ablates and burns away surface contamination, leaving a clean surface for subsequent laser pulses for LIBS analysis. For aluminum alloys it is usually sufficient to select preburn which is about 2 to 3 times longer than the time needed for analytical burn.

5.2. Homogeneity of sample and beam rastering

Another factor that affects representativeness of results is inherent nonhomogeneity of sample itself. Figure 9 shows example of large crystallites of silicone in aluminum matrix. This particular alloy contained 17% of silicon. Red circle imitates diameter of laser beam focused on alloy surface. It is obvious that results of analysis will strongly depend on the location of laser beam. It is therefore recommended to take more than one measurement and at different locations so the average may be more representative of the bulk composition. It is worth to note that some degree of averaging is already provided by rastering the laser beam across sample surface.

Beam rastering is requirement with micro-power lasers. If the laser beam is stationary, the intensity of plasma decreases very fast with each consecutive scan as is shown in Figure 10 by blue data points. This is because consecutive laser pulses striking the same location deepen the crater on sample surface and negatively affect laser-sample coupling efficiency. When laser beam moves across the sample it always strikes new, solid spot on its surface.

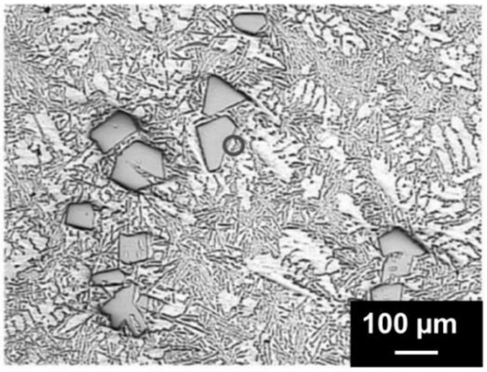


Fig. 9. Nonhomogeneity of sample

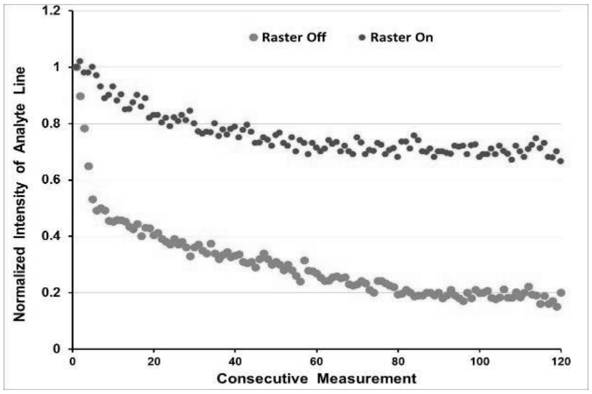


Figure 10. Effect of rastering of laser beam.

6. Conclusions

Laser-Induced Breakdown Spectroscopy successfully migrated from laboratory to industrial environment in the form of a handheld LIBS analyzer. This ergonomically designed instrument can analyze composition of aluminum and other alloys in less than two second per sample. Good accuracy of analysis combined with sophisticated identification algorithm allow the instrument to identify alloy grades with 95 to 100% success rate, making it into excellent alloy sorting tool. This is especially true for sorting aluminum grades as many of them contain magnesium and silicon. As new elements, such as boron, lithium, are being introduced to aluminum alloys family one should anticipate µLIBS to become more and more useful.

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