A compact LIBS system for industrial applications

B. Noharet[a], C. Sterner[a], T. Irebo[b], J. Gurell[b], A. Bengtson[b], R. Vanik[b], H. Karlsson[c], E. Illy[c]
[a]Acreo Swedish ICT, Box 1070, Isafjordsgatan 22, SE-164 25 Kista, Sweden
[b] Swerea KIMAB, Box 7047, Isafjordsgatan 28A, SE-164 07 Kista, Sweden
[c] Cobolt AB, Vretenvägen 13, SE-171 54 Stockholm, Sweden

ABSTRACT

In recent years, laser-induced breakdown spectroscopy (LIBS) has been established as a promising analytical tool for on-line chemical analysis. The emitted light spectrum is analyzed for instantaneous determination of the elemental composition of the sample, enabling on-line classification of materials. Two major strengths of the technique are the possibilities to perform both fast and remote chemical analysis to determine the elemental composition of the samples under test. In order to reduce the size of LIBS systems, the use of a compact Q-switched diode-pumped solid-state laser (DPSSL) in a LIBS system is evaluated for the industrial sorting of aluminum alloys. The DPSSL, which delivers 150µJ pulses of high beam quality at more than 7KHz repetition rate, provides irradiance on the target that is appropriate for LIBS measurements.

The experimental results indicate that alloy classification and quantitative analysis are possible on scrap aluminum samples placed 50 cm apart from the focusing and collecting lenses, without sample preparation. Similar calibration curves and limits of detection are obtained for the DPSSL evaluated in this paper and the LIBS setup in previous work by Gurell et.al[1] , showing the applicability of compact diode-pumped lasers for industrial LIBS applications.

Keywords: LIBS, laser-induced breakdown spectroscopy, chemical analysis, on-line monitoring, recycling.

1. INTRODUCTION

Laser-induced breakdown spectroscopy (LIBS) enables both fast and remote chemical analysis to determine the elemental composition of the samples under test, without the need for prior sample preparation. LIBS is an attractive technology for a wide range of scientific and industrial analytical applications, including metal-content analysis, solar silicon quality control, plant and soil analysis, mining and prospecting, forensic and biomedical studies, and explosives and biological warfare detection. It is particularly well-suited to the on-line monitoring of industrial processes, especially for the metal industry. LIBS can, for example, be applied to monitor and optimize critical metallurgical processes (slag or molten metal analysis), to control the quality of metal products (rolls, tubes, foils, and so on), or to analyze and sort metal scrap before recycling.

Traditional LIBS set-ups are based on the use of flash-pumped Q-switched lasers that deliver pulses with energy levels of hundreds of millijoules at relatively low pulse rates, typically 20 to 30Hz. Although flash-pumped lasers are robust and have been successfully demonstrated in LIBS systems for industrial applications, their size and water-cooling system make them cumbersome for many applications where compactness is critical. Moreover, their limited repetition pulse rate sets a bound to their analysis capacity in terms of material throughput.

The steady progress in compact diode-pumped solid-state lasers in terms of cost-to-performance ratio, maturity and robustness makes them attractive for the commercial deployment of LIBS systems in a wide range of industrial application, and may provide competitive and practical solutions in particular to the recycling industry owing to their compactness and high pulse repetition rate.

The suitability use of a compact, high-repetition-rate diode-pumped solid-state laser in a LIBS set-up for the remote chemical analysis of aluminum samples is investigated in this paper.

In section 2, a brief description of the aluminum recycling study case is provided. The basic properties of LIBS are reviewed in section 3, and a discussion on the key parameters of lasers for LIBS is provided. Finally, experimental results obtained with a compact diode-pumped solid-state laser are introduced and discussed in section 4.

2. ON-LINE CHEMICAL ANALYSIS FOR IMPROVED ALUMINUM RECYCLING

An example of an application that would strongly benefit from the availability of more compact and industrial-grade LIBS systems is aluminum recycling. Aluminum is in principle 100% recyclable; its recycling involves the collection of waste and subsequent use as secondary material in the production of new products. The use of recycled aluminum requires only 5% of the energy used in extraction of virgin minerals to produce aluminum, thus enabling large savings in energy consumption.

A large part of the aluminum scrap on the market today is delivered from shredding mills, in which cars as well as industrial and household goods are cut into small pieces. The shredded material is inhomogeneous and, today, mostly sorted by visual inspection or coarse sorting techniques. The uncertainties in alloy composition of scrap materials set an upper bound to the amount of recycled aluminum used in production, where very stringent compositions are required.

Due to the lack of efficient aluminum scrap-sorting methodology, today only a limited fraction of recycled aluminum can be efficiently used in aluminum production. The potential for direct classification and sorting of recycled aluminum flows is therefore huge, both in terms of economic benefits to the aluminum producers and minimized environmental impacts, as represented schematically in figure 1.

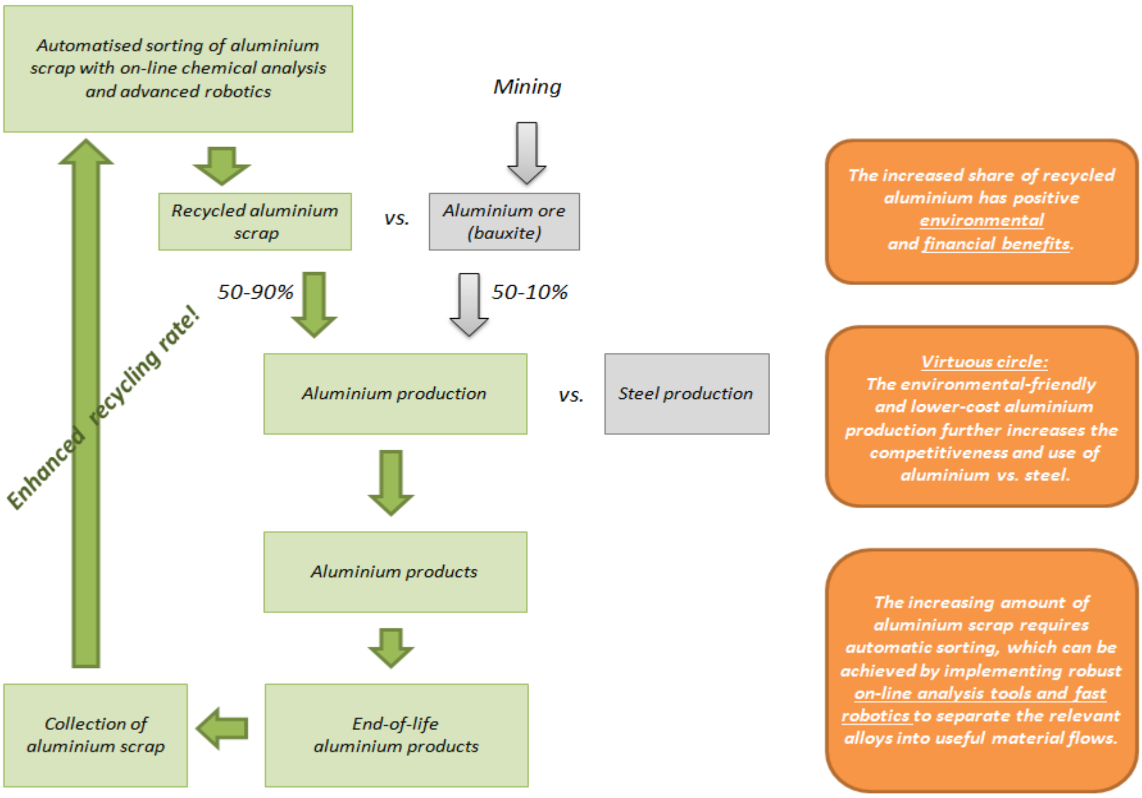

Figure 1. Impact of automatized alloy sorting on the aluminum material flow

3. LASER-INDUCED BREAKDOWN SPECTROSCOPY

3.1 Measurement principle

Laser-induced breakdown spectroscopy (LIBS) is based on laser pulses, directed and focused onto a surface, which induces a plasma that emits element-specific optical radiation from the sample material. The spectral information is detected with an optical spectrometer and the spectral information is used to deduce the elemental composition of the scrap piece under investigation, as shown in figure 2 - left.

Prototypes of LIBS systems have already been proposed and successfully demonstrated in the laboratory and at test sites for rapid classification of aluminum alloys, clearly showing the benefits of using LIBS to efficiently sort different alloys and dynamically handle and manage recycled material flows in scrap yards or production plants.

Our LIBS prototype (see figure 2 - right) has been designed for the on-line automatic analysis of metal scrap pieces carried on a fast conveyor belt. Careful optical design was performed to optimize the photon budget and thereby enable high signal-to-noise ratios. The operating distance between the LIBS instrument and the sample can be tuned between 0.5 and 1 m, however, the distance is kept constant under operation. Experimental results obtained with this LIBS prototype to analyze steel scrap have already been reported (see [1]).

In order to operate the LIBS prototype in a fully automated mode, a range measuring device, based on triangulation, was used to continuously monitor the distance between the instrument and the scrap pieces. Distance measurement is used as a trigger to the laser and the spectrometer which therby leads to firing of the laser when an object is placed at the focal distance of the laser focusing lens, as shown in figure 1 (left). Analysis of the plasma was performed with a compact spectrometer covering wavelengths between 220 and 440nm.

The two major strengths of the technique are the possibilities to perform both fast and remote chemical analysis. The practical implementation and widespread use of LIBS as an on-line tool at scrap-yards or at production sites requires, however, the development of more robust, faster, and most of all more-compact LIBS systems.

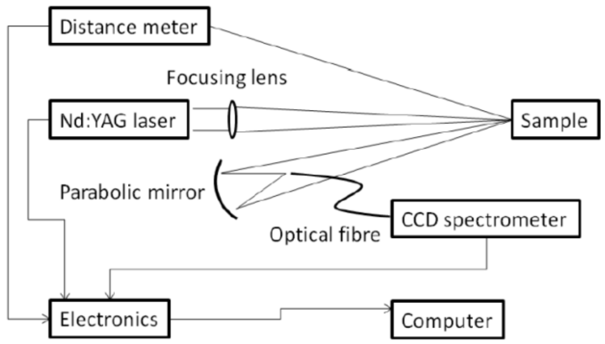

Figure 2. Portable LIBS prototype for industrial on-line applications.
Left: schematic view of the different components Right: photograph of LIBS prototype

3.2 The pulsed laser: a key component for LIBS

In our previous prototype, as well as in many other LIBS system reported in the literature, a flashlamp-pumped Q-switched laser was used. The laser delivers up to 30 pulses per second at energy levels up to 330mJ per pulse. In order to enable faster as well as more compact and versatile systems, we have replaced our flashlamp-pumped laser by a diode-pumped laser (Cobolt Tor laser). This laser is a new class of compact, high-performance diode-pumped Q-switched lasers that can help advance the trend of extending the use of LIBS systems from laboratory work to industrial applications. The laser design provides a combination of stable multikilohertz repetition rate (greater than 7 kHz with less than 1µs pulse-to-pulse jitter), pulse energies in the 100 µJ range at 1064 nm, pulse widths of a few nanoseconds, and a high beam quality ($M^2 < 1.3$).

A key advantage of the laser is its substantially more compact size compared to traditional high-pulse-energy Nd:YAG lasers. The laser head measures 125 × 70 × 45 mm and is accompanied by an electronics unit for supply of drive currents and control signals measuring 190 × 72 × 28 mm. Typical heat load of the laser head is less than 30 W, which, when combined with the small size, allows for compact integration into portable industrial LIBS systems. The laser is manufactured into hermetically sealed packages to ensure robust performance and long lifetime in varying ambient conditions such as those that exist for demanding industrial applications.

Figure 3 provide a schematic comparison between the two laser types.

	Flash-pumped	Diode-pumped
Peak power	Very high	Medium
Beam quality	Poor	Very good
Pulse repetition rate	Low	High
Cooling	Water	Air
Laser+driver size	Large	Compact

Figure 3. Comparison of flash-pumped and diode-pumped lasers

Owing to its high repetition rate, air cooling and compactness, the diode-pumped laser offers a promising alternative for industrial LIBS applications. However, some questions needs to be answered:

- Is the irradiance large enough to enable good material ablation and plasma formation at distances over 50cm and on dirty scrap samples?
- The high pulse repetition rate significantly increases the analysis capacity in terms of material throughput. However, when using compact CCD spectrometers, it is very challenging to filter out the contribution from the continuum emission spectrum that originates from the very early phase of the plasma and that contribute to a larger background noise at high pulse repetition rates. Is the continuum background contribution too high to enable good LIBS signal detection?
- Finally, is it possible to make reliable calibration curves to quantify the alloy contents?

3.3 Experimental results

Several laboratory tests were performed to assess the performance and limitations of the diode-pumped laser in a LIBS system for aluminum scrap analysis. Certified reference materials with known elemental compositions were used in the laboratory tests to calibrate the system.

Light from the diode-pumped laser was focused by a single lens onto the surface of test samples. The distance between the lens and the sample was 50cm. Light from the plasma was collected by another lens, also placed at 50cm from the sample, focused into an optical fiber, and conveyed to a compact spectrometer.

Figure 4 provides examples of detected spectra from different samples collected at a scrap yard. Clear plasmas are obtained both on reference samples and on dirty scrap samples, as shown in figure 4 (left), and the different material composition can be clearly resolved.

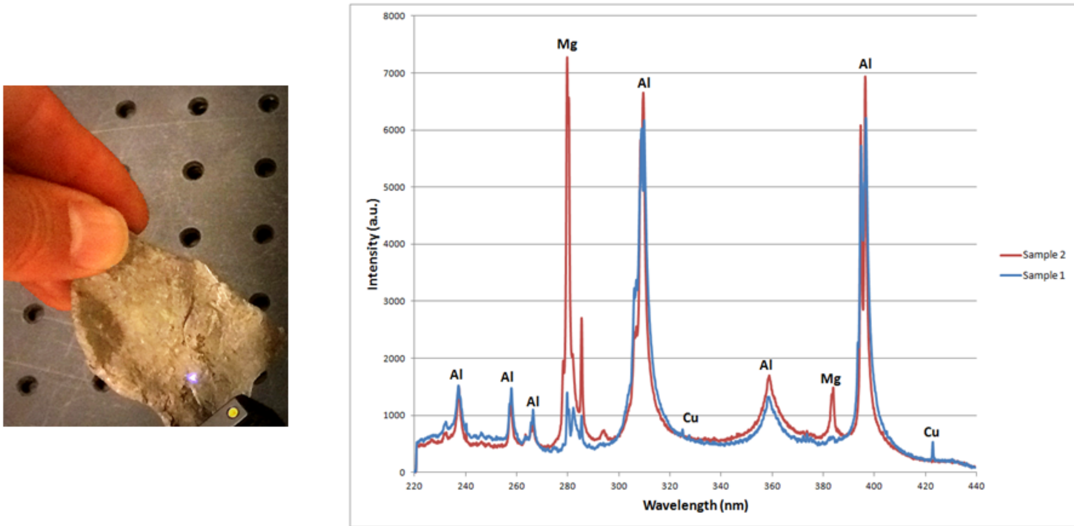

Figure 4. Experimental results with the LIBS prototype on aluminum scrap
Left: Plasma obtained on an aluminum scrap sample
Right: Spectra collected for 2 different scrap samples with different contents in magnesium and copper.

Further experiments were conducted on reference samples. An example of calibration curve is provided below, for the detection of magnesium in aluminum. Magnesium has a strong emission peak around 280nm that was used to quantify its concentration. Figure 5 shows the different magnesium lines obtained for the different reference samples.

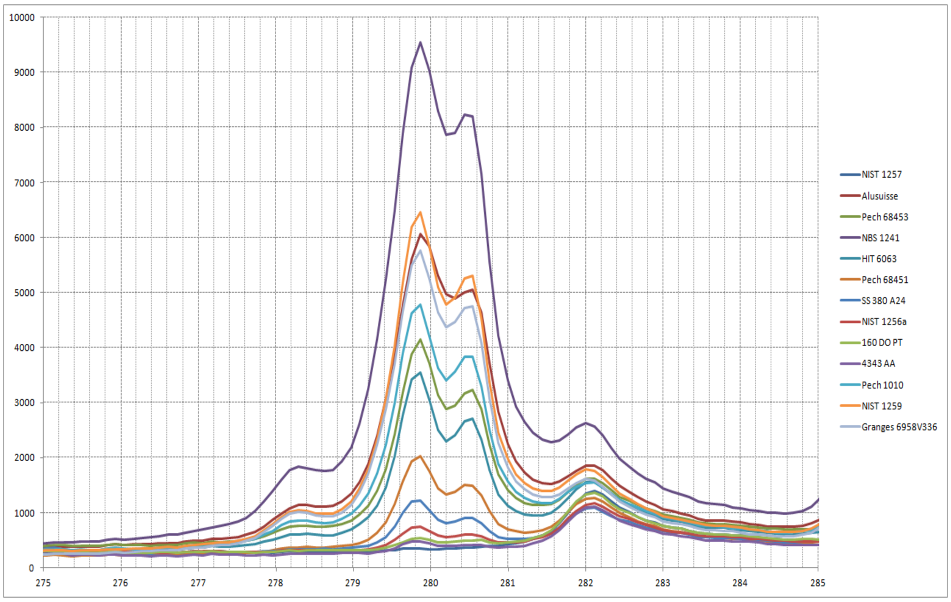

Figure 5. Magnesium emission peaks obtained for different reference samples.

The ratio of the line intensity of magnesium to the emission line of aluminium is plotted as a function of the known concentration ratios of the reference samples in figure 6. The 256.8nm Al I line was chosen.

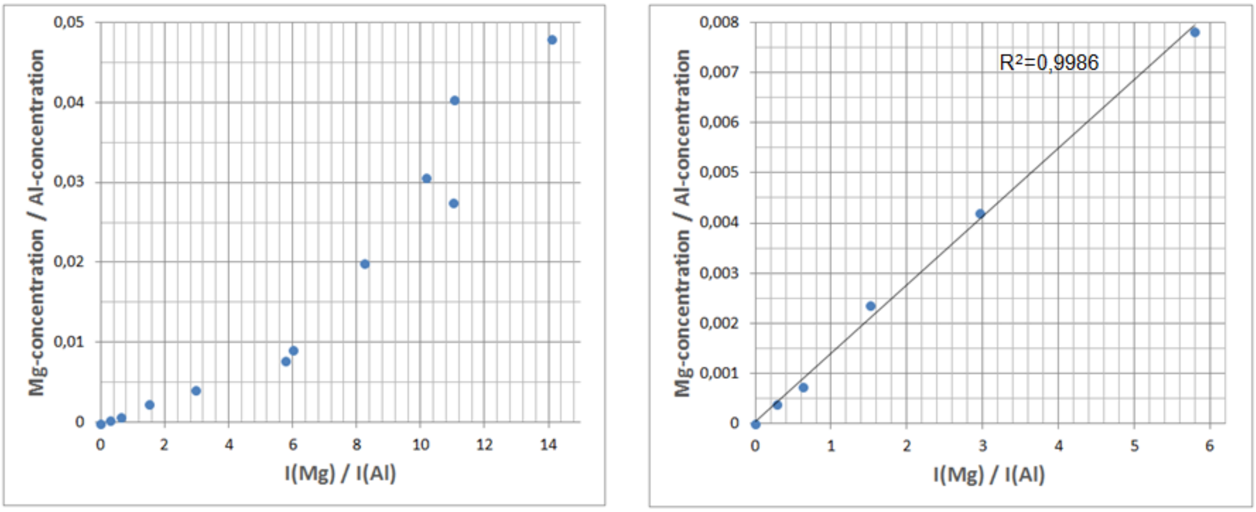

Figure 6. Calibration curve for magnesium
Left: over a large range of Mg content, showing a non-linear effect probably due to self-absorption
Right: for limited range of low concentrations, showing a linear behavior

For low magnesium concentration, the calibration curve shows a very good linearity.

Further measurements were conducted to compare calibration curves obtained with a flashlamp-pumped laser and a diode-pumped laser. The following emission lines were selected: Si (288nm), Mg (280nm), Cu (325nm) and Al (309.5nm). Note that no post processing operation (e.g. offset, baseline removal) were implemented, only the ratio of the detected raw emission line intensities are plotted. Two different sets of reference samples were used.

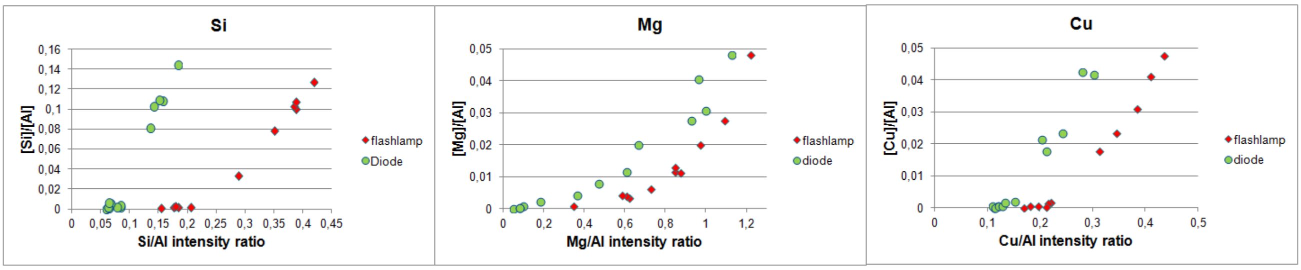

Figure 7. Calibration curves for silicom (left), magnesium (center), and copper(right), obtained with a flashlamp-pumped laser and a diode-pumped laser.

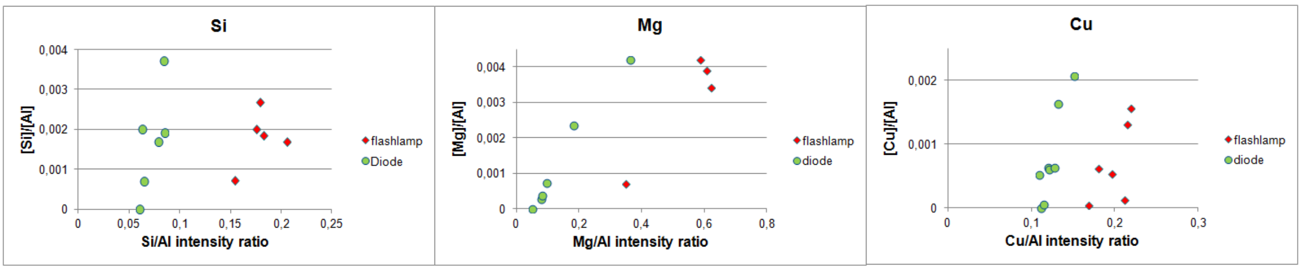

Figure 8. Calibration curves for silicom (left), magnesium (center), and copper(right), obtained with a flashlamp-pumped laser and a diode-pumped laser at low element concentrations

While the low-repetition-rate flashlamp-pumped laser enables time gating of the spectrometer, the high-repetition-rate diode-pumped laser was run without synchronization with the spectrometer. Similar curves and slopes are obtained for each element, showing similar performances (see figure 7 and 8). In particular, figure 8 shows linear responses obtained with the diode-pumped laser, and indicate limits of detection in the range of a few hundreds ppm for each element.

The experimental results therefore indicate that:

- Good plasma conditions are obtained on dirty scrap aluminum samples placed 50 cm apart from the focusing and collecting lenses, without sample preparation.
- It is possible to correctly classify different aluminum dirty scrap samples with different alloy compositions.
- Quantitative analysis is possible after calibration. Similar calibration curves are obtained with a low-frequency (30Hz) high-energy (330mJ) flashlamp-pumped laser and a high-frequency (7kHz) low-energy (150µJ) diode-pumped lasers. Noise levels at low concentrations indicate similar limits of detection for each system, in the order of a few hundreds of ppm. Note that acquisition was performed within a fraction of a second, at a distance of 50cm.
- Detection without gating does not change the results significantly.

The very strong performance of this compact high-repetition-rate laser in LIBS applications is most likely related to its very good beam quality, which enables high irradiance and fluence values. It is also believed that its relatively low-energy pulses create short-lived continuum plasma backgrounds (see [2]), which allows the use of non-gated detectors also for quantitative analysis, greatly simplifying the detector requirements and system cost. The high repetition rate of the laser also contributes to enhancing the signal-to-noise ratio at the detector level.

4. CONCLUSION

LIBS has become a promising analytical tool for on-line chemical analysis. It is a material analysis technique that uses short laser pulses to locally ablate the material sample and create plasmas. While flashlamp-pumped Q-switched Nd:YAG lasers that deliver high-energy pulses at low repetition rate are traditionally used in industrial applications of LIBS, we have shown that smaller and faster diode-pumped solid-state lasers may become a very interesting alternative, when compactness and speed are critical. The diode-pumped laser has been integrated into a LIBS set-up for remote analysis of aluminum scrap pieces. Classification and quantitative analysis of various aluminum alloys were demonstrated. We have shown that the use of compact high-repetition-rate pulsed lasers with a high-quality beam can provide quality LIBS results while drastically reducing the system size, allowing for integration into portable LIBS systems suitable for use in industrial environments. Another advantage of this laser type is that its lower-energy pulses minimize the size of the ablation volume and therefore enable a nearly nondestructive analysis compatible with product quality control.

ACKNOWLEDGEMENTS

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REFERENCES

[1] J. Gurell et al., “Laser induced breakdown spectroscopy for fast elemental analysis and sorting of metallic scrap pieces using certified reference materials”, Spectrochimica Acta Part B: Atomic Spectroscopy, Vol. 75-76, pp. 46-50 (August-September 2012)

[2] G. Cristoforetti et al., “Quantitative analysis of aluminum alloys by low-energy, high-repetition rate laser-induced breakdown spectroscopy”, Journal of Analytical Atomic Spectrometry, Vol. 21, pp. 697-702 (June 2006)