Laser-induced breakdown spectroscopy for identification and characterization of aluminum

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Abstract. Identification of aluminum is required to evaluate the quality of metallic products in industry. In this study, identification and characterization of aluminum has been carried out by using Laser Induced Breakdown Spectroscopy (LIBS). LIBS can be analyzed elements in metal rapidly and does not require more sample preparation, and is a low-cost compared to other conventional methods. The samples used in this study were pure aluminum plate and Indonesian currency coin. Experimentally, a pulse neodymium yttrium aluminum garnet (Nd:YAG laser, 1064 nm) was irradiated on a metal sample surface at a reduced pressure of air to produce a luminous plasma. The plasma was then detected by optical multichannel analyzer to get emission spectrum. Emission spectrum of neutral and ionic aluminum (Al) lines of Al I (309,28 nm), Al II (359,75 nm), Al I (396,15 nm), Al II (448,98 nm), Al II (561,32 nm), Al II (660,96 nm), Al II (781,23 nm) was clearly detected from the pure aluminum plate. The same spectrum of Al was also detected from the Indonesian currency coin. However, the emission intensity of Al is lower for Indonesian currency coin.

Keywords: Laser induced breakdown spectroscopy; LIBS, identification of aluminum; Nd:YAG laser

1. Introduction
Identification of metal elements is very important for applications in science and industry. Aluminum is one of the most abundant metals in the world and is the third most common element, comprising 8% of the Earth’s crust. The flexible nature of aluminum makes it the most widely used metal after steel. Identification of aluminum metallic is required in industry such as food industry [1], aluminum alloy industry [2-4], and automotive aluminum industry [5].

Existing methods used for identification of aluminum metal are magneto-rheological (MR) [6] and X-ray fluorescence spectroscopy (XRF) [7]. However, identification of aluminum element using MR method needs magnetic field, fluid, aluminum and system of MR. The weakness of the MR method is that it requires more preparation and takes a longer time to perform aluminum metal analysis. XRF is a tool used to analyze the chemical composition along with the concentration of elements contained in a sample by using spectrometry method. XRF is commonly used to analyze elements in minerals or rocks. The elemental analysis is done both qualitatively and quantitatively. Qualitative analysis is done to analyze the type of elements contained in the material and quantitative analysis is performed to
determine the element concentration in the material. However, XRF method needs more costs for analysis.

Laser-induced breakdown spectroscopy (LIBS) is efficient and effective method for identification of elements in metals [8]. LIBS can be used to analyze elements in metal rapidly and does not require a high-cost compared to other conventional methods. The sensitivity of LIBS method can achieve tens to hundreds part per million (ppm) level. LIBS has also been applied for identification and analysis of impurities in aluminum alloys without internal calibration [9]. LIBS also can be used for applications of any kind of material including metal [10] and non-metal [11, 12]. In the study, an experiment was conducted at atmospheric pressure.

In this study, we applied LIBS technique for identification of aluminum in metal aluminum at low pressure of surrounding air. A comparative study was made between aluminum with high-purity of 99% and Indonesian currency coin. A pulse neodymium yttrium aluminum garnet (Nd:YAG) laser with wavelength 1064 nm was used as an ablation source for aluminum metal with high-purity of 99%. Aluminum metal was then characterized elementally by scanning optical multichannel analyzer (OMA). With the same method was used for 500 coin metal to compare characteristic of both metal. The present method using Nd:YAG laser with wavelength 1064 nm effectively reduce cost and not take a lot of time to analyzing aluminum metal and money 500 rupiah coin metal.

2. Experimental setup

Basic experimental setup used in this research is shown in Fig. 1(a). A high-purity aluminum metal sheet (99%) was placed inside of a chamber. The dimension of aluminum metal sheet are 30 mm x 30 mm x 1 mm. A Nd:YAG laser beam (wavelength of 1064 nm and energy of 40 nJ) was focused on the surface of sheet by convex lens (focal length are 100 m) to ablate the sheet to produce plasma. Figure 1(b) shows the photograph of plasma taken from the aluminum sheets. Light blue color plasma clearly appears with hemispherical shape. The color contributed from the emission lines of Zn at the wavelength of around 400 nm.

![Fig 1.](image-url)

The repetition rate and energy of laser beam used in this study were 5 Hz and 95% (40 mJ). The spectra of the plasma was read by an optical multichannel analyzer (OMA) than fed into the computer. The other sample used was Indonesian currency coin (500 rupiah). All experiments were carried out at reduced pressure of air (0.267 kPa).

The emission spectra of plasma was obtained by scanning laser plasma radiation using OMA. The light emitted from the laser plasma was collected by an optical fiber and fed into the OMA system. One end of the fiber was placed at 15 cm distance from the focusing point of the laser light and set perpendicularly to the path of laser beam.
3. Results and discussion
The LIBS method can be used to identify the element content in the aluminum metal sample. From the experimental results by using high-powered Nd-YAG laser pulse (1,064 nm, 40 mJ, 7 ns) on the sample of pure alumina (99.9%) and Indonesian currency coins, a beautiful color and shape of the plasma photograph was produced. Figure 1(b) shows the plasma photograph obtained from the pure alumina sheet using present method of LIBS employed at low pressure. Bright light color is mainly contributed from the Zn emission at the wavelength of around 400 nm. Hemispherical shape of plasma proved that a shock wave is induced in this present study as reported by Kagawa et al […] .

In a shock wave plasma, the plasma consists of 2 distinguished regions namely primary plasma and secondary plasma. A primary plasma emits high-intense continuous emission (small and white color plasma just above the sample surface) contributed from the Bremsstrahlung and free-bound transition processes. A secondary plasma has a wide region with beautiful color (light blue color) contributes discrete emission lines via dissociation and excitation processes of fine particles ablated from the sample.

Figure 2 shows emission spectra of aluminum obtained from the aluminum sheet sample (99.9%). Neutral and ionic Al lines at Al I (309.28 nm), Al II (359.75 nm), Al I (396.15 nm), Al II (448.98 nm), Al II (561.32 nm), Al II (660.96 nm), Al II (781.23 nm) clearly appear with high emission intensities and low background emission.

![Figure 2](image-url)

Fig 2. (a) spectra plasma of aluminum, (b) spectra plasma of coin 500 rupiah, (c) comparison spectra plasma of aluminum 99% and coin 500 rupiah.
The spectra characteristics of the aluminum metal show different intensities. There are several internal and external factors affecting the intensity of the spectra. Influencing internal factors includes the atomic electronic energy level, the ability to transition cross section, and the atomic population at each energy level. The external factors are laser energy, laser wavelength, laser repetition rate, and sample characteristics.

From the experiments it was found that LIBS can be used to determine the element of aluminum from the pure aluminum. Based on the data above, then we continued an experiment by using the other sample of Indonesian currency coin. Figure 2 (b) shows the emission spectra obtained from the Indonesian currency coin (500 rupiah). Neutral and ionic Al lines at Al I (309.28 nm), Al II (359.75 nm), Al I (396.15 nm), Al II (448.98 nm), Al II (561.32 nm), Al II (660.96 nm), and Al II (781.23 nm) clearly appear as in the case of pure aluminum sheet. However, it can clearly be seen that the emission spectra of Al obtained from the currency coin has lower intensity than the case of pure aluminum sheet as shown in Fig. 2(c). This is because the currency coin contains various elements not only Al, even though the aluminum is major element in the sample.

| Ion | Wavelength (nm) | Energy Level | Intensity (arb. unit) |
|-----|----------------|--------------|----------------------|
|     |                | Ei (eV)      | Ek (eV)              |                      |
| Al I| 309.28         | 0.0138938    | 4.0214836            | 478.7               |
| Al II| 359.75        | 15.062034    | 18.50749             | 139.6               |
| Al I| 396.15         | 0.0138938    | 3.1427212            | 718.4               |
| Al II| 448.98        | 15.6057688   | 18.366415            | 124.4               |
| Al II| 561.32        | 15.472500    | 17.680649            | 43.8                |
| Al II| 660.96        | 15.472500    | 17.347742            | 84.6                |
| Al II| 781.23        | 15.585203    | 17.171798            | 56.4                |

As shown in Fig. 2, Al lines have various emission intensities depending on their wavelength. For example, the neutral Al line at 396.15 nm has highest intensity than others. This is because the Al I 396.15 nm line has lowest excitation energy than others as shown in Table 1. Therefore the probability of the emission is much higher for the emission lines having lower excitation energy. This results certified that identification and characterization of aluminum element in pure Al metal sheet and Indonesian currency coin can be made by using LIBS technique.

4. Conclusion
Identification of Al can be made from the pure Al metal sheet and Indonesian currency coin by using LIBs method operated at low pressure. Shock wave plasma with beautiful light blue color was produced from the pure Al metal sheet. Neutral and ionic Al lines at Al I (309.28 nm), Al II (359.75 nm), Al I (396.15 nm), Al II (448.98 nm), Al II (561.32 nm), Al II (660.96 nm), and Al II (781.23 nm) were clearly identified from both pure Al metal sheet and Indonesian currency coin. However, the intensities of Al obtained from Indonesian currency coin are lower compared to that of pure Al sheet. Furthermore, the result certified that the emission intensity of Al having lower excitation energy has higher intensity.

Acknowledgment
Part of this study was financially supported by Ministry of Research and Technology and Higher Education, Indonesia under the project of PUPT scheme (Contract No. 007/SP2H/LT/DRPM/IV/2017).

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