Emission characteristics of copper using laser-induced breakdown spectroscopy at low pressure

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Abstract. Identification of copper (Cu) in metal is necessary to evaluate the quality of metal products. High-concentration of Cu in metal can make easily fragile of the metal. In this study, identification and emission characteristics of Cu were carried out by using laser-induced breakdown spectroscopy (LIBS). The sample used was Cu plate (99.99%) and Indonesian currency coin containing Cu. Experimentally, a pulse laser beam (Nd:YAG laser, 1064 nm, 7 ns) was irradiated on the material surface to induce a plasma. The plasma emission was detected by optical multichannel analyzer system to obtain emission spectrum of Cu. The results certified that many neutral Cu lines at 324.75, 327.40, 510.55, 515.32, and 521.82 nm, and ionic Cu lines at wavelengths of 406.81, and 657.71 nm were successfully detected. It has been confirmed that the Cu lines at the same wavelength was also detected from the Indonesian currency coin. However, the intensity of the Cu lines are much weaker for the case of coin target. Furthermore, the other element of aluminum (Al) was also identified in the coin sample at wavelength of 309.28 nm and 396.15 nm for neutral Al lines, and ionic Al line at wavelength of 660.92 nm.

1. Introduction
Nowadays, rapid identification of metal is very necessary to be carried out because of its usability in material characterization that can be applied in scientific and industrial sector. Each metal element has specific atomic and mass number which affects to their physical properties. Therefore, it becomes easy to say that mechanical properties of metals (e.g. hardness, tensile strength, thermal conductivity, etc.) can be determined by identifying their element characteristics [1].

There are several metal identification methods such as inductively coupled plasma (ICP), laser-induced fluorescence (LIF) imaging spectroscopy, and x-ray fluorescence (XRF) spectroscopy. However, an ICP method needs complicatedly dissolved sample preparation and requires additional gas flowing during the examination as well as in LIF imaging spectroscopy [2-5]. XRF employs high energy of x-ray beam bombarding a fine-homogenized sample to identify elements composition in the sample by measuring x-ray energy level emitted from its element [2].

Laser-induced breakdown spectroscopy (LIBS) is a well-known emission spectroscopy for rapid identification of elements contained in a sample. In this method, high-power laser beam is used to ablate the sample surface to induce a plasma [2]. Emission characteristics of elements can be obtained by detecting a plasma emission containing atoms ablated from the material surface. It should be emphasized that compared to the other identification methods such as ICP, LIF, XRD and XRF, LIBS can be applied without complicated sample preparation [2-6]. LIBS had been applied for Cu detection in various sample including chromated copper arsenate (CCA) used as preservatives agent inside
wood wall surface. In that research, LIBS technique using Nd:YAG laser was compared with laser-induced gas plasma spectroscopy using transversely excited atmospheric (TEA) CO\(_2\) laser [7]. It can be clearly seen that Nd:YAG is able to detect Cu spectrum even though its detection limit is not as well as TEA CO\(_2\). However, in that LIBS technique, the pressure surrounding the sample was set at standard pressure (1 atmosphere). Furthermore, LIBS was also been employed to analyze Cu content in beef, trace metal elements (including Cu) in infant milk, and examine archeological coin, etc. [8-9].

In this study, LIBS operated at low pressure will be applied for rapid identification and characterization of Cu. The sample targets used in this study were pure Cu plate (99.99%) and a material containing copper (Indonesian currency coin). Characteristics of Cu lines in both samples were discussed.

2. Experimental Setup
The basic experimental setup employed in this research is shown in Fig. 1(a). Nd:YAG laser pulse (New Wave Research, 1845L, wavelength of 1046 nm, pulse energy of 50 mJ, pulse duration of 7 ns) was employed in this research as an energy source to evaporate, ionize and excite atoms and molecules from the sample surface. Laser pulse was reflected by mirror and focused onto the sample by using multicoating-convex lens of 100 mm in focal length. Energy and repetition rate of the laser pulse were arranged to 40 mJ and 10 Hz, respectively. The sample used in this study was high purity copper plate (Hikari, HC0326, Cu contents of 99.99 %) and Indonesian currency coin (500 rupiah). The sample was placed in vacuum tight chamber connected to compressor as vacuuming instrument andULVAC GP-1000G as a vacuum gauge was employed to monitor air pressure in the chamber. Air inside the chamber was compressed until the number of pressure pointed on vacuum gauge of 1.7 torr (about 267 kPa).

Figure 1(b) shows the plasma photograph obtained from the Cu plate. The plasma consisting of atoms, electrons, ions, molecules was induced when the laser was focused on a sample target [10]. This emission spectrum of plasma was detected by optical multi-channel analyzer (OMA system, Lambda Vision, SA-100W-HPCB1024/C), which one of its end was connected to the optical fiber to detect plasma emission and the other was connected to the computer system.

![Figure 1](image.png)

3. Result And Discussion
Characterization of materials is very important to be conducted, and one of the most prevalent characterizing method is LIBS due to its simplicity that does not need any complicated sample preparation. Sample placed in vacuum tight chamber was bombarded by Nd:YAG laser beams (pulse wavelength of 1064 nm, pulse energy of 30 mJ, pulse duration of 7 ns). Due to the laser bombardment, fine particles of the sample were evaporated. Following the process, evaporated particles was atomized and ionized in the plasma region.

The plasma was induced on the material target at low pressure air surrounding gas (267 kPa). The low pressure was chosen because plasma induced at low pressure will produce a secondary plasma,
which will not appear in the plasma at atmospheric pressure. In the low pressure, primary plasma induced by initial laser bombardments freely moves forward with very high velocity to induce a strong shock wave and finally produce a secondary plasma. In this process, a kinetic energy of the ablated atoms transforms into thermal energy. The atoms are excited in the secondary plasma.

Element contained in materials can be determined by identifying its spectrum line. Relative intensity shown in Y axis represents amount of photon emitted from each element in the material. Difference of the spectrum intensity is affected by internal factor e.g. atoms population, excited energy state, and probability of the atoms to excite to higher energy level, and external factor e.g. laser energy, laser wavelength, and emission affectivity.

Figure 2. Plasma spectrum of high purity Cu plate

Figure 2 shows emission spectrum of neutral copper (Cu I) at the wavelengths of 324.75, 327.40, 510.55, 515.32, and 521.82 nm taken from the high purity copper. The ionic line of Cu II also appears at the wavelengths of 406.81 and 657.71 nm. Based on Fig. 2, total intensities of Cu I line is much higher than that of Cu II. These results indicated the plasma induced in this study containing more atomic Cu than that of ionic Cu. In the plasma generation process, ionization process occurs very short time of less than 1 milliseconds before atomization. Electrons ejected by atoms during the ionization are further captured by ions and combine with it, so this process is well known as recombination process. Due to the recombination, ions release their energy as photon emission. Besides that, Cu has high ionization energy level, hence it requires a high energy to eject its electron. The higher the energy needed to ionize, the lower the possibility of the atoms to be ionized. This might be the reason why the ratio between Cu I and Cu II becomes so high. These results also confirm that Cu used in this study is a high purity copper because there are no other elemental lines observed in the spectrum line. Hydrogen existence in the spectrum line is neglected since this element normally appears in the air and attached to the copper surface [4]. The spectrum emission certified that present LIBS method can be used to identify Cu elements in the material target.

Table 1 shows the energy level of excited electrons of atoms in high purity copper. Based on the table, it can be seen that the probability of the electrons in ground state to be excited due to laser bombardment is very high, meanwhile the electrons excited at the higher level energy gives much lesser intensities in spectrum than the lower energy level case.
Table 1. Copper wavelengths, their kinetic energy, and intensities obtained in this study.

| Atom   | Wavelength (nm) | $E_i - E_k$ (eV) | Intensity (arb. unit) |
|--------|-----------------|------------------|----------------------|
| Cu I   | 324.754         | 0 – 3.817        | 12240                |
| Cu I   | 327.395         | 0 – 3.786        | 15860                |
| Cu II  | 406.811         |                  | 4420                 |
| Cu I   | 510.554         | 1.389 – 3.817    | 6570                 |
| Cu I   | 515.324         | 3.786 – 6.191    | 6960                 |
| Cu I   | 521.820         | 3.817 – 6.192    | 7780                 |
| H      | 656.279         | 10.198 – 12.088  | 3940                 |
| Cu II  | 657.708         |                  | 3160                 |

To examine the ability of the present LIBS method for detection of Cu element in other material containing various elements, an Indonesian currency coin was employed as a sample target. Figure 3 shows neutral Cu emission spectrum obtained from the Indonesian currency coin (red line). An emission spectrum of Cu taken from the high-purity Cu plate was also shown to compare with the spectrum from the coin. It can clearly be seen that the Cu lines appear from the coin target. However, the intensity of Cu lines from currency coin is much lower than that of Cu plate. This is because the currency coin contains much lower concentration of Cu than the plate case. The other element also appears in the coin target, namely atomic aluminum (Al I) at wavelengths of 309.28 nm and 396.15 nm, and ionic aluminum (Al II) at wavelength of 660.92 nm; the currency coin also contain Al with quite high concentration. The results confirmed that the present method can be used to identify Cu element in metal target containing Cu at quiet high concentration.

Figure 3. Emission spectra of Cu obtained from the high purity Cu plate (red line) and Indonesian currency coin (blue line)

4. Conclusion

Identification of Cu in high purity copper and Indonesia currency coin have been successfully demonstrated by using laser-induced breakdown spectroscopy at low pressure. High purity copper spectrum line shows neutral Cu I emission at the wavelengths of 324.75, 327.40, 510.55, 515.32, and
521.82 nm, and ionic Cu II emission at the wavelengths of 406.81, 655.13, and 657.71 nm. Total intensity of Cu I is much higher than the Cu II case. The other metal of Indonesian currency coin was also used as a sample target. The emission spectrum of coin target shows that Cu I and Cu II emission lines clearly appear in the wavelength as same as in the high purity copper case. However the Cu I emission intensities at wavelength of 324.75 and 327.40 nm from high purity copper is much higher than in the currency coin case. The emission spectrum obtained from the Indonesian currency coin also shows the other elements emission, such as atomic aluminum (Al I) at wavelengthof 309.28 nm and 396.15 nm, and ionic aluminum (Al II) at wavelength of 660.92 nm. These results indicate that present method can be employed to identify Cu element in metal target containing Cu at quiet high concentration.

Acknowledgement
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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