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Identification heavy metal pollution in biological samples around cement plant in Aceh, Indonesia using Laser Induced Breakdown Spectroscopy (LIBS)

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Abstract. A study was conducted for identification of heavy metal pollution from biological sample as a potential proxy of environmental pollution due to industrial waste. The identification was conducted using the emerging analytical tool, namely laser induced breakdown spectroscopy (LIBS). The sample was collected from seawater near a cement plant in Aceh. Samples is a conch shell. The sample was dried in the open air and then prepared in the form of a pellet. The analysis was made by generating a plasma on the pellet sample using an Nd-YAG laser with a wavelength of 1,064 nm which is focused with a lens that has a focal length ($f = 15$ cm) by varying laser energy under low pressure of 3 Torr of air surrounding gas. Emission from the generated plasma was transmitted to the Maya2000 spectrometer optical detector using an optical fiber and then the emission spectrum of each element is displayed on the monitor. The results showed that the snail shell contained the salts and heavy metal elements K, Pb, Gd, Se, Mg, Rb, Fe, and Xe. Thus, it can be concluded that the heavy metal elements Pb and Fe can be detected LIBS technique from the biological sample.

1. Introduction

Industrial plants not only have a positive impact but can also have a negative impact on the communities. Waste disposal that ignores environmental health will no doubt cause contamination to the environment. Some factory probably uses dangerous chemicals such as non-essential heavy metals that are still unknown to the body's benefits and even toxic. One example of non-essential heavy metal elements is lead, Pb. Pb accumulation in the body can cause poisoning of seizures and even death [1]. Thus, chemicals used in the industrial process make it possible to produce wastes contaminated by chemical elements that are highly harmful to human health. Therefore, one way to address the problem is to identify the chemical content of the environment.

Cement is powder or flour made of chalk and other materials used to make concrete glue bricks together or make walls. While the raw material used in cement is limestone and clay, it does not



eliminate the possibility of the burning process for making cement emit such dangerous chemical elements as heavy metals (Cu, Pb, Cr, etc) into the surrounding ecosystem. Some study using well established analytical tool such as atomic absorption spectroscopy (AAS), X-ray fluorescence (XRF), etc. has been made for examining the heavy metals around cement plants especially Padang cement and found that presence of heavy metals such as Al, Cd, Cr, Cu, Pb, and Zn in the environment surrounding the cement plants [2, 3].

It is considered the biological samples live in the environment surrounding the cement plane can be good proxy for detecting the emission of the poisonousness element into the environment. The conch samples such a snail or gastropods are generally a waterpot that is lightweight and easily affected by the presence of a chemical pollutants. Also mentioned that molluscs such as snails is the right bioindicators [4, 5]. Thus, analysis of the biological samples is useful for evaluating the possible heavy metal pollution in the surrounding area. In this study, detection of heavy metals will be carried out using an emerging analytical tool, namely laser induced breakdown spectroscopy on biological sample collected from the sea shore near a cement plant in Aceh, namely Andalas cement plant located in Lhoknga, Aceh Besar Regency. The biological sample used is a conch shells.

LIBS technique is a technique used to detect various chemical elements with a certain intensity contained in a material based on the resulting plasma ablation. Plasma is an ionized gas containing electrons, ions, neutral atoms and excited atoms, emitting specific emission spectra. The intensity of emission lines represents the concentration of the element in the material and the wavelength represents the type of the element [8]. The plasma characteristics is important to make LIBS analysis [6,8]. This technique promises many excellences over well-established analytical tools such as capability to detect almost all chemical elements that exist in the periodic table simultaneously and to analyse any samples in solid, liquid or gas phases without complex sample preparation and without damaging the sample [8]. Some study on the use of LIBS for biological samples of the river shells has been conducted and found that heavy metal can be detected [9, 10].

2. Method

The conch samples were taken from the seawater of Lhoknga Aceh Besar, in adjacent with Andalas cement plant Aceh. A sample is taken in slightly flooded waters by predicting all the elements found in the water which can be thoroughly absorbed by the sample and thus can produce a more accurate result [9]. The conch samples that had been taken was dried in the open air for approximately 12 hours. The sample is put inside a chamber.



Figure 1. (a) The sampling process and (b) the process of drying samples.

The LIBS experiment was conducted at the Nano Laser Laboratory of the Center for Physics Research (P2F) at the Indonesian Institute of Sciences (LIPI) PUSPIPTEK Serpong, South Tangerang. The experimental setup used in this work is illustrated in Fig. 2. In this LIBS technique, excitation source is an Nd-YAG laser (Q-Smart 850 model). The laser operated at the fundamental wavelength of 1064 nm with pulsed duration of 5.5 ns, and a repetition rate of 10 Hz. The laser is focused with the lens focal distance ($f = +15$ cm) towards the sample.

The measurement was under air surrounding at a pressure of 3 Torr. The generated plasma emission is transmitted by optical fiber into the spectrometer (Maya2000). Then the emission spectrum of each element is displayed on the monitor. This study will be repeated 5 times with variations in energy of 12 mJ, 45 mJ, 70 mJ, 93 mJ and 120 mJ. The obtained spectrum were processed with Origin Lab software and the wavelengths obtained were confirmed with Atomic spectrum data base, NIST [11].

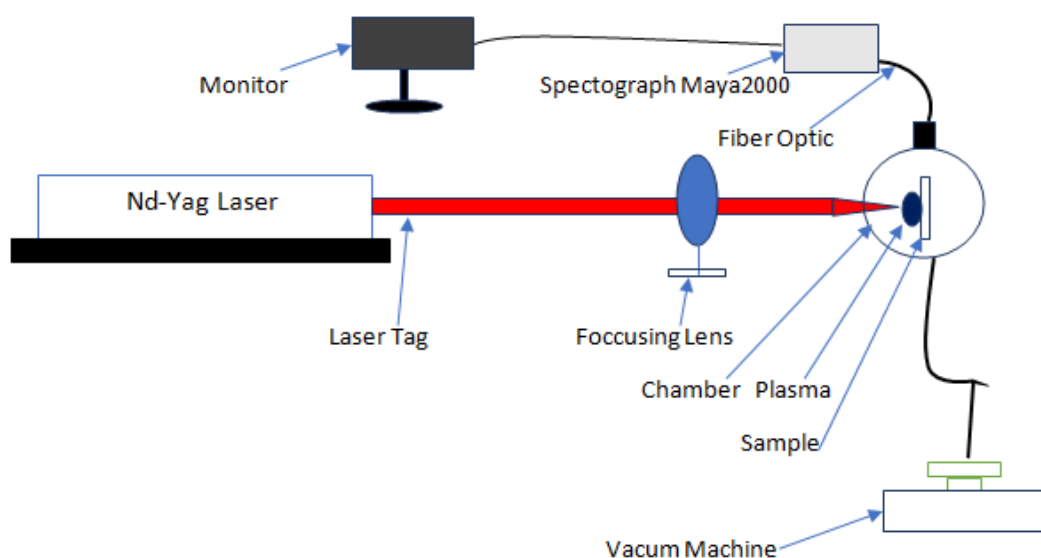


Figure 2. Arrangement of LIBS apparatus used in this work.

3. Results and discussions

The plasma emission produced by irradiation of Nd-YAG (Neodymium-doped yttrium aluminium garnet) laser on the biological sample was observed. The pictures of plasma produced from the biological sample is displayed in Fig. 3. The plasma was generated using a laser pulse of (a) 12 mJ and (b) 45 mJ, respectively, under air surrounding at a pressure of 3 Torr. It is observed clearly that the plasma size increase with laser energy. A visual observation on the plasma implies that the emission intensity is very strong, thus implying that biological sample can be excited well using the Nd-YAG laser. The characteristics of plasma are very dependent on the temperature and electron density [12]. Thus, the features of the emission spectrum depend strongly on the plasma characteristics. The chemical elements which are the main focus in this study are the presence or absence of heavy metal content in the biological material under study. Figure 4 shows the emission spectrum detected from the biological samples in a wavelength region, starting from 100 nm to 1200 nm, precisely from 300 nm to 1000 nm.

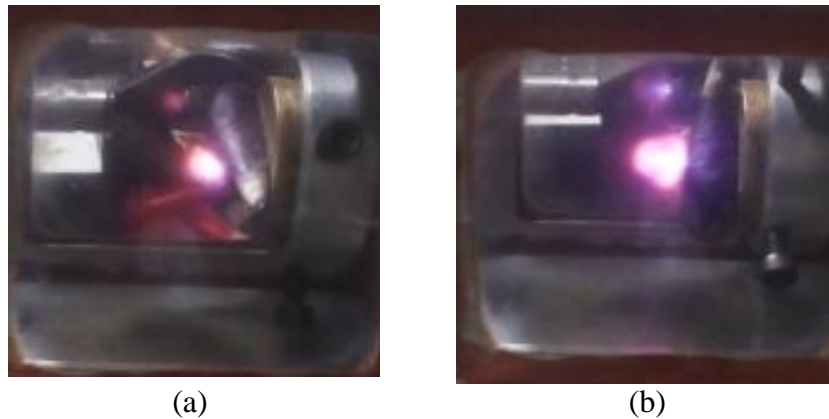


Figure 3. Photograph of plasma produced on biological sample, the sea conch shell, using the Nd-YAG laser of (a) 12 mJ and (b) 45 mJ.

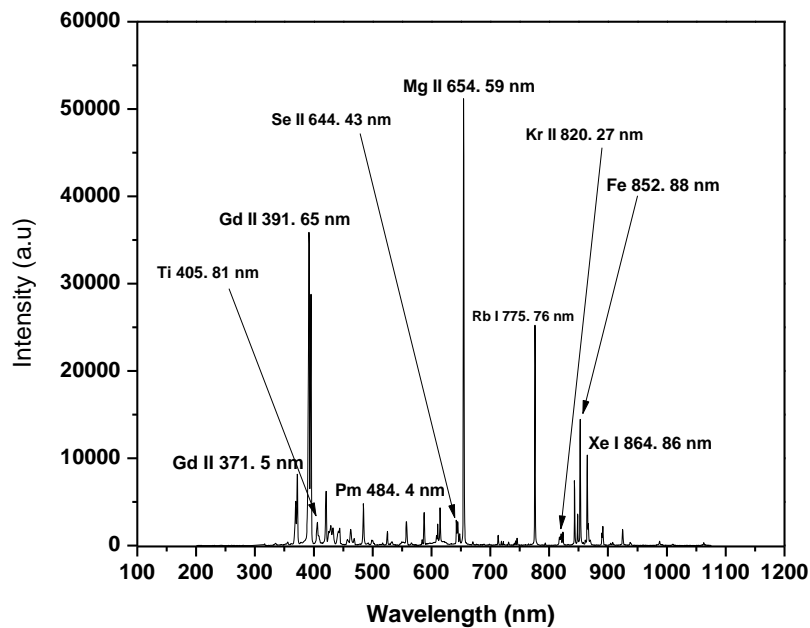


Figure 4. The emission spectrum taken from plasma produced on biological sample, the sea conch shell, using the Nd-YAG laser of 120 mJ under air surrounding gas at a pressure of 3 Torr.

The emission spectrum figure out that the conch shell from that waters contains chemical elements such as Gd (Gd II 395.65 nm, Gd II 371.95 nm), Mg (Mg II 654.59 nm), Rb (Rb I 775.76 nm) and Fe (Fe I 852.88 nm). The emission intensities due to the elements are relatively high. Along with the emission lines, other emission lines, namely Ti 405.81 nm, Se II 644.43 nm, Pm I 484,4 nm, Kr II 820.27 nm and Xe I 864.86 nm with relatively low intensity was found. Based on the guidelines from the directorate for the supervision of dangerous products and substances, the Indonesian National Drug and Food Control Agency explains that Se II 644.43 nm and Fe I 852.88 nm are included in the heavy metal category. The plasma characteristics produced on the sea conch shell and the emission spectrum features under different experimental condition will be studied in greater details.

4. Conclusion

LIBS has been used to analyse biological sample, namely the sea conch shell. Plasma can be produced well on the biological sample without tiring, complex sample preparation. Many elements can be found in the obtained emission spectrum, including Gd, Mg, Rb, Fe, Ti, Se, Pm, Kr and Xe. The elements were detected simultaneously in a single spectrum. Thus, LIBS can be used for analysis of biological sample. This work reveals the presence of heavy metals such as Se and Fe in biological sample taken in the environment around the cement plant in Aceh at Lhoknga Aceh. This indicates that the environment is contaminated with heavy metals.

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