Effect of pressure of laser-induced plasma spectroscopy for zinc element identification in multivitamin

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Abstract. Identification of zinc elements in 99.9% pure zinc metal and zinc multivitamin tablet samples has been done using Laser Induced Plasma Spectroscopy (LIBS) method. Plasma is generating by laser firing Nd: YAG (1064 nm, 50 mJ, 7 ns). Optimization of laser plasma was performed by varying environmental air pressure and on the spectrum of zinc. The character of samples is displayed in the spectrum line. Spectrum line of 99.9% pure zinc metal shows neutral zinc (Zn I) emission at wavelengths of 280.08, 330.25, 334.50, 472.21, 481.05 and 636.23 nm, and ionic zinc (Zn II) emission of 99.9% pure zinc metal at wavelengths of 250.19 and 255.79 nm. Zinc multivitamin tablet spectrum line shows Zn I emission at the wavelengths as same as 99.9% pure zinc metal of 334.50 and 481.05 nm, which is the intensities of Zn I at a wavelength of 334.50 and 481.05 nm in zinc multivitamin tablet is much higher than in the 99.9% pure zinc metal. The higher the given environmental air pressure, the higher the intensity of the zinc emission spectrum accompanied by high background emission intensity.

1. Introduction
Zinc has been studied extensively in recent years, as it plays an important role in human food products such as pharmaceutical products [1]. Pharmaceutical products are fundamental and important for the treatment of diseases and are used as complementary and alternative products for health care the expansion of production and use of pharmaceutical products and herbal medicines around the world, making their quality, efficacy, and safety an important concern for the public and health authorities. It is necessary to keep the products safe, effective, and quality [2]. To ensure the effectiveness, safety, and developed methodologies in assessment and quality control of pharmaceutical products and herbal medicines, has conducted various studies. Pharmaceutical analysis can be used as an important approach to understanding the active pharmaceutical ingredients and the trace elements contained therein [3].

The techniques used to identify the zinc in pharmaceutical products are Spectrophotometric method [1] and Multivariate (Chemometric) Methods in NMR Spectroscopic to detect the authenticity and quality control of pharmaceutical products. This technique can be performed to analyze pharmaceutical products because it is supported with a powerful tool [4]. (Laser-induced plasma spectroscopy / LIBS) is a better method to identify the zinc element in a multivitamin, in which a short pulse laser is a focus to the sample surface. This technique has advantages including less sample preparation, low cost in the analysis [5]. In this study, detection of zinc element in multivitamin will be carried out using the LIBS technique conducted at high and low pressure. The identification of zinc
emission spectrum will also be studied. The comparison of zinc emission characteristic obtain from multivitamin and zinc metal plate will be made.

2. Experimental Setup

The basic experimental set-up is showed in Fig.1. A pulse Nd-YAG is focused on the sample surface by using the convex lens of 100mm to produce a plasma. The repetition rate and energy of the laser beam were 10 Hz and 45 mJ. The sample used in this study are 99.9% pure zinc metal plate and zinc multivitamin tablet. The sample was placed in a vacuum chamber connected to the compressor as vacuuming instrument. The value of air pressure is displayed on Pirani vacuum gauge employed to monitor air pressure in the chamber. Experimentally, after plasma produced, the plasma emission was detected by using Optical Multi channel Analyzer via an optical fiber connected to the computer. The experiment was conducted at high and low pressure of $10^5$ Pa and 400 Pa. The emission spectra obtained in this study was confirmed with the data reference of NIST and Kurucz database.

![Figure 1. Experimental Set-up used in this study](image)

3. Result and Discussion

The plasma generated from the generation mechanism by firing a laser beam has unique characteristics. This is because ionized and excited gases from the material constituents emit specific elements of wavelength with the color and size of the laser plasma varying according to the transition energy level. The laser firing of the samples was obtained visually differently, according to the given air pressure values. As shown in Figure 2 (a) the resulting plasma is bright white with a diameter of 2 mm. If plasma generation is carried out under high-pressure air pressure environment of $10^5$ Pa. Plasma is generated has the shape of a small ball of white light with a radius of the order of millimeters and has a high density [6].

Figure 2 (b) shows that the plasma is generated at a low pressure of about 400 Pa has a size larger than the plasma generated at a pressure of 105 Pa. The plasma diameter at low pressure is 11 mm and has a bright blue color. The bright blue color is generated from the wavelength of the zinc elements with a wavelength range between 450 - 495 nm.
Figure 2. Plasma photo obtained from the 99.9% pure zinc metal plate at an air pressure of (a) $10^5$ Pa (b) 400 Pa

Plasma generation at a low-pressure condition consists of two distinct areas, namely the area of primary plasma and secondary plasma. The first area (center) is called the primary plasma is a narrow region located right area the laser interaction with the sample and bright white because it emits a continuous emission spectrum in a short time [6,7].

Figure 3. Emission of spectrum line obtained from 99.9% pure metal zinc plate at a high pressure of $10^5$ Pa
Figure 3 shows an emission spectrum of zinc obtained from 99.9% pure metal zinc plate at high pressure of $10^5$ Pa. Very clear atomic Zn lines at 280.08, 330.25, 334.50, 472.21, 481.05 and 636.23 nm and ionic Zn lines at 250.19 and 255.79 nm appear with high emission intensity.

As shown in Figure 4, the emission spectrum of zinc obtained from 99.9% pure metal zinc plate at a low pressure of 400 Pa displayed discrete spectrum lines with a low background spectrum and formed sharp intensity peaks. Atomic Zn lines at 330.25, 334.50, 472.21, Zn I 481.05 and 636.23 nm appear with high emission intensity. There is a difference in the background spectrum detected by OMA at a pressure of $10^5$ Pa and 400 Pa. Only a few affect the intensity of the spectrum for each pressure variation. This is because the plasma volume at 400 Pa is greater than the plasma volume at $10^5$ Pa. Thus causing the emission intensity spectrum at a pressure of 400 Pa lower than the pressure of $10^5$ Pa.

Khumaeni et al., state about increasing LIBS emissions can be explained by changes that are dependent on pressure from the evaporated sample target and collision frequency between species in the plasma. At high pressures, the resulting plasma cannot expand freely so that the plasma density produced is high and makes the plasma shielding effect high. This causes the plasma produced at high pressure can absorb a laser beam so that it becomes a shield for the laser beam to reach the sample target. At low pressure, the plasma produced can expand freely so that the plasma density produced is low and the electron population is very low. This process produces shock waves with very low densities and will reduce the plasma shielding effect and allow photons to reach the target sample directly from the laser beam. More photons that interact with the surface of the sample will more abrasive the surface and produce a more intense spectrum. The intensity of emissions reduced at low pressure is caused by shock waves from the plasma and freely expand, reducing the frequency of collisions between species in the plasma such as electrons and ions. The reduced frequency of collisions between species will reduce the emission intensity of the spectrum obtained [7, 8].
To prove that the zinc elements detected in a zinc multivitamin tablet sample are a zinc element then the emission spectrum of zinc multivitamin tablet is compared with the emission spectrum of 99.9% pure zinc metal as shown in Figure 5.

Figure 5 shows that the wavelength of zinc consistently appears in the emission spectrum of 99.9% pure zinc metal also appears in the emission spectrum of zinc multivitamin tablet. The same wavelength detected for each sample was Zn I 334.50 nm and Zn I 481.05 nm. Zinc multivitamin tablet spectrum line also shows another elements emission, such as atomic magnesium (Mg I) at wavelengths of 385.39 nm and 821.30 nm, and atomic sodium (Na I) at a wavelength of 589.59 nm.

Zinc multivitamin tablet sample has a content equivalent to 54.9 mg of zinc sulfate (ZnSO4). The spectrum of zinc multivitamin tablet shows broadening lines in the wavelength range of 350 nm to 500 nm. The broadening line of zinc multivitamin tablet spectrum has similarities with ZnS pure spectrum in the research of Iranmanesh et al., which shows the spectrum of photoluminescence of ZnS nanoparticles that have been synthesized to investigate luminescence. ZnS pure in bulk and nano crystals shows the main emission bands, namely blue bands. Although not specific shows the ZnSO4 compound, but the broadening line of spectrum that appears for ZnSO4 and ZnS compounds is similar [9]. Broadening line in LIBS spectrum due to the effect of Stark Broadening and Doppler Broadening effects. Stark Broadening occurred due to interference from the two levels of heavy particles (ions or atoms) are involved in the radiation transition, during collisions with charge particles. Doppler Broadening occurred due to the Doppler effect caused by the velocity distribution of atoms, ions or molecules [10].

It should be informed that zinc tablet contains zinc with a concentration of 3.7%. Zinc multivitamin tablet that used in this research is produced by Kimia Farma Company, and it included a group of generic pharmaceutical product. This result certified that the LIBS technique could be employed to detect elements in pharmaceutical products.

4. Conclusion
Identification of zinc element in 99.9% pure zinc metal plate and zinc multivitamin tablet has been demonstrated by using laser-induced breakdown spectroscopy at high pressure and low pressure. The emission spectrum of zinc multivitamin tablet at Zn I 334.50 nm and Zn I 481.05 nm appear with high intensity. In plasma optimization, variations of air pressure affected the zinc emission spectrum.
variations of air pressure, the higher the given environmental air pressure, the higher the intensity of the zinc emission spectrum accompanied by high background emission intensity. Thus, it affected the accuracy of emission spectrum identification of zinc element with low intensity.

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