

Elemental Characterization Of Human Blood Using Laser- Induced Breakdown Spectroscopy Utilizing 355 Nm Nd Yag Operated At Reduced Pressure Of He Gas

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ELEMENTAL CHARACTERIZATION OF HUMAN BLOOD USING LASER-INDUCED BREAKDOWN SPECTROSCOPY UTILIZING 355 NM Nd: YAG OPERATED AT REDUCED PRESSURE OF He GAS

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ABSTRACT

The human blood serum has often been used as a medium for diagnoses of various diseases based on elemental composition. In this paper, elemental identification and analysis of human blood serum have been performed using a standard LIBS technique utilizing 355 nm Nd: YAG laser under He surrounding gas. Experimentally, human serum was homogeneously dropped on a copper metal plate to produce a thin film. The film was then evacuated in a sample chamber, which is filled with He gas at 5-3 torr. A Nd:YAG laser was bombarded on a film to produce a breakdown plasma. Some elements in the serum from the normal and tuberculosis (TB) patients have successfully been identified, including C, H, O, Ca, and Na. The analyte intensities from the human serum of TB patients have good stability with laser shot dependence in different positions. A preliminary test to distinguish the TB patient from normal patient was made based on Ca elements in the blood serum. Namely, the Ca intensities from TB patient is much higher than the case of a normal patient.

Keywords: Human Blood Serum, TB Patient, LIBS, Laser-induced Plasma Spectroscopy, 355 nm Nd:YAG Laser

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INTRODUCTION

Elements deposited in the human blood serum have attracted many researchers, especially in the field of medical researches.¹ The human serum contains essential elements, which are very important for human life. Some imperative elements are nitrogen, oxygen, hydrogen, carbon, potassium, phosphorus, chlorine, and magnesium, while the essential trace elements are calcium, iron, zinc, manganese, chromium, iodine, silicon, and arsenic. These elements should be present in the human blood in a fair constant concentration. Nutritional elemental deficiency or abundance in the human body, including human blood serum, leads to susceptibility to infectious diseases. The human serum has often been used as media for diagnoses of various diseases based on elemental composition.² Therefore, sensitive and accurate elemental identification and analysis of blood serum are indispensable.

Some imaging and spectroscopic methods have been commercially purchasable and employed in the study of disease diagnosis based on elemental composition. These ICP-OES and NAA spectroscopy. Such methods are widely adopted for accurate and sensitive elemental analyses. However, tedious sample pretreatments are needed and the techniques suffer from serious spectra interference because of multi-elements present in the sample target.³⁻⁵

Laser-induced breakdown spectroscopy (LIBS) is a rising-star technique for elemental analysis in many kinds of samples such as gases, liquids, and solids.⁶⁻¹⁰ Experimentally, a pulse Nd:YAG laser 1064 nm is used to induce a breakdown plasma, which plays a role as an excitation source of atoms from the material target. The applications of LIBS to elemental analysis of human blood serum have been reported in some literature. However, it is known that LIBS has a limitation for the analysis of liquid samples such as blood

serum, due to the low sensitivity and delicate sample preparations. Furthermore, a standard LIBS technique operated at atmospheric ambient air is very delicate to detect H and C, which are the main elements in the blood serum, because of the time mismatch effect.¹¹⁻¹²

In this work, we proposed laser-induced plasma spectroscopy using 355 nm Nd:YAG laser in reduced pressure of He gas for identification and analysis of elements in the blood serum, including human blood serum from the normal patient and tuberculosis patients. The use of He gas in the study is to produce lots of He metastable atoms (He* atoms) in the plasma. The He* atoms work, assisting a process of atomic excitation of the analyte atoms, including light atoms of carbon and hydrogen. The sample was made as a film deposited on a copper metal subtarget. The result certified that the element intensities of C and H in both human blood serum of normal and TB patients are successfully enhanced with optimum S/N ratio and without any broaden line. Furthermore, the human blood serum of the TB patients can be distinguished from the blood serum of normal patients based on trace elements of Ca identified in the spectrum.

EXPERIMENTAL

Figure-1 displays a setup used in this paper. First, an Nd:YAG laser (355 nm, 10 Hz, energy of 70 mJ) was irradiated and focused on a sample target using a quartz lens ($f = 150$ mm) to initiate and produce a breakdown plasma. Experimentally, the sample target was put in a chamber, in which the helium gas (air-liquid, purity of 6N) was used as an environmental gas of sample with a flowing rate of 10 liters per minute and gas pressure of 5 torr.

The human blood serum collected from the normal patients and TB patients at Diponegoro National Hospital was used as a sample target. For the experiment, 1 ml liquid serum was poured on a copper metal plate (99.9 % purity) with a dimension of $0.1 \times 20 \times 20$ mm³. The serum was homogeneously spread on the surface of Cu plate. The serum was then placed at room temperature for 30 minutes to produce a serum film. During data acquisition, the sample was put in a chamber and was rotated with a rotation rate of 2 rotations per minute (rpm).

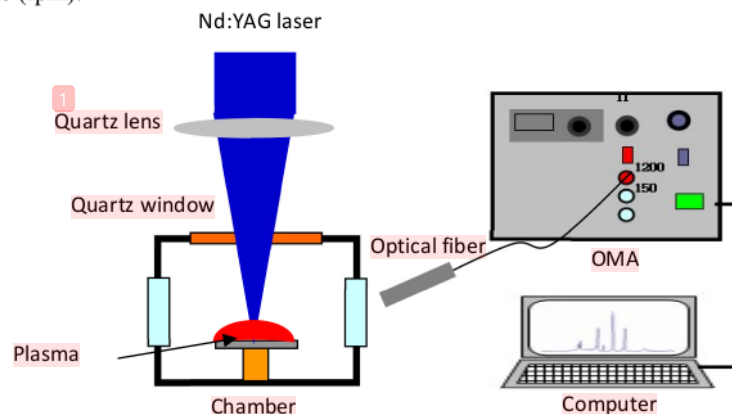


Fig.-1: Experimental Setup used in this Work

The atomic emission spectrum was obtained from the breakdown plasma by using an Echelle spectrograph (Mechelle M5000, Andor) via an optical fiber that is connected to the spectrograph. The delay time and gate widths are $1 \mu\text{s}$ and $5 \mu\text{s}$, respectively.

RESULTS AND DISCUSSION

Initially, spectrochemical characteristics of Cu metal plate as a metal sub-target during the study were examined. Figure-2 displays the analytical spectrum of Cu taken from the Cu metal plate only. Typical resonance lines of neutral Cu occur at 324.7 nm and 327.4 nm. The other lines of typical neutral Cu are also detected at 510.5 nm, 515.3 nm, and 521.8 nm. These lines are contributed from the Cu plate used as a sub-target. No other elements are identified from the Cu sub-target.

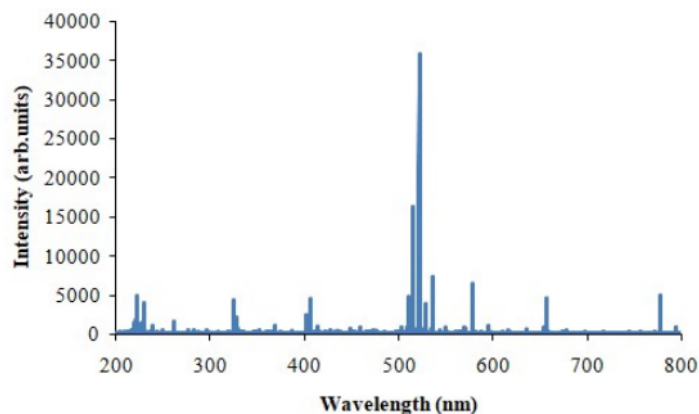


Fig.-2: An Analytical Spectrum is taken from the Cu Metal

Further work was the identification of elements from the human blood serum. Figure-3 displays an emission spectrum of the human blood serum of normal patients using the present LIBS technique. The laser energy used was 70 mJ. The analytical lines of neutral C, H, and O occur clearly at 247.8 nm, 656.3 nm, and 777.7 nm, respectively. The other lines of neutral sodium at 588.9 nm and 589.5 nm, ionic Ca at 393.3 nm and 396.8 nm appear faintly in the spectrum. Those elements are major and minor elements in the human blood serum, as reported here.¹³ In addition, typical lines of neutral Cu clearly occur at 324.7 nm, 327 nm, 510.5 nm, 515.3 nm, and 521.8 nm. These lines are contributed from the Cu plate used as a sub-target.

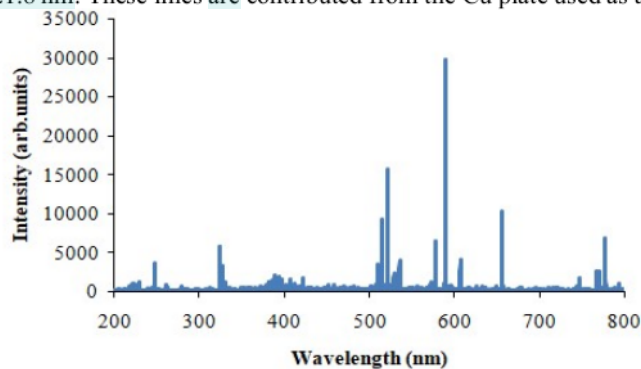


Fig.-3: The emission spectrum is taken from the human blood serum of a normal patient at a reduced pressure of ambient air

To obtain optimum intensity and S/N ratio of the analyte, the effect of laser energy on emission intensities of major and trace elements in normal human blood serum was examined. Figure-4 shows the laser energy dependence to emission intensities of C, H, and O at 247.8 nm, 656.3 nm, and O I 777.7 nm, respectively, and Ca I 393.3 nm. It can clearly be seen that the S/N ratio of all elements increases with increasing the laser energy from 30 to 70 mJ. As reported in the paper,¹⁴ atomic excitation in the plasma region effectively happens with an increment of laser energy. However, it should be mentioned that the intensities of atoms remained stable when the laser energy was much more increased, which might be due to saturation. Also, when laser energy was more increased, the ablation of the Cu sub-target metal increased, increasing the ablated Cu intensities and thus disturbing the emission lines of analytes. Therefore, in this present work, the laser energy of 70 mJ was selected during the experiment for obtaining the optimum emission intensities and S/N ratio of analytical lines.

The effect of ambient He gas in the intensity enhancement was also studied. The use of He as a surrounding gas can produce He metastable atoms, which play a role in the excitation process.¹⁵⁻¹⁶ Figure-5 displays the human blood spectrum of a normal patient. It appears that the total emission intensities of analytical lines

in He gas increased almost 4 times compared to the case of ambient air (Fig.-3). All major and trace elements, including neutral C at 247.8 nm, ionic C at 393.3 nm and 396.8 nm, H I 656.3 nm, He I 667.8 nm, neutral Na at 588.9 nm and 589.5 nm, and O I 777.7 nm are clearly identified with increasing the intensities compared to the case in ambient air.

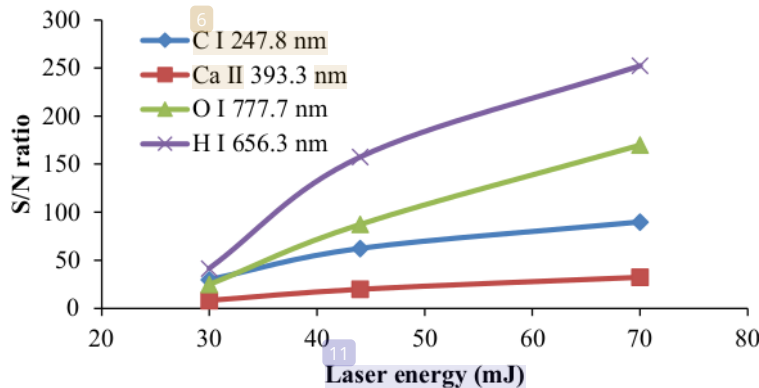
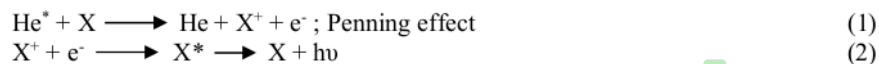


Fig.-4: Laser energy dependence of the emission intensities of analyte taken from the human blood serum of the normal patient

It is assumed that the increment of the total emission intensities happens in the He plasma due to the different excitation processes. Namely, the excitation process in the He plasma region takes place through He metastable atoms (He* atoms).¹⁷⁻¹⁸ In this process, lots of He metastable atoms, which have a very high potential energy of 19.8 eV, produce in the plasma region. He* atoms collide with analyte atoms and by transferring the potential energy of He* atoms, the analyte atoms are excited and ionized via the penning effect. The ionized analyte atoms are then recombined to produce atomic emissions. All the process follows the question below,

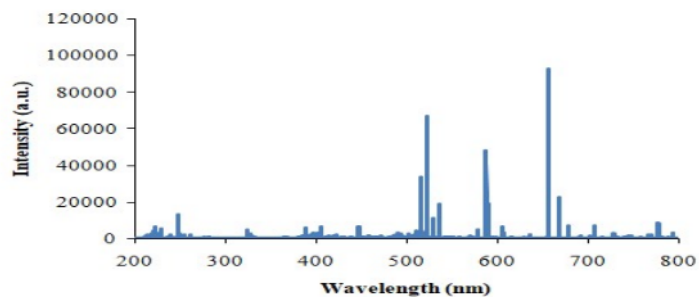


Ablated X atom from the material target collides via penning effect with the metastable He atoms accumulated in the He gas plasma region, resulting in X ion and free-electron (Eq. 1). Multiple collisions among free electrons, He metastable atoms, and other constituents in the plasma region reduce electron's energy and finally electron recombines with the X ion to produce X*, which results in the emission of X atom as displayed in Eq. 2. Figure 5(b) shows a zoomed area of Fig. 5(a) in the range of 390 nm to 400 nm. It is seen that the emission intensities of ionic Ca at 393.3 nm and 396.8 nm only faintly occur with quite noise.

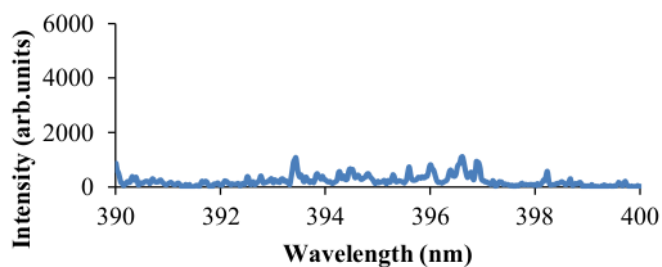
The present technique was then employed to identify and analyze elements in the blood serum obtained from tuberculosis (TB) patient. Figure-6 is a spectrum taken from the human blood serum of TB patients and zoomed area of Fig.-6 in the wavelength region of 390 nm to 400 nm (Fig. 6b). Total emission intensities of major and minor elements including C, Na, H, and O obtained from both blood serum of normal and TB patients are almost the same. However, it should be noticed that the intensity of Ca as a trace element in the human blood serum of TB patients is significantly different from the normal patient case. Namely, the ionic Ca emission intensity in TB patients is almost four times higher than the case of a normal patient. Therefore, the existence of Ca atom in human blood serum can be used to distinguish the serum from the TB patient to a normal patient. The human blood of TB patients contains Ca as a trace element.¹⁸ Further detailed study on analysis of human blood serum from the TB patients will be carried out in the near future.

The reproducibility of the analytical intensities obtained from the human blood serum was then examined. Figure-7 shows the laser shot dependence to the S/N ratio of the analyte, including ionic Ca 393.3 nm,

neutral O 777.7 nm, neutral H 656.3 nm, and neutral C 247.8 nm obtained from the blood serum of TB patients. Intensities of Ca, O, H, and C have good stability with the number of laser shots in a different position.



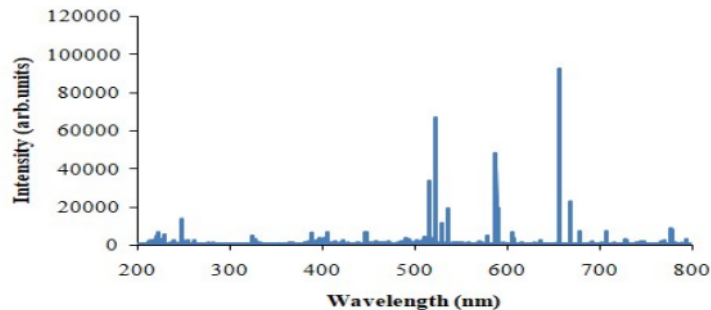
(a)



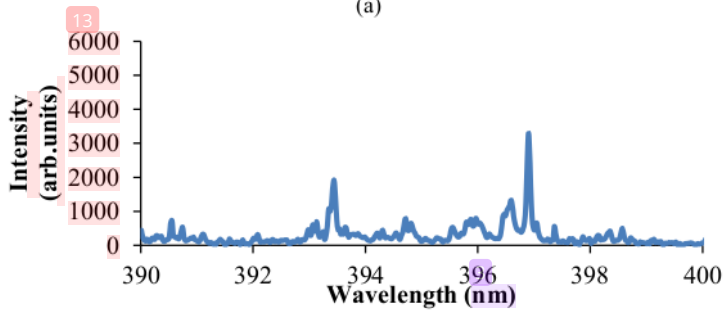
(b)

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Fig.-5: The emission spectrum is taken from the human blood serum of a normal patient at a reduced pressure of He gas, (a) 200-800 nm and (b) 390-400 nm



(a)



(b)

Fig.-6: Emission spectrum is taken from the human blood serum of TB patients at a reduced pressure of He gas, (a) 200-800 nm and (b) 390-400 nm

The present technique has good precision in the analytical result and thus, it can be employed to the analysis of organic liquid material such as human blood serum, which is usually difficult to perform using the standard LIBS technique.

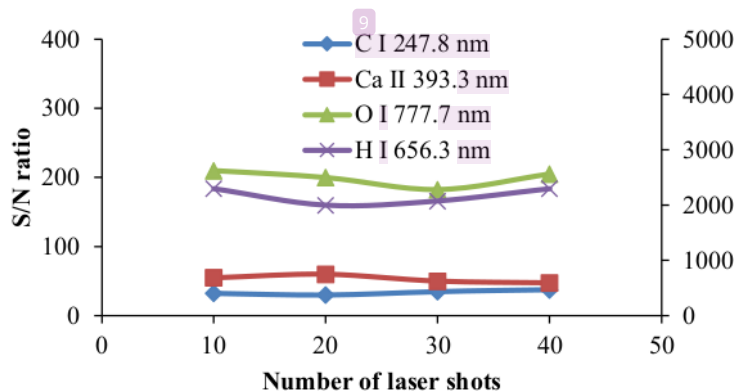


Fig.-7: Laser shot dependence of the emission intensities of analyte taken from the human blood serum of TB patient at a reduced pressure of He gas

CONCLUSION

Identification and analysis of human blood taken from the normal and TB patients have been realized by LIBS utilizing 355 nm Nd:YAG laser at a reduced pressure of He surrounding gas. Identification of elements including C, H, O, and Na in human blood serum was successfully performed. The intensities of those elements are very stable with the number of laser shots in different positions. It was also found that based on trace elemental identification of Ca, the human blood serum from the TB patient contains a higher concentration of Ca compared to the case of a normal patient. This present method has a high possibility to be applied to the analysis of TB patients based on human blood serum as an early diagnosis of TB disease.

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