Identification of elements in liquid-immersed particles by pulse CO$_2$ laser-induced breakdown spectroscopy

Ali Khumaeni, Asep Yoyo Wardaya and Wahyu Setia Budi
Department of Physics, Faculty of Science and Mathematics, Diponegoro University Jl. Prof. Soedharto, SH, Tembalang, Semarang 50275, Indonesia
E-mail: khumaeni@fisika.undip.ac.id

Abstract. New devised metal subtarget technique has been developed for specific applications of liquid analysis. Experimentally, liquid material was homogeneously poured on a surface of metal plate, which functions as a metal subtarget. The metal surface was then dried using drying machine. When a pulse CO$_2$ laser (10.64 μm) was irradiated on a metal subtarget, a large-volume plasma was induced. During laser irradiation, a material target was vaporized and moved into the plasma region to be dissociated and excited. The technique was successfully used to identify major elements such as Ca and Mg in cement and to identify light elements such as C and H in gasoline liquid. Finally, the technique was also successfully employed to detect impurity element of Ca in human blood. This method is very potential to be applied for the analysis of liquid without tedious sample pretreatment.

1. Introduction

Examination of chemical properties in liquid-immersed particles is very important for specific purpose in some fields including science and industries [1-3]. In medical field, the elemental analysis of blood can be used to diagnose a specific disease in human being such as cancer. In environmental field, analysis of liquid-immersed fine particles is necessary to determine the impurity in the environment including soils and waters. In industry, analysis of liquid is also imperative for impurity detection in industrial products.

The methods often employed to liquid analysis is atomic spectrometry and mass spectrometry [4,5]. The methods offer high-sensitivity and high-precision analysis of liquid. However, the technique needs delicate pretreatment and is highly priced. The other method, which is recently used to analysis of liquid, is laser-induced breakdown spectroscopy (LIBS) [6,7]. In this method, a neodymium yttrium aluminium garnet (Nd:YAG) laser is generally employed as an energy source to induce a luminous plasma on material surface. Compared to other mentioned method, the LIBS can be employed for analysis with less sample preparation, quiet cheap experimental tools. Especially for applications on liquid analysis, some sample devices has been developed including liquid jet and wood-immersed liquid.

In this work, a new devised technique using metal subtarget was introduced to analysis of liquid-immersed fine particles utilizing a pulse transversely excited atmospheric (TEA) CO$_2$ laser. In the study, the liquid was poured on a metal surface and then was dried to deposit on the surface. The results indicated that rapid analysis of liquid can be successfully demonstrated.
2. Experimental Method
Experimental arrangement used in this work is illustrated in Fig. 1(a). A pulse CO\textsubscript{2} laser was directed and focused using a ZnSe lens (focal length of 200 mm) on a sample target to induce a luminous laser plasma on metal surface. The energy of laser was 750 mJ and duration of laser pulse was 200 ns. The optical fiber connected to optical multichannel analyzer (OMA) system was used to collect plasma emission to get an emission spectrum of plasma obtained from the sample target.

![Experimental arrangement](image)

**Figure 1.** (a) Experimental arrangement, (b) Sampling technique used in this work

The samples used in this work included cement powder, firework powder, gasoline, and blood. For analysis of fine particles and liquid samples, fine particles were immersed in a liquid with saturated concentration. The liquid sample was then homogeneously poured on a Cu metal plate, with a function as a metal subtarget. The sample was then dried for 10 minutes at 100\textdegree C to get fine particles deposited on the metal. The sample was then placed into a metal chamber with a diameter of 12 cm, which can be evacuated with various gas environments. During experiment, He gas (99.999 \%) was introduced into the metal chamber to remove the dust impurity in the chamber.

3. Results and Discussion
The use of metal subtarget in LIBS using TEA CO\textsubscript{2} laser is very unique, namely the metal functions to deposit a sample target and to induce a large-volume and high-temperature gas plasma as successfully studied in the report [8].

![Spectrum obtained from the Copper metal subtaget using this present technique](image)

**Figure 2** Spectrum obtained from the Copper metal subtaget using this present technique

In this present work, the metal was used to deposit fine particles and liquid film used as the sample. It is hypothesized that once a TEA CO\textsubscript{2} laser is focused on metal subtarget, on which the fine particles and liquid film were deposited, a luminous plasma is induced just above the subtarget by the assisting of metal subtarget. The fine particles and liquid film are then vaporized into the area of plasma to be
atomized and excited. It should be informed that the Cu metal subtarget used in this study is never ablated and atomized in the plasma region because the power density of laser on the metal surface is much lower than the density of the metal. The metal only functions to initiate and induce a plasma and therefore, the emission spectrum of Cu does not detected as displayed in Fig. 2. The spectrum emission ranging from 480 to 550 nm displayed that no neutral Cu I emission at the wavelength of 510.5 nm, 515.5 nm, and 521.8 nm was detected. This spectrum proved that the Cu was not ablated by CO$_2$ laser and it only functions as a subtarget to induce a luminous plasma.

Figure 3 Emission spectra of nitrogen and potassium obtained from the liquid-immersed fireworks powder at the wavelength of (a) 735-755 nm and (b) 760-800 nm.

The metal subtarget technique was then applied to rapid identification of elements in liquid immersed fine particles and liquids. First, the fireworks powder was used as a sample. Figure 3 shows emission spectra obtained from the fireworks powder at the wavelength of (a) 735-755 nm and (b) 760-800 nm. Fireworks powder is chemical explosive, which consist of a mixture of potassium nitrate, charcoal, and sulphur. The sulphur functions as fuels and the potassium nitrate is as an oxidizer. As is seen in Fig. 3(a), nitrogen (N) emission lines clearly appeared at the wavelength of 742.4, 744.2, and 746.8 nm. Also, potassium (K) emission lines occurred at 766.5 and 769.9 nm, while the oxygen (O) line was detected at 777.7 nm. The elements of K, N, and O are the element component composing fireworks powder. The results confirmed that the presented technique can successfully be employed to identify the elements in fireworks.

Figure 4 Spectra obtained from the liquid-immersed cement powder at the wavelength of (a) 360-440 nm and (b) 270-300 nm.
The technique was then used to detect elements in other fine powder of cement powder. Figure 4 shows emission spectra obtained from the cement powder. Cement powder contain Ca and Mg at around 50 % and 5 %, respectively. High-intensity emission lines of Ca II 393.3 and 396.8 nm and Ca I 422.6 nm occurs in the spectrum as shown in Fig. 4(a). For Mg detection, the OMA system was set at the wavelength from 270 to 300 nm as displayed in Fig. 4(b). Ionic Mg lines at 279 nm and 280 nm are clearly observed with high emission intensity, while the neutral Mg line 285.3 nm appears faintly. As obtained in the spectra (Fig. 4), the ionic elements are dominant in the plasma region, certifying that the ionization process of atoms most often takes place in the plasma. This is because the temperature of laser-induced plasma generated by TEA CO₂ laser on metal surface is quiet high of around 5000 K. This high-temperature plasma can effectively be used to excite and ionize atoms ablated from the materials, resulting in high emission intensity of analytes.

![Emission spectra](image1)

**Figure 5** Emission spectra taken from the gasoline liquid using the present technique at the wavelength of (a) 220-270 nm and (b) 620-700 nm.

The present technique was employed to identification of light elements in liquid material. Identification of light elements such as C and H is very delicate to be realized by using conventional LIBS method utilizing Nd:YAG laser due to the mismatching effect of light elements in the laser plasma. For this purpose, gasoline sample and blood sample were used. Figure 5 displays emission spectra obtained from the gasoline liquid. It is known that gasoline contains carbon (C), hydrogen (H), and oxygen (O) as major elements. Emission line of C at 247.8 nm appears with quiet high background emission. The H line at 656.7 nm is also clearly detected with high intensity. Unidentified lines also appear around 650 nm and 660 nm. This result certified that this present technique can successfully be employed to identification of light elements even in liquid material.

![Spectrum](image2)

**Figure 6** Spectrum obtained from the human blood using the present technique.

Finally, the technique used to detect impurity elements in liquid. To this end, identification of Ca in human blood is demonstrated. The blood of normal adults contains Ca at concentration of around 50
mg/L [9]. Figure 6 shows the spectrum of Ca obtained from the human blood. Ionic Ca lines at 393.3 nm and 396.8 nm are identified with high signal peak and low background emission.

4. Conclusion
Detection of elements in liquid material has been demonstrated using new devised technique of metal subtarget. In this work, liquid-immersed fine particles and liquid material was homogeneously poured on a metal subtarget and finally dried by drying machine. A large-volume plasma was generated when the TEA CO₂ laser was irradiated on the metal surface. The dried fine particles and liquid was vaporized and enter into the plasma region to be dissociated and excited. Using this technique, identification of elements in some liquid materials including liquid-immersed fireworks, liquid-immersed cement, gasoline, and human blood have been made. Identification of light elements such as C and H, which is usually difficult to be carried out using conventional LIBS method, can be realized by using gasoline liquid. The impurity element of Ca in human blood can also be identified clearly using this present metal subtarget technique. Therefore, this present technique is very powerful for specific application on analysis of liquid without tedious sample pretreatment.

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6. References
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