TRANSVERSELY EXCITED ATMOSPHERIC CO$_2$ LASER-INDUCED PLASMA SPECTROSCOPY FOR THE DETECTION OF HEAVY METALS IN SOIL

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A rapid detection of heavy metals in soil was presented by the metal-assisted gas plasma method using specific characteristics of a pulsed, transversely excited atmospheric (TEA) CO$_2$ laser. The soil particles were placed in a hole made of acrylic plate. The sample was covered by a to prevent the soil particles from being blown off. The mesh also functioned to initiate a luminous plasma. When a TEA CO$_2$ laser (1500 mJ, 200 ns) was focused on the soil sample, passing through the metal mesh, some of the laser energy was used to generate the gas plasma on the mesh surface, and the remaining laser energy was employed to ablate the soil particles. The fine, ablated soil particles moved into the gas plasma region to be dissociated and excited. Using this technique, analysis can be made with reduced sample pretreatment, and therefore a rapid analysis can be performed efficiently. The results proved that the signal to noise ratio (S/N) of the emission spectral lines is much better for the case of the present method (mesh method) compared to the case of standard laser-induced breakdown spectroscopy using the pellet method. Rapid detection of heavy metal elements in soil has been successfully carried out. The detection limits of Cu and Hg in soil were estimated to be 3 and 10 mg/kg, respectively. The present method has good potential for rapid and sensitive detection of heavy metals in soil samples.

Keywords: *heavy metal detection, soil analysis, laser-induced plasma spectroscopy, laser-induced breakdown spectroscopy, TEA CO$_2$ laser.*

Introduction. Analysis of complex matrices such as soil is of great interest from the point of view of hazard material analysis. Soil pollution by chemicals and heavy metals such as mercury (Hg) and copper (Cu) has increased greatly due to mining, manufacturing, and industrial waste [1, 2]. Environmental pollution by heavy metals, especially in soil, can cause serious problems for human health [3, 4]. Thus, the analysis of metal pollution in soil is urgently required.

Various methods have been applied to perform soil analysis, such as X-ray fluorescence spectrometry (XRF) and inductively coupled plasma optical emission spectroscopy (ICP-OES) [5–7]. These methods have high precision and high sensitivity for the detection of major and minor elements in a target sample. However, they require delicate sample pretreatment and are labor intense. Recently, laser-induced breakdown spectroscopy (LIBS) has become a popular method for qualitative and quantitative analyses of sample targets for various kinds of samples including liquids [8, 9], metals [10, 11], and solids [12, 13]. In this technique, a pulse neodymium yttrium aluminum garnet (Nd:YAG) laser is focused on/in a sample to induce a luminous plasma. In the plasma region, molecules and atoms ablated from the sample can be effectively dissociated and excited [14, 15]. Compared to other conventional analytical methods, standard LIBS is superior because rapid analysis can be performed without tedious sample preparation and it requires only low-cost experimental equipment [15]. Several studies have reported on the application of standard LIBS for the analysis of soil targets [16, 17]. Del′Agglio et al. have detected heavy metals elements such as Cr, Cu, Pb, and Zn in soil. Comparative studies have been undertaken using ICP-OES. The correlation between ICP-OES and LIBS was confirmed by the satisfactory agreement observed [18]. However, in the standard LIBS method, using a pulsed Nd:YAG laser, the soil sample should be prepared in the form of pellets for effective dissociation and the excitation process [19, 20].

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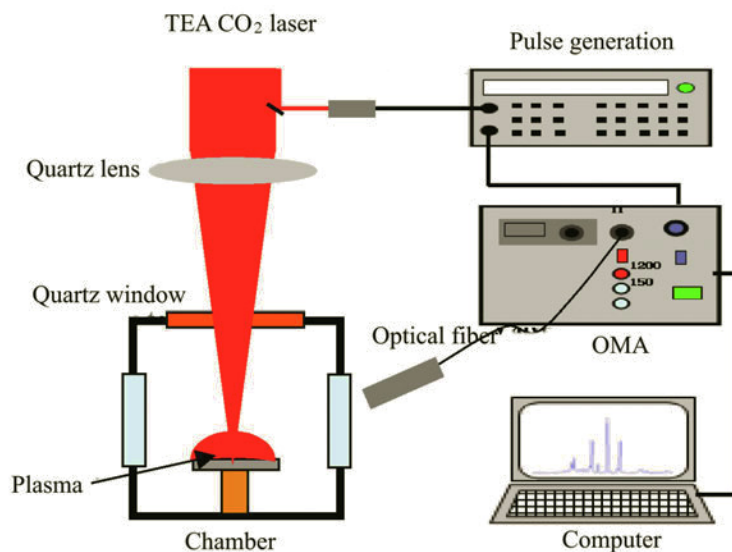
Fig. 1. Experimental setup used in this work.

On the other hand, we noticed that a pulsed transversely excited atmospheric (TEA) CO_2 laser has different specific characteristics compared to the case of Nd:YAG laser. Namely, the pulse duration (200 ns) and wavelength (10.64 μm) of the TEA CO_2 are much longer than those of a Nd:YAG laser (10 ns and 1.064 μm in pulse duration and wavelength, respectively). The TEA CO_2 laser has higher absorption in powder samples such as soil and thus is suitable for soil analysis. By using the TEA CO_2 laser, we have developed a novel method for powder analysis [21–23] and soil analysis [21].

In the present study, we performed a rapid and direct detection of heavy metals in soil by a metal mesh-assisted gas plasma method using the specific characteristics of the pulsed CO_2 laser. The soil sample was placed in a hole made of acrylic plate. A metal mesh covered the sample to prevent the soil particles from being blown off. The mesh also functioned to initiate a luminous gas plasma. Using this technique, the sample could be prepared with reduced pretreatment, and therefore a rapid analysis can be performed efficiently.

Experimental procedure. The experimental setup used in this research is shown in Fig. 1. A pulse TEA CO_2 laser (Shibuya SQ 2000 laser, pulse energy of 3 J, wavelength of 10.64 μm, pulse duration of 200 ns in full width at half-maximum, beam cross section of 30×30 mm) was employed in this study. The laser was directly focused on a metal surface through a ZnSe window using a ZnSe lens with a focal length of 200 mm. During the experiment, the laser energy was fixed at 1500 mJ by inserting an aperture in the path of laser beam.

The samples used in this study were clean soil and oil-contaminated soil obtained from the area near Diponegoro University, Central Java, Indonesia. Other standard soils containing heavy metals of Hg (50, 500, and 1000 mg/kg) and Cu (50 mg/kg) were also used. Prior to experiment, the soil was prepared using two different preparation methods. One batch of soil was prepared in the form of pellets (10 mm in diameter and 2 mm in thickness) and the other was prepared in the form of powder particles by using our present method, namely, the metal mesh method, as illustrated in Fig. 2. In the case of the mesh method, the soil was placed into a hole which was made in an acrylic plate, with a diameter of 6 mm and a depth of 10 mm.

A metal mesh made of stainless steel wires (a lattice constant of 0.4 mm with wires of 0.1 mm in diameter) was used to cover the soil to protect the particles from being blowing off. It should be noted that the metal mesh is not ablated during the laser bombardment because the ablation threshold of the mesh is higher than the power density of laser beam. This is due to the fact that the greater part of the laser energy is absorbed by the gas plasma [21].

The emission spectrum was obtained by using an optical multichannel analyzer (OMA) system (ATAGO Macs-320) consisting of a 0.32 m focal-length spectrograph with a grating of 1200 groves/mm, a 1024-channel photodiode detector array, and a microchannel plate image intensifier to detect the laser plasma radiation. The spectral resolution of the OMA system was 0.2 nm. The light emission of the laser plasma was collected by using an optical fiber (27° solid angle), which fed into the OMA system. One end of the fiber was placed at a distance of 3 cm from the focusing point of the laser light and set perpendicularly to the path of the laser beam. The gate delay time and gate width of both OMA systems were set at 1 and 100 μs, respectively for an exposure time of 1 s under the laser operating at 10 Hz.
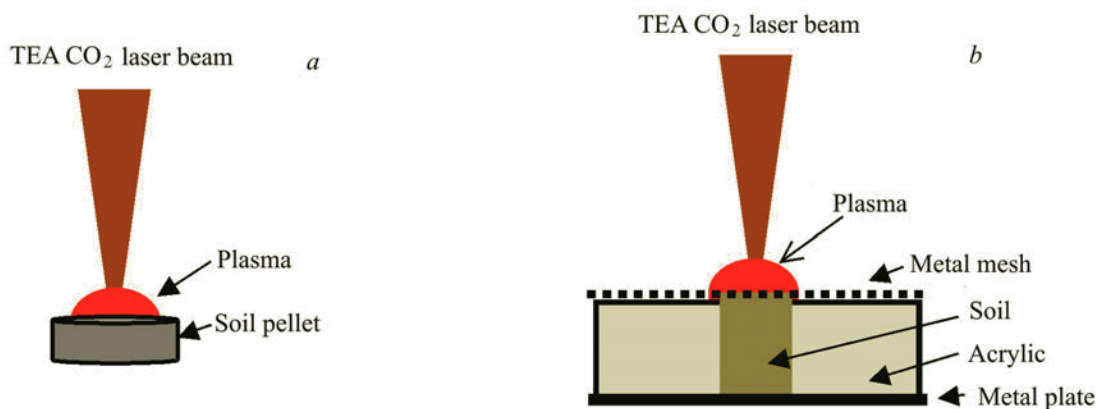
Fig. 2. Sample preparation using (a) pellet method and (b) metal mesh assisted gas plasma method.

Results and Discussion. First, the analytical spectra obtained by using a standard LIBS method, in which the sample is usually prepared in the form of pellets, and the mesh method presented in this work, were compared. Figure 3 shows the emission spectra of Ca obtained from the uncontaminated soil using the pellet method (standard LIBS method) and the metal-mesh-assisted gas plasma method. Ionic Ca lines (Ca II) at 393.3 and 396.8 nm clearly appear in the emission spectrum with low background emission both for the pellet and mesh methods. Also, neutral Al lines (Al I) at 394.4 and 396.2 nm appear very sharply near the Ca II lines both in Fig. 3. However, it should be noticed that the signal to noise ratio (S/N) of the Ca II and Al I lines for the mesh method (Fig. 3b) is much better than the case of the pellet method (Fig. 3a). Furthermore, the emission spectrum for the mesh method is less noisy than the case of the pellet method. Ca and Al are major elements in soil. The experimental result above supports our hypothesis as described in a previous study [24, 25], namely that shock waves play an important role for plasma generation using the standard LIBS technique using pellets. In the pellet method, when a pulsed laser is focused on the surface of a pelletized soil sample, atoms are emitted from the sample surface due to the repulsion force. The propelled atoms then move with very high speed, pushing the surrounding gas like a piston. The expansion of the propelling atoms, being impeded by the surrounding gas, gives rise to compression processes. As a result of this compression, a blast wave is generated in the surrounding gas with its wave front almost coinciding with the front of the propelling atoms. The most important point regarding the shock wave model is that the energy required to produce the plasma is supplied in the form of kinetic energy from the propelling atoms. Due to this compression process, the kinetic energy of the propelling atoms is converted into thermal energy in the plasma, by which atoms are excited. However, it should be noted that the emission spectrum of soil for the case of the pellet sample (Fig. 3a) is much weaker and noisier than the case of the mesh method. This result confirms the previous results [24]. Namely, even though the soil samples are pressed into pellets, the samples are still not as hard as other solid samples, such as glass or ceramic. Thus, a strong shock wave, which is necessary to induce a high-temperature plasma, cannot be produced due to the lack of repulsion forces originating from the pelletized soil sample. It is assumed that in the case of a soft sample, the forward momentum of the atoms propelled from the sample is weak. On the other hand, when the sample is very hard, such as would be the case with metal or ceramic, the forward momentum of the strongly propelled atoms is enhanced by the repulsion force supported by the hard sample, generating a strong shock wave. Furthermore, we noticed that ablation sometimes happens in the form of fine particles, resulting in a lack of dissociation.

This mechanism of plasma generation for the pellet method (standard LIBS) is quite different from that of the mesh method case (Fig. 3b). In the case of the mesh method, it is assumed that the plasma generation takes place through the following process [22, 26]: when a pulsed laser is focused onto soil particles passing through a metal mesh, half of the energy of the laser pulse is used to initiate a gas plasma assisted by the metal mesh, and the rest of energy is used to ablate the soil particles. In the gas plasma generation, just after the laser beam impinges on the metal mesh surface, electrons are released from the surface due to a multiphoton absorption process that occurs at the focusing point of the laser light without ablating the metal surface. These electrons are then accelerated to high energy in the electric field of the laser light, which induces cascade ionization of the atoms in the gas and generates an initial gas plasma. Once this initial plasma has been produced, the laser light is completely absorbed in the gas plasma by inverse bremsstrahlung via free–free transitions. This absorption is much stronger for the TEA CO_2 laser than for the Nd:YAG laser as the plasma absorption coefficient is proportional to the
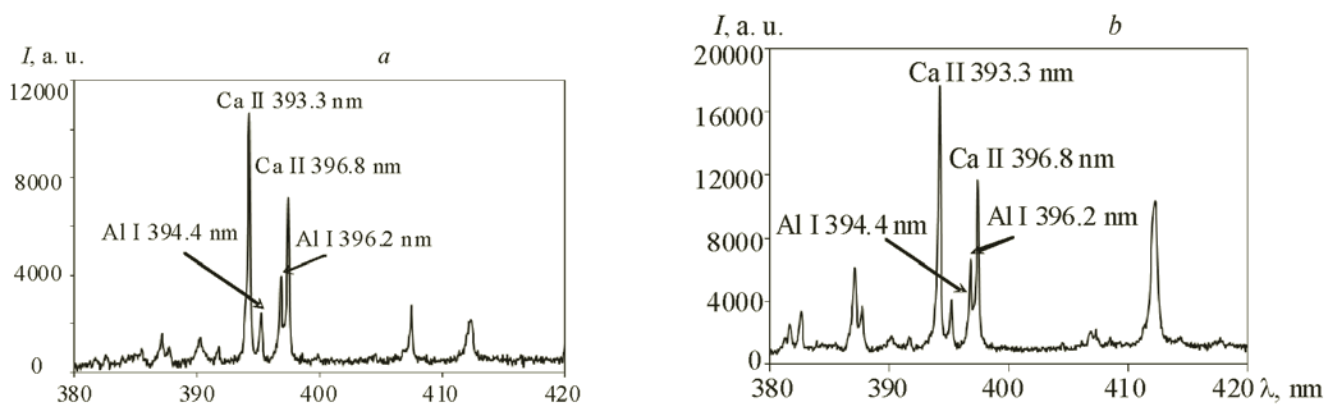
Fig. 3. Emission spectrum of Ca obtained from the soil taken by using (a) pellet method, and (b) metal-mesh-assisted gas plasma method.

inverse square of the frequency of the laser light. Furthermore, the pulse duration of the TEA CO_2 laser is relatively long (200 ns), about 20 times longer than that of the Nd:YAG laser, which means that almost all the energy from the TEA CO_2 laser is absorbed by the gas plasma, resulting in a large volume and high-temperature gas plasma. The fine particles of soil ablated by the rest of the laser energy move to the gas plasma region to be dissociated and excited.

Further study was made to estimate the gas plasma temperature generated by the assisting metal mesh. To this end, we sent the copper atom in the gas plasma. This is because by using two lines of Cu emission (Cu I 510.5 and Cu I 521.8 nm), which can be obtained simultaneously in one frame of display of our OMA system, the temperature of the gas plasma can be easily derived by assuming a Boltzmann distribution. The sample used to estimate the plasma temperature was $CuSO_4$ powder. Figure 4a shows the emission spectrum of Cu obtained from the $CuSO_4$ powder. The gate delay time and gate width of the OMA system were 10 μs and 1 μs, respectively. Typical triplet neutral Cu lines (Cu I) at 510.5 nm, 515.5 and 521.8 nm clearly appear with very low background emission. The gas plasma at 10 μs was estimated to be at a temperature of 7000 K; the plasma temperatures were derived from the ratio of the emission intensity of Cu 521.8 nm (excitation energy of 6.2 eV) to that of Cu I 510.5 nm (excitation energy of 3.8 eV), with the assumption of a Boltzmann distribution. This result showed that the TEA CO_2 laser-induced gas plasma resulting from the use of the mesh method has high enough temperature to dissociate and excite the fine particles in the soil samples.

In order to examine the capability of the present method for the rapid detection of heavy metals in soil, analyses of Cu and Hg in soil samples were performed. Cu and Hg are toxic heavy metals and are very dangerous to human health if they are present at high concentration [3]. Figure 4b shows the emission spectrum of Cu obtained from the standard soil sample containing 50 mg/kg Cu. High-intensity Cu I lines at 324.7 and 327.4 nm can be clearly detected with quite a low background emission. Many neutral Fe (Fe I) lines also occur with very sharp emission lines and narrow spectral width. As is already known, the soil contains Fe with high enough concentration.

A further experiment was undertaken to detect other heavy elements in the soil samples. Figure 5a shows the emission spectrum of Hg taken from a standard soil sample containing 500 ppm of Hg. A very clear neutral Hg (Hg I) line at 435.8 nm was detected. However, the background emission line is very strong, which is due to the bremsstrahlung effect and free–free recombination processes [14, 15]. The other lines of neutral Fe (Fe I) at 432.0, 433.7, and 436.7 nm occur with a high emission intensity.

Finally, a semi-quantitative analysis of soil samples containing different concentrations of Hg was made. A good linear calibration curve of Hg from the soil sample was successfully determined, as displayed in Fig. 5b. For standardization, the neutral emission line of Fe at 436.7 nm, which is a major element contained in soil, was employed. Non-intercept zero of the calibration curve might be due to the high background emission produced from the soil samples which include high matrix samples, as described above. The LOD of Cu and Hg in the soil sample using this present method were estimated to be 3 and 10 mg/kg.

The detection limit was derived by calculating the concentration where the signal had an intensity three times that of the noise level because this represents a clear signal that can be distinguished from the noise [27]. The mesh method presented in this study has high potential for application to rapid direct analysis of heavy metal elements in soil at low concentration levels and without tedious sample preparation.
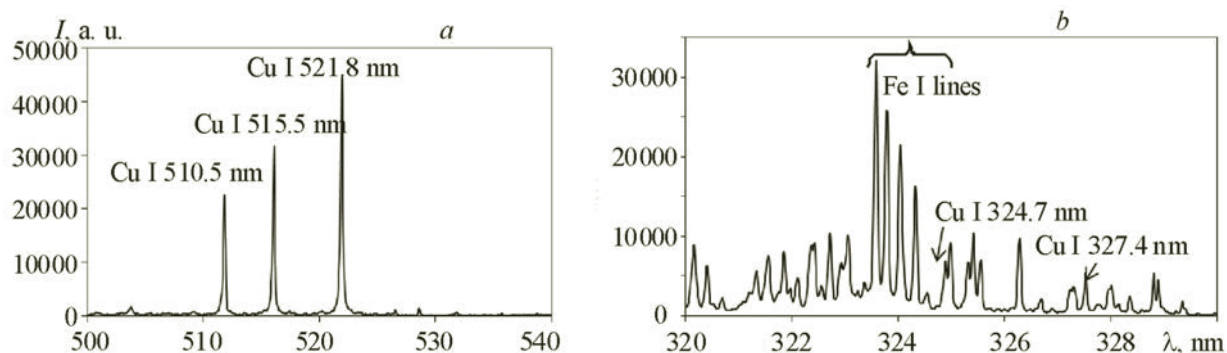
Fig. 4. Emission spectrum of Cu obtained (a) from the powdered $CuSO_4$ using mesh assisted gas plasma method, and (b) from the standard soil containing 50 mg/kg Cu.
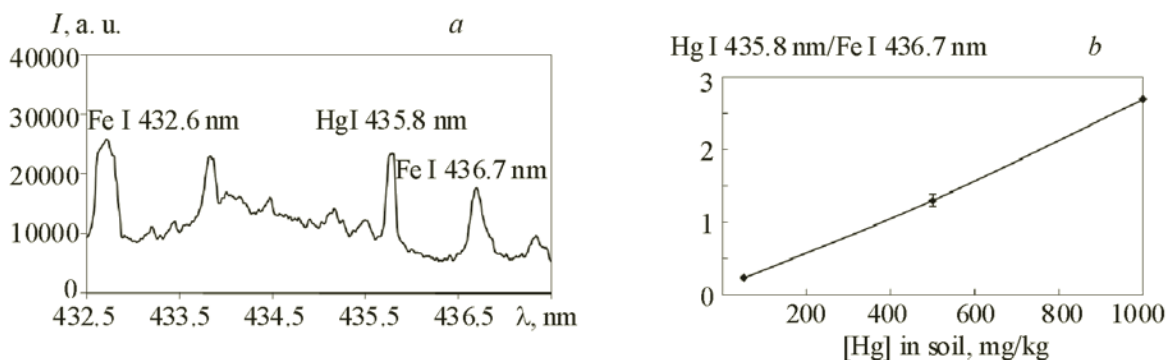

Fig. 5. Emission spectrum of Hg obtained from the standard soil containing 500 mg/kg Hg (a), calibration curve of Hg obtained from the standard soil containing 50, 500, and 100 mg/kg Hg (b).

Conclusions. A rapid analysis of heavy metals in soil samples has been performed by a mesh method using the specific characteristics of a TEA CO_2 laser. A high-temperature and long-lifetime gas plasma was generated by an assisting mesh metal just in front of the mesh, which functions as a cover for the soil particles. Fine soil particles were ablated by a laser beam and moved into the gas plasma region to be dissociated and excited. Using this method, rapid detection of heavy metals in soil has been successfully performed. The result proved that the S/N of the emission spectral lines is much better for the case of the present method (mesh method) compared to the case of standard LIBS using pellets method. Very rapid detection of heavy metal elements in soil has been made by using the present mesh method. The detection limits of Cu and Hg in soil were estimated to be 3 and 10 mg/kg, respectively. The present method has very high potential for rapid and sensitive detection of heavy metals in soil samples.

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