Detection of salts in soil using transversely excited atmospheric (TEA) carbon dioxide (CO₂) laser-induced breakdown spectroscopy (LIBS) by the aid of a metal mesh

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Abstract. In this work, a nickel metal mesh was used to allow a direct detection of salt in soil sample by LIBS utilizing unique characteristics of a TEA CO₂. The metal mesh is placed in the front of the soil sample to prevent the soil sample from blowing off upon focusing the high pulsed laser beam irradiation. LIBS apparatus used in this work is a TEA CO₂ laser operated at wavelength of 10.6 μm with pulse energy and duration of 3J and 200 ns, respectively. The laser beam was focused using a ZnSe lens (f = 200 mm) onto soil sample after passing through the metal mesh. The emission spectrum from the induced plasma was detected using an optical multichannel analyzer (OMA) system consisting of a 0.32-m-focal length spectrograph with a grating of 1200 graves/mm and a 1024-channel photodiode detector array with a micro-channel plate intensifier. The soil sample used is a standard soil and ordinary soil containing several salts such as Ca, Mg at high concentration. The LIBS experiment was carried out at high pressure surrounding gas of 1 atmosphere. It was observed that by the aid of the metal mesh, strong breakdown gas plasma can be produced just after TEA CO₂ laser irradiation on soil sample without significant sample blowing off. It was found that emission lines from salts, Ca (Ca II 393. 3 nm, Ca II 396.3 nm, Ca I 422.5 nm), and also other salts including Mg and Na can clearly be detected with strong emission intensity and narrow spectral width. This result implies that a TEA CO₂ LIBS assisted by the metal mesh (metal mesh method) can be used for direct analysis several salts such as Ca, Mg, and Na in soil sample.

1. Introduction
Due to the physical and chemical properties namely soft matrix and containing many element of organics and inorganics at various levels including major, minor and trace elements, soil is considered as complex sample. Thus, it is basically difficult to make direct analysis even using laser induced breakdown spectroscopy (LIBS). One serious problem in analysing soil sample using LIBS is sample blowing off upon direct focusing a high power laser beam on the soil sample. This problem is actually general problem in LIBS when dealing with powder sample. Therefore, several schemes have been adopted in LIBS to suppress the sample blowing effect to allow direct analysis of powder sample including soil. General approaches are making the powder sample in the form of pellet and employing...
binder materials such as potassium bromide, poly(vinyl alcohol), starch, silver and aluminium [1]. A neodymium yttrium aluminum garnet (Nd-YAG) laser with typical wavelength and pulse duration of 1064 nm and 10 ns, respectively, is normally adopted in LIBS as an excitation source. On the other hand, in previous study it was found that LIBS using a TEA CO$_2$ shows very promising analytical performance for soil pollution analysis [2]. It is considered due to unique characteristics of the CO$_2$ laser pulse. The TEA CO$_2$ laser has a far longer wavelength and pulse duration of 10.6 m and 200 ns, respectively. Moreover, it was also found a unique phenomenon in laser induced breakdown spectroscopy (LIBS) using the TEA CO$_2$ laser on metal sample at atmospheric pressure, namely strong gas breakdown plasma can be induced when the TEA laser beam focused on the metal sample while leaving the metal sub target without any damage [3-4]. The unique phenomenon has been utilized for various unique applications of the TEA CO$_2$ LIBS [5]. Recently, the unique metal sub target effect in the TEA CO$_2$ LIBS was studied for detecting salt in soil sample [6]. In the study, for escaping from blowing off effect, the soil sample was mixed with silicon grease as binder material and then the soil mixed with silicon grease sample is attached on a nickel metal sub target. It was found that the soil sample can be fixed with high stability on the metal sub target without any blowing off effect. It was also found that strong plasma can be induced from the soil sample mixed with silicon grease (SMS) by attaching the SMS to the nickel sub target effect. The plasma produced is very strong, resulting in strong salt emission lines allowing a quantitative analysis, such as Ca, Na, Mg. In this study, the unique phenomenon in the TEA CO$_2$ LIBS on a metal sample at atmospheric pressure is utilized with different strategy, namely a metal mesh is used for covering the soil sample for avoiding the soil sample from blowing off while at the same time the metal mesh works to enhance plasma generation.

2. Experimental Procedure
The basic experimental setup used in this work is similar to the previous study [6]. However, instead of the metal mesh sub target, the nickel metal mesh was used in this study. The soil sample and the metal mesh configuration are shown in Figure 1. The LIBS apparatus consists of a TEA CO$_2$ laser (3 J, $\lambda$=10.6 $\mu$m, $\Delta t$= 200 ns) as a plasma excitation source and an optical multichannel analyzer (OMA) system as an optical detector for the plasma emission. The TEA CO$_2$ laser is a Shibuya SQ-4000 laser actually constructed for laser marking application. The OMA system (ATAGO Macs-320) consists of a spectrograph (0.32-m-focal length) with a grating of 1200 graves/mm, and a photodiode detector array (1024-channel) equipped with a micro-channel plate image intensifier. The spectral resolution of the OMA system is 0.2 nm at 500 nm.

There used in this study is the standard soil sample, the same as used in the previous study [6]. The standard soil sample is produced by Japan Industrial Test Powder (Japan Industrial Standard Test Powders 1 Class 7) with a specified chemical composition as displayed in Table 1. There are two kinds of the nickel metal mesh used in this study, namely metal mesh no. 40 (equivalent to 0.420 mm particle size) and no. 50 (equivalent to 0.297 mm particle size). The soil sample in amount of 3 mg is inserted in a hole with a diameter of 15 mm and a depth of 50 mm made on a metal plate as shown in Figure 1. The soil sample was pressed manually to put in the hole. The soil sample in the metal hole is then covered by the metal mesh. The sample on the metal holder is situated in a circular metal chamber with a diameter of 120 mm. The circular metal chamber is equipped with several windows and valves for filling different kinds of surrounding gases in the chamber and evacuating the gas. This experiment was carried out at high pressure of 1 atmosphere under helium surrounding gas flowing at a rate of 5 L/min.
In order to produce plasma from the soil sample, the CO$_2$ laser beam was focused by a zinc selenium (ZnSe) lens ($f = 200$ mm) through a ZnSe window onto the metal mesh covered-soil sample in the chamber. Small part of the laser beam was intercepted by a photon drag detector (Hamamatsu Photonics, B749) and sent to the OMA system for synchronizing the data acquisition. It is considered that most part of the focused laser beam passes through the mesh reaching the soil sample inducing the soil plasma. The plasma emission was collected and delivered to the spectrograph of the OMA system using an optical fibre. One end of the optical fibre was set at an inclined position of about 45° to the laser beam path, and around 7.5 cm apart from the centre of the plasma, as displayed in Fig. 1, to allow collection the entire plasma emission into the fibre optic core ($\theta = 27^0$ in solid angle). The output optical signal from the other end of the optical fibre was then fed into the entrance slit of the spectrograph. The photodiode array was installed at the exit slit of the spectrograph for detecting the plasma emission spectrum. The OMA system was operated by a personal computer using SpectraView software. The emission spectrum was displayed on the computer monitor and was recorded in the computer memory. The detector was run in gated mode. The gate delay and gate width of the OMA system was set mostly at 1 $\mu$s and 50 $\mu$s, respectively during the experiment. The emission spectrum acquisition was carried out by 10 accumulations and was repeated 3 times. It was estimated the fluctuation of intensity of the emission lines is approximately 5%.

3. Results and Discussion

It was observed during this experiment that strong, luminous plasma can be produced from the soil sample covered by the nickel metal mesh after focusing the TEA CO$_2$ laser beam. The plasma generation was made under helium surrounding gas at atmospheric pressure, since preliminary experimental results show the emission intensity is boldly increased in case using helium as surrounding gas. Figure 2 shows emission spectrum taken from the plasma produced on the metal mesh covered-soil sample. The metal mesh used in this experiment was no. 40. This mesh is equivalent to a nominal sieve opening of 0.42 mm. It can clearly be seen the atomic and ionic emission lines due to salt, Ca, namely Ca I 422.67 nm, Ca II 393.36 nm, and Ca II 396.84 nm. The emission lines due to other soil constituents also appears together with the salt emission lines, namely Al atomic emission lines (Al I 394.40 nm and Al I 396.15 nm) and Si ionic emission lines (Si II 412.80 nm). The emission lines feature strong intensity especially Ca lines due to its low excitation energy. It can also be seen the emission lines exhibit narrow spectral width with relatively low background. It is interesting since the emission spectra were acquired under almost time integrated mode, namely the delay and the width of the gate time of the OMA system were set at 1 $\mu$s and 50 $\mu$s, respectively as
normally adopted in LIBS without a gating function. It is assumed that most part of the laser beam passes through the mesh and arrive on the soil sample, ablating the soil sample. Almost simultaneously, the long pulse duration of the TEA CO$_2$ laser interacts with the metal mesh inducing strong gas breakdown through initial electron liberation by multiphoton ionization from the metal mesh in the focusing region of the laser beam. This initial electrons promote avalanche or cascade ionization by collision and further absorption of the later part of the pulse energy of the laser light through free-free transition, inverse Bremsstrahlung, resulting strong gas breakdown plasma [3]. In the case of the sample covered by the metal mesh, strong helium gas breakdown plasma produced on the metal mesh, just in front of the soil sample. After the strong helium gas breakdown plasma produced, the laser energy is then reserved in helium metastable excited states. It is considered that the helium metastable excited states play important role in plasma excitation process [7-8]. Thus, the ablated atoms from the sample populated in the helium gas plasma will be excited effectively by the helium metastable excited states. In case of the soil sample covered by the metal mesh, the ablated soil atom moves into the region of helium gas breakdown plasma located just in front of the soil sample, and then are excited by the helium metastable excited states. This results in strong emission intensity with a narrower spectral width and low background since the emission takes place through a delayed excitation mechanism by the helium metastable excited states.

![Figure 2](image1.png)  ![Figure 3](image2.png)  ![Figure 4](image3.png)

**Figure 2.** Emission spectrum taken from the plasma induced on the soil sample when the metal mesh no. 40 used.  **Figure 3.** Emission spectrum taken from the plasma produced on the soil sample when the metal mesh no. 50 employed.  **Figure 4.** Photograph from the top view of the interior situation of the circular metal chamber including the sample on the metal holder and the optical fibre probe taken just after focusing the TEA CO$_2$ laser on the metal mesh covered-soil sample. The metal mesh used in this case is no. 40.

When using the metal mesh no. 40, the soil sample blowing off still occurs significantly as shown in Figure 4. As it can be seen in Fig. 4, the soil sample was scattered on the interior bottom of the sample chamber just after focusing the laser beam onto the soil sample covered by the metal mesh. We then tried to use the metal mesh no. 50 which its nominal sieve opening is 0.297, about 25% smaller than that of the metal mesh no. 40. It is expected the soil sample blowing off effect will be suppressed further while keeping an optimal laser pulse energy passing through the metal mesh for producing...
strong plasma. Figure 3 shows emission spectrum taken from the plasma produced on the soil sample when the metal mesh no. 50 employed. It can be observed in Figure 3 that the emission lines from Ca and other constituents of the soil sample appears with similar features to the spectrum detected when using the metal mesh no. 40. The difference is only in the emission intensity, which is around 25% lower than that of using the metal mesh no. 50. This is consistent with the difference in the nominal sieve opening between the two metal meshes, affecting to the portion of the laser pulse beam passed through the metal mesh. It is considered that in case of using the metal mesh no. 50, the laser pulse energy passed through the mesh is about 25% lower than that of using the metal mesh no. 40. Nevertheless, as shown in Figure 3 although the laser energy passes through the metal mesh no. 50 is lower, the produced plasma exhibits a useful emission spectrum with favorable features for spectrochemical analysis. The emission lines from other salts, namely Mg and Na can also clearly be detected at different wavelength measurement ranges with similar emission spectral line features. Thus, the TEA CO$_2$ LIBS employing the metal mesh method can be used for carrying out quantitative analysis of salt in soil sample.

4. Conclusions

The nickel metal mesh was employed to allow direct analysis of soil sample using a TEA CO$_2$ laser. The blowing off effect can be suppressed substantially by using the metal mesh for covering the soil sample. It is found that by applying the metal mesh on the soil sample, strong, luminous plasma can be produced, resulting in strong emission intensity of salt, Ca (ionic lines: Ca II 393.36 nm, and Ca II 396.84 nm, and atomic line: Ca I 422.67 nm) and other constituents. The emission lines feature a narrow spectral width and low background, implying the essential role of the delayed excitation through helium metastable excited states produced in the strong helium gas breakdown plasma. The dimension of the metal mesh must be carefully selected to obtain optimal condition namely it can passes through sufficient laser pulse energy to the soil sample surface while it is able to prevent the soil sample blowing off. This TEA CO$_2$ laser induced breakdown spectroscopy utilizing the unique metal mesh can be used for conducting a direct analysis on soil sample. A quantitative analysis is being conducted and will be reported elsewhere.

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