Preliminary Study on Possibility Cl Detection in Soil by Means of The Unique Sub-target in a Transversely Excited Atmospheric Pressure (TEA) Carbon Dioxide (CO₂) Laser Induced Breakdown Spectroscopy

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Abstract. A preliminary study on Cl detection in soil sample using LIBS has been carried out. The soil sample was mixed with silicon grease to allow attachment to the surface of a nickel plate acting as a sub-target. The laser used in this work is a TEA CO₂ laser that operates at wavelength of 10.6 μm with energy and pulse duration of 2.5 J and 200 ns, respectively. The laser beam was focused onto the sample using a zinc selenium lens (f = 200 mm) under air and helium surrounding gas at atmospheric pressure. The emission spectrum from the generated plasma was detected using an optical multichannel analyser (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. Soil sample used in this work is a standard soil sample mixed with NaCl solution at various concentrations. The results show that many emission lines due to salts such as Ca, Mg, Na and K can be detected clearly. Nevertheless, Cl emission line cannot be detected in soil sample, although the sample has been intentionally mixed with Cl, even when Cl content reaching 1000 ppm. It is therefore necessary to develop a new approach to allow LIBS techniques for detecting Cl in soil samples.

1. Introduction

Soil is a very important matter to support the life of all living things on the earth. For grown plants, soil is primary base of macronutrients and micronutrients. In the natural state, the soil contains elements of salt at normal concentrations. However, the addition of salt in the soil may occur through industrial waste disposal and natural disasters. One of the most dangerous elements of salt is Cl. The Cl element is widely used in many industries. Soil with high concentration of Cl will bring about bad impact not only to the grown plants, but also to the building making it more susceptibility to corrosion due to ion chloride intrusion [1]. Therefore, monitoring of Cl content in the soil is very important.

The soil sample is a very difficult sample to analyse because of its complex matrix [2]. There are several conventional techniques currently used for soil salinity detection such as EC (Electrical...
Conductivity) and AAS (atomic absorption spectroscopy), but the technique requires lengthy sample preparation and uses a strong chemical acid in the sample preparation process. In addition, this technique only detects one element in a single measurement, making it less effective for monitoring the concentration of salt in the soil. Therefore, the technique takes an appropriate analytical technique for detection of salt content in soil samples. On the other hand, due to many excellences over the conventional analytical, laser induced breakdown spectroscopy (LIBS) technique offers bright potential for this purpose [3].

LIBS technique is part of atomic emission spectroscopy. LIBS technique detects the content of the sample by analyzing the emission spectra of the plasma generated from the sample. LIBS technique is known as a technique that has many unique advantages such as not requiring complicated sample treatment and can detect multielement in one measurement [3]. LIBS technique has been widely used in chemical analysis of various types of samples such as solid, liquid and gas [4-6]. This technique has also been commonly used for qualitative and quantitative analysis of the content of geological and environmental samples. In some studies, this technique has been used for monitoring and chemical analysis of soil samples [7-8].

In many studies, spectrochemical analysis of various samples employing LIBS technique generally uses Nd-YAG laser as a plasma generation source. In previous studies, Nd-YAG laser was used to detected Cl at wavelengths of ultraviolet and near infrared regions [9-12]. However, in that study, only Cl atomic emission lines can be detected at Cl I 133.6 nm and 837.36 nm and no report on detect ionic Cl emission line using Nd-YAG LIBS. The Cl ionic emission line cannot be detected at atmospheric pressure, and LIBS technique commonly conducted at atmospheric pressure cannot be used for Cl ionic emission line detection.

In some previous studies it was found that LIBS performance achieved improvement by using a TEA CO₂ laser [13-17]. Thus, TEA CO₂ LIBS is also widely used in spectrochemical analysis of various samples including complex samples, such as environmental and geological samples. The TEA CO₂ LIBS has been successfully used for inspection of carbonation in concrete [13]. Moreover, although Cl element is basically difficult to detect in spectrochemical analysis because of its high lying excitation level of the ionic emission lines and its chemical properties, however in previous study the ionic emission lines of Cl in visible wavelength region can be detected unequivocally from plasma generated on plastics sample using the TEA CO₂ LIBS [14]. Furthermore, the TEA CO₂ LIBS has then been used for analysis heavy metal pollution such as Cr and Hg in soil sample by employing a unique approach of the microstructured hole on a metal sub-target [15].

In recent experiment, LIBS techniques utilizing a sub-target effect using TEA-CO₂ laser have been successfully used to detect salts such as Mg, Na and Ca in soil samples [16]. In the study, to avoid samples from blowing off that will be resulting in the difficulty of obtaining accurate emission signal, in turn a high sensitive analysis, soil samples were mixed with silicon grease and then attached to a nickel plate. The nickel plate works only as sub-target aiding the plasma generation process from powder and soft samples [17]. Referring to the previous results, a preliminary work is carried out to study possibility for detecting the difficult salt, Cl using the TEACO₂ LIBS on complex sample, namely soil sample. As the initial stage, the soil samples used in this study was a standard soil samples intentionally added with Cl at different concentrations.

2. Experimental Procedure
Basic LIBS experimental setup used in this work is similar to that used in previous study [16]. The arrangement of the LIBS system used in this study is shown in Figure 1. In order to generate plasma, TEA-CO₂ laser (2.5 J, 10.6μm, 200 ns) beam was focused on the sample placed in a circular metal chamber using a zinc selenium (ZnSe) lens with a focus of 200 mm.

The plasma emission was collected using an optical fibre and delivered to the spectrograph of an optical multichannel analyser (OMA) system. The OMA system consists of a spectrograph (focal length 0.32 m) with a grating (1200 graves / mm), and a photodiode detector arrays (1024-channel) for
detecting the emission spectrum. One end of the fibre is placed at a distance of 7.5 cm from the center of the plasma with an angle position of 45° to allow to collect all plasma emissions. The other end of the optical fibre was connected to the spectrograph where on the output slot has been installed a photodiode array as light detector to detect the plasma emission. The time delay and gate width of the OMA system was set at 1 μs and 50 μs, respectively. The OMA system is operated on a personal computer using SpectraView software. For synchronizing the spectral acquisition, some part of the TEA- CO₂ laser beams was intercepted by a photon drag detector and delivered to the OMA system. The results were stored in computer memory for data processing purposes. The recorded spectrum is identified and compared to atomic spectral database from NIST (National Institute of Standard and Technology), United States of America (USA) [18].

![Experimental setup of LIBS apparatus using a TEA CO₂ laser for Cl detection](image)

**Figure 1** Experimental setup of LIBS apparatus using a TEA CO₂ laser for Cl detection

| Chemical composition | Percentage (%) |
|----------------------|---------------|
| SiO₂                 | 34 – 40       |
| Fe₂O₃                | 17 – 23       |
| Al₂O₃                | 26 – 32       |
| CaO                  | 0 – 3         |
| MgO                  | 3 – 7         |
| TiO                  | 0 – 4         |
| Misc                 | 0 – 4         |

As a preliminary study, the soil sample used was a standard soil sample (Japan Industrial Standard Test Powders 1 Class 7) with a given chemical composition, as showed in Table 1. The standard soil sample does not contain Cl. Normal uncontaminated soil generally contains Cl at concentration a few tens ppm. Thus, in this preliminary study the standard soil was intentionally added Cl at very significantly higher concentrations to understand and estimate quickly the LIBS technique capability for
Cl detection. The standard soil sample was added with a salt solution of NaCl at certain proportion to obtain soil samples with Cl concentration of 200 ppm and 1000 ppm, consecutively. The soil sample mixed with NaCl solution then was dried up in the electric oven set at a operating temperature of 150\(^\circ\) for 1 hour. The soil sample containing Cl was then mixed with silicon grease in a proportion of 50% : 50% (soil : silicon grease) and attached onto the nickel plate for plasma generation. The nickel plate serves as a sub target. The nickel plate dimension is 2.5 cm x 3 cm. The soil sample can be bound well to the sub target surface, resulting in a layer of the soil mixed with silicon grease with a dimension of 2.5 x 3 cm x 1 mm on the plate surface. The nickel sub target is then placed on the sample holder inside the metal chamber. In addition, plastics sample namely plastic plate PVC (vinyl chloride resin) was used for confirmation of the ionic emission lines of Cl in the visible wavelength region. In this experiment surrounding gas used was air and high purity helium (99.999 %) at 1 atmospheric pressure, alternatively.

3. Results and discussion

For conducting an analysis of soil samples using LIBS techniques, the samples generally were made in pellet form. This is done to bind samples thus avoiding scattering of samples upon irradiation of a laser beam with high energy onto the soil sample. However, in this study, as mentioned above, to bind samples of powder such as soil, an alternative, simple method was used namely mixing soil sample with silicon grease and attached to the surface of the nickel plate. Figure 2 shows the spectral emission line taken from plasma emission produced on the soil sample containing Cl at 200 ppm mixed silicone grease attached on the nickel plate sub target by focusing the TEA-CO2 laser beam. The measurements were made under air as the surrounding gas at a pressure of 1 atmosphere. The displayed spectrum was accumulated for 50 laser shots. It can clearly be seen that in Figure 2 there are many emission lines due to salts can be detected. The emission lines are very strong and well resolved with narrow spectral widths. After matching the emission lines to NIST database, the salt emission lines were confirmed. Calcium emission occurs at wavelength of Ca II 393.36 nm and Ca II 396.84 nm and the atomic Ca line at Ca I 422.67 nm, Fig. 2(a). Fig. 2(b) shows clearly the triplet Mg atomic emission lines, namely Mg I 516. 73 nm, Mg I 517.27 nm and Mg I 518.36 nm. The typical sodium emission lines of Na I 588.99 nm and Na I 589. 59 nm can also be detected featuring well resolved pair with strong emission intensity. Furthermore, although it not clearly visible because of the high background emission and many overlapping line emission lines in the wavelength, emission lines from potassium (K) can also be identified at wavelengths of 766.49 nm (K I) and 769. 90 nm (K I). In addition to the salt emission lines, the emission lines due to other soil constituent such as Al, Fe and O can also be detected with very strong intensity, the emission spectrum not shown in this manuscript.

This result confirms that CO\(_2\) LIBS utilizing the unique sub target effect aided by the silicone grease as binder material can be used to generate strong plasma from soil sample useful for spectrochemical analysis of salts. Many salts contained in the soil samples, namely Ca, Mg, Na, K can clearly be detected. The detected emission spectrum lines display favorable features for qualitative and quantitative analysis. Also, it is still required a simple and easy sample preparation of the soil sample, namely mixing the soil sample with silicone grease as the binder material, however this unique sub target effect confirm the main advantage of LIBS technique namely the freedom from tiring and environmentally unfriendly sample preparations comparing the conventional analytical tool. Encouraging by this experimental results, the experiment then was further extended to detection of Cl. The coverage of the wavelength region of the OMA system used in this experiment is basically ranging from 200 nm till 850 nm. The ordinary OMA system cannot be used for detection of Cl emission line is the vacuum ultraviolet (VUV) wavelength region and also the fiber optics is not able to delivered the emission of the wavelength region. On the other hand, the emission line of Cl in the near infrared region is also not detected since the emission line detected is weak and the sensitivity of the optical detector of the OMA system in the infrared region is also relatively low. Thus, the detection of Cl emission lines was focused on a wavelength region centered at 480 nm, since based on the atomic database (NIST) there are several Cl ionic emission lines with high relative intensities are expected to occur in this wavelength region. It was actually proved in the previous experiment of the plastics samples detected the ionic emission lines of
Cl, namely Cl II 479.40 nm, Cl II 480.0 nm and 480.94 nm with very strong emission intensities using CO$_2$ LIBS and the unique sub-target effect [14]. The results of Cl emission lines detection from the soil sample intentionally added Cl are shown in Figure 3.

![Emission spectrum of the TEA- CO$_2$ LIBS detected from plasma generated on the standard soil sample containing Cl at 200 ppm attached to the sub-target of a nickel metal plate with silicon grease. The spectrum measurement was conducted under air as the surrounding gas at atmospheric pressure. The measurement was made at several wavelength regions centered at (a) 410 nm, (b) 515 nm, (c) 575 nm, and (d) 770 nm, respectively.](image-url)
Figure 3 Emission spectrum from taken from plasma produced on the standard soil sample added intentionally Cl at concentration of (a) 200 ppm, and (c) 1000 ppm, respectively after focusing the TEA CO2 laser beam. The spectrum was expanded for detailed observation of Cl wavelength emission region, (b) the expanded spectrum of (a) while (d) the expanded spectrum of (b). The spectral acquisition was made under air as the surrounding gas at a pressure of 1 atmosphere.

Figure 3(a) shows the emission spectrum taken from plasma generated on the soil samples intentionally added Cl with concentration of 200 ppm. The measurement was conducted under air surrounding gas at atmospheric pressure. It can be in the emission spectrum, there is no emission lines due to Cl, and even after enlarging the emission spectrum, Fig. 3(c), no any emission lines due to Cl can be detected. Nevertheless, the soil sample was intentionally added Cl at high concentration of 200 ppm, about 20 times higher than the natural concentration of Cl in the ordinary uncontaminated soil. The concentration of Cl in the standard soil sample then was very significantly increased to 1000 ppm, unfortunately as it can be observed in Figure 3(c), there is no single Cl emission lines can be detected. Even after the spectrum in Fig. 3(c) was enlarged, there is no Cl emission lines can be detected though there are actually Cl concentration has increased 5 times than that in the previous soil sample. After having these results, a study for confirmation of the Cl emission lines was conducted using the plastics
plate sample. The measurement was carried out under the same experimental conditions, and the results is displayed in Figure 4.

![Figure 4](image)

**Figure 4** Emission spectrum of taken from plasma produced on the plastic sample PVC containing Cl as host element after focusing the TEA CO\(_2\) laser beam at atmospheric pressure under surrounding gas of (a) air and (b) helium.

Figure 4 displays Cl emission line detected from the plasma produced using the TEA CO\(_2\) laser beam on the plastic sample at atmospheric pressure under two different surrounding gas. Previously, Cl emission lines was observed clearly from the plastic sample using the TEA CO\(_2\) LIBS [14]. It can be seen that the Cl emission lines with very weak emission intensity can be observed under air surrounding gas, Figure 4 (a), is very low. However, when the air was replaced by helium as the surrounding gas, the Cl emission lines appear very clearly with dramatically increased intensities. This enhancement actually was also absorbed in case of Nd-YAG LIBS for Cl emission line in infrared region [18]. These results led us to try to detect Cl in the soil sample adopting helium as surrounding gas. The results are exhibited in Figure 5.

Figure 5 shows the emission spectrum detected from the plasma produced on the standard soil sample containing Cl at concentration of 200 ppm after irradiation of the focused TEA-CO\(_2\) laser beam under helium as the surrounding gas. The plasma generation and the spectral acquisition were made at atmospheric pressure, the same as in the case using air as the surrounding gas. The detection wavelengths is just similar to the case of using air, namely (a) 410 nm for Ca emission lines, (b) 515 nm for magnesium triplet emission lines, (c) 575 nm for sodium emission lines, and (d) 770 nm for potassium emission lines, respectively. From the figure it can be seen that all emission lines of salts appearing in the case of using air as the surrounding gas can be observed clearly in this case of helium surrounding gas. Moreover, the emission intensity of the salt emission lines remarkably increases in helium gas case, more than 4 folds for calcium emission lines, more than 7 folds for magnesium lines and sodium emission lines and potassium emission lines, respectively. The background emission intensity is also very low in helium gas case compared to the air case. The emission lines of potassium now appear clearly, very different spectral features than that in case of air surrounding gas. This indicates that the helium surrounding gas plays an important role in observing the increase in the emission intensity of analytical lines in LIBS. Actually, the dramatic enhancement of the emission lines characteristics in LIBS using helium as the surrounding gas was observed in several works both using a TEA CO\(_2\) laser or a Nd-YAG laser as excitation sources. The enhancement is attributed to the crucial contribution of the helium metastable excited states produced after the helium gas breakdown, providing a delayed excitation mechanism resulting in strong emission lines with narrow spectral width and low background
emission favorable for spectrochemical analysis of various samples using LIBS technique [19-22]. It is expected that a similar enhancement occurs in Cl emission, allowing detection of Cl emission lines in various samples. Previous LIBS study using a Nd-YAG laser actually found the important contribution of inert gas as the surrounding gas, namely helium in enhancing Cl emission lines [23]. Thus, the next experiment was focused on detection of Cl from the standard soil sample under helium surrounding gas, and the results are shown in Figure 6.

![Emission spectra](image)

**Figure 5** Emission spectrum detected from the plasma produced on the standard soil sample containing Cl at 200 ppm after focusing the TEA-CO$_2$ laser. The plasma generation has conducted under helium surrounding gas at atmospheric pressure. The spectral acquisitions were made in wavelength region centered at (a) 410 nm, (b) 515 nm, (c) 575 nm, and (d) 770 nm, respectively.

Figure 6 shows the emission spectrum measured in wavelength region centered at 480 nm from plasma produced on the standard soil sample intentionally mixed with different concentration Cl when the surrounding gas of the plasma has replaced by helium instead of air. It has been seen in Figure 6(a), there is no emission lines due to Cl has be detected from the standard soil sample intentionally added 200 ppm Cl. The similar result was also obtained even after the concentration of Cl in the soil sample was increased very significantly to 1000 ppm, 5 times higher than the first sample, as shown in Figure
6(b) there is also no any emission lines due to Cl can be detected. On the other hand, a dramatic improvement in emission characteristics of the other salts as mentioned above was clearly observed in the case of using helium surrounding gas. Considering closely the emission spectrum, Figures 6 (a) and 6 (b), the emission intensity of the plasma actually increases enormously, about 10 folds, in comparison with the case of using air as the surrounding gas. However, the emission lines due to Cl can scarcely not detected, nevertheless Cl has intentionally added in the soil samples. This is probably due to the chemical and physical properties of Cl which is very volatile nature and very high excitation level and the characteristics of the studied sample since Cl emission lines can definitely be detected from the plastics sample. These results actually confirm the difficulty faced in detecting Cl especially for complex samples such as soil sample. Therefore, a further study on the emission dynamic and nature of Cl in soil sample is required to find a way allowing detection of Cl using LIBS. On the other these results also confirm the TEA- CO\textsubscript{2}LIBS can be used for salts detection in soil sample employing the unique sub target effect aided by silicon grease as binder.

![Figure 6](image_url)

Figure 6 Emission spectrum detected from plasma produced by focusing the TEA- CO\textsubscript{2} laser beam on the standard soil sample, added intentionally with (a) 200 ppm and (b) 1000 ppm of Cl, respectively under helium surrounding gas at atmospheric pressure.

4. Conclusion

It was found in this study that strong plasma can be generated by using a TEA-CO\textsubscript{2}laser from the soil sample containing Cl mixed with silicon grease and attached onto the nickel plate surface. The mixture of the soil sample with silicone grease effectively avoids blowing off of the soil sample upon focusing the TEA-CO\textsubscript{2} laser beam. The many emission line of salts such as Ca (Ca I 422.67 nm, and Ca II 393.36 nm and Ca II 396.84 nm), Mg (Mg I 516.73 nm, Mg I 517.26 nm and Mg I 518.36 nm), Na (Na I 588.99 nm and Na I 589.59 nm), and K (K I 766.49 nm and K I 769.9 nm) can clearly be detected when using air as the surrounding gas. The emission lines due to salts were largely enhanced when helium used instead of air as the surrounding gas. The emission lines of Cl in the visible region centered at 480 nm can unambiguously be detected from the plastics plate sample, especially under helium surrounding gas. However, no emission lines due to Cl can be detected from the standard soil samples, intentionally Cl at concentration of 200 ppm and even from the soil sample containing 1000 ppm Cl. It is therefore necessary to study further the dynamic of Cl emission lines and also the chemical and physical properties of Cl in soil sample to make possible Cl detection using LIBS.
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