Analyzing silver concentration in soil using laser-induced breakdown spectroscopy

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Abstract. Determination of concentration of heavy metal ions in soil, such as silver, is very important to study soil pollution levels. Several techniques have been developed to determine silver ion concentration in soil. In this paper, we utilized laser-induced breakdown spectroscopy (LIBS) to study silver concentration in soil. We used four different data analysis methods to calculate silver concentration. In this case, we prepared soil samples with different silver ion concentrations from 400 ppm to 1000 ppm. Our analysis was focused on the 843.15 nm silver atomic absorption line. We found that plasma intensity increased as silver concentration increased. Our findings were based on our analysis using four different analysis methods. We believe that these analysis methods are able to calculate silver concentration in soil using LIBS.

1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is a fast technique for studying elements in materials. The plasma spectrum, which is generated from laser-matter or photon-atomic interaction, provides essential information such as excitation and de-excitation processes of electrons in materials and elemental information. In principle, materials produce photons when electrons undergo de-excitation. Photons produced from de-excitation process are unique; therefore the energy of the produced photon provides information regarding specific elements in the material [1].

Rapid development of LIBS was significantly achieved due to its great potential applications. In comparison to other spectroscopy technique such as X-ray fluorescence spectroscopy (XRF), LIBS can detect elements with low atomic numbers. The plasma spectrum generated from photon-atomic interaction is mostly in the ultraviolet (UV), visible, and near infrared (NIR) regions, which aids detection. In addition, LIBS can be applied to various types of materials, including solids, liquids, and gases. Generally, LIBS measurements do not require extensive sample preparation. Most samples only require one preparation step before LIBS measurement. Low preparation time makes LIBS a powerful and fast spectroscopy technique.

LIBS can be utilized to detect almost all elements in nature, e.g., heavy metal. Detection of heavy metal elements in nature, such as soil, is crucial for determining contamination levels. Several
techniques have been developed to detect heavy metals content in soil. Chemical analysis requires complicated and time consuming procedures. XRF and X-ray diffraction (XRD) techniques require an X-ray source and detector, which are expensive. Detection of elements in UV-visible-NIR range is one of the easiest detection techniques. LIBS offers fast detection of heavy metals contained in soil since detection is done in UV-visible-NIR range.

However, analysis of low heavy metal concentration in soil using LIBS is not an easy task. Therefore, there are not many reports related to the determination of heavy metal concentrations in soil. A calibration curve constructed from known concentrations is required to quantitatively analyse LIBS data. A problem that often occurs in LIBS measurement is that plasma formed from natural materials is unstable due to the heterogeneity of the sample. One way to analyse plasma spectra is by using a normalization technique [2]. Gornushkin et al. reported that normalization of surface density by considering mechanical effects of ablated mass provides a simple solution for analyzing plasma spectra of low concentration elements in a matrix [3].

For a specific case, silver element causes pollution in the environment and severe negative effects. Silver pollutants are known to accumulate in plants and animals and can cause serious illness in humans at the top in the food chain [4 – 6]. In this work, we will focus on analyzing plasma spectrum of low concentration of silver (Ag) ion in soil matrix using several data analysis techniques. The purpose of this work is to find the optimum analysis method of plasma spectra, which was obtained using LIBS measurement, for determining Ag ion concentration in soil.

2. Sample preparation and measurements
We utilized ordinary soil from local tropical farm fields as the sample matrix. The soil was ground and filtered to obtain soil particles of uniform size at 1 mm. 15 g of prepared soil was then mixed with 10 ml of various AgNO₃ concentrations, enabling calculation of Ag ion concentration in soil in unit of ppm. The mixture was then blended to make homogeneous Ag-embedded soil samples. The sample was then heated in oven at 100 °C for 1 hour to reduce water content. In order to ease plasma generation and analysis, the Ag-embedded soil was transformed into a pellet using pellet press with a pressure of 25 bar. The surface of pellet was flat, smooth, and ready for LIBS measurements. Low water content and flat pellet surface improved the quality of LIBS measurements [7 – 8].

![Figure 1. LIBS experimental setup.](image)
LIBS measurement was done using setup shown in figure 1. A Quantel Nd:YAG laser operating with a 10 Hz repetition rate, a 532 nm wavelength, and a 24 mJ energy, was focused onto sample pellets using a 100 mm focusing lens. The sample was placed in a vacuum chamber and rotated during LIBS measurement to ensure that laser is incident on a new surface of the sample for each laser pulse. A spectrophotometer with integration time of 100 ms was used to detect and record emission spectra of generated plasma. It was assumed that for every 100 ms there was only one laser pulse to generate plasma. For analysis purposes, 250 plasma spectra were recorded for one sample. We also conducted LIBS measurements of a 99.99% pure silver plate to obtain silver lines in plasma spectrum.

3. Results and discussion
First, we analyzed the plasma spectrum of the Ag plate, shown in figure 2. We obtained seven detectable Ag atomic lines from plasma spectrum, i.e., Ag (I) 405.54 nm, Ag (II) 418.54 nm, Ag (II) 519.81 nm, Ag (II) 544.09 nm, Ag (I) 768.77 nm, Ag (II) 825.47 nm, and Ag (I) 843.15 nm. We also noticed that these Ag ion lines were detectable in low laser fluence.

![Figure 2. LIBS emission spectra from Ag plate.](image-url)

Every recorded plasma spectrum was then analyzed to study Ag ion concentration in soil. Plasma peaks were then confirmed and corrected using the National Institute of Standards and Technology (NIST) atomic line database. We also confirmed the recorded plasma peaks using the silver plate spectrum. This confirmation was required since there was random shot-to-shot variation of plasma peak intensity due to the heterogeneity of the sample. Therefore, we calculated and normalized 250 spectra to get a single spectrum for every soil sample.

Plasma spectra obtained from soil samples were quite different compared to those from the Ag plate. We assumed that this was because matrix effects influenced generated plasma. Soil and other elements in the matrix could form new and different plasma lines [9]. A lot of spectral lines that are not linearly dependent on Ag concentration could occur in a complex sample such as soil. This complicated spectrum is difficult to understand and analyze. The set-up and spectrophotometer position will also affect recorded spectrum. This is the reason that 250 spectra were collected for each
sample. By confirming soil sample spectra with the silver plate spectrum and NIST atomic database, we selected the Ag plasma line at 843.15 nm wavelength for further analysis. This line was chosen because intensity increased with increasing concentration as can be seen in figure 3. This means that it was an appropriate peak for analyzing silver ion concentration. We selected this peak wavelength since this peak was always detectable in all measurements and there was no overlapping with peaks from other elements. Therefore, it made analysis easier.

![Ag II 843.15 nm](image)

**Figure 3.** LIBS emission spectra of Ag ion at 843.15 nm wavelength for various Ag ion concentrations.

We used four methods to analyse plasma spectra, i.e. uncorrected, discard 20% of outlying data, peak-to-background ratio, and a combination of the final two methods [10]. The number of scans was chosen to be 250 as this was reported by Body [10] to improve data analysis. 250 scans was an optimal number as more scans could potentially damage the sample and affect the results. In uncorrected method, we calculated area under Ag ion line using trapezium formula for all 250 spectra and took the average as the peak area. In the discard 20% method, we discarded 10% of highest data and 10% of lowest data from calculation results of uncorrected method. It is assumed that the highest and lowest 10% data from the median contains potential outliers that can introduce error into the calculation of the mean. In the ratio method, we compared the peak area of Ag ion line to total plasma spectrum area. This method is to minimize laser power and matrix effect. In the last method we applied discard 20% method to results obtained from the ratio method.

The precision of analysis is given by the relative standard deviation (RSD) value as shown in figure 4. The accuracy of calculations of the 843.15 nm Ag (II) ion line in soil is shown in figure 5. The uncorrected method gives the worst calculation result, as expected. After applying the discard 20% method, the accuracy improves. The ratio and combined ratio and discard 20% methods also give good results.

Figure 5 shows analysis results of silver concentration in soil using discard 20% and ratio with discard 20% methods. There is a weak linear correlation between plasma intensity increasing as silver...
concentration is increased. However, the correlation is weak and non-linear due to many factors, such as the uncontrolled heterogeneity of silver concentration in soil.

![Graph showing RSD for different methods](image)

**Figure 4.** Precision calculation of Ag atomic line using four different methods.

![Graph showing Ag 843.15 nm Response](image)

**Figure 5.** Calibration curves for a 843.15 nm Ag atomic line present in various Ag ion concentrations.

4. **Conclusion**

Ag emission lines were detected in soil samples using a 532 nm wavelength laser. Using Ag atomic lines from Ag plate and NIST database, we have confirmed and analyzed plasma spectra from soil to determine Ag content from 400 ppm until 1000 ppm. Analysis of 250 plasma spectra Ag at 843.15 nm
was carried out using four different methods. We found that the discard 10% method gives better analysis than other methods. It requires more experiments by varying more Ag concentration to show linearity between Ag concentration and plasma intensity.

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