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Elemental Analysis of Soils Using Laser-Induced Breakdown Spectroscopy (LIBS)

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Abstract

Laser-induced breakdown spectroscopy (LIBS) has been applied for the quantitative analysis of various samples, but it is controversial for chemically-complex soils. In order to study the effect of delay time, gate width, and repetition rate on the LIBS signal in soil, the emission line at 396.84 nanometer was selected. The results indicated that repetition rate, delay time, and gate width significantly affected the LIBS signal, delay time was more important than gate width in controlling the LIBS signal. The optimum instrumental parameters for soil analysis were obtained when repetition rate, delay time, and gate width equaled 10 hertz, 1 microsecond, and 10 microsecond, respectively. In order to compare the analytical ability of univariate and multivariate approaches in analyzing the LIBS spectral data and to quantitatively determine copper and zinc concentrations in soils, 12 samples with different copper and zinc concentrations were analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES) and LIBS, respectively. The univariate and the partial least square (PLS) regression were coupled with LIBS to build the calibration models and to predict copper and zinc concentrations. The background-subtracted signal intensity at 324.75 nanometer (copper) and 334.59 nanometer (zinc) were used for the univariate analysis, and the full spectral range 200-600 nanometer and the reduced spectral ranges 250-450 nanometer and 300-350 nanometer were used for the PLS analysis. Copper and zinc concentrations predicted by LIBS were compared with those measured by ICP-OES. The results demonstrated that (1) the PLS regression was powerful in analyzing the LIBS spectral data, and compared to the univariate regression, it improved the normalized root mean square error of calibration (NRMSEC) about 15% and the normalized root mean square error of prediction (NRMSEP) about 10% respectively; (2) The PLS regression using the reduced spectral range (300-350 nanometer) containing copper and zinc peaks produced the best results among all

the spectral ranges, which indicated that use of the suitable spectral range in the PLS regression improved the LIBS analytical ability; (3) The implementation of multivariate approaches in analyzing the LIBS spectral data made the quantitative analytical ability of LIBS promising and comparable to that of ICP-OES.

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General Introduction

Laser-induced breakdown spectroscopy (LIBS) is also called laser-induced plasma spectrometry (LIPS) or laser spark spectrometry (LSS). It is a total multi-elemental analytical technique based on atomic emission spectroscopy (AES). It utilizes a high-energy laser pulse as the vaporization, atomization, and excitation source to create a high-temperature micro-plasma at the surface of the target (Cremers and Radziemski, 2006). The elements contained in the sample are vaporized and excited in the hot plasma to generate an atomic and ionic spectrum which is characteristic of the elemental composition of the target. Each element has its unique emission lines working as the "fingerprint" of the element. After being spectrally-resolved, the wavelength of the emission line is used to identify the existence of the elements, and the background-subtracted peak intensity at the chosen emission line is used to quantify the elemental composition of the target.

Conventional atomic spectroscopic techniques such as inductively coupled argon plasma-optical emission spectroscopy (ICP-OES), ICP-mass spectroscopy (ICP-MS), and atomic absorbance spectroscopy (AAS) have excellent analytical performance, but their sample preparation method is destructive and environmentally hazardous. It normally involves the acid-digestion of the silicate and organic matrix under conditions of elevated temperature and pressure, requires hazardous chemical use and disposal and is time-consuming as well. Compared to the conventional elemental analytical methods, LIBS has numerous potential advantages such as simple and compact experimental setup, less sample preparation, less-destructive surface analysis, remote in-situ analysis in hostile environments for hazardous or inaccessible targets, etc. Due to its inherent advantages, LIBS developed very fast since its invention in 1960's and had been successfully applied for both qualitative and semi-

quantitative analysis in a wide range of areas, including environmental monitoring (Hahn and Lunden, 2000; Samek et al., 2000; Hettinger et al., 2006), industrial monitoring (Grant et al., 1991; Kraushaar et al., 2003; García et al., 2004), space exploration (Cremers and Radziemski, 2006), and various material analysis such as pigments identification in painted artworks (Anglos et al., 1997), archaeological excavations (Melessanaki et al., 2002), biological (Labbé et al., 2008), geological (Anzano et al., 2006), and agricultural materials (Vadillo et al., 1999; Sirven et al., 2006; Kaiser et al., 2007), etc. Although LIBS has tremendous advantages over the other spectroscopic techniques, it has limitations also. For example, unstable signal intensity, the relatively high limit of detection (LOD), repeatability of results, and matrix-dependency of measurement. Many studies have investigated the environmental factors and the instrumental parameters that influence the analytical performance of LIBS, and the solutions used to reduce and solve the problems included the application of a rotating stage, the average of accumulated laser shots, and the homogenization of samples.

The LIBS spectrum contains large, redundant, and complex information describing the elemental composition of the target (Labbé et al., 2008). If accurately and efficiently analyzed, the spectral information can be used to quantitatively analyze the elemental composition of the target. Multivariate analysis (MVA) is a powerful chemometric analytical technique that takes into account all the possible variables, removes the redundant and correlated variables, and fully utilizes the LIBS spectral information. It has been reported that MVA worked very well for the analysis of the LIBS spectra collected from several materials, including bacterial spores, molds, pollens, and protein (Samuels et al., 2003), bacterial deposits and aerosols (Leone et al., 2004), preservative-treated wood (Martin et al., 2005), cremains and prosthetic implants (Martin et al., 2007), and lignin (Labbé et al., 2008). Soil is

a chemically-complex matrix, and only a few studies coupled MVA and LIBS together such as soil carbon analysis (Martin et al., 2007). Therefore, to implement MVA in the analysis of the LIBS spectral data collected from soil samples is of great significance in evaluating the quantitative analytical ability of LIBS in soil metals analysis. Our goals were (1) to study the effect of repetition rate, delay time (t_d), and gate width (t_w) on signal intensity, the relative standard deviation (RSD%) of signal intensity, and signal-to-noise ratio (SNR); (2) to compare the analytical ability of univariate and multivariate approaches in analyzing the LIBS spectral information and to quantitatively determine Cu and Zn concentrations in soils.

This thesis is composed of two parts. Part 1 studied the effect of the instrumental parameters (repetition rate, t_d, and t_w) on signal intensity, the RSD% of signal, and SNR using soil. Our results indicated that repetition rate significantly affected the LIBS signal intensity and t_d was more important than t_w in controlling the LIBS signal. The optimum instrumental parameters for soil analysis were obtained when repetition rate, t_d, and t_w equaled 10 Hz, 1 μs, and 10 μs, respectively.

Part 2 compared the analytical ability of univariate and multivariate approaches in analyzing the LIBS spectral information and to quantitatively determine Cu and Zn concentrations in soils. Twelve soil samples with different Cu and Zn concentrations were analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES) and LIBS, respectively. The univariate and the partial least square (PLS) regression techniques were implemented to analyze the LIBS spectral data, the calibration models were developed relating Cu and Zn concentrations with the LIBS spectral information (background-subtracted signal intensity at 324.75 nm (Cu) and 334.59 nm (Zn), the full spectral range 200-600 nm, and the reduced spectral ranges 250-450 nm and 300-350 nm). The calibration models were used to predict Cu and Zn concentrations in the same soil samples, and the predicted Cu and Zn

concentrations by LIBS were compared with those measured by ICP-OES. The results clearly demonstrated that (1) the PLS regression was powerful in analyzing and extracting the useful LIBS spectral information, and compared to the univariate regression, it improved NRMSEC about 15% and NRMSEP about 10%, respectively; (2) The PLS regression performed on the reduced spectral range (300-350 nm) containing Cu and Zn peaks produced the best results among all the spectral ranges, which indicated that use of the suitable spectral range in the PLS regression improved the LIBS analytical ability; (3) The implementation of multivariate approaches in analyzing the LIBS spectral data made the quantitative analytical ability of LIBS promising and comparable to that of ICP-OES.

Literature Review

Introduction

Laser-induced breakdown spectroscopy (LIBS) is a total multi-elemental analytical method based on the measurement of atomic emission lines from laser plasma generated at a sample surface. Due to its tremendous potential advantages over the conventional elemental analytical techniques, LIBS related research and applications have been widely investigated since its invention in 1960's. From the previously published papers and books, it is easy to conclude that LIBS is a versatile quantitative multi-elemental analytical approach that can be applied in many areas for the analysis of almost all kinds of samples. In this literature review, the LIBS related research and studies are organized into three categories: (1) Factors affecting the analytical performance of LIBS; (2) Analytical methods suitable for analyzing the LIBS spectral data, including univariate analysis and multivariate analysis (MVA); (3) The application of LIBS for the elemental analysis of samples with different states in various research areas.

Factors Affecting the Analytical Performance of LIBS

Laser-induced breakdown spectroscopy (LIBS) is a sensitive elemental analytical technique whose analytical performance can be significantly affected by the environmental factors, the instrumental parameters, the chemical and physical properties of the sample, the homogeneity and the ambient states of the sample, etc. For example, air humidity, air temperature and pressure (Iwasaki et al., 2009), laser pulse energy (Charfi and Harith, 2002; Gondal et al., 2008), pulse duration (Margetic et al., 2000; Yamamoto et al., 2005), pulse repetition rate (Wisbrun et al., 1994), laser wavelength (Cabalín and Laserna, 1998), delay time (t_d) and gate

width (t_w) (Radziemski and Loree, 1981; Eppler et al., 1996; Dudragne et al., 1998), and the number of laser shots (Wachter and Cremers, 1987). Signal intensity and stability are the most important factors that influence the analytical results of LIBS, and a lot of research has been focused on this area. Gondal et al. (2008) studied the relationship of signal intensity and laser pulse energy, and the results showed that signal intensity linearly (r^2=0.996) increased with increasing pulse energy from 10 mJ to 30 mJ. Cabalín and Laserna (1998) studied the effect of laser wavelength on plasma initiation threshold at infrared (1064 nm), visible (532 nm), and ultraviolet (266 nm) regions using metal samples, and the results showed that laser wavelength was an important factor in affecting plasma initiation threshold, and a shorter laser wavelength enhanced the ablation process of metal samples. Margetic et al. (2000) studied the effect of pulse duration with 170 fs and 6 ns laser pulses on the ablation of brass samples in argon shield gas, and the results showed that fs- laser pulse was more reproducible than ns- laser pulse. Due to the presence of the continuum "white light" at the very beginning of the plasma formation, there is little intensity variation as a function of wavelength, and thus the detection of the relatively weaker emission lines from minor and trace elements is often interfered. Delay time (t_d) is the time between plasma formation and the start of the observation of the plasma light, and gate width (t_w) is the time period over which the plasma light is recorded (Miziolek et al., 2006). By using a time-resolved detection system to control t_d and t_w, the intense initial continuum emission at the early stage of the plasma formation can be gated off, and SNR can be improved dramatically. Wisbrun et al. (1994) investigated the effect of repetition rate, t_d, and t_w on signal intensity and SNR using soil and sand samples, and the results showed that the optimum repetition rate for soils was 1 Hz, the optimum time parameters were element-dependent, but a common setup could be found, and t_d was more significant than t_w in controlling the LIBS signal intensity and stability. Eppler et al. (1996)

reported that t_w longer than 50 μs was unnecessary because most of the analytical emission lines had completely decayed. Watcher and Cremers (1987) studied the effect of the number of laser pulses on the RSD% of signal intensity, and they found that with the increase of laser shots from 50 to 1600, the RSD% of signal intensity decreased from 13.3% to 1.8%. Castle et al. (1998) reported that the best precision occurred at 325 laser shots for the stationary sample, but for moving samples, the general trend was the same, the best precision occurred at varying laser shots ranging from 50 to 400 shots.

Normally, repetitive single spark (RSS) works very well in determining the elemental composition of a sample. However, it is very difficult to obtain an emission line if the target is submerged in water. In order to enhance the analytical performance of LIBS, repetitive spark pair (RSP) is developed. It may be generated by a single laser or by two separate lasers at a certain time delay. Pichahchy et al. (1997) reported that the first laser pulse could create a bubble inside the water bulk, the second laser pulse could go through the bubble and create higher excitation plasma at the sample surface, and thus enhance signal intensity. Due to its ability to enhance signal intensity and overall analytical performances, RSP has been widely used for liquid samples (Kumar et al., 2003), solid samples submerged in liquid (Giacomo et al., 2005; Lazic et al., 2007), and solid samples (Casavola et al., 2005; Amal et al., 2006).

During the vaporization process, each laser pulse only ablates a tiny amount of material, which means each laser pulse does not always vaporize a mass that is representative of the composition of the sample. Therefore, the homogeneity of the sample is of great importance for measurement accuracy and precision. In the last few years, different kinds of sample preparation methods have been developed. For solid samples, grinding (Hilbk-Kortenbruck et al., 2001; Anzano et al., 2006) and sieving were used in the homogenization, and mechanical pressure (Bustamante et al., 2001; Gondal et al., 2008) was used in the uniformization of the

sample surface. For liquid solution, it could be converted to solid-matrix by different binders (Cáceres et al., 2001; Pace et al., 2006; Gondal et al., 2007) or transformed to flowing surface or jet (Jer et al., 2002; Kumar et al., 2003; Fang et al., 2007). Pace et al. (2006) added calcium oxide to aqueous solution, and after stirring and drying, the precipitate was pressed into pellets and analyzed. Jer et al. (2002 and 2007) used an electro-spray ionization needle (anode) to generate a stream of micro-droplets at a controlled loading speed toward the other metal base (cathode), thus providing a flowing surface in a micro-column. St-Onge et al. (2004) used NaCl solution to study the effect of sample present geometry, including bulk liquid in a closed glass bottle, flowing horizontal surface, and non-flowing surface in a container, and the results showed that the conversion of liquid to a flowing horizontal surface was the most promising approach in liquid sample analysis. Schmidt and Goode (2002) used an ion exchange membrane to pre-concentrate and immobilize the analyte in a liquid solution and to analyze the membrane. Yaroshchyk et al. (2005) used the absorbent paper substrate to analyze the used engine oil, and the results showed that this method provided the better LODs than those obtained by flowing liquid jets.

LIBS Spectral Data Analytical Methods

The LIBS spectrum contains large and complex information about the elemental composition of the target, which can be used for the qualitative and as well as the quantitative analysis of a wide range of samples. In a matter of microseconds, tens of thousands of data points can be collected. For example, a spectrum collected with a spectrometer covering a wavelength range of 200-600 nm and having a wavelength resolution of 0.012 nm contains more than thirty thousand points. Therefore, use of the suitable data analytical method to efficiently and accurately analyze the complex LIBS spectra is of great importance in evaluating the analytical ability of LIBS. Most researchers (Barbini et al., 1997; Xu et al., 1997; Vadillo et

al., 1999; Kaiser et al., 2007) used the univariate approach (single emission line) to analyze the LIBS spectra which caused the loss of much useful information. With the development of statistical analytical methods, many other analytical approaches are successively applied in the analysis and extraction of the useful spectral information, including MLA (Essington et al., in press) and MVA (Wisbrun et al., 1994; Martin et al., 2005; Bousquet et al., 2007; Labbé et al., 2008). Martin et al. (2003 and 2007) applied MVA in the LIBS spectra analysis, and the results showed the possibility that MVA could construct a "universal calibration curve" for elements in different matrix. Labbé et al. (2008) reported that using several emission lines in combination could produce dramatically better results than using any of the individual emission line alone. The univariate analysis and MVA will be described in the following part.

Univariate Analysis

Univariate analysis is based on the analysis of a single emission line of the element of interest. Any detected emission line can be used to construct a calibration model, in which the elemental concentration is the independent variable (x-axis) and the background-subtracted peak intensity is the dependent variable (y-axis). The calibration model can be expressed as a linear and first-order equation *(1)*

$$y = ax + b \qquad (1)$$

where a is the slope of the calibration curve, b is the intercept.

The average relative error of prediction (*REP%*) is used to evaluate the predictive ability of the calibration model. The *REP%* is calculated with equation *(2)*:

$$REP(\%) = \frac{100}{N_p}\sum_{i=1}^{N_p}\left|\frac{p_i - c_i}{c_i}\right| \qquad (2)$$

where N_v is the number of validation spectra, p_i is the predicted concentration, c_i is the true concentration.

The LOD is calculated from the IUPAC definition (Mocak et al., 1997) with equation *(3)*:

$$LOD = 3\sigma/S \qquad (3)$$

where σ is the standard deviation of the background, and S is the slope of the calibration curve.

Multivariate Analysis

Multivariate analysis (MVA) is a powerful chemometric analytical technique which takes into account all the variables in the whole spectra, removes the redundant and correlated information, and extracts the most important information from the original LIBS spectra. It makes LIBS more feasible in the determination of elemental composition and the differentiation of different samples. Principal component analysis (PCA) and the partial least squares (PLS) regression are the most often used multivariate approaches. Principal component analysis (PCA) is a data decomposition method involving a mathematical procedure that orthogonally transforms a large number of possibly correlated independent variables into a smaller number of uncorrelated independent variables, also called principal components (PCs) or latent variables. The application of PCA can remove the redundant and less important while retain the most important and original information, interpret the interrelationships among different variables, uncover unknown trends, and differentiate groupings (Mark, 2001; Romanenko and Stromberg, 2007). The PLS regression linearly relates the variations of dependent variables to the variations of independent variables, and it works especially well when independent variables are large in number and carry common information such as correlations and collinearity (Wold et al., 2001). Different from PCA, the

PLS regression actively uses dependent variables to help estimate the "latent" variables (PLS components) from the original independent variables, and the first PLS component contains the most relevant information predicting the dependent variables. The PLS regression simplifies the interpretation of the relationship between independent variables and dependent variables, because this relationship is interpreted with the smallest number of PLS components. The application of MVA in extracting and analyzing the LIBS spectral information will definitely improve the quantitative analytical ability of LIBS and make it more promising.

Application of LIBS in Elemental Analysis

The first laser ablation experiment was reported in 1962 (Brech and Cross, 1962) which described the analytical application of laser in solid samples. One year later, Runge et al. (1963) reported that the spectra produced by laser excitation had very good reproducible quantitative relationships among the various elemental constituents of the sample which showed great potential for LIBS as a quantitative elemental analytical method. With the advances of the LIBS components and statistical analytical approaches, LIBS has dramatically improved with its quantitative analytical ability becoming more robust. During the last decade, LIBS has dominated the analytical atomic spectroscopy scene.

As a total multi-elemental analytical method, LIBS has been successfully applied in many areas for the elemental analysis of solids, liquids, gas, and aerosol (Cremers et al., 1984; Eppler et al., 1996; Pichahchy et al., 1997; Kumar et al., 2003; Martin and Cheng, 2000). Sabsabi and Cielo (1995) and Aragón et al. (1999) quantitatively analyzed the composition of aluminum alloys and steel by LIBS respectively, and both studies obtained satisfactory analytical results. Laser-induced breakdown spectroscopy (LIBS) was also applied to detect elements in different liquids (Fichet et al., 1999), and the LOD of chromium was 20 ppm in

water and 30 ppm in oil, which made LIBS an alternative tool for the quantitative analysis of liquid samples. Martin and Cheng (2000) used LIBS to detect Cr in aerosol, and the results showed that the LOD of Cr determined by LIBS was even better than that determined by ICP-AES. In agricultural science, quick and accurate analysis of the elemental composition of the agricultural samples is very important for nutrition management, fertilization practices, and contaminant monitoring. Sun (2000) directly analyzed P, Al, Ca, Cu, Mn, Zn, Mg, and Fe in plant leaves using NIST-SRM (tomato leaves, spinach leaves, apple leaves, and peach leaves). Loose leaf powder was spread on a double-sided tape with one side attached on a glass microscope slide, and after the excess powder was shaken off, the tape with a uniform thin layer of powder was measured by LIBS. A major problem with phytoremediation of toxic metals is lack of the information on how the ions transport and where they are stored within the plant, which is very important for plant scientists to answer many questions about plant metabolism. Current analytical techniques normally use the whole plant organs or tissue, therefore, precise spatial and depth resolution is hard to obtain. However, LIBS makes high spatial (size of laser beam diameter) and depth (tens of nanometer deep depending on laser pulse energy in the sampling site) resolution both accessible (Galiová et al., 2007). Kaiser et al. (2007) investigated the bioaccumulation of Pb and Cd in the different parts of leaf samples using a femto-second laser pulse, and the results showed that LIBS had great potential in analyzing the spatial and lateral distribution of the element within different plant components. As an atomic emission spectroscopy technique, LIBS is especially good at metal analysis. Therefore, studies about soil analysis were mainly focused on metals. Through comparing the LOD of As, Ba, Cd, Cr, Cu, Zn, Hg, Ni, Pb, Tl, and Sr determined by LIBS in different soils, some studies (Barbini et al., 1999; Vadillo et al., 1999; Sirven et al., 2006; Hussain and Gondal, 2008) concluded that the quantitative analytical ability of LIBS was very promising,

but others (Capitelli et al., 2002; Essington et al., in press) insisted that LIBS was only successful at qualitative or semi-quantitative levels and not at quantitative levels. Reasons for this contradiction include the differences in soil matrix, reference emission line, analytical methods, etc.

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Part 1 Instrumental Parameter Analysis of Laser-Induced Breakdown Spectroscopy (LIBS) in A Complex Soil Matrix

This part is a paper to be submitted to Communications in Soil Science and Plant Analysis.

Ningfang Yang, Neal S. Eash, Jaehoon Lee, Forbes R. Walker, Madhavi Z. Martin. Instrumental Parameter Analysis of Laser-Induced Breakdown Spectroscopy (LIBS) In A Complex Soil Matrix.

Abstract

Laser-induced breakdown spectroscopy (LIBS) is a sensitive elemental analytical technique. The analytical figure of merit of LIBS such as precision, accuracy, and the limits of detection (LOD) are not as satisfactory as that of the conventional analytical techniques. There are many factors that influence signal intensity, signal stability (the relative standard deviation of signal intensity, the RSD% of signal intensity), and signal-to-noise ratio (SNR), including the physical and chemical composition of the sample, the environmental conditions, and the instrumental parameter. In order to improve the analytical ability of LIBS, a strong, stable, and sensitive emission signal must be obtained. This research studied the effect of instrumental parameter, including repetition rate, delay time (t_d), and gate width (t_w) on the LIBS signal intensity, the RSD% of signal intensity, and SNR in a complex soil matrix, and the optimum instrumental parameter for soil analysis was determined. Standard reference material (SRM-2586) was used to prepare pellets for the parameter analysis. To study the effect of repetition rate, t_d was set to 1 μs, t_w was set to 20 μs, and repetition rate was varied from 1~15 Hz. To study the effect of t_d and t_w, repetition rate was set to 10 Hz, t_d was varied from 0.5~5 μs, and t_w was varied from 5~50 μs. For each set of parameters, four spectra were collected. The results indicated that repetition rate, t_d, and t_w significantly affected the LIBS signal intensity, t_d was more important than t_w in controlling the LIBS signal. The optimum instrumental parameters for soil analysis were obtained when repetition rate, t_d, and t_w equaled 10 Hz, 1 μs, and 10 μs, respectively.

Keywords: LIBS; signal intensity; RSD% of signal intensity; SNR

Introduction

Laser-induced breakdown spectroscopy (LIBS) is a promising and sensitive elemental analytical technique which has been applied for the analysis of the elemental composition of samples in various states such as solid, liquid, and aerosol (Sabsabi and Cielo, 1995; Schmidt and Goode, 2002; Martin and Cheng, 2000). The potential advantages of LIBS such as less-destructive surface analysis, minimum sample preparation, small amount of sample requirement, and multi-elemental analysis, are also responsible for the unsatisfactory analytical ability of LIBS including high limit of detection (LOD), low precision and accuracy, and low measurement reproducibility. Factors influencing the analytical ability of LIBS include the physical parameters of the target (state and homogeneity), the chemical composition of the target, the environmental conditions (atmospheric pressure, temperature, and gas composition), and the instrumental parameters (delay time, gate width, repetition rate, laser pulse wavelength, pulse energy and duration). In order to obtain satisfactory and reproducible analytical results, a strong, stable, and sensitive emission signal must be obtained. So far, several researchers systematically studied the effect of instrumental parameter on the signal intensity and stability (Wachter and Cremers, 1987; Castle et al., 1998; Charfi and Harith, 2002), but only a few using soil matrices (Wisbrun et al., 1994; Eppler et al., 1996). Wisbrun et al. (1994) studied the precision of LIBS measurements on soil and sand samples as a function of repetition rate, delay time (t_d), and gate width (t_w). The results indicated that the optimum repetition rate for soils was 1 Hz, and the optimum t_d and t_w were element-dependant but a common setup could be found. Eppler et al. (1996) reported that most analytical emission lines had completely decayed when t_w was longer than 50 μs. In this study, the effect of repetition rate, t_d, and t_w on the signal intensity, the RSD% of signal

intensity, and signal-to-noise ratio (SNR) were studied in a complex soil matrix, and the optimum instrumental parameter of LIBS for soil sample analysis was determined.

Materials and Methods

LIBS Setup

The LIBS setup employs a Q-switched Nd: YAG pulsed laser (Minilite II, Continuum, Santa Clara, CA) with a fundamental wavelength of 1064 nm which is frequency doubled to 532 nm and used as the excitation wavelength. The laser pulse energy is 25 mJ, the laser pulse width is 3~5 ns, and the repetition rate ranges from 1 to 15 Hz. Laser pulse was guided and focused at the target's surface by a plano-convex quartz lens and a focusing lens to form a high-temperature plasma for vaporization and atomization of the target material. A fused-silica fiber-optic cable (Glenair, Inc., Glendale, CA) was mounted at a ~45° angle to the target's surface. The light released from the plasma containing the emission spectrum was delivered by the fiber-optic cable to a spectrometer (SE 200 Spectrograph with High Order Dispersion Module, Catalina Scientific Corporation, Tucson, AZ) which was connected to an intensified charged coupled detector (ICCD, Apogee Intensity Camera, Catalina Scientific Corporation, Tucson, AZ). The ICCD camera records the emission lines and allows the identification of the elements through their unique spectral signatures. The spectrometer covers a wavelength range of 200~600 nm, including the spectral lines of almost all the elements. It means that LIBS is capable of detecting all chemical elements because all elements emit light somewhere in that spectral range. The wavelength resolution is about 0.012 nm. The opening of the camera shutter was controlled by a delay generator (Model 500C Pulse Generator, Berkeley Nucleonics, San Rafael, CA), and the LIBS system was controlled by computer using KestrelSpec Apogee for Windows Version 4.12 software

(Catalina Scientific Corporation, Tucson, AZ). Figure A.1 is a schematic diagram of the LIBS system which describes the major components of LIBS setup.

Sample Preparation

We used a Standard Reference Material (SRM-2586) purchased from the National Institute of Standards and Technology (NIST) as the soil sample. SRM-2586 is a blended mixture of soil samples collected from an urban area with a particle size of less than 75 μm. This standard soil contains all the major metals (Ca, Fe, Al, Na, Mg, and Si) and high-concentrations of trace metals (Pb, Cr, Cu, Zn, Ba, Mn, and Cd) in soil. A sample of 0.3 g SRM-2586 was placed into a steel cylindrical mold (Figure A.2) and compressed under a mechanical pressure of 1.5×10^7 kg for 5 min to make a soil pellet (13-mm in diameter and 1-mm thick). For parameter analysis, 20 soil pellets were prepared. Each pellet was placed on a rotating stage which continuously rotated to provide a fresh surface for every laser shot for the LIBS analysis.

Results and Discussion

The RSD% of signal intensity represents the LIBS signal stability, and the high RSD% value means the low signal stability, and vice versa. The SNR compares the level of desired signal to the level of background noise, and the higher the ratio, the less obtrusive the background noise is, and vice versa. The SNR represents the sensitivity of signal, and the high SNR value means the high signal sensitivity, vice versa. In order to obtain accurate and precise analytical results, a strong, stable, and sensitive signal must be obtained. Therefore, in this study, the standards used to determine the optimum instrumental parameters are “to maximize the signal intensity and SNR, and to minimize the RSD% of signal intensity”. For each set of parameters, four spectra were collected, and the average signal intensity, the RSD% of signal

intensity, and SNR at 396.84 nm (emission line of calcium) was used to analyze the instrumental parameters.

Effect of Repetition Rate on Signal Intensity, the RSD% of Signal Intensity, and SNR

t_d and t_w were fixed to 1 and 20 μs respectively for the detector and to study the effect of repetition rate by varying it from 1 to 15 Hz. Figure A.3 showed the effect of repetition rate on the average signal intensity. Figure A.4 showed the changes of the RSD% of signal intensity and SNR as a function of repetition rate. As seen in Figure A.3, the average signal intensity increased with increasing repetition rate, but the increasing rate gradually decreased when repetition rate exceeded 10 Hz. This is caused by the aerosol produced by the laser breakdown of soil material (Wisbrun et al, 1994). Generally, with the increase of repetition rate, the aerosol production rate increases and the steady-state aerosol concentration above the sample surface increases. Aerosol at the sample surface can increase the signal because some of the soil material is already ablated and available in the plasma spot location before the next laser pulse arrives. It means the process of aerosol production supplies materials into the hot plasma which is a critical process to obtain a LIBS spectrum. However, an aerosol concentration beyond a certain value can decrease the signal due to the absorbance of laser light by the aerosol along the laser pass which causes the reduction of the energy available at the focal location. At high repetition rate, the production of aerosol above the sample surface can easily be observed by eye. Other variables need to be considered in determining the optimum repetition rate include the RSD% of signal intensity and SNR. As seen in Figure A.4, the lowest RSD% of signal intensity was obtained at a repetition rate of 10 Hz, at which the highest SNR was also obtained. It means the most stable and sensitive LIBS signal for soil analysis is obtained at a repetition rate of 10 Hz which is in agreement with the value used in many studies (Multari et al., 1996; Harris et al., 2004). However, Wisbrun et al. (1994)

reported that the optimum repetition rate for soil analysis was 1 Hz. Due to the difference in physical- and chemical-matrices of soils, it is quite possible that different soil samples have different optimum repetition rate.

Effect of t_d and t_w on Signal Intensity, the RSD% of Signal Intensity, and SNR

There are two important time parameters, t_d and t_w, need to be optimized before the LIBS analysis. To study the effect of t_d and t_w, repetition rate was fixed to 10 Hz (the optimum repetition rate for the standard soil according to the above analysis). Figure A.5, A.6, and A.7 are the three-dimensional graphs depicting the changes of the signal intensity, the RSD% of signal intensity, and SNR as a function of both t_d and t_w. As seen in Figure A.5, the signal intensity had no significant changes as a function of t_w, but it significantly increased with decreasing t_d, which indicated that t_d was more important than t_w in affecting the signal intensity. The lifetime of the plasma generated at soil surface is shorter than that generated at metal surface which means the plasma of soil matrix cools down much faster and t_d is the major concern in selecting the optimum time parameters. Figure A.6 showed that the RSD% of signal intensity irregularly changed with the change of t_b and t_w, and its values were generally low at low t_d (0.5~1.5 μs) which indicated that the stable signal was generally obtained at low t_d. The lowest RSD% of signal intensity is 5% which is obtained when t_d and t_w equal to 1 μs and 10 μs, respectively. To maximize the signal intensity and the RSD% of signal intensity is not the only standard to decide the optimum LIBS signal, and SNR must also be considered. As the signal intensity increases, the signal background noise also increases. Normally, the signal background noise decays faster then the emission signal, therefore, the LIBS measurements are gated and delayed with respect to the laser pulse to obtain the optimum SNR. Figure A.7 showed that the highest SNR of 19 was also obtained when t_d and t_w equaled to 1 μs and 10 μs, respectively. Therefore, the optimum time

parameters for soil analysis were obtained when t_d and t_w equaled to 1 μs and 10 μs, respectively.

Statistical Analysis of Signal Intensity, the RSD% of Signal Intensity, and SNR

To determine the statistical significance of repetition rate, t_d, and t_w on affecting the signal intensity, the RSD% of signal intensity, and SNR, the ANOVA analysis was applied at 95% confidence interval using SAS software. The ANOVA analytical results indicated that repetition rate, t_d, and t_w could significantly affect the signal intensity ($P<0.001$) (Table A.1), t_d had significant influence on the RSD% of signal intensity ($P=0.035$) but not on SNR ($P=0.089$), and t_w was not significant on affecting both the RSD% of signal intensity ($P=0.643$) and SNR ($P=0.680$) (Table A.2). The statistical analysis confirmed the results that t_d was more important than t_w in controlling the LIBS signal.

Conclusions

The effect of instrumental parameters (t_d, t_w, and repetition rate) on the LIBS signal intensity, the RSD% of signal, and SNR were analyzed using soil samples (SRM-2586), and the optimum set of instrumental parameters for soil sample analysis were determined according to the standards that "to maximize the signal intensity and SNR, and to minimize the RSD% of signal". The results of this study indicated that (1) repetition rate, t_d, and t_w significantly affected the LIBS signal intensity; (2) t_d was more important than t_w in controlling the LIBS signal intensity, the RSD% of signal intensity, and SNR; (3) the optimum instrumental parameters for soil analysis were obtained when repetition rate, t_d, and t_w equaled 10 Hz, 1 μs, and 10 μs, respectively.

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Appendix A

Table A.1 ANOVA analysis of signal intensity using SAS (α=0.05).

Source	Degree of Freedom	F-value	P-value
Repetition rate	13	149.95	<0.001
t_d	4	382.25	<0.001
t_w	5	6.18	<0.001

Table A.2 ANOVA analysis of the RSD% of signal intensity and SNR using SAS (α=0.05).

Source	Degree of Freedom	RSD% of Signal Intensity		SNR	
		F-Value	P-value	F-Value	P-value
t_d	4	3.2	0.035	2.35	0.089
t_w	5	0.68	0.643	0.63	0.680

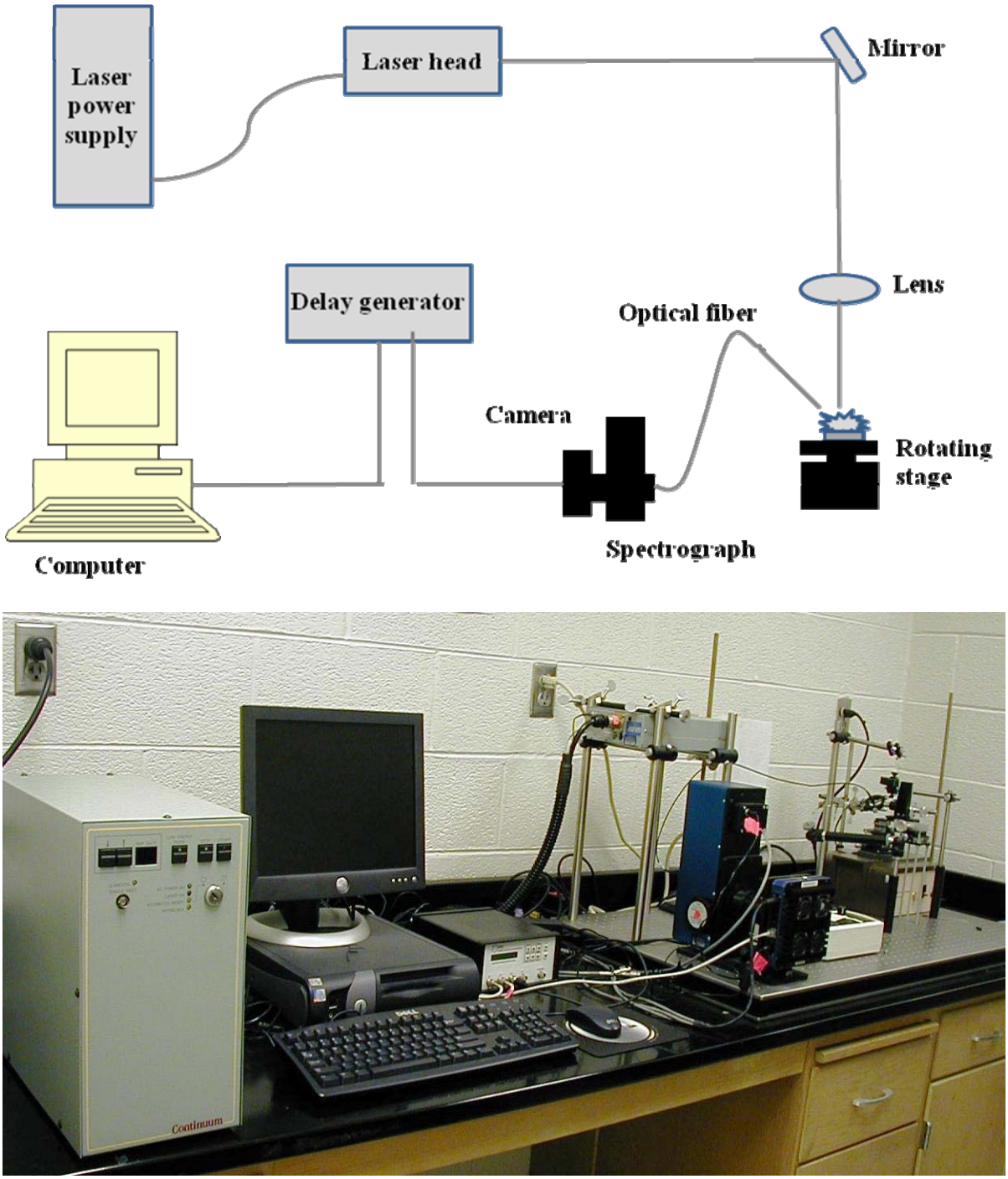


Figure A.1 Schematic diagram of the LIBS system and its major components.





Figure A.2 Sample compressor.

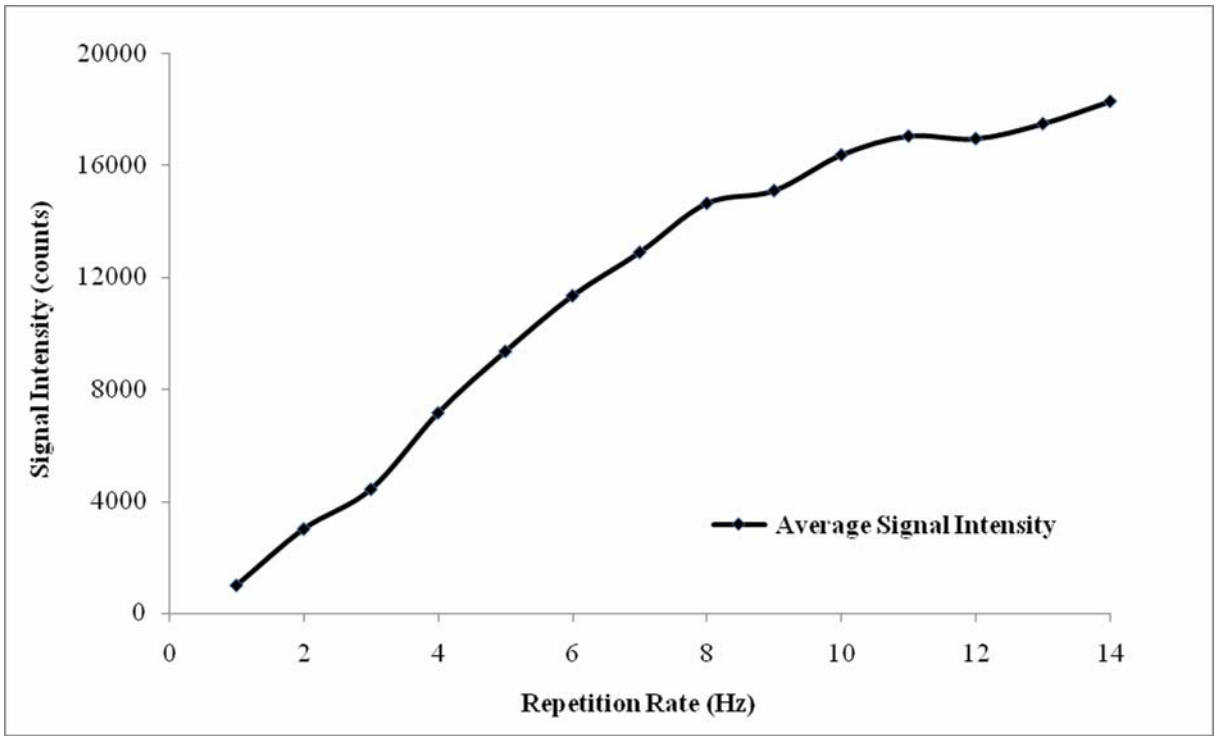


Figure A.3 Effect of repetition rate on the average signal intensity.

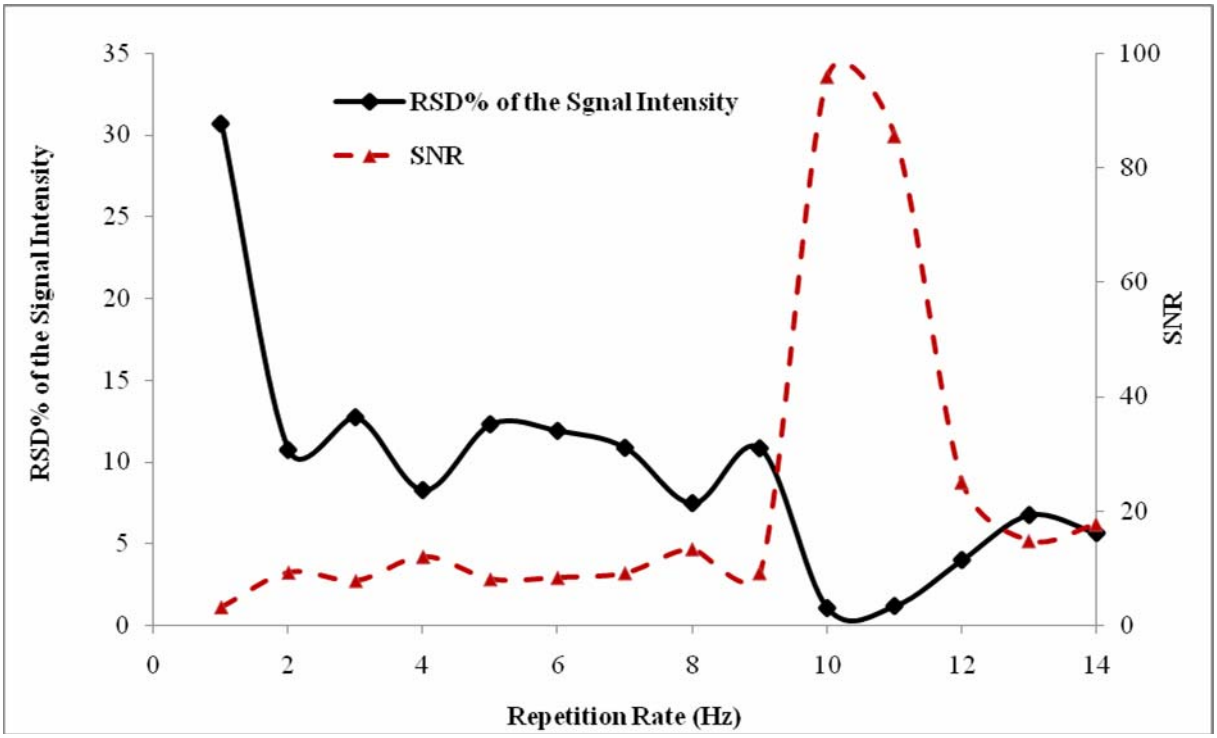


Figure A.4 Effect of repetition rate on the RSD% of signal and SNR.

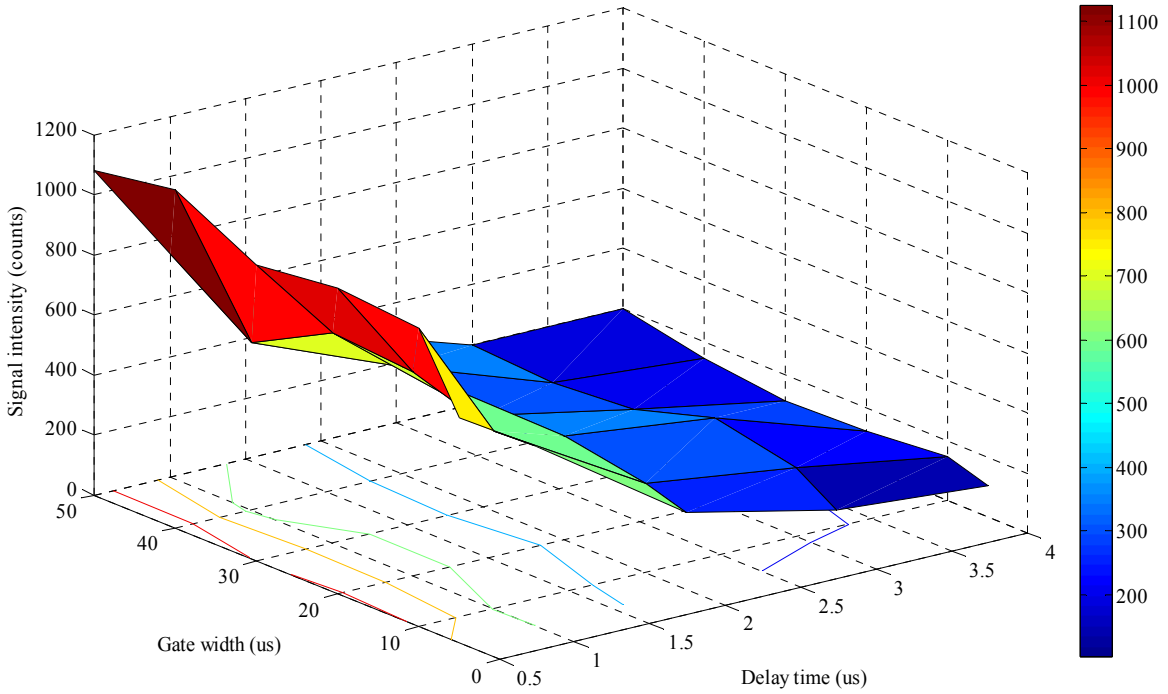


Figure A.5 Changes of signal intensity as a function of delay time and gate width

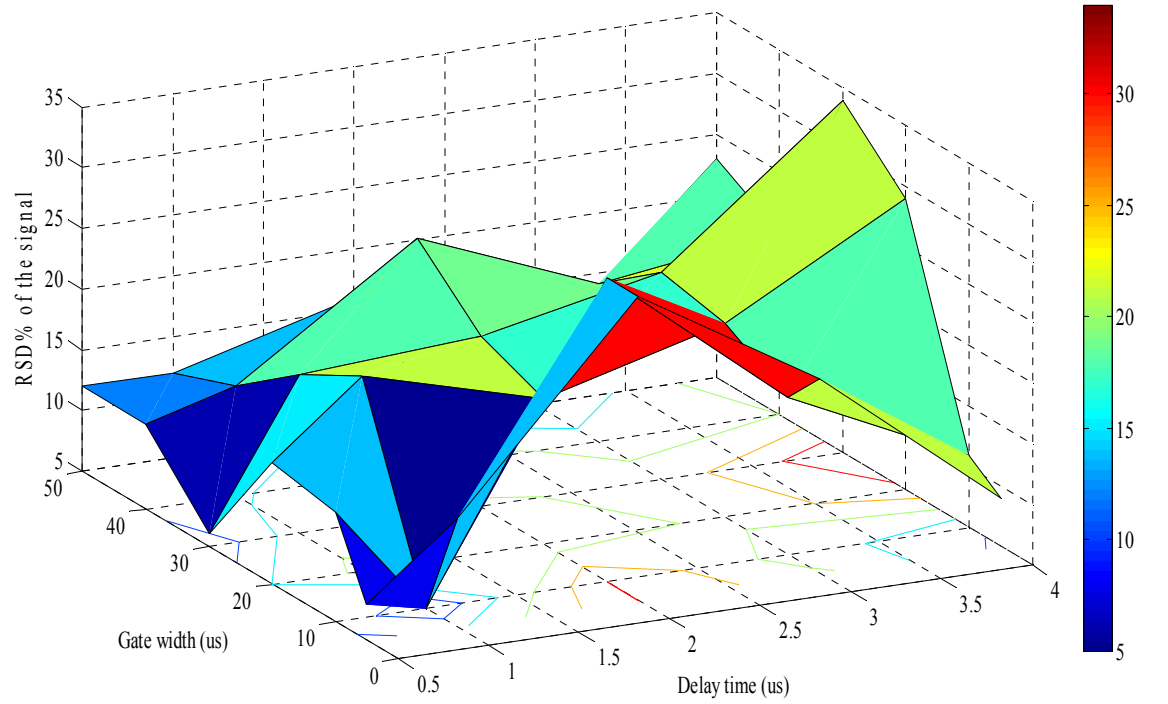


Figure A.6 Changes of the RSD% of signal intensity as a function of delay time and gate width

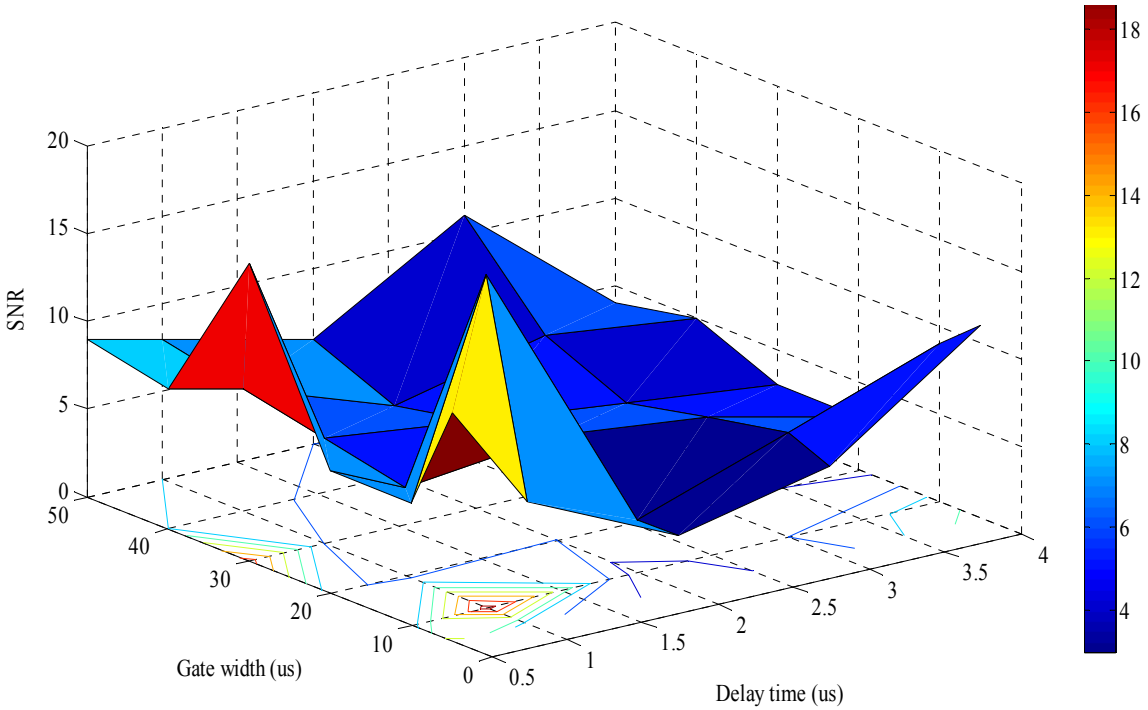


Figure A.7 Changes of SNR as a function of delay time and gate width

Part 2 Analysis of Soil Cu and Zn by Multivariate Analysis of Laser-Induced Breakdown Spectroscopy (LIBS) Spectral Data

This part is a paper to be submitted to Soil Science Society of America.

Ningfang Yang, Jaehoon Lee, Neal S. Eash, Forbes R. Walker, Madhavi Z. Martin. Analysis of Soil Cu and Zn by Multivariate Analysis of Laser-Induced Breakdown Spectroscopy (LIBS) Spectral Data.

Abstract

Laser-induced breakdown spectroscopy (LIBS) is a promising quantitative analytical technique which has been successfully applied in many areas for the quantitative analysis of various kinds of samples, but for chemically-complex soils, its quantitative analytical ability is controversial. In order to evaluate the quantitative analytical ability of LIBS in soil metals analysis, 12 soil samples (homogenous mixture of standard reference material 2586 and an agricultural soil) with different Cu and Zn concentrations were measured by LIBS and ICP-OES. The univariate and the PLS regression techniques were coupled with LIBS to build the calibration models relating Cu and Zn concentrations with the LIBS spectral information (background-subtracted signal intensity at 324.75 nm (Cu) and 334.59 nm (Zn), the full spectral range 200-600 nm, and the reduced spectral ranges 250-450 nm and 300-350 nm). The calibration models were used to predict Cu and Zn concentrations in the same soil samples. The Cu and Zn concentrations measured by ICP-OES were compared with those predicted by LIBS, and the results clearly demonstrated that (1) the PLS regression was powerful in analyzing and extracting the useful LIBS spectral information, and compared to the univariate regression, it improved NRMSEC about 15% and NRMSEP about 10%, respectively; (2) The PLS regression performed on the reduced spectral range (300-350 nm) containing Cu and Zn peaks produced the best results among all the spectral ranges, which indicated that use of the suitable spectral range in the PLS regression improved the LIBS analytical ability; (3) The implementation of multivariate approaches in analyzing the LIBS spectral data made the quantitative analytical ability of LIBS promising and comparable to that of ICP-OES.

Keywords: LIBS; PLS regression; soil

Introduction

Due to the longtime application of sewage sludge, livestock manure, and industrial wastewater irrigation in the agricultural land, heavy metal contamination in soil has become more serious (Nicholson et al., 2003). A method that both fast and accurate is needed for detection of heavy metals in agricultural systems. Conventional atomic spectroscopic techniques have excellent analytical performance, but their sample preparation method is destructive. It involves the acid-digestion of the silicate and organic matrix under conditions of elevated temperature and pressure, requires hazardous chemical use and disposal, and is time-consuming as well. Laser-Induced Breakdown Spectroscopy (LIBS) is a total-elemental analytical technique which has numerous potential advantages over the conventional elemental analytical techniques such as simple and compact experimental setup, less sample preparation, less-destructive, remote in-situ analysis in hostile environments and hazardous or inaccessible targets. So far, LIBS has been successfully applied in the elemental analysis of samples in various states such as solids (Cáceres et al., 2001; Gornushkin et al., 2002), liquids (Cremers et al., 1984; Jer et al., 2002 and 2007; Yueh et al., 2002; Fang and Ahmad, 2007, gases (Dudragne et al., 1998), and aerosols (Martin and Cheng, 2000).

The LIBS spectrum contains large and complex information, for example, tens of thousands of data points can be collected in less than a second (Labbé et al., 2008). For a simple spectrum such as pure zinc, it is possible to build models with every single emission line and then choose the emission line giving the best analytical result. But for a complex spectrum such as soil, it is not possible to compare the analytical results of every possible emission line for each element. Soil is a chemically-complex matrix which contains almost all the elements discovered so far on the earth. Essington et al. (in press) reported that the soil spectra were dominated by the emission lines of Al, Ca, Mg, and Fe, and some of which had more than a

hundred emission lines. The existence of these major elements in soil interferes and over-shadows most of the other elements that might be of interest, and thus makes them hard to be isolated and identified. Many studies (Wachter and Cremers, 1987; Hussain et al., 2007; Lazic et al., 2007; Alamelu et al., 2008) only used one emission line in the spectral analysis and thus lost a large amount of useful information.

One of the methods for preventing the loss of useful spectral information is to implement multivariate approaches in the LIBS spectral analysis. Multivariate approaches are powerful chemometric analytical tools which are especially useful to resolve and extract information from large and complex LIBS spectra (Labbé et al., 2008). MVA takes into account all the variables in the whole spectra, and removes the redundancy, correlation, and collinearity of all the variables. With the development and optimization of various robust statistical analytical methods, LIBS becomes more promising in determining elemental composition and differentiating samples. Principal component analysis (PCA) is a data decomposition method that involves a mathematical procedure that orthogonally transforms a large number of correlated independent variables into a smaller number of uncorrelated independent variables, also called principal components (PCs) or latent variables. The application of PCA can interpret the interrelationships among different variables, uncover unknown trends, and differentiate groupings (Mark, 2001; Romanenko and Stromberg, 2007). The partial least squares (PLS) regression is a two-block regression method that linearly relates the variations of dependent variables to the variations of independent variables, which works especially well when independent variables carry common information such as correlations and collinearity. Different from PCA, the PLS regression actively uses dependant variables to help estimate the “latent” variables (PLS components) from the original independent variables. The first PLS component contains the most relevant information predicting the

dependant variables. So far, only a few studies coupled the multivariate approaches and LIBS together (Martin et al., 2005; Bousquet et al., 2007; Labbé et al., 2008). Martin et al. (2005) successfully differentiated the different preservative-treated wood using PCA. Martin et al. (2007) applied PCA and the PLS regression in the analysis of wood, human cremation remains, and prosthetic implant, and the results showed the possibility of using multivariate approaches to build a "universal calibration curve". Labbé et al. (2008) reported that using several emission lines in combination could produce dramatically better results than using any of the individual emission line alone. Our main objective is to implement the PLS regression in the analysis of the LIBS spectral information and to evaluate the quantitative analytical ability of LIBS in the analysis of soil metals.

Materials and Methods

LIBS Setup

The LIBS setup employs a Q-switched Nd: YAG pulsed laser (Minilite II, Continuum, Santa Clara, CA) with a fundamental wavelength of 1064 nm which is frequency doubled to 532 nm and used as the excitation wavelength. The laser pulse energy is 25 mJ, the laser pulse width is 3~5 ns, and the repetition rate ranges from 1 to 15 Hz. Laser pulse was guided and focused at the target's surface by a plano-convex quartz lens and a focusing lens to form a high-temperature plasma for vaporization and atomization of the target material. A fused-silica fiber-optic cable (Glenair, Inc., Glendale, CA) was mounted at a ~45° angle to the target's surface. The light released from the plasma containing the emission spectrum was delivered by the fiber-optic cable to a spectrometer (SE 200 Spectrograph with High Order Dispersion Module, Catalina Scientific Corporation, Tucson, AZ) which was connected to an intensified charged coupled detector (ICCD, Apogee Intensity Camera, Catalina Scientific Corporation, Tucson, AZ). The ICCD camera records the emission lines and allows the

identification of the elements through their unique spectral signatures. The spectrometer covers a wavelength range of 200~600 nm, including the spectral lines of almost all the elements. It means that LIBS is capable of detecting all chemical elements because all elements emit light somewhere in that spectral range. The wavelength resolution is about 0.012 nm. The opening of the camera shutter was controlled by a delay generator (Model 500C Pulse Generator, Berkeley Nucleonics, San Rafael, CA), and the LIBS system (Figure A.1) was controlled by computer using KestrelSpec Apogee for Windows Version 4.12 software (Catalina Scientific Corporation, Tucson, AZ).

Soil Sample Preparation

We used a Standard Reference Material (SRM-2586) purchased from National Institute of Standards and Technology (NIST) as the polluted soil. SRM-2586 is a blended mixture of soil samples collected from an urban area with a particle size of less than 75 μm, and it contains all the major metals (Ca, Fe, Al, Na, Mg, and Si) and high-concentrations of trace metals (Pb, Cr, Cu, Zn, Ba, Mn, and Cd) in soil. A natural agricultural soil (Fargo silty clay loam) collected at surface 1~15 cm from the Red River Valley (Crookston, MN) with low-concentrations trace metals works as a dilution. After sieving the large root and debris, the air-dried agricultural soil is proportionally mixed with SRM-2586 to make 12 soil samples with different concentrations of copper and zinc (Table B.1). De-ionized water was added into each sample to uniformly mix it, and after thoroughly stirred and oven-dried, each sample was homogenized by grinding in a mortar and pestle.

Soil Sample Treatment and ICP-OES Analysis

All the soil samples were microwave digested in *aqua regia* (3:1:1 HCl:HNO_3:H_2O) and HF (Ammons et al., 1995). After the excess HF was neutralized with boric acid, the solution samples were filtered to 0.45 μm and diluted as needed for the ICP-OES analysis. The total

elemental content was determined with a Spectro DIROS ICP-OES (Fitchburg, MA) using commercially-available ICP standards and protocol established in USEPA Method 6010C (USEPA, 2007).

LIBS Analysis

A sample of 0.3 g SRM-2586 was placed into a steel cylindrical mold (Figure A.2) and compressed under a mechanical pressure of 1.5×10^7 kg for 5 min to make a soil pellet (13 mm in diameter and 1 mm thick). For each soil sample, duplicate pellets were prepared. The pellets were placed on a rotating stage for the LIBS analysis. The rotating stage was continuously rotating to provide a fresh surface for every laser shot. Base on the preliminary study, the repetition rate, delay time and gate width of the ICCD camera were set to 10 Hz, 1 μs, and 20 μs, respectively. Alignment of the optics and camera calibration was accomplished by maximizing the intensity and minimizing the shift of the emission lines at 546.07 nm and 579.07 nm from an Hg vapor lamp. If the wavelength error of all the major Hg emission lines is less than 0.5%, the ICCD camera calibration was considered adequate (Essington et al., in press). For each soil sample, 5 spectra were collected, and each spectrum was the average of 50 laser shots. All the measurements were conducted at the same time at the atmospheric air pressure in laboratory. Elemental spectral lines were identified according to the most frequently used spectral lines in the previously published literatures, and then confirmed using the NIST atomic spectra database and the Kurucz spectra database. Once the element is identified and the emission line used for the quantitative analysis is decided, the background-subtracted intensity of each spectral peak is determined using the KestrelSpec Imageing Spectroscopy Software (Catalina Scientific Corporation, Tucson, AZ).

Analysis of the LIBS Spectral Data by the PLS Regression

The PLS regression is performed using The Unscrambler (version 9.8) software (CAMO, Woodbridge, NJ). The LIBS spectral data are first averaged to one spectrum per sample and reduced to 0.048 nm wavelength spacing. Models are constructed with the PLS regression using 12 soil samples, and the predictive ability of the PLS models is evaluated by full cross-validation (Shao, 1993), which systematically leaves one sample out from the original samples as the validation data, and uses the remaining samples as the training data. This procedure is repeated until every sample is used once as the validation data. Full cross-validation is a conservative model evaluation method which helps to select the model with the best predictive ability. The results from the PLS analysis are typically presented as the number of PCs, correlation coefficients (r^2), the root mean square error of calibration (RMSEC), and the root mean square error of prediction (RMSEP). The RMSEC is a measure of how well the model fits the calibration data, and the RMSEP is a measure of the average prediction error. Both are expressed in the same unit as the dependent variables. The root mean square error (RMSE) is calculated with equation *(1)*.

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n}(P_i - C_i)^2}{n}} \qquad (1)$$

where P_i is the predicted value, C_i is the true value, and n is the number of samples. A model with high r^2 and low RMSEC and RMSEP values is an ideal model. In our study, the univariate and the PLS regression methods are used to build the calibration models and to predict the elemental concentrations of the same soil samples.

Results and Discussion

Twelve soil samples with different copper and zinc concentrations were analyzed by ICP-OES and the results were compared with those measured by LIBS. Figure B.1 is a LIBS spectrum in the range 300-400 nm collected from SRM-2586 which contains the highest concentrations of copper (81 mg/kg) and zinc (352 mg/kg) among the tested samples. As shown in Figure B.1, Cu emission lines at 324.75 and 327.38 nm and Zn emission lines at 334.50 and 334.59 nm were observed, and the major soil metals, Ca, Al, Mg, and Fe were also observed. The existence of these major metals interferes and overshadows Cu and Zn peaks, therefore, the peak intensity is very small and even hard to identify at low concentrations. The univariate models were developed by relating the intensity of the emission lines at 324.75 nm (Cu) and 334.59 nm (Zn) with the measured concentrations, and then the models were used to predict Cu and Zn concentrations in the same soil samples. The signal intensity was poorly correlated the concentration in the calibration models, with r^2 of 0.7067 and 0.6165, RMSEC of 9.1304 and 54.2550, and NRMSEC of 16.6007% and 18.9703% for Cu and Zn, respectively.

Multivariate approaches such as the PLS regression can simultaneously analyze all the emission lines, select the most important and relevant emission lines from the original spectral information, and finally establish a linear model to predict the elemental concentrations from a new measured spectrum. Due to the robust and powerful analytical ability of multivariate approaches, the PLS regression normally yield better results then the univariate regression. The PLS regression was initially performed on the full spectral range (200-600 nm) and the results indicated that PLS models were significantly better than the univariate models, with r^2 of 0.9936 and 0.9935, RMSEC of 1.2696 and 6.6255, and NRMSEC of 2.3084% and 2.3166% for Cu and Zn, respectively. Figure B.2 described the

relationship of the residual variance as a function of the number of PCs for the PLS calibration and validation models performed on the full spectral range (200-600 nm). Figure B.2 indicated that three PCs were enough to obtain a calibration model with the optimum predictability. Regression coefficients represent a direct linear relationship between the LIBS spectra and the elemental concentrations, and the peaks assigned show an insight on which emission lines are important and relevant to the changes of the elemental concentrations. Large absolute values indicate large importance and small values indicate less importance. Figure B.3 depicted the regression coefficients corresponding to the PLS calibration models performed on the full spectral range (200-600 nm). As seen from Figure B.3, most peaks having strong influence on the variation of Cu and Zn concentrations and being used to build the PLS calibration models on the full spectral range appeared in the spectral range 250-450 nm. In order to reduce the interference of irrelevant emission lines and to the time for the complex calculation, the PLS regression was performed on the reduced spectral range 250-450 nm. In order to compare the predictability of the PLS models performed on different spectral ranges, three PCs were selected to build all the PLS calibration models. The PLS models using the 250-450 nm spectral range performed as well as the full spectral range models, with r^2 of 0.9932 and 0.9931, RMSEC of 1.3910 and 7.2781, and NRMSEC of 2.5291% and 2.5449% for Cu and Zn, respectively.

Figure B.4 is a plot of regression coefficients from the PLS models performed on the reduced spectral range (250-450 nm) which shows the importance of each emission line in building the PLS models and predicting Cu and Zn concentrations. From Figure B.4 we can see that Ca, Al, Fe, and Mg play an important role in building the calibration models. In most kinds of soils, Ca, Al, Fe, and Mg are the major soil metals which appear as the most intense peaks in the soil spectra, therefore, they can be used as predictors to predict the elements of interest.

However, it is not reasonable in theory. In order to reduce the influence of these major metals and to make the PLS models practically reasonable, a smaller spectral range (300-350 nm) containing more Cu and Zn peaks are selected to build the PLS models. The PLS models using the 300-350 nm spectral range performed better than the PLS models using the full spectral range (200-600 nm) and the reduced spectral range (250-450 nm), with r^2 of both 0.9960, RMSEC of 1.0679 and 5.5453, and NRMSEC of 1.9416% and 1.9389% for Cu and Zn, respectively.

Labbé et al. (2008) reported that a good fit of the calibration data by a PLS model did not necessarily imply a good fit of the future data, therefore, the validation of the calibration model using samples that were not included in the calibration model were highly recommended when possible. However, due to the small sample size in our study, the validation was performed using the same soil samples. To compare the analytical ability of LIBS, Cu and Zn concentrations predicted by LIBS and those measured by ICP-OES were plotted together (Figure B.6). From Figure B.6 we can see, Cu and Zn concentrations predicted by the univariate regression were poorly correlated with the measured concentrations, with r^2 of 0.6240 and 0.4457, RMSEP of 10.3382 and 65.2229, and NRMSEP of 18.7967% and 22.8054% for Cu and Zn (Table B.2), respectively. The concentrations predicted by the full spectral range models were significantly improved, with r^2 of 0.9026 and 0.8990, RMSEP of 5.7410 and 30.3760, and NRMSEP of 10.4382% and 10.6210% for Cu and Zn (Table B.2), respectively. The concentrations predicted by the reduced spectral range (250-450 nm) models were as good as those of the full spectral range models, with r^2 of 0.9107 and 0.9061, RMSEP of 5.4953 and 29.2844, and NRMSEP of 9.9915% and 10.2393% for Cu and Zn (Table B.2), respectively. The concentrations predicted by the reduced spectral range (300-350 nm) models were the best results we obtained, with the

highest r^2 of 0.9442 and 0.9407, the lowest RMSEP of 4.3429 and 23.2801, and the lowest NRMSEP of 7.8962% and 8.1399% for Cu and Zn (Table B.2), respectively. The concentrations measured by ICP-OES were highly correlated with the measured concentrations of the samples, with r^2 of 0.9745 and 0.9947 for Cu and Zn (Table b.2), respectively. Compared to the univariate results (Figure B.6), NRMSEP by LIBS using the PLS regression improved about 10% and 12% for Cu and Zn, respectively. The implementation of the PLS regression makes the analytical ability of LIBS comparable to that of ICP-OES.

Conclusions

The univariate and the PLS regression techniques were implemented to analyze the LIBS spectral data that were collected on 12 soil samples, the calibration models were developed relating Cu and Zn concentrations with the LIBS spectral information (background-subtracted signal intensity at 324.75 nm (Cu) and 334.59 nm (Zn), the full spectral range 200-600 nm, and the reduced spectral ranges 250-450 nm and 300-350 nm). The calibration models were used to predict Cu and Zn concentrations in the same soil samples. Twelve soil samples were also analyzed by ICP-OES, and the measured Cu and Zn concentrations were compared with those predicted by LIBS. The results clearly demonstrated that (1) the PLS regression was powerful in analyzing and extracting the useful LIBS spectral information, and compared to the univariate regression, it improved NRMSEC about 15% and NRMSEP about 10%, respectively; (2) The PLS regression performed on the reduced spectral range (300-350 nm) containing more Cu and Zn peaks produced the best results among all the spectral ranges, which indicated that use of the suitable spectral range in the PLS regression improved the LIBS analytical ability; (3) The implementation of multivariate approaches in analyzing the

LIBS spectral data made the quantitative analytical ability of LIBS promising and comparable to that of ICP-OES.

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Appendix B

Table B.1 Measured Cu and Zn concentrations (mg/kg) in soil samples.

Sample #	1	2	3	4	5	6	7	8	9	10	11	12
Cu	26	27	29	33	36	39	43	48	54	59	70	81
Zn	66	72	83	100	117	135	152	180	209	238	295	352

Table B.2 Comparison of the analytical ability of the PLS and the univariate regression.

Metals	Spectral range	PCs	Calibration			Prediction		
			r^2	RMSEC (mg/kg)	NRMSEC (%)	r^2	RMSEP (mg/kg)	NRMSEP (%)
	Univariate (324.75 nm)	N/A	0.7067	9.1304	16.6007	0.6240	10.3382	18.7967
Cu	PLS (200-600 nm)	3	0.9954	1.1403	2.0733	0.9026	5.7410	10.4382
	PLS (250-450 nm)	3	0.9932	1.3910	2.5291	0.9107	5.4953	9.9915
	PLS (300-350 nm)	3	0.9960	1.0679	1.9416	0.9442	4.3429	7.8962
Zn	Univariate (334.59 nm)	N/A	0.6165	54.2550	18.9703	0.4457	65.2229	22.8052
	PLS (200-600 nm)	3	0.9943	6.6344	2.3197	0.8990	30.3760	10.6212
	PLS (250-450 nm)	3	0.9931	7.2781	2.5449	0.9061	29.2844	10.2393
	PLS (300-350 nm)	3	0.9960	5.5453	1.9389	0.9407	23.2801	8.1399

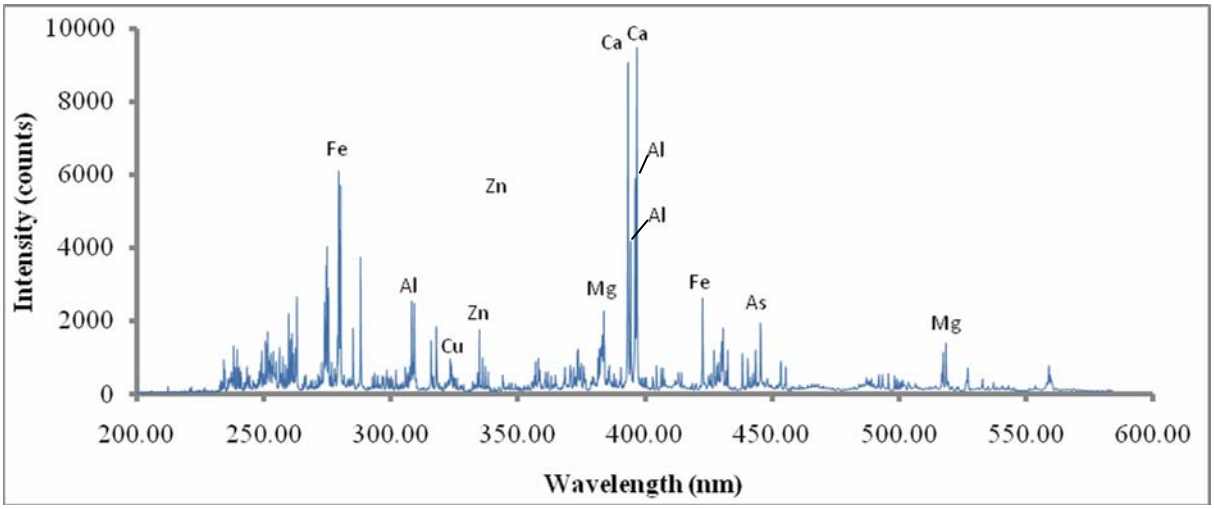


Figure B.1 LIBS spectrum (200-600 nm) collected from SRM-2586 with 81 mg/kg Cu and 352 mg/kg Zn.

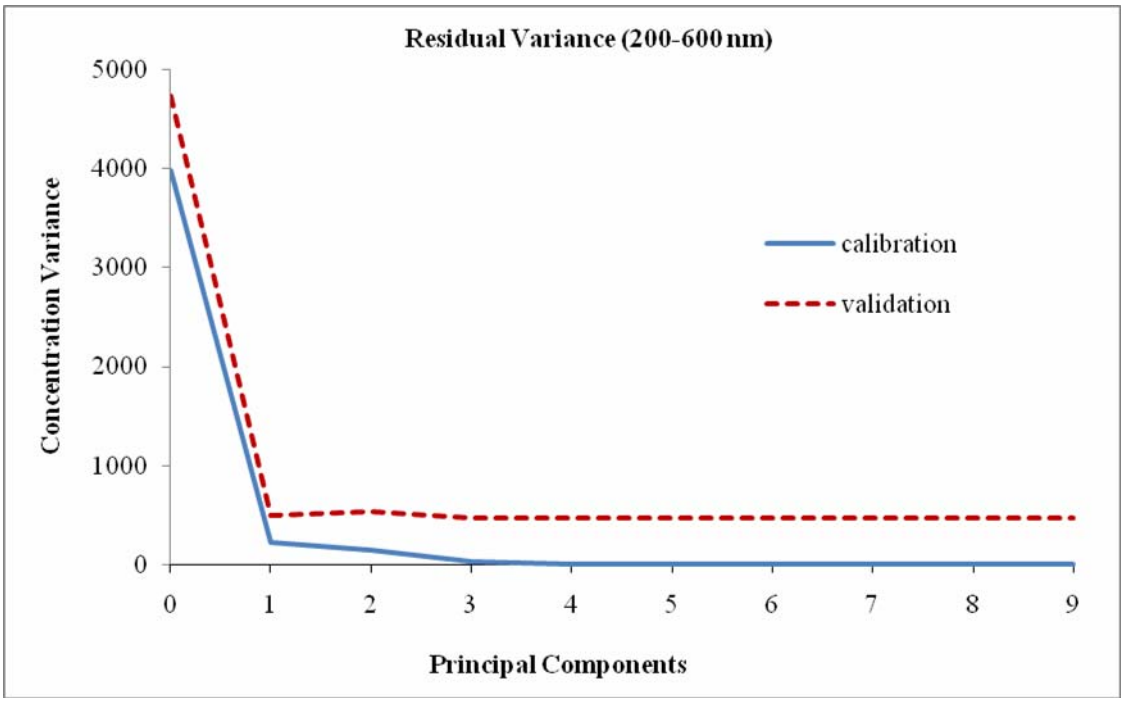


Figure B.2 Residual variance plot for the PLS calibration and validation models using the full spectral range 200-600 nm.

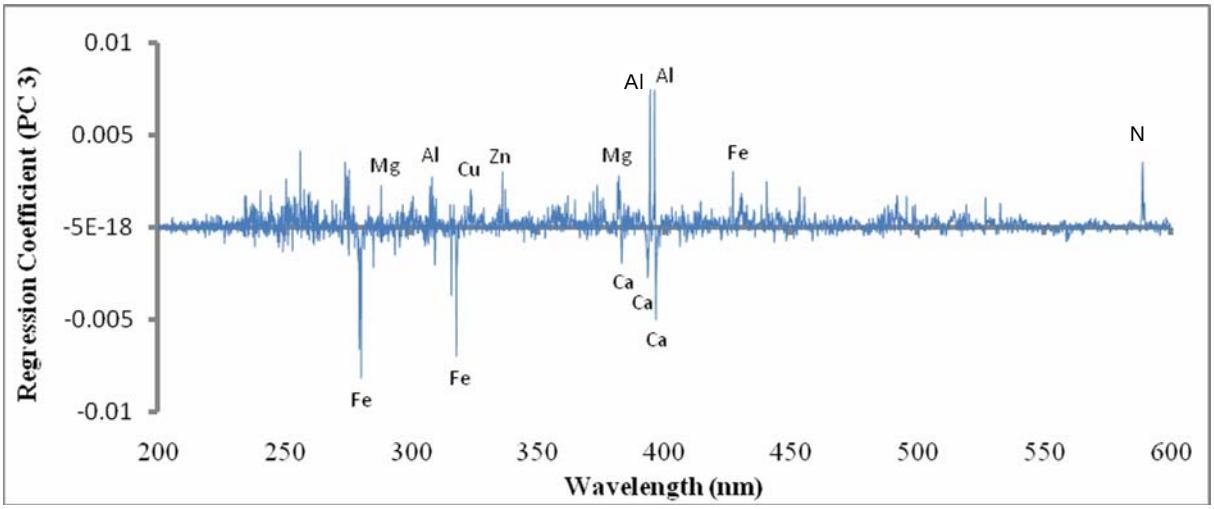


Figure B.3 Regression coefficients from the PLS calibration models using the spectral range 200-600 nm.

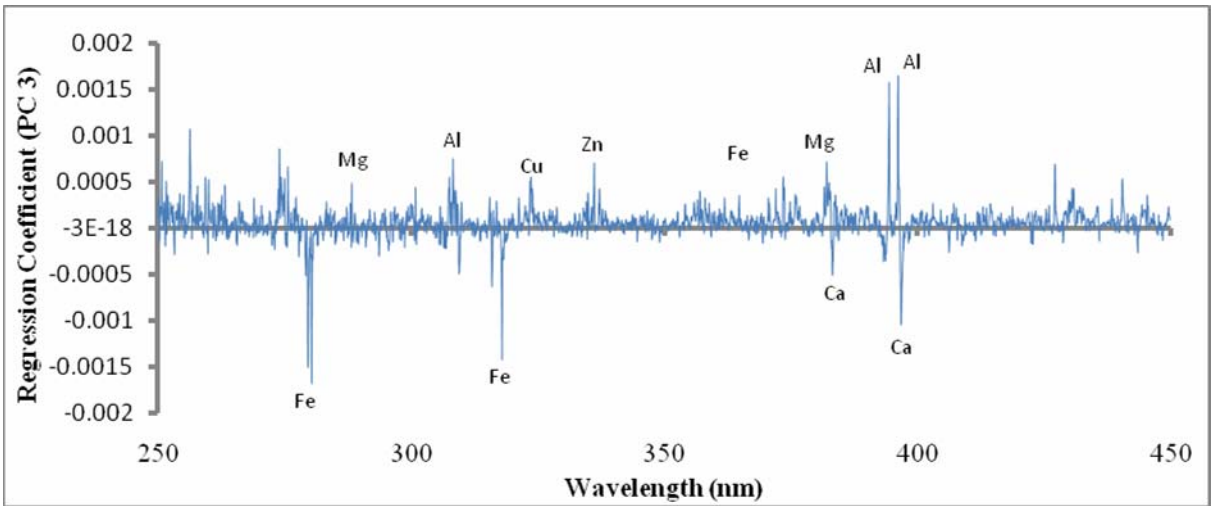
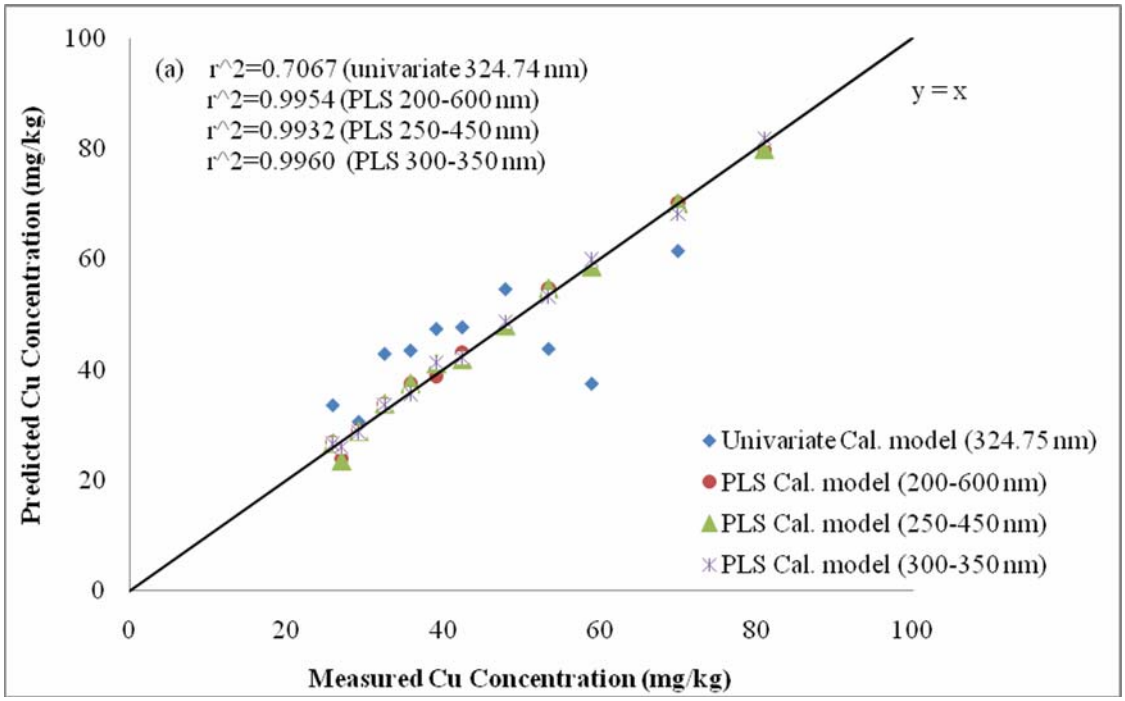


Figure B.4 Regression coefficients from the PLS calibration models using the spectral range 250-450 nm.



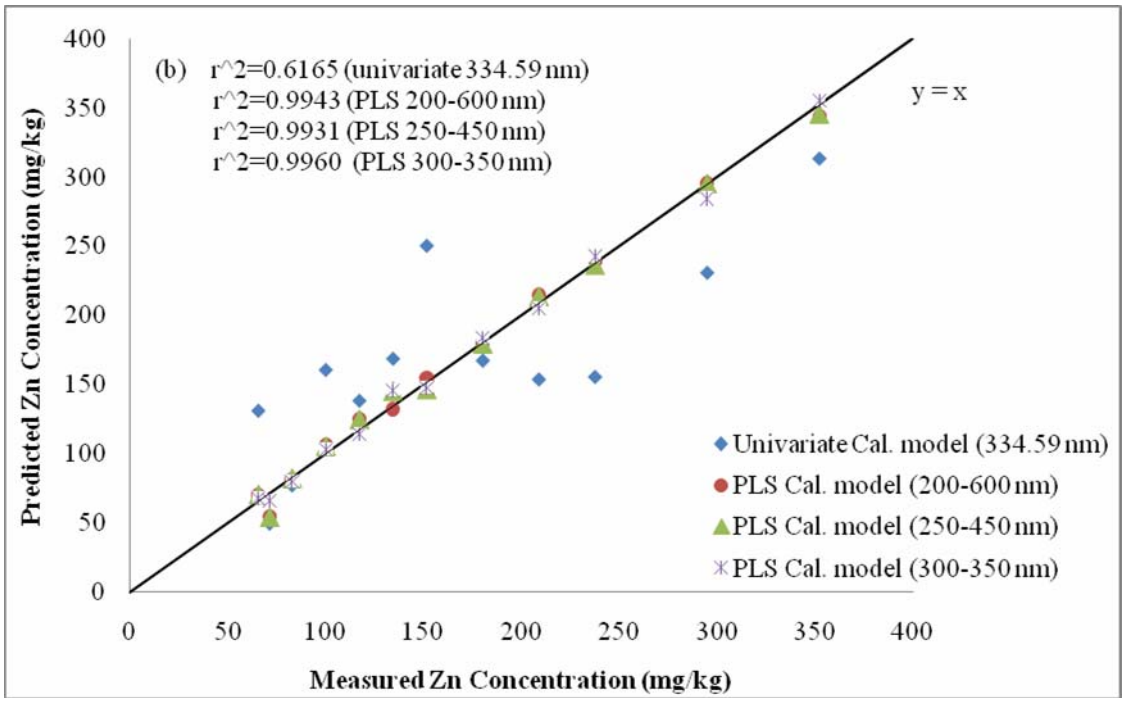
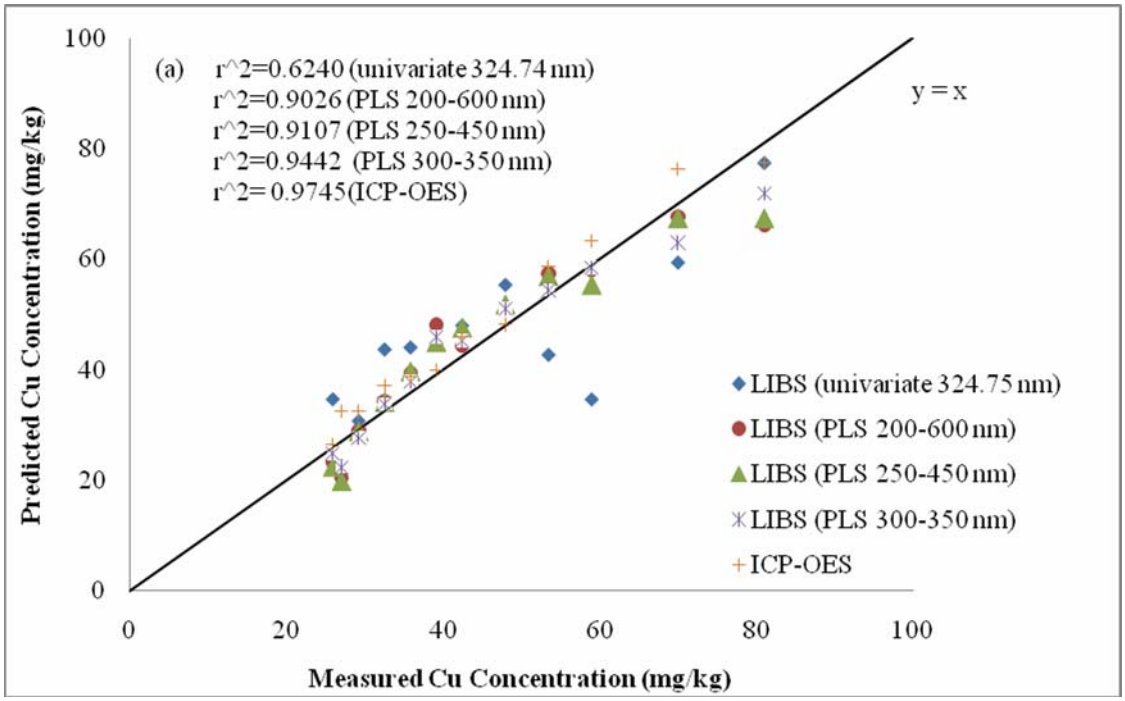


Figure B.5 The PLS calibration models constructed using the spectral ranges 200-600 nm, 250-450 nm, and 300-350 nm, and the univariate calibration models constructed using the emission lines at 324.75 nm (a) and 334.59 nm (b).



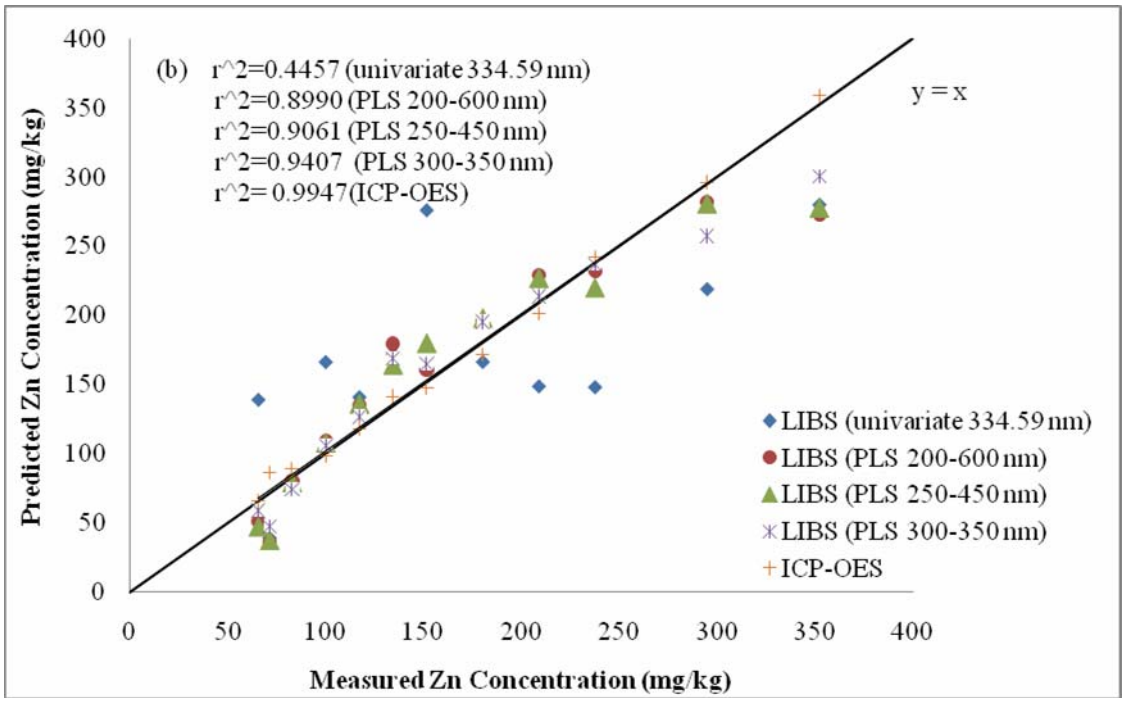


Figure B.6 Correlation between Cu (a) and Zn (b) concentrations measured by ICP-OES and LIBS (the PLS regression using the spectral ranges 200-600 nm, 250-450 nm, and 300-350 nm and the univariate regression at 324.75 nm and 334.59 nm).

Vita

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