

Estimation of Soil Nitrate (NO₃) Level Using Laser-Induced Breakdown Spectroscopy (LIBS)

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Abstract. Laser-Induced Breakdown Spectroscopy (LIBS) is a method for measuring level of nitrogen (N) in the soil in the form of N-nitrate (NO₃) rapidly without going through the process of sieving and drying. The sample soil in the form of pellets subjected to laser pulses using a wavelength of 532 nm, pulse duration 5.5 ns, repetition rate of 10 Hz, and Q-switch delay of 150 μs. Emissions are captured by the spectrometer with the wavelength range of 190-1130 nm. Spectrum characterization was processed through the second derivative in order to obtain a wavelength identity that could be rapidly used to estimate the nitrate content of the soil with a determination coefficient of (R²) 0.9254 and a coefficient of variation (CV) of 8.41%. The results of this study are very potential to be applied for rapid measurement of soil nitrate.

1. Introduction

Laser-Induced Breakdown Spectroscopy (LIBS) is a method for measuring content of nitrogen (N) in the soil in the form of N-nitrate (NO₃) rapidly without going through the process of sieving and drying, providing a fertilizer recommendation which is immediate and specific locations in order to implement precision farming. The conventional soil testing soil analysis are relatively expensive and took a long time, in addition the availability of soil testing laboratories are very limited. This led to generalization and uniformity of crop fertilizer throughout Indonesia archipelago [1].

Tools or methods that can measure the levels of nitrogen in the soil immediately and cheap is needed today in order to provide specific fertilization recommendations. According to Yoshida [2], the plants can absorb and use various forms of N such as: N-ammonium-nitrate N, N-urea and N-amino acids. N-ammonium is the form of the N most prevalent and has stable form in flooded soils (wetland), while the N-nitrate is most often found on dry land (upland).

One way to determine the nitrogen content in the soil immediately is using electromagnetic waves (UV-Vis-NIR) which can interact with atoms and chemical molecules electromagnetically. Ehsani et al. [3] determined the levels of nitrogen in the soil in the form of ammonium and nitrate compounds using NIR with a wavelength of 1800-2300 nm. Russell et al. [4] used the NIR wavelength range of 350-2500 nm to measure the uptake of nitrogen in a single season rice crop. While Hernandez et al. [5] used NIR to measure total nitrogen and total carbon in wetlands in Ohio United States. Determination of nitrogen in corn crop soil marks using Vis-NIR wave in the wavelength range of 400-2500 nm carried out by Kusumo et al. [6]. Mahmood et al. [7] measured the total of N content in soil samples (0-30 cm depth) using a wavelength of 350-2500 nm by drying in an oven at a temperature of 40 °C for 72 hours and



sieved using a 2 mm sieve. Recent research conducted by Abdi et al. [8] further reaffirmed that the NIR could predict precisely the total nitrogen and nitrogen available in the soil. In another study, Xuemei et al. [9] measured the content of organic matter, nitrogen, phosphorus and potassium in the soil using Vis-NIR wave at a wavelength of 325-1075 nm by drying and sifting the ground using 1 mm sieve. Other than the dry land, research that measured levels of nitrogen in paddy fields is done by Wenjun et al. [10] using a wavelength of 350-2500 nm with a sampling soil from fields that have been dried for 10 days and sieved using a 2 mm sieve. Until now, studies to determine the composition of the nutrient content in the soil using NIRS in Indonesia is only done by Angkat [11] at a wavelength of 1000-2500 nm as well as determined a single wavelength 1506 nm to predict soil N content in the form of N total.

All methods that have been done are still in the development phase, that makes this study has not yet realized in a measurement tool that can be used in the field. This condition caused by several things such as expensive equipment as well as the high level of difficulty in the research and development of these methods. So that there is still room to determine new methods that are easier to be realized as a measuring tool in the field, one of them using the technique of Laser-Induced Breakdown Spectroscopy (LIBS).

Laser-Induced Breakdown Spectroscopy (LIBS) is a potential method to be developed to measure levels of N in the soil. LIBS is useful for determining the elemental composition of materials in solid, liquid and gas by focusing a high power laser pulse at the sample to create a spark plasma or laser to be captured by the detector. LIBS method provides an opportunity to measure the levels of nitrate (NO_3) in the form of solid or soil samples as the original form field without going through the process of drying and sieving. Although the soil samples used in several studies using LIBS methods still going through drying and sieving process, such as research conducted by Yang [12], Knadel et al [13] and Haddad [14]. In general LIBS produces a spectrum UV-Vis and NIR fraction. UV-Vis spectrum can be used to determine the characteristics of the atomic wave to the N element. This process is difficult to do since NIR is molecular and very sensitive to H_2O to verify the elements of N in the form of chemical bonds, because the chemical bonds of N in the soil are very diverse.

This study aimed to characterize the soil samples LIBS spectra of the N elements without sifting and drying, so it has some single wavelengths that interact electromagnetically with atoms or molecules of N in the soil to build a prediction model of N levels in the soil in the form of N- nitrate.

2. Materials and methods

2.1. Samples preparation

The sample for the characterization of the spectral UV-Vis-NIR soil to the element N is 10 soil samples weighing 0.5 kg that taken at a depth of 0-30 cm composite of 10 different pick-up points on dry land. The soil samples were made in the form of pellets with a diameter of 3.2 cm and 0.5 cm thick with a pressure of 4245.61 psi using a manual hydraulic press without drying and sieving the soil.

2.2. Setup of LIBS and experimental steps

The spectra soil of UV-Vis-NIR is collected through Laser-Induced Breakdown Spectroscopy (LIBS) using Nd-YAG Laser Q-Smart 850 model which resulted in a wavelength of 1064 nm, 532 nm and 266 nm. In this study, a soil sample in pellet form subjected to laser pulses using a wavelength of 532 nm, pulse duration of 5.5 ns, repetition rate of 10 Hz, the Q-switch delay of 150 μs and total energy of 15 mJ/pulse. Before subjected to the laser, the soil sample was put into a vacuum chamber with pressure of 5.75 torr. The laser will pass through the focusing lens with a focal length of 10 cm. Soil samples were subjected to laser pulses will release a plasma caused by the collapse of chemical bonds plasma chemical bonds resulting in ionization process. Plasma containing information of the elements contained in the soil sample including its concentration will be collected through the collecting lens and lens filter 532 nm which captured by the detector to measure the light intensity in the wavelength range of 190 nm - 1130 nm.

2.3. Data processing

2.3.1. Characterization spectrum UV-Vis-NIR against the elements of soil N. Spectrum characterization of UV-Vis-NIR soil against the N elements in the soil is done by identifying the peaks wave of UV-Vis-NIR with a specific wavelength that has electromagnetic interaction with the N in the soil based on the manual book written by Sansonetti [15]. Characterization spectrum of UV-Vis-NIR soil is done on the original spectrum, the first derivative spectrum, and the second derivative spectrum through the identification of peaks spectrum at certain wavelengths according to the manual book.

2.3.2. Determination of the soil nitrate (NO₃) level estimation model. Soil nitrate (NO₃) content estimation model is built using multiple linear regression. The intensity of a specific wavelength that emerges from the process of characterizing the spectral UV-Vis-NIR in the original spectrum, first derivative spectrum, and the second derivative spectrum will be the independent variables. Wavelength intensity value is used as an independent variable in the original spectrum, first derivative spectrum, and the second derivative spectrum is the intensity of a specific wavelength in the original spectrum based on the characterization of the spectral UV-Vis-NIR. The concentration of NO₃ in soil samples will be the dependent variable. The coefficient of determination (R²) and coefficient of variability (CV) will be the parameters of the model built to measure the concentration of NO₃ soil. If the value of R² is getting closer to 1 the changes of NO₃ level in soil will cause changes in the content of NO₃ amount, otherwise, if the CV value is declining close to 0, thus the data generated will be more homogeneous.

3. Results and discussion

3.1. Characterization of spectrum UV-Vis-NIR of the elements of soil N

The detector captures the wave beam in the form of plasma in the range of 190-1130 nm. The spectrum is obtained in the range of UV (130-400 nm), Vis (400-750 nm) and NIR (750-1130 nm). Certain wavelengths that have strong electromagnetic interaction of the elements of N is verified based on wave peaks that appear based on the manual book written by Sansonetti [15]. Identification of the emerging wave peak produced 3 wavelengths on raw spectrum, i.e. 463.054 nm, 567.602 nm and 843.874 nm (figure 1).

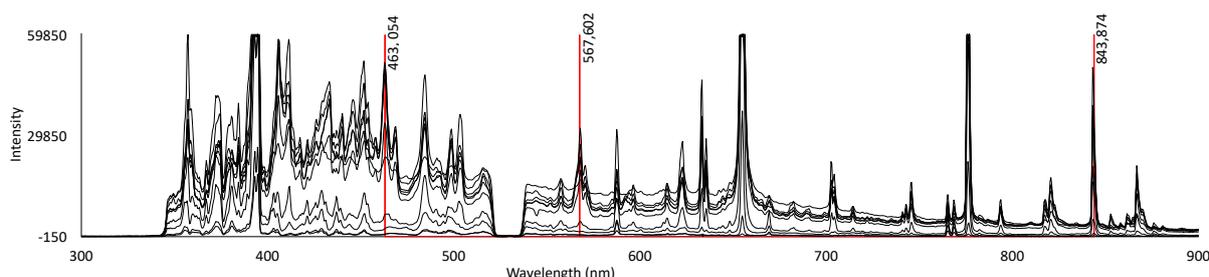


Figure 1. Raw UV-Vis-NIR spectrum.

Identification of wave peaks is also performed at the first derivative spectrum from the raw spectrum to see specific wavelengths that have interactions with atoms or molecules of N soil. First derivative spectrum can be used to remove the effects of additive baseline [16]. First derivative spectrum can reduce the effects of baseline and improve absorption peaks (figure 2). Normalization is used to reduce the variations of baseline in order to identify the wave peaks (figure 3). Normalization spectrum obtained by scaling each of spectrum in the range of 0 and 1 [17]. The identification of wave peaks in the first derivative spectrum generates 5 wavelengths i.e. 395.585 nm, 499.436 nm, 504.510 nm, 571.077 nm and 862.924 nm.

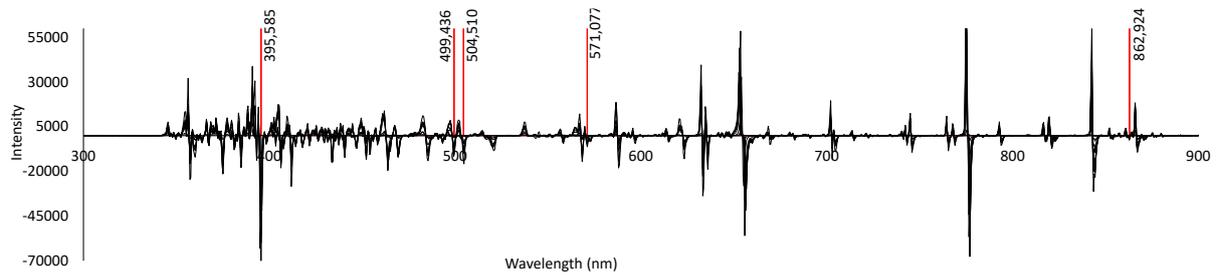


Figure 2. First derivative UV-Vis-NIR spectrum.

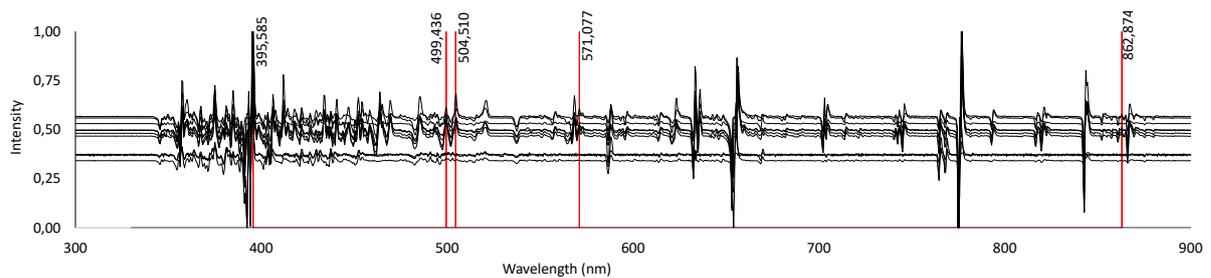


Figure 3. First derivative UV-Vis-NIR spectrum normalization.

The same principle is also applied on the second derivative spectrum to increase the absorption peaks in order to identify peak-peak waveform appears (figure 4). The second derivative to dump slope additive baseline [16]. Normalization is also performed on the second derivative spectrum to eliminate variations of baseline (figure 5). Identification of the wave peak in the second derivative produces 8 pieces wavelength, i.e. 399.500 nm, 444.703 nm, 463.054 nm, 496.398 nm, 567.480 nm, 742.364 nm, 822.314 and 843.874 nm.

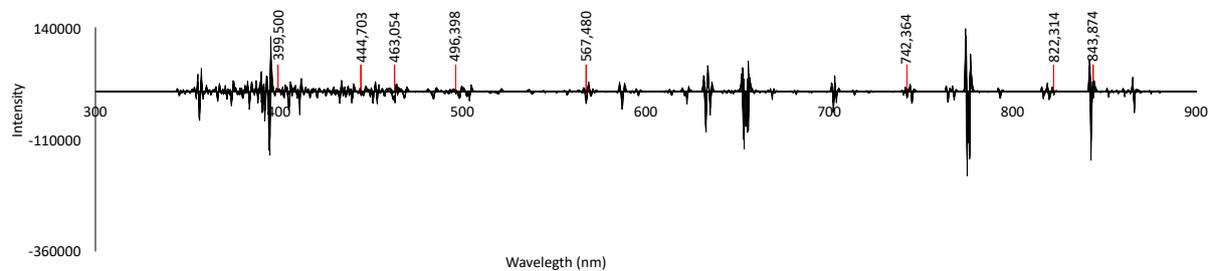


Figure 4. Second derivative UV-Vis-NIR spectrum.

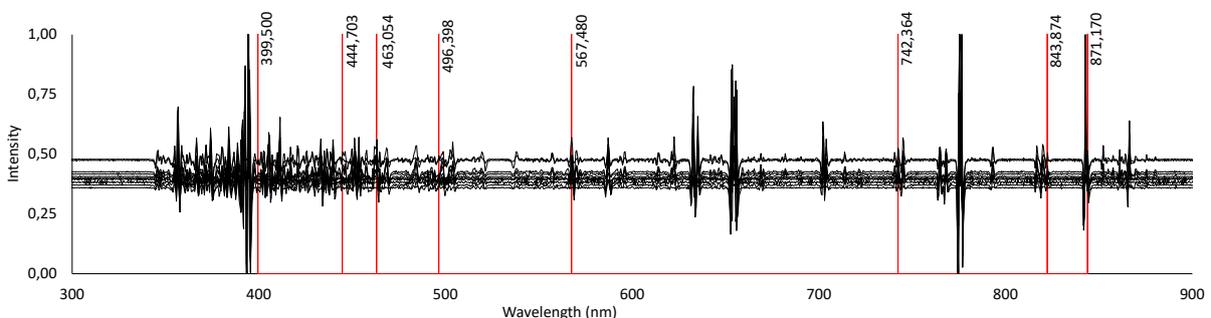


Figure 5. Second derivative UV-Vis-NIR spectrum normalization.

3.2. Nitrate (NO_3) Level Estimation Model

The NO_3 level estimation model is built using multiple linear regression model with intensity value from a specific wavelength as an independent variable. NO_3 concentration values are collected through

the calculation of soil laboratory as the dependent variable. Minitab software is used as a tool to process the data to build a prediction model equations levels of NO_3 soil. The best prediction model based on coefficient of determination (R^2) and coefficient of variation (CV).

In the raw spectrum uses three variable independent which is the intensity value of the wavelength 463.054 nm, 567.602 nm and 843.874 nm 10 locations soil samples to produce the following equation :

$$\text{NO}_3 = 52.84 + 0.00211\lambda_{463.054} + .00557\lambda_{567.602} - 0.00115\lambda_{843.874} \quad (1)$$

While in the first derivative spectrum using 5 independent variables which is the intensity value of the wavelength 395.585 nm, 499.436 nm, 504.510 nm, 571.077 nm and 862.924 nm of 10 soil samples to produce the following equation :

$$\text{NO}_3 = 51.1 + 0.000936\lambda_{395.585} - 0.00568\lambda_{499.436} - 0.00496\lambda_{504.510} + 0.0180\lambda_{571.077} - 0.0116\lambda_{862.924} \quad (2)$$

Then second derivative spectrum uses 8 independent variables is the value of the intensity of the wavelength 399.500 nm, 444.703 nm, 463.054 nm, 496.398 nm, 567.480 nm, 742.364 nm, 822.314 and 843.874 nm of 10 samples of soil which produces the following equation :

$$\text{NO}_3 = 57.8 + 0.0119\lambda_{399.500} + 0.0238\lambda_{444.703} - 0.00358\lambda_{463.054} - 0.0152\lambda_{496.398} - 0.00087\lambda_{567.480} - 0.0332\lambda_{742.364} - 0.0487\lambda_{822.314} + .00895\lambda_{843.874} \quad (3)$$

Where λ is the wavelength identity intensity. equation 1, 2 and 3 are used to calculate the value of NO_3 estimated for comparison with NO_3 measured. The relationship between NO_3 measured, and NO_3 estimated presented in figure 6.

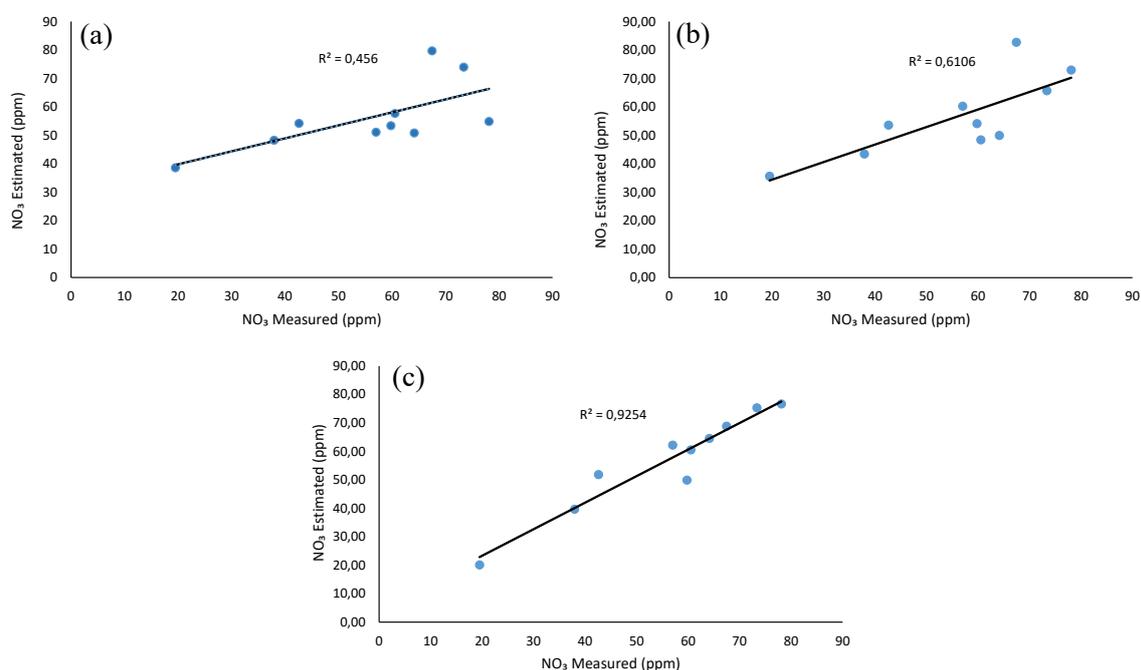


Figure 6. The relationship between the measured and the estimated NO_3 in the (a) raw spectrum, (b) first derivative spectrum and (c) second derivative spectrum.

The results show the value of R^2 is the highest in the second derivative spectrum of 0.9254 with the smallest CV value of 8.41%. So the best model to estimate the levels of NO_3 ground using equation 3 with the intensity at a wavelength of 399.500 nm, 444.703 nm, 463.054 nm, 496.398 nm, 567.480 nm, 742.364 nm, 822.314 and 843.874 nm as independent variables.

4. Conclusions

Second derivative UV-Vis-NIR spectrum has more wave peaks that consist of electromagnetic interaction with soil N elements. The level of NO₃ in the soil can be estimated by value intensity of wavelength 399.500 nm, 444.703 nm, 463.054 nm, 496.398 nm, 567.480 nm, 742.364 nm, 822.314 and 843.874 nm on soil nitrate estimation equation model in the second derivative spectrum.

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