Formulation, configuration, and utilization of Laser Induced Breakdown Spectroscopy (LIBS) to analyze nitrogen particles in soil

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Abstract. The use of Laser Induced Breakdown Spectroscopy (LIBS) method for real-time analysis of Nitrogen particles in soil is proposed. This study aims to find the optimal LIBS formulations and configurations for analyzing soil particles, mainly Nitrogen particles. The LIBS hardware used in this research Nd-YAG Laser model Q-Smart 850. The optimization was done through laser pulse shooting to a pellet-shaped soil sample within a 5.75 torr pressurized vacuum chamber with 532 nm wavelength, 5.5 ns pulse duration 5.5 ns, 10 Hz repetition rate, Q-switch delay 150 µs and energy of 15 mJ/pulse.

Keywords: laser pulse, soil plasma, soil organic particle

1. Introduction
Laser Induced Breakdown Spectroscopy (LIBS) is an atomic emission spectroscopy equipment that uses lasers as a source of energy ablation [1]. The laser is fired towards the surface of the samples, some of which were distilled to form plasma. A plasma contains electrons, neutral atoms, ions and excited atoms. Excitation process is one of the methods in which material absorbs electromagnetic energy pulse (photon). In atoms, the excitation energy is absorbed by orbiting electrons which are lifted to different higher energy levels. These excited atoms in a very short time cause the electrons to return to the ground state while emitting photon emissions. When the electrons in the excited atom go down to the ground state it releases energy in the form of photons and is captured by the spectrometer displayed in the intensity of the wavelength function [2].

The LIBS method can be used to determine the composition of an element in solids, liquids and gases by focusing high-power laser pulses on a sample to make a plasma or spark a laser to be captured by a detector. Therefore, the LIBS method provides an alternative opportunity to analyze organic particles in soil samples in the field without having to go through the drying and sifting process which is usually done in laboratory based soil analysis.

Organic particle analysis in soil samples using LIBS will be effective if an appropriate LIBS configuration is obtained which can give rise to a soil plasma containing electrons, neutral atoms, ions and optimally excited atoms [3, 4, 5]. Therefore, this study aims to find the right LIBS formulations and configurations for LIBS utilization in analyzing soil particles.
2. Material and Methods

2.1. Soil Sample Preparation
The soil samples were shaped into pellets with diameter and thickness of 3.2 cm and 0.5 cm respectively, using a manual hydraulic press with a pressure of 29.272 Mpa. These pellets are required in laser firing in order to get the LIBS spectrum of soil.

2.2. Formulation and LIBS Configuration
Formulation and configuration optimization of LIBS is done by firing laser pulses on soil samples using the Nd-YAG Q-Smart 850 Laser model with output wavelengths of 1064 nm, 532 nm and 266 nm. Sample soil pellets in pressurized space, were shot by laser pulses using wavelength of 532 nm, a pulse duration of 5.5 ns, a repetition rate of 10 Hz with a focal length of 10 cm. The soil pellets shot with laser pulses produce plasma due to damage to chemical bonds so that they undergo an ionization process. Plasma containing information about soil elements was concentrated in the lens collector by measuring light intensity in the wavelength range of 190 nm - 1000 nm. The best LIBS configuration is obtained by identifying the maximum spectra produced in different Q-switch conditions and chamber pressures.

3. Result and Discussion
Plasma formation occurred when a laser fired to a soil pellet reaches a certain threshold for optical damage. The threshold is mostly influenced the environment and the target material [6]. If the constituents of the material analyzed are known, LIBS can be used to evaluate the relative abundance of each organic nutrient element, or to detect the presence of nutrients in soil. In practice, the detection limit is a function of plasma excitation temperature, light collecting window, and the strength of the transition line visible.

3.1. Second Harmonic
The acquisition of ground LIBS spectra uses second harmonics at 532 nm waves to minimize the energy required when firing lasers in order to obtain a certain energy output. The second harmonic of two photons (ωp) with the same frequency interacts with nonlinear material and produces new photons (2ωp), whereas in fundamentals one photon (ωp) will produce one new photon (ωp) (figure 1). So that the second energy input is harmonic (532 nm) half of the energy required when using the fundamental (1064 nm) to produce the same energy output.

![Figure 1. Second harmonic and fundamental harmonic](image-url)

Besides that, second harmonic at 532 nm wave is a green light in a visible light spectrum that is easily found as a laser source when making tools (figure 2). The use of second harmonics can prevent the use of infrared as a laser source which is more difficult to obtain and more expensive.
3.2. Pulse Duration
Pulse duration 5.5 ns is the default setting when taking soil samples using Nd-Yag. Pulse duration is the time interval required by the pulse in the process of increasing the amplitude from a certain level to the level of a particular fraction and the time to decrease the amplitude of the pulse to the same level. Usually 50% of the maximum amplitude is used as the starting point and the endpoint determines the duration of the pulse (figure 3).

![Figure 3. Pulse duration (t-t₀) [8].](image)

Pulse duration is an important parameter in micromaching applications. Shorter pulse duration generally results in better spatial resolution, depth control, edge quality and minimizes peripheral thermal damage. One reason is that each material has an ablation threshold (minimum peak intensity needed to remove material). For pulse energies which are given shorter pulses, they are desirable because they are more efficient at material removal in particular, shorter pulses give more total energy above the threshold strength, where absorption becomes increasingly nonlinear because of the higher electric field generated from higher peak forces. Conversely, most of the energy from longer pulses is wasted and is only used to heat the material (figure 4) [9].

![Figure 4. The impact of pulse width on LIBS spectra retrieval process [10].](image)
3.3. **Q-Switch Delay**

The optimal Q switch delay to be used during the LIBS ground spectra retrieval process of 150 µs with an energy of 15 mJ (figure 5). Q-switch delay of 150 µs has the most intensity based on experiments conducted using 3 variations of Q-Switch delay, namely 150 µs, 160 µs and 180 µs. Q-switch delay that is smaller than 150 µs has energy greater than 15 mJ which causes soil samples to break. The smaller the Q-switch value, the greater the energy and vice versa.

![Figure 5. Soil LIBS spectrum on different Q-Switch delay but same pressure.](image)

Laser pulses are usually made with the aim of producing very large laser power with a short radiation time. The Q-switch process occurs in the laser resonator from the modulation of the electrooptic effect which aims to produce laser light in the form of short pulses with high power.

Initially the laser media was pumped while the Q-switch was set to prevent an increase in light feedback to the media (resulting in a low Q-laser resonator). This results in population inversion, but the laser cannot be operated due to no feedback from the resonator. Due to losses from spontaneous emissions and other processes, the stored energy will reach the maximum level at a certain period. In the period that the medium reaches saturated conditions, the Q-switch device quickly changes from low to high allowing feedback and the amplification process by stimulating emissions to start. Due to a large amount of energy is stored in media amplification, the light intensity in the laser resonator accumulates very quickly, causing the energy stored in the medium to run out as soon as possible. The end result is a short pulse of light output from a laser, known as a giant pulse, which may have a very high peak intensity (figure 6). Factor value of Q can be explained through the following formula [11]:

$$Q(\omega) = \omega \times \frac{\text{max energy stored}}{\text{power loss}}$$

Where $\omega$ is the angular frequency in rad / s when measuring energy stored in the system and the energy lost in joules. The Q value is affected by the Q-switch delay time, the longer the time delay the Q value gets smaller and vice versa. A higher Q value produces a shorter duration pulse and vice versa.
3.4. **Pressure inside Vacuum Chamber**

Pressure in the vacuum chamber plays an important role in producing a plasma with maximum wave intensity to be captured by the detector. Based on the experiments carried out, it can be seen that the more vacuum the sample space is the greater the intensity of the wave and vice versa (figure 7). So that the pressure in the sample room should approach the vacuum. The difficulty lies in the time needed to make a vacuum sample room of 3 Torr takes quite a long time. Through repeated experiments it is known that the sample room pressure is smaller than 5.75 Torr has almost the same wave intensity. In taking the next soil sample spectra, the maximum sample chamber pressure is 5.75 Torr to produce a plasma with maximum wave intensity.

Figure 6. Process of laser pulse generation using Q-switch delay [12].
4. Conclusions

With the Nd-YAG Q-Smart 850 Laser model, the formulation, configuration, and optimal use of LIBS to obtain maximum soil plasma is carried out by photographing laser pulses to soil pellets in a 5.75 torr pressurized vacuum using a wavelength of 532 nm, pulse duration 5, 5 ns, 10 Hz repetition rate, 150 µs Q-switch delay and 15 mJ/pulse energy.

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Acknowledgement
I would like to express my gratitude to the Ministry of Agriculture of the Republic of Indonesia for the awarding of Doctoral Program scholarship, Physics Research Center for the support of spectroscopic lab in the collection of soil LIBS spectrum, Department of Land and Land Resources IPB for the support of soil fertility laboratory in the measurement of soil nitrogen content.