Studies of laser induced-breakdown spectroscopy of holly leaves

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Abstract. The LIBS spectra of holly leaves produced by Nd:YAG nanosecond laser has been investigated. More than 20 elements and molecules were identified from the spectra. The influence of laser wavelength upon analysis of plant samples via LIBS technique has been investigated. The comparison of LIBS spectra shows that the spectrum for 1064 nm irradiation is more intense than the one for 266 nm irradiation by the same pulse energy in the near-UV region. Investigation of the influence of laser wavelength for LIBS can help to improve the analytical capabilities of LIBS.

1. Introduction
The laser-induced breakdown spectroscopy (LIBS) is a laser-based versatile elemental and molecular analysis tool. It has attracted substantial attention nowadays for a wide range of applications such as measuring of the microelements in solids, liquids and gases and for discrimination of microorganisms and bacteria[1-4]. It is a relatively new task to use the LIBS technique in plant samples[5-7].
In this paper, we present some experimental results on analysis of LIBS spectra of holly leaves. The interactions between the incoming irradiation and the sample depend upon numerous variables such as laser wavelength, pulse energy and the surrounding atmosphere, etc [8]. We also show the influence of laser wavelength for LIBS spectra of plant samples.

2. Experimental technique
The experiments were carried out with a Nd:YAG laser (Quanta-Ray, USA) that can deliver fundamental wavelength of 1,064 nm (IR) with a pulse duration of ~10ns and a repetition rate of 10Hz. Forth harmonic 266 nm (UV) with maximum pulse energy of 100mJ was acquired by KDP (Potassium Dihydrogen Phosphate) crystal. The energy of the laser pulse was monitored by an energy meter (3sigma, Coherent) during experiment. The beam was focused on the sample using a quartz lens (f=100mm). Fig.1 shows a schematic drawing of the LIBS system. All of the experiments were carried out in air without any control of the surrounding atmosphere. Plasma emission was collected by two plano-convex lenses to bifurcated fiber cable. The latter was mounted onto the entrance slits of a four-channel fiber optic spectrometer (Avantes, Nethlans). In this work the master channel (230–343nm) and first slave channel (340–438nm) were used. The CCD detector of the spectrometer was triggered with the laser lamp signal which was delay for 500ns and the gate for acquisition was set to 2ms for IR and UV laser. Before measurement, the sample leaves were cleaned by distilled water to remove the dust on their surface and dried. The leaf sample of holly was mounted on a stage with precision...
movements and continuously moved across the laser beam in order to provide a fresh surface for each shot. This improves the reproducibility of mass ablation by avoiding the formation of deep craters by successive ablation[9].

![Schematic setup of the LIBS system for plant sample.](image)

**Figure 1.** The schematic setup of the LIBS system for plant sample.

3. **Results and discussions**

3.1. **Spectra lines identification**

In the experiment, more than 430 lines in the range of 230–438 nm were found and more than 20 elements and molecules were identified from spectra of holly leaves samples according to the spectroscopy data of NIST[10]. A typical spectrum of the holly leaves sample is shown in Fig.1. The lines from different metal elements such as K, Ca, Na, Mg, Fe, Al, Mn, Ti, Mo, Ni, Cr, Co, Zn, Cu, V and nonmetal elements such as C, O, Si were identified according to their wavelengths. Two weak Pb lines were also found which may be used to analyze air pollution. Some molecular spectra from C2 and CN were observed. Normally, C2 is emitted from the leaves surface or formed in its vicinity, while part of CN is due to carbon recombination with atmospheric nitrogen in the plasma through the reaction $\text{C}_2 + \text{N}_2 \rightleftharpoons 2\text{CN}$ [11, 12]. Some species observed in the holly leaves samples are listed in table 1.

![LIBS spectrum of holly leaves.](image)

**Figure 2.** The LIBS spectrum of holly leaves.
### Table 1. Some peaks identification of species observed in the holly leaves samples.

| Wavelength (nm) | Species | Wavelength (nm) | Species | Wavelength (nm) | Species | Wavelength (nm) | Species |
|----------------|---------|----------------|---------|----------------|---------|----------------|---------|
| 232.74         | Fe II   | 281.34         | Fe I    | 313.064        | Ti II   | 383.491        | Fe I    |
| 234.39         | Fe II   | 281.66         | Al II   | 317.964        | Ca II   | 387.166        | CN      |
| 239.59         | Fe II   | 282.83         | Ti II   | 322.815        | Mn I    | 387.889        | Fe I    |
| 243.27         | Fe I    | 284.39         | Fe I    | 323.436        | Ti II   | 388.372        | CN      |
| 243.51         | Si I    | 285.19         | Mg I    | 327.401        | Cu I    | 388.675        | Fe I    |
| 247.89         | C I     | 286.95         | Fe I    | 330.27         | Na I    | 390.354        | Mo I    |
| 249.34         | Na I    | 288.18         | Si I    | 334.204        | Zn I    | 396.214        | Al I    |
| 254.92         | Al II   | 297.91         | Na II   | 334.487        | Ca I    | 396.876        | Ca II   |
| 257.61         | Mn II   | 298.36         | Fe I    | 334.931        | Ti II   | 402.474        | Ti I    |
| 259.31         | Fe II   | 298.49         | Fe II   | 338.603        | Ti I    | 403.094        | Mn I    |
| 259.93         | Fe II   | 298.77         | Si I    | 346.377        | Co I    | 405.789        | Pb I    |
| 266.06         | Al I    | 299.73         | Ca I    | 347.499        | Fe I    | 407.76         | Sr II   |
| 268.463        | Fe I    | 300.12         | Fe I    | 350.34         | Co I    | 416.689        | CN      |
| 271.44         | Fe II   | 300.27         | Ni I    | 356.448        | Fe I    | 418.027        | CN      |
| 272.12         | Fe I    | 304.77         | Fe I    | 357.296        | Pb I    | 422.636        | Ca I    |
| 272.72         | Fe II   | 305.89         | Fe I    | 357.824        | Cr I    | 423.559        | Fe I    |
| 275.55         | Fe II   | 306.21         | Co I    | 358.024        | Fe I    | 427.465        | Cr I    |
| 276.77         | Fe I    | 306.61         | V I     | 359.582        | Ti II   | 430.327        | Ca I    |
| 279.57         | Mg I    | 307.55         | Ti II   | 364.284        | Ti I    | 436.309        | C2      |
| 279.82         | Mn I    | 309.29         | Al I    | 373.762        | Fe I    | 438.387        | Fe I    |

3.2. **The characters of the spectra produced by different wavelength laser**

![Figure 3](image-url) shows parts of LIBS spectra produced by IR and UV laser. Fig.3 shows parts of the LIBS spectrum averaged for 3,000 laser shots with 45mJ pulse energy. From plot (a), the spectrum in the near-UV region for 1,064nm irradiation is more intense than the one for 266nm irradiation. Abundant ionic lines were identified in this region. This is due to the higher absorption in the plasma caused by the inverse bremsstrahlung (IB), whose cross-section is proportional to cube of the laser excitation wavelength. Thus, the higher temperature caused by the
greater absorption of the IR laser light was reached and rapidly converted into kinetic energy and ionization [8, 13, 14]. The similar phenomenon was observed in the LIBS analysis of ancient bronzes spectra [8].

Although IR laser can produce higher intensity lines which may be helpful to find weak lines in near-UV region, stronger continuum spectrum in visible region was also produced which has disadvantage to the signal-noise ratio of lines as shown in plot (b). However, one should be careful at this point, the reproducibility of LIBS spectra produced by IR laser is worse than those produced by UV laser [13]. Because the plasma shield to IR laser is much stronger.

4. Summary
The LIBS spectra of holly leaves have been investigated and more than 430 line were found and more than 20 elements and molecules were identified from spectra of holly leaves samples in the range of 230–438nm. The influence of laser wavelengths upon analysis of plant samples has been investigated. The comparison of LIBS spectra shows that the spectrum for 1,064nm irradiation is more intense than the one for 266nm irradiation by the same pulse energy in the near-UV region, and stronger continuum spectrum in visible region was also produced by 1,064nm irradiation. Thus, 266nm irradiation will be better for qualitative analysis of micro-elements in plant sample than 1,064nm irradiation for less influence of the plasma shield. Investigates of the influence of laser wavelength for LIBS can help to improve the analytical capabilities of LIBS.

Acknowledgements
The work is supported by the Natural Science Foundation of China (Grant No. 10605034)

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