

# Rapid identification of macro nutrients in pharmaceutical medicine using laser-induced plasma spectroscopy

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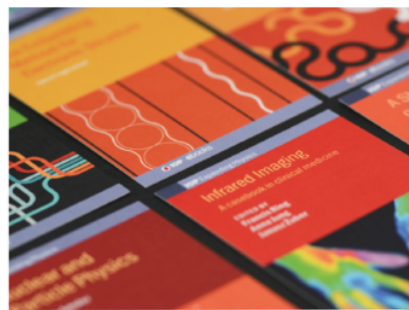
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## Rapid identification of macro nutrients in pharmaceutical medicine using laser-induced plasma spectroscopy

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**Abstract.** Identification of macro nutrients in medicine is really necessary for healthy purpose. In this study, identification of macro elements in pharmaceutical products was carried out by laser-induced plasma spectroscopy (LIPS). A comparative study was made by employing different types of laser, namely an Nd:YAG laser and a pulse TEA CO<sub>2</sub> laser. Experimentally, the laser beam was directed and focused by a convex lens on a mineral supplement tablet. A luminous plasma was induced on the tablet's surface. Sharp and high-intensity emission spectra of macro elements including Ca and Mg were detected both in LIBS using Nd:YAG and pulse CO<sub>2</sub> lasers. However, the intensities of Ca and Mg spectra are much higher for the LIBS using CO<sub>2</sub> laser. Based on the analysis, the plasma temperature plays important role in the spectra. Namely, the plasma induced by a TEA CO<sub>2</sub> laser is much higher than that of Nd:YAG laser; the plasma temperature for the case of TEA CO<sub>2</sub> laser and Nd:YAG laser were 6400 K and 4500 K, respectively.

### 1. Introduction

Identification of macro elements in pharmaceutical products is urgently necessary because of the importance of elements for human body. The macro elements include calcium, magnesium, zinc, potassium, and sodium, which are strongly beneficial for human health [1]. Therefore, periodical check of quality of pharmaceutical products containing macro elements is greatly important.

There are various techniques used for identification of elements including inductively coupled plasma (ICP). The techniques are very sensitive for elemental detection and are powerful to be employed for elemental detection [2,3]. However, the techniques need complicated and tedious sample pretreatment. They are also very expensive in experimental equipments.

Laser-induced plasma spectroscopy (LIPS) that is usually called laser-induced breakdown spectroscopy (LIBS) is new method in analytical spectroscopy. In LIBS, pulse laser usually uses to induce a luminous plasma [4,5]. The plasma is sent to the optical multichannel analyzer (OMA) system to obtain an emission spectrum. Compared to other conventional method, LIBS enables one to perform an analysis of elements rapidly and without any delicate sample pretreatment. [6,7]. Furthermore, the LIBS system is much cheaper than that of other spectrochemical equipments such as ICP and x-ray fluorescence spectroscopy.



Some researchers have employed LIBS for the detection of elements in pharmaceutical products [8]. However, in the study, a pulse Nd:YAG laser was used. In this present research, a comparative study on LIBS for detection of macro elements in pharmaceutical product was conducted using pulse Nd:YAG laser and transversely excited atmospheric (TEA) CO<sub>2</sub> laser. It was found that the emission spectra of macro elements such as Ca, Mg, and Zn in mineral supplement are much better for the pulse CO<sub>2</sub> laser case, namely the emission intensities are much higher with low background emission than that of Nd:YAG laser.

## 2. Methods

Figure 1(a) displays setup used in this research. The lasers applied in this research were Nd:YAG laser (1.064  $\mu\text{m}$ , 60 mJ, 10 ns,) and TEA CO<sub>2</sub> laser (10.64  $\mu\text{m}$ , 1500 mJ, 200 ns.). The laser was irradiated and focused onto sample surface by using a lens (quartz lens for Nd:YAG and ZnTe lens for CO<sub>2</sub> laser as illustrated in Fig. 1(b) to induce a luminous plasma. The diameter of focal spot of Nd:YAG laser on sample surface was 0.1 mm, while for the TEA CO<sub>2</sub> laser was 2 mm, resulting in the laser fluence of 0.38 GW/cm<sup>2</sup> and 0.18 GW/cm<sup>2</sup> for the YAG laser and TEA CO<sub>2</sub> laser, respectively.

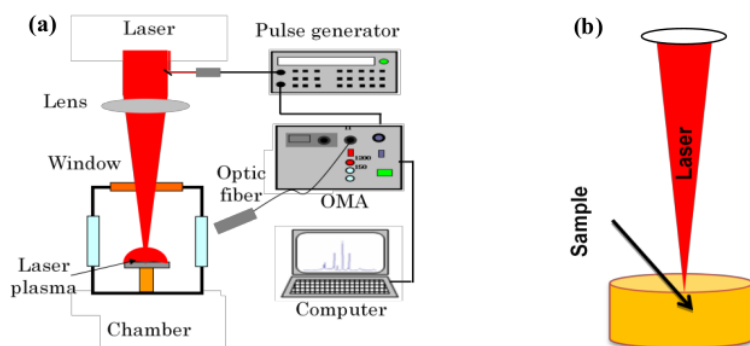


Figure 1. (a) experimental arrangement, (b) focusing laser on sample target

The sample used in this work was mineral supplement tablet containing around 2.5 % Ca and 1 % Mg. The sample was put in a holder put in a chamber (12 cm x 12 cm x 12 cm). The plasma was produced at 1 atm air.

To obtain the spectral emission, the plasma emission obtained from the sample was sent onto the spectrograph system via optical fiber. The gating function of OMA was 1-100  $\mu\text{s}$  for Nd:YAG case and it was 10-100  $\mu\text{s}$  for TEA CO<sub>2</sub> case.

## 3. Results and discussion

At initial, emission spectra of Ca obtained from the supplement target taken by using TEA CO<sub>2</sub> LIBS and Nd:YAG LIBS were compared. The emission spectra of Ca by LIBS method using (a) TEA CO<sub>2</sub> laser and (b) Nd:YAG laser were shown in Fig. 2. Ca II 393.3 nm and Ca II 396.8 nm emission lines appear clearly both in Nd:YAG and TEA CO<sub>2</sub> laser cases even though the Ca has high ionization energy. Ca II 393.3 nm has excitation energy of ionic Ca at 393.3 nm has higher level energy  $E_k$  of 3.2 eV and lower level energy  $E_l$  of 0 eV from the ground state of ionic state of Ca. First ionization energy of Ca is 6.1 eV. From this result, it certified that the plasmas induced in the present study have good plasma with high temperature to ionize the Ca atoms as macro nutrient. In addition, neutral Ca line at 422.6 nm was also sharply detected both in two lasers. The excitation energy of neutral Ca 422.6 nm is 2.9 eV from the ground state of Ca neutral. However, for the case of TEA CO<sub>2</sub> laser, the intensity of ionic Ca lines (Fig. 2a) are slightly higher and the intensity of neutral Ca line is slightly lower than Nd:YAG laser case (Fig. 2b). This indicates that the plasma temperature produced by TEA CO<sub>2</sub> laser

is quiet higher than that of Nd:YAG laser. Therefore, the degree of ionization is higher for the TEA CO<sub>2</sub> laser, resulting in higher emission intensity. The lower intensity of neutral Ca lines in TEA CO<sub>2</sub> laser case also proves that the temperature is higher in the plasma induced by TEA CO<sub>2</sub>. In the plasma with high temperature, the ionization process of atoms effectively takes place, resulting in optimum emission intensity of ionic lines as reported in our previous work [9].

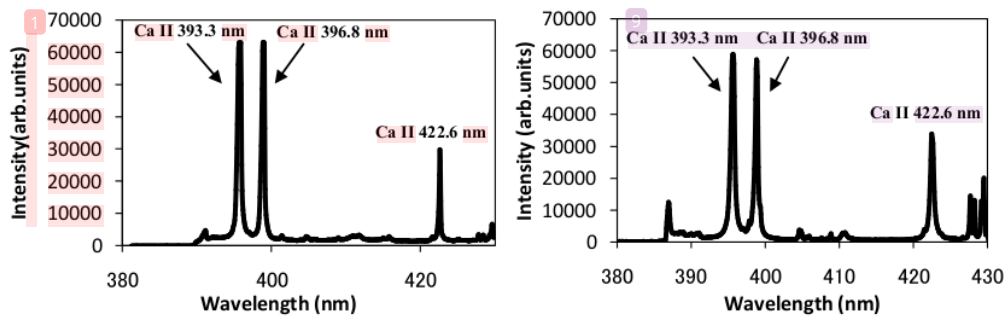


Figure 2. Emission spectra of ionic and neutral Ca obtained from mineral supplement by LIBS using (a) TEA CO<sub>2</sub> laser and (b) Nd:YAG laser.

To support our assumption that the plasma in TEA CO<sub>2</sub> laser LIBS has higher temperature than Nd:YAG laser case, detection of Mg as macro nutrient in mineral supplement was made. Mg emission spectrum obtained from the supplement tablet by (a) TEA CO<sub>2</sub> LIBS and (b) Nd:YAG LIBS were shown in Fig. 3.

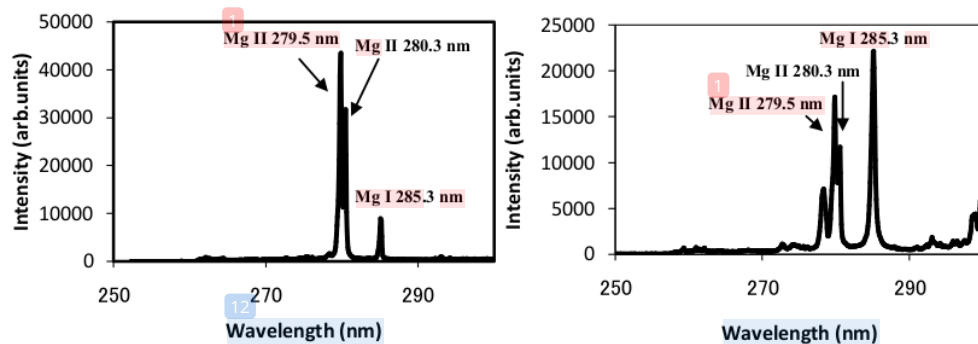


Figure 3. Emission spectra of ionic and neutral Mg obtained from mineral supplement by LIBS using (a) TEA CO<sub>2</sub> laser and (b) Nd:YAG laser.

High-intensity of ionic Mg lines at 279.5 nm and 280.3 nm clearly appear together with neutral Mg I line at 285.3 nm both in TEA CO<sub>2</sub> laser and Nd:YAG laser cases. The excitation energies of Mg II lines at 279.5 nm and 280.3 nm are 4.4 eV from the ground state of ionic level. However, it should be pointed out that the intensity of ionic Mg lines by using TEA CO<sub>2</sub> laser is higher than that of Nd:YAG laser (Fig. 3a). Furthermore, the intensity of neutral Mg line is significantly lower for TEA CO<sub>2</sub> laser case as same tendency with the case of Ca atom shown in Fig. 2. It should be mentioned that the Mg lines has first ionization energy of 7.6 eV. Due to this high degree of ionization, ionization process of Mg is more effective in TEA CO<sub>2</sub> laser because the plasma has quiet high-temperature, resulting in high-emission intensity of ionic Mg.

The plasma temperature was further calculated by using Boltzmann's method using neutral Zn emission obtained from the mineral supplement. Neutral emission lines of Zn and their spectroscopic data from NIST database as shown in Table 1 are applied to calculate the plasma temperature.

Table 1. Emission lines of neutral Zn and their spectroscopy data

Elements	Wavelength (nm)	Upper level energy (eV)	Upper level degeneracy	Transition probability ( $s^{-1}$ )
Zn I	328.2	7.7823	3	$8.7 \times 10^7$
Zn I	330.2	7.7827	5	$1.1 \times 10^8$
Zn I	334.5	7.7834	7	$1.5 \times 10^8$

Considering the plasma in local thermodynamic equilibrium (LTE), the Boltzmann equation can be written as follows

$$\ln\left(\frac{I\lambda}{g_k A_k}\right) = -\frac{1}{k_B T} E_k + C \quad (1)$$

Where  $\lambda$  is wavelength of the transition line,  $I$  is the line intensity occurring between the upper energy level  $k$  and lower energy level  $i$ ,  $A_k$  is the transition probability,  $g_k$  is the degeneracy of the upper energy level,  $T$ ,  $k_B$ , and  $E_k$  are plasma temperature, Boltzmann constant and energy of the upper energy level, respectively,  $C$  is a constant for a given atomic species. The temperature  $T$  can be estimated from Eq.2 as follows

$$y = mE_u^i + y_0 \quad (2)$$

Based on spectral lines shown in Table 1, the Boltzmann plots of the Zn neutral by LIBS using TEA CO<sub>2</sub> laser and Nd:YAG laser was shown in Fig. 4(a) and (b), respectively. The slopes of the curves give a temperature of plasma of around 6400 K in TEA CO<sub>2</sub> laser and 4500 K in Nd:YAG laser.

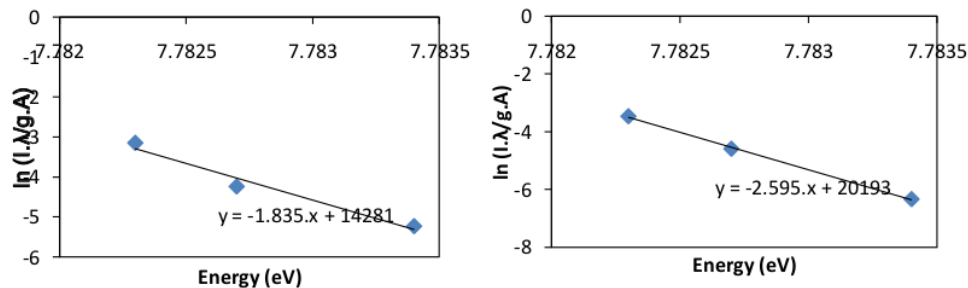


Figure 4. Boltzmann method from the identification of Zn neutral obtained from the mineral supplement by LIBS using (a) TEA CO<sub>2</sub> laser and (b) Nd:YAG laser.

By the Boltzmann plot, the temperature of plasma induced by LIBS using TEA CO<sub>2</sub> laser and Nd:YAG laser were estimated to be 6400 K and 4500 K, respectively. This result confirmed our assumption that the plasma induced by TEA CO<sub>2</sub> laser has higher temperature than the case of Nd:YAG laser and therefore, the emission intensities of spectra obtained by LIBS using TEA CO<sub>2</sub> laser is higher than that of Nd:YAG LIBS.

#### 4. Conclusion

A comparative study on detection of macro nutrients of Ca and Mg in mineral supplement has been carried out by LIBS using TEA CO<sub>2</sub> laser and Nd:YAG laser. The emission spectra of Ca and Mg obtained by using TEA CO<sub>2</sub> LIBS has much higher intensity than the case of Nd:YAG LIBS. By experiment, it was proved that the plasma temperature gives significant contribution to the emission spectra. Namely, the higher the plasma temperature, the higher the intensity of observed spectra. Based on calculation of plasma temperature by using the Boltzmann method, it was obtained that the temperatures of plasma induced by TEA CO<sub>2</sub> laser and Nd:YAG laser are 6400 K and 4500 K, respectively.

#### Acknowledgment

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