Quantitative analysis of titanium concentration using calibration-free laser-induced breakdown spectroscopy (LIBS)

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Abstract. Laser-induced breakdown spectroscopy (LIBS) can be used for quantitative and qualitative analysis. Calibration-free LIBS (CF-LIBS) is a method to quantitatively analyze concentration of elements in a sample in local thermodynamic equilibrium conditions without using available matrix-matched calibration. In this study, we apply CF-LIBS for quantitative analysis of Ti in TiO₂ sample. TiO₂ powder sample was mixed with polyvinyl alcohol and formed into pellets. An Nd:YAG pulsed laser at a wavelength of 1064 nm was focused onto the sample to generate plasma. The spectrum of plasma was recorded using spectrophotometer then compared to NIST spectral line to determine energy levels and other parameters. The value of plasma temperature obtained using Boltzmann plot is 8127.29 K and electron density from calculation is 2.49×10¹⁶ cm⁻³. Finally, the concentration of Ti in TiO₂ sample from this study is 97% that is in proximity with the sample certificate.

1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is one of the methods that can be used for quantitative and qualitative analysis. The advantages of LIBS are less destructive and more efficient. For qualitative analysis using LIBS, further preparation sample is not required. Until now LIBS has been successfully used for testing several types of samples such as gases, liquids, and solids.

For quantitative analysis LIBS, standardization is needed, such as using calibration curves. The commonly used calibration curve is matrix-matched standards [1]. When matrix-matched is used in LIBS analysis then the advantages of LIBS are reduced because it is no longer efficient. The use of calibration standards should meet several attempts of plasma spectral emission, such as the state of plasma temperature. To overcome these issues, a calibration-free LIBS (CF-LIBS) method can be used for solution. CF-LIBS was proposed by Ciucci et al. in 1999 [2]. Until now, quantitative analysis using CF-LIBS has been applied in a number of studies and some analytical methods for CF-LIBS have been proposed [3]. Dong et al. [4] in 2015 developed a procedure using determined plasma temperature by genetic algorithm (GA). Bulajic et al. [5] in 2002 proposed a procedure for correcting self-absorption in CF-LIBS. Self-calibrated LIBS was proposed by De Giacomo et al. [6] in 2007.

Using CF-LIBS for quantitative analysis must meet several circumstances, such as the laser induced plasma must be in local thermodynamic equilibrium (LTE) condition [7]. LTE condition is characterized with the achievement of the value of electron density (Ne) ≥ 1.6×10¹⁶ cm⁻³ [8]. The
concentration of a specific element of interest is given by the sum of the concentrations of neutral and singly ionized species.

In this paper, we used CF-LIBS for analyzing concentration of Ti in TiO$_2$ sample. The purpose of this work is to find the successive CF-LIBS as quantitative analysis without calibration curve. The standard sample used in this work was high purity TiO$_2$ powder from MERCK (99.99%).

2. Experimental methods

TiO$_2$ powder was mixed with polyvinyl alcohol (PVA) as a binding material for better compactness and then pressed into pellet by hydraulic pressing machine. The sample was pressed for 10 minutes at 48.78 MPa at room temperature. Diameter and thickness of the pellet are 29 mm and 3 mm, respectively.

LIBS setup scheme is shown in figure 1. Nd: YAG Q-Smart 850 laser from Quantel was used in this work, with laser wavelength of 1064 nm and repetition rate of 10 Hz. Laser beam was focused onto sample using 100 mm focusing lens. The energy of laser was 45 mJ and the pellet sample was placed in a vacuum chamber. Ocean Optics spectrometer was used to detect and record emission spectrum of generated plasma with integration time 100 ms.

![Figure 1. LIBS setup.](image)

The CF-LIBS method as quantitative analysis is based on the assumption that laser induced plasma is optically thin and under LTE condition [7]. When the conditions are accomplished, the integrated intensity of spectral emission line can be expressed by Saha-Boltzmann Equation [9]:

$$I = F C s A_{ki} \frac{g_k}{U(T)} \exp \left( - \frac{E_k}{kT} \right)$$  (1)

Where $I$ is the measured integrated spectral line intensity, $F$ is constant, $C_s$ is the number density of an atomic or ionic species $s$, $A_{ki}$ is transition probability, $g_k$ is the statistical weight for the upper level, $U(T)$ is the partition function, $E_k$ is energy of the upper energy, $k$ is Boltzmann constant, and $T$ is the plasma temperature.

For a plasma in LTE conditions, plasma temperature is calculated according to:

$$ln \frac{I}{A_{ki}} = - \frac{1}{kT} E_k + ln \frac{F C s}{U(T)}$$  (2)
In a linear form $y = mx + bs$, plasma temperature can be obtained from the slope of the Boltzmann plot with $m = -1/kT$ [10]. The concentration of a specific element in plasma can be calculated following the steps prescribed by equations 3 – 5:

$$U(T) = \sum g_i e^{-E_i/kT}$$ (3)

$$Cs = \frac{1}{F_{np}} U(T) e^{bs}$$ (4)

$$Cs = \frac{U(T) e^{bs}}{\sum U'(T) e^{bs'}}$$ (5)

3. Result and discussion

First, pellet samples of TiO$_2$ were shot with a laser beam from Nd: YAG with wavelength 1064 nm and energy of laser beam 45 mJ. Emission spectrum of generated plasma from the sample was detected and recorded by spectrophotometer. Emission spectrum was converted to graphic using Ocean Optics spectrophotometer program. Graphic of emission spectrum is shown in figure 2.

**Figure 2.** Graphic of emission spectrum.

Graphic of emission spectrum was analyzed to obtain spectroscopic constants using NIST database as a reference. Required spectroscopic constants are transition probability, energy in upper level, and degeneracies. The analysis result is shown in table 1.

Based on the literature, CF-LIBS can be used as a method for quantitative analysis with some conditions. One of the conditions is that the LTE state of plasma is fulfilled. Plasma can be considered in LTE state if the value of $Ne \geq 1.6 \times 10^{16}$ cm$^{-3}$, and $Ne$ can be calculated according to equation 6 [8]:

$$Ne \geq 1.6 \times 10^{12} T_e^{1/2} (\Delta E_{nm})^3$$ (6)

where $Ne$ is electron density, $T_e$ is electron temperature, and $\Delta E_{nm}$ is the largest gap between adjacent energetic levels.
Table 1. Spectral lines considered for the analysis.

| Species | Wavelength (nm) | $A_{k_i}$ (s$^{-1}$)$\cdot10^6$ | $E_k$ (eV) | $g_k$ |
|---------|-----------------|---------------------------------|------------|------|
| Ti I    | 320.90219       | 16.3                            | 5.8310053  | 3    |
| Ti I    | 363.79650       | 0.93                            | 3.4070939  | 3    |
| Ti I    | 366.06929       | 3.0                             | 3.4070939  | 3    |
| Ti I    | 387.32011       | 50.5                            | 5.19706946 | 4    |
| Ti I    | 451.2733        | 9.86                            | 3.5826547  | 5    |
| Ti I    | 517.3740        | 4.23                            | 2.3957447  | 2    |
| Ti I    | 549.0148        | 3.69                            | 3.7178148  | 3    |
| Ti I    | 842.6504        | 1.20                            | 2.2968146  | 2    |
| Ti II   | 332.33879       | 1.02                            | 4.89451479 | $\frac{5}{2}$ |
| Ti II   | 335.20693       | 15.2                            | 4.91904347 | $\frac{1}{2}$ |
| Ti II   | 348.36246       | 97                              | 7.86630466 | $\frac{3}{2}$ |
| Ti II   | 373.9599        | 1.71                            | 5.90475341 | $\frac{3}{2}$ |
| Ti II   | 442.19384       | 1.85                            | 4.86432351 | $\frac{3}{2}$ |
| Ti II   | 498.279         | 4.20$\cdot10^{-7}$             | 3.09479323 | $\frac{3}{2}$ |
| Ti II   | 622.724         | 2.7$\cdot10^{-8}$              | 2.59768654 | $\frac{5}{2}$ |

To fulfill LTE condition, the most crucial factor is plasma temperature. Plasma temperature can be obtained from the slope of the Boltzmann, a plot between $\ln (I/\lambda A_{k_i} g_k)$ and $E_k$. Boltzmann plot is shown in figure 3.

![Figure 3. Boltzmann Plot.](image)

The result of plasma temperature in this work is 8127.29 K. Using value of plasma temperature, the obtained electron density is $2.49\times10^{16}$ cm$^{-3}$. The Ne result is greater than $1.6\times10^{16}$ cm$^{-3}$, which means LTE condition of plasma in this work is fulfilled. Furthermore, CF-LIBS can be used as quantitative analysis in this work.

Concentration of the species Cs can be calculated using the intersection value $b_s$ of the linear regression in the Boltzmann in equations 3 – 4. From calculation result, concentration of Ti in TiO$_2$
sample in this work is up to 97%, which is very close from known concentration of certified samples, i.e. 99%.

4. Conclusion
In this work, the best linear fit is obtained in calculating temperature plasma. The value of $Ne$ is $2.49 \times 10^{16}$ cm$^3$, which means that LTE condition of plasma in this work is fulfilled. In this work, quantitative analysis for concentration of Ti in TiO$_2$ sample using CF-LIBS is successful. The results of concentration Ti is obtained 97% which is very close from known concentration of certified samples, i.e. 99%.

Acknowledgments
The authors are grateful to Unggulan Program and Penguatan Kompetensi Program Research Center of Physics, Indonesian Institute of Science (LIPI) for financial support of this research.

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