

Controlled calibration method for laser induced breakdown spectroscopy

Li Wang (汪力)¹, Chijian Zhang (张持健)¹, and Yuan Feng (冯源)²

¹The Intelligence Measure-Control Technique Research Center, Anhui Normal University, Wuhu 241000

²Institute of Atomic and Molecular Physics, Anhui Normal University, Wuhu 241000

Received July 17, 2007

Laser induced breakdown spectroscopy (LIBS) is a potential technique for rapid analysis of samples present in solids, gases and liquids. In the last two decades it was an object of extensive studies. Controlled calibration method used to analysis the LIBS spectra is investigated. Compared with the inner calibration and calibration-free (CF) methods, this new method overcomes “matrix effect”, and demonstrates a better ability to cope with the spectra. It is used to analyze natural soil, and errors of the concentration are decreased about 5%. The result shows that the new method is feasible and accurate.

OCIS codes: 140.3440, 020.0020, 350.5400, 300.0300.

Laser induced breakdown spectroscopy (LIBS) was proposed by Brech and Cross^[1] in 1962. This technique is based on the spectroscopic analysis of the atomic or ionic emission lines from the intense plasma or weak plume generated when a pulsed laser beam is focused on a sample. It has been a potential technique for rapid analysis of materials in a wide range^[2–12]. The merits of non-invasive analysis, suitability to remote measurement, and minimal sample preparation have made this technique increasingly attractive. At present, there are two methods applied to analyzing spectra of LIBS. One is the inner calibration LIBS method which has been allowed to perform quantitative analysis using calibration curves obtained from reference samples of known composition. However the concentration of major components is difficult to measure by this method because of the so-called “matrix effect”, and it cannot be applied in the case of unknown samples. Another is the calibration-free LIBS (CF-LIBS) method which has been developed to determine, without calibration curves, the concentration of atomic components^[13–15] on the promise of detecting all the elements. But CF-LIBS method has several disadvantages, for example, all the elements’ spectra must be detected in the soil sample, and the accuracy of detecting concentration of samples is not satisfying compared with other methods — inner calibration LIBS method, inductively coupled plasma mass spectrometry (ICP-MS) and atomic absorption spectrometry (AAS).

We put forward a new method on the basis of the two methods above, which is called “controlled calibration LIBS” temporarily. The concentration of element can be calculated from reference element directly by this new method. This avoids the “matrix effect” and improves the accuracy of concentration of atomic components.

The CF-LIBS method used for the analysis of the LIBS spectra has been described in detail elsewhere^[13], therefore here we will only describe this approach briefly. At first, self-absorption is not considered in the method. By assuming the plasma to be in local thermodynamic equilibrium (LTE) in the temporal window of signal acquisition, the LIBS line integral intensity corresponding to the transition between two levels E_k and E_i can be expressed

as

$$\overline{I}_{\lambda}^{ki} = FC_s A_{ki} \frac{g_k \exp(-E_k/K_B T)}{U_s(T)}, \quad (1)$$

where $\overline{I}_{\lambda}^{ki}$ represents the measured integral line intensity; λ is the wavelength of the transition; C_s is the concentration of the emitting atomic species; A_{ki} is the transition probability for the given line; g_k is the degeneracy of the k level; F is a constant to be determined after the species concentrations have been normalized; T is the electron temperature; K_B is the Boltzmann constant; and $U_s(T)$ is the partition function for the emitting species, which is defined as

$$U_s(T) = \sum_k g_k \exp(-E_k/K_B T). \quad (2)$$

Defining the following quantities,

$$y = \ln \frac{\overline{I}_{\lambda}^{ki}}{g_k A_{ki}}, \quad (3)$$

$$m = -\frac{1}{K_B T}, \quad (4)$$

$$x = E_k, \quad (5)$$

$$q_s = \ln \frac{C_s F}{U_s(T)}. \quad (6)$$

Taking the logarithm of Eq. (1) and substituting the above definitions, we obtain the following linear relationship between the x and y parameters:

$$y = mx + q_s. \quad (7)$$

According to Eqs. (3)—(6), the slope of the curve m is related to the temperature of the species, while the intercept q_s parameter is proportional to the logarithm of the species concentration via the constant factor F . The F factor can be determined by normalizing to unit the sum of the species concentrations as

$$\sum_s C_s = \frac{1}{F} \sum_s U_s(T) \exp(q_s) = 1. \quad (8)$$

Finally, the concentration of all the atomic species of the sample can be obtained as

$$C_s = \frac{U_s(T)}{F} \exp(q_s). \quad (9)$$

According to Eqs. (8) and (9), we can obtain

$$\frac{U_s^1(T) \exp(q_s^1)}{C_s^1} = \frac{U_s^2(T) \exp(q_s^2)}{C_s^2} = \dots = \frac{U_s^s(T) \exp(q_s^s)}{C_s^s}. \quad (10)$$

Assuming that the concentration of one element called reference element (marked as C_s^0) is known, the corresponding partition function is $U_s^0(T)$ and intercept is q_s^0 . Then the other elements' concentration can be obtained as

$$C_s^i = C_s^0 \frac{U_s^i(T) \exp(q_s^i)}{U_s^0(T) \exp(q_s^0)}, \quad (i = 1, 2, \dots, s-1) \quad (11)$$

where all the factors are known. The concentration value determined by Eq. (11) refers to one species: in order to obtain the elemental composition, it is sufficient to add the values corresponding to the neutral and single ionized species of the same element, for example, the total concentration for a given element M is given by

$$C_M^{\text{total}} = C_M^{(\text{I})} + C_M^{(\text{II})}. \quad (12)$$

The characteristics of this method are as follows. Firstly, compared with the inner calibration LIBS method, this method avoids "matrix effect". Secondly and also obviously, we do not need to detect all the elements in the soil sample in this method, which is difficult to achieve in experiment. Thirdly, the concentration of the determined element can be calculated only from the spectral lines of the determined element and the reference element in the sample. Finally, the method avoids the step of calculating the factor F which is the systematic error in the CF-LIBS method, so the result is simpler, more rapid and more accurate than CF-LIBS.

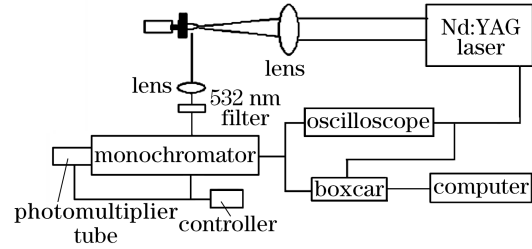


Fig. 1. Experimental setup used for the LIBS measurements on the soil samples.

The experimental setup used for the LIBS measurements in the soil samples is sketched in Fig. 1.

The Nd:YAG laser was operated at 532 nm with energy of 170 mJ per pulse at a maximum repetition rate of 10 Hz, which was focused with a 68 mm focal length lens on the soil sample surface. The soil sample was fixed to a rotary holder (1 r/min) so that every laser shot could hit on a flash site. The plasma light was collected perpendicular to the direction of laser beam, focused it by a lens of 67 mm focal length and 532 nm filter into the entrance slit of single grating monochromator (AC-TON, SP-2750) whose width of entrance slit is 80 μm . The detector was a photomultiplier tube (PMT, R376) whose signal is time resolved and averaged with a boxcar. Spectra were recorded and processed by a computer, at the same time, the time-resolved LIB signal transported by the PMT can be observed by the digital memory oscilloscope (TEK460A). In this experiment, we made the soil sample from local natural soil, and the shape of soil sample was cylindrical (the inner diameter is 6 mm and thickness is 3 – 5 mm).

In the soil sample, Pb was used as reference element whose concentration is 210 ppm. In the experiments, the time delay of intensity measurements was 600 ns, the laser was focused on the soil sample interior, the distance is 1 mm from the surface, which could avoid breaking down the air, and the laser energy was 22 mJ. The spectra were shown in Fig. 2.

Figures of $\ln(I_{\lambda}^{ki}/g_k A_{ki})$ versus E_k could be constructed by the intensity of LIBS experimental spectral lines. Curves of Fe(I), Al(I), Mn(I) and Ca(II) were depicted in Fig. 3, from which T and q_s^i could be calculated. T was 4200 – 4500 K. The power density of laser was $2.2 \times 10^9 \text{ W}\cdot\text{cm}^{-2}$.

Table 1. Composition of the Soil Sample Calculated by Two Methods

	Controlled Calibration	Calibration-Free	ICP ^a	
	O	46.65	48.85	46.99
	Si	33.49	35.07	34.118
	Al	6.35	6.65	6.13
Major Elements (%)	Fe	2.56	2.68	2.87
	Ca	0.543	0.569	0.536
	Mg	0.562	0.589	0.534
	Ti	0.504	0.528	0.516
	Mn	460	482	465
Trace Elements (ppm)	Pb	210	220	210
	Cr	85	89	80.5

^aICP: Checking results of sample by Nanjing Soil Institute of Chinese Academy of Science).

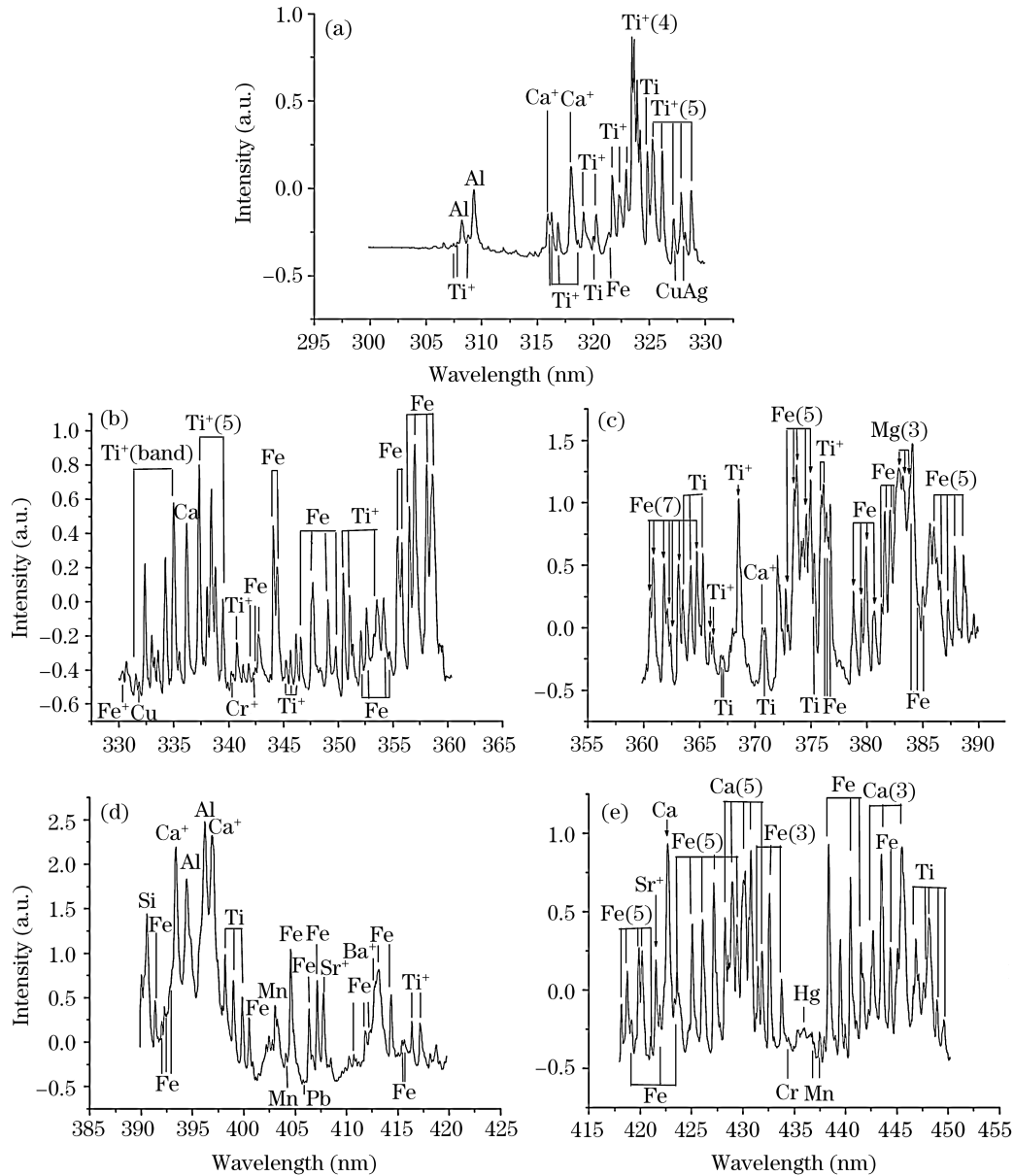


Fig. 2. LIBS spectra of soil samples in 300 – 450 nm: (a) 300 – 330 nm; (b) 330 – 360 nm; (c) 360 – 390 nm; (d) 390 – 420 nm; (e) 420 – 450 nm.

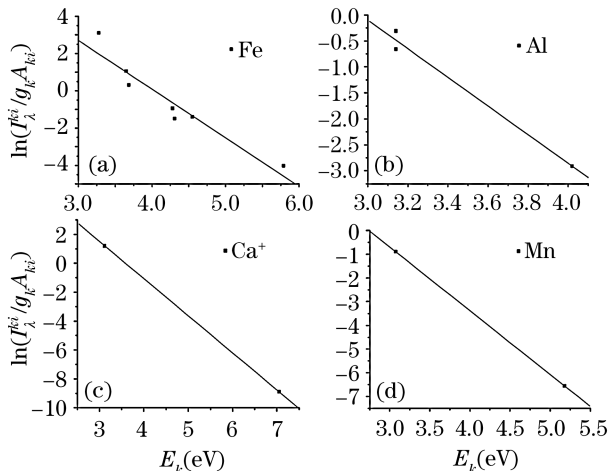


Fig. 3. Curves of $\ln(I_{\lambda}^{ki}/g_k A_{ki})$ versus E_k of four elements. (a) Fe(I); (b) Al(I); (c) Ca(II); (d) Mn(I).

Results of the CF-LIBS method and the controlled calibration method are listed in Table 1 for comparison. We can see that errors of the concentration of seven elements are all decreased about 5% by applying the controlled calibration LIBS approach. Most of the concentrations of elements are more accurate compared with the CF-LIBS method. Actually, because we do not need to calculate all the elements which are difficult to achieve in experiment, in addition, the error of calculating the factor F is avoided.

In conclusion, we present a new approach for the analysis of LIBS, and this approach is verified to be feasible in theory and experiment. Firstly, the controlled calibration LIBS method overcomes “matrix effect”. Secondly, it is allowed to perform quantitative analysis using reference element. The result shows that this method is simple and rapid, and the accuracy is better than CF-LIBS. More

importantly, all further improvements of CF-LIBS analysis are fit for the controlled calibration LIBS method. The further work will be focused on improving the accuracy and practicability.

This work was supported by the National Natural Science Foundation of China (No. 60475017), the Key Subject of Molecular and Atomic Physics of Anhui Province, and Anhui Normal University Doctor Research Foundation 2006. The authors gratefully acknowledge Hong-guang Xu (Institute of Atomic and Molecular Physics, Anhui Normal University) for supporting the experimental data. C. Zhang is the author to whom the correspondence should be addressed, his e-mail address is whzcj_cn@sina.com. L. Wang's e-mail address is wangli_tl@163.com.

References

1. F. Brech and L. Cross, *Appl. Spectrosc.* **16**, 59 (1962).
2. L. St-Onge, M. Sabsabi, and P. Cielo, *Spectrochim. Acta Part B* **53**, 407 (1998).
3. M. Hanafi, M. M. Omar, and Y. E. E.-D. Gamal, *Radiation Physics and Chemistry* **57**, 11 (2000).
4. H. Sun, Z. Xu, T. Jia, X. Li, C. Li, D. Feng, S. Xu, and X. Ge, *Chin. Opt. Lett.* **3**, 60 (2005).
5. G. Hubmer, R. Kitzberger, and K. Mörwald, *Anal. Bioanal. Chem.* **385**, 219 (2006).
6. M. A. Gondal and T. Hussain, *Talanta* **71**, 73 (2007).
7. L. Fomarini, F. Colao, R. Fantoni, V. Lazic, and V. Spizzicchino, *Spectrochim. Acta Part B* **60**, 1186 (2005).
8. P. Yaroshchuk, D. Body, R. J. S. Morrison, and B. L. Chadwick, *Spectrochim. Acta Part B* **61**, 200 (2006).
9. Z. Cui, X. Zhang, G. Yao, X. Wang, X. Xu, X. Zheng, E. Feng, and X. Ji, *Acta Phys. Sin.* (in Chinese) **55**, 4506 (2006).
10. Z. Wang and J. Wang, *China Science and Technology Information* (in Chinese) (9), 21 (2007).
11. J. Li, C. Lin, and S. Li, *Spectroscopy and Spectral Analysis* (in Chinese) **26**, 944 (2006).
12. L. Yu, J. Lu, W. Chen, L. Huang, J. Li, and C. Xie, *J. Appl. Opt.* (in Chinese) **27**, 147 (2006).
13. A. Ciucci, M. Corsi, V. Palleschi, S. Rastelli, A. Salvetti, and E. Tognoni, *Appl. Spectrosc.* **53**, 960 (1999).
14. L. Yu, J. Lu, W. Chen, G. Wu, K. Shen, and W. Feng, *Plasma Science & Technology* **7**, 3041 (2005).
15. V. S. Burakov and S. N. Raikov, *Spectrochim. Acta Part B* **62**, 217 (2007).