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用卤钨灯对激光诱导击穿光谱探测系统进行绝对效率标定

费腾[1],潘从元[2],曾强[1],杜学维[1],王秋平[1]
(1 中国科学技术大学 国家同步辐射实验室, 合肥 230029)
(2 安徽大学 电气工程与自动化学院, 合肥 230601)

摘 要:基于辐射度学理论搭建了用于激光诱导击穿光谱探测系统的绝对效率标定装置.用卤钨灯配备紫外玻璃滤光片和熔融石英漫射片作为标定的标准光源,标定了配备 Czerny-Turner 型紫外波段光谱仪的激光诱导等离子体光谱探测系统.测得了系统在 310～385 nm 波长范围内的绝对光谱响应,不确定度小于 7%(在标准偏差为 2 的条件下).绝对效率标定可为激光诱导击穿光谱探测系统硬件评估提供一种手段.

关键词:激光诱导击穿光谱;绝对标定;卤钨灯;绝对光谱响应
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Absolute Calibration of Laser-induced Breakdown Spectroscopy Detection System by Using a Tungsten Halogen Lamp

FEI Teng[1], PAN Cong-yuan[2], ZENG Qiang[1], DU Xue-wei[1], WANG Qiu-ping[1]
(1 *National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei* 230029, *China*)
(2 *College of Electrical Engineering and Automation, Anhui University, Hefei* 230601, *China*)

Abstract: An absolute calibration setup for laser-induced breakdown spectroscopy detection system is built based on the radiometry theory. A tungsten halogen lamp equipped with an ultraviolet glass filter and a fused silica diffuser is used as standard light source for the calibration. Absolute calibration of a laser-induced breakdown spectroscopy detection system with a Czerny-Turner spectrometer in the ultraviolet range is performed. The absolute spectral response of the system in the range of 310～385 nm is obtained with an uncertainty less than 7% by 2 standard deviation estimate. The absolute spectral calibration provides a way to evaluate the hardware of the laser-induced breakdown spectroscopy detection system.

Key words: Laser-induced breakdown spectroscopy; Absolute calibration; Tungsten halogen lamp; Absolute spectral response
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0 Introduction

Laser-induced Breakdown Spectroscopy (LIBS) technique is a promising analytical method that can be

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First author: FEI Teng (1986—), male, Ph.D. degree candidate, mainly focuses on laser-induced breakdown spectroscopy. Email: feiteng@mail.ustc.edu.cn
Supervisor (Contact author): WANG Qiu-ping (1963—), male, professor, mainly focuses on grating design & grating based monochromator development, precision machinery development and measurement related to spectrometer. Email: qiuping@ustc.edu.cn

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used in many fields, including metallurgy[1-3], combustion[4], environmental monitoring[5-6], space exploration[7], etc. LIBS obtains the component concentrations of a sample by analyzing the spectra from laser induced plasma. In the analysis, the intensities and intensity ratios of spectral lines are used for plasma characterizing or quantitative calculation, in which the spectral response calibration of the LIBS system is needed at the measured wavelength. In HAHN D W′s review of LIBS, several calibrations of the detection system were summarized[8]. Most of them adopted relative calibration by a certified standard light or branching ratios. However, TASCHUK M T, et al. used a radiometric approach to characterize the absolute calibration of several laser-induced breakdown spectroscopy detection systems and obtained their absolute responsivities[9]. Relative calibration normalizes the spectral response of different channels of the detection system, while absolute calibration establishes the numerical relations between the input radiometric values and output data of the detection system. Relative calibration is sufficient for spectral intensity ratio calculations, whereas absolute calibration can well characterize the entire LIBS detection system that could provide the absolute emission intensity of spectra in radiometric units. In TASCHUK M T′s opinion, quantitative comparisons can be performed between different experimental groups or with theoretical predictions by applying absolute calibration on LIBS[9]. Thus, absolute calibration is an excellent tool for the research of laser-induced plasma. In this paper, the structural rationality of the absolute calibration setup is investigated, and the uncertainty of the absolute spectral response results is estimated.

For the absolute calibration setup, a certified quartz-halogen, tungsten coiled filament lamp (FEL-type tungsten halogen lamp, or FEL lamp) is used as the standard source. FEL lamps with a nominal electrical power of 1000 W are used worldwide as standard of spectral irradiance[10-12]. They are used as radiometric calibration sources in operations that cover the spectral range from 250 nm to 2 500 nm[13-15] due to their low cost, availability in any electronic stores[16], and excellent stability[13].

A common LIBS detection system is selected for calibration, and it consists of an optical lens, a fiber, and a common Czerny-Turner spectrometer with an unintensified Charge-Coupled Device (CCD) array. In terms of practical application, calibrating the entire detection system is simple and accurate. An optic filter and a diffuser are used; therefore, the absolute spectral response of the LIBS detection system is obtained. The uncertainty of the absolute spectral response is estimated based on the experimental setup and noise characteristics of the spectrometer. Finally, an example is given to show the application of the absolute spectral response in LIBS.

1 Absolute calibration theory

1.1 Absolute spectral response

According to Ref.[12] about radiometry, when calibrating the absolute spectralresponse of an instrument, the incident standards could be radiance ($W/(m^2 \cdot sr)$), irradiance (W/m^2), or power (W). For a LIBS system, power is selected as the measurement of the incident standard, as it is suitable in LIBS application. Then, the absolute spectral response of the system is absolute spectral power response. For a single detector, the absolute spectral response is expressed as

$$R_{\Phi}=V/\Phi \tag{1}$$

where Φ is the input power from the standard source; V is the instrument output, which is expressed in volts, amperes, or other arbitrary units; and spectral response R_{Φ} is the spectral power response[18].

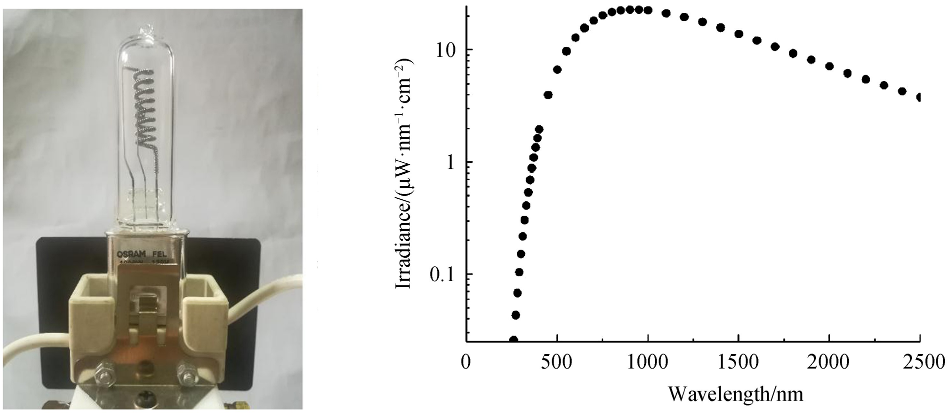
For the detection system equipped with a linear CCD array, the absolute spectral response is converted to the formula given by

$$R_{\Phi,\lambda}=\frac{V_{\lambda}/t}{\Phi_{\lambda}\Delta\lambda_{\lambda}} \tag{2}$$

where subscript λ is the wavelength corresponding to the CCD pixel. Instrument output V_{λ} is the integrated intensity through integral time t by the spectrometer. The unit of V_{λ} is a.u. by the spectrometer software, which is insignificant in the calibration. In addition, $\Delta\lambda_{\lambda}$ is the CCD pixel resolution; Φ_{λ} is the input power versus the wavelength, which is expressed in W/nm; and $R_{\Phi,\lambda}$ is the spectral power response of the detection system.

1.2 FEL lamp

In 1975, a 1 000 W tungsten halogen lamp was converted to a FEL lamp as a commercial irradiance standard[12]. The lamp used in the experiment and its calibrated standard value are shown in Fig.1. The lamp was calibrated by the National Institute of Metrology, China, with the calibration distance of 500 mm and uncertainty of 1.1%～2.1% (by 2 standard deviation estimate) in the range of 250～400 nm. The calibrated standard value is irradiance at the calibration distance.



(a) FEL lamp used in the experiment (b) Calibrated standard value of FEL lamp

Fig.1 FEL lamp and its standard irradiance at the calibration distance

2 LIBS detection system and the calibration method

2.1 LIBS detection system to be calibrated

The LIBS detection system consists of a collection lens, a fiber, and a spectrometer. The collection lens is a UV-fused silica lens (focal length: 35 mm). The fiber is a 0.5 m long UV fiber with a core diameter of 200 μm. The collection lens and the fiber are fixed in a tube, and the effective lens aperture is determined to be 17.5 mm. These parameters define a detection distance of 300 mm, an object surface area of Φ 1.5 mm and an angle of 1.5°. The spectrometer is a Czerny-Turner spectrometer (Avantes AvaSpec-ULS2048, 300～400 nm), which uses a 2048-pixel CCD array as a detector.

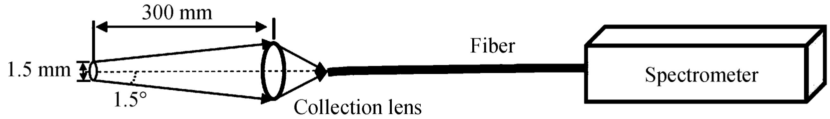


Fig.2 LIBS Detection system

2.2 Input standardpower Φ

An optical filter and a diffuser are required to generate the standard input power Φ for the calibration.

2.2.1 *Optical filter*

Tungsten-halogen lamps are long wavelength rich, so sometimes the well-characterized spectral filters are required[20-21]. In our detection system, the spectrometer has a stray light level of 0.04%～0.1%. For the input long wavelength rich spectral distribution in Fig. 1, the wavelength components out of the spectral range of the spectrometer is so strong that the output results are affected. Therefore, it is difficult to obtain a short-pass filter only with the transmission in the range of UV, a UV glass (Model ZWB1 according to Chinese color filter glass standard GB15488-2010) is used as a filter. A typical ZWB1 UV glass has a main transmission wavelength ranging from 250 nm to 400 nm and another transmission wavelength ranging from 650 nm to 850 nm with a transmission below 30%. In our experiment, this UV glass filter can reduce the stray light to the noise level.

2.2.2 *Diffuser*

As mentioned in Section 1.1, the input value for the detection system is expressed in power (W). Thus, the standard irradiance from the tungsten halogen lamp must have several conversions. In practice, an integral sphere or a diffuser is used to provide a secondary source of standard power. A diffuser is cheap and operates well compared with an integral sphere[10, 19]. In this investigation, a UV-fused silica diffuser (Model DGUV10-220 from Thorlabs Inc.) is placed at the calibration distance of the lamp and on the object surface of the collection optics. The incident irradiance to the diffuser is the calibrated value, and a portion of emitted light from the diffuser is collected by the detection system. By measuring the diffuser transmission versus output angle data (Fig.3), the input power for the detection system can be calculated and then used as the input standard for the calibration.

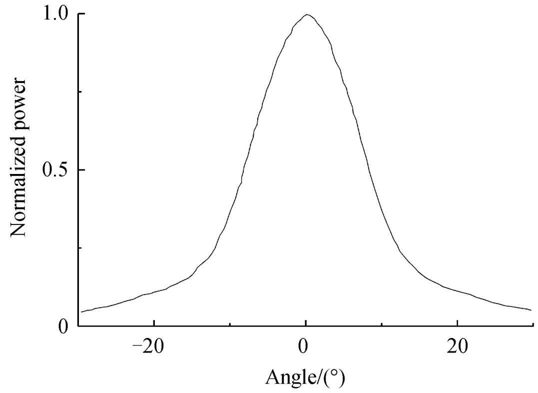


Fig.3 Diffuser transmission versus output angle

2.2.3 *Input standard power Φ*

Input power Φ in Eq. (2) can be expressed by the formula

$$\Phi_\lambda = P_\lambda S T_\lambda \tag{3}$$

where P is the standard irradiance value at the calibration distance, which is provided by the certificate of the FEL lamp. S is the effective area of the secondary source, which is a Φ 1.5 mm circuit based on the optics of the detection system (Fig.2). Transmission T is the product of three factors that can be measured or calculated: the spectral transmission of the filter, the spectral transmission of the diffuser, and the power ratio of collected input light to the total light from the secondary source. Combining these factors, the input power which as a function of wavelength (Φ_λ) is shown as Fig.4. The uncertainty of Φ_λ mainly comes from the uncertainty of the irradiance of the standard source and the uncertainty of T_λ from the filter and diffuser, and it changes little in the spectral range, so the uncertain value of Φ_λ rise high around 375 nm simultaneously with the value of Φ_λ.

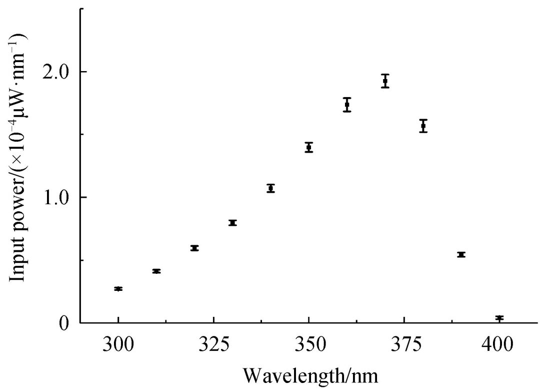


Fig.4 Input power versus wavelength Φ_λ

2.3 Experimental setup

Based on the methods mentioned above, the absolute calibration setup is shown in Fig.5. The lamp equipped with an 8.1 A, 1 000 W current power source is placed on a poster at a certain distance from the collection system. The collection system is placed in a black oxide iron box to avoid the stray light in the room. The aperture of the box is Φ 20 mm. The diffuser, filter, and collection lens are placed behind the aperture . The distance between the diffuser and lamp filament center is 0.5 m, which is the calibration

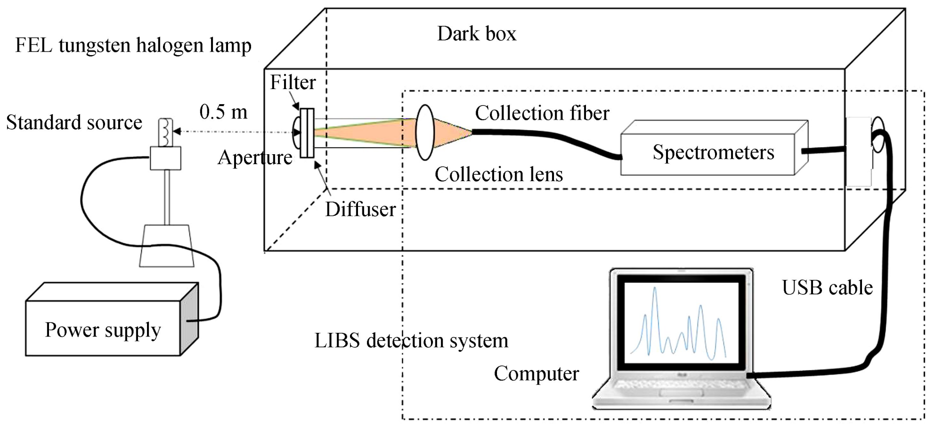


Fig.5 Experimental setup for the calibration

distance. The spectrometer is also placed in the box, and its USB cable (for data transmission) is inserted through another hole in the box.

3 Results and discussion

3.1 Absolute spectral response of the detection system

Instrument output V_λ is 10 times average of the spectral intensity obtained through the spectrometer software (Fig.6), and integral time is 3.5 s. In Fig.6, the low intensities around 400 nm proves that the filter works well in reducing the stray light. Then, the absolute spectral response of the LIBS detection system is obtained by Eq. (2) shown in Fig.7. The spectral response is the discrete values corresponding to each CCD pixel, and it is the characteristics of the entire detection system. The uncertainty of the spectral response increased according to the uncertainty of the incident power and the error of the detected instrument output. The lower output intensities near 300 nm and 400 nm caused the greater uncertainty. Thus, only the wavelength range from 310 nm to 385 nm is considered, with the Relative Standard Deviation (RSD) less than 3%, which means the uncertainty is 2.15% (2 standard deviation estimate). In order to calibrate the other spectral ranges, the filter should be replaced.

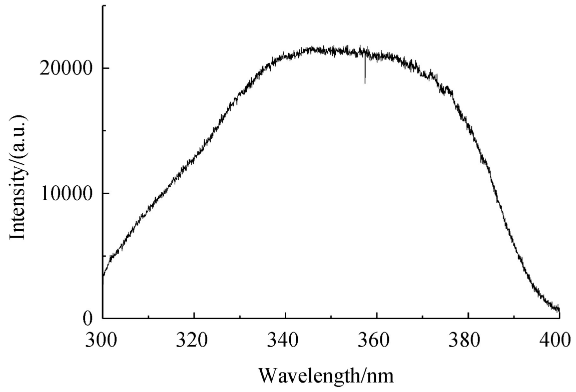


Fig.6 Instrument output V_λ

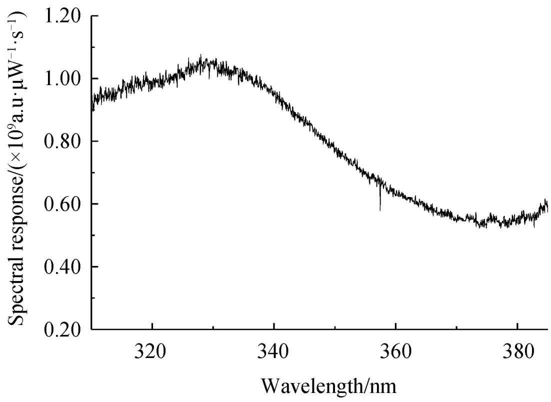


Fig.7 Absolute spectral response of the LIBS detection system in the range of 310～385 nm

3.2 Uncertainty of the absolute calibration

The absolute spectral response of the LIBS detection system is obtained in the range of 310～385 nm. On the basis of Eqs. (2) and (3), the uncertainty of absolute spectral response R has many sources, in which several of them are difficult to be calculated. Thus, a rough value of uncertainty is estimated by considering the main sources.

Firstly, the uncertainty of input irradiance P in Eq. (3) is obtained from the uncertainty of the certified irradiance value (1.1%～2.1% mentioned in Section 2.2.2) and the uncertainty of the alignment of the experimental setup, and based on the results of several studies[13], the latter is small and the former is dominant. Secondly, the primary noise sources are dark current, readout, and A/D converter noises for an unintensified CCD[9]. The uncertainty of spectrometer output V is obtained from these noises. By taking these noises as normal distribution, the 10 times averaged RSD 1%～3% in the range 310～385 nm result in an uncertainty of 0.72%～2.15% (2 standard deviation estimate). By the same method, the recalibrated transmissions of the filter and diffuser are estimated to have uncertainties less than 2.3% and 1%, respectively (2 standard deviation estimate). At last, the diffuser transmission versus output angle data from THORLABS Inc. is supposed to be less than 5%. Combing these uncertainties, according to Eqs. (2) and (3), the uncertainty transfer formula should be as

$$\Delta R_{\Phi,\lambda}=\sqrt{(\Delta V_\lambda)^2+(\Delta P_\lambda)^2+(\Delta T_\lambda)^2}=\sqrt{(2.1\%)^2+(2.15\%)^2+[(2.3\%)^2+(1\%)^2+(5\%)^2]}=6.35\% \tag{4}$$

where Δ refers to the uncertainty of the following value, the other characters are the same with previous equations. Eq. (4) ignores several minor factors, so the uncertainty of the absolute spectral response is less than 7% (2 standard deviation estimate) for a rough estimation. To take the diffuser transmission as a function of the output angle data into consideration by further determinations, the uncertainty value can be improved. However, the noise from the spectrometer limits the accuracy both in the absolute and relative spectral response.

3.3 Using absolute spectral response in LIBS

The absolute spectral response shown in Fig.7 is used to correct the spectral data from a LIBS setup. The LIBS setup is shown in Fig.8 including the detection system. It is operated in normal atmosphere. The laser pulse is of 1 064 nm, 1 Hz and 12 mJ. The target is a Fe plate. At a delay time 0.5 μs from the generation of the laser induced plasma, the spectrometer begins measurement.

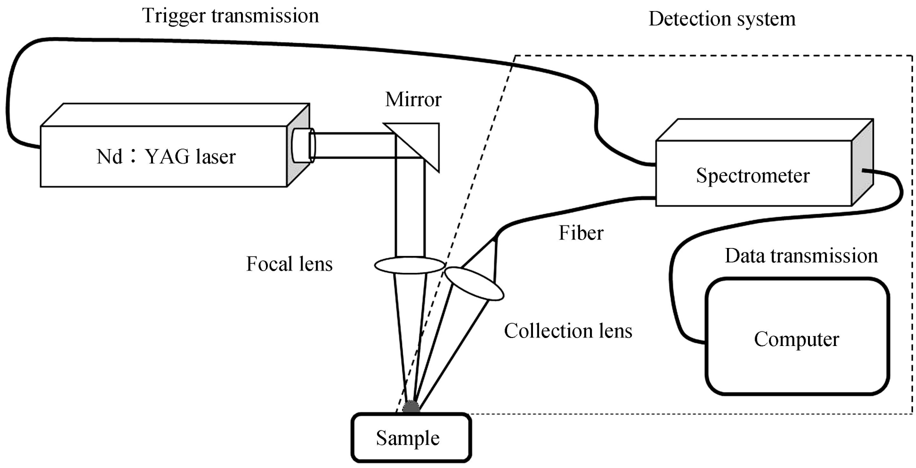


Fig.8 LIBS setup

When the setup is operated, instrument output V'_λ is obtained. The output is corrected to get real spectral distribution collected by the detection system by formula

$$I_\lambda = \frac{V'_\lambda}{R_\lambda \cdot \Delta\lambda_\lambda} (\mu\text{J/nm}) \tag{5}$$

or

$$I_\lambda = \frac{V'_\lambda}{R_\lambda \cdot \Delta\lambda_\lambda \cdot h\nu} (\text{Photons/nm}) \tag{6}$$

where I refers to the real spectral distribution by unit of energy or number of photons, R refers to the spectral response, $\Delta\lambda$ refers to the spectral resolution, $h\nu$ refers to the energy of a single photon, and subscript λ refers to the wavelength corresponding to the CCD pixel. The real spectral distribution is shown in Fig. 9. It is the characteristic of the laser induced plasma, so that the data can be compared between the different setup.

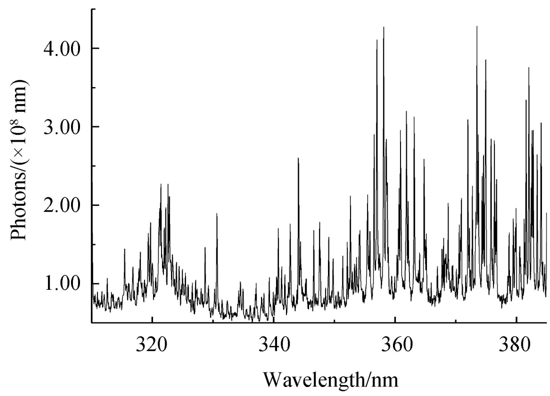
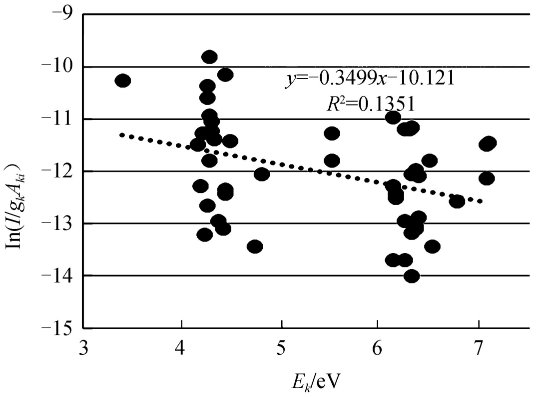


Fig.9 Corrected spectral data (Real spectral distribution collected by the detection system)

The absolute spectral response can also normalize the spectral response of the channels of the detection system (In this study, a channel is related to a CCD pixel). Boltzmann plot is used to show this. Boltzmann plot is commonly used to compute the plasma temperature. Though the integral time of the unintensified CCD in the detection system is quite long (at least 2 ms), it still shows that the temperature computing is greatly improved by using the absolute spectral response. In Fig.10, the plots are Boltzmann plot using Fe I lines identified from Fig.9, I is the intensity of the spectral line by number of photons, g_k is the degeneracy of the upper energy level k, A_{ki} is the transition probability and E_k is the upper energy by unit of eV; then the slope of the fitted straight line is $1/T$, where T is the plasma temperature by unit of eV. As shown in Fig.10, when using instrument output directly, the correlation coefficient R^2 of the fitted line is very small, but when using spectral data corrected by absolute spectral response, R^2 grows quite large. This proves the necessity of spectral calibration of LIBS detection system.



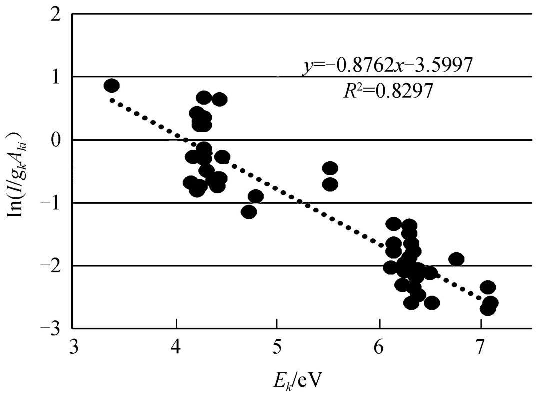


Fig.10 Boltzmann plot made using Fe I lines

4 Conclusion

In this paper, an absolute spectral calibration setup is built to calibrate the LIBS detection system. The FEL lamp equipped with a UV glass filter and a diffuser provides an economical standard source. The absolute spectral response of the LIBS detection system is obtained in the range of 310～385 nm, and its uncertainty is estimated to be less than 7% (2 standard deviation estimate). The absolute calibration of the LIBS detection system satisfies the calculations using the spectral intensity ratios and also aids to obtain the absolute intensities in radiometric units. Therefore, it serves as a significant tool to the quantitative analysis of LIBS and also provides a way to evaluate the hardware of the LIBS detection system.

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