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Effects of experimental parameters on elemental analysis of coal by laser-induced breakdown spectroscopy

Jie Li [a], Jidong Lu [a,*], Zhaoxiang Lin [b], Shunsheng Gong [c], Chengli Xie [a], Liang Chang [b], Lifei Yang [a], Pengyan Li [a]

[a] State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, Wuhan 430074, China
[b] Laboratory for Laser Spectrum Research, South-Central University for Nationalities, Wuhan 430074, China
[c] Wuhan Institute of Physics and Mathematics, Chinese Academy of Sciences, Wuhan 430071, China

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ABSTRACT

The purpose of this work is to improve the precision of the elemental analysis of coal using laser-induced breakdown spectroscopy (LIBS). The LIBS technique has the ability to allow simultaneous elemental analysis and on-line determination, so it could be used in the elemental analysis of coal. Organic components such as C, H, O, N and inorganic components such as Ca, Mg, Fe, Al, Si, Ti, Na, and K of coal have been identified. The precision of the LIBS technique depends strongly on the experimental conditions, and the choice of experimental parameters should be aimed at optimizing the repeatability of the measurements. The dependences of the relative standard deviation (RSD) of the LIBS measurements on the experimental parameters including the sample preparation parameters, lens-to-sample distance, sample operation mode, and ambient gas have been investigated. The results indicate that the precision of LIBS measurements for the coal sample can be improved by using the optimum experimental parameters.

1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is a laser based, rapid and sensitive optical diagnostic technique used to detect certain atomic species. The foundation for LIBS is a solid state, short-pulsed laser that is focused on a sample to generate a high-temperature plasma. When the plasma cools, the excited atomic, ionic, and molecular fragments produced within the plasma emit radiation that is characteristic of the elemental composition of the material in the volatilized sample. The LIBS technique has been used extensively for analysis of elemental concentrations in a variety of solid [1], liquid [2], gas [3], and aerosol [4] samples.

Simultaneous elemental analysis is required in the assessment of the quality of coal. Laser-induced breakdown spectroscopy has ability to allow simultaneous determination and detect the low-atomic number elements, so it could be used in the on-line elemental analysis of coal. Many researchers have investigated the analysis of coal by means of laser-induced breakdown spectroscopy [5–15]. The coal sample form can be lump, powder or pellet. Zhang et al. [15] used a powder coal sample, but more researchers such as Wallis [8] and Mateo [12] have used the pellet coal sample for the LIBS measurements. The characteristics of the laser-induced plasmas may be different for different coal sample forms. The different coal sample forms influence the precision of LIBS measurements in different ways. A pellet coal sample is frequently used, but it differed from the pellet sample made from a homogeneous mixture. Many investigations have been undertaken on the effects of experimental parameters on alloy samples or homogeneous pellets [16,17]. It is difficult to guarantee precise and accurate quantitative results in LIBS measurements, especially for the heterogeneous materials such as coal. As far as we know, there are no papers that consider the effects of the experimental parameters on the precision of coal analysis by LIBS.

The focus of the present paper is to identify and quantify the variables that affect the precision of LIBS measurements for pellet coal samples. Important analysis parameters which influence the precision of coal analysis by LIBS include the sample preparation parameters, lens-to-sample distance (LTSD), sample operation mode, and ambient gas. These parameters have been investigated in this study and it is shown that their control can improve the precision of LIBS measurements. Furthermore, the calibration is closely related to the accuracy which is also important for LIBS analysis. The calibration curves of the coal sample are given in this paper to allow the comparison between the LIBS analytical results and the certified analytical results.

* Corresponding author.
E-mail address: jdlu@mail.hust.edu.cn (J. Lu).

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2. Experimental

A schematic diagram of the experimental set-up is shown in Fig. 1. A pulsed Q-switched Nd:YAG laser (Spectra-Physics, model Pro 290) is used to generate the plasma. The laser operates at the 1064 nm with 10 ns pulse width and 600 mJ pulse energy. The laser energy is reduced to approximately 30 mJ by means of an optical attenuator (Beamtech), consisting in a half-wave plate that rotates the polarization plane of the laser light and a polarizing beamsplitter cube. The laser beam is focused on the sample via a lens with 195 mm focal length. The sample is positioned on a rotation stage. The power density (calculated at the focal length of the lens) on the sample is on the order of 10^{10} W/cm^2.

The light emitted by the plasma is collected by an optical collector, and is fed to the slit of an Echelle spectrograph (Andor, model Mechelle 5000) through a 2-m-long optical fiber. The spectrograph provides a constant spectral resolution ($\lambda/\Delta\lambda$) of 4000 over a wavelength range 200–900 nm. The plasma dispersed light is detected by using a gated, intensified charge-coupled device (ICCD), Andor, model DH 734. The ICCD consists of 1024×1024 elements, the size of the detector chip is 13 mm $\times$ 13 mm and the spectral response range is 185–850 nm. The ICCD intensifier has a diameter of 18 mm, ensuring that all pixels of the array are active. Before the experiment, a wavelength calibration using an Hg lamp (Ocean Optics, model HG-1) and a spectral response calibration using a deuterium–halogen lamp (Avantes, model AvaLight-DH-CAL) are carried out. A digital delay/pulse generator (Stanford Research Systems, model DG535) is used, and the Q-switch is triggered by the DG535 synchronized to the data acquisition system controlled by a computer. An optimum delay time of 0.5 μs was selected to avoid the continuum emission. A gate width of 2 μs was used which collected a large fraction of the elemental emission. Fifty summed spectra comprised one measurement, which was then repeated five times.

One bituminous coal sample from Pingxiang mine in China was received and used in this study. The coal sample was analyzed by a certified chemical analysis method before the LIBS experiments were undertaken.

The sample preparation parameters, lens-to-sample distance, sample operation mode, and ambient gas can affect coal analysis by LIBS. In this study, these parameters were systematically changed and their effects on the repeatability were studied. The results of repeated measurements were used to determine the repeatability of LIBS measurement. The relative standard deviation (%RSD) was used to evaluate the repeatability, and it can be computed as

$$\%\mathrm{RSD} = 100\% \times \left[\sum (x_i - M)^2/(n-1)\right]^{1/2} \Big/ M \quad (1)$$

where n is the number of a set of measurements; x_i is the result of each measurement; M is the arithmetic mean value of the set of repeated measurements.

3. Results and discussion

3.1. Spectrum analysis

The basis of LIBS measurement is the analysis of the plasma spectrum which contains information about the elements in the sample. This information is in the form of emission lines, located at specific wavelengths [18]. The emission spectra of coal obtained by laser-induced breakdown spectroscopy were recorded. A representative spectrum of coal in the 240–850 nm spectral region is shown in Fig. 2, where the main peaks were identified using the National Institute of Standards and Technology (NIST) electronic database [19]. This spectrum shows a high density of emission lines resulting from the complex composition of coal, and the spectrum reveals the key inorganic components of coal such as Ca, Mg, Fe, Al, Si, Ti, Na, and K. In addition, organic

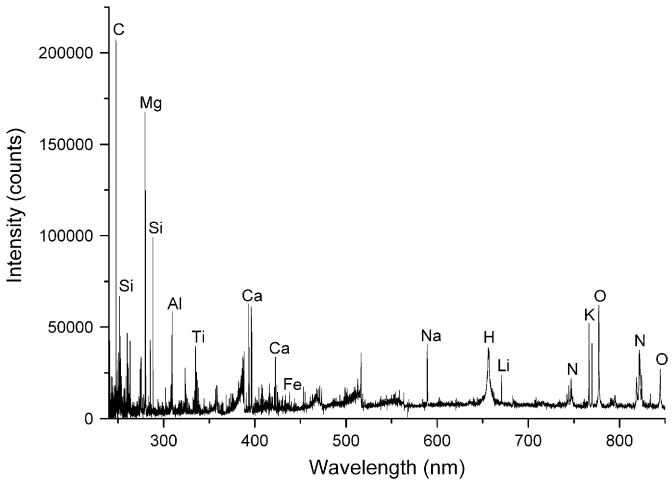

Fig. 2. Emission spectrum of the coal sample by laser-induced breakdown spectroscopy.

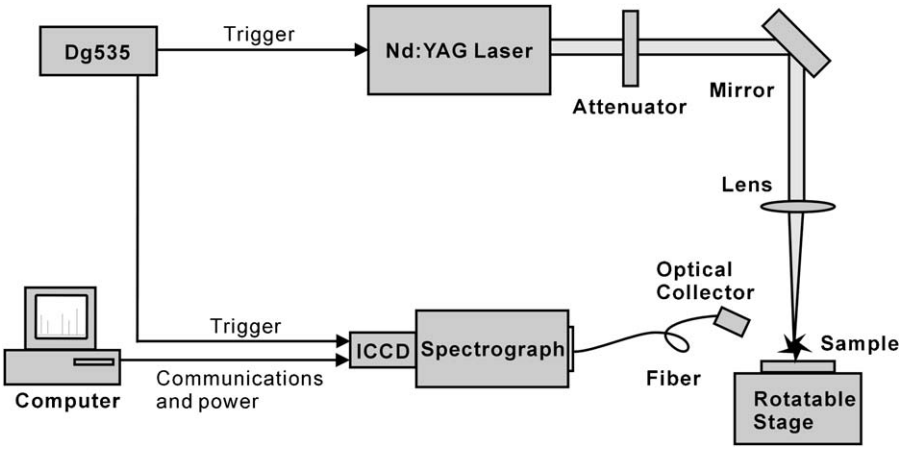

Fig. 1. LIBS experimental set-up.