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Rapid analysis of heavy metals in the coal ash with laser-induced breakdown spectroscopy

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ABSTRACT

In this study, laser-induced breakdown spectroscopy (LIBS) was applied for the qualitative elemental analysis of coal ash. The spectrum of the ordinary coal ash indicated that coal ash contains elements of Al, Fe, Cu, Ca, Mn, Ti and so on. Sulfates produced by the reaction of metal oxides in coal ash with the acid gases in the atmosphere are the main causes of haze-fog formation. To simulate the haze, eight solutions with different Pb concentrations were prepared and coal ash samples were soaked in solutions and then dried thoroughly. The spectra were obtained from these contaminated coal ash samples with the LIBS technique. To accurately identify the spectral lines of Pb in the spectrum, the spectrum of pure Pb were selected as a reference and the spectral lines of Pb were determined. At the same time, an internal standard method was used to quantitatively analyze the value of the component of Pb/Al with a calibration curve that had a linear correlation coefficient (R^2) of 0.98648, which indicates rough estimation of Pb content can be achieved by the intensity of Pb in the spectrum. The results of the experiments show that LIBS technique can be employed for the rapid detection and analysis of metal elements in coal ash and provide a brand-new method for the detection of atmospheric environment based on the content of Pb.

1. Introduction

The coal ash is the product of the complete burning of coal, mainly including various metals and non-metal oxides and salts, which is an important parameter in coal utilization. Coal was widely used for industrial production beginning with the industrial revolution in the late 18th century, which brought great productivity to the society and promoted the development of industrialization [1,2]. Combustion of coal, however, as the largest source of secondary particles and a main emission source of primary particles, a large amount of coal ash reacts with various substances in the atmosphere to form haze, which has caused a huge threat to human health [3,4].

Pb is one of those carcinogenic and toxic heavy metal elements, seriously damaging human health and even causing cancer [5–7]. In addition, it also has negative impact on ecosystem and severely pollutes environment [8]. Nevertheless, due to heavy metal

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elements such as Pb in haze, it is of great significance to conduct qualitative analysis [9].

Laser-induced breakdown spectroscopy (LIBS) is a type of the atomic emission spectroscopy that applies highly energetic pulses to various samples in solid, liquid, gaseous and aerosol forms [10–12]. In comparison with other techniques, LIBS technique has many advantages such as rapid and precise response, simultaneous muti-element analysis, high sensitivity, cost effective and so on [13–15]. As a new material identification analysis technology, LIBS can be used both in the laboratory and on-line detection in industrial sites [16]. What's more, LIBS has been widely applied in hydrology, geological prospecting, environmental monitoring, scientific research and other fields of application successfully [17,18]. What's more, the determination of coal ash content by LIBS technology is of great significance for the correct evaluation of coal quality and processing and utilization [19,20]. In recent years, domestic and foreign researchers have made some attempts on the application of LIBS technology in coal quality analysis and made some progress. Feng et al. [21] proposed a method of PLS quantitative analysis based on dominant factors for low accuracy of LIBS analysis of coal quality components, which improved the measurement accuracy to some extent. Mateo et al. [22] analyzed the influence of different laser wavelengths and sample placement in the measurement process on the measurement of some secondary elements contained in coal and they found that the short wave length laser is more favorable for accurate measurement. These findings provide a favorable reference for the application of LIBS in coal ash.

In the present work, a sample of coal ash obtained from a steel company was tested based on laser-induced breakdown spectroscopy and the spectra of the elements were analyzed. To simulate haze containing Pb, the Pb compound was added to the coal ash. To verify the accuracy of LIBS technology, test samples were compared with the ordinary coal ash, which does not contain Pb. In this paper, a calibration curve was obtained and can be taken as a reference line for Pb detection in the future by quantitative analysis of Pb in coal ash. LIBS technology provides a new method for the detection and analysis of coal ash.

2. Experimental

2.1. Experimental setup

The schematic diagram of experimental setup is shown in Fig. 1. The Q-switched Nd: YAG laser used as the excitation laser was operated at a fundamental wavelength of 1064 nm, the maximum energy is 600 mJ in a single laser pulse and the pulse energy for the employed laser beam in the current measurement is around 100 mJ per pulse with 10 ns duration at a frequency of 5 Hz. The laser beam was focused onto the sample surface using a focusing lens (f = 300 mm), of which the irradiation energy was collected with a fiber-optical probe. The emission signal from the plasma was transferred via a fiber to a spectrometer system, at the same time, the experimental platform keeps moving to reduce the influence of sample on spectral signal after being bombarded by pulse laser. The spectrum was recorded on a computer, and the PLSUS software was utilized to identify emission lines. The possible elements could be identified according to the spectrum. The spectrometer and wavelength shift were calibrated via the pure metal sample. The optical fiber spectrometer we used is called AVANTES and its model number AvaSPEC-ULSi2048-USB2-SPC-1*. The spectral resolution of spectrometer and the detection delay are 1 nm and 1.5 μs, respectively. To increase the stability and reduce the standard deviation of the spectral intensities, 10 measured spectra were averaged.

2.2. Sample preparation

The experimental samples from a steel company are powdered coal ash collected after organized discharge, which were divided into 8 groups based on different concentrations of Pb acetate solution. These solutions with different quantity of $(CH_3COO)_2Pb{\bullet}3H_2O$ were prepared and the concentration of these solutions were 100 ppm, 200 ppm, 0.2%, 0.4%, 0.6%, 0.8%, 1%, respectively. These samples were dried at a drying temperature of 120 degrees for 24 h after mixing. To obtain a better LIBS signal, the tablet machine was used to press the coal ash into coal lump of 10 mm in diameter and 10 mm in thickness. Finally, these block samples were performed by LIBS test.

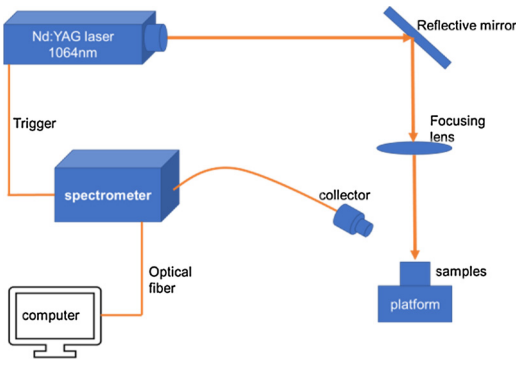

Fig. 1. Schematic diagram of the LIBS setup.