

Rapid Detection of Zinc in Coal Ash by Laser Induced Breakdown Spectroscopy

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Abstract The composition of coal ash refers to complete combustion of the minerals in the coal, producing a variety of metals and non-metallic oxides and salts, which is an important parameter when using coal. Coal has been widely used in the production and people's life, as an important energy substance. A large amount of coal dust (coal ash) from coal combustion was released into the atmosphere and interacted with various substances in the atmosphere to form haze. A series of physico-chemical reactions take place between metal oxides in coal ash and small droplets in the air, which result in the formation of haze. In this study, laser induced breakdown spectroscopy (LIBS) was employed to analyze the elements in coal ash. The experimental samples were provided from a steel company, which was divided into seven parts. Distilled water and 0.1%, 0.2%, 0.2%, 0.4%, 0.8%, 1% zinc sulfate solution were added into samples, which were labeled with number 1~7 respectively. In order to obtain a better LIBS signal, the sample was powdered. The water in the solution was used to thoroughly mix zinc with coal ash. In the experiment, the coal ash was pressed into 10mm diameter and 10 mm thick coal ash blocks by using a tableting machine. In order to get accurate elemental results, X-ray fluorescence spectroscopy were also employed for reference, and the original sample did not contain zinc. Due to the uncertainty of spectral analysis and wavelength shift phenomenon, qualitative analysis of element was inaccurate. To solve this problem, four kinds of high-purity elements including iron, calcium, titanium and aluminum were separately selected. Under the same experimental conditions, four measured elemental spectral lines were compared with the corresponding spectra in the NIST atomic spectral database. All the spectra in the experiment were corrected according to the wavelength difference or shift. At this point, the elemental spectrum of pure elements can be aligned with the samples' spectrum. The samples then can be identified and confirmed when the characteristic line in the elemental spectrum is aligned with the spectrum in the samples. Because Al has similar chemical and physical property with target element, and Al is one of the major elements in coal ash and the crust, and has moderate spectral intensities. For quantitative analysis, the internal standard calibration method was used to determine the concentration of zinc in the samples. The results of simulating zinc-containing atmospheric aerosols were achieved by adding zinc to coal ash. Some other related metal elements, including iron, calcium, manganese, titanium and aluminum were also used to spike into coal ash to

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simulate atmospheric aerosols. The relative difference between the two methods is 1.78%, 3.39%, 5.17%, 0.20%. The reason for the difference may be due to the lack of resolution of the spectrometer or the impact of background noise, which could lead to the measurement error. Due to the limitations of laboratory conditions, we can't be sure whether the influence of matrix will affect the experiment results, and which will be further confirmed by future experiments. The linear correlation coefficient of zinc in coal ash was determined to be 0.995 72, indicating that the rough estimation of zinc content can be achieved by the intensity of zinc in the spectrum. The experiment concluded that LIBS technology can be used for the rapid detection of metal elements in coal ash, and this work provides a novel method for the detection of atmospheric environment based on the content of zinc. After establishing the calibration curve of the elements, the LIBS technique can be used to conduct a rapid and accurate quantitative analysis in the future.

Keywords Laser-induced breakdown spectroscopy; Coal ash; Metal; Zinc; Aerosols; Quantitative analysis
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Introduction

The composition of coal ash refers to complete combustion of the minerals in the coal, producing a variety of metals and non-metallic oxides and salts, which is an important parameter when using coal. Since the Second Industrial Revolution, coal has been widely used in the production and people's life, as an important energy substance. A large amount of coal dust (coal ash) from coal combustion was released into the atmosphere and interacted with various substances in the atmosphere to form haze^[1].

There is plenty of heavy metal-zinc in the haze. Even if zinc is one of the indispensable trace elements in human life, it will also do great harm to the human body when exceeding a certain dose^[2]. The absorption of iron in human body could be inhibited because of excessive zinc, resulting in the involvement of iron in the hematopoietic system; there by intractable iron deficiency anemia appears. In the case of high levels of zinc in human body, it is difficult to cure anemia even with iron preparations^[3]. Similarly, the atmosphere with excessive zinc will be dissolved in water, which could cause great damage to the aquatic animals and plants^[4]. In addition, the corrosion to outdoor buildings and accelerations of the aging of materials will be aroused because of a large amount of zinc present in haze^[5-6].

Conventional detection of zinc includes inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS)^[7-8]. However, these conventional methods are cumbersome, and the sample needs to be pre-processed and cost too much. Laser Induced Breakdown Spectroscopy (LIBS) is a novel elemental detection method that uses high-energy laser pulses to act on a sample to be measured, collected with a spectrometer. The atomic and ion spectra in the plasma are obtained to achieve material characterization and quantitative analy-

sis^[9-10]. LIBS technology has the advantages such as simple operation, short detection time, multi-element detection and so on, which enable rapid detection of the sample components^[11].

In this paper, a sample of coal ash obtained from a steel company was tested based on LIBS technology. The elements were analyzed, and also the spectra of these elements were obtained. To simulate haze containing zinc, the zinc compounds were added to the coal ash. In order to verify the accuracy of LIBS technology, test samples were compared with the ordinary coal ash, which did not contain zinc. After the quantitative analysis of zinc in coal ash, a calibration curve can be obtained as a reference line for zinc detection in the future. LIBS technology provides a new method for the detection and analysis of coal ash afterwards.

1 Experimental setup

The schematics of the LIBS experiment are shown in Figure 1. The spectrometer was provided by Avantes, and its grating is from 200 to 850 nm. The fixed delayed time is 36.8 μ s. The Q-switched Nd-YAG laser was used in the experiment, which is operated at a fundamental wavelength of 1 064 nm, and 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 is focused on the surface of the samples by a lens with a focal length of 300 mm to form a focal spot of about 100 μ m in diameter. The resulting laser plasma spectral signal is coupled to an optical fiber through a quartz lens with a focal length of 50 mm and then it is transmitted to a spectrometer for spectral splitting and detection. To increase the stability and reduce the standard deviation of the spectral intensities, 10 measured spectra were averaged. The spectrometer and wavelength shift were calibrated via the pure metal samples.

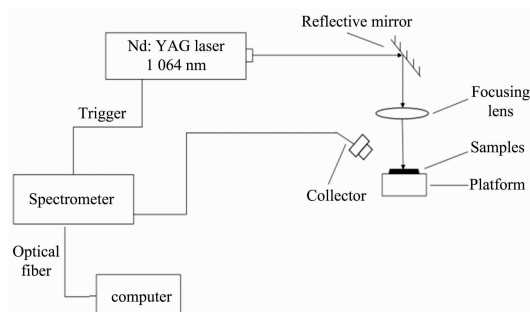


Fig. 1 Experimental Device

2 Sample preparation

The experimental samples were provided from a steel company, which was divided into seven parts. Distilled water and 0.1%, 0.2%, 0.2%, 0.4%, 0.8%, 1% zinc sulfate solution were added into samples, which were labeled with number 1~7 respectively. After mixing well, these samples were dried. In order to obtain a better LIBS signal, the sample was powdered. The water in the solution is used to thoroughly mix zinc with coal ash. In the experiment, the coal ash was pressed into 10 mm diameter and 10 mm thick coal ash blocks by using a tableting machine. In order to get accurate elemental results, X-ray fluorescence spectroscopy were also employed for reference, and the original sample did not contain zinc.

3 Results and discussion

3.1 LIBS elemental analysis of ordinary coal ash

Figure 2—Figure 4 show the LIBS spectra of coal ash. It can be seen from the figures that the experiment has detected the characteristic spectra of Ca, Fe, K, Mn, Ti and Al were indicated in Figure 2. Undetected elemental sulfur is because the characteristic line of elemental sulfur is mainly in the infrared band, which is beyond the spectral range of this experiment.

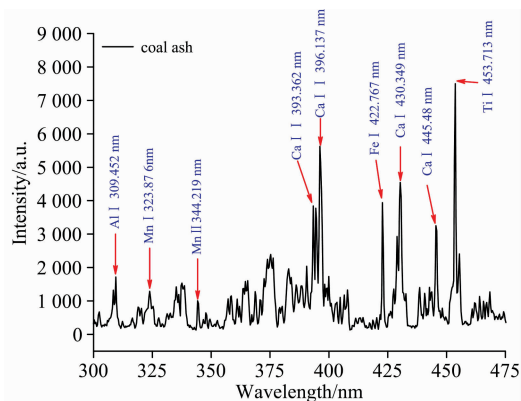


Fig. 2 The LIBS spectrum of coal ash in 300~475 nm

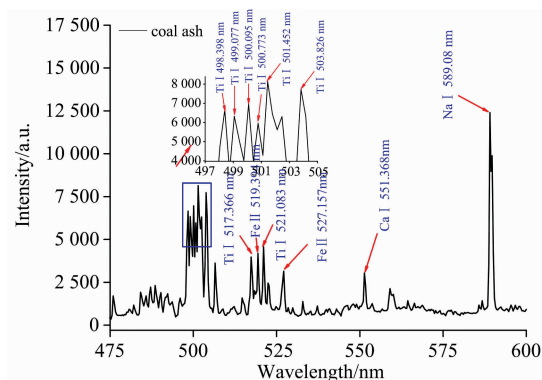


Fig. 3 The LIBS spectrum of coal ash in 475~600 nm

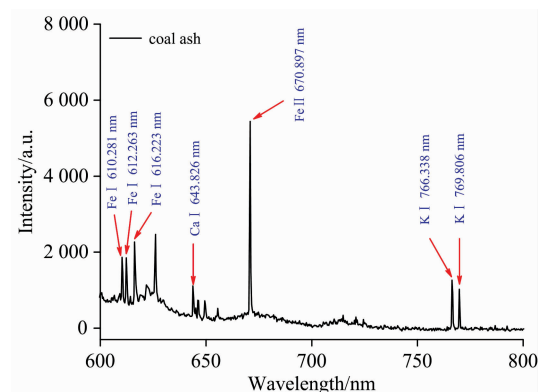


Fig. 4 The LIBS Spectrum of coal ash in 600~800 nm

Due to the uncertainty of spectral analysis and wavelength shift phenomenon, qualitative analysis of element was inaccurate. To solve this problem, four kinds of high-purity elements including iron, calcium, titanium and aluminum were separately selected. Under the same experimental conditions, four measured elemental spectral lines were compared with the corresponding spectra in the NIST atomic spectral database^[12]. All the spectra in the experiment were corrected according to the wavelength difference or shift. At this point, the elemental spectrum of pure elements can be aligned with the samples' spectrum. The samples then can be identified and confirmed when the characteristic line in the elemental spectrum is aligned with the spectrum in the samples.

Figure S1—S4 show the comparative spectra of normal coal ash, pure Al, Ca, Mn and Fe, respectively. Al has characteristic peaks at 396.137, 394.403, 309.452 and 308.395 nm, which can be aligned with the characteristic peaks of the sample. Ca has characteristic peaks at 430.349 and 445.48 nm. Fe has characteristic peaks at 519.394, 527.157, 610.281, 612.263 and 616.223 nm. Ti has characteristic peaks at 453.713, 498.398, 500.095, 501.452, 506.537, 517.366, 519.394 and 521.083 nm.

3.2 Element Analysis of LIBS Containing Zinc in Coal Ash

The experimental results show that there is no zinc in the

coal ash. In the second experiment, industrial zinc-containing atmospheric haze was simulated by adding zinc sulfate to the coal ash. To verify the accuracy of the LIBS measurement, the spectrum of coal ash was compared with the spectrum of the ash containing 1% zinc sulfate, which are shown in Fig. 5 and Fig. 6.

To accurately identify zinc in the spectrum of the coal ash immersed in zinc solution, pure zinc was conducted to obtain the spectra to calibrate the spectrum of zinc in coal ash, which is shown in figure 5. Eight spectral lines of zinc were observed (328.441, 330.548, 334.758, 468.086, 472.562, 481.053, 589.080, 636.289 nm).

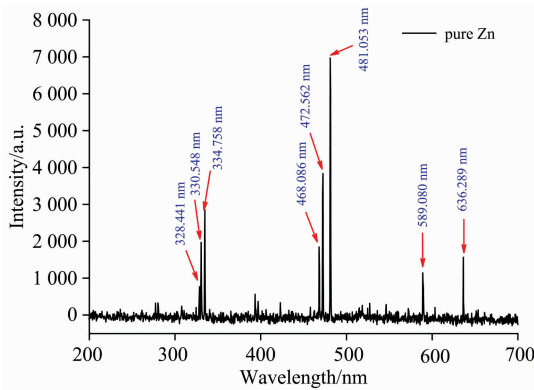


Fig. 5 The spectrum of pure zinc

3.3 Quantitative Analysis of Zinc in Coal Ash

Figure 6 shows the spectra in the 300 to 495 nm bands of normal coal ash, coal ash in a 1% zinc solution and pure zinc. By comparing these three spectra, four lines (330.548, 334.758, 473.526 and 481.053 nm) in the sample spectrum can be easily identified. The spectrums of zinc are also confirmed in the literature^[13]. As can be seen from Figure 6 characteristic spectrum line with the highest sensitivity is 481.053 nm. After comparative analysis of the experimental data, it was found that the characteristic line of zinc (Zn I : 481.053 nm) is the least affected by the other elements in the experiment. And that's why we chose this peak to calculate the content of zinc.

Figure S5 shows the relative intensities of the two zinc lines, and the relative intensity increases with the concentration of zinc. For quantitative analysis, the internal standard calibration method was used to determine the concentration of zinc in the samples.

The estimated detection limit for LIBS technique is about 0.2%. According to the experimental results, when coal ash is 0.2% zinc solution, it can be detected. Due to experimental conditions and some instrumental reasons, when the concentration of zinc in the coal ash is as low as 0.1%, the zinc emission intensity is very low, almost consistent with the noise.

The quantitative analysis formula of LIBS is Lomakin-Scheibe formula^[14]

$$I = ac^b \tag{1}$$

where I is the observed intensity of the spectral line, a is the experiment constant, c is the concentration of the objective element, b is the self-absorption coefficient. At the same time due to the content of zinc is low, the self-absorption phenomenon is not obvious, so its influence is ignored, so the self-absorption coefficient can be ignored, $b=1$.

$$I = ac \tag{2}$$

The element of Al was chosen as the internal standard for the experiment because Al has similar chemical and physical property with target element, and Al is one of the major elements in coal ash and the crust, and has moderate spectral intensities. So the above equation becomes

$$\sum (I_{Zn}/I_{Al}) = a_{Zn}c_{Zn}/a_{Al}c_{Al} \tag{3}$$

In Figure 7, the calibration curve was fitted by fitting the data with the concentration ratio of Zn/Al as an independent variable and $\sum (I_{Zn}/I_{Al})$ as a dependent variable. And the concentration of Zn/Al in coal ash was chosen as abscissa and the laser intensity of spectrogram as ordinate, then the calibration curve of zinc was fitted. As can be seen from Figure 7, the linear correlation coefficient (R^2) of the curve is 0.99572, which means that the intensity of zinc in the LIBS spectrum is proportional to the concentration of the corresponding zinc solution.

Table 1 Comparison of standard and LIBS results

Concentration of experimental configuration/%	LIBS measurement results/%	Relative error/%
10.00	10.18	1.78
8.00	7.73	3.39
4.00	4.21	5.17
2.00	1.99	0.20

To test the accuracy of the calibration curve, the calculated value was obtained from the curve and compared with the standard value, and the results can be seen from Table 1. The exact values of zinc content are 10%, 8%, 4%, 2% and that measured values by LIBS are 10.178%, 7.729%, 4.207%, 1.996%. The relative differences between the two methods are 1.78%, 3.39%, 5.17%, 0.20%, but the results are still within the margin of error. The reason for the difference may be the lack of resolution of the spectrometer or the impact of background noise, which could lead to the measurement error. Because of the limitations of laboratory conditions, we can't be sure whether the influence of matrix will affect the experiment results, and which will be further confirmed by future experiments.

Therefore, it can be considered that the zinc concentration in the coal ash could be determined by the quantitative analysis of the zinc line by the LIBS technique.

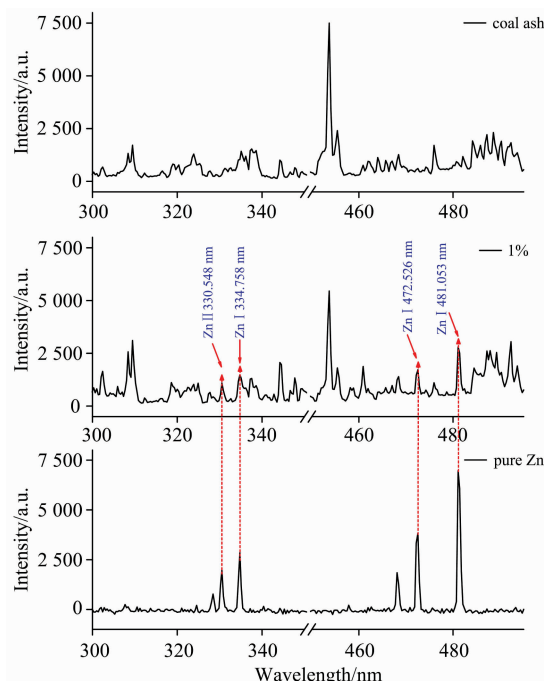


Fig. 6 The spectrum of ordinary coal ash, zinc-containing coal ash and Pure zinc

4 Conclusion

In this experiment, the elements of aluminum, iron, sodium, potassium, calcium, and manganese were found by elemental analysis of coal ash. Aluminum, iron, manganese

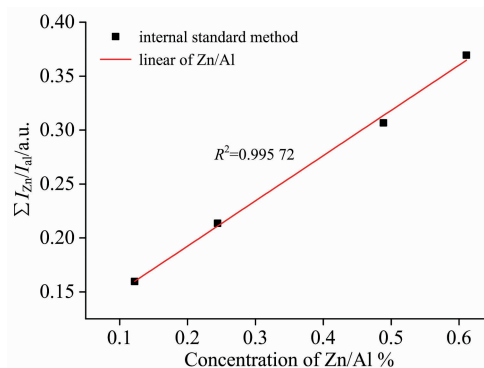


Fig. 7 Calibration curve of zinc

and calcium can be identified accurately in the experiment. By adding zinc element to the coal ash to simulate the atmospheric haze with zinc content and analyzing its content, a number of characteristic spectra of zinc and coal ash were obtained, and the linear correlation between zinc and coal ash was obtained. The coefficient was 0.99572, indicating that the content of zinc in the coal ash can be indirectly measured by the intensity of the characteristic peak of the spectrum. And the relative error from the exact value was within the error range. The experiments showed that the LIBS technology can be used for rapid detection of the composition and content of the elements in coal ash discharged by the enterprise. After establishing the calibration curve of the elements, the LIBS technique can be used to conduct a rapid and accurate quantitative analysis in the future. Furthermore, due to the high efficiency and real-time character of LIBS, this technique can also be applied to food safety, soil testing and other fields. Specific research will be further developed in the future.

References

- [1] Ma Jianzhong, Xu Xiaobin, Zhao Chunsheng, et al. *Advances in Atmospheric Science*, 2012, 29(2): 1006.
- [2] Zhang Enlou, Liu Enfeng, Shen Ji, et al. *Journal of Environmental Sciences*, 2012, 24(7): 1189.
- [3] Fekiacova Z, Cornua S, Pichat S. *Science of the Total Environment*, 2015, 51(1): 96.
- [4] Liu Mingda, Li Yue, Zhang Wei, et al. *Procedia Environmental Sciences*, 2013, 18(2013): 283.
- [5] Beata Klimek. *Bulletin of Environmental Contamination and Toxicology*, 2012, 88(4): 617.
- [6] Peng Meng, Zhu Kun, Chen Lianhong, et al. *Physical Testing and Chemical Analysis Part B: Chemical Analysis*, 2012, 48(9): 1039.
- [7] Yang Yuewei, Zhang Yuxia, Yang Xiaohong, et al. *Physical Testing and Chemical Analysis Part B: Chemical Analysis*, 2016, 52(4): 427.
- [8] Choi JaeJun, Choi Soojin, Jack J Yoh. *Applied Spectroscopy*, 2016, 70(9): 1411.
- [9] Wang Li, Xu Li, Xu Weiqing, et al. *Spectroscopy and Spectral Analysis*, 2018, 38(1): 314.
- [10] Uzma G, Junaid M, Khalid Alamgir, et al. *Spectroscopy and Spectral Analysis*, 2017, 37(10): 3266.
- [11] Farooq W A, Tawfik W, Alahmed Z A, et al. *Journal of Russian Laser Research*, 2014, 35(3): 252.
- [12] NIST Atomic Spectra Database, https://physics.nist.gov/PhysRefData/ASD/lines_form.html.
- [13] Johansson I, Contreras R H. *Ark. Fys*, 1968, 37: 513.
- [14] Lomakin B A. *Zeitschrift fur Anorganische und Allgemeine Chemie*, 1930, 187(75).

激光诱导击穿光谱技术快速探测煤灰中的重金属锌

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摘要 煤灰的成分指的是煤中矿物质的完全燃烧, 产生各种金属和非金属氧化物和盐, 这是使用煤时的重要参数。煤被广泛用于生产和人民生活, 作为重要的能源物质。大量来自燃煤燃烧的煤尘(煤灰)被释放到大气中并与大气中的各种物质相互作用而形成雾霾。煤灰中的金属氧化物和空气中的小液滴之间发生一系列物理化学反应, 这导致了雾霾的形成。在实验中, 采用激光诱导击穿光谱(LIBS)分析煤灰中的元素。实验样品由某钢铁公司提供, 分为七个样品, 并标上序号。样品分别加入蒸馏水和 0.1%, 0.2%, 0.2%, 0.4%, 0.8%, 1% 硫酸锌溶液, 分别用 1~7 号标记。为了获得更好的 LIBS 信号, 样品被研磨为粉末状, 并使用蒸馏水使硫酸锌与煤灰充分混合。通过使用压片机将煤灰压制成 10 mm 直径和 10 mm 厚的煤灰块。为获得准确的元素结果, X 射线荧光光谱也被用作参考, 并且原始样品不含锌元素。由于光谱分析和波长漂移现象的不确定性, 因此实验中, 分别选择了铁, 钙, 钛和铝四种高纯单质。在相同的实验条件下, 将四条测量的元素谱线与 NIST 原子光谱数据库中相应的谱图比较。实验中的所有光谱根据波长差或偏移进行校正。此时, 纯单质的元素谱线可以与样品的光谱对齐。当元素谱中的特征线与样品中的谱线对齐时, 样品就可以被识别和确认。由于铝元素与目标元素具有相似的化学和物理性质, 铝元素是煤灰和地壳中的主要元素之一, 具有中等的光谱强度。因此将铝元素作为内标元素, 运用内标校准方法来确定样品中锌的浓度。模拟含锌大气气溶胶是通过向煤灰中添加含锌元素来实现的。还有一些其他的金属元素, 包括铁, 钙, 锰, 钛和铝也被用来加入煤灰中, 用以模拟大气气溶胶。两种方法的相对差异分别为 1.78%, 3.39%, 5.17%, 0.20%。造成差异的原因可能是由于光谱仪缺乏分辨率或背景噪声的影响, 这是可能导致测量误差的原因之一。由于实验室条件的限制, 无法确定基底是否会影响实验结果, 这将在未来的实验中得到进一步的证实。实验拟合曲线测得煤灰中锌的线性相关系数为 0.995 72, 这表明可以通过粗略估算锌的激光强度来估计煤灰中的锌含量的实现。实验结果证明 LIBS 技术可用于煤灰中金属元素的快速检测, 为基于锌含量的大气环境检测提供了一种新方法。在建立元素的校准曲线后, LIBS 技术将来可以用来进行更快速, 更准确的定量分析。

关键词 激光诱导击穿光谱; 煤灰; 重金属; 锌; 气溶胶; 定量分析

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