Effects of KCl and KI additives on soil breakdown spectroscopy characteristics*

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In order to enhance the spectral characteristics of the laser-induced breakdown spectroscopy (LIBS), the spectral signals of soil samples with different concentrations of KCl and KI additives were analyzed. The optimal laser energy, the lens to sample distance (*LTSD*) and the delay time were determined. Under the optimum experimental conditions, the spectral intensity, signal-to-noise ratio (*SNR*) and plasma characteristics of Cd I 288.08 nm and Al I 394.40 nm in soil samples with 0%, 5%, 10%, 15%, 20%, 25% and 30% KCl and KI additives were analyzed. The experimental results show that the spectral intensities of Cd and Al in soil samples with 15% KCl are 1.33 times and 1.61 times of that of the original sample, while those with 15% KI are 1.84 times and 1.81 times. The *SNR*, plasma temperature and electron density are improved. This provides an experimental reference for improving the accuracy of LIBS in soil detection.

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Laser-induced breakdown spectroscopy (LIBS) is a spectral technology for qualitative and quantitative analysis of material components through the time-detection and measurement of the plasma emission spectrum generated by the interaction between high-energy laser and material. LIBS has the advantages of simple sample pretreatment, simple operation, real-time online detection, and simultaneous detection of multiple elements. It has been widely used in many fields such as environment[1], metallurgy[2], coal[3], agriculture[4], biomedicine[5], and space detection[6].

In order to obtain higher quality breakdown spectroscopy signal and further improve the detection ability of LIBS, the radiation intensity of the plasma can be improved to a certain extent by optimizing the experimental conditions, selecting the appropriate laser pulse energy, changing the environmental atmosphere of the sample ablation, applying the electric field and magnetic field in the laser plasma area and adopting the dual laser technology. Methods such as multi-pulse excitation[7], reducing the environmental pressure[8], and enhancing the cavity constraint[9] are all effective. There are many studies on the optimizing of the LIBS experimental parameters to enhance the detection accuracy. ZHOU et

al[10] explored the changes of spectral characteristics of laser-induced soil plasma by comparing different working parameters. The optimal operating parameters of the LIBS were determined by experiments. GUO et al[11] studied the effect of sample morphology on the characteristics of laser induced soil plasma. The results showed that the laser plasma temperature and electron density of silty soil samples were higher than those of flake soil samples under the same experimental conditions, but the element characteristic line intensity of flake soil samples was larger and less affected by soil particle size.

Pre-treatment of samples is an effective method to improve the detection accuracy. Many scholars have conducted related studies on adding effective auxiliary matrix to the samples. CHEN et al[12] studied the influence of the laser output energy (100—500 mJ) and NaCl sample additive (mass fraction 0—20%) on plasma radiation intensity. The optimal laser energy and the influence of NaCl additive on spectral quality were obtained. SONG et al[13,14] studied the influence of CsCl as a soil sample additive on plasma radiation characteristics. By comparing the plasma characteristics with and without additives, the optimal CsCl additive content was obtained. SHI et al[15] used epoxy resin adhesive and traditional polyethylene as the binders

of soil powder samples, respectively, and used LIBS technology to analyze the Fe, Ca and Cr elements in the bonded soil. The results showed that the spectral intensity of each element in the sample using epoxy resin as the binder was about twice that in the sample using traditional polyethylene as the binder, and the calibration curve of the former has better linearity and lower detection limit. JIA et al[16] prepared four groups of samples with the same graphite content using mixtures of different rock powders and graphite powders with different contents (0%, 25%, 50%, 75%). To reduce some of the pulse-to-pulse fluctuation, the internal standardization method was adopted. Four sets of calibration curves of Ca and Mg were prepared using pellet samples with the same graphite content. The effect of graphite content on laser induced plasma temperature and electron density was further studied. The results showed that the determination coefficient of the standard curve after the doping graphite is greater than that of the standard curve without doping graphite, and the stability of the spectral intensity, plasma temperature and electron density after doping were also improved. The influence of additives on the detection accuracy of the LIBS technology remains to be improved. It is rare to study the influence of additives on the spectral quality of soil samples.

In order to obtain high-quality laser spectrum and further improve the detection ability of LIBS, the relationship between laser energy, delay time, *LTSD* and spectral characteristics is investigated in this study by optimizing the experimental conditions. The optimal laser energy, delay time and *LTSD* were determined. Under these conditions, the effects of KCl and KI additives on LIBS technology in soil detection were studied. The optimal additive content was obtained by comparing the effects of KCl and KI additives on spectral characteristics. The effects of different additives on the quality of plasma emission spectrum were analyzed, and the optimization conditions for improving the quality of laser spectrum were obtained.

The main instruments in the experiment include an Nd: YAG pulse laser with the output wavelength of 532 nm, pulse width of 8 ns, pulse repetition rate of 6 Hz, and output energy of 0—100 mJ. It also includes a marine optical MX2500 spectrometer with wavelength range of 200—960 nm and resolution of 0.1 nm, a spectral acquisition and data processing system. The schematic diagram of the experimental system is shown in Fig.1. The laser beam is vertically concentrated on the surface of the sample through the focusing lens with a focal length of 100 nm after passing through the mirror. The excited plasma signal is coupled to the spectrometer through the optical fiber to complete the spectral detection and splitting process.

The samples used in the experiment were from Hebei University. The samples were naturally dried, purified, screened, and ground. Unequal amounts of KCl additive and KI additive were added, and the additive contents were 0%, 5%, 10%, 15%, 20%, 25% and 30%, respectively. The samples were divided into three groups, each containing seven samples. The sample was ground uniformly in agate,

and a suitable amount of saturated sucrose solution was added as adhesive. The prepared sample was pressed into a wafer with a diameter of 15 mm and a thickness of 7 mm by 769YP-15A tablet press. Finally, the pressed round flake samples were placed in the GZX-9070MBW type digital drum dryer for drying.
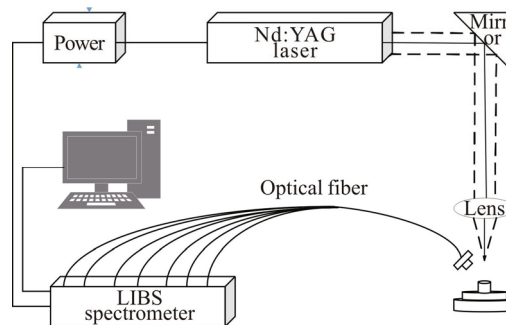

Fig.1 Schematic diagram of the experimental system

By querying the National Institute of Standards and Technology (NIST) atomic spectrum database, Cd and Al with larger emission intensity and larger transition probability were selected as the analytical lines. The plasma will be produced when the power density of the laser incident on the sample surface is greater than the critical energy density of the sample. By changing the laser energy from 44.44 mJ to 99.99 mJ, the variation trends of two Cd and Al spectral lines with laser energy were obtained, as shown in Fig.2. It can be seen that the spectral intensities of Cd and Al increase with the increase of laser energy (44.44 mJ, 55.55 mJ, 66.66 mJ, 77.77 mJ, 88.88 mJ, 99.99 mJ). As the laser energy increases from 44.44 mJ to 99.99 mJ, the intensities of Cd and Al atomic lines increase by 47.21 and 53.73 times, respectively. The analysis shows that with the increase of laser energy, the ablation amount of the sample increases, which increases the transition probability of atoms and molecules, generates more high-energy electrons, and leads to the increase of the spectral intensity of the plasma. When the laser energy reaches 99.99 mJ, the plasma produces self-absorption effect and the line intensity reaches saturation as shown in Fig.3. Therefore, the laser energy of 88.88 mJ is the most suitable choice in this study.
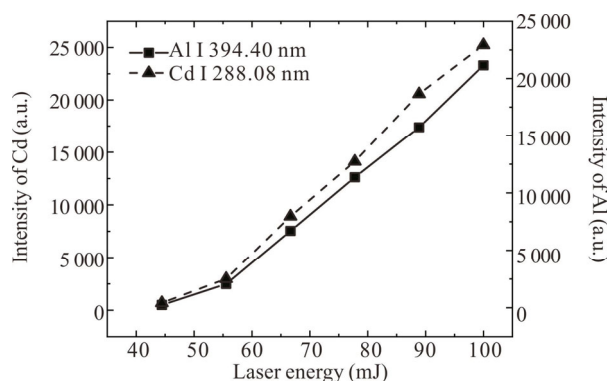

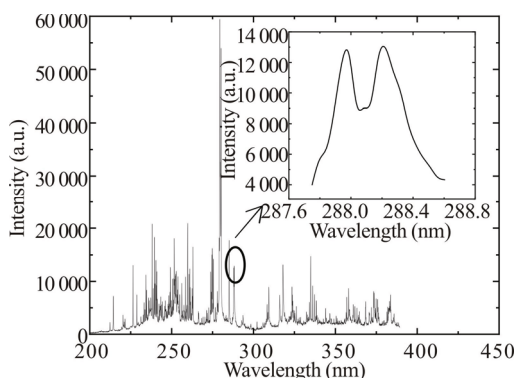**Fig.2 Spectral intensities of Cd and Al versus laser energy**

Fig.3 Spectral intensity at the laser energy of 99.99 mJ versus wavelength

Cd and Al were measured by different delay time. Fig.4 shows the change trends of signal-to-noise ratio (*SNR*) of Cd and Al with delay. Since there is a time difference between the continuous background spectrum and the characteristic spectrum, the intensity of the continuous spectrum increases first and then decreases gradually with the delay time when the optical breakdown occurs. The spectral intensity of the characteristic spectrum in the continuous background decreases gradually and then increases before decreasing again with the increase of the delay time. Therefore, the influence of continuous background spectra on the atomic emission spectra is reduced by controlling the delay time. The optimal delay time is when the *SNR* of the atomic characteristic line reaches the maximum. Under the delay time of 0—2.0 μs, the *SNR* curve of Cd increases, reaching the maximum value at 1.6 μs before decreasing. The *SNR* of Al also reaches the maximum value at the delay time of 1.6 μs. Therefore, 1.6 μs was selected as the optimal delay time of this experiment.
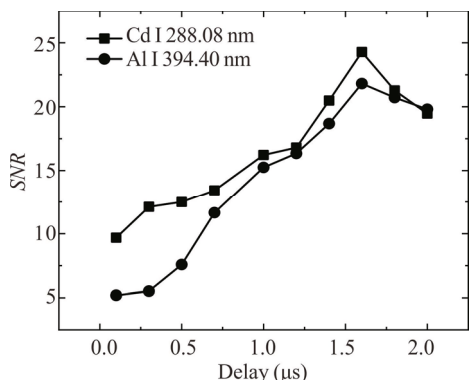

Fig.4 *SNR* versus delay time

In the experiment, when the focusing lens is used to focus the laser, the focusing lens should be placed on the focal plane theoretically. However, due to the differences in the samples and other external factors, the distance between the sample and the lens affects the size of the spot size. The larger the spot size is, the easier the atom transitions, and the better the plasma signal is. Therefore, it is

extremely important to select the optimal *LTSD*. Fig.5 shows the change trend of the 200—400 nm spectral line intensity under different *LTSD* conditions. When the *LTSD* is 91—104 mm, with the increase of *LTSD*, the intensities of Cd and Al increase first and then decrease. When the *LTSD* is 98 mm, the intensities of Cd and Al reach the maximum. Fig.6 shows the variation curves of *SNRs* of Cd and Al with the change of the *LTSD*. When the *LTSD* increases from 91 mm to 104 mm, the *SNRs* of Cd and Al reach the maximum of 10.58 and 9.15 at 98 mm. The analysis shows that compared with other *LTSD*, when *LTSD* is 98 mm, the experimental data are the optimal.
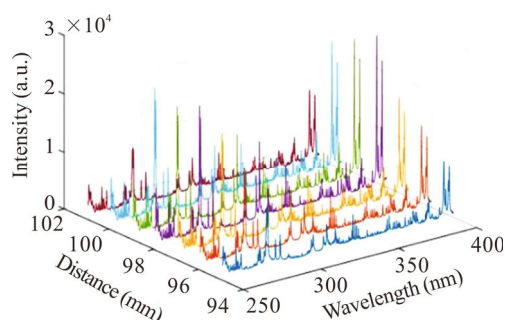

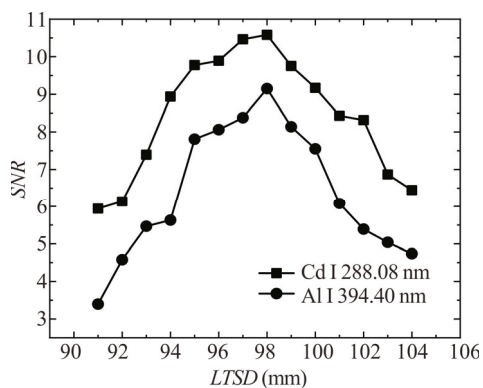**Fig.5 250—400 nm spectral intensity curves of different *LTSDs***

Fig.6 *SNR* curves of Cd and Al under different *LTSDs*

The experiments to investigate the KCl and KI influence were conducted under standard atmospheric pressure with the laser energy of 88.88 mJ, the delay time of 1.6 μs, and the *LTSD* of 98 mm. Using a 532 nm YAG laser and an MX2500 spectrometer, soil samples with different concentrations of 0%, 5%, 10%, 15%, 20%, 25% and 30% KCl and KI additives were tested. In order to obtain high-quality spectral signals and improve the accuracy of the analysis results, the spectral intensity and *SNR* were used to evaluate the spectral signals. In order to analyze the influence of the additives KCl and KI on the detection of heavy metal elements in soil by LIBS, the Cd and Al spectral intensities were obtained, and the trend of the spectral intensities of different additive contents was analyzed. Fig.7 shows the Cd and Al spectral line intensity curves of KCl and KI additives. It can be seen that

when the content of additives KCl and KI is 0—15%, the spectral intensity of Cd gradually increases. When the content of KCl and KI is 15%, the spectral intensity of Cd reaches the maximum. When the concentration of KCl and KI is 15—30%, the spectral intensity of Cd gradually decreases. It also shows the intensity curve of the Al spectrum of KCl and KI additives. When the concentration of the additive KCl and KI is below 15%, the intensity of the Al spectrum increases with the increase of the additive concentration. When the concentration of additive KCl and KI is higher than 15%, the line strength of the Al spectrum gradually decreases. When the concentration of KCl and KI equals 15%, the line strength reaches the maximum.

The analysis shows that the maximum intensities of Cd and Al spectral lines of KCl and KI additives are 0.33 times, 0.84 times, 0.61 times, and 0.81 times higher than those of samples without additives respectively. Effect of KI additive on soil breakdown spectral strength is greater than KCl additive. This greatly improves the accuracy of the LIBS for soil detection, and is of great significance for the spectrum detection of low-element samples.

As shown in Fig.8, the *SNR* trends of KCl and KI additives at Cd and Al are the same as the spectral intensity curves, showing a peak at 15% concentration, when the *SNR* is the largest. Experiments have proved that adding additives to the sample will improve the quality of the spectral signal, which is conducive to reducing the detection limit of the spectral analysis.
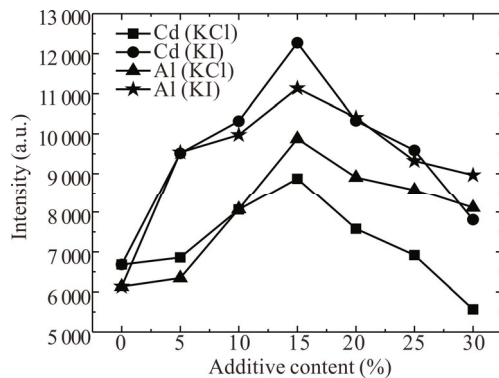

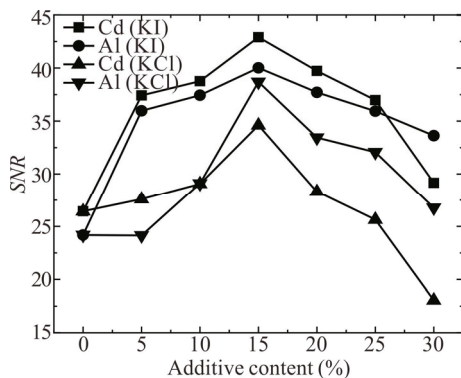**Fig.7 Cd and Al line intensity curves for KCl and KI additives**

Fig.8 Cd and Al *SNR* curves for KCl and KI additives

The temperature and electron density of laser-induced plasma are important indicators to describe the excitation characteristics of the light source and are the main parameters that determine the intensity of the spectral line. In order to explore the mechanism of the increase of the plasma radiation intensity by sample additives, the changes of electron temperature and electron density with the contents of KCl and KI were studied.

In the process of plasma formation, a large number of kinetic reaction rates will be affected by the electron density (N_e), so electron density is one of the important parameters of plasma and is calculated by the broadening of the characteristic spectral line Stark shown as[17]

$$\Delta\lambda_{1/2} = \frac{2\omega N_e}{10^{16}}, \tag{1}$$

where $\Delta\lambda_{1/2}$ is the full width at half maximum of the spectral peak, ω is the collision parameter, and N_e is the electron density. In this experiment, the electron density of Cd was calculated. As shown in Tab.1, the samples of KCl and KI additives reach the maximum when the content is 15%. The electron density changes all present a trend of first increasing and then decreasing.

Tab.1 Electron densities under different contents of different additives

Content	N_e (KCl) ($\times 10^{15}$ cm^{-3})	N_e (KI) ($\times 10^{15}$ cm^{-3})
0%	6.540 06	6.540 06
5%	7.976 32	6.457 71
10%	8.080 66	6.523 52
15%	8.425 39	6.809 45
20%	8.131 35	6.616 26
25%	7.565 79	5.963 00
30%	6.965 89	5.938 62

The laser plasma satisfies the local thermodynamic equilibrium (LTE) condition during the evolution process. Under the approximate condition of the local thermal equilibrium, the plasma temperature can be obtained from the diagram of Boltzmann[18], and the equation is as follows

$$\ln\left(\frac{\lambda I_{ki}}{g_k A_{ki}}\right) = \frac{-E_k}{K_B T} + C, \tag{2}$$

where λ is line voltage distribution wavelength, I_{ki} is spectral intensity, g_k is the energy level degeneracy on the spectral line, A_{ki} is transition probability, E_k is the energy level on the spectral line, K_B is a constant, and T is plasma temperature.

By querying the NIST database, the relevant data of Fe I at 272.09 nm, 252.28 nm, 248.95 nm, 267.90 nm, and 245.34 nm is obtained, and the electron temperature at different concentrations of different additives is calculated, as shown in Fig.9.

It can be seen from Fig.9 that the electron temperature of soil samples with 15% KCl and KI additives is the highest, and it is 1.07 times and 1.17 times that of no

additives samples. The electron temperature of the three additive soil samples increases first and then decreases. The analysis shows that the three kinds of KCl and KI added to the soil samples are all low boiling point additives. Different additives change the volatilization degree of the sample to different levels and reduce the laser ablation threshold of the sample. Carrying effect can make more samples evaporate into the plasma. Adding luminescent particles KCl and KI can improve the thermal coupling efficiency of laser energy and the sample, which significantly increases the amount of sample ablation, the electron temperature and the electron density of the plasma. It also improves the excitation conditions of the luminescent particles, which leads to a higher quality sample composition spectrum. The laser excites the sample to generate plasma.
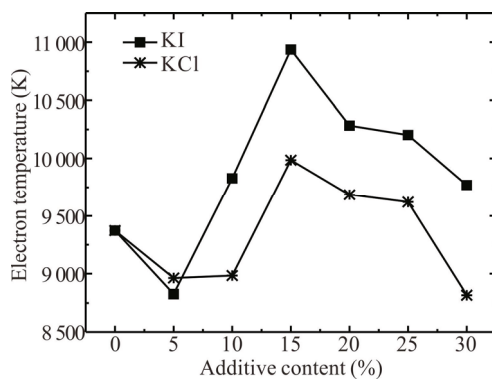

**Fig.9 Electron temperatures of KCl and KI additives**

The continuous radiation background light in plasma comes from the ductile radiation of high energy electrons and the recombination of electrons and ions. Because the energy of laser photon is less than the ionization energy of Al and Cd, the ionization of Al and Cd requires Nhv ($N \geqslant$ 2) photon energy. The ionization process of Z is as follows

$$Z^{n+} + Nhv \rightarrow Z^{(n+1)+} + \text{e}, \tag{3}$$

where $N=2, 3, 4...., n=1, 2, 3, 4$, h is the Planck constant, v is frequency, Z represents Al and Cd, and e is electron. Due to the addition of low boiling point KCl (boiling point is 1 420 °C) and KI (boiling point is 1 330 °C) additives below the boiling point of the sample, KCl and KI are ionized at the moment of the laser bombardment of the sample, where K is the easily ionized element. The ionization energy of K is 4.34 eV, and the ionization process is shown as

$$\text{K} + nhv \rightarrow \text{K}^+ + \text{e}. \tag{4}$$

At this time, K in the sample is ionized to form a gas-phase plasma, and electron e will absorb the laser energy at a high speed through the toughening radiation effect. After adding low boiling point additives, the ionization process of Z in the sample can be expressed as Eq.(5) due to the photon energy and kinetic energy excited by electron collision:

$$Z^{n+} + Nhv + E \rightarrow Z^{(n+1)+} + \text{e}, \tag{5}$$
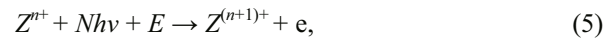
where E is the energy generated by the fast electron e collision. Therefore, the addition of additives reduces the threshold of laser ablation on the sample. High-energy electrons move rapidly in the environment of dense electrons and ions. The collision of electrons and ions can stimulate the recombination of electrons and ions, and the characteristic radiation rays of atoms and ions increase after the combined excitation. Therefore, compared with the sample without additives, the target with additives has less demand for photon energy, which reduces the condition of plasma excitation. Under the same laser condition, the plasma obtained increases. The addition of KCl and KI additives with high absorption can improve the thermal coupling efficiency of laser energy and samples, increase the ablation amount of samples, and make more samples evaporate into the plasma to produce stronger atomic emission lines.

Experiments were conducted on samples containing different concentrations (0—30%) of KCl and KI additives at the optimal laser energy of 88.88 mJ, the optimal *LTSD* of 98 mm, and the delay time of 1.6 μs. The experimental results showed that the appropriate laser energy, *LTSD*, and delay time can improve the reliability of the experiment. The KCl and KI additives have different effects on the spectral quality characteristics of the sample, and when the content of KCl and KI is 15%, the spectral signals and signals of Cd and Al have the highest *SNR*, the optimal plasma density and electron temperature. Effect of KI additive on soil breakdown spectral properties is better than the KCl additive. The method of adding KCl and KI additives on the spectral enhancement of soil samples can be further applied to the field of breakdown spectroscopy detection of different types of samples.

Statements and Declarations

The authors declare that there are no conflicts of interest related to this article.

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