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Heavy Metal Detection in Soils by Laser Induced Breakdown Spectroscopy Using Hemispherical Spatial Confinement

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Abstract Spatial confinement has great potential for Laser Induced Breakdown Spectroscopy (LIBS) instruments after it has been proven that it has the ability to enhance the LIBS signal strength and repeatability. In order to achieve in-situ measurement of heavy metals in farmland soils by LIBS, a hemispherical spatial confinement device is designed and used to collect plasma spectra, in which the optical fibers directly collect the breakdown spectroscopy of the soil samples. This device could effectively increase the stability of the spectrum intensity of soil. It also has other advantages, such as ease of installation, and its small and compact size. The relationship between the spectrum intensity and the laser pulse energy is studied for this device. It is found that the breakdown threshold is 160 cm^{-2}, and when the laser fluence increases to 250 J/cm^2, the spectrum intensity reaches its maximum. Four different kinds of laser pulse energy were set up and in each case the limits of detection of Cd, Cu, Ni, Pb and Zn were calculated. The results show that when the laser pulse fluence was 2.12 GW/cm^2, we obtained the smallest limits of detection of these heavy metals, which are all under 10 mg/kg. This device can satisfy the needs of heavy metal in-situ detection, and in the next step it will be integrated into a portable LIBS instrument.

Keywords: laser induced breakdown spectroscopy, hemispherical spatial confinement, laser fluence, limit of detection

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1 Introduction

As industrialization and urbanization gradually advanced, the heavy metal pollution of soil has become a serious environmental problem all around the world. Many activities, such as industrial production, improper stacking of solid waste, mining, and wastewater irrigation, will bring a lot of heavy metals into the soil. Heavy metals in soil will be enriched by crops and infiltrated into groundwater, so heavy metals in the soil may enter the human body from water and food, and then threaten human health.

Laser induced breakdown spectroscopy (LIBS) is a new material elements detection method. It can achieve real-time, in-situ measurement quickly and conveniently. It has already been applied in many fields, such as the iron and steel smelting, environmental monitoring, art appraisal and aerospace, in recent years [1−3]. In LIBS a high energy laser pulse is used to impact at the sample surface. The sample is ablated and ionized to generate plasma in the laser focus area. After the laser pulse, the induced plasma starts to cool down and releases spectral lines with element characteristics. After the spectral lines of the plasma are detected, the species and its contents of the elements in the plasma will be known. Assuming that the composition of the plasma is equal to the sample, the elements and contents of the sample will be known.

Laser induced breakdown spectroscopy is applied for qualitative and also quantitative analysis of soils by many scholars [4,5]. Several spectral enhancement methods have been used, such as microwave-assisted LIBS [6,7] and spatial confinement LIBS. Since Corsi and Zeng studied confinement in a crater that had a very small size [8,9], spatial confinement has made big progress. Andrey M. Popov [10] used a small cylindrical chamber with a 4 mm diameter to confine the laser-induced plasma, and his laser pulse energy was up to 400 mJ. Shen [11] used a cylindrical pipe with 10.8 mm diameter and a KrF excimer laser with 100-600 mJ pulse energy. L. B. Guo et al. [12,13] combined spatial and magnetic confinement together and used a hemispherical cavity, while they also combined spatial confinement and dual-pulse irradiation to further enhance the optical emission in LIBS. Zhe Wang et al. [14] used a polytetrafluoroethylene (PTFE) plate with cylindrical cavities of 3 mm diameter to regularize the laser induced plasma for signal strength enhancement and precision improvement. Zongyu Hou et al. [15,16] demonstrated that the cavity could increase the signal repeatability, they also combined spark discharge and moderate cylindrical confinement to improve the signal repeatability and enhance the signal and SNR. Xuejiao Su et al. [17,18] also investigated the spatial confinement with a small cavity and determined the optimized confinement cavity size, which was 1 mm in height and 3 mm in diameter.

Spatial confinement has great potential for LIBS instruments after its great ability to enhance the LIBS signal strength and repeatability has been proven. However, it has not yet been used in a LIBS instrument. In order to explore its effect in a LIBS instrument and achieve in-situ measurement of heavy metals in farmland soils by LIBS, a hemispherical confinement device is designed and applied to a handheld LIBS instrument. Referring to L. B. Guo, who used an aluminum hemispherical cavity with diameter of 11.1 mm to confine plasmas [19], a hemispherical chamber is used in the present device with a diameter of 10 mm. The whole device is 5 cm tall with a diameter of 3 cm. Unlike the experimental setups mentioned above, the focusing lens, the hemispherical cavity, and the fibers are all integrated together into the device. This is much more concise than the experimental setups mentioned above. The laser used in the experiment is an Nd:YAG laser with 100 mJ pulse energy, which is much cheaper than a KrF excimer laser. The fibers are much closer to the laser-induced plasma, and a much better signal can be achieved on the premise of small volume. This device can be taken out from the laboratory and used for in-situ measurement.

In the soil experiments this device was directly placed on the surface of the sample. Plasma was generated at the sample surface after being impacted by a laser pulse, which was focused by a lens. The fibers were inserted into the four small holes around the device and aimed at the center position of the plasma. This device is highly integrated, small and compact, the light-path is fixed, it is easy to install, and it also has a spectral enhancement effect. The limits of detection of Cd, Cu, Ni, Pb, and Zn in soil with this device were 4.1 mg/kg, 5.5 mg/kg, 6.2 mg/kg, 4.5 mg/kg, and 7.0 mg/kg, respectively.

2 Experiment

The block scheme of the present LIBS experimental apparatus is depicted in Fig. 1. The system includes a laser, a spectrometer, a rotary platform, and a computer. A Q-switched Nd:YAG laser (Brilliant, Quantel) operating at 1064 nm and 1 Hz is used as the ablating source. The laser pulse is reflected by a total reflecting mirror placed 45 degrees to the hemispherical device, which has a focusing lens with 100 mm focal length. The plasma emission was focused into an optical fiber linked to a spectrometer (Avantes), which provided a wavelength range of 200-500 nm and a resolution of less than 0.1 nm. The sample was placed on a rotary platform in order to avoid the laser focusing on the same point and ensure the uniformity of measurement. A digital delay generator (DG535, Stanford Research System) was used to ensure the synchronization of the platform and laser pulse.

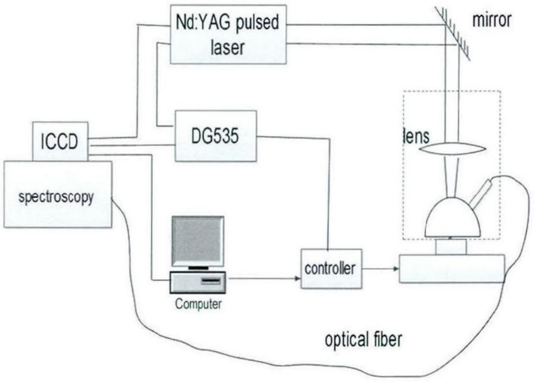

Fig.1 Schematic diagram of experiment setup

A schematic of the hemispherical spatial confinement device is depicted in Fig. 2 and the picture of the device is shown in Fig. 3. This device has mainly three effects. First, it enhances the stability of the spectrum since the focusing lens is integrated with the device and the light path is fixed. For example, with this device, the relative standard deviation (RSD) of the spectral line 214.44 nm of Cd is 4.31%, when the laser pulse energy is 100 mJ. While without the device the RSD could be up to 6.7%. Second, this device is highly integrated, small and compact, and easy to install. Hence, it would be much easier to transplant to another platform. Third, there is a hole on the upper part of the device in order to inflate the semicircular cavity with a certain kind of gas, such as argon and nitrogen. If the cavity is filled with argon, then the plasma will be generated in the environmental atmosphere of argon and the plasma emission can be greatly strengthened [20]. As for soil, in an argon gas environment, the spectral lines intensity of the major elements such as Fe, Ca, Al will increase significantly [21], while the spectral line intensity of trace heavy metal elements such as Pb, Ni, Zn will not have as obvious an enhancement effect as Fe. Under this circumstance, the spectral lines of the major elements will cover the spectral lines of trace elements. Otherwise, these lines cannot be separated; for example, the 327.4 nm spectral line of Cu blends with the 327.83 nm spectral line of Ti and the two spectral lines become a single peak. Since the first laser pulse will generate a huge wave at the surface when it impacts the soil sample, a hole will appear in the sample surface, and a lot of dust will be generated and distributed to the whole hemispherical space. When the second laser pulse comes, it will ablate the dust first instead of the soil sample, this can greatly reduce the energy impacting at the sample. In order to avoid the occurrence of this situation, in this experiment an air blower was used to blow the dust away from the cavity.

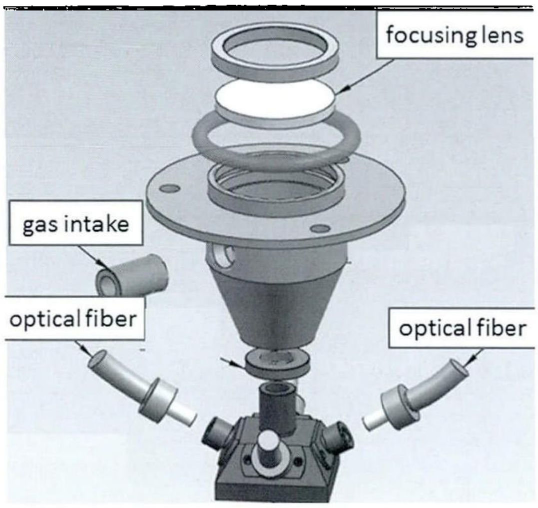

Fig.2 Schematic diagram of the hemispherical spatial confinement device

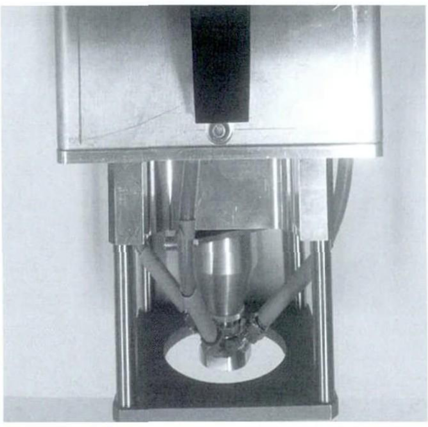

Fig.3 Picture of the spatial confinement device

All of the soil samples used in the experiments were collected in Yingshang County, Anhui, China by our research group. Heavy metal elements including Cd, Cu, Ni, Pb, and Zn in the samples were detected in Yangzhou Environmental Monitoring Center Station by inductively coupled plasma optical emission spectroscopy (ICP-OES). The detection results were considered as reliable and used to compare with the present LIBS results. All of the chosen soil samples were first ground and pressed into pellets with a diameter of 30 mm and a height of 2.5 mm under 10 MPa pressure. The crater size produced by the laser pulse under this spatial confinement has a diameter of 0.5 mm, which is much larger than the size of the laser's focus.

The delay time and the gate time chosen of the experiment were 1.5 μs and 1.05 ms, respectively. Each spectral data obtained from the experiment was the average of the effect of 20 laser pulses. Each heavy metal element had several characteristic spectral lines in the spectral range of 200-500 nm and only one line of each element was chosen for analyses. The spectral lines selected for element analyses are listed in Table 1.

Table 1. Characteristic spectral lines of five heavy metal elements

Element	Spectral line (nm)	Initial concentration (ppm)
Cd	214.44	0.327
Cu	324.75	19.36
Ni	341.48	23.14
Pb	405.78	19.72
Zn	213.86	42.6

3 Results and discussion

According to a few scholars' papers, the spatial-confinement of plasma is a potential method to improve the detection sensitivity of LIBS. Under different spatial confinement parameters, the temporal conditions (gate and delay) and the most suitable laser pulse energy required also differ. Since the gate time was long enough and the delay time was short enough to contain the whole evolution process of the plasma in the experiment, the spectral intensity enhancement would be obvious if any enhancement happened in the experiment. Significant enhancement effects for heavy metal elements in soil have been observed. As shown in Fig. 4, an increase in the intensities of Cr I lines of 2.5 times was observed for soil samples using the device, while the intensities of Fe I lines were increased 3-5 times. The intensities of Cd, Cr, Cu, Ni, Pb, Zn spectra lines all had a 2-3 times increase, but for Fe, Al, Ti in soil samples the increase was 3-5.

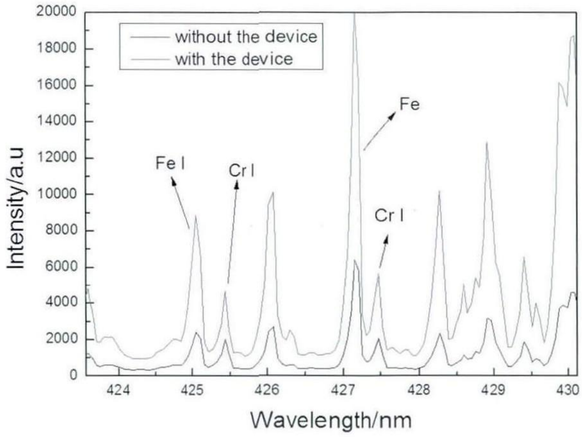

Fig.4 LIBS spectra of soil samples obtained by using the device and without it

Due to the advantages mentioned above, it is still necessary to find the most suitable laser fluence for this hemispherical spatial confinement device [22]. The laser pulse action point at the sample has a diameter of 200 μm through lens focusing. The laser pulse energy had a tunable range of 30 mJ to 125 mJ, and when the laser pulse energy was 30 mJ, the corresponding laser fluence was 75 J/cm^2. The curves of the spectral line intensity versus the laser pulse energy in the case of Ni and Pb are plotted in Fig. 5.

As shown in Fig. 5, when the laser pulse energy was between 30 mJ and 100 mJ, the characteristic lines intensity of Ni and Pb increased gradually with the increase of laser pulse energy. But when the laser pulse energy was above 100 mJ, the spectral line intensity would keep stable or fall slightly with the increase of the laser pulse energy. Other elements, including Cd, Cr, Cu, and Zn, had the same variation character of spectral intensity as Ni and Pb. When the laser pulse energy was 100 mJ, the corresponding laser fluence was 250 J/cm^2. The reason for this is probably as follows. First, high density plasma has a strong absorption of laser energy, the ablation amount of soil sample will tend to be stable with the increase of laser pulse energy. Second, after the laser pulse energy is increased, it will produce more significant physical effects on the sample surface, such as a greater pit in the sample surface or more dust in the hemispherical cavity. These would all hinder the optical fiber to receive the plasma spectrum and cause the spectral intensity to keep stable when the laser pulse energy keeps rising.

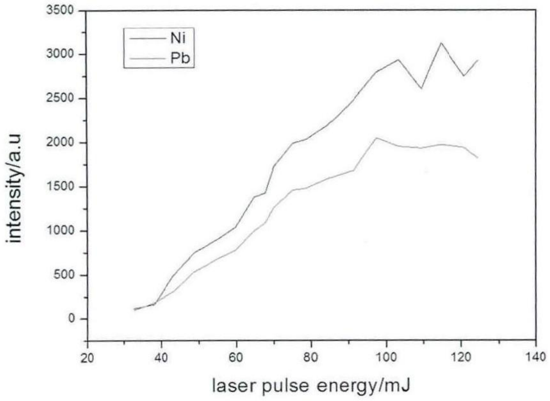

Fig.5 Spectral line intensity of Ni and Pb versus laser pulse energy

As shown in Fig. 6, with this hemispherical device, the ratio of signal and background (SBR) of Ni in soil increases with the increase of laser pulse energy, but when the energy is above 65 mJ (laser fluence 160 J/cm^2) the SBR will keep stable. The reason for this is that the increase of laser pulse energy causes the increase of plasma temperature, and then strengthens the spectral background and self-absorption effect.

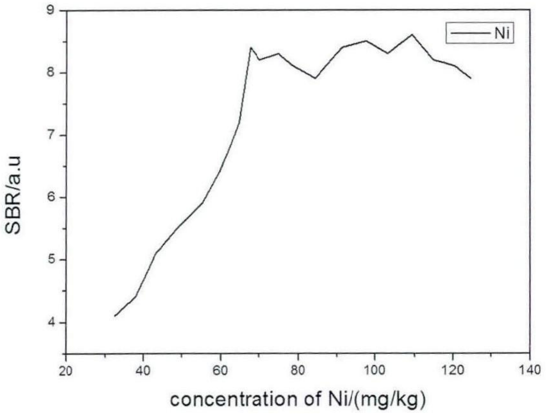

Fig.6 The SBR of Ni versus laser pulse energy

3.1 Relationship between limit of detection (LOD) and energy pulse energy

The limit of detection is an important parameter to evaluate the performances of LIBS. When the concentration of the element under test in the sample is low, the spectral lines intensity is proportional to the concentration of the element. According to the regulation of international union of pure and applied chemistry (IUPAC), LOD is obtained under the condition of low concentration. The computation formula is as follows:

$$C_{\mathrm{L}}=\frac{KS_{\mathrm{b}}}{M}, \tag{1}$$

In formula 1, the parameter K is a constant and equal to 3 in most circumstance, the parameter M is the value of the calibration curve and represents the sensitivity of detection, S_{b} is the standard deviation of the background. The calibration curve is drawn with the concentration of the element as the x axis and the spectral line intensity as the y axis.

The calibration curves of Ni and Pb were drawn, respectively, for the laser pulse energy of 53 mJ, 74 mJ, 103 mJ, 123 mJ, as shown in Fig. 7 and Fig. 8.

As shown in Fig. 7 and Fig. 8, when the laser pulse energy is 54 mJ, the calibration curves of Ni and Pb all have good linearity, but the slopes are much smaller than those with larger laser pulse energy. The small slope means that the sensitivity is lower, in other words, spectral intensity does not change significantly with the change of element concentration. As shown in Fig. 5, spectral intensity increases significantly with the increase of laser pulse energy when the energy range is 60-80 mJ per pulse. Within the range, any small changes of the laser pulse energy will produce significant spectral intensity changes. The laser pulse energy will have slight changes during the work, when the laser pulse energy is 74 mJ, the stability of the corresponding spectral intensity will be much poorer than those whose laser energy is not in the range, and the linearity of the calibration curve is also much poorer, as shown in Figs. 7 and 8. When laser pulse energy is 103 mJ, the spectral line intensity reaches its maximum and its stability is acceptable, the slope of the calibration curve is the largest, and the linearity is acceptable. When the laser pulse energy is 123 mJ, the spectral line intensity and stability are similar to the case of 103 mJ laser pulse energy, but the slope and linearity of the calibration curve are not as good.

When laser pulse energy is 103 mJ, the RSD of Ni 352.454 nm is 4.55% with the device, while without the device, the RSD can be 6.56%. When the spectra line of Fe 356.54 nm is chosen as the internal standard, the RSD of Ni line can be reduced to 3.25% with the device, which is still better than the result of without the device whose RSD is 5.21%.

Table 2 shows the limits of detection of Ni and Pb under different laser pulse energy. As described above, when laser pulse energy is 103 mJ, and the LOD is the best.

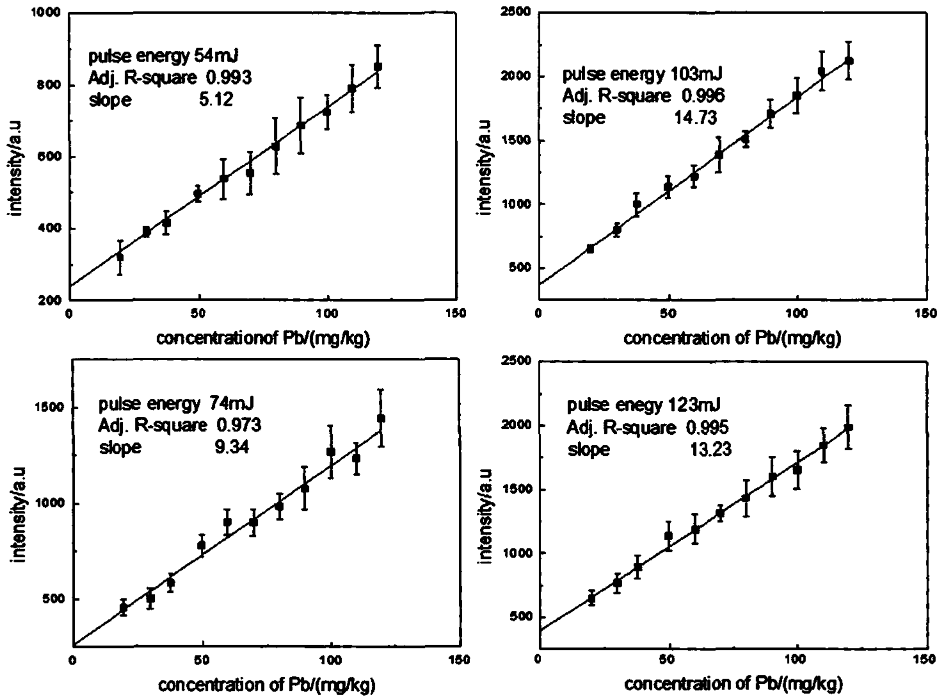

Fig.7 The calibration curve of Ni under different laser pulse energies

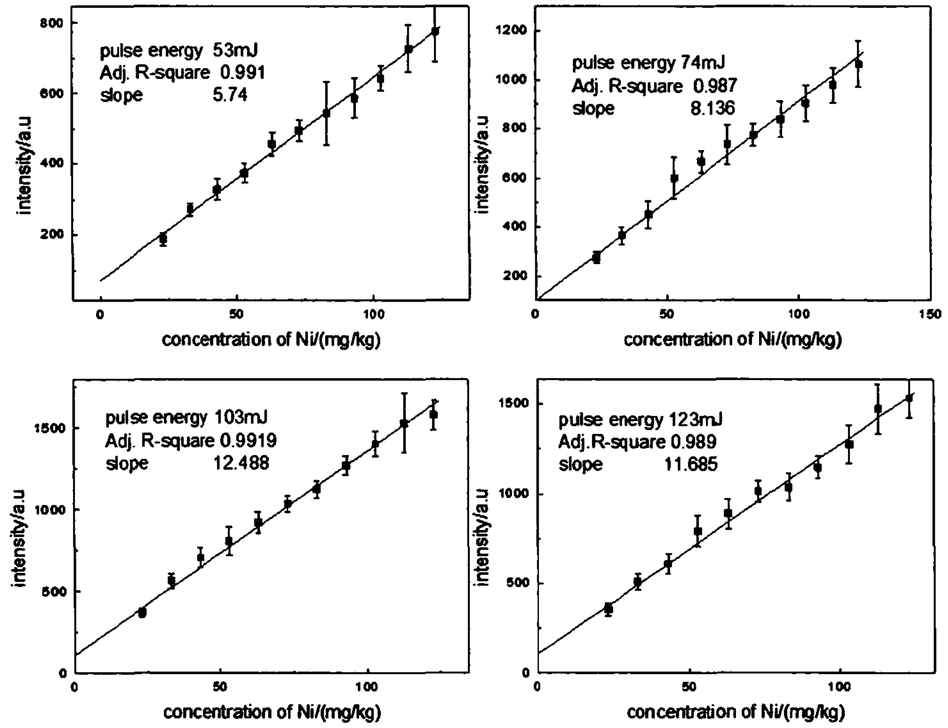

Fig.8 The calibration curve of Pb under different laser pulse energies

Table 2. The LOD of Ni and Pb under different laser pulse energies

Element	Laser pulse energy (mJ)	Slope	Adjust r square	LOD (mg/kg)
Ni	53	5.74	0.991	8.6
	74	8.14	0.987	9.1
	103	12.49	0.9919	6.24
	123	11.69	0.989	6.35
Pb	53	5.12	0.993	8.3
	74	9.34	0.973	4.67
	103	14.73	0.996	4.54
	123	13.23	0.995	5.4

When laser pulse energy was 103 mJ, we obtained the best results. Table 3 shows the limits of detection of Cd, Cu, Ni, Pb and Zn under this circumstance.

Table 3. The LODs of five heavy metal elements when the laser pulse energy is 103 mJ

Element	Cd	Cu	Ni	Pb	Zn
LOD (mg/kg)	4.58	3.21	6.24	4.45	2.6

3.2 Accuracy of the LIBS system

In order to test the precision and accuracy of the LIBS system with the spatial confinement device, the concentrations of Pb and Ni in soils obtained by LIBS and ICP are compared. The relative accuracy (RA) can be calculated using the following equation [23]:

$$RA = \frac{|d| + SD \times t_{0.975}/\sqrt{n}}{M}. \tag{2}$$

In Eq. (2), d is the difference between the measurement results of LIBS and ICP, SD is the standard deviation of LIBS measurement, n is the measurement number, $t_{0.975}$ is the t value at 2.5% error confidence, M is the measurement result of ICP, which is regarded as the standard method. The relative accuracy of this LIBS system is 0.092 for Ni and 0.101 for Pb, which is acceptable. The RSD of 10 times measurement results for Ni is 6.52%, while it is 4.67% for Cr.

4 Conclusions

In this article a hemispherical spatial confinement device is designed and used for laser focusing and spectrum collection. Since the light path and optical fiber are integrated together with the hemispherical cavity, the spectral line intensity is much more stable than in the case without the spatial confinement device. The device also has other advantages, such as ease of installation, and its small and compact size. When this device was used, the most suitable laser pulse energy would be 100 mJ, while the laser fluence was 250 J/cm^2. The limits of detection of Cd, Cu, Ni, Pb and Zn in soils were calculated, and the results are all under 10 mg/kg. This proves that spatial confinement can be applied to a LIBS instrument and used to detect heavy metal in soils.

This device will be applied to field test of heavy metal elements in soil in the future, and it will continue to be optimized by our research team.

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