

# Determination of Heavy Metals in Cultivated Land Using Laser-Induced Breakdown Spectroscopy

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**Abstract** A laser-induced breakdown spectroscopy (LIBS) system is developed for the determination of heavy metals in cultivated land around the city of Baoding, China. The element composition of the soil is determined by a quantitative spectrum analysis. The results show that the concentrations of Cd and Hg in three base soil samples do not exceed the limits specified by the second-class soil standard “Environmental quality standard for soils” (GB 15618-1995) issued by the state.

**Key words** laser technology; spectrum; quantitative analysis; detection

**OCIS codes** 300.6356; 300.6170; 300.6540

# 激光诱导击穿光谱法对产粮基地土壤中重金属元素含量检测

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**摘要** 采用激光诱导击穿光谱法(LIBS)检测保定周边三个产粮基地土壤中的重金属元素,并利用光谱定量法分析元素浓度。结果表明,三个基地中元素Cd和Hg的含量均未超过国家颁布的《土壤环境质量标准》(GB 15618-1995)中二类土壤标准。

**关键词** 激光技术; 光谱; 定量分析; 检测

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## 1 Introduction

Owing to the worldwide growth of the petroleum industry, garbage disposal and excessive pesticide using in cities and towns have caused environmental pollution by heavy metals. Consequently, the soil contamination in China is considerable. A survey indicates that one fifth of the cultivated land in China has been polluted<sup>[1-3]</sup>. Laser-induced breakdown spectroscopy (LIBS) is a fast, non-contact, and simple technology for preparing and analyzing samples, and is suitable for online analysis of soil composition. In this study, LIBS is used to determine the soil-sample composition. The emission spectra of soil samples are recorded by a spectrometer, and the contents of different elements are measured.

## 2 Experiments

### 2.1 Setup

NaCl and ZnO are added to the soil of the national-standard samples GBW-07401, GBW-07402, GBW-07408, GBW-07410, and GBW-07411, and the content of Zn and NaCl in the sample is 10% and 15%,

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respectively. The doped powder samples are subjected to agate–mortar grinding to ensure their uniformity. Using GBW–07401 as a test sample, the elements Cd and Hg—varying in content among GBW–07402, GBW–07408, GBW–07410, and GBW–07411—are used to draw  $\lg R \sim \lg C$  calibration curves. In addition, soil samples are acquired from the Wangdu Science and Technology Demonstration Park, Dingzhou vegetable base, and Baoding suburb wheat base. Small amounts of a saturated sucrose solution are added to the soil powder samples. The samples are mixed evenly and placed in a HGY–15 type tablet machine, under a pressure of 14 MPa for 10 min. They are pressed into round sheets and then placed in an electric blast–drying oven.

## 2.2 Spectral data collection

A NDZ–10 neodymium glass laser is focused onto the sample surface. The laser has an energy of 10 mJ and repetitive frequencies of 1/3 min. Air at atmospheric pressure is inserted into the chamber as a buffer gas, and the WDS–8 complex spectrograph had an entrance–slit width of 70  $\mu\text{m}$ . The fourth sequential laser–pulse action at a certain position on the soil–sample surface is recorded. The spectral lines of Cd I 340.3653 nm and Hg I 335.130 nm, representing non–self–absorption and non–interference, are used for spectral quantitative analysis. The spectroscopic–analysis formula, which is based on the internal standard principle, is given as follows:

$$\lg R = \lg \frac{I}{I_0} = b \lg C + \lg A, \quad (1)$$

where  $R$  is the analyzed line–intensity ratio;  $I$  and  $I_0$  are the analyzed line intensity and the internal standard line intensity, respectively;  $A$  is a constant; and  $C$  is used for the analysis of the element composition<sup>[4]</sup>. We select Zn I 330.258 nm and Zn I 328.233 nm as the internal standard line and Cd I 340.3653 nm/Zn I 330.258 nm, Hg I 335.130 nm/Zn I 328.233 nm as analytical line pairs, on the following grounds: (1) by adding the same content of Zn in the soil samples, the requirements match those of the internal standard method; (2) Zn, Cd, and Hg are zinc–group elements, and their physical and chemical properties are known; (3) Zn, Cd, and Hg atoms have a similar ionization potential; and (4) the analytical line pairs have similar wavelengths, which is convenient for the measurement.

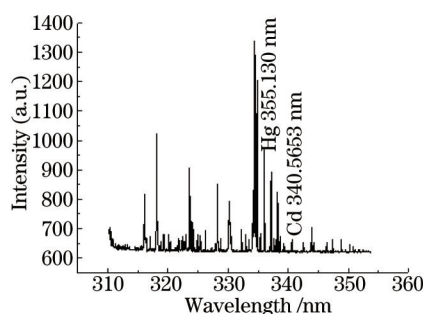


Fig.1 Typical LIBS spectrum of the sample (GBW–07401)

## 2.3 Measurement and calculation

In order to reduce the experimental error, three measurements are performed for each sample. The intensity ratios of the analysis elements to the internal standard element are calculated and averaged. As shown in Fig.2, an  $\lg R(I/I_0) \sim \lg C$  calibration curve is obtained according to the experimental data. The spectral data for the elements Cd and Hg in the sample GBW–07401 are measured, and the element compositions are determined using the calibration curve.

According to the experimental results, the Cd and Hg calibration curves shown in Fig.2(a) and (b), respectively, are formed. The concentrations of Cd and Hg in the GBW–07401 sample are calculated, and the precision and accuracy of the quantitative–analysis results are evaluated, as shown in Tables 1 and 2.

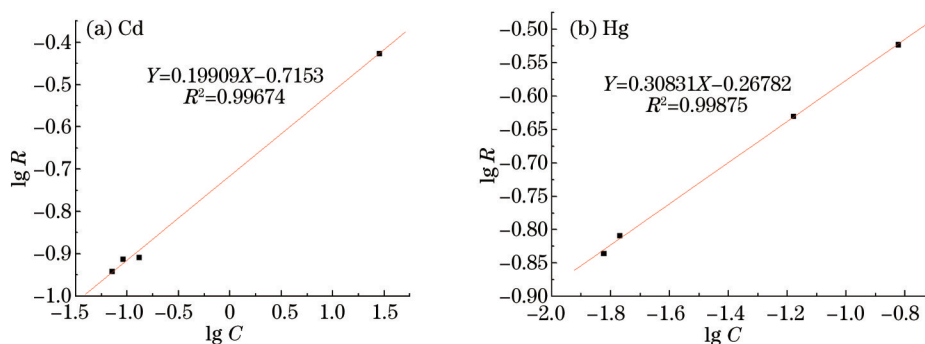
Fig.2 Cd and Hg  $\lg R(I/I_0) \sim \lg C$  calibration curve

Table 1 LIBS results for Cd in the GBW-07401 sample

Standard value / $10^{-6}$	Measured value / $10^{-6}$	Relative error (RE) /%	Relative standard deviation (RSD) /%
	3.945	8.256	
4.238	4.335	0.814	3.457
	4.252	1.116	
Average	4.194	2.470	—

Table 2 LIBS results for Hg in the GBW-07401 sample

Standard value / $10^{-6}$	Measured value / $10^{-6}$	Relative error (RE) /%	Relative standard deviation (RSD) /%
	0.030	6.563	
0.031	0.029	8.125	7.193
	0.034	7.500	
Average	0.031	2.500	—

According to the aforementioned quantitative spectrum analysis, the measurement results for heavy metals in the national standard soil samples (GBW-07401) are presented. The relative standard deviations (RSDs) of Cd and Hg are 3.457% and 7.193%, and the relative error (RE) between the measured value and the relative standard value is less than 9%. The experimental results suggest a good linear relationship between the spectral intensity and the element content, indicating the high precision and accuracy of the spectral analysis.

## 2.4 Results and discussion

Using the aforementioned method, the concentrations of the heavy metals Cd and Hg in soil from the Wangdu Science and Technology Demonstration Park, Dingzhou Xinxing vegetable base, and Baoding suburb wheat base are measured, as shown in Table 3.

Table 3 Concentrations of Cd and Hg in three soil samples

Analysis sample	Concentration of Cd / $10^{-6}$	Concentration of Hg / $10^{-6}$
Wangdu	0.0399	0.0400
Dingzhou	0.2178	0.0223
Baoding suburb	0.3069	0.0371

The results indicate that for all three base soil samples, the concentrations of Cd and Hg do not exceed the limits specified by the second-class soil standard of “Environmental quality standard for soils” (GB 156181995) issued by the state. This indicates good environmental quality.

## 3 Conclusion

A method involving the “confinement effect of the laser-induced crater on plasma” and the “influence of the sample additive” is employed to enhance the laser plasma radiation intensity. Trace heavy metals in soil are detected under atmospheric pressure, indicating the usefulness of the LIBS system for instantly analyzing the content of heavy metals in cultivated land.

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