Plasma Science and Technology

PAPER

Detection of heavy metals in water samples by laser-induced breakdown spectroscopy combined with annular groove graphite flakes

To cite this article: Li FANG *et al* 2019 *Plasma Sci. Technol.* **21** 034002

© 2018 Hefei Institutes of Physical Science, Chinese Academy of Sciences and IOP Publishing Printed in China and the UK Plasma Science and Technology

Plasma Sci. Technol. **21** (2019) 034002 (7pp) https://doi.org/10.1088/2058-6272/aae7dc

Detection of heavy metals in water samples by laser-induced breakdown spectroscopy combined with annular groove graphite flakes

Li FANG (方丽)[1,3], Nanjing ZHAO (赵南京)[1,3,5], Mingjun MA (马明俊)[1,2,3], Deshuo MENG (孟德硕)[1,3], Yao JIA (贾尧)[1,2,3], Xingjiu HUANG (黄行九)[4], Wenqing LIU (刘文清)[1,3] and Jianguo LIU (刘建国)[1,3]

[1] Key Laboratory of Environmental Optics and Technology, Anhui Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Hefei 230031, People's Republic of China
[2] University of Science and Technology of China, Hefei 230026, People's Republic of China
[3] Key Laboratory of Optical Monitoring Technology for Environment, Hefei 230031, People's Republic of China
[4] Institute of Intelligent Machines, Chinese Academy of Sciences, Hefei 230031, People's Republic of China

E-mail: njzhao@aiofm.ac.cn

Received 18 May 2018, revised 28 September 2018
Accepted for publication 2 October 2018
Published 23 November 2018

Abstract

The use of laser-induced breakdown spectroscopy (LIBS) for the analysis of heavy metals in water samples is investigated. Some factors such as splashing, surface ripples, extinction of emitted intensity, and a shorter plasma lifetime will influence the results if the water sample is directly measured. In order to avoid these disadvantages and the 'coffee-ring effect', hydrophilic graphite flakes with annular grooves were used for the first time to enrich and concentrate heavy metals in water samples before being analyzed by LIBS. The proposed method and procedure have been evaluated to concentrate and analyze cadmium, chromium, copper, nickel, lead, and zinc in a water sample. The correlation coefficients were all above 0.99. The detection limits of 0.029, 0.087, 0.012, 0.083, 0.125, and 0.049 mg l^{-1} for Cd, Cr, Cu, Ni, Pb, and Zn, respectively, were obtained in samples prepared in a laboratory. With this structure, the heavy metals homogeneously distribute in the annular groove and the relative standard deviations are all below 6%. This method is very convenient and suitable for online *in situ* analysis of heavy metals.

Keywords: laser-induced breakdown spectroscopy, quantitative analysis, heavy metals, graphite flake

(Some figures may appear in colour only in the online journal)

1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is a widely used technique due to its unique characteristics such as simple sample preparation, noncontact measurement, and fast and multi-elemental analysis [1]. It can be used as a fast method for elemental analysis of various forms of samples such as solid, liquid, and gas. Also, multiple elements can be detected simultaneously by this method. In this technique, a high power pulsed laser beam is focused onto the surface of the samples. Radiation energy is locally coupled into the sample and it starts to be ablated, resulting in the vaporization and

---

[5] Author to whom any correspondence should be addressed.

Table 1. The actual concentration of the heavy metals in the standard solutions (unit: mg l^{-1}).

Sample number	Cd	Cr	Cu	Ni	Pb	Zn
1	0.0578	0.0513	0.0534	0.0521	0.0503	0.0493
2	0.1156	0.1027	0.1068	0.1042	0.1006	0.0987
3	0.2312	0.2054	0.2136	0.2084	0.2012	0.1973
4	0.58	0.51	0.53	0.52	0.5	0.49
5	1.16	1.03	1.07	1.04	1.01	0.99
6	2.31	2.05	2.14	2.08	2.01	1.97
7	5.78	5.13	5.34	5.21	5.03	4.93
8	11.56	10.27	10.68	10.42	10.06	9.87
9	23.12	20.54	21.36	20.84	20.12	19.73
10	57.8	51.34	53.41	52.11	50.30	49.33

ionization of the sample in hot plasma. The plasma is then analyzed by a spectrometer. Each element has a unique spectral signature that allows its identification [2].

At present the LIBS technique is applied in different fields such as industry [3–5], environmental monitoring [6], biomedicine [7], archeology [8, 9], aerospace [10, 11], food [12, 13], and so on [14], but researchers still must strive to improve the stability, sensitivity, and accuracy of the technique. Take a liquid sample for example, several inherent drawbacks such as splashing, surface ripples, quenching of emitted intensity, and a shorter plasma lifetime restrict the use of LIBS [15]. All these drawbacks degrade the analytical performance of the technique. For a long time, several methods have been investigated to solve those difficulties. For example, double-pulse techniques [16, 17], jet technology [18], high frequency atomization technology [19], and the ring-oven based preconcentration technique [20] have been used for analysis of liquid samples. These strategies are high cost or involve a troublesome operation, and the reproducibility is still poor [21]. The transfer of a liquid sample to a solid sample has been reported in many studies in the literature. The methods used are as follows: enrichment with filter membrane [12, 22, 23], freezing samples [24], surface liquid layers evaporated onto a substrate [7, 25, 26], electrochemical preconcentration [27], ion exchange membranes [28], extraction technology [29], and so on. Yang and his team applied chemical replacement for the detection of trace heavy metal elements in aqueous solutions, in which a magnesium alloy was chosen as the substrate, and the limits of detection (LODs) obtained were 0.25 μg mL^{-1} for Cu, 0.118 μg mL^{-1} for Pb, 0.420 μg mL^{-1} for Cd, and 0.025 μg mL^{-1} for Cr [21]. Sarkar and co-workers employed spectroscopically pure graphite planchets of 32 mm diameter and 1.6 mm width as a solid sample support to quantify platinum group metals in simulated nuclear waste [30] and boron in groundwater samples [31]. A round flat solid state graphite was used as the solid sample support for analyzing Ni [32], Pb [33, 34], and Cr [35] in water by Zhao's team, and the LODs of Ni, Pb, and Cr were 0.28, 0.0665, and 0.52 mg l^{-1}, respectively. However, using these supports without any treatment may result in inhomogeneous distribution [31]. Bae and his team used a laser-patterned silicon wafer (LPSW) to analyze a small amount of liquid sample [36]. An LPSW with 40 × 40 trenches was devised for spreading a water droplet, and the LOD of potassium was 0.53 ppm and the relative standard deviation (RSD) was 4%. Lin detected ultra-trace amounts of Ag, Cu, and Cr in a water-based liquid using LIBS based on the utilization of a PVA material [37]. The LODs for Ag, Cu, Cr, Pb, Ni, Co, and Cd obtained were 1 ng ml^{-1}, 8 ng ml^{-1}, 16 ng ml^{-1}, 1 mg ml^{-1}, 1 mg ml^{-1}, 2 mg ml^{-1}, and 5 mg ml^{-1}, respectively. Daniel [38] also used a similar method to test fertilizer samples, which demonstrated a good agreement between the results of LIBS and inductively coupled plasma optical emission spectrometry for Cu, K, Mn, Mg, and Zn.

In this work, highly pure graphite flakes are used to concentrate and enrich heavy metals (Cd, Cr, Cu, Ni, Pb, and Zn) in a water sample. In order to improve the homogeneity of the enrichment, graphite flakes were treated with sodium hydroxide solution, and they changed from hydrophobic to hydrophilic. The new structure of the graphite flakes was used to enrich heavy metals, namely graphite flakes with an annular groove, which confined the solution in the space to ensure homogeneous distribution. Calibration curves in the range of about 0.05–50 mg l^{-1} were constructed using reference samples with known amounts of Cd, Cr, Cu, Ni, Pb, and Zn in order to evaluate the analytical performance of the method.

2. Experimental

2.1. Sample preparation

The nitrate and sodium hydroxide used in the experiment were purchased from Tianjin Guangfu Fine Chemical Research Institute (99.99% purity). The stock solution of the mixed heavy metals was prepared by dissolving 196.2 mg of $Cd(NO_3)_2 \cdot 4H_2O$, 409.6 mg of $Cr(NO_3)_3 \cdot 9H_2O$, 219.9 mg of $Cu(NO_3)_2 \cdot 3H_2O$, 289.7 mg of $Ni(NO_3)_2 \cdot 6H_2O$, 92 mg of $Pb(NO_3)_2$ and 233.2 mg of $Zn(NO_3)_2 \cdot 6H_2O$ in a beaker and was added to a 1000 ml volumetric flask, diluted with deionized water to volume, and mixed. For standard solutions preparation, different volumes of this solution were added to 11 100 ml volumetric flasks, respectively, and diluted with deionized water to volume. The actual concentration of the heavy metals in these standard solutions are listed in table 1.

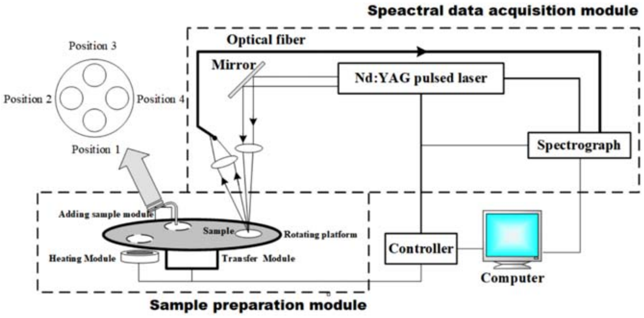

Figure 1. Schematic diagram of the LIBS system.

Then the standard solutions were added into the graphite flakes, dried, and analyzed.

The hydrophilic graphite flakes were prepared as follows: the graphite flakes were placed in a Teflon reaction kettle, 1 mol l^{-1} of sodium hydroxide solution was added until all the graphite flakes were immersed in the solution, and then the reaction kettle was put in the oven and heated at 80 °C for 12 h. Finally, the graphite flakes were taken out and washed with deionized water.

2.2. Experimental setup

A LIBS schematic diagram of the experimental setup is shown in figure 1, which is divided into two parts: the enrichment module and detection module. For the enrichment module, there is a disk in the center, as seen in figure 1, and four locations respectively for stowing the blank graphite flakes, sample injection, sample drying, and analysis. Blank graphite flakes were stored at position 1, and then rotated around the center of the disk to position 2 for sample injection, and then rotated to position 3 for sample drying, after which the solution was dried and the graphite flakes were rotated to position 4 for analysis by LIBS. During the analysis, the graphite flakes were rotated around the center of themselves at position 4 to avoid laser repetition on the same site, which enabled the laser pulses to be equally spaced in the annular groove. After the analysis was completed, the graphite flakes were rotated to position 1 again and put into the accumulator at position 1.

The detection module is composed of a pulsed laser, focusing system, transmitter system, optical receiving system, spectral detection system, and computer-control system. A 1064 nm Nd:YAG laser (BIGSKY, Ultra-100, 3 Hz repetition rate, 100 mJ/pulse and 6 ns pulse width) was focused by a lens with a 100 mm focal length to ablate the sample and generate plasma. The signal is collected and detected by a spectrometer (Avantes, AVS-DESKTOP-USB2, three channels, 200–500 nm spectral range, and 0.08–0.12 nm spectral resolution). The experiment is performed at the rate of 2 Hz, the laser energy is 100 mJ, the delay time is 1.5 μs, and the gate time is 1.05 ms. The diameter of the focal spot on the graphite flake is 0.7 mm.

2.3. Enrichment with graphite flakes

Graphite flakes have many favorable characteristics for use as a substrate to concentrate heavy metals, namely, not easily perforated, easy to handle, low cost, simple composition with few spectral lines, low interference, and so on. The graphite flakes we used were purchased from Xinfei Mechanical and Electrical Company. The graphite flakes are highly pure, with a carbon content higher than 99.99%. Trace calcium, manganese, and silicon in them will not affect the detection of heavy metals.

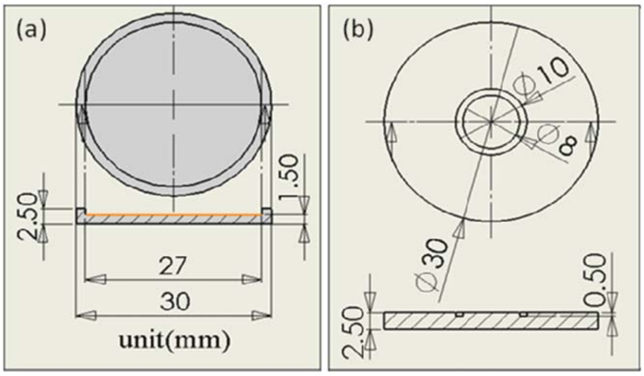

Figure 2. Graphite flake with a circular groove.

The graphite flakes with a circular groove are shown in figure 2(a), the diameter of which is 27 mm, and the depth is 1 mm. Two milliliters of Pb-containing solution is spotted into the circular groove, dried with electromagnetic heating, and then analyzed by LIBS. To get a 2D distribution of the Pb on the surface of the graphite flakes, the graphite flakes were placed in a program-controlled 2D rotating testbed to avoid repeat sampling on the trajectory (the maximum radius of the trajectory is 13 mm, the minimum radius is 2 mm, and the step size is 1 mm), and the distance between each laser spot was 1 mm, ensuring uniformity and stability of the sample measurements. Five-hundred sixty-five laser pulses were fired on this type of graphite flake, and one spectrum for each laser pulse was obtained for analysis.

The structure of the graphite flake with an annular groove is shown in figure 2(b). The graphite flake has a diameter of 30 mm and the annular groove has an internal radius of 4 mm, an outer radius of 5 mm, and a depth of 0.5 mm. The diameter of the focal spot completely falls inside the annular groove. A 16 μl sample solution is spotted into the annular groove, dried with electromagnetic heating, and then simultaneously analyzed by LIBS. The whole analysis time is about 5 min for every sample. Forty laser pulses were fired on this type of graphite flake. At the same time, the graphite flake was rotated to avoid laser repetition on the same site, so that the laser pulses were equally spaced in the annular groove.

3. Result and discussion

3.1. Emission lines

The LIBS spectra of the blank graphite flakes and the graphite flakes enriched with heavy metals are shown in figure 3. The concentrations of Cd, Cr, Cu, Ni, and Zn were 0.5 mg l^{-1}, and Pb was 0.8 mg l^{-1}. The features of the Cd, Cr, Cu, Ni, Pb, and Zn lines at 214.44, 425.43, 324.75, 341.48, 405.78,

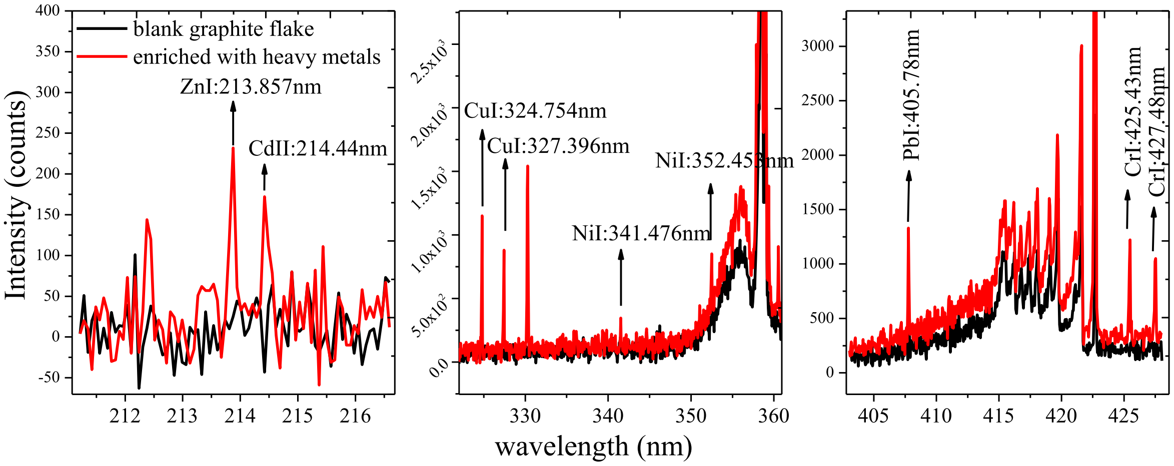

Figure 3. The spectra of the blank and the heavy metal enriched graphite flakes.

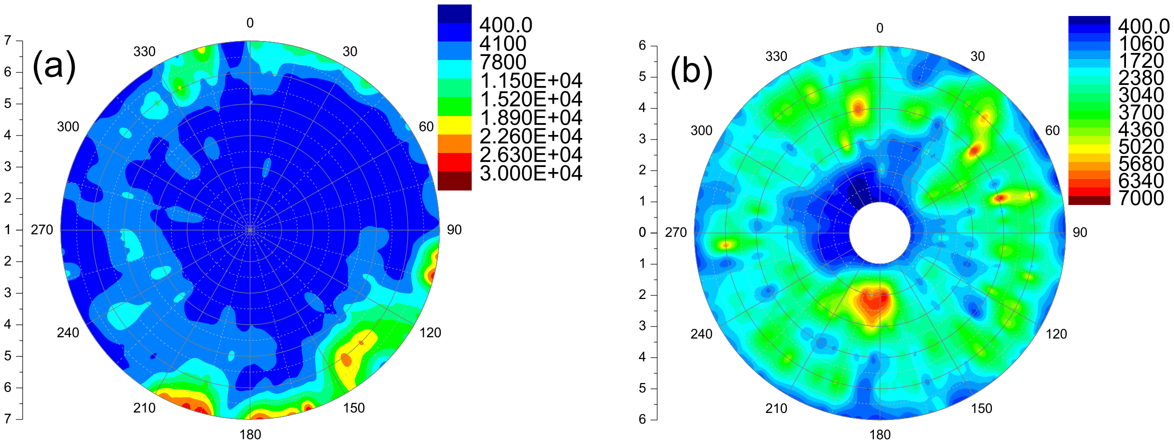

Figure 4. The distribution of Pb on the graphite flakes with circular grooves.

and 213.86 nm, respectively, are selected for analysis. There are no other lines around the analysis lines of the LIBS spectra of the blank graphite. So the graphite could be used for analyzing the concentration and enrichment of heavy metals in the water samples.

3.2. Graphite flakes with a circular groove

When we started the experiment, we used hydrophobic graphite flakes with a circular groove to gather heavy metals, and the 2D distribution of Pb on the surface of the graphite flake is shown in figure 4(a). We can see that the concentration of Pb at the margin is higher than that in the center of the circular groove. This is due to the 'coffee-ring effect' [12], like a drop of coffee has dripped onto a flat surface, the particle was inhomogeneously distributed on the flat surface when it dried. The color of the margin is darker than that in the center of the drop of the coffee stain. Because of the existence of the 'coffee-ring effect', the heavy metals cannot homogeneously distribute in the circular groove. We found that the graphite flake was hydrophobic. There was a large contact angle when solution was spotted in the circular groove. During the drying process, the solution gradually tapered and the margin of the graphite flake dried before the center, as shown in figure 5(a). This is the main reason for the nonuniformity of the distribution. While being enriched with hydrophilic graphite flakes, the contact angle obviously decreased, as can seen in figure 5(b). The margin and center of the graphite flake dried almost simultaneously. We could see the distribution of Pb changes, as shown in figure 4(b). The Pb concentration at the margin shown in figure 4(b) is lower than that at the same place in figure 4(a), and the Pb concentration in the center is higher than that at the same place in figure 4(a). The differences between the minimum and maximum of the intensity of Pb in the two figures are 37 268.99 counts and 9889.14 counts, respectively. From this we can see that the distribution of Pb on the hydrophilic graphite flake is much more homogeneous than that on the hydrophobic graphite flake. The hydrophilic graphite flake is better than the hydrophobic one, but still not good enough.

3.3. Graphite flakes with an annular groove

When enriching the heavy metals using the hydrophilic graphite flakes with an annular groove, the homogeneity improved dramatically. In comparison with the graphite flakes

Figure 5. The difference between the water on hydrophobic and hydrophilic graphite flakes.

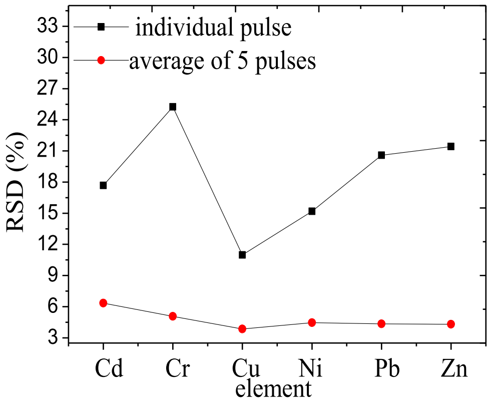

Figure 6. The RSD between the laser pulses and measurements

Table 2. The parameters of formula (1) and the correlation coefficients.

Elements	*a*	*b*	*c*	*R*
Cd	77.823	208.825	11.949	0.9955
Cr	−19.94	2783.724	5.746	0.9985
Cu	471.4671	817.1036	7.9715	0.9909
Ni	16.051 48	742.159	5.925 72	0.9982
Pb	−463.6877	187.8793	-1.8654×10^{13}	0.9930
Zn	58.7462	85.0048	13.4643	0.9991

with a circular groove, the heavy metals in the graphite flakes with an annular groove were distributed much more evenly. The RSDs of the 40 laser pulses are 17.68% for Cd, 25.24 for Cr, 10.98% for Cu, 15.18% for Ni, 20.59% for Pb, and 21.4% for Zn, respectively, as shown in figure 6. This instability is due to the poor stability of LIBS [3, 39], mainly caused by the fluctuation of laser energy and plasma, and so on. Data processing could reduce this instability, executed as follows: the results were averaged over five laser shots and eight spectra data were obtained. The RSDs of these eight spectral data are all below 6% for the six heavy metals. Based on the above statement, one can draw the conclusion that with this structure, the 'coffee-ring effect' can be avoided and the heavy metals can homogeneously distribute in the annular groove after being dried.

3.4. Calibration curves

The working curves are shown in figure 7. Each experimental point was obtained from the peak intensity of the line minus the background intensity. Three parallel samples were made for each value of concentration, and the results were averaged over the 40 laser shots.

In this work, linear fitting did not apply, so a nonlinear function is employed [40]:

$$y = a + bc(1 - \mathrm{e}^{-x/c}), \tag{1}$$

where y represents the line intensity and x the concentration of the element, c is the concentration at which the slope of the curve decreases at a factor of $1/\mathrm{e}$ from the value at $x = 0$. For low concentrations, the above formula is approximated by the following:

$$y = a + bx. \tag{2}$$

The fitting parameters of a, b, and c, and the correlation coefficients of R are listed in table 2. The values of R are all above 0.99. Being different from other elements, the calibration curve of Pb is nearly linear. This is because the experimental concentration did not reach the saturation concentration of Pb.

3.5. Detection limits

For determining the detection limits, low concentrations of the elements shown in figure 7 except Pb were used and linear fittings were done. The LOD is calculated according to the following expression:

$$\mathrm{LOD} = \frac{3\sigma_\mathrm{B}}{s}, \tag{3}$$

where σ_B is the standard deviation of the background of the spectrum, and s is the sensitivity which is given by the slope of the calibration curve. The LODs of the six elements are shown in table 3, and the LODs reported in other literature studies are also shown in the table. It can be seen that the LOD of Pb is much higher, and this is because the spectrometer used in this experiment had a weak spectral response of around 405 nm in the case of the Pb lines. Taking into account the cost, complexity, and detectability, the method of concentrated heavy metals in the water samples with graphite flakes is comparable to other methods.

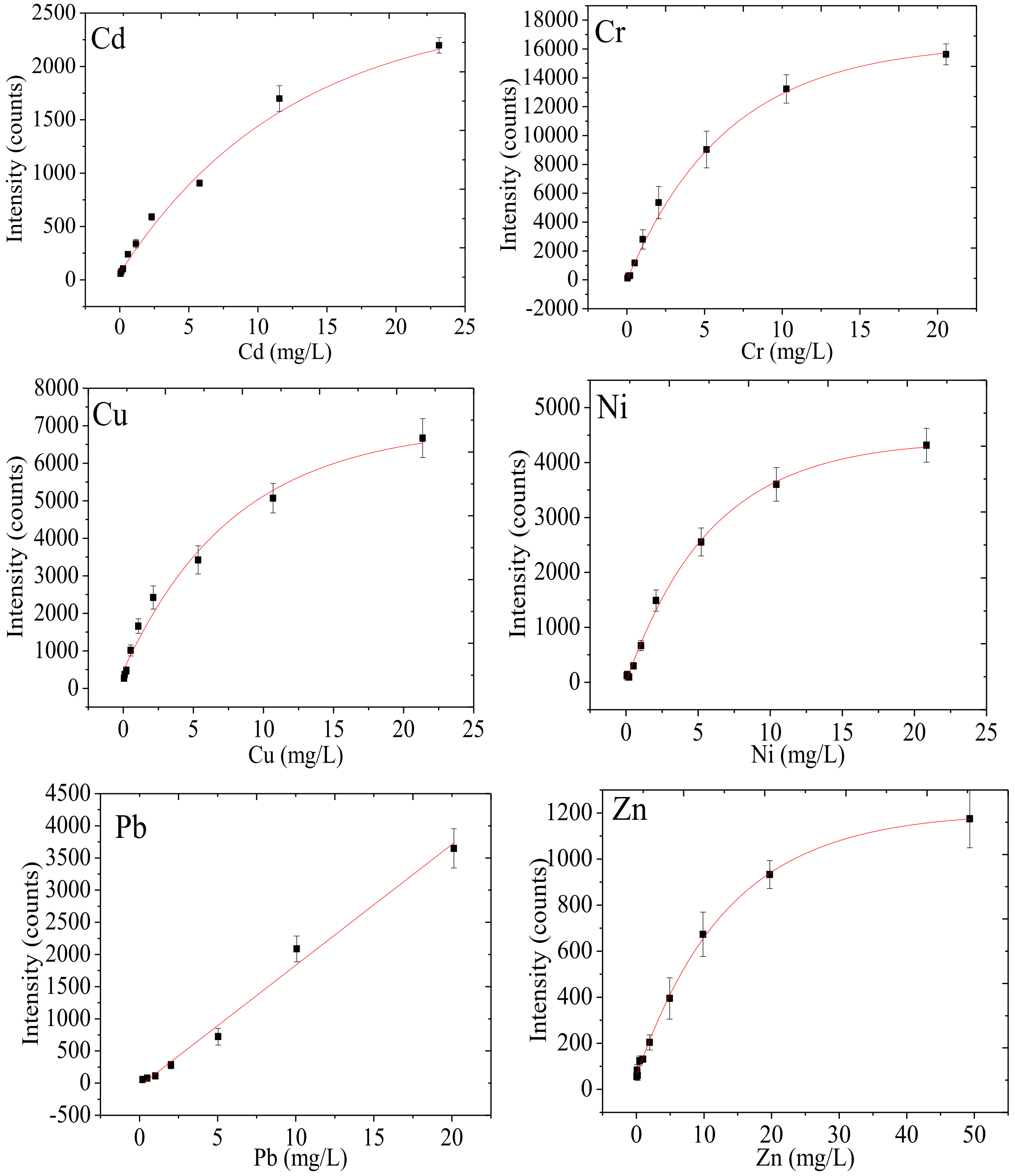

Figure 7. Calibration curves of Cd, Cr, Cu, Ni, Pb, and Zn.

4. Conclusions

Cd, Cr, Cu, Ni, Pb, and Zn are detected simultaneously by the LIBS technique. The solution is concentrated with hydrophilic graphite flakes with an annular groove. The RSD of the data is below 6%, and the LOD of the six heavy metals are 0.029, 0.087, 0.012, 0.083, 0.125, and 0.049 mg l^{-1} respectively. This concentrated method is very convenient and could be applied to *in situ* analysis.

Table 3. LOD of the elements (unit: mg l^{-1}).

Elements	This work	Other literature studies	Lines used in other literature studies (nm)	Comments
Cd	0.029	0.067 [41]	Cd I 228.802	Electrochemistry enrichment
		0.0031 [25]	Cd I 228.802	Electrochemistry enrichment
		4.43 [42]	Cd II 226.502	Water
		0.420 [21]	Cd I 508.58	Chemical replacement
Cr	0.087	0.004 44 [43]	Cr I 425.43	Hydrogel-based solidification
		1.26 [18]	Cr I 425.43	Liquid jets
		0.33 [44]	Cr I 425.43	Montmorillonite enrichment
		0.025 [21]	Cr I 520.84	Chemical replacement
		0.001 29 [23]	Cr I 425.43	Membrane separation
Cu	0.012	0.016 [45]	Cu I 324.75	Enrichment with aluminum target
		1.5 [46]		Enrichment with filter paper
		0.131 [47]		Enrichment with wood
		0.25 [21]		Chemical replacement
		0.002 59 [23]		Membrane separation
Ni	0.083	0.0017 [14]	Ni I 341.476	Electrochemistry enrichment
		0.28 [32]		Enrichment with graphite planchets
Pb	0.125	0.035 [33]	Pb I 405.78	Electrochemistry enrichment
		2.93 [48]		Ultrasonic atomizer
		0.118 [21]		Chemical replacement
Zn	0.049	13.67 [43]	ZnII 206.20	Water

Acknowledgments

This work is supported by National Natural Science Foundation of China (No. 21735005), the Science and Technology Program of Anhui Province (No. 1501041119), the Science and Technology Major Special Program of Anhui Province (No. 15CZZ04125), and National Key Research and Development Plan of China (No. 2016YFD0800902-2).

References

[1] Wang Z *et al* 2014 *Front. Phys.* **9** 419
[2] Hu L *et al* 2015 *Plasma Sci. Technol.* **17** 699
[3] Wang Z, Dong F Z and Zhou W D 2015 *Plasma Sci. Technol.* **17** 617
[4] Wang Y J and Yuan X Q 2013 *J. Gems Gemmol.* **15** 18 (in Chinese)
[5] Noll R *et al* 2001 *Spectrochim. Acta* B **56** 637
[6] Hassan H E *et al* 2013 *J. Appl. Sci. Res.* **9** 1074
[7] Metzinger A *et al* 2014 *Appl. Spectrosc.* **68** 789
[8] Giakoumaki A, Melessanaki K and Anglos D 2007 *Anal. Bioanal. Chem.* **387** 749
[9] Lazic V *et al* 2005 *Spectrochim. Acta* B **60** 1014
[10] Cremers D A *et al* 2004 LIBS analysis of geological samples at low pressures: application to Mars, the Moon, and asteroids *Proc. of the 35th Lunar and Planetary Science Conf.* (Houston, TX: Los Alamos National Laboratory) p 35
[11] Lazic V *et al* 2007 *Spectrochim. Acta Part B At. Spectrosc.* **62** 1546
[12] Abdel-Salam Z, Al Sharnoubi J and Harith M A 2013 *Talanta* **115** 422
[13] Yang H *et al* 2017 *Laser Opt. Prog.* **54** 083002 (in Chinese)
[14] Guo Y M *et al* 2016 *Front. Phys.* **11** 114212
[15] Pace D M D *et al* 2006 *Spectrochim. Acta* B **61** 929
[16] Pace D M D *et al* 2017 *Spectrochim. Acta* B **131** 58
[17] Wu Y Q *et al* 2016 *Chin. J. Anal. Chem.* **44** 1919 (in Chinese)
[18] Xu L *et al* 2012 *J. Anhui Norm. Univ. Nat. Sci.* **35** 438 (in Chinese)
[19] Serrano J, Moros J and Laserna J J 2016 *Phys. Chem. Chem. Phys.* **18** 2398
[20] Cortez J and Pasquini C 2013 *Anal. Chem.* **85** 1547
[21] Yang X Y *et al* 2016 *Opt. Express* **24** 13410
[22] Choi D *et al* 2015 *Appl. Spectrosc.* **68** 198
[23] Wang X *et al* 2015 *Anal. Chem.* **87** 5577
[24] Cáceres J O *et al* 2001 *Spectrochim. Acta* B **56** 831
[25] Wang Y Y *et al* 2017 *Spectrosc. Spect. Anal.* **37** 884 (in Chinese)
[26] Alamelu D, Sarkar A and Aggarwal S K 2008 *Talanta* **77** 256
[27] Jiang T J *et al* 2016 *Electrochim. Acta* **216** 188
[28] Schmidt N E and Goode S R 2002 *Appl. Spectrosc.* **56** 370
[29] Aguirre M A *et al* 2015 *Talanta* **131** 348
[30] Sarkar A *et al* 2009 *J. Anal. At. Spectrom.* **24** 1545
[31] Sarkar A *et al* 2010 *Microchim. Acta* **168** 65
[32] Shi H *et al* 2012 *Spectrosc. Spect. Anal.* **32** 25 (in Chinese)
[33] Wang C L *et al* 2012 *Proc. of SPIE 6th Int. Symp. on Advanced Optical Manufacturing and Testing Technologies: Optical Test and Measurement Technology and Equipment* **8417** 84171G
[34] Wang C L *et al* 2011 *Chin. J. Lasers* **38** 252 (in Chinese)
[35] Wang Y *et al* 2013 *Laser Technol.* **37** 808 (in Chinese)
[36] Bae D *et al* 2015 *Spectrochim. Acta* B **113** 70
[37] Lin Q Y *et al* 2016 *Anal. At. Spectrom.* **31** 1622
[38] Andrade D F, Sperança M A and Pereira-Filho E R 2017 *Anal. Methods* **9** 5156
[39] Guo L B *et al* 2016 *Front. Phys.* **11** 115208
[40] Aragón C, Aguilera J A and Peñalba F 1999 *Appl. Spectrosc.* **53** 1259
[41] Cheng Y K *et al* 2017 *Technol. Dev. Enterp.* **36** 5 (in Chinese)
[42] Song C, Zhang Y W and Gao X 2017 *Spectrosc. Spect. Anal.* **37** 1885 (in Chinese)
[43] Lin Q Y *et al* 2017 *J. Anal. At. Spectrom.* **32** 1412
[44] Wu Q F *et al* 2017 *Laser J.* **38** 21 (in Chinese)
[45] Lu Y *et al* 2010 *Appl. Opt.* **49** C75
[46] Zheng M L *et al* 2013 *Laser Optoelectron. Prog.* **50** 073004 (in Chinese)
[47] Tawfik W and Sawaf S 2014 *Proc. of SPIE Sensing Technology and Applications* **9101** 91010L
[48] Zhong S L *et al* 2016 *Front. Phys.* **11** 114202