

**QUANTITATIVE ANALYSIS OF TRACE METALS IN AQUEOUS SOLUTIONS  
BY LASER INDUCED BREAKDOWN SPECTROSCOPY COMBINED  
WITH FILTER PAPER ASSISTED ANALYTE ENRICHMENT**

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*The sensitive quantitative analysis of trace heavy metallic elements (Cd, Mn, Cr, and Cu) in aqueous solutions was achieved successfully through the combination of filter paper enrichment with laser induced breakdown spectroscopy. Filter paper was enriched with 0.4 mL aqueous solutions to form a homogeneous sample layer on the surface of the metallic target. Considering the limits of detection, the values deduced with calibration curves already exhibited the high performance of the proposed method at several hundred or 10 µg/L (Cd 0.165, Mn 0.035, Cr 0.012, and Cu 0.078 mg/L), lower than or comparable to those using other similar methods. The LIBS results agreed reasonably well with those from ICP-MS for real samples. All results showed that our method was suitable and accurate for rapid on-site detection of trace metals in aqueous solutions. This indicates that filter paper enrichment combined with laser induced breakdown spectroscopy is a feasible approach to wastewater quality monitoring.*

**Keywords:** heavy metals, laser induced breakdown spectroscopy, water quality monitoring.

**КОЛИЧЕСТВЕННЫЙ АНАЛИЗ СЛЕДОВ МЕТАЛЛОВ В ВОДНЫХ РАСТВОРАХ  
МЕТОДОМ ЛАЗЕРНОЙ ЭМИССИОННОЙ СПЕКТРОСКОПИИ В СОЧЕТАНИИ  
С ОБОГАЩЕНИЕМ АНАЛИТА С ПОМОЩЬЮ ФИЛЬТРОВАЛЬНОЙ БУМАГИ**

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*Осуществлен чувствительный количественный анализ микроэлементов тяжелых металлов (Cd, Mn, Cr и Cu) в водных растворах с помощью спектроскопии индуцированного лазерным излучением пробоя, дополненной использованием фильтровальной бумаги. Водный раствор объемом 0.4 мл пропускали через фильтровальную бумагу для образования на поверхности металлической мишени гомогенного слоя (образца). Показана высокая эффективность предлагаемого метода с учетом пределов обнаружения (Cd 0.165, Mn 0.035, Cr 0.012 и Cu 0.078 мг/л), что ниже или сравнимо с аналогичными методами. Результаты лазерно-индуцированной спектроскопии достаточно хорошо согласуются с результатами ICP-MS для реальных образцов. Предлагаемый метод подходит для быстрого и точного обнаружения следов металлов в образцах водных растворов и может применяться как возможный подход к контролю качества сточных вод.*

**Ключевые слова:** тяжелые металлы, спектроскопия индуцированного лазерным излучением пробоя, контроль качества воды.

**Introduction.** Heavy metal pollution of water poses a serious threat to the health of humans. For example, cadmium (Cd), copper (Cu), manganese (Mn), and chromium (Cr), which are common heavy metal elements in industrial wastewater from the electroplating and mineral processing industry, can be extremely harmful to the aquatic environment when their concentrations exceed the national standard. Sensitive and

quantitative analysis of trace metals in water is vital for environmental monitoring and process control [1], drinking water quality analysis [2], and industrial wastewater detection [3, 4]. Therefore, concentration monitoring and determination of trace metals in water provide an efficient way to identify and mitigate adverse consequences.

The laser induced breakdown spectroscopy (LIBS) technology has seen rapid development in recent decades and has been extensively applied for a wide range of scientific and industrial purposes [5–10]. However, the plasma emission in bulk is difficult due to the complex process of ablation in bulk, so the detection sensitivity is relatively low [6, 11].

In order to improve the detection sensitivity of LIBS to liquid samples, a variety of methods have been developed and lower detection limits have been obtained. Among these methods, converting liquid samples into solid ones is available and effective to improve the LIBS sensitivity to liquid samples. The limits of detection (LoDs) of trace metals in liquid samples have been improved effectively by LIBS via solid substrates, such as wood [12], graphite [13], metal electrode [14], bamboo [15], ion exchange membrane [16, 17], ice [18], carbon [19], and paper [20–23] for aqueous solutions. However, obtaining accurate measurement results of heavy metals in water using LIBS is still a serious challenge for analytical chemistry.

Recently, a solid metallic target or a silicon target was used as a substrate to assist LIBS analysis of aqueous solutions [24–27] in a process named surface-enhanced LIBS (SENLIBS). The detection sensitivity was improved greatly compared with direct analysis for liquid due to the high-temperature laser induced plasma. However, it was hard to confine the liquid samples in a settled area on the surface of the polished target. Only liquid droplets with a smaller volume of the aqueous solution was dropped onto the target surface, causing an inhomogeneous distribution of liquid samples. Based on the improvement of SENLIBS, some methods such as chemical replacement-SENLIBS [28] and laser-pretreated metallic target-SENLIBS [29] were developed to obtain better detection results. The detection sensitivity of LIBS for heavy metals in aqueous solutions was improved further.

In this work, filter paper enrichment was introduced as a sample pretreatment method to be combined with LIBS. Aqueous solution samples were dropped onto the filter paper placed on the surface of the metallic target. Then the filter paper was dried and the metallic target was taken off. A homogeneous sample layer was formed on the surface of the metallic target. In our previous reports, the filter paper adhered to the metallic target surface and absorbed aqueous solutions of heavy metals. Then the laser pulse was focused on the filter paper to induce plasma. The LoDs of Mn, Cr, Cd, and Cu in aqueous solutions were up to the level of sub mg/L [23, 30]. Also, indirect ablation laser induced breakdown spectroscopy has been demonstrated to be an efficient way for precise and sensitive analysis of wear metals in oils. We obtained the best LoDs of metal determination in viscous liquids [31]. In this paper, filter paper enrichment combined with LIBS was used to detect Cd, Mn, Cr, and Cu elements in aqueous solutions, and the detection sensitivity of this method to these heavy metals in aqueous solutions was also investigated. The detection accuracy of this method was verified by the concentration determination in real samples, the results of which were compared with those obtained by inductively coupled plasma mass spectrometry (ICP-MS).

**Experimental.** *Sampling.* Commercially medium speed quantitative filter papers (202, Hangzhou Fuyang Filter Paper Co. Ltd. Hangzhou, China) were used as the enrichment and transmission medium between the aqueous solution samples and the metallic substrate (Fig. 1). A pure aluminum target (Al 99.99%, Techlab, France) with a size of 21×22 mm was used as the metallic substrate. The commercial analytical reagents  $\text{CdCl}_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ ,  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Cr}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ , and  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (Sinopharm Chemical Reagent Co. Ltd., China) were dissolved with deionized water with a concentration of 100 mg/L each, which was used to obtain a set of reference samples by dilution for Cd, Mn, Cr, and Cu concentrations with 6, 5, 4, 3, 2, 1, and 0.5 mg/L, respectively. At first, the aluminum substrate was polished and cleaned, and then the dry filter paper (20×20 mm) was placed on the surface of the aluminum substrate as shown in Fig. 1a.

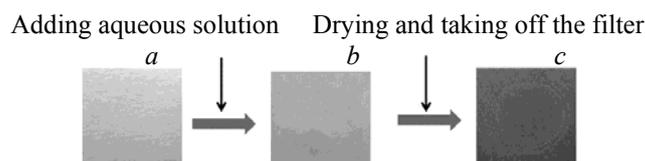


Fig. 1. Schematic diagram of the sample pretreatment procedures: dry filter paper (a) and wet filter paper (b) on the surface of the Al-metal substrate, c – Al-metal substrate with laser ablation.

During sample preparation, the enrichment effect of the filter paper was assessed to avoid the deposition of a part of the analyte on the fibers of the filter paper. The maximum volume of aqueous solutions absorbed on the filter paper was obtained. In our experiment, the evolution of the line intensity of the Cu I 324.7 nm at different sample dropping volumes ranging from 0.05 to 0.50 mL was achieved, as shown in Fig. 2. The concentration of Cu in an aqueous solution sample was 20 mg/L. Each point represents the average value of seven measurements ablated on the same Al substrate, and the error bars represent the associated standard deviations. We can see that the line intensity increases sharply before the dropping volume of 0.3 mL, and its rate decreases when the volume is between 0.30 and 0.45 mL. When the dropping volume is from 0.45 to 0.50 mL, the water enrichment saturation of filter paper occurred, possibly leading to decreased or unstable intensity. For Cd, Mn, and Cr, the line intensities are all higher and more stable at 0.4 mL. Moreover, in order to detect different elements simultaneously, it is necessary to set an agreed volume. According to the analysis above, the sample dropping maximum volume was therefore set as 0.4 mL.

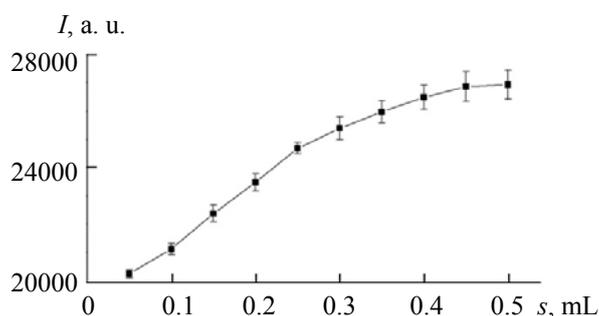


Fig. 2. The evolution of the line intensity of Cu I 324.7 nm at different sample dropping volumes ranging ( $s$ ) from 0.05 to 0.5 mL. The concentration of Cu in the aqueous solution sample was 20 mg/L, and each point represented the average value of seven measurements abating the same Al substrate.

The aqueous solution with a volume of 0.4 mL was dropped onto the filter paper placed on the surface of the aluminum substrate, as shown in Fig. 1b. The aluminum metallic substrate with the filter paper was heated by a heating plate at a temperature of 70 deg centigrade. After 5 min, the filter paper was removed, and a sample layer was formed on the surface of the aluminum metallic substrate, as shown in Fig. 1c. Then the aluminum target was placed on a rotating motor (60 rpm) to be ablated, as shown in Section 2.2. The surface morphology of the aluminum target after ablation exhibits good uniformity (Fig. 1c), making it possible to obtain good data reliability and reproducibility (as described in Section 3.1).

**Experimental.** A standard LIBS setup experiment was used in this experiment (Fig. 3). Its detailed description can be found elsewhere [32]. Briefly, a  $Q$ -switched Nd:YAG laser (1064 nm) was used for ablation with a laser pulse energy of 90 mJ. The laser pulse was focused slightly on the surface of samples by lens L1 ( $f=50$  mm). The Al metallic target covered with a sample layer was mounted on a rotating motor with a speed of 60 rpm. The plasma emission was collected by a combination of two lenses L2 and L3 with a focal

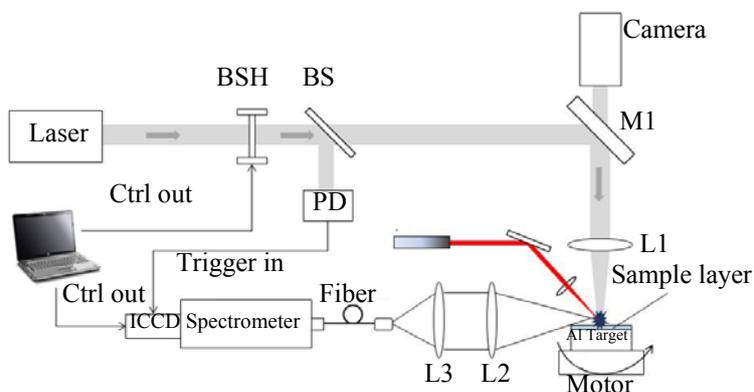


Fig. 3. Schematic diagram of the experimental setup. M1 – mirrors; BSH – beam shutter; BS – beam splitter; L1, L2, L3 – lenses.

length of 100 and 50 mm, respectively, and it was coupled into the entrance of a spectrometer (Andor, Mechelle 5000), which was in turn coupled with an intensified charge-coupled device camera (ICCD, iStar, Andor Technology). Each spectrum was obtained by the accumulation of over 200 single-shot ablations at different craters. A photodiode was used to detect the part of the laser pulse that provided the trigger signal for the ICCD camera. The detection window was set from 1.0 to 3.0  $\mu\text{s}$  after the impact of the laser pulse on the target. The experimental conditions, including the laser parameters and detection parameters such as the detection gate and the gain applied to the ICCD, were kept identical for all the samples.

**Results and discussion.** *Spectral line selections.* In order to obtain high performance for quantitative analysis, it is necessary to select a sensitive and available spectral line for the analytical element. In our work, the echelle spectrometer was used to record the emission spectrum over a wide spectral range from 220 to 850 nm. Figure 4 shows the spectrum of 200 single-shot LIBS obtained while 0.4 mL aqueous solutions were dropped onto the filter paper on the surface of the Al target with Cd, Mn, Cr, and Cu at a concentration of 10, 50, 30, and 20 mg/L, respectively. The spectrum of the most interesting spectral range for each element is presented.

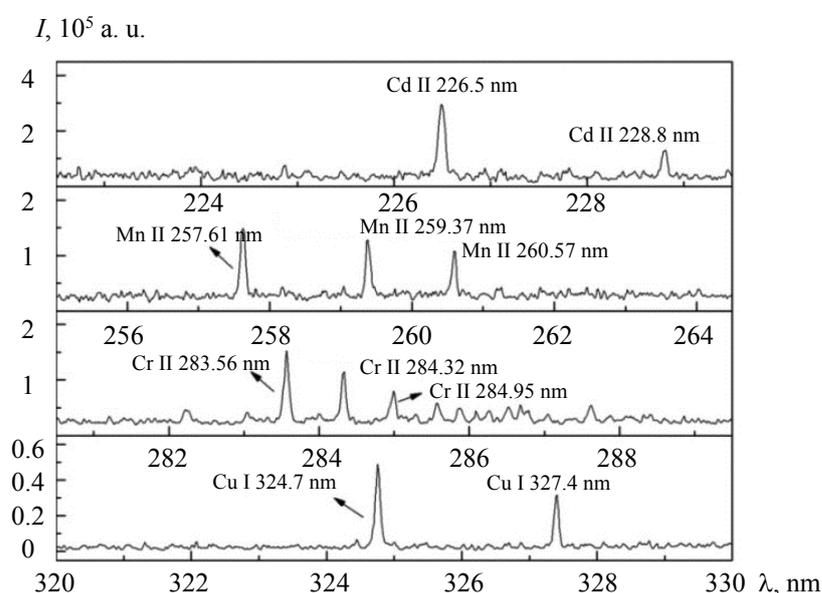


Fig. 4. Typical 200 single-shot LIBS spectra obtained while 0.4 mL aqueous solutions were dropped onto the filter paper on the surface of the Al target with Cd, Mn, Cr, and Cu concentrations at 10, 50, 30, and 20 mg/L, respectively.

In our experiment, the optimal emission lines of the four metals were selected. They were selected to be independent for avoiding any interference with other spectral emissions. The other important criterion was that the spectral lines would not be affected by the self-absorption effect. The shape of spectral lines was first observed to avoid strong self-absorption. Later, the calibration curves were plotted, and the linear fitting of the curves provided a negligible self-absorption effect for the selected lines. Finally, the spectral lines for the quantitative analysis of the four metal elements to be detected spectral lines CdII 226.5, MnII 257.61, CrII 283.56, CuI 324.7 nm are selected in our experiment.

*Calibration curves and LoDs for different elements.* For quantitative analysis, a series of experiments was carried out with the same experimental parameters, and the calibration curves were plotted. Figure 5 shows the calibration curves of Cd, Mn, Cr, and Cu in aqueous solutions under the normalized intensities with the Al I 396.2 nm as the internal reference. In Fig. 5, each data point represents the mean value of seven replicate measurements, and the error bars are their standard deviation. Calibration curves were fitted with a linear function:

$$y = b + ax, \quad (1)$$

where  $y$  is the normalized intensity of the emission line,  $x$  is the concentration of the element, and  $b$  and  $a$  are the intercept and slope of the calibration curves, respectively. The linear correlation coefficient  $R^2$  of the ca-

libration curves is also presented for each element in Fig. 5. The correlation coefficient  $R^2$  was improved to be 0.99 for each element. Both the reliability and reproducibility of the plotted data were improved due to the normalization procedure.

In the calibration curves plotted in Fig. 5, the LoDs of Cd, Mn, Cr, and Cu in aqueous solutions were calculated by the formula

$$\text{LoD} = 3\sigma/s, \quad (2)$$

where  $\sigma$  is the standard deviation of the background signals. In this experiment,  $\sigma$  was calculated from 10 measurements of background signals under the same experimental conditions. Here  $s$  denotes the slope of the calibration curves. We remarked that the determined concentration of the elements in the samples on the surface of the Al substrate was inconsistent with the real one in the aqueous solutions due to the different ability of paper to absorb different elements. However, in our work, the detected concentration on the surface of the Al substrate could be in line with that in real aqueous solutions, as the excess and the same volumes of samples were absorbed onto the filter paper. Therefore, the horizontal axis of the calibration curves represents the real concentration of elements in aqueous solutions, which could be determined by LIBS analysis.

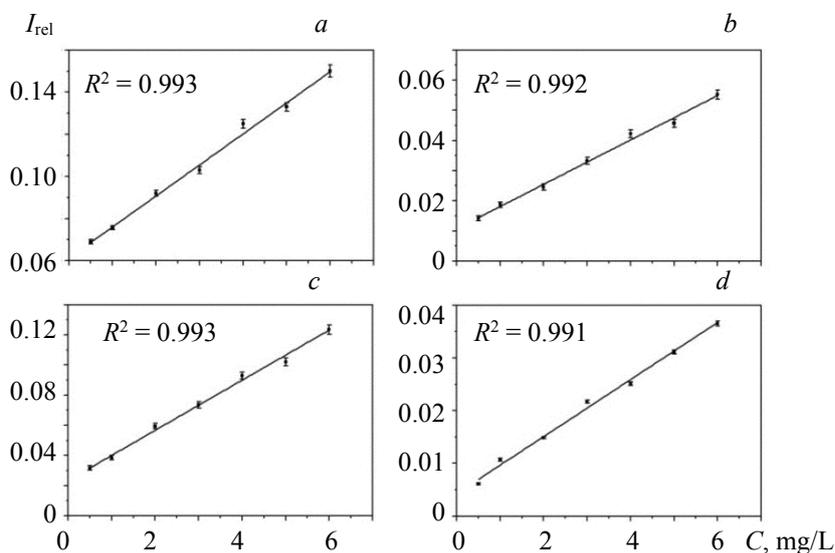


Fig. 5. Calibration curves of (a) Cd, (b) Mn, (c) Cr, and (d) Cu in aqueous solutions with line intensity normalization.

Table 1 shows an LoDs comparison between the present work and other similar works under different sampling configurations (e.g., wood slice substrate, filter paper substrate, other metallic substrates, ice substrate, and so on). It shows that the LoDs obtained from our method are lower or comparable to those using other similar methods. Even when the same metallic substrate was used for the aqueous solution deposition, the presented results are more precise compared with the reported results. We remarked that the LoDs values obtained from every method were not equal because of different experimental parameters (e.g., laser energy, detection delay and gate width, pulse accumulation, etc.) The detection sensitivity of these methods can be assessed by the LoDs of each element. Therefore, it was concluded that the detection sensitivity of this method was comparatively high. Moreover, filter paper enrichment combined with LIBS can be done within 5 min, shorter than the preparation time of other methods (e.g., ice, membrane,  $\text{Ca}(\text{OH})_2$ , dispersive liquid-liquid micro-extraction with SENLIBS (DLLME/SENLIBS) and single-drop micro extraction SENLIBS methods (SDME/SENLIBS)). The LoDs of Cd, Mn, Cr, and Cu obtained from this method are close to or lower than the level of the discharge standard of pollutants for the municipal wastewater treatment plant of China (No.GB/T 18918-2002), in which the highest discharge concentrations of Cd, Mn, Cr, and Cu are 0.01, 2.0, 0.1, and 0.5 mg/L, respectively. Moreover, the lower LoDs can be achieved through two-layer filter paper depositing more solutions on the surface of the aluminum metallic substrate in our further work.

TABLE 1. LoDs (mg/L) Comparison between the Present Work and Other Similar Works Corresponding to the Different Sampling Configurations

Methods	Elements			
	Cd	Mn	Cr	Cu
This method	0.165	0.035	0.012	0.078
Filter paper [30]	0.4	0.13	0.52	0.39
Wood slice [12]	0.59	0.036	0.034	0.029
DLLME/SENLIBS [26]	—	0.049	0.041	0.023
SDME/SENLIBS [27]	—	0.301	0.05	0.054
CR-SENLIBS [28]	0.386	—	0.016	0.257
Laser-pretreated Al target [29]	0.184	—	0.019	—
Ice [18]	1.4	—	1.4	2.3
Carbon planchet [19]	0.1	—	0.1	0.01
Membrane [16]	—	—	0.13	—

Note. DLLME/SENLIBS: dispersive liquid–liquid micro extraction with surface-enhanced LIBS; SDME/SENLIBS: single-drop micro extraction with surface-enhanced LIBS; CR-SENLIBS: chemical replacement with surface-enhanced LIBS.

*Accuracy of the concentration determination in the real samples.* To assess the accuracy of this approach, we present the results of measurements obtained by LIBS and inductively coupled plasma mass spectrometry (ICP-MS) on real samples from the wastewater collected from a local electroplating industry. The real samples were purified and collected when the heavy metals in wastewater were removed after biological adsorption. The commercial analytical reagents  $\text{CdCl}_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ ,  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , and  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  were dissolved with the wastewater purified with the concentration of 1.5 mg/L for Cd, Mn, Cr, and Cu to prepare the real samples measured. The concentrations of Cd, Mn, Cr, and Cu in real samples were determined by the above-established calibration curves shown in Fig. 5. The calculated results are shown in Fig. 6. In order to assess the accuracy of the results of LIBS with other methods, the same real samples were detected by inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7500ce, USA).

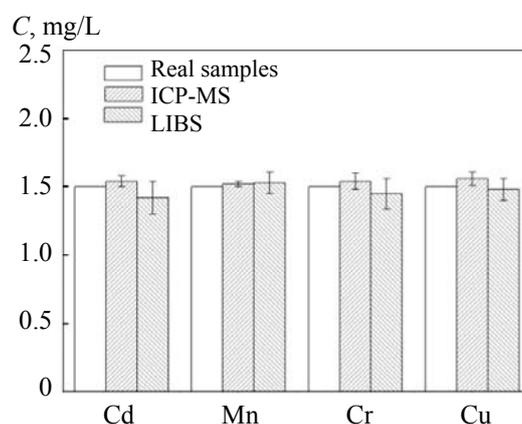


Fig. 6. Measurement results on real samples with the prepared concentration using LIBS and ICP-MS.

In Figure 6, the LIBS and ICP-MS results are both the average of seven replicate measurements, and error bars represent intensity ratios of seven replicate measurements. The average values obtained by ICP-MS are slightly higher than those from the prepared concentration of real samples, probably due to some residuals after the biological absorption of wastewater. However, based on comparison with the prepared concentration of real samples, good agreement was obtained between the LIBS and the ICP-MS results, although the error bars from the LIBS results are higher.

Firstly, the filter paper enrichment technology was used to convert liquid sample detection to solid sample detection by LIBS, which enhanced sample ablation efficiency and greatly improved detection sensitivity.

ty. Moreover, the filter paper was used as a transmission and enrichment medium through which more liquid samples were enriched on the surface of the metallic substrate. This can further improve the detection limits of trace elements in aqueous solutions. In addition, the filter paper was used to place the liquid samples onto the surface of the metallic substrate, thus helping the formation of a more uniform sample layer on the substrate surface, and good data reliability and reproducibility were obtained. This indicates that filter paper enrichment combined with LIBS is applicable to sensitive and quantitative analysis of trace metals in real environmental water with accurate results.

**Conclusions.** LIBS technology combined with filter paper enrichment was applied successfully to detect sensitively Cd, Mn, Cr, and Cu in aqueous solutions. Calibration curves were plotted for Cd, Mn, Cr, and Cu at a trace level of sub-mg/L to several mg/L levels. The limits of detection were calculated with calibration curves, which already exhibited high performance at the several hundred or 10  $\mu\text{g/L}$  level (Cd 0.165 mg/L, Mn 0.035 mg/L, Cr 0.012 mg/L, and Cu 0.078 mg/L). According to the comparison with the data previously published for LIBS analysis of trace metals in aqueous solutions, the LoDs obtained from our method are lower than or comparable to those using other similar methods. Even when the same metallic substrate was used for aqueous solution deposition, the presented results are more precise compared with the reported results. The LIBS results agree reasonably well with those from ICP-MS for real samples compared to the prepared concentration of real samples. This indicates that our method is suitable for sensitive and quantitative analysis of trace metals in aqueous solutions and can achieve accurate results.

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