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Improving the Sensitivity of Surface-Enhanced Laser-Induced Breakdown Spectroscopy by Repeating Sample Preparation

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To further improve the detection sensitivity of surface-enhanced laser-induced breakdown spectroscopy (SENLIBS), the number of repeating sample preparations in a fixed area was increased. The trace elements in an aqueous solution were quantitatively analyzed successfully. The results showed that the spectral intensities were strengthened. The limit of detection (LoD) values of Cu, Pb, Cr, and Cd were reduced from 0.072∼0.36 to 0.027∼0.057 μg/mL by increasing the number of repeating sample preparations from 1 to 8. This demonstrated that quantitative analytical sensitivity of SENLIBS could be improved by repeating sample preparations without increasing the cost of equipment.

Keywords: laser-induced breakdown spectroscopy, surface-enhanced, sensitivity, aqueous solution, sample preparation

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INTRODUCTION

Spectral analysis technology has been applied to the analysis of gas, solids, and liquids [1–4]. Laser-induced breakdown spectroscopy (LIBS) as a booming analysis technology has been proven as a promising method for waste-water monitoring [5]. Although LIBS has unique advantages such as micro-volume sample analysis, *in situ*, online, and stand-off analysis capabilities [6–10], it still faces a technical bottleneck of poor sensitivity in determining trace elements in aqueous solutions [11–13]. To improve the detection sensitivity, some methods have been proposed, such as changing the liquid samples from a static liquid to dynamic liquid using sampling equipment (e.g., meinhard nebulizer, pump, and nozzle) [14–16], assisting LIBS with additional equipment (e.g., magnetic field, electric field, and laser) [17–19], and converting the liquid samples from liquid phase to solid phase using liquid nitrogen, adsorbent materials, electrodeposition, and non-absorbent materials [20–23] etc.

Recently, surface-enhanced LIBS (SENLIBS), as a new liquid-to-solid phase transition method, has been considered as a versatile analytical technique for liquid samples [24–35], power samples [36], and solid samples [37]. The powder sample was mixed with viscous liquid as the liquid sample. The solid sample was changed to the liquid sample by chemical treatment. Next, the liquid sample was dried as a solid layer or deposited as the gel-like layer on a non-absorbent substrate surface, and then analyzed by LIBS. Up to now, many methods have been proposed to further improve detection sensitivity or the spectrum intensity of SENLIBS, which included the liquid microextraction (e.g., single drop microextraction and dispersive liquid–liquid microextraction) [29, 38, 39], chemical replacement [27], and double-pulse LIBS (DP-LIBS) [35]. However, liquid microextraction will introduce additional chemical agents, as chemical replacement is only suitable for analysis of inert metal ions, and DP-LIBS will increase the cost of equipment.

To further improve the detection sensitivity of SENLIBS, a sample preparation method was introduced in this work, which will increase the element concentration per unit area by increasing the number of sample preparations in a fixed point. Therefore, experimental conditions, spectral enhancement, and quantitative analysis of the trace elements in aqueous solution were investigated and discussed in detail.

EXPERIMENTAL

LIBS Instrument

The experimental setup for LIBS is schematically illustrated in **Figure 1A**, which was described in our previous work [40]. Briefly, the Q-switched Nd:YAG laser was used as an ablation source to ablate the samples. The laser beam was reflected and focused on the sample by a reflector mirror and a plano-convex lens (f = 100 mm). The defocusing amount for ablation of the sample is 4 mm. The speed of the 2D motorized translation stage loaded with samples is 5 mm/s. The plasma emission was coupled into an echelle spectrometer (Andor Tech., Mechelle 5000) through the light collector (f = 200 mm) and optical fiber (50 μm × 200 cm). An intensified charge-coupled device camera (ICCD) (Andor Tech., iStar 334T) was attached to the spectrometer, which can convert the optical signal into an electrical signal for analysis.

Sample Preparation

The stock solution was prepared with the analytical reagents [$CrCl_3$, $CdCl_2$, $CuCl_2$, and $Pb(NO_3)_2$]. The concentration of each element (Cu, Pb, Cd, and Cr) in the stock solution was 500 μg/mL. The stock solution was diluted with deionized water to prepare 11 standard aqueous solutions. The concentration range of each element in the standard solutions ranged from 0.1 to 10 μg/mL.

A zinc target, without analytical elements, was used as a metallic substrate. To increase the sample preparation repeatability, a 6 mm diameter filter paper was placed on the surface of the Zn-metal substrate as reported in our previous work [40]. The sample pretreatment procedures of each aqueous solution are shown in **Figure 1B**, which included: (1) the Zn-metal substrate with filter papers was placed on a heating plate; (2) a microdroplet of standard solution was deposited on the filter paper by a micropipette; (3) After drying, step 2 was repeated as needed; (4) finally, the filter paper was taken off. The standard aqueous solution was prepared as a 6 mm diameter solid prepared layer on the surface of the Zn-metal substrate.

To further improve the LIBS spectral stability, the spectral was obtained by concentric analysis of each droplet deposition area as shown in our previous work [40]. Each spectrum was accumulated for 90 shots. **Figure 2** shows the optimization of sample preparation conditions. As shown in **Figure 2A**, the maximum spectral intensities of trace elements increased with the sample volume. As shown in **Figure 2B**, the higher the temperature is, the less time is needed for drying. In this work, 40 μL was selected as the sample volume for each microdroplet, 70°C was chosen as the drying temperature, and the drying time for each sample preparation was about 4 min.

RESULTS AND DISCUSSION

Optimization of the Analytical Parameters

For high detection sensitivity, a higher signal-to-noise ratio (SNR) is needed. The laser energy and gate delay time were optimized for the highest SNR. **Figure 3** shows the evolution trends of SNRs of analytical lines (Cu I 324.75 nm, Pb I 405.78 nm, Cd I 508.58 nm, and Cr I 520.84 nm) on laser pulse energies (gate delay: 3 μs; and gate width: 0.5 μs) and gate delay times (laser energy: 40 mJ; and gate width: 0.5 μs). The SNR values were calculated based on the ratio of the maximum analytical line intensities and the noise calculated by

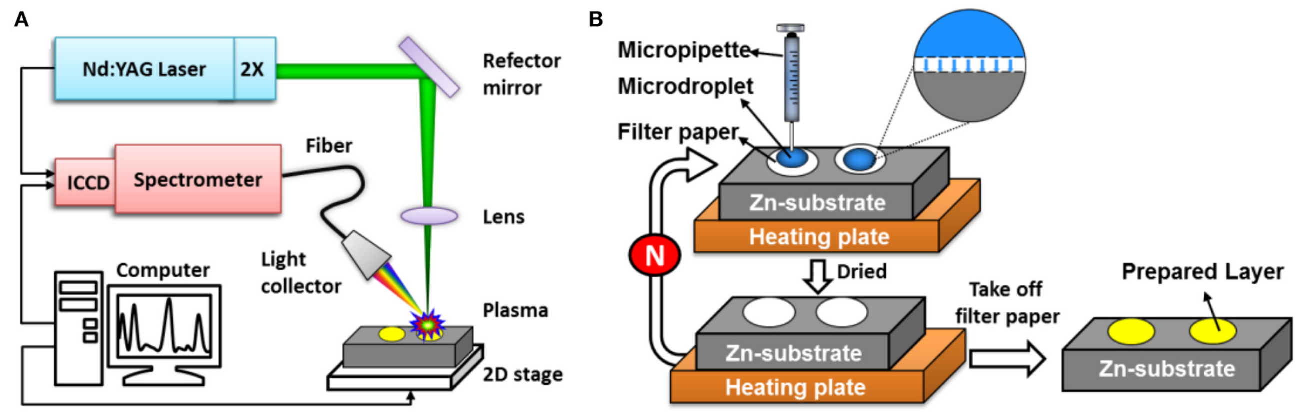

FIGURE 1 | Schematic of the experimental setup **(A)** and the sample pretreatment **(B)**.

the background near the analytical lines. The 369.43–369.61 nm for Cu, 398.66–398.55 nm for Pb, and 537.23-537.33 nm for both Cd and Cr were chosen as the background. As shown in **Figure 3**, the SNRs of all analytic lines increased first and then decreased with increasing laser energy and gate delay time, respectively. Therefore, 40 mJ of laser energy, the 2 μs of

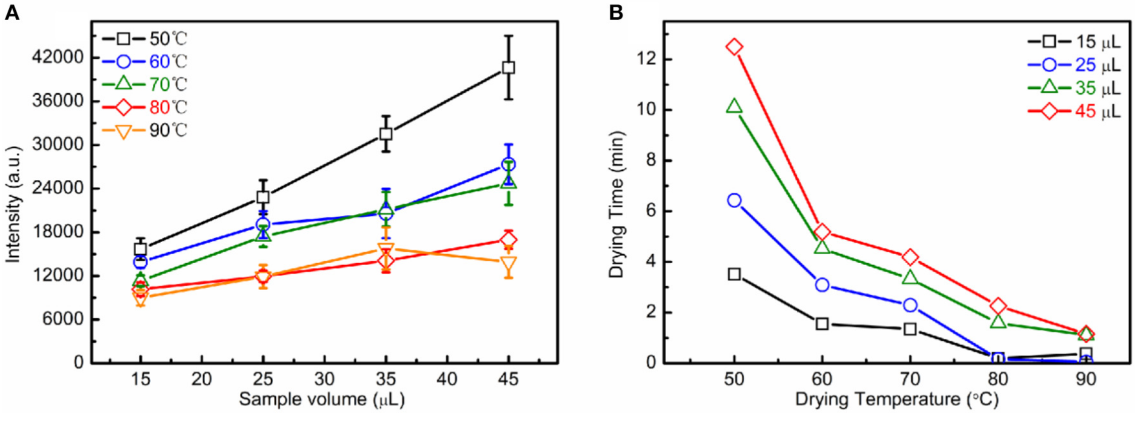

FIGURE 2 | Optimization of sample preparation conditions: the effect of sample volume on the spectral intensity **(A)**; the drying temperature on the drying time **(B)**.

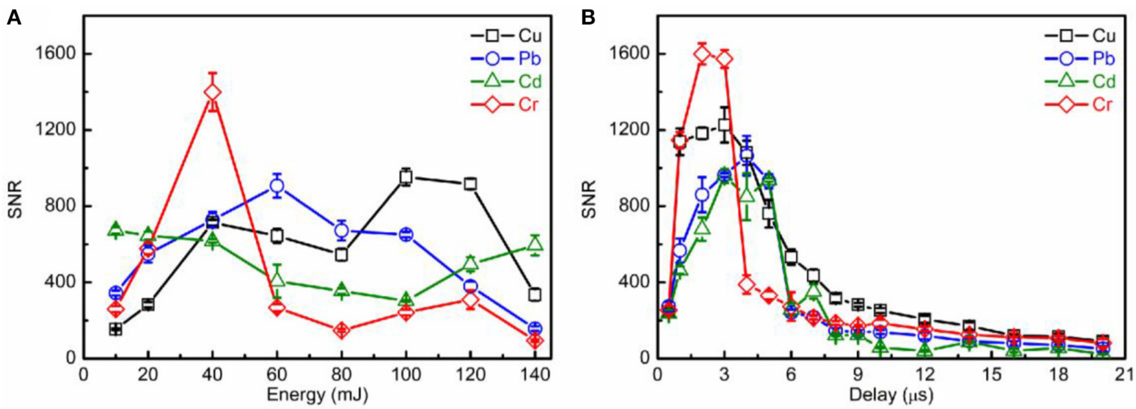

FIGURE 3 | Evolution trends of SNRs for analytical lines (Cu I 324.75 nm, Pb I 405.78 nm, Cd I 508.58 nm, and Cr I 520.84 nm) on laser energy **(A)** and gate delay time **(B)**.

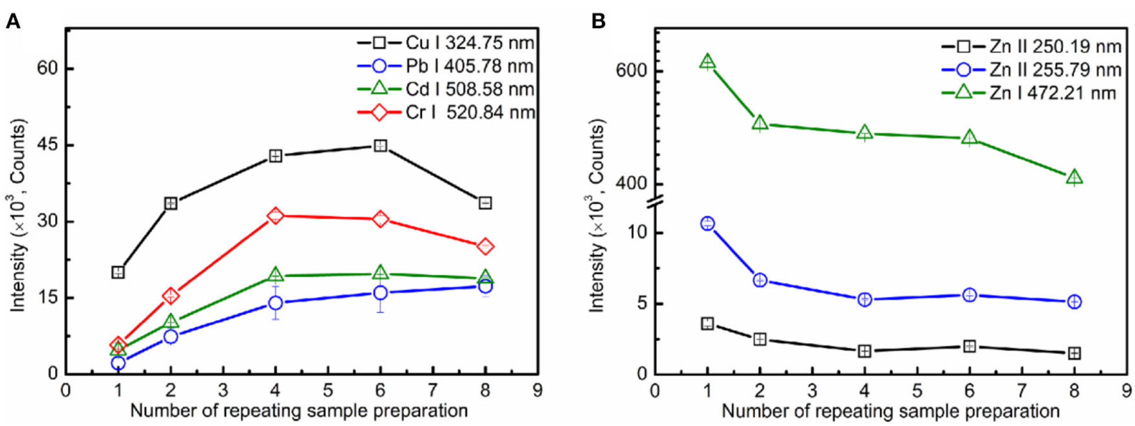

FIGURE 4 | Evolution trends of spectral intensity for analytical lines **(A)** and substrate element lines **(B)** on the number of repeating sample preparations.

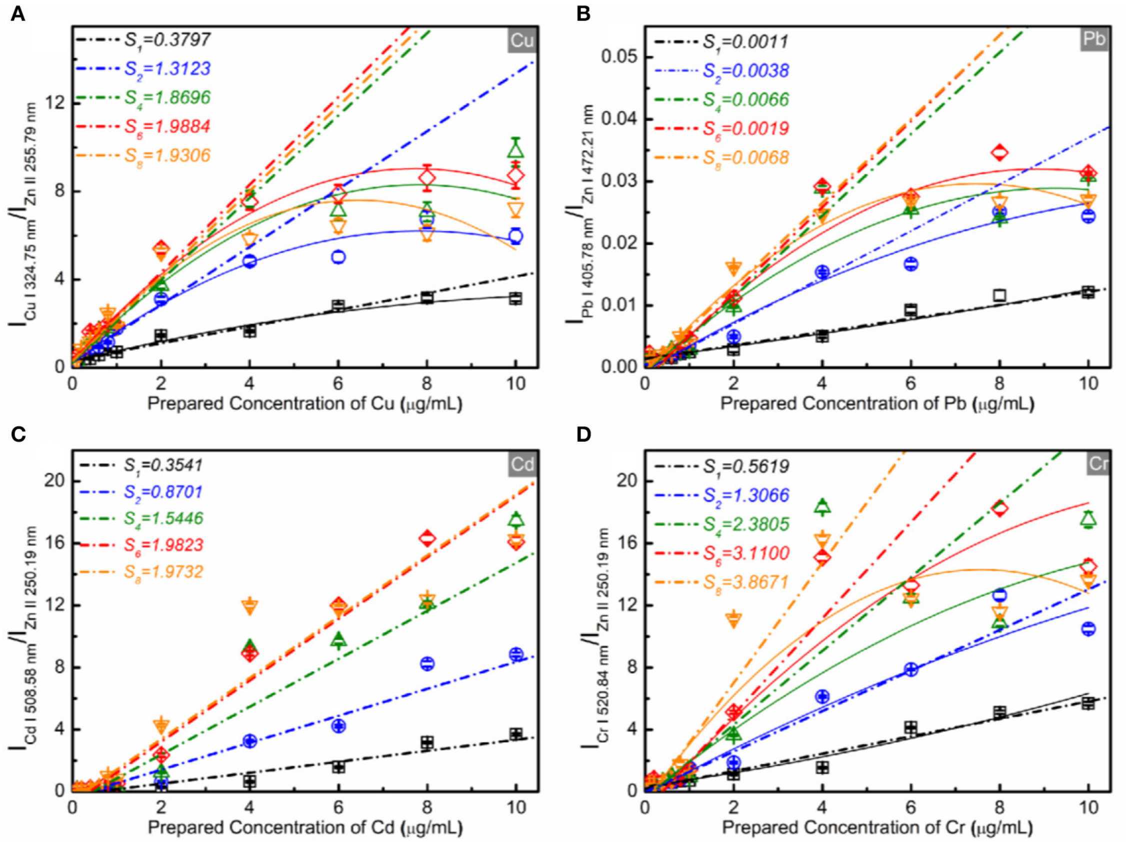

FIGURE 5 | Calibration curves with linear fit (short dash dots line) and a quadratic fit (solid line) of trace elements [Cu **(A)**, Pb **(B)**, Cd **(C)**, and Cr **(D)**] in the standard samples analyzed by SENLIBS with different number of repeating sample preparations.

both gate delay and gate width were selected as the optimum experimental parameter.

Spectral Enhancement

As is widely known, as the element concentration per unit area on the metal surface enlarged, the spectral intensity will be enhanced. With an increase in the number of repeating sample preparations within a fixed range, the element concentration per unit area will be enlarged. As the results, the spectral intensity will be strengthened. **Figure 4A** shows the relationship between spectral intensities and the number of repeating sample preparations. As shown, the spectral intensities for each element were increased with the number of repeating sample preparations. However, the spectral intensities of the substrate element lines (Zn II 250.19 nm, Zn II 255.79 nm, and Zn I 472.21 nm) decreased with the number of repeating sample preparations, as shown in **Figure 4B**. For SENLIBS, the prepared layer and the metallic substrate were ablated simultaneously. The ablation amount of the substrate decreased with the increase of prepared layer thickness, with the increase of the number of repeating sample preparations under the same experimental conditions.

Calibration Curves and Limits of Detection

As is well-known, the detection sensitivity will be improved with the spectral intensity enhancement. For SENLIBS, the ablation amount of the substrate will be reduced with the increase in thickness of the prepared layer under the same experimental conditions. To reduce the effect of different thicknesses of the prepared layer, the substrate element Zn was selected as the reference element for quantitative analysis as shown in our previous work [40]. **Figure 5** shows the calibration curves of analytical lines (Cu I 324.75 nm, Pb I 405.78 nm, Cd I 508.58 nm, and Cr I 520.84 nm) analyzed by SENLIBS with different number of repeating sample preparations. As shown the slope of the calibration curve (S) with linear fit, increased with the number of repeating sample preparations. The self-absorption effect increased with the number of repeating sample preparations, which was evident from the bend of calibration curves with the quadratic fit. As shown in **Figure 6**, the LoDs for SENLIBS were decreased with the number of repeating sample preparations. And the LoDs were improved from 0.072∼0.36 to 0.027∼0.057 μg/mL. The results demonstrate that the sensitivity of SENLIBS could be improved by increasing the element concentration per unit area through increasing the number of sample preparations, and the

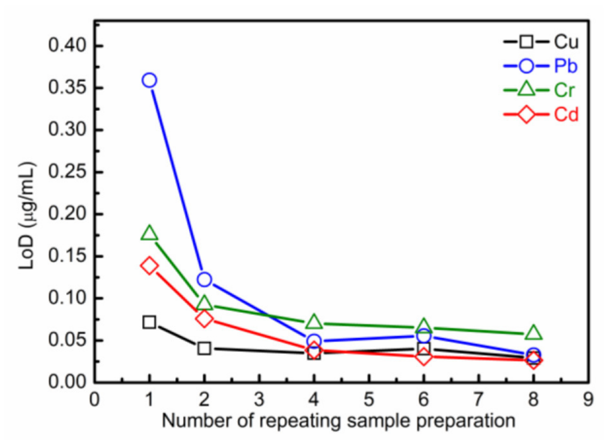

FIGURE 6 | Evolution trends of LoDs for analytical lines (Cu I 324.75 nm, Pb I 405.78 nm, Cd I 508.58 nm, and Cr I 520.84 nm) on the number of repeating sample preparations.

saturation of sensitivity would be reached owing to the self-absorption effect.

As reported, sensitivity of LIBS for analysis of aqueous solution could be improved by use of supplementary instrumentation [16–18], e.g., DP-LIBS, LIBS-LIF, LIBS combined with magnetic field etc. Therefore, those reported methods could be introduced to reduce the sample preparation time and to improve the sensitivity of SENLIBS. Although the sample preparation time with repeating sample preparations is about 16 min, both the cost and complexity of equipment was reduced compared to those of reported methods. As is generally known, the sample preparation time of SENLIBS depends on the liquid volume and spreading area. Therefore, the number of repeating sample preparations, with the same element concentration per unit area, could be reduced by reducing the spreading area with the same liquid volume. As the results, the sample preparation time will be decreased. These results showed that the introduced method is a feasible method in improving the sensitivity of SENLIBS.

CONCLUSIONS

A new sample preparation method for improving the sensitivity of SENLIBS was proposed, by repeating sample preparations in a fixed point. Using this method, both the spectral intensity and detection sensitivity of trace elements (Cu, Pb, Cd, and Cd) in aqueous solution, using SENLIBS, were improved by increasing the number of sample preparations in a fixed point. The unique advantages of this method include the low cost of equipment and its higher sensitivity. Accordingly, this proposed method is an economical method for the analysis of trace elements in a liquid sample.

DATA AVAILABILITY STATEMENT

The datasets generated for this study are available on request to the corresponding author.

AUTHOR CONTRIBUTIONS

XY, XL, and ZC planned and supervised the experiments, processed the raw data, and wrote and revised the manuscript. GY, ZZ, and KL advised on data processing. All authors contributed to the article and approved the submitted version.

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.