SENSITIVE ANALYSIS OF COPPER IN WATER BY LIBS-LIF ASSISTED BY SIMPLE SAMPLE PRETREATMENT[**]

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Laser-induced breakdown spectroscopy (LIBS) combined with laser-induced fluorescence (LIF) is applied to realize sensitive analysis of trace copper in water for the first time. A wood slice substrate is selected as water absorber to convert liquid sample analysis to solid sample analysis to eliminate drawbacks of the water matrix in direct analysis of liquid samples by the LIBS or LIBS-LIF technique. Copper atoms in the laser-induced plasma are resonantly excited at 324.75 nm from the ground state to a higher state with a tunable dye laser. The fluorescence of copper atoms from this higher state to a lower state at 510.55 nm is selectively monitored with high detection sensitivity. A calibration curve of copper in water analyzed with the LIBS-LIF technique has been built and the limit of detection reaches 3.6 ppb, which is 4–5 orders better than that obtained in direct analysis of aqueous solutions by the LIBS technique. The combination of this simple sample pretreatment method with the LIBS-LIF technique demonstrates rapid, sensitive, and reliable analysis of trace copper in water.

Keywords: laser-induced breakdown spectroscopy, laser-induced fluorescence, wood slice, copper in water, sensitive detection.

ЧУВСТВИТЕЛЬНЫЙ АНАЛИЗ СОДЕРЖАНИЯ МЕДИ В ВОДЕ С ПОМОЩЬЮ МЕТОДОВ СПЕКТРОСКОПИИ ЛАЗЕРНО-ИНДУЦИРОВАННОЙ ПЛАЗМЫ В СОЧЕТАНИИ С ЛАЗЕРНО-ИНДУЦИРОВАННОЙ ФЛУОРЕСЦЕНЦИЕЙ ПРИ ПРОСТОЙ ПРОБОПОДГОТОВКЕ

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Для реализации чувствительного анализа следов меди в воде применена спектроскопия лазерно-индуцированной плазмы (LIBS) в сочетании с лазерно-индуцированной флуоресценцией (LIF). Для устранения недостатков использования водяной матрицы при непосредственном анализе жидких образцов методами LIBS или LIBS-LIF в качестве поглотителя воды выбрана тонкая подложка из древесины, что позволяет превратить анализ жидкой пробы в анализ твердых образцов. Атомы меди в лазерно-индуцированной плазме резонансно возбуждаются из основного состояния в верхнее состояние излучением перестраиваемого лазера на красителе на λ = 324.75 нм. Флуоресценция атомов меди из верхнего состояния в нижнее на λ = 510.55 нм регистрируется избирательно с высокой чувствительностью. Построена калибровочная кривая для анализа содержания меди в воде с использованием метода LIBS-LIF. Достигнут предел обнаружения 3.6 ppb, что на 4–5 порядков лучше, чем при непосредственном анализе водных растворов методом LIBS. Показано, что сочетание выбранного простого метода предварительной обработки образца с методикой LIBS-LIF обеспечивает быстрый, чувствительный и надежный анализ следового содержания меди в воде.

Ключевые слова: спектроскопия лазерно-индуцированной плазмы, лазерно-индуцированная флуоресценция, древесная подложка, содержание меди в воде, чувствительная регистрация.

Introduction. Although copper is an essential nutrient for plants and animals, including human beings, copper overdose is harmful. High levels of copper in the human body can cause some detrimental pathological reactions such as vomiting, diarrhea, stomach cramps, nausea, liver cirrhosis, and even death. According to the regulations set by the Environmental Protection Agency (EPA) of the Unite States, the threshold value of copper in drinking water is 1.3 mg/L, or 1.3 ppm [1]. In order to avoid copper overdose in drinking water that originates mainly from industrial effluents, sensitive detection of trace copper in natural water is very important and necessary.

Several state-of-the-art analytical methods can be utilized to analyze copper in water, such as flame atomic absorption spectrometry (FAAS) [2], inductively coupled plasma mass spectrometry (ICP-MS) or inductively coupled plasma optical emission spectrometry (ICP-OES) [3], and energy dispersive X-ray fluorescence (EDXRF) [4]. These methods can realize trace metal analysis of water with high sensitivity, but most of them must be carried out in laboratories. Laser-induced breakdown spectroscopy (LIBS) has also been developed for more convenient and rapid analysis of copper in water over the past decades because of its potentials for *in situ* or field analysis.

However, two problems of direct LIBS analysis of water samples still exist if the laser beam is focused on a water surface: (i) water splashing will seriously affect light collection of the optical system, leading to low signal reproducibility; (ii) water molecules or OH radicals in the laser-induced plasma will quench the atomic emission of the analytes, leading to low analytical sensitivity. Thus the limits of detection (LODs) of copper in water obtained in the direct LIBS analysis of water samples are usually at ppm levels [5]. Analysis of ultrasonic-nebulization samples [6] or ices [7] with LIBS can only solve the first problem; the quenching effect still exists in the laser-induced plasma, and the LODs of copper are still at ppm levels.

The analytical sensitivity of metals in water by LIBS can be improved from two aspects. The first is adopting different methods of liquid-to-solid sample convertion to remove the interference from water matrix. Different solid substrates have been used as water absorber to convert liquid sample analysis to solid sample analysis, such as ion exchange membrane [8] or crosslink PVA polymer membrane [9], carbon planchet [10], wood slice [11], filter paper [12], fish bone [13], and hydrogel [14]. A 2–3 orders improvement factor can be achieved using these sample pretreatment methods. Except the ion exchange membrane and fish bone, sample pretreatment using the above-mentioned substrates usually takes a few minutes, which is acceptable for daily applications. It is worthwhile to mention that an electrical-deposition preconcentration method can be used to improve analytical sensitivity of metal ions in water by LIBS significantly; however, tens of minutes is required for sample preparation, and other ions may interfere with the electrical-deposition preconcentration of the analytes [15, 16].

The second one is developing more sensitive spectroscopic techniques to enhance analytical sensitivity of metals in water. The double-pulse LIBS (DP-LIBS) has been applied to analyze copper in water samples, and better results could be achieved than single-pulse LIBS (SP-LIBS) [17, 18]. Excitation of the atoms in the laser-induced plasma with a second laser source and monitoring the atomic fluorescence can also enhance the analytical sensitivity. Cheung et al. [19–21] have developed the plum laser excited atomic fluorescence (PLEAF) technique in which the atoms in the laser-induced plasma are excited by a 193 nm laser with high photon energy, and enhanced atomic emissions are observed for the elemental analysis. In a typical laser-induced fluorescence (LIF) technique, the atoms are resonantly excited from the ground state to a higher state with a tunable laser, and the fluorescence emissions from the upper states are selectively monitored. The LIF technique has been applied to analyze atoms or molecules in laser-induced plasma, which is termed with the laser-ablation-LIF (LA-LIF) or LIBS-LIF. In the past decades, the LIBS-LIF technique has been applied to analyze heavy metals in soil [22], lead in water [23–27], and phosphorus [28], boron [29], and cobalt [30] in steel. Aside from higher analytical sensitivity, the spectral interference from other species can be eliminated due to the selective atomic excitation in LIBS-LIF [31]. The spatially selective excitation has also been proposed to get better analytical performance [32].

This work will test the possibility of using the LIBS-LIF technique for the sensitive detection of trace copper in water samples. In order to eliminate the drawbacks of the water matrix, a wood slice will be selected as the water absorber to realize the liquid-to-solid sample conversion. The sample pretreatment schedule will be introduced, and the analytical characteristics, performance, and application of this technique for analyzing natural water samples will be evaluated.

Experiment. A schematic diagram of the LIBS-LIF experimental setup used for copper analysis in our laboratory is shown in Fig. 1. The 532 nm output of an electro-optical Q-switched Nd:YAG laser (Nd:YAG 1) with 12 ns pulse width and 5 Hz repetition rate was used as the LIBS laser source to ablate and break down

the samples. The laser beam was focused by a plano-convex lens L1 (quartz, f = 50.8 mm) onto the sample surface. The sample was mounted on an x-y translation platform which was moving at a linear speed of 0.5 mm/s during the experiment to ensure a fresh spot for each laser shot. A homemade dye laser consisting of an oscillator, an amplifier, and a second harmonic generation (SHG) unit was used as the resonant excitation laser source in LIF. The dye laser was pumped by the 532 nm outputs of a second similar electro-optical Q-switched Nd:YAG laser (Nd:YAG 2). The DCM (6-(4-dimethylaminostyryl)-4H-pyran) laser dye was dissolved in ethanol to prepare the dye solutions with concentration of 1.5×10^{-3} mol/L for the oscillator and 1.4×10^{-4} mol/L for the amplifier. In this dye laser, the resolution power of the grating is 24000, and the line width of the output dye laser at 649.50 nm was estimated to be ~0.03 nm.
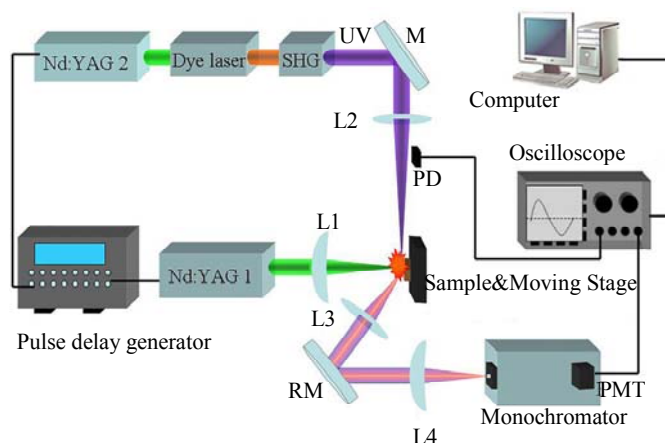

Fig. 1. Schematic diagram of the LIBS-LIF experimental setup.

The output of the dye laser was frequency-doubled with a SHG unit (BBO crystal) to generate the UV laser emission to be used as the resonant excitation laser source in LIF. For description convenience, this UV laser was called the LIF laser, and the 532 nm laser used to ablate and break down the samples was called the LIBS laser in the following text. The LIF laser was slightly focused on the plasma produced by the LIBS laser with a plano-convex lens L2 (quartz, f = 150 mm) along the direction parallel with the sample surface. The pulse energy of the LIF laser was ~110 μJ and it could be attenuated with two Glan-Taylor polarizers. A 4-channel pulse delay generator (Quantum Composers, model 9520) was utilized to synchronize these two Nd:YAG lasers and to control the interpulse delay between the LIF laser pulse and the LIBS laser pulse.

Plasma emission was optically collected onto the entrance slit of a 30 cm monochromator equipped with a 1200 line/mm diffraction grating for wavelength selecting. Both the widths of the entrance and exit slits of the monochromator were set at 100 μm, and the resolution was better than 0.3 nm, both predicted theoretically and demonstrated by observing the sodium D line of a discharge lamp. The output signal of a photomultiplier tube (PMT) (Hamamatsu, CR114) was monitored by a 500 MHz digital storage oscilloscope (Gw Instek, model GDS-3502). A fast photodiode (PD) receiving the scattered dye laser generated a trigger source for the oscilloscope. The signal recorded by the oscilloscope could be transferred to a computer for further analysis.

A set of aqueous solutions of copper in water were prepared by dissolving analytical pure $CuCl_2 \cdot 2H_2O$ (>99%) in deionized water. Commercially available wood slices made with poplar were selected as water absorbers. The concentration of copper in these wood slices was checked with the LIBS-LIF technique before the sample preparation to make sure that the copper concentration in these wood slices was very low and the influence on the quantitative analysis could be ignored. Each wood slice was cut to the size of $40 \times 25 \times 1$ mm^3 and dipped into the prepared aqueous solution for 2 min, and then it was taken out and baked for 3 min using a 100 W infrared lamp to evaporate the water molecules. Finally, the prepared wood slice was mounted on the sample platform for immediate analysis.

Figure 2 shows a simplified energy level diagram of copper atoms relative to this work. The copper atoms can be excited from the $^2S_{1/2}$ ground state to the $^2P_{3/2}$ upper state at 324.75 nm with the frequency-doubled tunable dye laser, and the LIF signal from the $^2P_{3/2}$ upper state to the $^2D_{5/2}$ lower state of copper atoms at 510.55 nm can be selectively monitored for the spectral analysis. As we know, in the emission spectrum of copper atoms, the line emission intensities at both 324.75 and 510.55 nm wavelengths are relative

strong. This implies a relatively high induced absorption coefficient for the excitation at 324.75 nm and a relatively high spontaneous emission coefficient for the 510.55 nm fluorescence, which is helpful for the highly sensitive detection of the trace copper atoms in the laser-induced plasma.
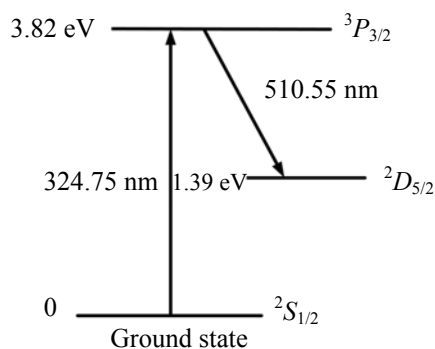

Fig. 2. Simplified energy level diagram of copper atoms in relation to this work.

Results and discussion. Typical temporal profiles of plasma emission for both LIBS-LIF and LIBS are shown in Fig. 3. In the experiment, the pulse energy of the LIBS laser and the LIF laser was ~8 mJ and ~110 μJ. The wavelength of the LIF laser was 324.75 nm, thus the copper atoms could be resonantly excited from the ground state to the $^2P_{3/2}$ upper state. The interpulse delay between the LIBS laser and LIF laser pulses was 8 μs. Since the oscilloscope was triggered by the dye laser, the plasma emission excited by the LIBS laser appeared ~8 μs ahead of the LIF laser. The copper fluorescence appeared at ~0 μs in LIBS-LIF.

The fact that the signal appearing at ~0 μs in Fig. 3 is due to the fluorescence of the copper atoms was double checked in two ways. The first was tuning the wavelength of the LIF laser to select resonant and non-resonant excitation for copper atoms, where the dye laser wavelength was measured with a monochromator. The fluorescence signal could be observed under resonant excitation. Without fluorescence signal could be observed under nonresonant excitation. The second was the observation of the signal at different monitoring wavelengths under resonant excitation. When the monitoring wavelength was set at 510.55 nm, the fluorescence signal could be observed, but if the monitoring wavelength was set at 509.55 or 511.55 nm, the signal disappeared in these cases. All these demonstrated that the observed signal appearing at ~0 μs in Fig. 3 was the fluorescence of the copper atoms. It is worthwhile to note that the time duration of the fluorescence of copper atoms was less than 30 ns, almost of the same order as the laser pulse width. It was found that,
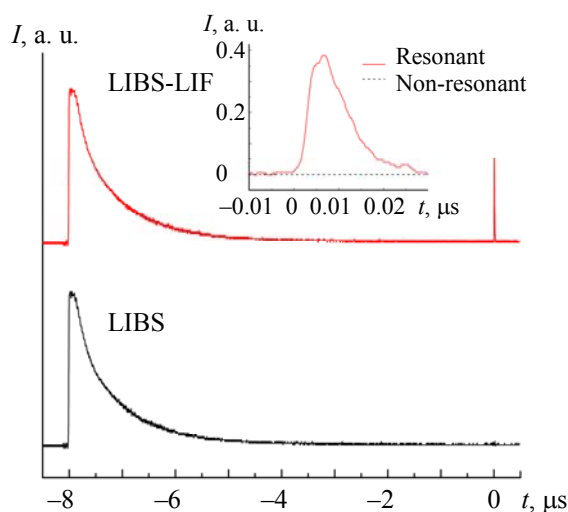

Fig. 3. Observed temporal profiles of the plasma emissions at 510.55 nm in LIBS and LIBS-LIF. The wavelength of the LIF laser was 324.75 nm. The inset shows the signal recorded at 510.55 nm under resonant excitation at 324.75 nm and nonresonant excitation at 325.0 nm for Cu atoms.

in the time window while the fluorescence appeared, the background was very weak. This provided almost background-free signal detection; thus the detection sensitivity could be improved significantly in comparison with that of conventional LIBS, which was affected by the strong background from the continuous bremsstrahlung emission of the laser-induced plasma. Below, all signal or background intensities are time integrated intensities of the observed signals and backgrounds.

In order to have an optimal analytical performance, some experimental parameters were first optimized, such as pulse energies of the LIBS and LIF lasers and interpulse time delay between the LIBS and LIF lasers. According to the experimental observation, the maximum signal-to-background ratio was reached when the interpulse time delay was 8 μs and the pulse energy was 12 mJ. Therefore, in the following experiments, the pulse energy of the LIBS laser was set at 12 mJ, and the interpulse time delay between two laser pulses was set at 8 μs.

The relationship of the signal intensity of copper fluorescence to the pulse energy of the LIF laser has also been investigated experimentally. The signal intensity increased monotonously and non-linearly with increasing pulse energy of the LIF laser. A slight saturation effect has been observed, which is similar to that reported in lead analysis with the LIBS-LIF technique [26]. Because the maximum output pulse energy of our dye laser was not high enough to introduce a significant saturation effect, the maximum pulse energy of 110 μJ was selected in the experiments for the LIF laser.

From the analytical point of view, the water-absorption characteristic of each wood slice will be the key point affecting the analysis accuracy. In order to evaluate the influence of the water-absorption characteristic of each wood slice on the analytical reproducibility after using the wood slice as a water absorber, ten pieces of the wood slices have been prepared and ten measurements on the LIF signals of copper were carried out repeatedly with each wood slice. The copper concentration of the tested sample was 2 mg/L. According to statistics, the overall relative standard deviation (RSD) of all the 100 measurements was ~6.5%. These results demonstrated that the influence of the water-absorption characteristic on the signal fluctuation was not obvious if the same type of wood slice was selected. Good analytical reproducibility can be achieved after using the wood slice as the water absorber for the analysis of copper in water by the LIBS-LIF technique.

A calibration curve is necessary to for quantitative analysis and sensitivity evaluation of this technique for the analysis of copper in water samples. For this purpose, a set of aqueous solutions with known copper concentrations from 5 to 150 mg/L was prepared for the experimental studies with LIBS and LIBS-LIF. Figures 4 a,b shows the calibration curves of copper in water obtained with the LIBS and LIBS-LIF technique. For convenience in comparing the sensitivity of these two techniques, the analytical line of copper at 510.55 nm was also selected in the LIBS technique. Each data point was the arithmetical average result for 64 laser shots. The number 64 was set on the digital oscilloscope to take account of both analytical speed and signal-to-noise ratio. The error bars were determined according to the signal fluctuation of three multiple repeated measurements. Both calibration curves can be fitted with direct lines, and the correlation coefficients are $R^2 = 0.998$ and 0.999 for LIBS and LIBS-LIF, respectively.
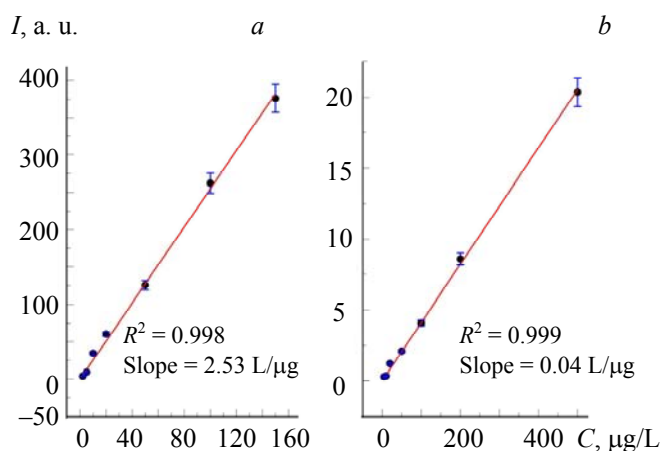

Fig. 4. Calibration curve of copper in water obtained by LIBS (a) and LIBS-LIF (b) techniques. The wavelength of the analytical line in both techniques was 510.55 nm. The time window of the data acquisition in LIBS analysis was from −7.0 to −6.0 μs as shown in Fig. 3.

The limits of detection (LODs) of copper in water determined with LIBS and LIBS-LIF were evaluated according to the IUPAC 3σ convention, that is,

$$LOD = 3\sigma_B/s, \qquad (1)$$

where σ_B is the standard deviation of the background, and s is the slope of the calibration curve. After the careful determination of σ_B based on ten repeated background measurements, the LOD of copper in water obtained by LIBS-LIF was 3.6 μg/L, or 3.6 ppb. Comparing with 3.5 mg/L, or 3.5 ppm, obtained by LIBS (also using the wood slice as the water absorber), the sensitivity has been improved 3 orders using LIBS-LIF compared to LIBS. Improvement factors of 4–5 orders have been achieved when comparing this result (3.6 ppb) with that obtained in the direct analysis of water samples with LIBS [5, 7].

The LODs of copper in water obtained with different LIBS-based techniques are listed in Table 1 for comparison. The analytical sensitivity of the LIBS-LIF technique combined with this matrix converting method is the best one except for the results obtained after preconcentration of the analytes with electrical deposition. In that work, tens of minutes is required for the sample preparation; however, in this work, only 5 min is required for the sample preparation.

TABLE 1. Comparison of LODs of Copper in Water Obtained
by Different LIBS-Based Analytical Techniques

Method	LOD, ppm	Reference	Notes
SP-LIBS	7	[5]	Tilted surface
	9.6	[7]	Static water
	19	[18]	Liquid jet
	1.7	[6]	Ultrasonic nebulization
	2.3	[7]	Ice
	0.008	[9]	Polymer membrane
	0.01	[10]	Carbon planchet
	0.029	[11]	Wood slice substrate
	4.69	[14]	Hydrogel
	8.3×10^{-5}	[15]	Electrical-deposition preconcentration
	3.5	This work	Wood slice substrate
DP-LIBS	2.0	[17]	Liquid jet
	13	[18]	Liquid jet
LIBS-LIF	0.0036	This work	Wood slice substrate

The copper concentrations of two natural water samples have been analyzed directly with this technique. One was tap water and another one was lake water taken from a small lake in our campus. For comparison, a deionized water sample was also analyzed to check the background level under exactly the same experimental condition. Based on the observed signal intensities and the calibration curve, the concentrations of copper were determined to be 9.6 ppb in the tap water and 17.5 ppb in the lake water. That is to say, the concentrations of copper in these two natural samples are below the threshold set by the EPA of the United States (1.3 ppm) for drinking water.

The most obvious characteristic of this technique is its high analytical sensitivity for analyzing trace metal elements in water samples. The analytical sensitivity has been improved significantly from two aspects. First, a wood slice was selected as the water absorber to convert liquid sample analysis to solid sample analysis. Thus, the influence of water splashing on the collecting optics of the spectroscopic analytical system could be eliminated and the signal stability could be improved. The quenching effect of the water molecules or OH radicals on the plasma radiation has also been eliminated, which partly contributed to the significant improvement of the analytical sensitivity. Second, the LIF spectroscopic analytical technique has been used to analyze trace copper atoms in the laser-induced plasma. Due to the high excitation efficiency from the resonant excitation and possible background-free signal detection in the LIF technique, the detection sensitivity in LIF is much higher than that in LIBS.

This sample pretreatment method is quite simple and very easy to carry out. Although five minutes sample pretreatment time is required, which slows down the analytical speed in comparison with that in the

direct analysis of liquid samples with LIBS or LIBS-LIF, this disadvantage can be partially eliminated by preparing multiple samples at the same time. If more than four pieces of wood slices are prepared at the same time, the required time for the sample pretreatment of each samples can be reduced to 1 min, or even less than 1 min.

Conclusion. The LIBS-LIF technique was applied to realize sensitive analysis of trace copper in water for the first time. By using a wood slice as the water absorber, the drawback of the water matrix in the direct LIBS analysis of liquid samples can be successfully eliminated. Together with the highly sensitive LIF technique, the analytical sensitivity of copper has been improved significantly. Under the current experimental condition, a calibration curve of copper in water has been constructed, and the copper LOD in water reached 3.6 ppb, which is 4–5 orders better than that obtained in the direct analysis of water samples by LIBS. The relative standard deviation of repeated measurements was determined to be ~6.5%, demonstrating good analytical reproducibility. The copper concentration of the natural water sample can be analyzed directly with this technique in a few minutes. This approach provides a sensitive and convenient way to analyze copper and other trace toxic metal or nonmetal elements in water, which can be potentially applied in the fields of water quality control, water environment monitoring, etc.

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