A Hydrogel’s Formation Device for Quick Analysis of Liquid Samples Using Laser-Induced Breakdown Spectroscopy

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Abstract The laser-induced breakdown spectroscopy technique has irreplaceable advantages in the field of detection due to its multi-phase specimen detection ability. The development of the LIBS technique for liquid analysis is obstructed by its inherent drawbacks like the surface ripples and extinction of emitted intensity, which make it unpractical. In this work, an in-situ hydrogel formation sampling device was designed and used the hydrogel as the detection phase of LIBS for Cu, Cr and Al in an aqueous solution. With the measured amount of resin placed in the device, the formed hydrogel could be obtained within 20 s after putting the device into water solution. The formed hydrogel could be directly analyzed by LIBS and reflect the elemental information of the water sample. The prominent performance made this hydrogel’s formation device especially suitable for quick in-situ environmental liquid analysis using LIBS.

Keywords: laser-induced breakdown spectroscopy, quick analysis, liquid samples, hydrogel formation

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

1 Introduction

Laser-induced breakdown spectroscopy (LIBS) is an atomic emission spectrometry technique for the direct qualitative as well as quantitative analysis of all-phases samples [1]. The LIBS technique is receiving more and more attention and has obtained remarkable development since its investigation in the early 1980s [2]. The most prominent advantages of the LIBS are in-situ analysis and no sample preparation time over many other conventional spectroscopic techniques, namely atomic absorption spectroscopy (AAS), laser ablation inductively coupled plasma optical emission spectroscopy (LA-ICP-OES) and spark-discharge optical emission spectroscopy (SD-OES) [3–5]. These unique characteristics make LIBS a promising analytical approach in some special fields [6–8].

Environmental concern is an international issue, especially the dissolved toxic heavy metals in different water bodies which threaten human health. Toxic elements will be accumulated in the human body and bring people disease or even death. In the work of environmental protection, the detection of the composition and relative abundance of toxic heavy metal elements in water bodies is of great importance.

The capabilities of rapid, multi-elemental analysis makes LIBS a preferred monitoring technique suitable for the qualification and quantification analysis of trace elements in solid, liquid and gaseous samples [9]. However, most researches are focused on solid samples due to their greater sensitivity and repeatability [10]. Thus a large number of reports emerged to demonstrate the different operation conditions involved in enhancement of plasma density and decrease of the limits of detection for a better performance. On the contrary, the advantages of LIBS are severely discounted to detect the trace elements in a liquid matrix. Laser-induced plasmas produced on the surface of liquids perform a shorter life-time due to the quenching effect of water or liquid, leading to lower sensitivity [5,10–12]. Furthermore, the optical detection system can be interfered by the splashing and surface ripples followed by shock waves, which will contribute to the poor repeatability in the direct detection of trace elements in liquid samples by LIBS [11]. The presented inherent drawbacks in direct analysis on liquid samples become obstacles, making LIBS meaningless.

Some strategies have been reported to eliminate the drawbacks in direct analysis on liquid samples. One of these strategies is using adsorbents to concentrate the
trace elements into the solid adsorbent and then the adsorbent would be dried for the LIBS analysis to improve the detection limit of liquid samples [11]. LIBS acquires the elements information of the liquid sample by analyzing the surface of the adsorbent indirectly. The adsorbents mainly include bamboo slice [12,13], filter paper [14,15], charcoal [16] and zinc oxide [11]. Together with other methodologies like freezing the liquid samples [17], drying the liquid samples [1,18−22], laminar flows [23], liquid jets [24−27], the double-pulse technique [28] and droplets [29], these processes need additional equipment as well as a complexity operation procedure which will add experimental effort and spend a great deal of time on the preprocessing of the samples. There was no department applied to in-situ analysis and most methods were just employed in the laboratory other than outdoor environment.

SAP (Super Absorbent Polymer) is a kind of weak cross linked polymer which has a three-dimensional network structure. Due to the excellent capacity of water absorbency and water retention, it is becoming more and more popular not only in daily life but also the scientific fields. Compared with the traditional adsorbents such as activated carbon and calcium oxide, the amount of the water adsorbed can be as high as dozens of times its own weight and can give a good performance even at high pressure [30−32]. Besides, most of the SAP materials are nontoxic thus have no negative influence on the environment during its application.

In the present work, we designed an in-situ hydrogel formation sampling device and used the hydrogel as the detection phase of LIBS for Cu, Cr and Al in an aqueous solution. With the help of the super absorbent polymer, this device transforms a liquid sample to a hydrogel formation. The hydrogel formation sample can be analyzed by LIBS directly and the inherent drawbacks in direct analysis on liquid samples would be eliminated. This work attempted to propose and demonstrate an approach for quick in-situ analysis on liquid samples using LIBS at the scene of the pollutant. This work creatively proposed a solution that combined the sample collection and the sample preparation. Moreover, at the scene of the contaminated water the formed hydrogel could be analyzed directly by LIBS apparatus making it possible to apply LIBS to rapid in-situ and on-site analysis for liquid samples.

2 Experiment

2.1 Instrument

The structure diagram of the LIBS experimental instrument is demonstrated in Fig. 1. A nanosecond Nd:YAG Q-switched laser (Lotis TII,1064 nm) was employed to generate a high energy laser pulse beam to focus onto the surface of the sample by means of a plano-convex quartz lens with a focal length of 50 mm between the lens to the sample surface. The characteristic atomic emission signal was collected and analyzed by an Echelle spectrometer (Aryelle 400, 220-800 nm, LTB Berlin) through an optic fiber system connected with an optical fiber collimating lens (74-UV, 200-2000 nm) which was placed with an angle of 50° with respect to the sample surface to increase the sensitivity of the analysis. The angle of the optical fiber collimating lens was optimized in our previous work [33]. The early plasma continuum background was filtered by a mechanical chopper and delay generator in front of the entrance slit. On account of the fact that the emission of continuum radiation of the plasma is a two-stage process, the process of characteristic radiation emerged after the emission of continuum radiation, and the characteristic atomic emission lines involving element information can only be detected in the characteristic radiation, so in order to enhance the signal-to-noise ratio, the time-delay device controls the working time of spectrometer after the laser ablation to reject the emission of continuum radiation and receive the characteristic radiation. The sample was located on a three-dimensional translational platform which shifted in the X-Y plane between two laser pulse beams. Here the laser was operated at an output energy of 175 mJ with the repetition rate of 5 Hz. Each atomic emission spectrum was obtained by accumulating 500 ablation events for the purpose of statistics and signal repeatability. In addition, a spectrum processing software pack was used to extract qualification and quantification information from characteristic atomic emission lines.

Fig. 1 Structure diagram of the LIBS experiment setup

2.2 Hydrogel formation device and in-situ sample preparation

The in-situ hydrogel formation device for direct detection of liquid samples mainly consists of two parts, demonstrated as part A (working above water) and part B (working under water). Part A was used to control the timing for water solution sampling and record the water depth while part B was used to take the liquid sample through emerging under water, river and lake, for example.

Each supporting bar was designed to be one meter long on with marked length calibration which makes it feasible to support part B to enter into deep water by linking several supporting bars together. The design of the hydraulic buffer is described in Fig. 2. In
consideration of the fact that our work aimed at toxic heavy metals dissolved in water, a steel ball buffer, a strainer and a filter paper were covered on top of the sampling container to filter out the impurities in water and control the flow speed of the water entering into the sampling container. The sampling container filled with super absorbent polymer in advance was replaceable to make sure that the operation of sampling is rapid and the sampling would be accomplished more than once at the same time. The diameter of the sampling container was 5 cm, with a height of 8 cm.

![Fig.2](image)

**Fig. 2** Design of hydraulic buffer: A Steel ball buffer, B Strainer, C Filter

When the device reaches the specified location in the river, a button in the device was pushed down to open the water valve to suck the water sample into the chamber, and then the water valve will be closed after a certain period with the timing controlled. With the measured amount of resin placed in the device, the formed hydrogel could be obtained within 20 s after putting the device into water solution. When the sample collection came to an end, the device was taken back from the river and the formed hydrogel was taken out from the device. By replacing the sampling container different samples were obtained. Meshed with a portable LIBS apparatus, at the scene of the contaminated water, LIBS could analyze the formed hydrogel directly and provide the elements information of the water sample. A better sensitivity and repeatability was accomplished in the whole process of measurement.

## 3 Results and discussion

### 3.1 The investigation of appropriate delay time

In this section we demonstrated the appropriate delay time between the laser ablation and the spectrometer acquisition to evaluate the best performance of the experiment setup under the conditions of 175 mJ per laser pulse, accumulating 500 shots signal and choosing Al (308.2 nm) as the reference element. The effects of delay time on the signal ration and background ratio are shown in Fig. 3. The SBR increased slowly at the preliminary period of the plasma because the spectra were dominated mainly by continuum emission other than the characteristic radiation. However, with a lower decay rate than the continuum emission, the characteristic radiation takes over the dominate position of the plasma after 2 \(\mu\)s demonstrated as a sharp increase of the signal to background ratio. Both the continuum emission and the characteristic radiation decayed quickly when the delay time was further increased, the SBR tended to decrease as a consequence. In consideration of the fluctuation of SBR, 2.7 \(\mu\)s was employed as the optimal delay time in our experiment.

![Fig.3](image)

**Fig. 3** Signal and noise ratio of Al (308.2 nm) at different delay times in the condition as follows: laser pulse energy = 175 mJ, shot accumulation = 500

### 3.2 Detection limits of Al, Cu, and Cr

mental elements

Synthetic sample representatives of polluted water with different element concentration of the Al, Cu, and Cr were made to estimate the limit of detection. Different spectra acquired with the hydrogel formation method with four levels of elements concentration in the ranges of 1 \(\mu\)g·mL\(^{-1}\) to 100 \(\mu\)g·mL\(^{-1}\). As the results demonstrated in Fig. 4, the signal of Al (308.21 nm, 309.28 nm) was actually better when the concentration was relatively low, which revealed the potential for a better limit of detection if we investigated further. Fig. 4 shows the spectra intensity of Al (308.21 nm, 309.28 nm), Cu (324.75 nm, 327.40 nm), and Cr (422.67 nm, 425.43 nm) with the concentration of 25 \(\mu\)g·mL\(^{-1}\). Because the spectra intensity of Al increased sharply with a high concentration, the signal tended to saturation due to self-absorption. As shown in Fig. 5, the emission of Cr at 425.43 nm had a better linearity range, which showed as a more stable increase at the concentration of 1 \(\mu\)g·mL\(^{-1}\), 5 \(\mu\)g·mL\(^{-1}\), and 25 \(\mu\)g·mL\(^{-1}\) \((y = 13.56 + 76.19x, R^2=0.9994)\). However, with the effect of self-absorption, the intensity of analytical lines reached saturation and the linearity range was impaired at the concentration of 100 \(\mu\)g·mL\(^{-1}\). According to the IUPAC definition, the LOD for each element was calculated as the following formula:

\[
\text{Limit of detection (LOD)} = \frac{3\sigma_B}{s},
\]

where \(3\sigma_B\) stands for the standard deviation of the background signal, and \(s\) is the sensitivity which is given by the slope of the corresponding calibration curve. In this work, \(\sigma_B\) was obtained from ten measurements of background signals under the same experimental conditions \(^{[14]}\). A comparison of the obtained
LODs for these three elements using hydrogel and other analytical matrices in the atmospheric environment was presented in Table 1. Considering the rapid procedure compared with those other ones, we could identify this one as the most applicable method for field-deployment.

![Fig.4](image_url) Different spectra acquired through the hydrogel formation method with the concentration of 25 $\mu$g·mL$^{-1}$ for Al, Cu and Cr elements

![Fig.5](image_url) The linearity range of spectra acquired through the hydrogel formation method with concentrations of 1 $\mu$g·mL$^{-1}$, 5 $\mu$g·mL$^{-1}$, 25 $\mu$g·mL$^{-1}$, 100 $\mu$g·mL$^{-1}$ for Cr element

3.3 The repeatability of the determination of Al, Cu, and Cr mental elements

Three water matrices with two different concentration levels for each element were established (Al: 1.00 $\mu$g·mL$^{-1}$ and 5.00 $\mu$g·mL$^{-1}$, Cr: 5.00 $\mu$g·mL$^{-1}$ and 25.00 $\mu$g·mL$^{-1}$ and Cu: 25.00 $\mu$g·mL$^{-1}$ and 100.00 $\mu$g·mL$^{-1}$), and 10 mL of the solutions was added to form the hydrogels. The average repeatability for these three elements expressed as the RSD (relative standard deviation) was Al 16.8%, Cr 14.4%, and Cu 26.6%, respectively. In consideration of that, the destructiveness from the laser pulse to the final specimen would probably influence the analytical results in our experiment, a better RSD could be acquired with fewer average pulse number. This novel device was shown to be a fast, simple and in-situ monitoring tool for liquid sample analysis.

4 Conclusions

Simple sample preparation and efficient detection are still unacceptable for LIBS to analyze the trace elements in a liquid matrix particularly. The common liquid sample preparation strategies usually need complicated apparatus and a long time procedure, leading to the unique characteristic of rapid measurement not being prominent anymore for LIBS. In the present work, we mainly focused on an in-situ hydrogel formation device which integrated sampling and sample preparation together for the direct and fast detection of aqueous solution samples by LIBS. The formed hydrogel can be detected directly, making in-situ analysis on liquid samples feasible within minutes in the outdoor environment. It has been proved that this method could be applied to quantitative analysis of aqueous samples for a better LODs and reproducibility has been acquired. In conclusion, the in-situ hydrogel formation device was unprecedented on making it possible to detect elements in a liquid matrix rapidly for field-deployment by LIBS, and the performance was brilliant to accomplish the in-situ analysis of water solution.

In this work the emphasis was aimed at the detection of toxic heavy metals dissolved in water, so the sampling container of the hydrogel’s formation device was covered with a filter paper to filter out the impurities in water. In practical applications, the heterogeneous distribution of particles induced a discrepancy of the LIBS analysis. In consideration of the fact that pollution can be in particles state, the focus will be concentrated on the analysis of particles in water samples in the following work. This work proposed an approach for quick in-situ analysis of liquid samples using LIBS. In this context, synthetic sample representatives of polluted water were applied in the experiment. The minimum detectable concentration is expected to be improved to make it possible to analyze the contaminated water in the next work.

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<th>Table 1. Comparison of LOD for Al, Cu, and Cr</th>
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<td>Element</td>
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References


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