



Laser-induced breakdown spectroscopic detection of trace level heavy metal in solutions on a laser-pretreated metallic target



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ABSTRACT

A fast and sensitive analysis for trace level heavy metals in aqueous solution was realized by using an improved laser induced breakdown spectroscopy (LIBS) methodology. Solutions containing heavy metal elements, Ni, Cr, and Cd, were concentrated in a laser-pretreated area ($25 \times 20 \text{ mm}^2$) of a polished aluminum target surface, wherein pretreated grooves enabled homogeneous distribution of the metallic solutions in the well-defined area, and laser ablation of the aluminum target produced unique plasma excitation of various metallic ions. For 1-mL solutions deposited, we obtained an analytical precision of about 7% relative standard deviation (RSD), and limits of detection (LODs) of 22, 19, and 184 $\mu\text{g/L}$ for Ni, Cr, and Cd, respectively. Moreover, the laser-pretreated metallic microstructure allowed more solution deposited with the help of a hot plate, which supported improvement of LODs to sub- $\mu\text{g/L}$ level for Cr and Ni and $\mu\text{g/L}$ level for Cd with about 20-mL solution engaged in the enrichment processes. The applicability of the proposed methodology was validated on certified reference materials and real river water.

1. Introduction

Water pollution control requires efficient techniques for in situ detection of water pollutants at trace level. LIBS seems to be a very useful tool for this purpose and a lot of work has been done for monitoring trace heavy metals, such as nickel, chromium, cadmium, lead, mercury, and zinc with LIBS [1–21,24–27]. As experimentally demonstrated, LIBS provides portable apparatus, convenient, fast, and reliable in situ detection of heavy metal elements in aqueous solutions. In LIBS detections on liquids, laser is either focused on the liquid surface [1,2] or in the liquid bulk [3,4]. On account of physical characteristics of liquid, the analytical performance of LIBS is deteriorated. These drawbacks that restrict directly analyzing liquids could be subdued by double-pulse LIBS techniques [5–7], or creating fluid jet streams [8]. Nevertheless, fluid jet streams need relatively large amount of samples, while double-pulse LIBS is difficult to control with requisite complicated setup.

On the other hand, numerous phase transformation methods have also been demonstrated for improvement of LODs. Materials, including filter paper [9–11], graphite [12], metal electrode [13], ion exchange membrane [14,15], bamboo [16], wood chip [17,18], silicon [19] and ice [20,21], have been used to transform liquid to solid and concentrate the samples. Zhao and coworkers [12] measured trace Pb element and obtained a LOD of 0.11 mg/L by using graphite substrate. Detection of

elements enriched with metal electrodes [13] was demonstrated and LODs of most detected metals reached up to sub- $\mu\text{g/L}$ levels. Ni et al. [16] used bamboo charcoal substrate for lead detection in solution and got a LOD of 8.5 mg/mL. These methods proved helpful in transformation of liquid samples into solid phase and their detections. However, some methods, like metal electrode and ion exchange membrane, need a relatively long time for sample preparation and complicated experiment setups. Although filter paper, graphite, bamboo and wood chip could enrich heavy metal elements, with these methods enrichment is limited and the substrates could only be used once. Also most of these materials are organic substrates, on which laser could only induce plasmas with a relatively low temperature and thus the analytical sensitivity is reduced. Moreover, it is difficult to get certified materials without heavy metal contamination.

Recently, a polished aluminum target was used as the substrate to assist spectroscopic analysis of oil [22,23] and liquid droplets [24–26]. With the help of aluminum substrates, laser induced plasmas of high temperature, resulting in significant sensitivity enhancement compared with direct analysis for liquid or oil. More interestingly, matrix effects brought by different salts could be overcome [27] because the properties of the induced plasma relied on the metallic target. But still this robust method has some constraints. It is hard to confine the liquid sample in a fixed area on a polished surface. In addition, only a less volume of solution was available for spectroscopic measurements, since

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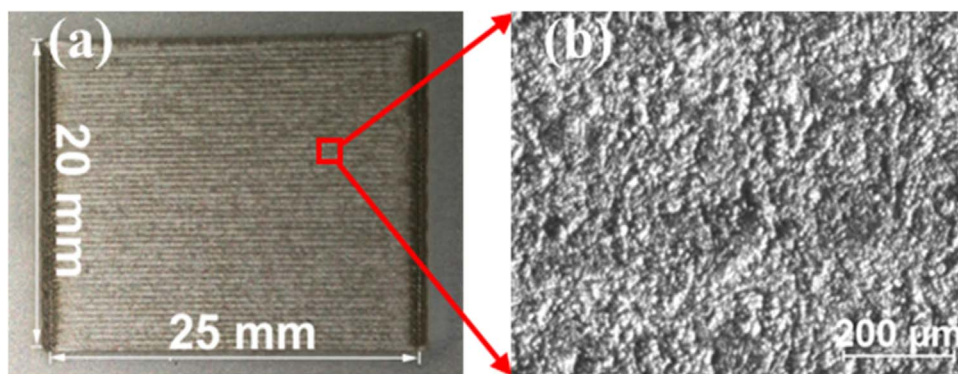


Fig. 1. Surface profiles (a) and microscopic images (b) for the laser-pretreated surface.

rapid drying process easily caused an inhomogeneous distribution of solution more easily on the bare polished surface, thus preventing from more sensitive measurements.

In this work, we demonstrated a robust technique to perform precise and sensitive LIBS detection of heavy metals in aqueous solutions. Aqueous samples were deposited and dried on a laser-pretreated aluminum substrate. Rough microstructure on the substrate surface trapped the solution in the laser-pretreated area and enabled a homogeneous distribution of the solution. Furthermore, it also supported the heavy metal enrichment by repeated solution deposition and evaporation, resulting in a dramatic improvement of LODs for heavy metal detections.

2. Experimental method

2.1. Experiment setup

A standard LIBS experimental setup was used for the present investigation. Its detailed description can be found elsewhere [27]. Briefly, the ablation source was a Q-switched Nd: YAG laser (Quantel Brilliant) operating at 1064 nm with repetition rates of 20 and 5 Hz (20 Hz for ablating the surface and 5 Hz for LIBS detection), pulse duration of 5 ns, and pulse energy of 60 mJ. The laser beam was focused slightly under the sample surface using a lens of 5-cm focal length to generate the plasma. The laser spot was estimated to be 400 μm in diameter on the target surface. The aluminum target was mounted on a 3-D motorized micrometric displacement stage. The plasma emission was collimated by a 4-f imaging system with focal lengths of 100 and 50 mm, respectively, which collected the emission into the entrance of an optical fiber of 50 μm in diameter. The fiber delivered the plasma emission into an echelle spectrometer (Mechelle 5000, Andor Technology) equipped with an intensified charge coupled device (ICCD; iStar, Andor Technology). A photodiode was used to detect a part of split laser pulse prior to focus and produced a trigger signal that was sent to the ICCD camera.

2.2. Sample preparation

In our experiments, three kinds of mineral salts with analytical reagent grade, $\text{C}_4\text{H}_6\text{NiO}_4 \cdot 4\text{H}_2\text{O}$, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, and $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ (all from Sinopharm Chemical Reagent Co., Ltd.) were used. They were dissolved together in deionized water with the concentration ranging from 0.005 to 200 mg/L for each mineral salt. The concentrations of analytical heavy metal elements were thus in the range of 0.00118 ~ 47.2 mg/L for Ni, 0.000975 ~ 39.0 mg/L for Cr and 0.00246 ~ 98.4 mg/L for Cd, respectively, according to their relative molecular masses. These solutions were prepared as the aqueous calibration standards for optimization and calibration. During the preparation process, accurate weight and complete digestion were noticed to avoid the uncertainty. In addition, certified reference materials, high-purity standards (Aladdin,

China; < <http://www.aladdin-e.com> >) and an ICP Multi-element Standard (GNM-M061504-2013, Aoke Biology Research (Beijing) Co., Ltd, China; < <http://www.bzwz.com> >) were used for validation experiments after appropriate dilutions. Since all the experiments in this work have been performed for over one month, sealed flasks were used and fresh solution was prepared for measurement each day avoiding possible evaporation loss. High purity aluminum block (TechLab, France) with a size of $43 \times 49 \text{ mm}^2$ was used as the substrate. This certified aluminum target (Al 99.99%, Cu 0.005%, Si 0.002%, Fe 0.001% and traces) does not contain these three elements to be measured. At first the aluminum substrate was polished and cleaned. Then the laser pulses were used to ablate the substrate surface to get rough structures on it. The related parameters were given in the Section 2.1. To evaluate the precision of multiple repetitions, a large rectangle area of $25 \times 20 \text{ mm}^2$ was well set to ablate as shown in Fig. 1(a). While being ablated, the substrate was kept moving at the rate of 0.5 mm/s with straight lines and parallel grooves were obtained in the well-defined area. Though the width of each groove was equal to the diameter of laser spot, $\sim 400 \mu\text{m}$, the distance between the center of each groove was fixed at 200 μm . Such an overlap ablation on the surface assure a homogeneous microstructure. Fig. 1 shows the straight-line grooved surface microstructure and its microscopic image. The central location of the grooved target could be seen explicitly and the rough surface in the form of concaves is evident from the micrograph. The microstructure was nearly uniform with respect to the laser spot size of 400 μm .

As the laser-pretreated surface area was only $25 \times 20 \text{ mm}^2$, we controlled repetitive solution deposition up to sufficient quantity as follows. A small volume of solution was deposited on the laser-pretreated area, followed by drying and then adding more solutions on the dried surface repeatedly. A hot plate at a temperature 90 $^\circ\text{C}$ was used to facilitate the evaporation process. By using the above-mentioned process, different volumes of solutions were deposited on the laser-pretreated area, ranging from 0.5 to 12 mL. The drying process took about 1 min for 1-mL solution and about 20 min for 12-mL solution. Deposition of less than 1-mL solution in such a large area took less drying time but might cause inhomogeneous distribution due to such a short time available to spread. In fact, the liquid volume needed and time consuming were dependent on the area pretreated. Thus the LODs and corresponding liquid volume were based on the area of $25 \times 20 \text{ mm}^2$ in this work.

3. Results and discussions

3.1. Optimization of signal and spectral-line selections

In order to avoid the impact of continuous background emission in the initial stage of plasma evolution, it is necessary to determine the optimal time delay between the laser impact and the beginning of signal acquisition and also the optimal acquisition window time width, which

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