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Simultaneous determination of La, Ce, Pr, and Nd elements in aqueous solution using surface-enhanced laser-induced breakdown spectroscopy

Xinyan Yang, Zhongqi Hao, Meng shen, Rongxing Yi, Jiaming Li, Huiwu Yu, Lianbo Guo, Xiangyou Li*, Xiaoyan Zeng, Yongfeng Lu

Wuhan National Laboratory for Optoelectronics (WNLO), Huazhong University of Science and Technology (HUST), Wuhan, Hubei 430074, PR China

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ABSTRACT

Determination of rare earth elements (REEs) plays an important role in the extraction process. In this work, surface-enhanced laser-induced breakdown spectroscopy (SENLIBS) was introduced to detect REEs (lanthanum, cerium , praseodymium , and neodymium elements) in an aqueous solution. The emission lines of La II 394.91 nm, Ce II 418.66 nm, Pr II 422.29 nm, and Nd II 406.10 nm were selected for quantitative analysis by drying the analytical samples on a Zn metal substrate surface and optimizing the experimental parameters. The results showed that the limits of detection (LoDs) for determining La, Ce, Pr, and Nd elements can reach to 0.85, 4.07, 2.97, and 10.98 μg mL^{-1}, respectively, which proved that SENLIBS is a feasible method for determining REEs.

1. Introduction

Products of rare earth elements (REEs) have been widely used in the fields of metallurgy, petroleum, textiles, agriculture, and especially high-tech industry (e.g., cars, flat display screens, phosphors, optical glasses, mobile phones, and disc drives) due to its chemical, catalytic, electrical, magnetic, and optical properties [1]. Since REEs usually exist as compound forms in mineral deposits, such as monazite, xenotime, and ion-adsorbed clay [2], obtaining pure REEs often requires a complex extraction process. Therefore, a method for rapid monitoring of the contents of REEs during the extraction process would be helpful for ensuring product quality and reducing production cost.

Laser-induced breakdown spectroscopy (LIBS) has been proven to be a competitive analytical technique due to its attractive features, such as rapid, simultaneous multi-element detection, in situ, and real-time analysis [3–5]. Therefore, LIBS has potential for the rapid analysis of REEs during the extraction process. Several researchers have reported the qualitative and quantitative determination of REEs in different solid matrixes with LIBS, such as phosphors [6], coal samples [7], sand [8], and graphite [9]. However, only a few reports have focused on the quantitative determination of REEs in an aqueous solution [10–12], especially for analysis of lanthanum (La), cerium (Ce), praseodymium (Pr), and neodymium (Nd) elements. The limits of detection (LoDs) for La, Ce, Pr, and Nd elements in a solid matrix were 10, 11,400, 40, and 500 μg mL^{-1} [13,14], respectively. However, the analytical performance of elements in an aqueous solution are poorer than those in a solid matrix due to the inherent drawbacks of water splashing, surface ripples, and intensity extinction in an aqueous solution [15,16].

To address these problems, several methods have been proposed, such as changing the static liquid sample to a dynamic liquid [17], using extra experimental equipment [18–20], and converting a sample from the liquid phase to the solid phase [21–23]. Among them, surface-enhanced LIBS (SENLIBS) is the most promising method due to its unique advantages, such as a simple preparation process and the ability to reuse the metallic surface by polishing. SENLIBS was successfully carried out to improve the LoD for direct analysis of a liquid droplet of manganese (Mn) just by drying a liquid droplet on a metallic surface [23]. However, the quantitative determination of REEs in an aqueous solution using SENLIBS has still not been investigated.

In this work, SENLIBS was applied for the determination of REEs (La, Ce, Pr, and Nd) in an aqueous solution. The selection of analytical lines, experimental conditions, and analytical performance were studied and discussed in detail.

2. Sample preparation and experimental setup

To make different liquid droplets spread on the metal substrate surface in a fixed area, fast-speed quantitative filter paper (201, Hangzhou Wohua Filter Paper Co. Ltd. Hangzhou, China) was chosen as the transmission medium between the standard solution and the metallic substrate and cut into 6-mm diameter round sheets. A zinc

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* Corresponding author.
E-mail address: xyli@mail.hust.edu.cn (X. Li).

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Table 1
The concentrations of each REE in standard solutions (μg mL^{-1}).

	1	2	3	4	5	6	7	8
La	6.00	8.00	10.00	20.00	40.00	60.00	80.00	100.00
Ce	11.04	14.72	18.40	36.81	73.61	110.42	147.22	184.03
Pr	1.13	1.50	1.88	3.76	7.52	11.28	15.03	18.79
Nd	3.38	4.50	5.63	11.25	22.50	33.75	45.00	56.25

target (Zn: 99.993–99.995%, Kurt J. Lesker Company) that contains no REEs (La, Ce, Pr, and Nd) was used as a metal substrate. It was cleaned using 1200-grit silicon carbide (SiC) abrasive paper and then washed with ethyl alcohol three times to remove surface impurities. A stock mixed solution of four REEs (290.40 μg mL^{-1}) was prepared by dissolving a given amount of La_2O_3, CeO_2, Pr_6O_{11}, and Nd_2O_3 in a 1.0 M hydrochloric acid solution. Thirteen standard aqueous solutions containing La, Ce, Pr, and Nd elements were prepared by diluting the stock solution with a 1.0 M hydrochloric acid solution. The concentrations of each REE in the standard solutions are listed in Table 1. Each sample for SENLIBS analysis was prepared using the following procedures (see Fig. 1(a)):

(1) A filter paper sheet was placed on the surface of the Zn metal substrate.
(2) The Zn metal substrate with filter paper was heated by a heating plate with a temperature of 70 °C.
(3) A 30 μL aqueous solution was deposited on the filter paper using a micropipette.
(4) After 4 min, the filter paper was removed and a solid prepared layer contained REEs was prepared on the surface of the Zn metal substrate.

The experimental setup for SENLIBS is schematically illustrated in Fig. 1(b), which was depicted in detail in our previous work [15].

3. Results and discussion

3.1. Selection of analytical lines

To obtain an accurate analysis, the spectral lines with less interference should be selected [24,25]. The time-integrated LIBS spectra from the Zn substrate and a solid layer prepared by a standard rare earth solution are shown in Fig. 2; and the characteristic spectral lines of La, Ce, Pr, and Nd elements are marked. It was shown that the spectrum of the prepared layer was free from interference by the Zn metal element lines. Moreover, the spectral line of Zn II 255.79 nm could be used as an internal line to reduce the effects of pulse-to-pulse fluctuation from laser energy. Furthermore, the spectral lines of REEs in the range of 378.20–448.90 nm were less interfered with by other REE lines. As the results, best analytical lines for quantitative analysis were selected and are listed in Table 2.

3.2. Optimization of the analytical parameters

Both the energy of ablation laser and delay time of acquisition were critical influencing factors for LIBS quantitative analysis due to the signal-to-noise (SNR) values of analytical lines can be significantly affected by the above two parameters [22]. Fig. 3 showed the evolution trends of SNRs of analytical lines (La II 394.91 nm, Ce II 418.66 nm, Pr II 422.29 nm, and Nd II 406.10 nm) on laser pulse energies (gate delay: 2 μs; and gate width: 2 μs) and gate delay times (laser energy: 60 mJ; and gate width: 1 μs). As shown in Fig. 3(a), the SNRs of all analytical lines increased first and reached a maximum at 60 mJ, then decreased with increasing the laser energy. Moreover, with the best energy of 60 mJ, the SNRs of analytical lines from 1 to 25 μs were reduced with increasing delay times. The highest SNRs were obtained when the delay time was 1 μs (as shown in Fig. 3(b)). Therefore, the optimized parameters of SENLIBS for quantitative determination of REEs in an aqueous solution were 60 mJ for laser energy and 1 μs for delay time.

3.3. Calibration curves and limits of detection

For SENLIBS, the aqueous solution was prepared by drying the liquid droplet on a metallic substrate, which converted the analytical sample as a solid layer on the metallic substrate surface. As reported in previous work, SENLIBS can provide a better LoD than that of direct analysis of a liquid droplet [23]. The main reason is that, the plasma of solid has a lower breakdown threshold than that of liquid [26]. Moreover, the volume of the liquid droplet used in SENLIBS is only several micro-liter in this work, which makes the thickness of the prepared layer thinner. When a laser focused on the prepared sample, the layer and metallic substrate would be ablated simultaneously. As the result, the ablation depth of metallic substrate is larger than that of dried liquid layer as studied in our previous work [15]. It can be concluded that another enhancement mechanism of SENLIBS is that

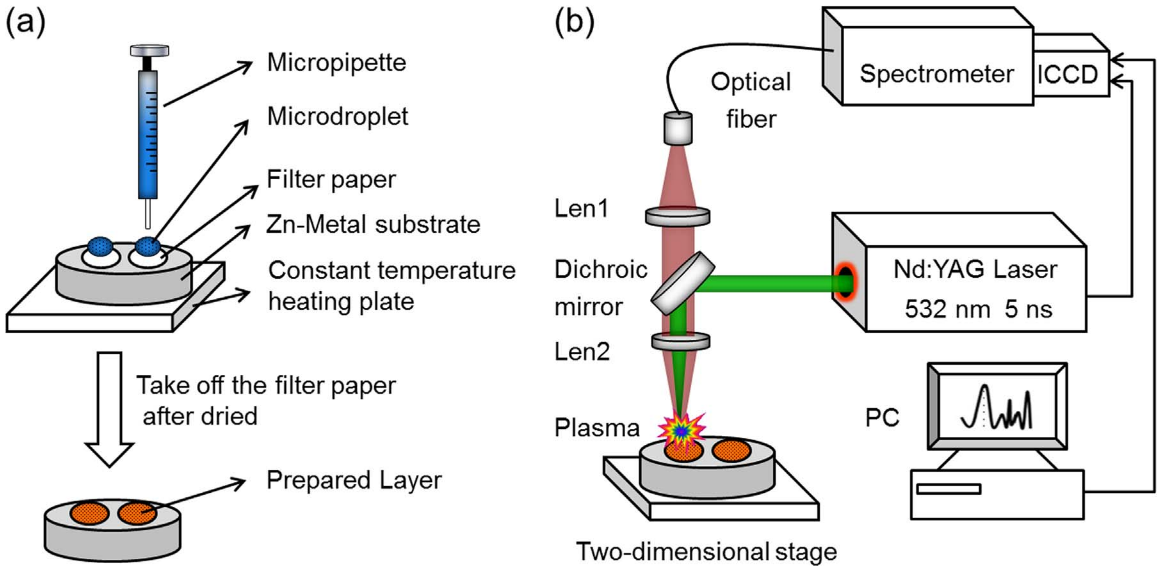

Fig. 1. Schematic diagram of sample pretreatment procedures (a) and experimental setup (b).