Ultrasonic Nebulizer Assisted LIBS: a Promising Metal Elements Detection Method for Aqueous Sample Analysis*

ZHONG Shilei (钟石磊)\textsuperscript{1,2}, ZHENG Ronger (郑荣儿)\textsuperscript{2}, LU Yuan (卢渊)\textsuperscript{2},
CHENG Kai (程凯)\textsuperscript{2}, XIU Junshan (修俊山)\textsuperscript{2}

\textsuperscript{1}College of Physics Science, Qingdao University, Qingdao 266071, China
\textsuperscript{2}Optics and Optoelectronics Laboratory, Ocean University of China, Qingdao 266100, China

Abstract A newly developed approach for trace metal elements detection for aqueous samples analysis is presented in this paper. The idea of this approach is to improve ablation efficiency by transforming the liquid sample into a dense cloud of droplets using an ultrasonic nebulizer. The resulting droplets are then subjected to analysis by laser induced breakdown spectroscopy (LIBS). A purpose-built ultrasonic nebulizer assisted LIBS (UN-LIBS) system has been applied to the analysis of aqueous samples at trace levels of concentration. Experimental investigations of solution samples were carried out with various dissolved trace metal elements (Mn, Zn, Cu, Pb, Fe, Mg and Na) using this approach. The characteristics of UN-LIBS signal of the elements were investigated regarding the lifetime and S/B ratio and the calibration curves for trace metal elements analyses. The obtained LODs are comparable or much better than the LODS of the reported signal enhancement approaches when the laser pulse energy was as low as 30 mJ. The good linearity of calibration curves and the low LODs shows the potential ability of this method for metal elements analysis application. The density of the electrons was calculated by measuring the Stark width of the line of H\textsubscript{α}. The possible mechanism of the LIBS signal enhancement of this approach was briefly discussed.

Keywords: LIBS, ultrasonic nebulizer, metal elements, water solution, Mn

PACS: 42.62.Fi

DOI: 10.1088/1009-0630/17/11/17

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

1 Introduction

Laser induced breakdown spectroscopy (LIBS) technology, as a quick, in-situ, sensitive and wide scope trace elements analysis method has received increasing attention in recent decades \cite{1,2}. It has been introduced into many fields with different degrees of success \cite{3–6}. However, owing to the interaction of complex factors in the liquid environment, the LIBS signal of aqueous samples shows more noise and less stability which results in lower sensitivity and higher limit of detection in comparison with the situation in air \cite{2}.

Many efforts have been made by researchers to improve the LIBS signal of an aqueous sample. Moving the breakdown point onto the surface of bulk liquid \cite{7} or inducing breakdown on the surface of liquid jet \cite{8,9} have been demonstrated as efficient ways to improve the sensitivity and stability of the LIBS signal in trace analysis of aqueous samples. Transforming liquid samples into solid samples is another alternative to improve LIBS signal. There are different forms of transformation, including solidifying the liquid sample with CaO before undertaking the detection of trace metal elements in the sample using LIBS \cite{10} and freezing the aqueous sample into ice to achieve good sensitivity in trace sodium detection \cite{11}. Double pulse LIBS (DP-LIBS) also demonstrates an advantage in liquid sample detection. It has been reported that in the detection of Mn dissolved in water using DP-LIBS, the LOD was found to be as low as 0.39 ppm \cite{12}. Experiments of LIBS for single droplet analysis showed that LIBS was capable of low volume sample analysis \cite{13}. Over the last several years, many efforts have been made in our laboratory in the hope of applying LIBS to ocean applications. Extensive experimental investigations have been carried out with different forms of liquid samples \cite{9,14,15}. A “guided conversion” method was established to achieve the LOD of 0.016 ppm in the detection of trace Cu ions in water \cite{14}. In an attempt to develop an on-line deck monitoring system using LIBS, a purpose-built sampling system in conjunction with LIBS setup was established in our laboratory to form a new enhancement approach, called ultrasonic nebulizer assisted LIBS (UN-LIBS). In the former study, some features of UN-LIBS and the relationship between the parameters of the ultrasonic nebulizer system and the

*supported by National Natural Science Foundation of China (No. 11104153)
signal of the UN-LIBS have been studied [15]. In this paper, the configuration of this approach will be presented in more detail.

2 Experimental arrangement and samples

2.1 Experimental setup

Fig. 1 is the experimental arrangement used for UN-LIBS, which consists of a purpose-built ultrasonic nebulizer sampling system and a conventional LIBS setup. In the sampling system, the target liquid sample was nebulized into liquid droplets by an oscillating plate operating at an ultrasonic frequency of 1.7 MHz. The plate is fixed at the bottom of the liquid sample cell and driven by a capacitance feedback oscillator. A couple of fans were used to drive the droplets off from the target sample cell to the analysis chamber and form a stable airflow perpendicular to the laser beam. The laser source used for UN-LIBS is a Q-switch Nd:YAG (Quantel, Brilliant, 10 Hz frequency, 10 ns pulse width) laser operated at 1064 nm with two typical pulse energies of 30 mJ and 60 mJ. A quartz convex lens with a focal length of 38 mm is used to focus the laser beam to the center of airflow and breakdown the dense cloud of droplets. The resulting plasma emission is collected and delivered by a fiber system with one end placed about 2.5 cm away from the centre of the plasma and at about 90° to the laser beam while the other end of the fiber is coupled into a spectrometer (Acton, SP 500i, 1200 lines/mm, 0.1 nm resolving power). The time resolved UN-LIBS spectra are recorded with an ICCD (Andor, DH734-18F-03) with a triggering signal from the Q-switch synchro-out signal. Each spectrum of the different elements is obtained with a similar process on the Q-switch synchro-out signal. The obtained spectra are processed with Origin software on a PC.

![Fig.1 Experimental arrangement used for UN-LIBS](image)

2.2 Sample preparation

Our investigations are focused on the most common elements (Zn, Cu, Pb, Fe and Mn) related to water pollution and the ubiquitous elements (Mg and Na) that are found in natural water. The analytical reagents used in the preparation of the samples are all commercially available, they are: ZnSO$_4$·7H$_2$O, CuSO$_4$·5H$_2$O, Pb(NO$_3$)$_2$·H$_2$O, FeSO$_4$·7H$_2$O, MnSO$_4$·H$_2$O, MgCl$_2$·6H$_2$O and NaCl. To prepare an investigated aqueous sample, the relevant analytical reagent is dissolved into deionized water with a certain concentration. It then takes several dilute procedures to get the samples with desired trace element concentrations.

3 Results and discussion

3.1 UN-LIBS spectra of metal elements dissolved in water

In our earlier study of UN-LIBS with a Mg target element, its ionic emission was found to be much stronger than its atomic emission [15]. The intensity of Mg II 295.5 nm was about 10 times higher than that of the atomic line at Mg I 285.21 nm. This feature was observed in the UN-LIBS investigation of most metal elements in this work. Fig. 2 depicts the typical UN-LIBS spectra obtained from seven individual samples prepared with the metal elements of interest dissolved in water at concentrations of around 1 ppm for the samples of (a) Zn(3.27 ppm), (e) Mn(1.09 ppm), (f) Mg(0.60 ppm), and (g) Na(1.15 ppm), or just above the LODs for the samples of (b) Cu(17.67 ppm), (c) Pb(48.64 ppm), and (d) Fe(22.34 ppm).

The signal to noise ratios for the emission lines were all fairly good, as shown in Fig. 2, and especially for the double atomic lines of the Na atom, which promises a LOD that is much lower than 1 ppm. The ionic lines of Zn II 206.19 nm, Cu II 213.59 nm, Pb II 220.35 nm, Fe II 259.94 nm, Mn II 257.61 nm, Mg II 279.55 nm and the atomic line of Na at 588.99 nm were taken as target lines to verify the LODs of each of the elements of interest.

3.2 Temporal evolution of the plasma

In the preliminary investigation, the UN-LIBS signal was found to have increased with the laser pulse energy. To make better understand power dependence, two laser pulse energies of 30 mJ and 60 mJ are chosen to make a comparison. The temporal evolution of the plasma of UN-LIBS was investigated using the sample of MnSO$_4$·7H$_2$O with Mn weight concentration of 55 ppm. Spectra were taken every 0.2 µs gate delay from 0.4 µs to 4 µs with the same gate width of 0.2 µs and ICCD gain level of 200. Fig. 3 shows four typical spectra of Mn II 257.61 nm taken at different gate delays with laser pulse energies of 60 mJ (S1 and S3) and 30 mJ (S2 and S4). Spectrum 1 and spectrum 2 demonstrate that the best signal to background ratio was obtained at gate delays of 2.0 µs and 1.2 µs, respectively, spectrum 3 and spectrum 4 were taken at a gate delay of 4 µs and the signals are still reasonably good.
As can be seen from Fig. 4(a) and Fig. 4(b), the emission intensity and background showed similar trends in temporal evolution for laser pulse energies of 30 mJ and 60 mJ. The emission intensity of Mn II at 257.61 nm went up steeply at the early period and reached a maximum at about 0.8 μs with 30 mJ (at 0.6 μs with 60 mJ), it then gradually fell down. The signal intensity was still reasonably good at a delay of 4 μs, as shown in S3 and S4. It was observed that the maximum of emission intensity was nearly doubled and the average intensity over all the investigated data became two times higher by increasing the energy from 30 mJ to 60 mJ.

It can be seen from Fig. 4(b) that the background was very strong at the initial stage and it dropped down at a very fast falling rate. From the point of view of the influence of the laser pulse energy, the dropping rate of a background with 60 mJ was higher than that with a lower energy, although the value of the former was higher throughout the investigation time. The ratio between the signal and the background exhibited an interesting feature, as shown in Fig. 4(c).

Fig. 4(c) is the signal to background ratio as a function of the gate delay time. Compared with the situation with higher energy, the S/B ratio with 30 mJ was higher before 2 μs and reached a maximum at 1.2 μs.
The maximum with higher energy occurred at about 2.0 µs. In Fig. 3 the spectra of S1 and S2 show the spectra at the two maximum S/B ratios (1.2 µs for 30 mJ and 2 µs for 60 mJ).

Fig. 3 and Fig. 4 suggest that higher excitation energy of laser pulse could induce a higher signal intensity of the spectra but, at the same time, could also lead to a lower S/B ratio in the investigation of Mn by UN-LIBS method. If signals with good quality or lower background are needed, then not only the absolute intensity of the targeted peak but also the effect of excitation energy of laser pulse on the S/B ratio should be considered. In consideration of these factors, we optimized the temporal parameters in the coming LOD investigation. With the principle that the S/B ratio should be higher than a half of its maximum, the integration time intervals were chosen to be from 0.6 µs to 2.6 µs for 30 mJ exiting energy and from 1.2 µs to 3.6 µs for 60 mJ. The other elements analyses showed similar features or trends in the experiments. The lifetime (time from the pulse arrived to the emission intensity) of each element was longer than 2 µs, except for the lifetime of Na, which was longer than 120 µs. These obtained lifetimes were longer than that obtained in bulk water experiments. The optimal detection parameters employed in experiments for different elements are listed in Table 2. 30 mJ of laser pulse energy was used to obtain higher S/B ratio.

According to the experimental data, the lifetime of the target signal is at least several microseconds long, even with a very low laser pulse energy of 30 mJ. This order of magnitude of lifetime is obviously longer than the several hundred nanoseconds of lifetime in conventional LIBS experiments for bulk water detection. A longer lifetime is good for avoiding the strong bremsstrahlung background in the incipient period. In the UN-LIBS detection, the sample is transformed from bulk water into a mass of droplets of several micrometers in diameter by an ultrasonic nebulizer. Compared with the situation in bulk water, the sample serving as dense but isolated droplets could be ablated in a lower heat conduction environment. Hence, the plasma induced by UN-LIBS could keep a high temperature state for a longer time. This mechanism is similar to the surface breakdown detection in a jet or the static surface method, but the interface of air and liquid sample is infinitely magnified in the UN-LIBS method.

3.3 Limit of detection

In order to explore the ability of detection of UN-LIBS, a series of experiments have been carried out with the optimized experimental parameters to calculate the LOD. Mn²⁺ solutions with weight concentrations from 2.2 ppm to 11 ppm were used as samples in these experiments. The intensities of ionic line of Mn at 257.610 nm and the two calibration curves are shown in Fig. 5. The slope with 60 mJ was about two times bigger than that with 30 mJ, which can be found from Fig. 5.

Table 1 gives the obtained parameters of the fitting curves shown in Fig. 5. The R value of each fitting line was higher than 99%. To get the limit of detection (LOD), the standard deviations of background were calculated and the results are also listed in Table 1. The LOD can be extrapolated by the function below:

$$\text{LOD} = 3\sigma/S,$$

where $\sigma$ is the standard deviation and $S$ is the slope of calibration curves. The LODs obtained were 0.232 ppm and 0.090 ppm for different laser pulse energies, as shown in Table 1. It could be found that even with very low laser energy of 30 mJ, the LOD of Mn was still slightly lower than that achieved in other studies. For example, Kumar et al. utilized the Meinhard nebulizer to improve the sensitivity of LIBS for liquid samples. Although the LOD of Mn reached 0.6 ppm, the laser pulse energy used was as high as 190 mJ [16]. Lazic et al. detected the element of Mn in bulk water with DP-LIBS by optimizing the laser pulse energy ($E_1=72$ mJ and $E_2=144$ mJ) and the LOD of Mn reached 0.390 ppm [12].

<table>
<thead>
<tr>
<th>$E$ (mJ)</th>
<th>$\sigma/S$ (ppm)</th>
<th>$R^2$</th>
<th>LOD (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>13848.18/178566.76</td>
<td>0.994</td>
<td>0.233</td>
</tr>
<tr>
<td>60</td>
<td>13960.93/465126.06</td>
<td>0.996</td>
<td>0.090</td>
</tr>
</tbody>
</table>

Table 2 shows the LODs of those elements detected by the UN-LIBS method and the parameters employed, such as gate delay time ($t$) and gate width ($\Delta t$). The LODs obtained were generally better than the LODs found in references and for several elements the LODs were one or two orders of magnitude lower. Considering the lower laser pulse energy and better LODs, it is reasonable to regard UN-LIBS as helpful for signal enhancement. At the same time, the coefficients of relationship of calibration curves were all greater than 0.99, which suggested good linearity in the range of very low concentration. This could be an advantage of UN-LIBS for quantitative detection in future research.
Table 2. The present LOD and those obtained in references. (Here $t$ and $\Delta t$ are gate delay time and gate width, respectively)

<table>
<thead>
<tr>
<th>Elements</th>
<th>Present work</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_{EM}$ (nm)</td>
<td>$t$ (µs)</td>
<td>$\Delta t$ (µs)</td>
</tr>
<tr>
<td>Mn</td>
<td>257.61</td>
<td>0.6/1.2*</td>
</tr>
<tr>
<td>Mg</td>
<td>279.55</td>
<td>0.6</td>
</tr>
<tr>
<td>Zn</td>
<td>206.19</td>
<td>0.3</td>
</tr>
<tr>
<td>Na</td>
<td>588.99</td>
<td>5.0</td>
</tr>
<tr>
<td>Pb</td>
<td>220.35</td>
<td>0.5</td>
</tr>
<tr>
<td>Cu</td>
<td>213.59</td>
<td>0.3</td>
</tr>
<tr>
<td>Fe</td>
<td>259.94</td>
<td>0.6</td>
</tr>
</tbody>
</table>

*Parameters employed or data obtained when the laser pulse energy is 60 mJ
**With double pulse LIBS method

3.4 Calculation of electron density

Electron number density is a very important parameter to understand the evolution of plasma. Measuring the width (FWHM) of the Stark profile has been regarded as a reliable and simple way to calculate the electron density. In many references, the hydrogen emission spectra in the Balmer series were used to calculate the electron density by measuring the Stark broadening [17,18]. In our experiments, the concentration of hydrogen in plasma was high, to a certain extent, as a consequence of the ultrasonic nebulizing process. So the lines of $H_\beta$ and $H_\alpha$ were very strong. Because the $H_\beta$ line was subjected to distortion by self-absorption, the line of $H_\alpha$ was utilized to calculate the electron density.

Fig. 6 shows the experimental data around the peak of $H_\alpha$ at 656.27 nm. These data could be fitted well with the Voigt function, which is depicted as a solid line in Fig. 6. The contributions of the Gauss function and the Lorentzian function to the width were then obtained. The electron density was calculated by:

$$N_e = C(N_e, T)(\Delta \lambda_{FWHM})^{3/2}.$$  

Here the $C(N_e, T)$ is a coefficient which is a weak function of the electron density and electron temperature. $\Delta \lambda_{FWHM}$ is the Stark width obtained from the experiment. The temperature of plasma in LIBS experiments was usually about 10000 K and the $C(N_e, T)$ could be found in Table 14-1 of Ref. [19]. The electron density calculated by the data given in Fig. 6 is $2.0 \times 10^{17}$ cm$^{-3}$.

Because the intensity of signal of $H_\alpha$ was too high to be detected in the initial period, Fig. 7 only shows the electron density calculated for gate delay ranging from 0.6 µs to 2.6 µs. The gate width employed was 200 ns. It is obvious that the electron density was lower than $3.0 \times 10^{18}$ cm$^{-3}$ [17], at which the self-absorption appears. Hence, the line of $H_\alpha$ is reliable for an electron density estimate.

4 Conclusion

A purpose-built ultrasonic nebulizer assisted LIBS (UN-LIBS) system has been applied to metal elements analysis of aqueous samples at trace levels of concentration. The experimental analysis of metal elements (Mn, Zn, Cu, Pb, Fe, Mg and Na) dissolved in aqueous samples showed that the lifetime of the signal was long enough to avoid the bremsstrahlung. The power dependence investigation indicated that although a higher energy could induce higher signal intensity it may also lead to lower S/B ratio. These characteristics are fac-
tors that should be considered in parameter optimization. With optimized experimental parameters, the signals of low concentrations obtained showed a very good linear relationship. The calculated LODs of most elements calculated by the $3\sigma$ method were at least one order of magnitude better than that obtained in other signal enhancement approaches even when the exiting energy was as low as 30 mJ. This has proven that this approach could offer a higher sensitivity. The electron density calculated by measuring the Stark width of line H$_\alpha$ showed that it was reasonable to consider the plasma of UN-LIBS as LTE plasma. All of these results suggest that UN-LIBS has a promising future in trace metal elements detection for aqueous sample analysis.

References


(Manuscript received 9 April 2015)
(Manuscript accepted 15 June 2015)
E-mail address of corresponding author
ZHENG Ronger: rzheng@ouc.edu.cn

984