Analysis of heavy elements in water with high sensitivity using laser induced breakdown spectroscopy

S. SAWAF[a,*], WALID TAWFIK[a,b]
[a]*Department of Physics and Astronomy College of Science, King Saud University, Riyadh, Saudi Arabia*
[b]*Department of Environmental Applications NILES National Institute of Laser, Cairo University Cairo, Egypt*

In this study, the quantitative analysis of heavy elementals contents available in drinking water are studied using one step technique; laser induced breakdown spectroscopy (LIBS) technique. This was done by developing a new method to improve the detection limits of LIBS for manganese (as example of heavy elements) in aqueous solutions with different concentrations. In this method a medium-density fiberboard (MDF) wood have been used as a substrate that absorbs the liquid sample to transform laser liquid interaction to laser solid interaction. LIBS parameters were optimized to achieve high sensitivity measurements. Thus, it was found that using a focused 180 mJ of laser pulses of Nd:YAG laser at wavelength 1064 nm with pulse duration of 6 ns at repetition rate of 10 Hz on the prepared samples enhanced the signal to background ratio at detection delay of 1 microsecond. The atomic spectral lines for Mn were resolved. Under local thermodynamics LTE conditions. The calibration Curves for Mn are observed, with correlation coefficient (R^2) values ~ 0.98. The limit of detections LOD of Mn value of 623 ppb is compared the previous published ones. The manganese plasma temperature reaches 0.6 eV. The obtained results are important for important for nondestructive in -situ environmental monitoring and analysis of manganese in water.

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1. Introduction

Manganese exists naturally in many sources of surface water and groundwater and in many types of soils that may corrode into these waters. Though, human actions are also liable for much of the manganese pollution in water in some areas. Many studies concluded that at high levels, it can cause damage to the brain, including changes in human behavior and losses in the ability to learn and remember [1]. The first study was in 1868, by Wanklyn and Chapman where they studied the adversarial effects of the heavy metals "iron, lead, copper, arsenic, manganese and zinc" in drinking water. Therefore, it is vital to determine the content of drinking water samples of such hazardous metal to make it healthy and eco-friendly [2-4].

Instrumental sensitivity for the detection of heavy metals in water is generally at sub-ppm levels, because of their concentrations. Consequently, finding a suitable method for water analysis and environmental monitoring in real-time led to the employment of laser-induced breakdown spectroscopy [LIBS] in water, in order to combine it with the instrumental analysis method. This is because LIBS attracts a lot of attention in the past few years, where several works on LIBS in fluids ranging from small aerosols and droplets to organic solution and molten steel have been reported [5]. However, the application of the LIBS technique in liquid sample analysis is not easy due to surface ripples, splashing, extinction of emitted intensity and a shorter plasma life-time [6–8]. Solid samples provide an identical surface for better sensitivity and repeatability [9-11]. In this work, MDF wood have been used as a liquid absorber that absorbs the liquid sample contains manganese traces to transform laser liquid interaction to laser solid interaction via LIBS technique. This development was introduce for highly sensitive measurements, good reproducibility and ease of handling. This technique can be applied in the fields of environmental pollution observing and monitoring of drinking water quality. By using a wood MDF slice substrate a lower LOD has been achieved in this work.

2. Experimental procedure

A. Samples

The calibration samples were prepared using a solution of manganese chloride $MnCl_2 \cdot 2H_2O_2$ (Sigma-Aldrich - United States) in deionized distilled water as a solvent. The concentration of analyte (manganese) ranged from 2000 to 16000 mg L^{-1}.

One type of commercially available non-contaminated wood slice, medium-density fiberboard (MDF) wood have been used as a substrate. The MDF wood slices were cut to 25×25 mm^2 with 2 mm thickness. These slices were dipped into the aqueous solutions for about 5 min to absorb the solution in order to avoid pre-concentration. Then taken out and put on a dry paper for 1 min before being mounted on rotating sample stage for immediate analysis with LIBS. The rotating holder speed of 5 revolutions/min to grantee to avoid surface inhomogeneity and surface burning.

B. The LIBS system

The schematic diagram of the used LIBS setup is shown in Fig. 1. The plasma were generated by an 8 ns Q-switched fundamental Nd:YAG laser pulse of energy 180 mJ with 10 Hz repetition rate. An energy meter (Nova 978, Ophir Optronics Ldt., USA) was employed to monitor the shot to shot pulse energy. Using 10 cm quartz convex lens, the laser pulse power density of 7.1 × 10^8 W cm^{-2} was reached at the MDF sample surface with a spot size of the laser of about 1 mm. Tight focusing was avoided to prevent burning the MDF wood samples. Moreover, the laser intensity of 7.1 × 10^8 W/cm^2 is optimized to be much lower than the breakdown threshold of 1064 nm in air (~ 1 × 10^{11} W/cm^2) [12]. A cylindrical lens was used to image the laser induced plasma 1:1 onto the optical fiber 600 µm diameter. This collected light was then delivered to a high-resolution (0.1 nm FWHM) spectrometer attached to a gated CCD. For each LIBS spectrum, an average of 10 collected spectra were recorded for the selected optical range. The used gateable intensified CCD camera, model DiCAM-Pro-12 bit, PCO Computer Optics, Germany. The overall linear dispersion of the spectrometer camera system ranges from 0.006 (at 200 nm) to 0.033 nm/pixel (at 900 nm). To avoid the electronic interference and jitters, the intensifier high voltage was triggered optically. The spectral lines identification was checked by the most up-to-date electronically published database [13].

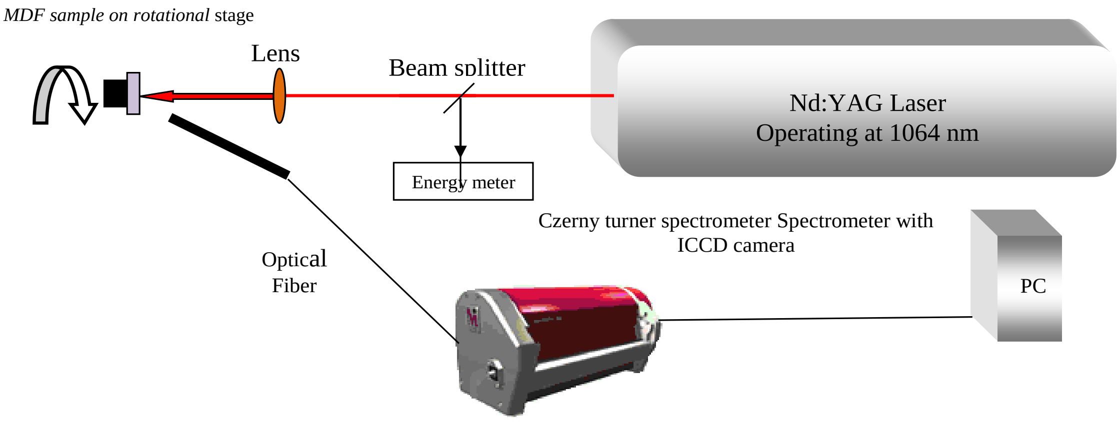

Fig. 1. Schematic of the LIBS experimental setup.

3. Results and discussion

3.1 LIBS spectrum

Fig. 2 shows a typical LIBS plasma emission spectrum of the prepared MDF wood slices samples (which contains solution of manganese traces with different concentrations). These spectra were observed at optimized conditions of 2.5 µs delay time and 10 µs gate width for best signal to noise ratio SNR. The optimized experimental parameters for laser pulse energy, gate delay time, gate width, number of accumulated single shot spectra, and geometrical arrangements are fixed for all experimental data acquisition procedures. As mentioned above, we found that using 180 mJ laser energy produce a beam waist w_0 ~ 1 mm FWHM at the surface of the sample. This in turn gives laser intensity of 7.1 × 10^8 W/cm^2 which is much lower than the breakdown threshold of 1064 nm in air (~ 1 × 10^{11} W/cm^2) [12]. In addition, we did not detect any significant emission atomic lines of oxygen or nitrogen in our LIBS spectrum of our samples. This indicates that environmental influences have been fully avoided due to optimized experimental conditions. The observed LIBS spectrum of manganese sample in the range 400-410 nm for the characteristic manganese lines 403 nm is observed at different manganese concentrations are shown in Fig. 2. The variation of the observed manganese lines intensities with the concretion is used to build the calibration curve of manganese as shown in Fig. 3.

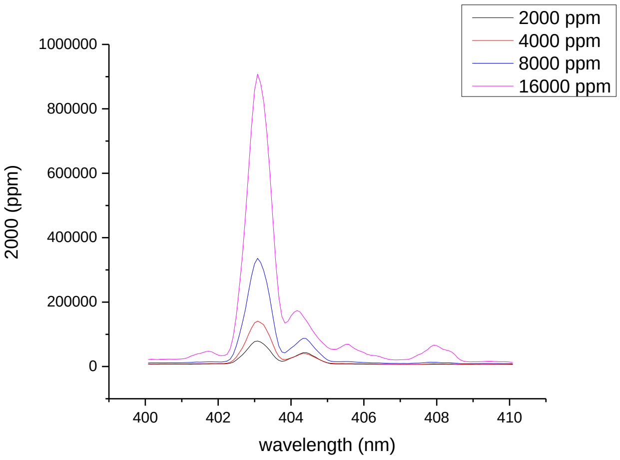

Fig. 2. LIBS spectrum for the characteristic manganese lines 403 nm at different concentrations of manganese in the MDF wood samples.

The given error bars show the calculated standard deviation for the measured LIBS intensities for each trace content of the manganese in the sample. They represent the variation in our measurements. To overcome the timing jitter and other fluctuations in laser intensity, the observed intensities are divided by the background intensity. Fig. 3 demonstrates the observation of good linear calibration equation and the correlation coefficient R^2 of 0.93 show good linearity within two orders of magnitude. The linearity of the calibration curves confirms that the obtained spectra are nearly continuum free [14, 15]. The observed result in fact, gives a prospect that the developed LIBS method has a capability for a good linearity of the calibration curves attaining a wide range of elemental concentrations.

The limit of detection could be determined from the formula [16]

$$\mathrm{LOD} = 3\,\sigma / s$$

Where σ is the background standard deviation and s is the slope of the calibration curve. We obtained detection limit of 0.623 mg/L or 623 ppb for manganese in water. The obtained LOD value for manganese is better than previously obtained value of 0.7 ppm by Yueh FY et al. [17] and lower than the J. Diedrich et al. [18] value of 36 ppb. The obtained results facilitates our proposed LIBS setup for in-situ measurements in drinking water monitoring.

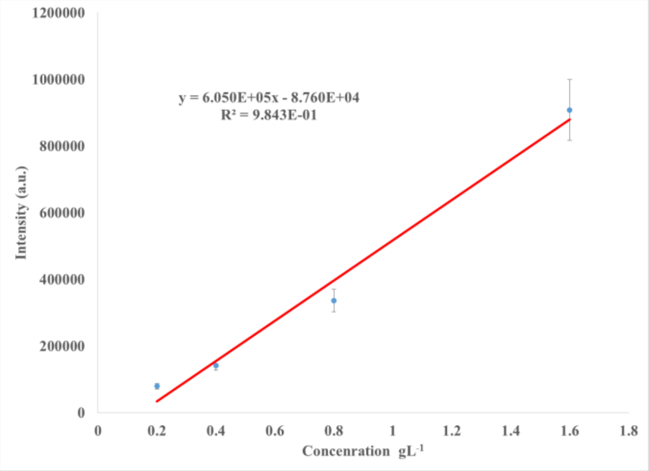

Fig. 3. The manganese calibration curve at 304 nm using LIBS technique.

3.2 Plasma temperature

To provide accurate measurements of plasma parameters, the LTE (local thermodynamic equilibrium) plasma assumption should be confirmed. Therefore, parameters such as plasma electron temperatures and electron density have to be considered and compared with the LTE condition.

Assuming the LTE assumption, the electron dominates the reaction rate, so that, the observed intensity of emission line of a single species is resulting from the Boltzmann equation as [6]:

$$I_\lambda = F.C_s \frac{A_{ki}\, g_k}{U_s(T)} \exp\left(-\frac{E_k}{KT}\right) \tag{1}$$

Where A_{ki} and g_k are respectively the probability of transition and the statistical weight for the upper energy level. E_k is the excited level energy, K is the Boltzmann constant and, T is the temperature. F is an experimental factor, C_s is the species concentration, and $U(T)$ is the partition function.

By considering the logarithm of equation (1), we got a linear relationship [6]:

$$\ln \frac{I_k}{A_{ki}\, g_k} = -\frac{1}{KT}.E_k + \ln \frac{C_s F}{U_s(T)} \tag{2}$$

A plot of the relation on the left side vs. the energy E_k has a slope of $-1/KT$. Therefore, the T plasma electron temperature can be obtained without expressive F, or the partition function $U(T)$. A typical Boltzmann plot of Mn lines is shown in Fig. 4. The curve slope yield a temperature of 7047 K or 0.6075 eV [17-20].

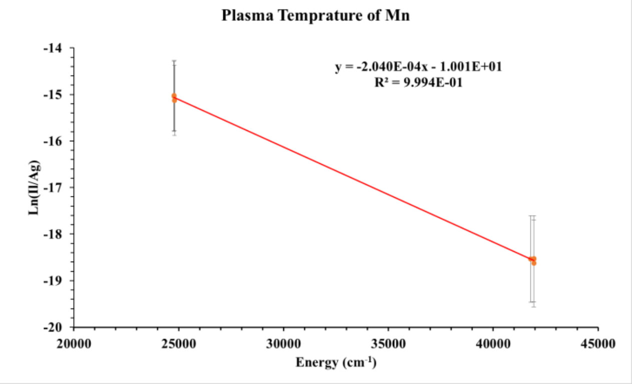

Fig. 4. The Boltzmann plot of manganese in the MDF wood samples.

4. Conclusion

In this study, a development of LIBS technique was used to analysis manganese in water and study the plasma characteristics of the generated plasma. The laser intensity was optimized to avoid the ambient air breakdown, which may influence the manganese plasma emission lines. The observed LIBS spectrum revealed well-resolved manganese spectral characteristic lines. The observed LOD for manganese 304 nm is 623 ppb. The plasma temperature reaches 0.6 eV. The obtained result is important for some environmental applications such as online monitoring of heavy elements in drinking water purification.

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*Corresponding author: sausan@ksu.edu.sa