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Detection of mercury in water by laser-induced breakdown spectroscopy with sample pre-concentration

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Abstract A method based on pre-concentration, using electrolysis, has been proposed and used for the improvement of detection sensitivity of mercury ions at ultra-trace level of concentration in an aqueous matrix by laser-induced breakdown spectroscopy (LIBS). The experimental evaluation of this method was carried out on mercury chloride ($HgCl_2$) in triple-distilled water for a concentration range of the element of 0.01–10 mg l^{-1}. A pre-concentration factor of ∼180 was obtained for LIBS detection of mercury emission line at 253.65 nm. The limit of detection (LoD) of ∼0.011 mg l^{-1} (or ∼11 ppb) for mercury in the water sample was achieved.

1 Introduction

Over the last few decades, laser-induced breakdown spectroscopy (LIBS) has become an important tool for elemental detection and analysis because of its advantages for in situ and real time analysis without or with little need for sample preparation. The applications of LIBS have widely covered different analytical demands for samples including solid [1–5] and liquid samples [6–9]. For most of the applications the laser beam is commonly focused onto a sample surface to induce micro plasma, which also allows higher detection sensitivity for aqueous sample than that when the laser beam is focused in an aqueous sample bulk [10]. One of the most important applications of LIBS is the determination of trace amounts of heavy metals in water for environmental monitoring. Concentrations of heavy metals in natural waters are very low, of the order of a few μg l^{-1}, and so are those in the waste water allowed for discharge. Therefore, the main emphasis for this analytical technique has been put into the improvement of detection capability with sufficiently low limit of detection.

Research at our laboratory has been carried out to explore the possibility of a LIBS system for sensitive detection of trace metals in surface water or in water effluent in sewage treatment plants. A critical effort is to sufficiently enhance some selected spectral signals of laser-induced atomic emission from trace elements in water and thus significantly lower the limit of detection. One of the most effective methods has been to pre-concentrate aqueous samples to increase the elemental contents for laser ablation and also transfer the sample phase to a solid one which favour LIBS for detection sensitivity. Such pre-concentration of trace elements prior to its detection has been achieved using a variety of methods, e.g. the use of mesoporous sorbent micro-column to obtain concentration factor of 150 thereby limiting the detection level down to ∼0.39 μg l^{-1} for mercury by inductively coupled plasma—optical emission spectroscopy [11] and the use of membrane filter for the ion determination of heavy metals (Pb, Cr, Co, Cu and Fe) by atomic absorption spectroscopy (AAS), with the pre-concentration factors of up to 250 [12]. Abdullin et al. [13] reported the detection of copper and cadmium in water within the concentration range of ∼1–10 μg l^{-1} (ppm) by AAS with electrochemical and sorption pre-concentration. For elemental detections by LIBS, a wood slice substrate [14] and graphite substrate [15] were also used to pre-concentrate and transfer sample phase from liquid to solid one, where the limits of detection for some metals in water were at least 2 orders better than those from direct detection on water surface. Typically for mercury (Hg), the limit of detection (LoD) of LIBS technique, using graphite substrate for pre-concentration and sample

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phase transfer, was decreased by more than 2 orders, to ~10 ppm, whilst it was undetectable directly in water bulk sample at a concentration of up to ~2000 ppm.

Mercury is one of the most toxic heavy metals in the environment and its susceptibility to bioaccumulation in water is one of the routes for its incorporation into the human body. Therefore detection of mercury in trace concentrations in water has become a priority task for the environmental protection agencies world wide. The task is, however, made difficult, particularly in water environment, due to its relatively low strength of its prominent emission lines, especially in water environment. This paper presents some experimental results and analysis on the detection of mercury in aqueous sample using electrolysis method to pre-concentrate the content onto a copper substrate prior to analysing the content on the dried substrate surface by LIBS. The detection limit for mercury in water samples has been significantly improved, indicative of the prospect of its commercial viability.

2 Experimental

Aqueous samples containing Hg at trace concentrations were prepared by dissolving the chemical powder of mercury chloride ($HgCl_2$) and diluting it in triple-distilled water for required concentrations. Two electrodes of copper strips were placed in the sample solution and a DC voltage was applied so that the metallic mercury was electroplated onto one of the strips as a thin layer on its surface. It was then removed out of the solution and the sample-coated surface was exposed to the focused laser beam for the LIBS analysis using a custom built laboratory system. The experimental set ups to achieve this are detailed below.

2.1 Pre-concentration

The pre-concentration was achieved by using the electrolysis arrangement as shown in Fig. 1. A glass container was filled with the sample solution of ~50 ml in which two copper strips of surface dimension ~20 mm × 8 mm were used as the electrodes. The voltage applied between these was 30 V across a gap of ~5 mm. In this electrolysis process the sample solution was an electrolyte and the metal element in the sample was deposited on the cathode strip as a result of reduction on the electrode as follows:

$$Hg^{2+} + 2e^- \rightarrow Hg^0$$

It is noted that the method adopted here not only allowed pre-concentrating the sample but also transferred the liquid sample phase to a solid one after the cathode strip is taken out of the sample solution and dried for LIBS detection.

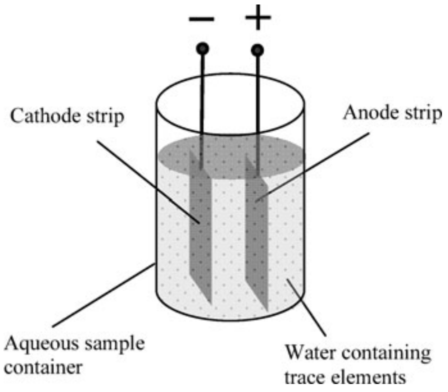

Fig. 1 Electrolysis for pre-concentration of trace elements in water

2.2 LIBS detection

The LIBS system used for this work is shown in Fig. 2. A Nd:YAG laser (Litron 200-UK) with maximum pulse energy of 200 mJ at 1064 nm was used as the exciting source and its pulse duration was ~6 ns (FWHM) at a maximum pulse repetition rate of 20 Hz. The beam diameter at the laser exit is 5 mm with a beam divergence of <2 mrad. A 25 mm focal length lens was used to focus the beam on to the sample surface, i.e. the surface of the copper strip used as a cathode during the pre-concentration process. The laser-induced plasma on the sample surface was imaged on to the entrance slit of a monochromator (SPEX 1404) with collecting lenses of 50 mm diameter, giving a f-number nearly matching that of the monochromator ($f/7.8$). The spectral dispersion of the system is achieved with high-resolution (maximum ~10 cm^{-1}) double gratings. The detector used here was an intensified diode array detector and coupled to an optical multi-channel analyser (EG & G OMA III) for spectral acquisition and analysis. A gating pulse having delay of ~2 μs and width of ~10 μs was applied to the detector through its control unit to achieve optimum S/N ratio. The sample stage was mounted on a linear translation base and moved constantly to allow a fresh sample point for each laser pulse during spectral acquisition which was done by a data average over 100 shots of laser pulses.

3 Results and analysis

Aqueous samples of triple-distilled water as a background matrix and Hg at different concentrations in triple-distilled water, from 0.01 $mg\,l^{-1}$ to 10 $mg\,l^{-1}$, were, respectively, used for the pre-concentration using the device in Fig. 1. The cathode strip surface as a substrate with trace mercury coated on it was placed on the sample stage in Fig. 2 for LIBS detection and spectral acquisition. The laser energy used to produce plasma in the experiment was 20 mJ at 20 Hz. The recorded spectra for the aqueous samples of

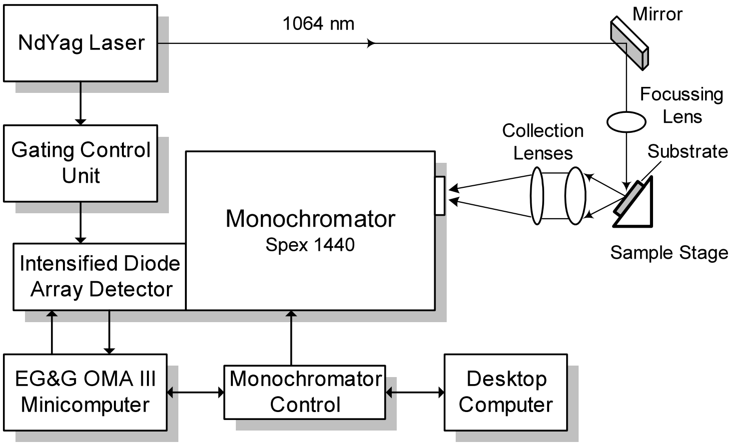

Fig. 2 Schematic of apparatus for LIBS experiments for elemental analysis

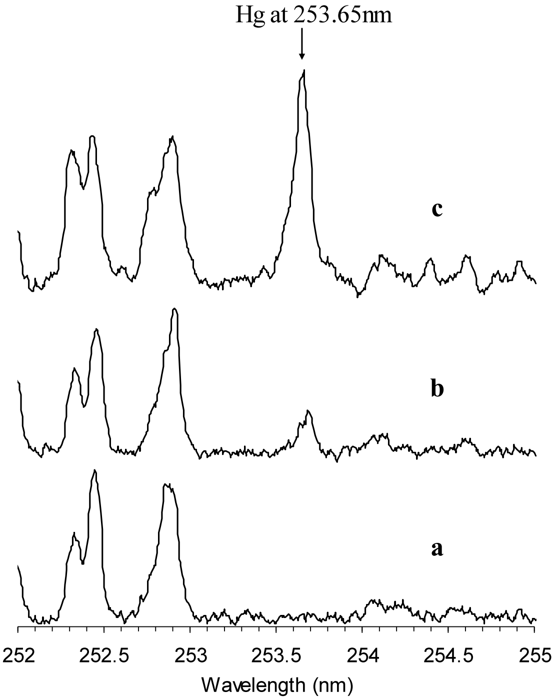

Fig. 3 Comparison of the spectra measured using sample pre-concentration and LIBS for: (**a**) triple-distilled water only, (**b**) and (**c**) the triple-distilled water with trace mercury additive at 10 mg l^{-1} when no voltage and a voltage of 20 V were applied for electrolysis, respectively

the triple-distilled water only and the water with 10 mg l^{-1} mercury additive are shown in Fig. 3 including the spectrum of the latter sample where no voltage was applied for pre-concentration.

The spectrum (a) in Fig. 3 shows the atomic emission of the copper substrate when there is no mercury deposited on it. This appears as a background of aqueous samples for the detection. For the sample of mercury in water at the concentration of 10 mg l^{-1} when the electrolysis voltage was not applied, the strong emission line of mercury at 253.65 nm was detected, as shown by the spectrum (b) in the figure, with a signal-to-noise ratio of ~15. The limit of detection in this case is roughly estimated as ~2 mg l^{-1} (e.g. 3×10 mg $\mathrm{l}^{-1}/15$) assuming a linear signal strength with the sample concentration (at low values). This also demonstrates the feasibility of transforming liquid phase into solid one to enhance detection sensitivity for a water bulk sample in which trace heavy metals, e.g. mercury, are difficult to detect at such concentration level. When the voltage was applied to the electrodes for sample pre-concentration, the acquired spectrum (c) in the figure shows a significantly higher signal peak at 253.65 nm with a signal-to-noise ratio of ~123. The limit of detection in this case was similarly estimated as 0.24 mg l^{-1} (3×10 mg $\mathrm{l}^{-1}/123$). This clearly indicates a significant increase of detection sensitivity for mercury by over 8 times when electrolysis method for pre-concentration was applied.

The results have, so far, demonstrated that the pre-concentration method allows enhancement of the detection sensitivity of mercury in water by LIBS. It was, however, noted that the target ions in the aqueous sample existing away from the vicinity of the electrodes may not be effectively deposited onto the cathode during the electrolysis process. It was envisaged that a slow circulation of the sample solution through the field may give more efficient pre-concentration. For this consideration, a pump was used to circulate the sample solution of 400 ml at a rate of ~0.6 l min^{-1} from another container into the electrolysis one. Figure 4 shows the recorded spectrum of the mercury in water at a much lower concentration, 0.05 mg l^{-1} when the sample was circulated during the electrolysis process for pre-concentration. The emission line of mercury at 253.65 nm was easily detected with a signal-to-noise ratio of ~13. To evaluate its limit of detection for mercury in water, its aqueous samples at various lower concentrations were spectrally analysed and their signal strengths at this emission line were measured for each concentration. These

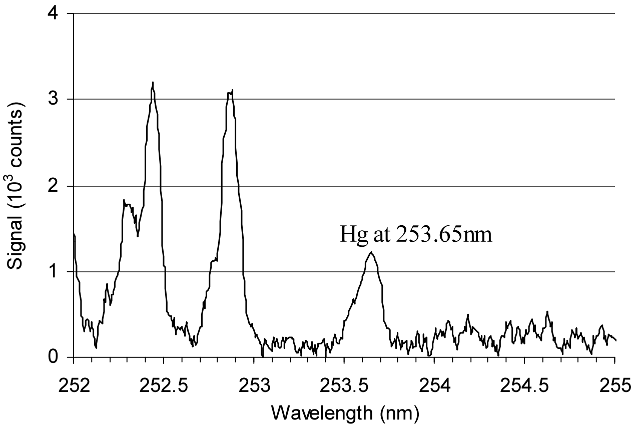

Fig. 4 LIB spectrum of mercury at a trace concentration of 0.05 mg l^{-3} when the aqueous sample of 400 ml was circulated during electrolysis

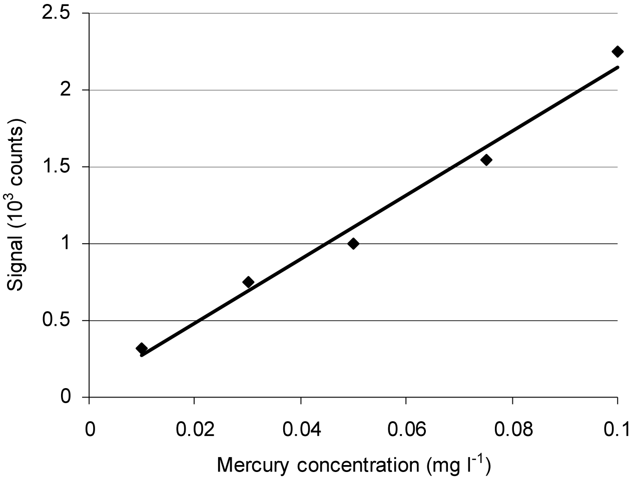

Fig. 5 Dependence of LIBS signal strength of the 253.65 nm Hg line on sample concentration in water

data are plotted in Fig. 5. The LIBS signal strength shows a linear increase with the mercury concentration in the water in the range of a sub-ppm level. The slope of the linearity was measured as $\rho = 20.8 \times 10^3$ counts/(mg l^{-1}). The standard deviation of spectral signal noise was measured as $\sigma = 75$ counts. Using these values, the limit of detection (LoD), based on the '$3\sigma/\rho$' criterion, is estimated to be ~0.011 mg l^{-1}. This corresponds to a decrease of LoD by a factor of ~180, compared to the LoD (2 mg l^{-1}) obtained from the measurement of spectrum (b) in Fig. 3 where the electrolysis voltage was not applied. It is, therefore, evident that with electrolysis method in circulated solution for pre-concentration, the limit of detection achievable for mercury using LIBS can be improved significantly to ppb (part per billion) concentration levels.

4 Conclusions

From the results obtained in this study, it has been proved that laser-induced breakdown spectroscopy allows detection of mercury in aqueous matrix at a ppb level of concentration using pre-concentration of target species. Pre-concentration has been most effectively carried out on a metal plate by electrolysis before subjecting the plate to LIBS analysis. A pre-concentration factor of ~180 for the mercury determination in triple-distilled water was achieved. This has greatly increased the capability and applicability of LIBS for trace metal detection in water. Such improvement has been achieved from its previous status where mercury detection in water at concentrations of even a few thousands ppm was difficult by direct LIBS probe in water bulk medium and for solid sample the reported limit of detection for mercury was just above ppm level. This study is an initial evaluation of the pre-concentration method as assistance for LIBS. The further investigation is being undertaken to optimise the technique to even further lower LoDs and improve the sensitivity and reproducibility of LIBS for the detection of heavy metals including mercury in water. Possible industrial applications of LIBS for aqueous samples with such pre-concentration method are also being explored.

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