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Detection of trace amount of arsenic in groundwater by laser-induced breakdown spectroscopy and adsorption

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ABSTRACT

LIBS technique coupled with adsorption has been applied for the efficient detection of arsenic in liquid. Several adsorbents like tea leaves, bamboo slice, charcoal and zinc oxide have been used to enable sensitive detection of arsenic presence in water using LIBS. Among these, zinc oxide and charcoal show the better results. The detection limits for arsenic in water were 1 ppm and 8 ppm, respectively, when ZnO and charcoal were used as adsorbents of arsenic. To date, the determination of 1 ppm of As in water is the lowest concentration of detected arsenic in water by the LIBS technique. The detection limit of As was lowered to even less than 100 ppb by a combination of LIBS technique, adsorption by ZnO and concentration enhancement technique. Using the combination of these three techniques the ultimate concentration of arsenic was found to be 0.083 ppm (83 ppb) for arsenic polluted water collected from a tube-well of Farajikandi union (longitude 90.64°, latitude 23.338° north) of Matlab Upozila of Chandpur district in Bangladesh. This result compares fairly well with the finding of arsenic concentration of 0.078 ppm in the sample by the AAS technique at the Bangladesh Council of Scientific and Industrial Research (BCSIR) lab. Such a low detection limit (1 ppm) of trace elements in liquid matrix has significantly enhanced the scope of LIBS as an analytical tool.

1. Introduction

Laser induced breakdown spectroscopy (LIBS) is a well established atomic emission spectroscopic technique where a high power, pulsed laser is used to produce weakly ionized plasma. As this plasma expands and cools, characteristic lines are emitted by the excited atomic/ionic species present in the sample which are the spectral fingerprints of those atoms or ions. Therefore LIBS can be used to determine the elemental composition of a sample. The concentrations of an element in the sample can also be determined by LIBS [1–4]. LIBS technique was used in a variety of applications, e.g., on-line analyses of industrial products [5–7], analysis of biological samples [8,9], detection of biologically hazardous elements [10], biomedical analysis [11,12], space exploration [13], and mineral analysis [14–17].

However, the scope of LIBS as an analytical tool is severely limited when it comes to trace element detection in liquid matrix. Direct detection of trace elements by LIBS in liquid with adequate sensitivity is extremely difficult due to quenching effect of water or liquid. Moreover, if the plasma is formed on the water surface, liquid may splash around due to shock waves, and severely interfere with optical detection system. As a result, the detection sensitivity of LIBS for a given element in water is usually several 100 ppm or more, and this is not enough in many cases. For these reasons, adsorbents have been used to concentrate the trace elements from water on to the surface of the adsorbent, and then LIBS were performed on these solid adsorbents. For example, Zhu et al. [18] detected trace metal elements (Pb) in aqueous solution by LIBS using bamboo charcoal as a solid-phase extraction adsorbent. In another experiment Zhu et al. [19] used paper as an absorbent for the determination of Ca and Mg in aqueous solution by laser-induced breakdown spectroscopy.

The problem of arsenic contamination in groundwater in Bangladesh came to light in 1993 in the Nawabganj district [20]. Arsenic contamination is present in the groundwater of 59 out of 64 districts of Bangladesh [21]. At present about 25 million people, out of a total population of ~160 million people of Bangladesh, are at risk due to arsenic contamination of drinking water [22]. The health effects of ingesting arsenic contaminated drinking water appear slowly. Short time effects cause diseases like stomach ache, diarrhea, muscle weakness, skin ailments etc. whereas long-term exposure can increase the risk of irregular heartbeat, liver and kidney damage, cancer etc. [23]. Skin changes including darkened patches and the appearance of areas of thickened skin, usually on the palms and soles are a common sign of chronic arsenic exposure.

Detection techniques of arsenic in the environment, including LIBS and chemical methods, are reviewed by Melamed [24]. The current

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recommended maximum permissible arsenic in drinking water is 10 ppb (parts per billion) [24]. In many districts in Bangladesh, arsenic in groundwater probably far exceeds this limit. It is mentioned that the detection limit for arsenic in solids is roughly 400 ppm [24], which is almost useless for sensitive detection of environmental contamination. In a more recent paper, Kwak et al. [25] discussed the various detection methods of arsenic in environment by the LIBS technique, and mentioned a similar detection limit (440 ppm) for arsenic in soil. As described in a NASA internal report, Vander Wal et al. [26] achieved a detection limit of 5 ppm in liquids. Using a graphite substrate, they evaporated a known amount of solution containing arsenic, and detection was achieved using LIBS analysis of this solid substrate.

In the present work, different types of adsorbent like tea leaves, bamboo slice, charcoal and zinc oxide had been used to improve the detection limit of arsenic in water by LIBS. The detection of trace elements is much easier because adsorption is a surface phenomenon i.e. it occurs only at the surface of the adsorbent and the concentration of trace elements on the surface of adsorbent becomes high enough to be detected by LIBS.

2. Experimental

The schematic of the experiment is shown in Fig. 1. The 2nd harmonic of a Q-switched Nd:YAG (Spectra-Physics LAB-170-10) laser at 532 nm with pulse duration of 8 ns, repetition rate of 10 Hz and maximum pulse energy of 450 mJ was focused on a circular spot of about 200 μm in diameter on the target sample by a convex lens of 10 cm focal length to produce an intense, transient and weakly ionized micro-plasma. The actual pulse energy used was 40 mJ. The beam has a Gaussian profile in the far-field with a beam divergence of less than 0.5 mrad. The experiments were performed in air [14].

The light emitted from the plasma was focused by a fused quartz lens ($f=5$ cm) and collected by a 300 cm long multimode silica fiber. The output end of the optical fiber was placed at the entrance slit of a 75 cm focal length computerized Czerny–Turner spectrograph (Acton Model SP-2758). The spectrograph was equipped with three ruled gratings: 2400, 600 and 300 grooves/mm blazed at 240, 500 and 300 nm, respectively, which were interchangeable under computer control, providing high-and low-resolution spectra in the wavelength range of 190–880 nm. In the present research work the 2400 grooves/mm grating was used covering a spectral width of ~9 nm (227–236 nm).

A gated and intensified CCD camera (ICCD camera, Princeton PI-MAX with Unigen II coating and programmable delay generator) was coupled to the output end of the spectrograph. The ICCD camera used has 1024 × 1024 pixels and was cooled to -20 °C by using Peltier cooling to reduce noise. The ICCD camera was electrically triggered by the Nd:YAG laser pulse after a software-controlled, adjustable time delay. In this way, the intense background radiation initially created by the high-temperature plasma was largely eliminated, and the atomic/ionic emission lines of the elements were more clearly observed. Usually, spectra from a number of laser shots (about 40–80) were obtained and an average was taken to increase the signal-to-noise ratio. Samples were manually moved between exposures to prevent crater formation and to avoid other harmful effects of the sample [17]. The spectrum, captured by the ICCD camera, was transferred to the personal computer by USB cable. A software (WinSpec/32) provided by the manufacturer was used to control all the functions of the gated ICCD camera and the Acton spectrograph [4].

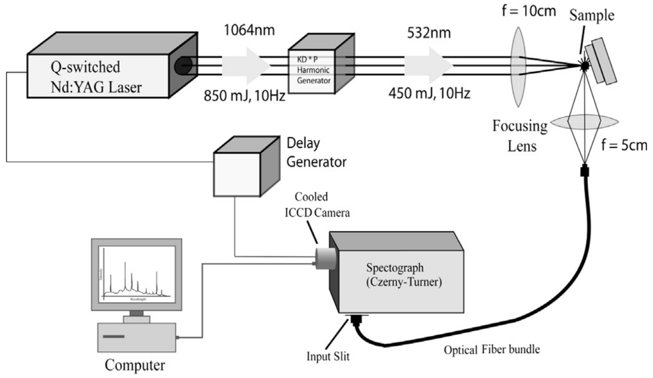

Fig. 1. Schematic diagram of the LIBS experimental setup.

2.1. Sample preparation

Aqueous solutions with different known concentrations of arsenic (1 ppm to 500/1000 ppm) were prepared in the laboratory by dissolving arsenic trioxide (As_2O_3, of the brand Loba Chemie Pvt. Ltd, India) in de-ionized distilled water. Zinc oxide (ZnO, of the brand UNI-CHEM chemical reagents, China) of fixed amount, thoroughly mixed with small (but fixed) amount of aluminum-trioxide (Al_2O_3, as internal standard, of the brand Merck Limited, Mumbai) was chosen as an adsorbent. A hand mortar was used to make the mixture of ZnO and Al_2O_3 uniform. Then this mixture of ZnO and Al_2O_3 was dipped into aqueous solutions (of fixed volume) of different concentrations of Arsenic for 20 h so that sufficient amount of adsorption could take place. The pH was maintained in the range of 2–3 to avoid possible precipitation of arsenic trioxide. Then the solution was filtered to get the adsorbent. After filtering, the adsorbent was dried at 80 °C for few hours. Finally, the sample was prepared by using a hand press and applying pressure of 80 bar to make the sample reasonably strong. The spectral emission line of As I at wavelength of 228.812 nm was used for drawing the calibration curve (the intensity of the arsenic emission line normalized by Al I emission line at 232.1562 nm versus the concentrations of added Arsenic in water). Similar procedures were followed in case of using charcoal (collected from pharmaceutical industry) as an adsorbent except the fact that no Al_2O_3 was deliberately mixed with it since aluminium was present as impurity in the charcoal.

The arsenic polluted groundwater was collected in plastic bottles from the Farajikandi union of Matlab Upazilla of Chandpur District of Bangladesh. The pH was maintained in the range of 2–3 to avoid possible precipitation of arsenic compound after collecting the arsenic polluted groundwater sample. The water sample was concentrated twenty times of initial volume by boiling in a glass beaker. Then ZnO adsorbent (along with aluminum trioxide) of the same amount as that in the case of solutions of known arsenic concentration was dipped into the arsenic contaminated water (same volume) for 20 h in order to adsorb arsenic from the polluted water and then filtered and dried in an oven. Finally small pellets were prepared from those ZnO as described above.

3. Results and discussions

A delay time of 800 ns (Fig. 2a) for the gated ICCD detector was found to be optimum for the line of AsI (at 228.812 nm) used for the calibration curve. In the present work the plotting of 'signal × S/N' as a function of delay time is a new idea which has been used, because of the fact that the strength of the signal is not constant rather decreases with increase of delay time. To illustrate this fact S/N as a function of delay time was also plotted in Fig. 2b which gives an optimized delay time of 1200 ns by maximizing the S/N ratio. At this delay time the signal strength was drastically reduced to 3644 whereas at the delay time of 800 ns the signal