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Ultrasonic nebulization-sample introduction system for quantitative analysis of liquid samples by laser-induced breakdown spectroscopy

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ABSTRACT

In this study, design and optimization studies of a sample introduction system based on ultrasonic nebulization of metal salts in aqueous environment for laser-induced breakdown spectroscopic detection were presented. The system consisted of an ultrasonic nebulizer connected to a tandem heater–condenser–membrane dryer unit that produces sub-micron size aerosols. Results indicate improvements in detection limits for some elements with the use of membrane dryer. Optimization studies were performed by systematical investigation of LIBS emission signal with respect to laser energy, carrier gas flow rate and detector timing parameters. Under optimized conditions, calibration graphs for Na, K, Mg, Ca, Cu, Al, Cr, Cd, Pb and Zn were constructed and detection limits were calculated. The applicability of the ultrasonic nebulization-LIBS system was tested on real water samples. This system establishes LIBS as an effective analytical tool for both qualitative and quantitative determination of metal aerosols in aqueous environments. This technique is sufficiently rapid to provide real-time monitoring of toxic metals.

1. Introduction

Sample introduction is one of the most problematical area in liquids analysis by laser-induced breakdown spectroscopy, LIBS. Analyzing elements directly from the bulk liquid [1,2] suffers from difficulties like splashing, bubble formation and shock wave formation after focusing the laser beam on liquids. In order to overcome those difficulties experienced in liquid analysis, plasma formation on liquid surfaces [3,4], on droplets [5,6], on flowing-jet liquids [7,8] and in cavitation bubbles [9] has been employed. Use of double pulses for plasma formation [10–12] has also been realized in liquid analysis by LIBS, with high sensitivity. Aerosol formation by suitable nebulization techniques [13–19] is another approach to liquid analysis by LIBS. Fine aerosol particles of micrometer to nanometer sizes can be obtained by pneumatic, ultrasonic and electrospray nebulization techniques. Studies based on the formation of volatile hydrides of some toxic elements from their solutions before laser-induced breakdown spectroscopic detection in aqueous environments have also been reported [20–22]. The sensitivity of LIBS for quantitative analysis of liquids compared to other atomic emission spectroscopic techniques, such as ICP-AES, is quite low and the limits of detection, (LOD) reported for several elements vary between high ppb(μg/L) to low ppm(mg/L) levels [4,23–26]. However, LIBS is a very convenient technique to develop portable sensors for detecting and monitoring of environmental pollutants in the field. In order to make LIBS applicable to liquid analysis at low concentrations, analytical capabilities of the LIBS technique needs to be improved with serious laboratory efforts.

In this study, a sample introduction system that utilizes ultrasonic nebulization for aerosol generation and a tandem heater–condenser–membrane dryer unit for desolvation and drying of aerosols has been realized for fast and sensitive analysis of metal salts present in aqueous environments by laser-induced breakdown spectroscopy. Variations of LIBS signal with respect to laser energy, carrier gas flow rate and detector timing parameters were systematically investigated. The effects of using membrane dryer on LOD values of Na, K, Mg, Ca, Cu, Al, Cr, Cd, Pb and Zn were evaluated. In order to overcome a common problem of plasma movement along the slit width, a telescopic system design that directs the laser beam from the top perpendicular to the sample flow was utilized. This way, plasma movement along the slit height and hence higher probability of obtaining LIBS signal from every single laser shot were achieved.

2. Experimental

The experimental set-up for ultrasonic nebulization-LIBS system, schematically shown in Fig. 1, consisted of a sample introduction, plasma formation and detection units. Metal aerosols produced in the sample introduction unit are coupled to a 5 armed teflon plasma cell. Laser pulses of 45–150 mJ energy were focused in the center of a teflon cell from the top arm by means of a 5 cm focal length lens and meet with a flow of dry aerosols at 90° angle to form plasma. Plasma emission was collected and spectrally resolved by an echelle type spectrograph and detected by a time gated ICCD detector. The

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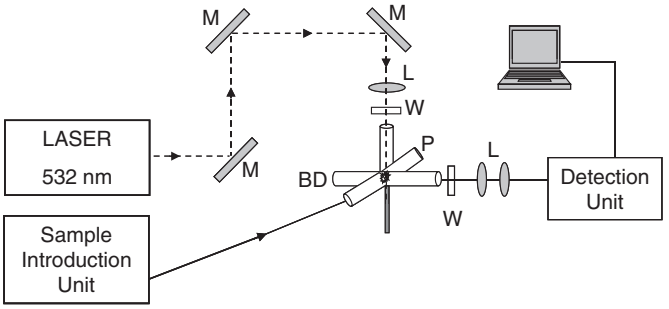

Fig. 1. Experimental LIBS set-up for the analysis of metal aerosols. M: 532 nm reflective mirrors, L: focusing and collimating lenses, W: quartz windows, P: pump, BD: Beam Dump.

details of each part of the experimental set-up are given in the following sections.

2.1. Sample introduction unit

Pictures of the sample introduction system consisting of an ultrasonic nebulizer, USN, desolvation unit and a membrane dryer connected to a teflon plasma cell are given in Fig. 2(a) and (b). Each part is explained below, in detail.

2.1.1. Ultrasonic nebulizer

An ultrasonic particle generator (*Sonaer, 241PG*), Fig. 2(a), with 50 mL of liquid sample capacity was used for production of micron sized aerosols from aqueous metal solutions. Some amount of liquid sample placed inside the particle generator was first converted into fine aerosol droplets by a piezo-electric crystal that vibrates at a frequency of 2.4 MHz. Aerosols generated inside the USN were carried into the *desolvation unit* by a flow of nitrogen gas at a rate of 3–5 L/min.

2.1.2. Desolvation unit

A compact heater/condenser desolvation unit [14,27], shown in Fig. 2(a), which consisted of heating and condensing tubes was constructed at the local glass shop for the removal of the solvent content of the metal aerosols. This unit was directly placed at the top of the USN and the aerosols formed inside the nebulizer travel through a 20 cm long glass tube placed on top of the nebulizer exit. Three meter long heating tape (*Cole-Palmer*), wrapped around this glass tube keeps the inside temperature of the tube around 110 °C. At this temperature, hot aerosols move through a 15 cm long condenser unit in which cooled water at 4 °C circulates outside (*PolyScience*). Here, the evaporated solvent condenses and is collected (drain) at the bottom end of the unit, while dry aerosols travel through the membrane dryer unit. The solvent removal efficiency of the desolvation unit has been tested via Atomic Absorption Spectrometric measurements of the drain solution. It has been found that 90% of the analyte solution is transported to the sample cell while 10% is lost to the drain during the desolvation process.

2.1.3. Membrane dryer

After passing the desolvation unit, dry aerosols travel through a naphion membrane dryer (*Perma Pure, PD50*), Fig. 2(a) and (b), for the removal of their excess moisture. Here, the aerosols flow within the nafion tubes while water vapor is carried away by a dry purge gas flowing over the exterior surface of the membrane tubing in counter-current direction with respect to the sample flow. Nitrogen gas flowing at flow rates smaller than the sample flow rate (typically 3.5 L/min) was used as a purge gas. The effect of membrane dryer on LIBS signal intensity is discussed in the Results and discussion section below. After passing the drying unit, aerosols are introduced into the sample/plasma cell from one side arm of the cell for plasma formation.

2.1.4. Teflon cell

The sample/plasma cell, Fig. 2(b), with five arms, each 5 cm length and 1 in. outer diameter, was machined from the teflon material in local machine shop and has been used previously [20] in another LIBS application of our group. The arms at which laser beam entering and plasma emission to be collected were covered with quartz windows. The medium inside the cell has been kept uniformly flowing using a vacuum pump (*Edwards*), connected to a third arm of the sample cell. It should be noted that the system was under atmospheric pressure due to the continuous nebulization of the sample during experiments. The aerosols were introduced into the sample/plasma cell from the one side arm of the cell and the remaining arm was blocked by a beam dump.

2.2. Plasma formation

A Q-switched Nd:YAG laser, (*Quanta-Ray, Lab 170, Spectra Physics*), working at the second harmonic wavelength, 532 nm, with 10 ns pulse duration and 10 Hz repetition rate was used for plasma formation. In order to overcome a common problem of plasma movement along the slit width, a telescopic system design, as shown in Fig. 1, was used. Here, three highly reflective mirrors placed successively at 45° angle with respect to incoming laser beam were used to direct laser beam from the top arm of the sample cell, perpendicular to the sample flow. This design enables plasma movement from one laser

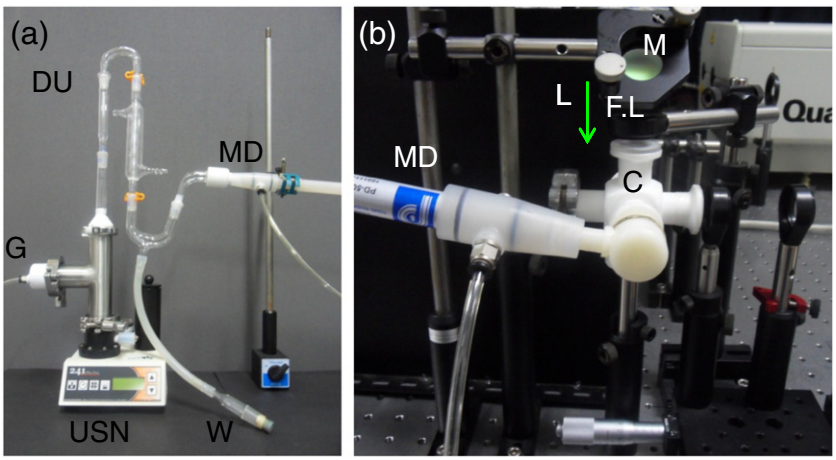

Fig. 2. Pictorial representations of sample introduction system. (a) USN particle generator desolvation unit (heater and condenser) connected to membrane dryer, (b) membrane dryer connected to 5 armed teflon plasma cell. G: gas inlet, DU: desolvating unit, W: waste, MD: membrane dryer, L: laser beam direction, C: sample cell, M: mirror, F.L.: focusing lens.