Laser-induced breakdown spectroscopy for monitoring heavy metals in soils

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Abstract

The quantification of Cr in soil was carried out using laser-induced breakdown spectroscopy (LIBS). A Q-switched Nd-YAG laser (10 Hz, $\lambda = 1064$ nm) has been employed for generation of laser-induced plasma on surface of soil sample. The atomic emission lines are recorded using an Andor Shamrock SR-303i spectrometer, fitted with a ICCD camera. In order to test the validity of LIBS results, inductively coupled plasma-atomic emission spectrometry (ICP-AES) was also employed for determination of Cr. The results obtained using LIBS found to be in good agreement with those of ICP-AES.

1. Introduction

Pollution of soils by heavy metals is a major public concern. In particular, the contamination of agricultural soils with heavy metals results in accumulation of toxic metals in food crops. Thus, soil-crop-food transfer, may be among the major exposure pathways of heavy metals to humans. The heavy metals can accumulate in human vital organs such as kidneys and liver, causing progressive toxicity.

Anthropogenic sources of heavy metals in the environment are combustion of fossil fuels, mining and smelting operations, processing and manufacturing industries and waste disposal including dumping, release of domestic sewage and scrap metal handling. Farming and forestry also contribute to the contamination of the milieu by toxic metals due to the use of fertilisers and pesticides [1]. Other materials used as soil amendments, irrigation water, and atmospheric deposition from urban and road emissions are also the possible sources of heavy metals [2]. The greatly increased circulation of toxic heavy metals in soil, water and air has raised considerable concern for environmental protection and human health. Thus, there is the need for rapid and accurate quantification of heavy metals in environmental matrices such as soils and sediments.

Laser induced breakdown spectroscopy (LIBS) is a laser based rapid and sensitive optical diagnostic technique in which any kind of sample can be easily analysed with little or no sample preparation. The dynamic range of LIBS technique is also remarkably wide: the technique simultaneously gives information about elements with concentrations ranging 100% down to parts per million [3]. As only a minute quantity of material is consumed in the process, LIBS is essentially a non-destructive technique. In addition, the technique may be applied for in situ analysis. The application of LIBS as a field sensor reduces sampling and sample preparation steps that consume both money and time.

In LIBS technique, a high powered laser pulse is focused onto a sample to create plasma, which results from vaporisation and atomisation of a small amount of target material. When a transient plasma, which contains neutral and ionised excited states cools down, the excited atomic, ionic and molecular fragments within the plasma emit light with the specific wavelength, which are the signatures of the elements in the sample. The emitted light can be recorded adequately, which provides spectra. Spectra obtained can then be analysed appropriately, providing qualitative and quantitative information on the elements contained in the sample [4, 5].

The main objective of this work is to evaluate the potential of LIBS technique for detection and quantification of heavy metals in soils with special emphasis on Cr. For this purpose, LIBS results were compared to the corresponding data obtained using conventional ICP-AES technique.

2. Experimental

The experimental set-up was designed using a Q-switched Nd-YAG laser (10 Hz, λ = 1064 nm) and the emission signals were collimated by a lens into an optical fibre coupled to an Andor Shamrock SR-303i spectrometer. The spectrometer is fitted with a DH734-18F-03 ICCD camera. In this study, 2399 l/mm grating of the monochromator and 50 μm entrance slit were used. Wavelength calibration was conducted with a low pressure Hg-Ar lamp. The beam from the laser was focused using a lens (f = 45 mm) onto the soil sample placed on a holder with a translational stage. The experimental set-up has been optimised adjusting lens-to-sample distance (LTSD), the position of collecting lens and fibre, and angle of light collecting fibre to assure a high signal-to-background ratio.

LIBS measurements were conducted by focusing pulses of laser energy of 150 mJ onto the sample surface. The emission spectra of plasma were collected with a delay time of 0.75 μs and gate width of 9 μs after optimisation for selected Cr I lines. At least 3 spectra of each sample were collected on different sample spots each resulting from 20 accumulations.

Soil samples were collected from areas close to mining activities. Soil samples were dried, finely ground, sieved and compacted to obtain pellets. Boric acid was used as a binder agent for preparation of pellets. Pellets of soil samples were prepared by pressing 4.00 g of soil mechanically for LIBS analysis. Soil and sediment certified reference materials were used for construction of calibration curves using LIBS.

Calibration standards were prepared from the 1000 mg/l stock solution of Cr for ICP-AES analysis. Millipore water, obtained from Milli-Q water purification system was used throughout this work. A blender was utilised to obtain fine soil samples. The combination of 3.00 ml HNO_3, 1.00 ml HCl, 1.00 ml HF and 1.00 ml H_3BO_3 were used for mineralisation of soil samples employing MARS 5 microwave digestion system.

3. Results and discussion

The assessment of interference free lines was conducted using standard reference materials of soils and sediments, which were purchased from NIST. Further assessment of experimental parameters has been carried out using soil samples since the matrix effect influences signal-to-background ratio of the analyte line. Suitable spectral lines of analyte have been identified with special focus on Cr, which is one of the potential pollutants of soil. Detailed investigation of experimental parameters such as gate width and gate delay time has been conducted. Gate width of 9 µs was employed after optimisation for selected Cr I lines. Gate delay times of 0.01 to 14 µs were studied as shown in Figure 1. The maximum signal-to-background ratio of Cr I 425.433, 427.481 and 428.971 nm lines was noticed at 0.75 µs gate delay time for Cr present in soil sample. Cr I 425.433 nm line showed the best signal-to-background ratio compared to 427.481 and 428.971 nm lines. Experimental parameters that revealed best signal-to-background ratio have been selected for subsequent analysis of Cr in soil samples using LIBS.

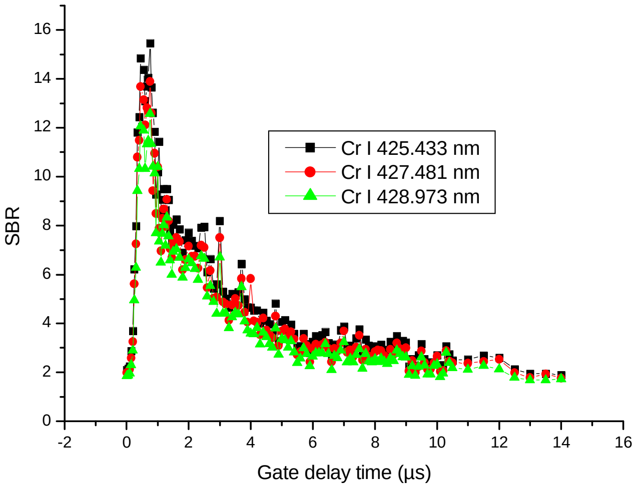

Figure 1. Effect of gate delay time variation on signal-to-background ratio of Cr I lines of soil sample.

Figure 2 shows LIBS spectra recorded in the specific 419.237 to 432.514 nm spectral region, where the three prominent lines of Cr exist. These strong emission lines of Cr I (425.433, 427.481 and 428.971 nm) were identified from soil samples employing our LIBS set-up. Other emission lines due to other elements do exist in this region, however, for this work we are interested in monitoring Cr. To identify Cr I lines, the LIBS spectra obtained analysing pure K_2CrO_4 was overlayed to the LIBS spectra of soil sample as shown in Figure 2. This clearly shows the presence of Cr I lines at 425.433, 427.481 and 428.971 nm in soil sample. All three lines are the intense lines of Cr I, which clearly demonstrates the presence of Cr in appreciable amount in soil sample collected from the vicinity of mining activities. The NIST atomic spectra database (http://physics.nist.gov/PhysRefData/ASD/lines_form.html) were also used to identify all the spectral lines recorded for Cr with our LIBS set-up. The results revealed the feasibility of our LIBS set-up for detection of heavy metals such as Cr. The spectral region for three Cr emission lines selected here has minimal interference with other weak emission lines from other elements.

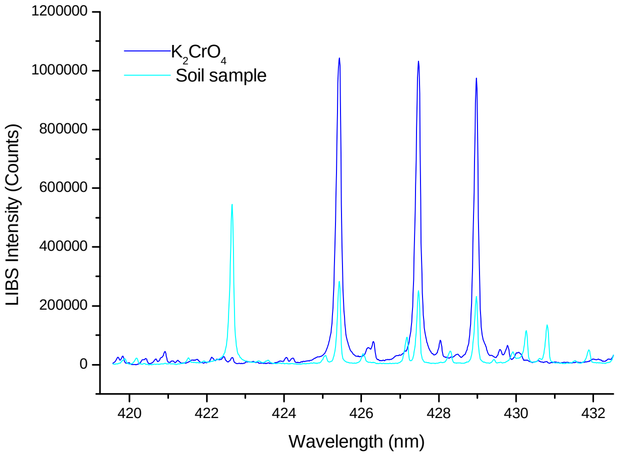

Figure 2. LIBS spectra of K_2CrO_4 and Soil sample.

A 425.433 nm Cr I line that showed best signal-to-background ratio during gate delay time optimisation has been selected for subsequent analysis. The calibration curve for Cr I 425.433 nm line was constructed using pellets of certified reference material of soils and sediments. The following certified reference materials were used: standard reference material of San Joaquin soil (SRM 2709a), certified reference materials of stream sediment (NCS DC 73316 and NCS DC 73374) and certified reference materials of soil (NCS DC 73322 and NCS DC 73325). Calibration curve for Cr I 425.433 line is presented in Figures 3. The calibration curve obtained showed strong linear dependence of LIBS signal on concentration as indicated by correlation coefficient (R=0.99646).

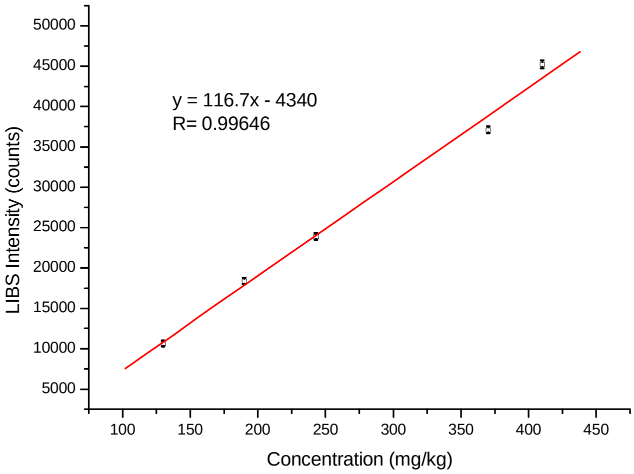

Figure 3. Calibration curve for Cr I 425.433 nm line.

The limit of detection (LOD) for determination of Cr in soil using LIBS, was determined from the calibration curve. The LOD is calculated by (3σ)/m, where σ is the standard deviation of the background signal and m is the slope of the calibration curve [6]. In this work, the LOD achieved for Cr in soil is 46.2 mg/kg.

Table 1. Comparison of LIBS and ICP-AES results.

Sample	Concentration (mg/kg) ± SD	
Soil sample 1	340 ± 37	371 ± 21
Soil sample 2	403 ± 43	426 ± 32
Soil sample 3	255 ± 41	269 ± 18

After calibration, the concentration of Cr was determined using LIBS setup and has been validated by the analysis of the same soil samples using ICP-AES. The concentration measured with our LIBS system as shown in Table 1 agrees with the concentration determined using ICP-AES. Thus, LIBS can be considered as an alternative technique for quantification of Cr in soil. On the basis of our experimental findings, it is concluded that to quantify Cr in soil, Cr I 425.433 nm line is more suitable in comparison to Cr I 427.481 and 428.973 nm lines as evidenced by its best signal-to-background ratio.

Acknowledgements

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