Original article

Spectroscopic Detection of Radioactive Elements within the Soil and Plant in Al-Hasahisa Locality

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Abstract

Laser Induced Breakdown Spectroscopy (LIBS) technique was used to determine the concentrations of different radioactive elements in within the same number of soil and plant (15 each). The sample were collected from Al-Hasahisa Locality, Jezara State, Sudan. Two radioactive elements: Uranium and berkelium were detected from the samples. The concentration of uranium equal 1.73 ppm in soil samples and 1.69ppm in plants samples while the concentration of berkelium equal 2.00ppm in soil samples and 1.99ppm in plant samples. The accuracy of LIBS system in range of 0.9687 - 0.9784 in soil sample and 0.9124-0.9177 for plants samples. This study display that LIBS is appropriate tool for detecting radioactive elements.

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Introduction

Laser-induced breakdown spectroscopy (LIBS) is a spectroscopic technique utilizing high power laser pulses. When a pulsed high power laser beam is focused on the material (Solid, Liquid, Gas and aerosols), a short lived (micro second) high temperature (few eV) and density $(10^{16}-10^{19} \text{ cm}^{-3})$ plasma is produced and expands perpendicular to the target surface (Qingyu and Pengkun. 2020, Zaitun *et al.*, 2018), German *et al.*, 2018). Such laser produced plasmas, which contains a diversity of atomic and ionic species as well as free electron emit radiation over an extensive spectral range stretching from infrared to the X-ray region. Although different materials have different breakdown thresholds, the plasma is typically generated when the laser irradiance exceeds ~ 10^8 MW/cm² (Zhou and Liu, 2021). The radiation emitted from excited/ionized species in the laser produced

plasma is spectrally resolved, and the individual neutral atoms and/or atomic ions in the plume are identified and quantified by their unique wavelengths and the line intensities respectively. The fundamental concept of LIBS is similar to that of conventional plasma-based methods of optical emission spectroscopy (OES). In practice this technique is calibrated through establishing a relationship between the observed spectral line intensities of a particular species and the corresponding concentration in the target sample material (Paullino and Villas-Boas, 2019). The graph that corresponds to this relationship is called the calibration curve and is used to determine the elemental contents of unknown sample by recording its LIBS intensity. Since it's starting LIBS technique has been employed for the direct qualitative as well as quantitative elemental characterization of almost every type of material using optical emission

spectroscopy. There are many reviews and books dedicated to basic principle and instrumentation of LIBS as well as to a wide range of applications (Vinicius et al., 2020). In the context of spectrochemical analysis of elements, LIBS has many advantages over other conventional spectroscopic techniques such as laser ablation inductively coupled plasma (LA-ICP), X-ray fluorescence (XRF), atomic absorption spectroscopy (AAS) and spark-discharge optical emission spectroscopy (SD-OES). These advantages generally include the fact that sample preparation is either not necessary or minimal. Sample excitation/ionization in the LIBS is carried out by optical energy. It is an almost non-destructive technique that provides direct characterization of the solid sample. The most important point about LIBS is that it has powerful capability in carrying out remote on line and in-situ analysis of the samples particularly situated in the hostile and harsh environments. However, it is lacking on the sensitivity front. Various techniques have been used to enhance the sensitivity of the LIBS. Some of them include expansion of plasma in the magnetic field, dual and multiple pulse excitation of plasma, spatial confinement of LIBS plasma as well as combination of LIBS with laser induced fluorescence technique (Zhou and Liu, 2021). The aim of this paper is to determine concentration of Erath Metal elements in Kadugli City soil and to calculate accuracy of the used LIBS system.

2. Theoretical Background

The concentration of any element detected through LIBS method can be calculated calibration function. Calibration curves for elements under investigation were also estimated by the total intensity of a spectral line 'I' from an excited atom or ion in homogenous and optically plasma for a transition from state $j \rightarrow i$, it is given by.

$$I = h v_{ji} A_{ji} N_i \tag{1}$$

Where v_{ji} is the frequency of the transition from state $j \rightarrow i$, A_{ji} the Einstein coefficient for spontaneous emission, N_j the population of the upper level j and h is the Planks constant (Hussain and Gondan, 2013).

If the energy levels concerned are in local thermodynamic equilibrium (LTE), then population density of upper level N_i

is related to ground level number density (N) by Boltzmann's equation

$$N_j = N_i g Q^{-1} \exp\left(\frac{E_j}{kT}\right) \tag{2}$$

Here g_j and E_j are the statistical weight and energy of upper level j respectively, Q is the partition function of relevant species, K is the Boltzmann's constant, and T is the electron temperature of the plasma. So, from above two equations, we get

$$I = h v_{ji} A_{ji} N_i g Q^{-1} exp\left(\frac{E_j}{kT}\right)$$
(3)

From Eq. (3), one can determine the population density of the relevant species (atoms or ions) for an element in plasma from a measurement of the absolute intensity of corresponding transition and the knowledge of the excitation temperature and atomic constants. However, it is not possible to derive a theoretical expression relating N and the concentration of the particular element (in samples) under investigation. Hence, in practice, an empirical relationship is required between the observed line intensity (Ij) and corresponding concentration (C), i.e.

$$I_i = F(C) \tag{4}$$

Here F (C) is called analytic calibration function and the graph between the LIBS intensity of a line of specific element and the concentration is called the calibration curve (Rosalba *et al.*,2010).

Standard Deviation

Standard deviation is a measure of amount of a variation or dispersion of a set of value, a low standard deviation indicates that the value tends to be close to the mean of the set, while out over a high standard deviation indicates that the values are spread over a wide range. Standard deviation can be calculated through formula

$$SD = \sqrt{\frac{(x-\bar{x})^2}{N}} \tag{6}$$

Where x is each value from the set, \bar{x} is the set mean and N is the number of set values.

Limit of detection

Limit of detection means the lowest concentration of particular element or compound and it is commonly used as evidence of the quality of the sensors, the limit of detection (LOD) of LIBS system can be estimated using the equation

$$LOD = \frac{2SD}{S} \tag{7}$$

Where (SD) is the standard deviation of the background and S is the sensitivity which is given by the ratio of the intensity to the concentration (Gondala *et al.*, 2010).

Materials and Methods

The experimental set up used for the analysis of (Soil and Plant) is depicted schematically in Figure 1 and is similar to published in earlier publications. The LIBS system consists of Ocean Optics LIBS 2000+ spectrometer, a sample holder, N2 - Laser and OOILIBS software. The 337.8 nm radiations emitted at fundamental frequency from N2- laser were applied for production of plasma spark at target surface. Laser beam was focused by a convex lens of focal length 30 mm onto the sample. The pulse energy utilized in these experiments was in the range of 100 mJ. The light from the plasma spark is collected by optical fiber with SMA connector. The USB 2000+ has four spectrometer modules to provide high resolution (FWHM 0.1 nm) with a gated CCD detector having 14,336 pixels for simultaneous recording of the spectrum in the 400 nm to 1150 nm wavelength region. The emission is collected at a 45° angle to the incident laser radiation. The spectrometer software reads the data from the detector and reconstructs



Fig. (1) The experimental set up LIBS used for the analysis of (Soil and Plant)

Results

A number of Thirteen samples (15 soil and 15 Plant) were collected from Al-Hasahisa governorate which located in Al-Jazeera state in middle of Sudan in the western bank of The Blue River at higher 40m from 13/6 feet above sea level, Sudan to detect radioactive by using Laser-Induced Breakdown Spectroscopy (LIBS) which used to measurements radioactive elements and to calculate concentrations of radioactive elements and limit of detection of LIBS system.



Fig (2) Typical LIBS spectra of berkelium in fifteen surface soil and plant samples were collected from Al-Hasahisa governorate.



Fig (3) Calibration curve for berkelium obtained by using analytic calibration function of (Bk) with known concentration.



Fig (4) Typical LIBS spectra of U in fifteen surface soil and plant samples were collected from Al-Hasahisa governorate



Fig (5) Calibration curve for Titanium (U) obtained by using analytic calibration function of (U) with known concentration

Table (1) radioactive elements of 30 samples (15 sample Soil and	d 15 sample Plant) were collected from Al-Hasahisa governorate
of detection and maximum detected concentrations and maximum	permissible concentration limit of detection (MPC).

Element	Main Concentration (ppm)		S.	S. D		LOD		R.S.D%		RA	
	Soil	Plant	Soil	Plant	Soil	Plant	Soil	Plant	Soil	Plant	
Bk	2.00	1.99	0.554	0.55	0.01368	0.01371	27.69	27.68	2.52	2.503	
U	1.73	1.69	0.028	0.02	0.00055	0.00034	1.60	1.01	6.31	2.941	

Discussion

In this experimental work, LIBS spectrum was applied in thirteen samples of soil and plant to detect radioactive elements. LIBS spectra of the samples containing Bk and U were measured in samples and compared to standard concentration in soil and plants. The recorded spectra of Bk and U were shown in fig (2) and (4) respectively.

The LIBS signal intensity showed linear dependence on the concentration of Bk and U as shown in fig (3) and (5) respectively, the concentration of Bk equal 2.00 ppm with accuracy 0.9687 by limit of detection 0.01368 in soil sample while for plant sample the concentration of Bk equal 1.99ppm with accuracy 0.9124 by limit of detection 0.01371,

the concentration of U in soil sample equal 1.73ppm with accuracy 0.9784 by limit of detection 0.00055but for plant sample the concentration equal 1.69ppm 73ppm with accuracy 0.9175 by limit of detection 0.00034. the concentration of all samples was obtained by using equation (4) and limit of detection by equation (7). According to Health Physics Society (HPS) in United States (specialist in radiation science research) the concentration of Bk and U under safety limit [HPS,2020]. If the concentration exceeded safety limit it will causes seriously diseases. Uranium has a chemical toxicity that independent of its radioactivity, Uranium affects all organs and tissues, as a cell poison, large doses of uranium can cause damage to the kidneys, it may also be associated with genotoxicity effects. At molecular level, Uranium may also include genomic instability by affecting pathways like DNA repair, gene expression regulation, reactive oxygen species generation by replacing essential metals in their metabolic pathways. All these affects may lead to the development serious disease such as cancer. The health effects of berkelium have not been studied in details, since it is radioactive, scientist assume that it is harmful to human health (Rakmetkazhy and Bulgakova, 2015). Due to that the time period for staying in this area must be considered to avoid cumulative effects, they also have to pay attention for dietary pattern.

Conclusions

In this study, the concentration of radioactive elements uranium (U) and (Bk) present in soil and plant samples collected from Al-Hasahisa governorate in Al-Jazeera state, Sudan was calculated using LIBS system. LIBS system occurs high efficiency to detecting radioactive elements, due to Health Physics Society (HPS) all detected elements under safety limit

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