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Identification of Heavy Metals in Some Water Sources in Khartoum State Using Laser Induced Breakdown Spectroscopy

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Abstract

Laser-induced breakdown spectroscopy (LIBS) is an atomic emission spectroscopy that can analyze any sample successfully and can be applied to gas, liquid, and solid samples. It can provide nonintrusive, qualitative and quantitative measurement of elements in various test environments .Due to rapid industrial growth, environmental pollution has increased tremendously over the years especially with heavy metals. This study was set up to use LIBS technique to identify the heavy elements in some water sources in Khartoum State. Four water samples collected from different locations in Khartoum were irradiated by Q-switched Nd: YAG laser to produce its plasma. The emission spectra of the plasma were collected via optical fiber and analyzed using the data base of National Institute of Standard Technology. The analysis of the spectra showed considerable amounts of (Ni, As, Ru, Th, Zr, Tb, Eu, Li, Xe, K , He, Ne, Cs, Hg, Cr, Cu, Na, Ra and Ca) elements in addition to (Ni+1, As+1, Th+1, Th+2, Zr+1, Cs+1, Cs+2, Cr+1and Cr+2) ions. The analysis of the four water samples led to efficient detection of different heavy metals using LIBS technique.

Keywords: LIBS; water sources in Khartoum; heavy metals.

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1. Introduction

In recent years, laser-induced breakdown spectroscopy (LIBS) was emerging as an important tool for the monitoring of trace pollutants in environment (liquid, soil, etc.) [1, 2].The principle of LIBS is based on the spectral analysis of radiation emitting from micro-plasma generated by focusing a high power pulsed laser beam on the surface of the sample. The characteristic emission from plasma provides finger print of constituents of target material. LIBS technique is unique in the sense that it requires no sample preparation and due to its capability of remote and in situ analysis of material in any phase [3,4]. This is in sharp contrast with conventional analytical techniques that require time consuming sample preparation and can be employed only in laboratory. Laser produced plasma of solid and liquid materials are also of much interest, especially in the field of laser diagnostic, thin film growth, and trace element analysis [5, 6]. Also LIBS is an emerging technique for quantitative analysis of heavy metals in environmental matrices [7]. Due to the rapid industrial growth, environmental pollution has increased tremendously over the years, especially the contamination of soil and ground water with heavy metals such as chromium, lead, copper, arsenic, nickel, beryllium, antimony, zinc, magnesium, mercury, aluminum, cobalt…..etc. These metals, are toxic even at low concentrations, may find their way into the human body via inhalation, ingestion, and skin absorption [8]. The analysis of wastewater for trace and heavy metal contamination is an important step in ensuring human and environmental health [9]. If accumulation of the heavy metal ions in the body tissues is faster than the body's detoxification, a gradual buildup of these toxins will occur. Long and even short term exposure to measurable quantities of various metals can lead to long term health problems and can cause irreversible damage [10]. In the dairy product industry, there is a need for an analytical technique to be able for on-line measurements of heavy metals and other trace elements in waste water coming from different processes involved. The amount of waste water generated by dairy industrial plant is of huge amount and it can have hazardous effects on environment [11].Recent researches in laser spectroscopy suggested the technique of LIBS, beside other spectroscopic techniques, to be used for the determination of these heavy metals in our environment [12]. This work aimed to use LIBS technique for the identification of heavy metals in some water sources in Khartoum State Republic of Sudan and to evaluate its efficiency in the identification of these elements.

2. The experimental part

2.1 The equipment

The LIBS setup used in this work is shown in Fig (1).It was consist of Ocean Optics 4000+ spectrometer. The USB 4000 interfaces to computer with Windows operating system connected with CCD camera, frequency doubled Q-switched Nd.YAG Laser (Laser Wavelength is 532 nm, pulse duration =10ns, Pulse Energy = 60 mJ, Spot size = 2-8 mm, repetition rate = 2 Hz), and finally glass cuvette as sample cell.

2.2 The Materials

Four water samples were collected from different water sources in Khartoum State and investigated by the LIBS system.

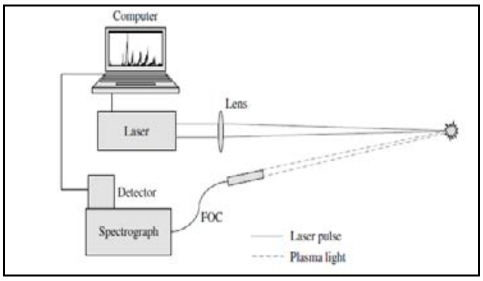

Figure 1: Schematic diagram of the LIBS setup.

2.3 Experimental Procedure

First of all, the background spectrum was recorded with the sample cell without sample. Then, each sample was put in the glass cuvette and irradiated by the Nd-YAG laser where the spark of the sample plasma was collected by a fiber optic connected with the spectrometer. In order to test the homogeneity of the samples, several LIBS measurements were performed at the surface of water samples. The recorded spectra of the samples were analyzed using Atomic spectra database line. 1.

3. Results and Discussion

Figures (2), (3), (4) and (5) show the LIBS emission spectra for the four water samples (1, 2, 3, 4), respectively, in the region from 200 nm to 850 nm. Table (1) lists the analyzed data. The analysis of the four spectra showed different kinds of elements like (Ni, As, Ru, Th, Zr, Tb, Eu, Li, Xe, K, He, Ne, Cs, Hg, Cr, Cu, Na, Ra and Ca) that were found in the samples. Beside neutral atoms, ions of different amounts and ionization stages also were found in the samples like (Ni+1, As+1, Th+1, Th+2, Zr+1, Cs+1, Cs+2, Cr+1and Cr+2). All these ions may not present in the samples originally, where some of them are produced due to the ionization of neutral atoms by the laser power density. The Nichel atom (Ni58.6) , Arsenic atom (As74.92), Ruthenium atom (Ru101.07), Zirconium atom (Zr91.22), Terbium atom (Tb158.92) , Europium atom (Eu151.96) , Xenon atom (Xe131.29), and Cesium atom (Cs132.90) they have big atomic weight and classify as heavy metals were found in all four water samples with nearly equal amount. In higher order of ionization the above heavy metals were excited because the irradiated pulse energy was sufficient to excite them. Lithium atom (Li6.94),Potassium atom (K39.09), Helium atom (He4.02) and Neon atom (Ne20.17) they have small atomic weight and not classify as heavy metals. They were found in all Samples with nearly equal amount. Thorium atom (Th232.03) has the biggest atomic weight found in the samples. It was found in all samples with nearly equal amount. Chromium atom (Cr51.99) with big atomic weight classify as heavy metal was found in all sample. Mercury atom (Hg200.59) with big atomic weight classify as heavy metal was found in sample (1, 2, 4) with nearly equal amount (this element is highly toxic even with little amount).Copper atom (Cu63.54) has big atomic weight classify as heavy metal was found in all sample with nearly equal amount. Sodium atom (Na22.98) with small atomic weight was found in sample (1, 4) with nearly small amount in them. Radium atom (Ra226) with big atomic weight was found in sample (3, 4) with high amount in sample3.Calsium atom (Ca40.07) with low atomic weight was found in sample3 only.

Table 1: The analyzed data of the four samples.

Element	λ nm	I(S1) a.u	I(S2) a.u	I(S3) a.u	I(S4) a.u
Ni I	222.29	125.91	125.68	125.66	125.88
Ni II	227.8	125.14	125.46	125.02	125.50
As I	234.98	125.43	125.46	125.48	125.51
As II	225.31	125.10	125.00	-------	125.01
Ru I	300.55	125.98	125.81	126.01	125.86
Th I	378.91	126.14	126.01	126.06	126.61
Th II	299.06 635.90	124.14 125.25	124.00	123.92 124.00	124.35
Th III	358.28	125.15	125.01	125.12	------
Zr I	384.30 457.55	------- 125.73	125.70 125.73	------- 125.98	------- 125.50
Zr II	738.28	124.95	124.59	124.78	124.99
Tb I	470.24	125.63	125.51	125.48	125.53
Eu I	537.69	126.26	126.06	------	125.83
Li I	548.51	125.96	125.58	125.83	125.68
Xe I	627.75	125.81	126.05	125.95	126.01
K I	693.87 534.29	125.81 126.79	126.01 126.71	126.01 -------	125.76 -------
He I	706.57	125.73	125.66	125.88	125.98
Ne I	772.46	125.98	125.78	125.53	125.73
Cs I	782.25	126.06	125.83	126.09	126.14
Cs II	358.28	125.30	125.83	125.30	125.49
Cs III	353.30	125.22	125.12	125.30	125.41
Hg I	313.18	125.68	125.70	-----	125.81
Cr I	391.62	125.83	125.71	125.81	125.73
Cr II	353.20	126.20	126.21	126.35	126.58
Cr III	204.84	124.83	124.56	124.66	124.34
Cu I	615..03 777.87	125.66 -------	125.86 125.80	125.91 126.00	126.15 126.10
Na I	654.77 541.45	-------- --------	------- -------	-------- 128.75	------- 125.61
Ra I	698.02	--------	-------	128.53	125.68
Ca I	518.88	--------	---------	130.33	---------

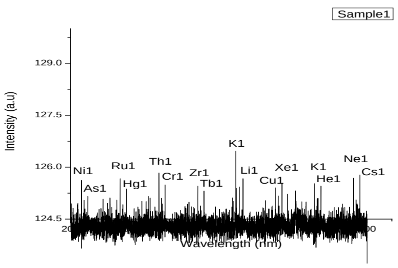

Figure 2: LIBS emission spectrum of sample 1.

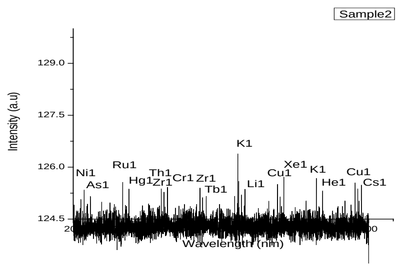

Figure 3: LIBS emission spectrum of sample 2.

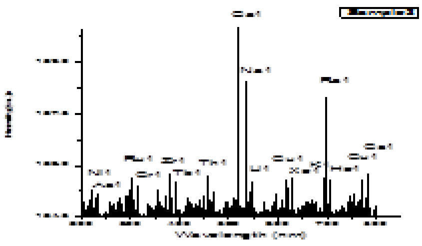

Figure 4: LIBS emission spectrum of sample 3.

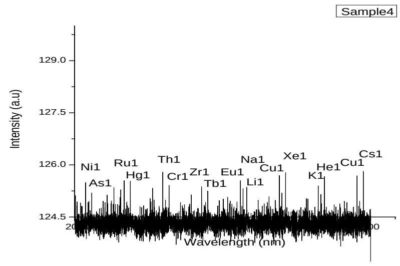

Figure 5: LIBS emission spectrum of sample 4.

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