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

Nafie A. Almuslet[1] and Ehessan B. Mirgani[2]
[1,2]Institute of Laser, Sudan University of Science and Technology, Khartoum / Republic of Sudan, P. O. Box (407)
mnmfa2008@yahoo.com, nafiealmoslot@sustech.edu

***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 designed 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, I, Cu, Xe, K, He, Ne, Cs, Hg, Cr, Tl, Cl, Na and Fe) elements in addition to (Ni^{+1}, As^{+1}, Th^{+1}, Th^{+2}, Zr^{+1}, Cs^{+1}, Cs^{+2}, Cr^{+1}, Cr^{+2}, Tl^{+1}, Tl^{+2}, Fe^{+1} and Fe^{+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, Analysis and Heavy Metals**

I. 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 fingerprint of constituents of targeted 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, and may find their way into the human body via inhalation, ingestion, and skin absorption [8].The analysis of wastewater for trace and heavy metals 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.

II. THE EXPERIMENTAL PART

The Equipments

The LIBS setup used in this work is shown in Fig. 1. It was consist of Ocean Optics 4000+ spectrometer, 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 =10 ns, pulse energy = 60 mJ, spot size = 2-8 mm, repetition rate = 2 Hz), and finally glass cuvette as sample cell.

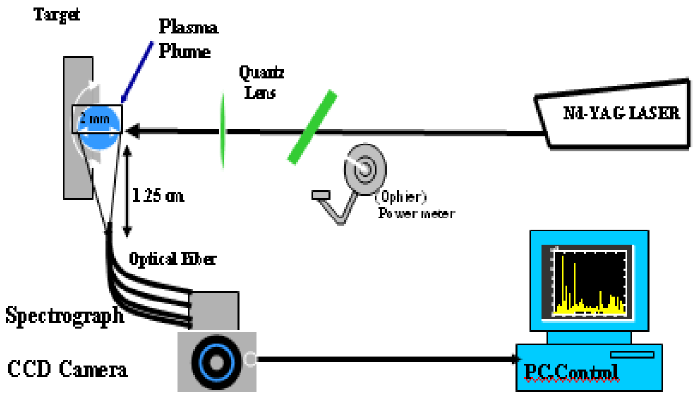

Fig. 1: Schematic diagram of the LIBS setup

The Materials

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

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.

III. RESULTS AND DISCUSSION

Fig. 2 – Fig. 5 show the LIBS emission spectra for the four water samples, 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, I, Cu, Xe, K, He, Ne, Cs, Hg, Cr, Tl, Cl, Na and Fe) that were found in the samples. Beside neutral atoms, ions of different amounts and ionization stages also were found; like (Ni^{+1}, As^{+1}, Th^{+1}, Th^{+2}, Zr^{+1}, Cs^{+1}, Cs^{+2}, Cr^{+1}, Cr^{+2}, Tl^{+1}, Tl^{+2}, Fe^{+1} and Fe^{+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 elements of: Ni, As, Eu,Tb, Xe, Zr, I, Cs have large atomic mass and considered as heavy metals They were found in the four water samples with nearly equal amounts. In higher order of ionization, the above heavy metals were excited because the irradiated pulse energy was sufficient to excite them. Lithium (Li), Potassium (K), Helium (He) and Neon (Ne) have small atomic masses and are not classified as heavy metals. They were found in all our samples with nearly equal amount. Thorium (Th) has the largest atomic mass found in the samples. It was found in all the samples but with high amount in samples (1 and 2) and low amount in sample (3,4).Chromium atom ($Cr_{51.99}$) with high atomic number classified as heavy metals was found in samples (2, 3, 4) only. Mercury (Hg) was found in samples (2, 3, 4) with nearly equal amounts (this element is highly toxic even with little amount). Chlorine (Cl), has small atomic mass and is not classified as heavy metal, was found in sample (3) only with high amount compared with the other elements. Copper (Cu) has high atomic mass and is classified as heavy metal, was found in samples (3, 4) with nearly equal amount. Sodium (Na) with small atomic mass was found in sample (3) only. Iron (Fe) which is one of the heavy metals, was found in samples (1, 4) with low amounts. Thallium (Tl) which is also a heavy metal, was found in sample (4) only with high amount.

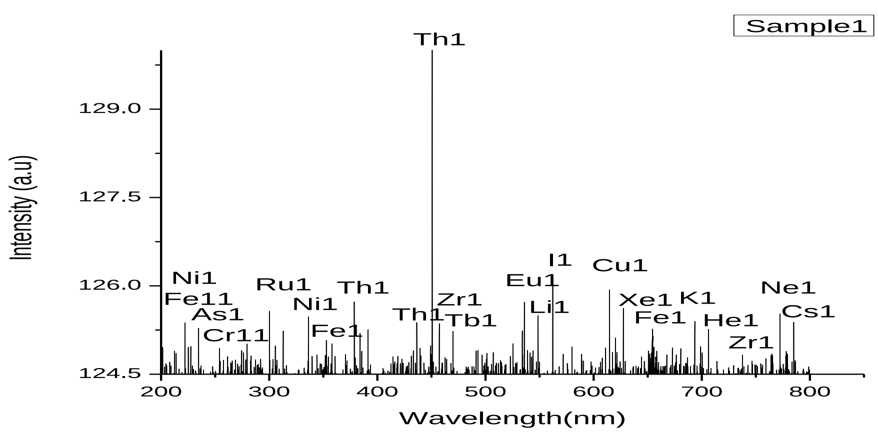

Fig. 2. LIBS emission spectrum of sample 1

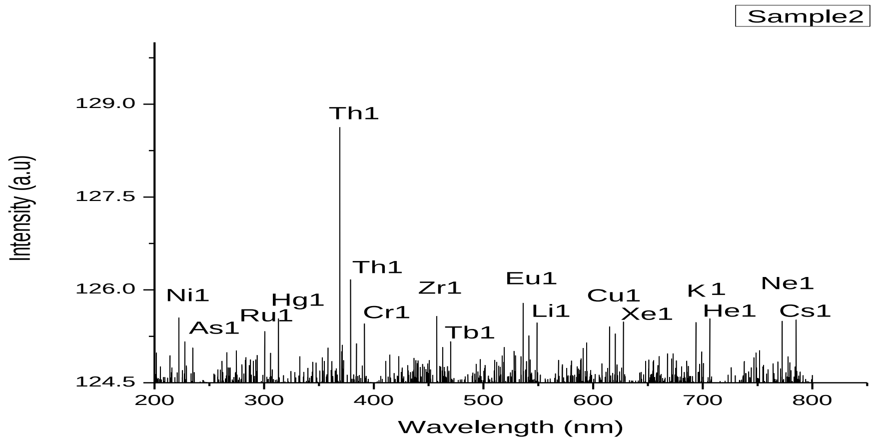

Fig. 3. LIBS emission spectrum of sample 2

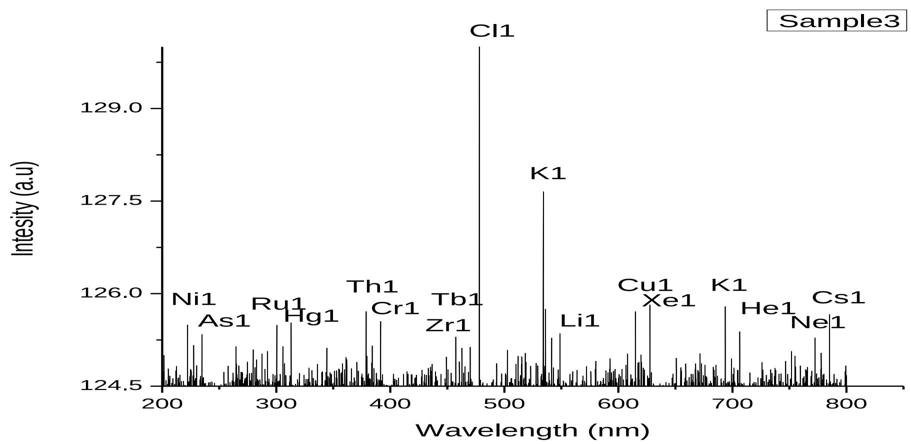

Fig. 4. LIBS emission spectrum of sample 3

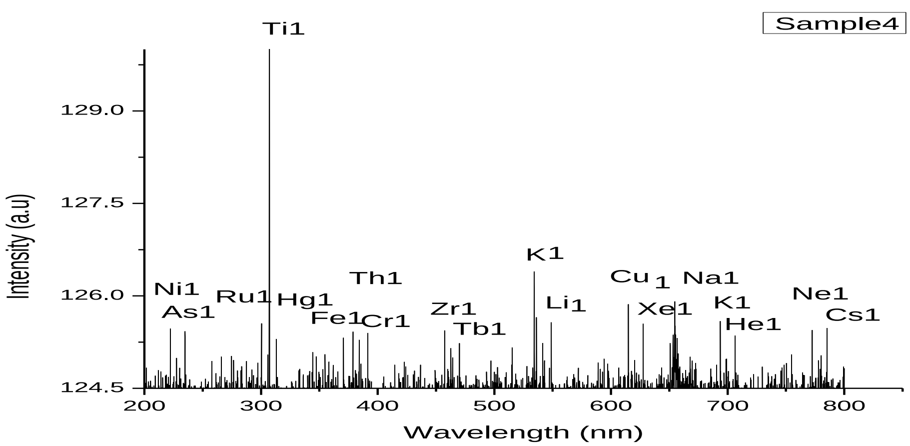

Fig.5. LIBS emission spectrum of sample 4

Table I: 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	222.29 336.57	125.63 125.51	125.81	125.76	125378
Ni II	227.8	125.14	124.99	125.02	125.50
As I	234.98	125.56	125.36	125.58	125.73
As II	225.31	125.10	125.00	-------	125.01
Ru I	300.55	125.89	125.61	125.81	125.81
Th I	378.91 436.59 451.05	125.71 125.68 130.26	128.90 126.44	125.98	125.76
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	457.55	125.66	125.83	125.33	125.76
Zr II	738.28	124.95	124.59	124.78	124.99
Tb I	470.24	125.53	125.43	126.01	125.48
Eu I	537.69	126.26	126.06	------	------
Li I	548.51	125.38	125.78	125.51	125.86
II	562.56	125.94	---------	------	------
Cu I	615.03	125.16	125.73	126.01	126.21
Xe I	627.75	125.26	125.78	126.11	125.83
K I	693.87 534.29	125.68	125.76	126.01	126.74
He I	706.57	125.53	125.81	125.61	125.66
Ne I	772.46	125.84	125.78	125.53	125.73
Cs I	782.25	125.71	125.83	125.94	125.78
Cs II	358.28	125.30	125.00	125.30	125.49
Cs III	353.30	125.22	125.12	125.30	125.41
Hg I	313.18	--------	125.86	125.76	125.61
Cr I	391.62	--------	125.76	125.81	125.66
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	--------	-------	126.11	126.21
Na I	654.77	--------	-------	--------	126.01
Fe I	370.79	--------	-------	-------	125.68
Fe II	369.84	124.98	124.50	--------	125.00
FeIII	208.59 227.81 492.65	124.88 124.98 125.07	125.00	124.98 125.02	125.02
Tl I	307.29	--------	---------	--------	130.33
Tl II	213.75	125.06	125.10	125.15	125.24
Tl III	391.56	125.40	125.53	125.59	125.63

IV. CONCLUSIONS

LIBS technique detected and identified heavy metals like; (Ni, As, Ru, Th, Zr, Tb, Eu, Li, I, Cu, Xe, Cs, Hg, Cr, Tl, and Fe) in water even those with little amounts.

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