

## ASSESSMENT OF THE CONCENTRATION OF Cr, Mn AND Fe IN SEDIMENT USING LASER-INDUCED BREAKDOWN SPECTROSCOPY

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**ABSTRACT.** In the present study, laser-induced breakdown spectroscopy (LIBS) has been applied for the determination of levels of Cr, Mn and Fe in sediment samples and the results have been compared with that of flame-atomic absorption spectroscopy (F-AAS). Fourteen sediment samples were collected from Tinishu Akaki River (TAR), Addis Ababa, Ethiopia. Pellets of 24 mm in diameter and 3–5 mm in thickness were prepared using a manual hydraulic press under a pressure of 8000 psi by mixing finely ground sediment samples with boric acid. The concentrations of Cr, Mn and Fe were successfully determined by Q-switched Nd:YAG laser at 1064 nm. Quantification of these metals was conducted against certified reference materials of sediments and soils. The LIBS results for the elements varied from 0.060–0.707 mg/g for Cr, 0.895–3.64 mg/g for Mn and 26.9–71.8 mg/g for Fe. The F-AAS results varied from 0.061–1.37 mg/g for Cr, 1.24–4.46 mg/g for Mn and 49.0–83.3 mg/g for Fe. TAR was found to be heavily polluted with Cr.

**KEY WORDS:** Laser-induced breakdown spectroscopy, Chromium, Manganese, Iron, Sediment, Tinishu Akaki River, Ethiopia

## INTRODUCTION

Sediments could be polluted by various means other than natural sources, such as *via* polluted river water, where the river could be polluted by the waste water outflows, airborne inputs, rainfall, dust precipitation, industrial sludge and transport activities [1]. Determination of the concentration of heavy metals in the sediment is important for assessing the nature and extent to which the aquatic environment is polluted. Furthermore, sediment reflects a record of past pollution since it has the capacity to bind several elements. Heavy metals are also present in natural uncontaminated sediments with dissimilar background concentrations. There is an increasing need to determine the degree of pollution quickly and accurately, in particular heavy metals in sediments. Heavy metal analysis can be carried out using flame-atomic absorption spectrometry (F-AAS), graphite furnace-atomic absorption spectrometry (GF-AAS), inductively coupled plasma-optical emission spectrometry (ICP-OES), inductively coupled plasma-mass spectrometry (ICP-MS), laser-induced breakdown spectroscopy (LIBS), X-ray fluorescence spectroscopy (XRF), electrochemical analysis and neutron activation analysis (NAA) where except LIBS the other techniques are the most commonly used [2–12].

Laser-induced breakdown spectroscopy is an atomic emission spectro-chemical technique useful for the analysis of various samples of environmental and geological interest and can be regarded as a universal sampling, atomisation, excitation and ionisation source, since laser-induced plasmas can be formed in gases, liquids, aerosols, slurries, conducting and non-conducting solid samples [13–19]. The basis for LIBS is a solid-state, short-pulsed, Nd:YAG laser that is focused on a sample to produce a high-temperature plasma, high electron density

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laser spark or microplasma. Upon cooling, the excited atomic, ionic and molecular fragments produced within the plasma emit radiation over a broad spectral range, from UV through visible to the near IR. This reflects the elemental composition of the material in the volatilised sample that can be gated off by the detection system [14, 15, 17, 20–23]. In this technique, powerful laser pulses evaporate a small amount of material (typically a few micrograms) during analysis creating a plasma plume. The emission from the plasma is spectrally resolved to determine the chemical composition of the sample. A range of processes such as sample heating, phase change, melting, atomisation, excitation, ionisation and thermo-ionic emission occurs [14–17, 19, 24]. The technique has proven capable of detecting many metals of environmental concern [23].

The key factors, which can affect the sensitivity of the LIBS system include the laser pulse characteristics (pulse width, energy, etc.), the sample homogeneity and the sampling geometry (distance from the focusing lens to the sample, focal length of the collecting lens, fiber optics, etc.), surrounding atmosphere and the binding material used for the pellet preparation of samples in powder forms [13, 16, 22, 25]. The application of LIBS to sediment samples has advantages such as rapid analysis technique, requires no or little sample preparation (except homogenisation and pellet preparation), portable, possibility of remote sensing and stand-off detection [20, 24, 26].

Currently, environmentally benign methods are important since they lead to cleaner environment. Due to this reason, methods that avoid acid digestion procedures or minimise excessive sample pre-treatment should be used as this would minimise the level of pollution. Direct solid analysis of environmental samples such as sediment by LIBS was selected as the alternative technique to be evaluated for the determination of heavy metals in sediment. The application of LIBS in the characterisation of heavy metals in sediment as reported in the literature are limited to a few applications [27–30]. Lazic *et al.* [27], Barbini *et al.* [28] and Lazic *et al.* [29] used LIBS for the determination of Cr, Cu, Mn, Fe, Ba and other metals in marine sediment samples. Similarly, Mohamed and Askar [30], Capitelli *et al.* [31], Santos *et al.* [32] and Senesi *et al.* [33] determined heavy metals (V, Cr, Mn, Fe, Ni, Co, Cu, Zn, Pb and Cd) in soil and sediment using LIBS.

Both Fe and Mn result in the coloration of the water where Fe results in red and brown color while Mn results in black due to the precipitation of their hydroxides. The colored water may stain textile and fixtures that can cause permanent damage on industrial boilers, equipment and tools which could lead to high consumption of energy because of the insulation caused by minerals (like Fe and Mn) present in water and hence reduces efficiency and life of the equipment [34, 35]. Both Fe and Mn produce odor and offensive taste that may affect animal intake [36] and their oxides play important role in the soil for fixing trace elements such as Co, Ni as well as pollutants like Pb [37]. Although Fe is an essential element for life, its excess in plant tissues may be responsible for a wide range of metabolic disorders, due mainly to its involvement in Fenton reaction leading to the production of high levels of toxic hydroxyl radicals and other reactive species [38]. Cr is an analyte of interest to the above industries and in the environment because, like other metals, it is not biodegradable. Once it enters the environment, its toxicity is determined to a large extent by its chemical form. Hexavalent Cr is much more toxic than trivalent Cr [39]. Cr(VI) is widely known to cause allergic dermatitis, as well as toxic and carcinogenic effects in humans and animals. Soluble and insoluble Cr(VI) salts have been demonstrated to induce morphological and neoplastic transformation and mutagenicity in murine and human cells [40].

The objective of this study was to quantify Cr, Mn and Fe in sediment samples collected from Tinishu Akaki River (TAR), Addis Ababa, Ethiopia using LIBS, and to evaluate how different areas of TAR are polluted with regard to Cr, Mn and Fe. For this purpose, sediment samples were collected from fourteen different sites, targeting point and non-point sources of

pollution in the study area. F-AAS was also used for analysis of the same sediment samples to compare the results.

## EXPERIMENTAL

### *Chemicals and reagents*

For preparation of pellets, boric acid (Merck, Germany) was used as binder and Cr, Mn and Fe metal powders with high purity (99.99%) (Alfa Aesar® A Johnson Matthey Company, USA) were used to identify emission lines of the analytes. The following soil and sediment certified reference materials were used for construction of calibration curves for LIBS analysis and for quality control: Certified Reference Material BCR®-320R No. 58 (IRMM, Belgium), San Joaquin Soil Standard Reference Material® 2709a (NIST, Gaithersburg, MD, USA), Standard Reference Material® 2587 Trace Elements in Soil containing Lead from Paint (NIST, Gaithersburg, MD, USA), Reference Material® 8704 Buffalo River Sediment (NIST, Gaithersburg, MD, USA), NCS DC 73322 Soil (China National Analysis Center for Iron and Steel, Beijing, China) and NCS DC 73374 Stream Sediment (China National Analysis Center for Iron and Steel, Beijing, China). For F-AAS analysis, 37% hydrochloric acid (Puriss, Sigma-Aldrich, Germany) and 69.5% nitric acid (Scharlau, reagent grade, ACS, ISO, Spain) were used for digestion of sediment samples. For construction of calibration curves for F-AAS analysis 1000 mg/L of standard stock solutions of Cr, Mn and Fe (Spectra AA – 20 plus, Varian Mulgrave Victoria, Australia) were used after appropriate dilution.

### *Study area, sample collection and pretreatment*

In Addis Ababa, the capital city of Ethiopia, the rapid population expansion, uncontrolled urbanisation and industrialisation, poor sanitation situation and uncontrolled waste disposal causes serious quality deprivation of surface and groundwater. Two major rivers flow through the city, namely Tinishu Akaki and Tiliku Akaki Rivers. Tinishu Akaki basin has a catchment area of about 540 km<sup>2</sup> and served as natural sewage lines for domestic and industrial wastes. A total of fourteen sampling sites (TAR at Biheiretsigie, Bulbula River, Gefersa, Kidanemihret River, Melkaqurani River, TAR at Alert area, TAR after mixing with Kidanemihret River, TAR after mixing with Melkaqurani River, TAR before mixing with Kidanemihret River, TAR before mixing with Melkaqurani River, Kebena River, Kera River, TAR at Kalti and TAR at Kolfe) were selected. The sampling stations were chosen to include hotspots of pollution around Addis Ababa city such as an industrial region, uncontrolled domestic wastewater discharge areas and rivers. Sediment samples were collected using ekman grab sampler at shallow depth from TAR and placed in double cap polyethylene bottles to avoid any type of external mixing or moisture. The collected sediment samples were air dried, homogenised using an agate mortar and pestle and passed through a 100-mesh sieve and transferred to polyethylene bottles for storage. The samples were sieved to remove coarse materials because the particles above 100 microns may consist of shells, rocks, wood and other detrital materials. In addition large debris, shells and visible organisms were removed prior to grinding.

### *LIBS instrumentation*

To carry out LIBS analysis, all fourteen sediment samples were dried and ground to suitable mesh size for pellet preparation. About 4 g of the sediment samples were accurately weighed and mixed thoroughly with about 0.3 g of boric acid as binder so as to ensure homogeneity. Care was taken to avoid any contamination due to mixing of other species during the pellet formation process. The pellets were made in a disc of cylindrical form having diameter 24 mm

and 3–5 mm thick using a hydraulic press (ENERPAC P142, International Crystal Laboratories, USA) with pressure of 8000 psi in order to ensure good mixing and homogeneity. Pellets of pure metal powders and certified reference materials were also prepared in similar way for identifying the emission lines and calibration purpose. A Q-switched Nd:YAG laser (Continuum Powerlite 9010, Continuum Inc., Santa Clara, USA) that can deliver a maximum pulse energy of 1 J operating at its fundamental wavelength (1064 nm) with pulse duration of 8 ns and 10 Hz pulse repetition rate was used for generating the sample plasma. The operating conditions for the LIBS system are summarised in Table 1. An energy meter (FieldMax<sub>II</sub>-TOP, COHERENT<sup>®</sup>, Portland, OR, USA) was used to monitor the dependence of the LIBS signal on incident laser energy. The laser beam was focused on the samples using a focusing lens of 25.4 mm diameter and 45 mm focal length to produce the plasma. In this experiment, a 2 mm diameter aperture was placed in the path of the laser beam before the lens in order to obtain a uniform beam shape. The emitted light was collimated by collecting lenses at a 45° angle to the incident laser beam, and thereafter a 2 m length fused-silica optical fiber was used to feed into an Andor Shamrock SR-303i spectrometer (Model SR-3031-A, Andor Technology, Ireland), equipped with an intensified charge coupled device (DH734-18F-03 ICCD, Andor Technology, Ireland) for detection of the dispersed light containing three different gratings (300, 1200 and 2400 grooves per mm), each one being blazed at 300 nm. An accumulation of 25 laser shots were recorded to complete one measurement so as to enhance the signal-to-background ratio. At least eight spectra of each sample were collected in eight different test portions of the pellet and averaged to decrease the shot-to-shot variations. All the spectral lines for the Cr, Mn and Fe were recorded for pellets of the metal powders and the certified reference materials and were identified using the NIST atomic spectral database. A schematic diagram of the experimental set-up is shown in Figure 1.

Table 1. Operating conditions of Q-switched Nd:YAG laser high power LIBS.

Operating parameters	Setting for		
	Cr	Mn	Fe
Laser pulse energy, mJ	53.5	53.5	53.5
Gate delay, $\mu$ s	0.9	1.4	1.0
Gate width, $\mu$ s	6	6	6
Gain level	150	150	100
Number of accumulation	25	25	25
Grating groove density, lines/mm	2400	2400	2400
Grating blaze, nm	300	300	300
Input side slit width, $\mu$ m	50	50	50
Wavelength range, nm	423–431	402–406	402–410

#### *Optimisation of LIBS parameters*

The experimental variables that can influence LIBS measurements are laser related (i.e. wavelength, energy, pulse duration and shot-to-shot power fluctuation), focusing spot size, ambient conditions, physical properties of the sample, amplification detector gain, ambient atmosphere, pressure and the detection window (delay time and gate width) [41]. The spectrometer was wavelength calibrated using mercury-argon lamp. Using metal powders emission lines with no or minimal interferences were selected. Moreover, pre-exposure was performed to set the response of the ICCD so that the camera would not over-saturate. For each new sample, before spectral collection, 10 laser pulses were performed to clean the sample surface and remove contamination. The delay times were chosen according to the maximum

LIBS signal intensity for each element present in the samples. Emission spectra at different laser energies were recorded to study the effect of the laser energy on the line emission intensity at a constant gate width of 6  $\mu\text{s}$  used throughout the study. To study the effect of laser energy on the line emission variation, laser produced plasma emission spectra from sediment samples were recorded from 20–190 mJ at the optimised delay times for each element.

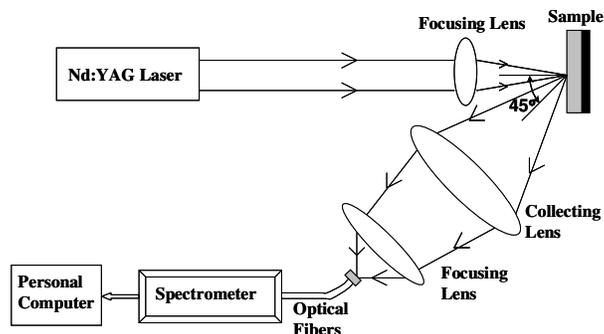


Figure 1. Schematic diagram of LIBS setup.

#### *Digestion of sediment samples for F-AAS*

For comparison, samples were also subject to acid digestion and the resulting solutions were analysed by F-AAS. Samples were prepared in triplicate according to the following procedure: about 0.5 g of dried and ground sediment samples was accurately weighed and placed in 100-mL beaker. Freshly prepared aqua regia (5 mL) was added. After the completion of the reaction, it was refluxed on a hot plate for 2 h at a temperature not exceeding 160 °C. The digest was filtered with No. 42 Whatman filter paper after cooling, diluted with deionised water to 50 mL and placed in the refrigerator prior to analysis using the F-AAS. Blanks were determined in similar fashion and all measurements were done in triplicate. For the calibration curve, a series of working standard solutions of metals (0, 1, 2, 5 and 10 mg/L for Cr; 0, 2.5, 5, 10 and 20 mg/L for Mn; and 0, 10, 50, 100 and 200 mg/L for Fe) were prepared by appropriate dilution with deionised water of the metal stock solutions of 1000 mg/L. The concentrations of Cr, Mn and Fe in the acid digested sediment samples were determined by F-AAS analysis, Varian Atomic Absorption Spectrometer (Spectra AA – 20 plus, Varian Mulgrave Victoria, Australia). The Buffalo River Sediment Reference Material<sup>®</sup> 8704 (NIST, Gaithersburg, MD, USA) was used for quality control purposes so as to monitor the accuracy of the F-AAS measurements.

## RESULTS AND DISCUSSION

#### *Optimisation of experimental conditions*

In order to enhance the sensitivity of the LIBS for analysing sediment samples, important experimental parameters such as laser pulse energy, gate delay time, gate width and gain level were investigated (Table 1). The spectrometer requires periodic internal calibration using mercury-argon lamp since the spectrum shifts due to variations in laboratory conditions [18]. Additionally, so as to obtain improved results, emission lines with no or minimal interference, due to the sample matrix and lines giving maximum signal intensity for metal powders were selected. The NIST atomic spectral database [42] was also used to identify all the spectral lines

recorded for analytes using the LIBS system. The most intense wavelength for each element was selected to study the effect of different experimental parameters. For quantification purpose, the selected wavelengths for Cr, Mn and Fe were 425.43, 403.076 and 404.58 nm, respectively. These emission lines had minimal interference from other emission lines.

In the early stages of plasma radiance, an intense continuum emission resulted and after an appropriate delay the plasma cooled to the point where atomic and ionic emissions could be observed. Hence, the study of delay time was fundamental and chosen according to the maximum LIBS signal intensity for each element present in the samples. The delay time with respect to the laser pulse had to be optimised to cut the continuum radiation. A typical plot of the dependence of LIBS signal intensity at the selected wavelengths on delay time, are presented in Figure 2. It is clear from the figure that the maximum LIBS signals are recorded at around 0.9  $\mu$ s, 1.4  $\mu$ s and 1.0  $\mu$ s for Cr, Mn and Fe, respectively, where maximum signal intensity-to-background ratios were observed.

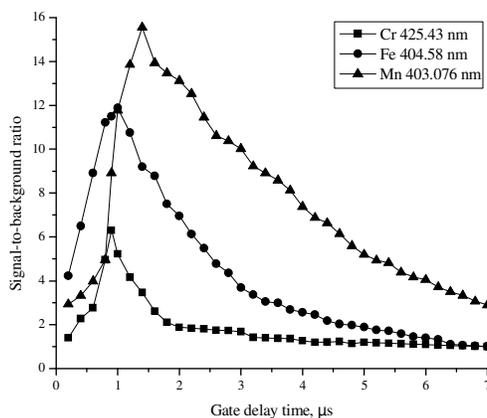


Figure 2. Dependence of LIBS signal intensity on gate delay time for Cr, Mn and Fe in sediment samples.

In LIBS, to produce the plasma and to excite the sample species into ionic and neutral atom electronic transitions, high-pulse energy of the laser beam is required. When a high-energy laser pulse is focused on a sample, the laser energy is deposited on a small area where local temperature rapidly rises above the vaporisation temperature and a laser-induced spark forms at the sample surface. The material is ablated and then atomised in the laser plasma [20]. Furthermore, the signal of the analyte lines is proportional to the laser energy. Emission spectra at different laser energies were recorded to study its effect on the line emission intensity at a constant gate width. The best signal-to-background ratio of analyte lines in sediment sample was obtained at laser pulse energy of about 53.5 mJ (Figure 3). The laser energy of 53.5 mJ was selected for subsequent analysis in all the cases (Table 1). The binding materials play an important role in efficiently coupling the laser energy to the sample, ablating a measurable quantity of mass, reducing fractionation and deviation between measurements [16]. Hence boric acid was used as binding material.

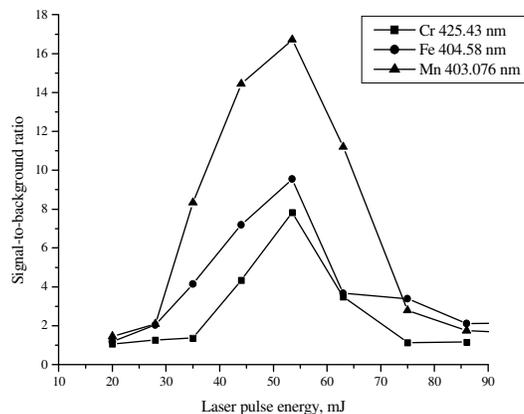


Figure 3. Effect of variation of laser pulse energy on the signal-to-background ratio of Cr, Mn and Fe lines of sediment samples.

#### *Spectral analysis*

Portions of the spectra of Cr, Mn and Fe metal powder standard, sediment samples and certified reference material are presented in Figures 4a-c. In the Figures, the spectra of metal powder were overlaid on to the spectra recorded for sediment samples in order to identify the prominent emission lines of the analytes. Additional lines due to the presence of other elements exist in the selected wavelength region; however, for this study, the best lines of the elements of interest are indicated. There are three strong emission lines of Cr, namely at 425.4 nm, 427.4 nm and 428.9 nm; four strong emission lines of Mn, namely at 403.076 nm, 403.3 nm, 403.4 nm and 404.136 nm; and two strong emission lines of Fe, namely at 404.58 nm and 406.357 nm [42]. Actually, the line at 425.4 nm, 403.076 nm and 404.58 nm exhibited highest intensity as shown in Figures 4a-c and were therefore selected for Cr, Mn and Fe, respectively, for this study. As it is known, spectral interference is the most severe problem for quantification due to interferences from the emission lines of other atoms. Thus, the above lines were chosen for the determination since they had minimal interferences from emission lines of other elements and are sufficiently intense.

#### *LIBS calibration*

The LIBS system should be calibrated prior to its application for the determination of heavy metals in sediment samples. The most common method for the calibration of a LIBS system for quantitative analysis is by measuring the spectral intensity at the most intense wavelength of that element with certified reference material after identifying the wavelengths using metal powders. Certified reference materials of soil and sediment were employed for construction of calibration curves. The calculations were based on the peak height measured at the selected wavelength of Cr line (425.4 nm), Mn line (403.076 nm) and Fe line (404.58 nm). The linear regression coefficient (R) values for all calibration curves were greater than 0.998, which showed strong linear dependence of the LIBS signal on the concentration of analytes and was acceptable for quantitative analysis.

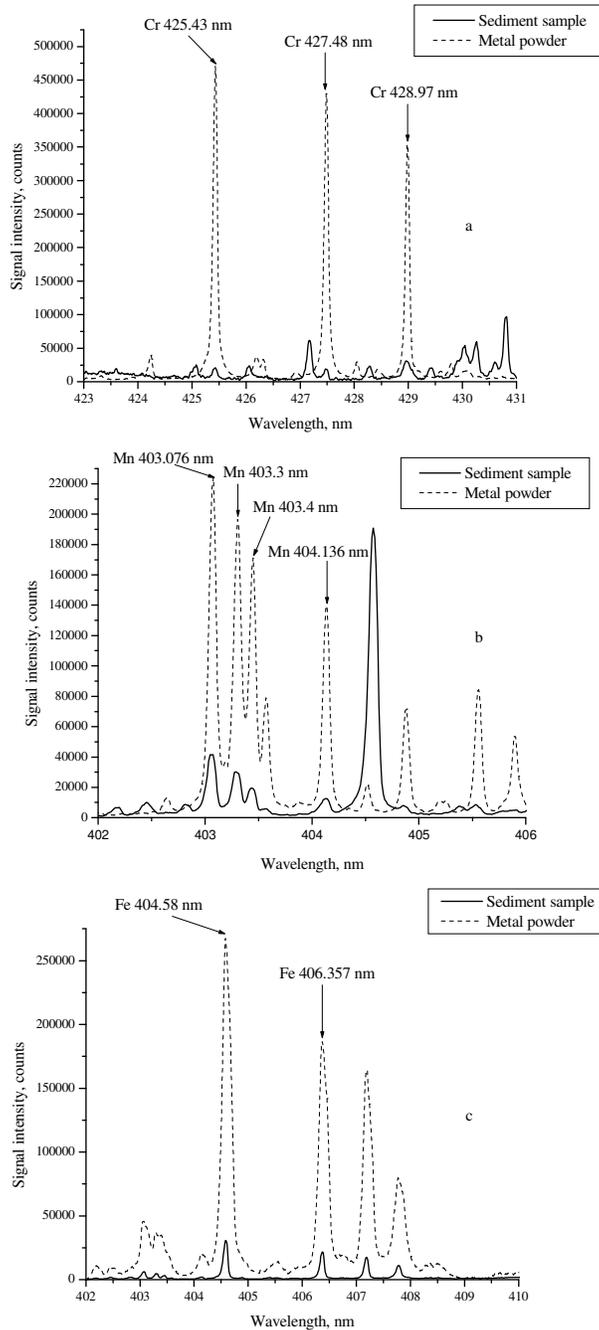


Figure 4. LIBS spectra of Cr (a), Mn (b) and Fe (c) in sediment samples and metal powders where corresponding main emission lines labeled.

### Limit of detection

The limit of detection of LIBS was calculated based on International Union of Pure and Applied Chemistry (IUPAC) definition using the certified reference materials used for calibration with the lowest concentration (mass fraction) of each analyte [13, 18, 43, 44]. Accordingly it was calculated using the equation: limit of detection (LOD) =  $3\sigma_b/S$ , where  $\sigma_b$  is the standard deviation of the background (noise level) and S is the calibration sensitivity (S = slope of the calibration curve) which is the ratio of the line intensity to the concentration. The obtained limit of detection for Cr, Mn and Fe were 0.043 mg/g, 0.039 mg/g and 0.079 mg/g, respectively. Lazic *et al.* [27] reported limit of detection of 0.375 mg/g for Mn in sediment samples, which is 9.6 times higher than the limit of detection achieved in this study.

### Quality control

The accuracy and precision in LIBS depends on the sample homogeneity, sample matrix, particle size and excitation properties of the laser. The self-absorption of emission lines is another impediment for the exact determination of elemental concentration due to non-homogeneous nature of the plasma. This could lead to non-linearity in LIBS signal intensity when plotted against concentration of the emitting elements and in turn affects the accuracy of quantitative analysis [18, 23]. The RSDs of the methods were  $\leq 20\%$  and  $\leq 5\%$  for LIBS and F-AAS, respectively. This shows the poor precision of LIBS compared to F-AAS. This high variation in LIBS measurements can be attributed to the unhomogeneity of the sample or non-uniform distribution of the analytes within the sample, variation in the amount of vaporised mass from shot-to-shot, deviation in laser energy and also changes in the distance between the focal plane and the sample surface [45–47]. The accuracy of the LIBS technique was compared with that of the conventional method, F-AAS using t-test at the 95% level of confidence. The calculated *p*-values were 0.46, 0.37 and 0.002 for Mn, Cr and Fe, respectively, where it can be concluded that the two methods are not significantly different for Mn and Cr, while were significantly different for Fe. The reason for the observed discrepancies between LIBS and F-AAS results could be attributed to the above stated factors and matrix effects (sample-plasma interactions) which in turn could be related to differences in absorptivity, particle size distributions and elemental composition of the evaluated matrices. The Buffalo River Sediment Reference Material<sup>®</sup> 8704 (NIST, Gaithersburg, MD, USA) was used for quality control purposes so as to monitor the accuracy of the F-AAS measurements. Results are presented in Table 2, and demonstrate that for the entire elements the determined results are well in agreement with the certified values.

Table 2. Quality control result (mean  $\pm$  standard deviation, mg/kg) for F-AAS using Reference Material<sup>®</sup> 8704.

No.	Element	F-AAS reading	Certified value	% Agreement
1	Cr	111 $\pm$ 5.2	122 $\pm$ 3.8	91.0
2	Mn	526 $\pm$ 34	544 $\pm$ 21	96.6
3	Fe	3.74 $\pm$ 1.5	3.97 $\pm$ 1.0	94.1

### Elemental analysis of sediment samples

The spectra for sediment samples were recorded under identical experimental conditions to those used for the metal powder and certified reference materials. The selected heavy metals present in the sediment sample were identified and the corresponding concentrations are listed in Table 3. All the data were presented after background correction of the signal intensity of the

sediment and certified reference materials. Net line intensities were calculated by subtracting the background intensities from the signal intensities prior to determining the concentrations of the selected elements. Referring Table 3, the concentration of the elements obtained using LIBS varied from 0.060–0.707 mg/g for Cr, 0.895–3.64 mg/g for Mn, and 26.9–71.8 mg/g for Fe, while F-AAS results varied from 0.061–1.37 mg/g for Cr, 1.24–4.46 mg/g for Mn and 49.0–83.3 mg/g for Fe. The mean concentrations of the metals obtained using LIBS were: Cr: 0.259 mg/g; Mn: 1.95 mg/g; and Fe: 52.4 mg/g, while the results obtained using F-AAS were: Cr: 0.369 mg/g; Mn: 2.15 mg/g; and Fe: 67.4 mg/g as summarised in Table 4. In general, areawise comparison shows that areas where less number of industries (such as Biheretsigie and Gefersa) have the lowest concentration while areas where large number of industries (such as AA TAR Kolfe and AA Melkaqurani) have the highest concentrations of the selected metals which indicate an increase in anthropogenic effects around the areas. Melaku *et al.* [5] determined selected heavy metals including Cr and Mn in sediment samples collected from TAR by ICP-MS. The reported values ranged from 0.061–16.3 mg/g and 1.20–6.48 mg/g, for Cr and Mn, respectively. These are comparable with results found in this study.

Table 3. Concentration of Cr, Mn and Fe (mean  $\pm$  standard deviation, in mg/g) in sediment samples from Tinishu Akaki River determined with LIBS and F-AAS.

Sample site name	Cr concentration		Mn concentration		Fe concentration	
	LIBS	AAS	LIBS	AAS	LIBS	AAS
AA* Biheretsigie	0.060 $\pm$ 0.012	0.116 $\pm$ 0.006	0.895 $\pm$ 0.027	1.88 $\pm$ 0.10	37.1 $\pm$ 2.7	52.4 $\pm$ 0.91
AA Bulbula	0.072 $\pm$ 0.001	0.137 $\pm$ 0.005	17.0 $\pm$ 0.23	1.64 $\pm$ 0.015	63.9 $\pm$ 3.7	64.0 $\pm$ 1.1
AA Gefersa	0.110 $\pm$ 0.008	0.086 $\pm$ 0.004	1.99 $\pm$ 0.25	2.05 $\pm$ 0.043	40.7 $\pm$ 0.66	71.0 $\pm$ 0.61
AA Kebena	0.116 $\pm$ 0.004	0.170 $\pm$ 0.002	1.86 $\pm$ 0.30	1.88 $\pm$ 0.032	42.1 $\pm$ 3.8	53.3 $\pm$ 0.59
AA Kera	0.138 $\pm$ 0.017	0.147 $\pm$ 0.008	1.91 $\pm$ 0.21	1.83 $\pm$ 0.043	69.5 $\pm$ 11	76.2 $\pm$ 1.3
AA Kidanemihret	0.181 $\pm$ 0.036	0.181 $\pm$ 0.003	1.29 $\pm$ 0.19	1.24 $\pm$ 0.026	26.9 $\pm$ 0.78	49.0 $\pm$ 0.57
AA Melkaqurani	0.082 $\pm$ 0.001	0.061 $\pm$ 0.003	3.64 $\pm$ 0.73	4.46 $\pm$ 0.22	58.4 $\pm$ 2.5	65.1 $\pm$ 3.26
AA TAR Alert	0.517 $\pm$ 0.084	0.591 $\pm$ 0.020	2.03 $\pm$ 0.34	1.97 $\pm$ 0.035	53.4 $\pm$ 4.8	73.0 $\pm$ 0.88
AA TAR and Kidanemihret	0.238 $\pm$ 0.048	0.182 $\pm$ 0.003	1.96 $\pm$ 0.14	2.01 $\pm$ 0.042	52.9 $\pm$ 2.7	69.2 $\pm$ 1.2
AA TAR and Melkaqurani	0.199 $\pm$ 0.010	0.209 $\pm$ 0.006	1.87 $\pm$ 0.089	2.85 $\pm$ 0.142	61.2 $\pm$ 8.4	75.0 $\pm$ 2.2
AA TAR before Kidanemihret	0.190 $\pm$ 0.096	0.366 $\pm$ 0.007	2.48 $\pm$ 0.31	2.50 $\pm$ 0.062	71.8 $\pm$ 10	72.0 $\pm$ 0.43
AA TAR before Melkaqurani	0.707 $\pm$ 0.072	1.08 $\pm$ 0.009	1.59 $\pm$ 0.14	1.52 $\pm$ 0.015	40.6 $\pm$ 4.3	65.6 $\pm$ 1.4
AA TAR Kalti	0.385 $\pm$ 0.059	0.481 $\pm$ 0.014	2.07 $\pm$ 0.24	2.23 $\pm$ 0.054	58.7 $\pm$ 5.5	74.9 $\pm$ 2.1
AA TAR Kolfe	0.638 $\pm$ 0.066	1.37 $\pm$ 0.014	2.03 $\pm$ 0.35	2.01 $\pm$ 0.026	56.6 $\pm$ 4.0	83.3 $\pm$ 1.2

AA\*, Addis Ababa

Table 4. Summary of the results obtained for the composition of Cr, Mn and Fe in sediment using LIBS and F-AAS.

Parameters	Element					
	Cr		Mn		Fe	
	LIBS	F-AAS	LIBS	F-AAS	LIBS	F-AAS
Selected wavelength, nm	425.43	357.9	403.076	279.5	404.58	248.3
Limit of detection, mg/g	0.043	0.00012	0.039	0.00025	0.079	0.00051
R for calibration curve	0.9981	1	0.9989	0.9999	0.9997	0.9997
Minimum concentration, mg/g	0.060	0.061	0.895	1.24	26.9	49.0
Maximum concentration, mg/g	0.707	1.37	3.64	4.46	71.8	83.3
Average concentration, mg/g	0.259	0.369	1.95	2.15	52.4	67.4
RSD	$\leq$ 20%	$\leq$ 5%	$\leq$ 20%	$\leq$ 5%	$\leq$ 20%	$\leq$ 5%
Correlation coefficient	0.94		-0.06		0.70	

*Assessment of sediment contamination based on sediment quality guidelines (SQGs)*

Numerical sediment quality guidelines (SQGs) have been used to identify contaminants of concern in aquatic ecosystem [48]. Sediments were classified as non-polluted, moderately polluted and heavily polluted, based on SQGs of United State Environmental Protection Agency (USEPA) [49]. The need for chemical guidelines that could be used to predict adverse biological effects in contaminated sediments led to the development of SQGs [50–55]. As can be seen from the results, with reference to sediment quality guidelines (Table 5), TAR is heavily polluted by Cr.

Table 5. Concentration (mg/g) of heavy metals in the core sediment and its comparison with sediment quality guidelines (SQGs).

Element	Mean LIBS	Mean F-AAS	SQG non-polluted	SQG moderate polluted	SQG heavily polluted
Cr	0.259	0369	< 0.025	0.025-0.075	> 0.075
Mn	1.95	2.15	-	-	-
Fe	5.24	6.74	-	-	-

## CONCLUSIONS

The concentration of Cr, Mn and Fe in sediment samples collected from Tinishu Akaki River (TAR), Addis Ababa, Ethiopia was determined using LIBS. The experimental parameters such as laser pulse energy, gate delay time and gate width were investigated, and the optimum parameters that improved the signal-to-background ratio of LIBS measurement were obtained. The LIBS results were compared with those obtained using a standard analytical technique, F-AAS. The proposed LIBS procedure is very simple, environmentally friendly and avoids the lengthy and corrosive acid digestion route. This allows for fast analysis and the results showed that LIBS can be applied as an alternative technique to other existing methods, like F-AAS, and does not require a sample decomposition step which is time consuming, expensive and may result in contamination of samples and the environment itself. With reference to SQGs, TAR is heavily polluted with Cr. Areas with less number of industries (such as Biheretsigie and Gefersa) have the lowest concentrations while those with large number of industries (such as AA TAR Kolfe and AA Melkaqurani) have the highest concentrations of the selected metals which indicate an increase in anthropogenic effects around the indicated areas.

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## REFERENCES

1. Ujevic, I.; Odzak, N.; Baric, A. *Water Res.* **2000**, 34, 3055.
2. Patnaik, P. *Dean's Analytical Chemistry Handbook*, 2nd ed. McGraw-Hill: USA; **2004**.
3. Rouessac, F.; Rouessac, A. *Chemical Analysis Modern Instrumentation Methods and Techniques*, John Wiley and Sons: Chichester; **2004**.
4. Sitko, R.; Zawisza, B.; Jurczyk, J.; Buhl, F.; Zielonka, U. *Polish J. Environ. Stud.* **2004**, 13, 91.
5. Melaku, S.; Wondimu, T.; Dams, R.; Moens, L. *Can. J. Anal. Sci. Spectrosc.* **2005**, 50, 31.
6. Ahuja, S.; Jespersen, N. *Modern Instrumental Analysis*, Vol. 47, Elsevier: Netherlands; **2006**.
7. Skoog, D.A.; Holler F.J.; Crouch, S.R. *Principles of Instrumental Analysis*, 6th ed. Thomson Corporation: Canada; **2007**.
8. Chen, D.; Hu, B.; Huang, C. *Talanta* **2009**, 78, 491.
9. Shibata, Y.; Suyama, J.; Kitano, M.; Nakamura, T. *X-Ray Spectrom.* **2009**, 38, 410.
10. Cevik, U.; Kozb, B.; Makarovska, Y. *X-Ray Spectrom.* **2010**, 39, 202.
11. Faraji, M.; Yamini, Y.; Saleh, A.; Rezaee, M.; Ghambarian, M.; Hassani, R. *Anal. Chim. Acta* **2010**, 659, 172.
12. Lepri, F.G.; Borges, D.L.G.; Araujo, R.G.O.; Welz, B.; Wendler, F.; Krieg, M.; Becker-Ross, H. *Talanta* **2010**, 81, 980.
13. Le Drogoff, B.; Margot, J.; Chaker, M.; Sabsabi, M.; Barthelemy, O.; Johnston, T.W.; Laville, S.; Vidal, F.; von Kaenel, Y. *Spectrochim. Acta, Part B* **2001**, 56, 987.
14. Cremers, D.A.; Radziemski, L.J. *Handbook of Laser-Induced Breakdown Spectroscopy*, John Wiley and Sons: Chichester; **2006**.
15. Miziolek, A.; Palleschi, V.; Schechter, I. *Laser-Induced Breakdown Spectroscopy (LIBS) Fundamental Applications*, Cambridge University Press: New York; **2006**.
16. Gondal, M.A.; Hussain, T.; Yamani, Z.H.; Baig, M.A. *Talanta* **2007**, 72, 642.
17. Singh, J.P.; Thakur, S.N. *Laser-Induced Breakdown Spectroscopy*, Elsevier: Amsterdam; **2007**.
18. Mohamed, W.T.Y. *Opt. Laser Technol.* **2008**, 40, 30.
19. Gondal, M.A.; Nasr, M.M.; Ahmed, Z.; Yamani, Z.H. *J. Environ. Sci. Health, Part A* **2009**, 44, 528.
20. Lal, B.; Zheng, H.; Yueh, F.Y.; Singh, J.P. *Appl. Opt.* **2004**, 43, 2792.
21. Gondal, M.A.; Hussain, T.; Yamani, Z.H.; Baig, M.A. *Talanta* **2006**, 69, 1072.
22. Bakry, A.H. *Pakistan J. Anal. Environ. Chem.* **2007**, 8, 7.
23. Gondal, M.A.; Hussain, T.; Yamani, Z.H.; Baig, M.A. *J. Hazard. Mater.* **2009**, 163, 1265.
24. Gondal, M.A.; Nasr, M.M.; Ahmed, M.M.; Yamani, Z.H.; Alsalhi, M.S. *J. Environ. Sci. Health, Part A* **2011**, 46, 42.
25. Gondal M.A.; Hussain, T. *Talanta* **2007**, 71, 73.
26. Liu, X.Y.; Zhang, W.J. *J. Biomed. Sci. Eng.* **2008**, 1, 147.
27. Lazić, V.; Barbini, R.; Colao, F.; Fantoni, R.; Palucci, A. *Spectrochim. Acta, Part B* **2001**, 56, 807.
28. Barbini, R.; Colao, F.; Lazić, V.; Fantoni, R.; Palucci, A.; Angelone, M. *Spectrochim. Acta, Part B* **2002**, 57, 1203.
29. Lazić, V.; Colao, F.; Fantoni, R.; Spizzichino, V.; Jovicevic, S. *Spectrochim. Acta, Part B* **2007**, 62, 30.
30. Mohamed, W.T.Y.; Askar, A. *Prog. Phys.* **2007**, 1, 46.
31. Capitelli, F.; Colao, F.; Provenzano, M.R.; Fantoni, R.; Brunetti, G.; Senesi, N. *Geoderma* **2002**, 106, 45.

32. Jr. Santos, D.; Nunes, L.C.; Trevizan, L.C.; Godoi, Q.; Leme, F.O.; Braga, J.W.; Krug, F.J. *Spectrochim. Acta, Part B* **2009**, *64*, 1073.
33. Senesi, G.S.; Dell'Aglio, M.; Gaudioso, R.; De Giacomo, A.; Zacccone, C.; De Pascale, O.; Miano, T.M.; Capitelli, M. *Environ. Res.* **2009**, *109*, 413.
34. Katsoyiannis, I.A.; Zouboulis, A.I. *Water Res.* **2004**, *38*, 1922.
35. Ghasemi-Fasaei, R.; Ronaghi, A. *J. Plant Nutr.* **2008**, *31*, 839.
36. Beutel, M.W.; Leonard, T.M.; Dent, S.R.; Moore, B.C. *Water Res.* **2008**, *42*, 1953.
37. Demirezen, D.; Aksoy, A.; *Ecol. Indic.* **2006**, *6*, 388.
38. De Dorlodot, S.; Lutts, S.; Bertin, P. *J. Plant Nutr.* **2005**, *28*, 1.
39. Gomez, V.; Callao, M.P. *Trend. Anal. Chem.* **2006**, *25*, 1006.
40. Bagchi, D.; Stohs, S.J.; Downs, B.W.; Bagchi, M.; Preuss, H.G. *Toxicology* **2002**, *180*, 5.
41. Godoi, Q.; Jr. Santos, D.; Nunes, L.C.; Leme, F.O.; Rufini, I.A.; Agnelli, J.A.M.; Trevizan, L.C.; Krug, F.J. *Spectrochim. Acta Part B* **2009**, *64*, 573.
42. Ralchenko, Y.; Kramida, A.E.; Reader, J.; NIST ASD Team. *NIST Atomic Spectra Database (ver. 4.1.0)*, [Online]. Available: <http://physics.nist.gov/asd3> [2011, June 20]. National Institute of Standards and Technology: Gaithersburg: MD; **2011**.
43. Sabsabi, M.; Heon, R.; St-Onge, L. *Spectrochim. Acta, Part B* **2005**, *60*, 1211.
44. Dell'Aglio, M.; Gaudioso, R.; Senesi, G.S.; De Giacomo, A.; Zacccone, C.; Miano, T.M.; De Pascale, O. *J. Environ. Monit.* **2011**, *13*, 1422.
45. Rossbach M.; Zeiller, E. *Anal. Bioanal. Chem.* **2003**, *377*, 334.
46. Trevizan, L.C.; Jr. Santos, D.; Samad, R.E.; Vieira, N.D.J.; Nomura, C.S.; Nunes, L.C.; Rufini, I.A.; Krug, F.J. *Spectrochim. Acta, Part B* **2008**, *63*, 1151.
47. Trevizan, L.C.; Jr. Santos, D.; Samad, R.E.; Vieira, N.D.J.; Nunes, L.C.; Rufini, I.A.; Krug, F.J. *Spectrochim. Acta, Part B* **2009**, *64*, 369.
48. McDonald, D.D.; Ingersoll, C.G.; Berger, T.A. *Arch. Environ. Contam. Toxicol.* **2000**, *39*, 20.
49. Perin, G.; Bonardi, M.; Fabris, R.; Simoncini, B.; Manente, S.; Tosi, L.; Scotto, S. *Environ. Technol.* **1997**, *18*, 593.
50. USEPA (United States Environmental Protection Agency). *Sediment Classification Method Compendium*, Environmental Protection Agency: Washington DC; **1992**.
51. Long, E.R.; Macdonald, D.D.; Smith, S.L.; Calder, F.D. *Environ. Manage.* **1995**, *19*, 81.
52. Long, E.R.; Macdonald, D.D. *Hum. Ecol. Risk Assess.* **1998**, *4*, 1019.
53. Bakan, G.; Ozkoc, H.B. *Int. J. Environ. Stud.* **2007**, *64*, 45.
54. Harikumar, P.S.; Nasir, U.P.; Rahman, M.P.M. *Int. J. Environ. Sci. Technol.* **2009**, *6*, 225.
55. Nasir, U.P.; Harikumar, P.S. *J. Environ. Prot.* **2011**, *2*, 710.