

SEMIQUANTITATIVE DETERMINATION OF CHROMIUM CONTENT OF RIVER BED SOIL OF BURIGANGA RIVER AT DIFFERENT LOCATIONS

M. E. SADAT, A. F. M. Y. HAIDER*, K. M. ABEDIN, M. WAHADOSZAMEN
AND A. I. TALUKDER

Department of Physics, University of Dhaka, Dhaka-1000, Bangladesh

ABSTRACT

Using the technique of Laser Induced Breakdown Spectroscopy, the chromium content of river bed sediment of the Buriganga River is determined at various locations. Hazardous element, chromium is found in addition to other elements such as calcium, magnesium, titanium, sodium etc. The source of this chromium is most likely to be the effluent discharge from the tanneries located nearby. Semi quantitative analyses showed the relative abundances of Cr, Mg, and Ca in the river bed sediment at Kamrangir Char and Shoari Ghat locations are in the ratios of 1:9:23 and 1:11:17, respectively.

Key words: Chromium content, River bed soil, Buriganga river

INTRODUCTION

Laser induced breakdown spectroscopy (LIBS) is a new analytical technique based on the analysis of light emitted from high temperature plasma (Radziemski and Cremers 2006, Singh and Thakur 2007) which is created by a high-powered pulsed laser. By spectrally analyzing the light emitted, it is possible to determine the elements present in the original sample. The technique is capable of performing both qualitative and quantitative analyses, i.e. it is possible to identify the elements present and to determine their respective concentrations. The technique has been applied in a variety of applications, ranging from industrial testing, archeology, to pollution monitoring (Andrzej *et al.* 2006, Singh and Thakur 2007).

Previously, the river water in and around Dhaka city were analyzed by using the LIBS technique, and the elements present in the suspended and dissolved materials in those waters were identified (Ahmed *et al.* 2009). In particular, it was found that the element chromium was present in high concentrations in the suspended component of water, but very little or none at all in the dissolved component. Since all the samples were collected in the general vicinity of tanning industries, and chrome alum is used in the tanning process, the authors surmise that the high concentration of chromium originated from the effluent of the tanneries. In the present work, it was found that high concentrations of chromium exist in soil of the river bed in the same general area.

* Author for correspondence: <yuhaider@univdhaka.edu>.

EXPERIMENTAL

The schematic diagram of the experimental LIBS system is shown in Fig. 1. The excitation laser is a Q-switched Nd:YAG laser system (Spectra-Physics LAB-170-10) which has output at fundamental wavelength of 1064 nm with pulse duration of 8 ns, repetition rate of 10 Hz and pulse energy of 850 mJ. The laser is also equipped with harmonic generators capable of generating the second and third harmonics of the fundamental at 532 nm and 355 nm by means of KDP crystals and producing energies of 450 mJ and 220 mJ per pulse, respectively. In the present experiment the second harmonic at 532 nm was used.

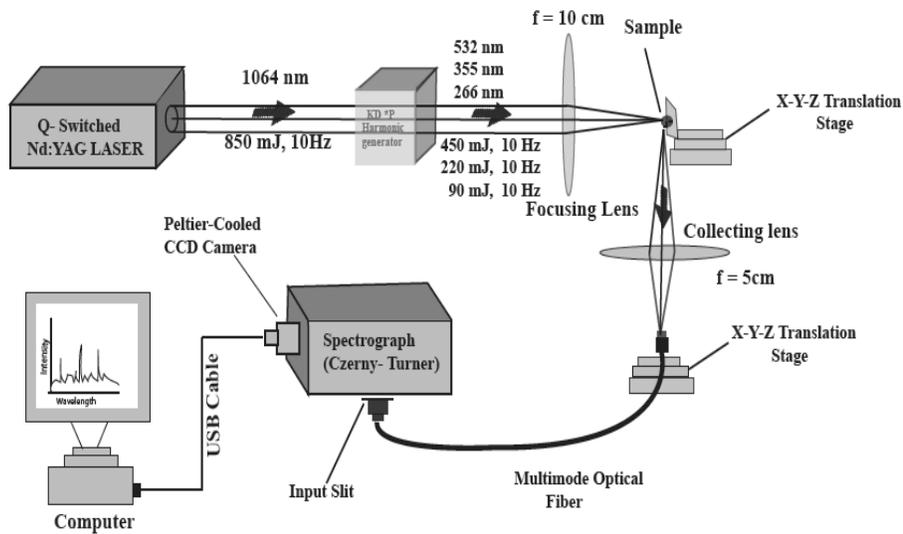


Fig. 1. Experimental setup of the LIBS experiment.

Intense, transient plasma is produced by focusing the laser beam on the sample by a convex lens of 100 mm focal length. The plasma is generated at the repetition rate of the laser, i.e. at 10 times per second. The light emitted by the plasma was collected by a short focal length lens and focused onto a 3 m long multimode optical fiber bundle. The light is transmitted through the fiber bundle to its other end which is placed at the entrance slit of a 750 mm focal length computerized Czerny-Turner spectrograph (Acton Model SP-2758). The spectrograph is equipped with two ruled gratings; 300 grooves/mm and 1200 grooves/mm, which are interchangeable under computer control, providing low resolution and high resolution spectra, respectively.

The output end of the spectrograph is placed in conjunction with a scientific-grade CCD camera (Roper Scientific PIXIS 100B). The CCD camera has 1340×100 pixels and is cooled to -68 C by a four-stage Peltier cooler to reduce noise. The spectral data

captured by the CCD camera is transferred to the personal computer by means of high speed USB connection cable. All the function of the PIXIS camera and the Acton spectrograph can be fully controlled by WinSpec software provided by the manufacturer. The CCD camera was usually set to spectroscopy mode. In this mode, all the 100 pixels in the vertical direction are summed (binned) in hardware before digitization is performed, resulting in an improved signal-to-noise ratio. The camera can support data acquisition rates (frame rates) as high as 500 Hz in this mode.

If 300 grooves/mm grating is used, a spectrum of about 120 nm width can be captured without moving the grating, and for the 1200 grooves/mm grating, it is only 30 nm. However, this width is insufficient to cover all the wavelengths of the emission spectrum from the sample. Hence, to cover a wider region, the grating was stepped under computer control, and data acquisition was performed at each grating position. Finally, the collected spectra were electronically glued. All this functions were performed by WinSpec software.

To find out all the elements within the sample we tried to acquire spectra covering as wide region as possible. But the higher limit of wavelength sensitivity of our detection system is determined by the drop-off of CCD sensitivity in the IR, limiting the useful operation to less than about 900 nm. The lower spectral limit is determined by loss of diffraction efficiency of the grating (blazed at 300 nm) and the absorption of the collection lens and the optical fiber in the UV. Overall, the lower limit of our system is about 200 nm.

The laser was operated at 10 Hz and the camera was allowed to operate in the free running mode without any synchronization of the laser (non-gated mode). Integration times of up to 10 sec were used to acquire spectra, and hence, an emission spectrum was accumulated from an average of up to 100 shots. This averaging process eliminates any short-term instability of the laser.

RESULTS

Samples were collected from two locations; one from Kamrangir Char and the other from Shoari Ghat (Fig. 2). For both locations, samples were taken from the river bed sediment by scraping. The location of the tanning factories are marked with an arrow in the figure. Low resolution LIBS spectra of the soil samples in the 400 - 530 nm range are shown in Fig. 3. Fig. 3(a) shows the spectra from the soil collected from Kamrangir Char and Fig. 3(b) shows that collected from Shoari Ghat. Because of the presence of a multitude of closely spaced spectral lines, it was not easy to identify individual lines of the elements present. Therefore, high resolution spectra (HR) using the 1200 lines/mm grating were acquired. The HR spectra centered around 415 nm and 522, of the soil samples collected from Kamrangir Char location are shown in Fig. 4a, b. Corresponding HR spectra of samples collected from Shoari Ghat location are shown in Figs 5a, b.

Spectral matching of the lines was performed for each of the emission lines with the NIST database, and the identified elements are shown in Table 1.

Table 1. Summary of the results of qualitative analyses.

(√ indicates the presence of the element in the sample)

Elements	Kamrangi Char (River bed sediment sample)	Shoari Ghat (River bed soil sample)	Major identifying line (nm)
Li	√	√	670.78
Na	√	√	589.00
Mg	√	√	518.36
K	√	√	766.49
Ca	√	√	393.37
Ti	√	√	453.32
Cr	√	√	425.43
Mn	√	√	403.08
Fe	√	√	438.35
Sr	√	√	460.73

Table 2. Concentration of Cr in the river bed soil samples of Buriganga.

Sample location	From first calibration curve (Fig. 6a, $\frac{[Cr]}{[Ca]} = x$)	From second calibration curve (Fig. 6b, $\frac{[Mg]}{[Ca]} = y$)	Approximate atomic ratios of Cr, Ca and Mg
Kamrangi Char	0.1120	2.5922	1:9:23
Shoari Ghat	0.0911	1.5636	1:11:17

A number of elements were detected, e.g. lithium, sodium, calcium, magnesium, titanium, manganese, iron, strontium and chromium. Most of these are found in normal soil, and are possibly not result of man-made contaminations (Baruthio 1992). Of the detected elements, chromium is not found in natural soil in significant quantities, and its origin is attributed to the effluent of the nearby tanneries.

A semi quantitative analysis from the spectra was performed. For this analysis, the calibration curve (plot of ratio of integrated line intensity vs concentration of Cr in Ca) drawn previously in our laboratory were used (Ahmed *et al.* 2009), where integrated intensity of a spectral line of interest was determined by multiplying the full width at half maximum (FWHM) of the line with its peak intensity. The calibration curve for Cr vs. Ca, where the integrated intensity ratios of Cr line at 425.43 nm to that of Ca at 422.67 nm was plotted against their respective atomic concentration ratios is shown in Fig. 6a. From the calibration curve, the measured concentration ratios of Cr to Ca (I_{Cr}/I_{Ca}) in the samples of Kamrangir Char and Shoari Ghat were: 0.112 and 0.0911, respectively.

Next, calibration of the magnesium concentration with respect to calcium in the samples was performed. The calibration curve for Mg (518.36 nm) in Ca (527.0270 nm) is shown in Figure 6 (b). From this graph, the measured concentration ratios of Mg to Ca (I_{Mg}/I_{Ca}) in the samples of Kamrangir Char and Shoari Ghat were: 2.5922 and 1.5636 respectively. Having obtained the concentration ratios of Cr/Ca (= x) [from Figure 6(a)] and Mg/Ca (= y) [from figure 6(b)] for the various samples, one can easily calculate the approximate atomic ratios of Cr, Ca and Mg in those samples. The result of this calculation is shown in Table 2 for the two locations (Kamrangir Char and Shoari Ghat).

DISCUSSIONS AND CONCLUSIONS

The result of qualitative analyses of the river bed soil collected from the Kamrangir Char and Shoari Ghat showed that, along with Ca, Mg, Ti, Fe, Na, K, Li, Sr, Mn, that are present in almost all the samples, hazardous element like Cr is also present. In the previous work done in this laboratory (Ahmed *et al.* 2009), Cr complex could not be identified as dissolved pollutant in river water although the particulate matters collected from the river water showed the presence of Cr in significant amounts. This indicates that salt of Cr that are present in the river water are either insoluble in water, hence remains suspended, or that the concentration of Cr complex as a dissolved pollutant was too low that it was beyond the detection limit of the present set up. So the purpose of this present research was to find out the concentration of the Cr present in the river bed soil of Kamrangir char and Shoari ghat, where the insoluble Cr complex is expected to have been precipitated down to the river bed and settle there. From the above data, it is proved that the chromium from the effluent is indeed precipitated as an insoluble compound on the riverbed.

The origin of Cr is undoubtedly the Cr salt that is being used in the tanneries of Hajaribag. The effluents of these tanneries are being discharged to the river without any kind of anti pollution treatment. Chromium can be found in three charged states *viz.* neutral chromium (Cr), trivalent Chromium (Cr III) and hexavalent chromium (Cr VI). The trivalent form occurs naturally in many fresh vegetables and fruits, meat, grains, and yeast. The trivalent form of chromium is relatively insoluble in water and is the most prevalent form in surface soils where oxidation processes, which convert chromium from the hexavalent to trivalent form, are most common mechanism. Hexavalent chromium occurs naturally, notably in water-saturated (reducing) conditions. This form is relatively soluble and can move more readily through soil to groundwater. The typical ratio of chromium in plants to chromium in soil is estimated to be 0.0045 (or 0.45%) (ANL 2005). A general assumption often made for chromium that is present in surface soil, is that 10 to 17% of the total chromium is in the hexavalent form (ANL 2005). Both acute and chronic toxicity (Baruthio 1992, Rai and Rai 2008, Nicola *et al.* 2007) are caused by hexavalent chromium compounds. The most important health hazard of chromium could be dermatological effects, lung cancers, pulmonary tract non-cancerous disorders, etc.

(Baruthio 1992). However, as LIBS is a technique for elemental profiling only, the charge state of the chromium present in the river bed soil could not be ascertained.

A semi quantitative analysis of the concentration of Cr present in the river bed of Buriganga was performed using the calibration curves drawn previously in the laboratory (Ahmed *et al.* 2009). The results of the analyses showed that, the ratios of relative abundances of Cr, Mg and Ca atoms are 1: 9: 23 and 1: 11: 17 at the two sampling locations, Kamrangir char and Shoari Ghat, respectively.

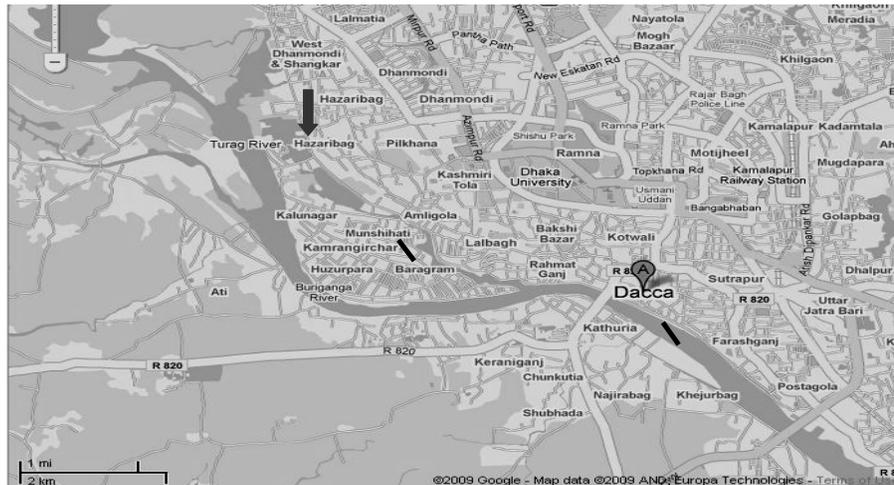
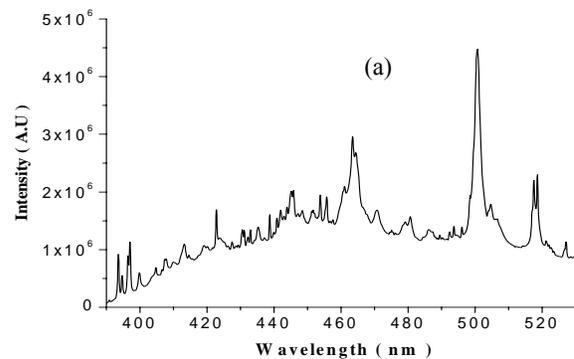


Fig. 2. Google map showing the sampling points of Kamrangir Char and Shoari Ghat (Red lines) and blue arrow indicates the position of the Tanneries.

In conclusion, it is stated that using the technique of LIBS, chromium can be detected in river sediment and it can be semi-quantitatively determined. The technique thus opens up the possibility of detecting other toxic elements discharged in the environment as a result of the activities of various industries, such as paint industries, electroplating industries, foundry and workshops etc.



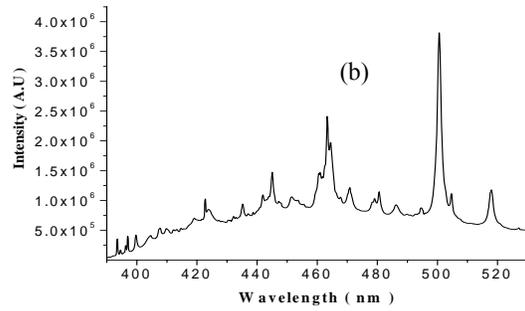


Fig. 3. Low resolution (LR) spectra of the river bed soil sample of (a) Kamrangir Char and (b) Shoari Ghat in the wavelength region of 390 nm to 530 nm.

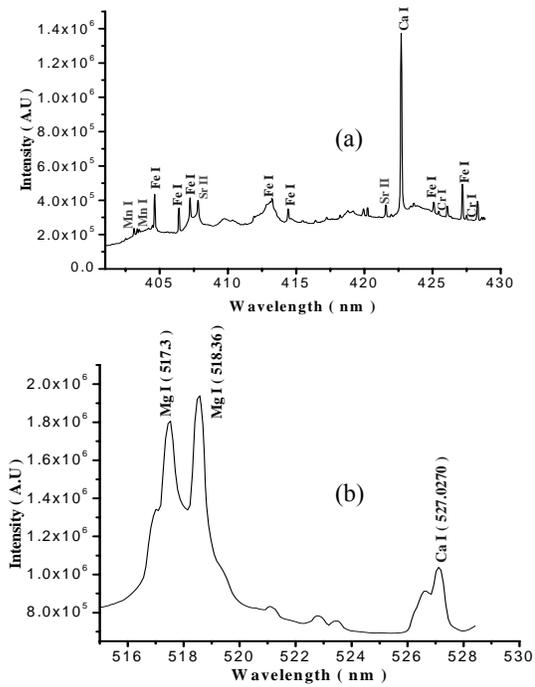
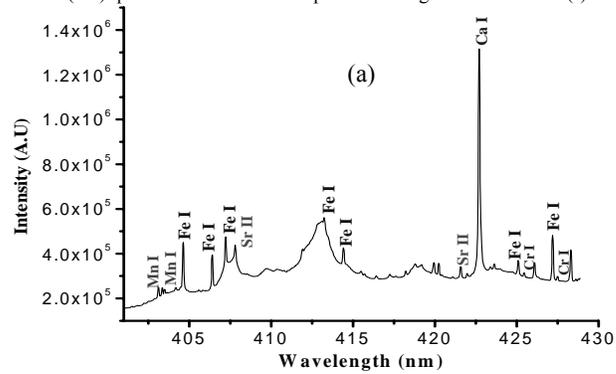


Fig. 4. High resolution (HR) spectra of river bed soil sample of Kamrangir Char centered at (a) 415 nm and (b) 522 nm.



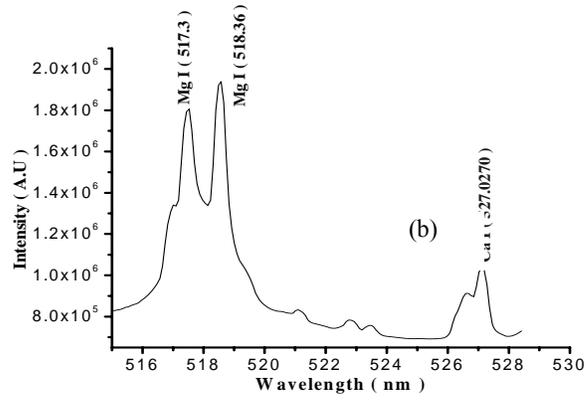


Fig. 5. High resolution (HR) spectra of the river bed soil sample of Shoari Ghat centered at (a) 415 nm and (b) 522 nm.

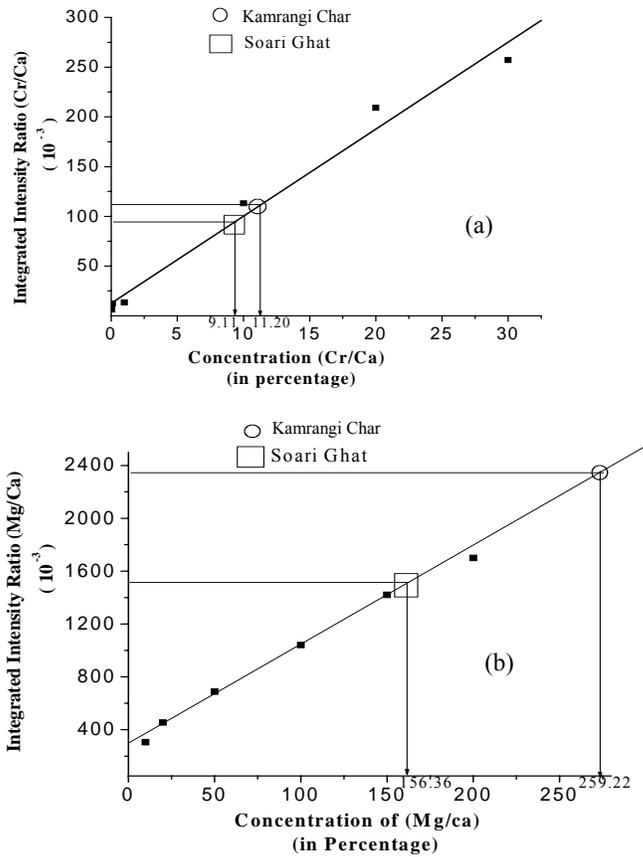


Fig. 6. Calibration curves of integrated line intensity ratio vs concentration of (a) Cr in Ca (with correlation co-efficient, $r = 0.99$) and (b) Mg in Ca (with Correlation co-efficient $r = 0.99$).

ACKNOWLEDGEMENTS

The experimental work was done by using the facilities of the Nonlinear Optics and Laser Spectroscopy Laboratory of the Center for Advanced Research in Physical, Chemical, Biological and Pharmaceutical Sciences (Center of Excellence) of Dhaka University.

REFERENCES

- Ahmed, M.F. K.M. Abedin, M.E. Sadat, A.I. Talukdar, M. Wahadoszamen and A.F.M.Y. Haider. 2009. Elemental Profiling of Surface Water Around Dhaka City By Laser Induced Breakdown Spectroscopy, *Journal of Bangladesh Academy of Science*. **33(2)**:209-218
- Andrzej W. Miziolek, Vincenzo Palleschi and Israel Schechter (ed.) 2006. *Laser-Induced Breakdown Spectroscopy: fundamentals and applications*, Cambridge University Press.
- Argonne National Laboratory. 2005. Human health fact sheet. EVS.
- Baruthio.F. 1992. *Toxic effects of Chromium and its compounds*, Biological Trace Element Research, **32**.
- Nicola, E.D. S. Meric, C.D. Rocco, M. Gallo and M. Iaccarino. 2007. *Wastewater Toxicity of Tannin-Versus Chromium-Based Leather Tanneries in Marrakesh, Morocco*, Arch Environ Contam Toxicol **53**: 321-328.
- Radziemski, L.J. and D. A. Cremers 2006. *Handbook of Laser Induced Breakdown Spectroscopy*. John Wiley.
- Rai, N.K. and A.K. Rai. 2008. LIBS-An efficient approach for the determination of Cr in industrial wastewater, *Journal of Hazardous Materials* **150**: 835-838
- Singh. J.P. and S.N. Thakur. (ed). 2007. *Laser Induced Breakdown Spectroscopy*, Elsevier.

(Received revised manuscript on 6 March, 2010)