

## **ELEMENTAL PROFILING OF SURFACE WATER AROUND DHAKA CITY BY LASER INDUCED BREAKDOWN SPECTROSCOPY**

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### **ABSTRACT**

Using the technique of Laser Induced Breakdown Spectroscopy (LIBS), which uses a pulsed laser to create plasma and advanced spectroscopic techniques, we analyzed the contents of surface water (river water) around the city of Dhaka. Several elements such as Li, C, Na, Mg, Al, K, Ca, Ti, Mn, Fe, Sr were identified in the water samples collected in addition to Cr, which was found at two locations at different concentrations. Chromium is a toxic element, and its presence at high concentrations is hazardous for human beings as well as the environment. Its presence in water is suspected due to the effluent discharge from the nearby tanning industries. Semi-quantitative analysis of the chromium present was performed. To our knowledge, this is the first example of the application of the LIBS technique in water analysis in Bangladesh.

### **INTRODUCTION**

Laser-Induced Breakdown Spectroscopy (LIBS) is a new and rapidly evolving technique useful for the detection of elements in many diverse situations<sup>(1-3)</sup>. The technique uses high power laser pulses for generation of plasma from samples and uses spectroscopic techniques for both qualitative and quantitative analysis for multiple elements. Since spectroscopic techniques are used, no chemical reagents are necessary. The technique is extremely versatile and powerful, and is capable of analyzing solid, liquids and gas samples. LIBS has been used, for example, for the detection of trace elements of soils<sup>(4-5)</sup>, geological analysis<sup>(6)</sup>, aerosol analysis<sup>(7-8)</sup>, analysis of industrial waste water<sup>(9-10)</sup> etc, to name a few.

Previously we have used a LIBS system for the elemental analysis of minerals in our laboratory<sup>(11)</sup>. In this paper, we used LIBS technique for the analysis of surface water from different sources in Bangladesh. To our knowledge, this is the first application of LIBS in the analysis of water in Bangladesh. We constructed a simple LIBS setup and performed both qualitative and quantitative analysis of various water samples, with a view to determine potentially harmful elements. We were successful in detecting at least one harmful element in different samples.

### **EXPERIMENTAL DETAILS**

The schematic diagram of the experimental LIBS system is shown in figure:1. The excitation laser which was used is a Q-switched Nd:YAG laser system (Spectra-Physics

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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 and 355 nm by means of KDP crystals and producing energies of 450 and 220 mJ per pulse, respectively.

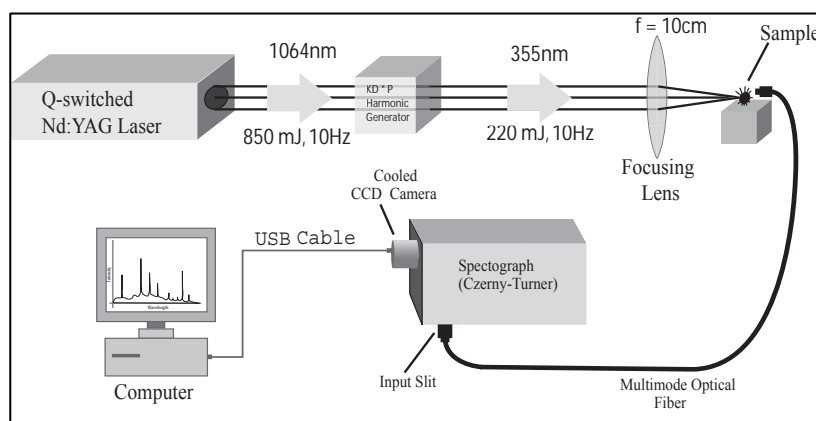


Fig. 1. Schematic Diagram of the experimental LIBS Set up

An 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 3 m long multimode optical fibre. The light is then transmitted through the fiber to its other end which is placed at the entrance slit of a 750 nm focal length computerized Czerny-Turner spectrograph (Acton Model SP-2758). The spectrograph is equipped by two ruled gratings; 300 grooves/mm and 1200 grooves/mm, which are interchangeable under computer control and 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 x 100 pixels and is cooled to  $-73$  C by a four-stage Peltier cooler to reduce noise. The image 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 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. All these functions were performed by WinSpec software.

To find out all the elements within the sample we tried to acquire spectra covering as wide a 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 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.

*Collection of Water Samples:* Water samples were collected from different areas in and around Dhaka city, which are known to be polluted, (Fig:2). Waters were collected from two different places of the river Buriganga, near Kamrangirchar and Shoari Ghat (points A and B), with a view to detect hazardous effluents discharged by the nearby tanneries situated around Hajaribag (point C). It may be mentioned here that Shoari Ghat is located downstream to Kamringir Char. Further samples were collected from Shitalakhya river near Narayangonj (D) and Hatir Jhil lake (E) which carries polluted waters from Tejgaon industrial area, respectively, and also from Dholai Khal (F) near Jatra Bari.

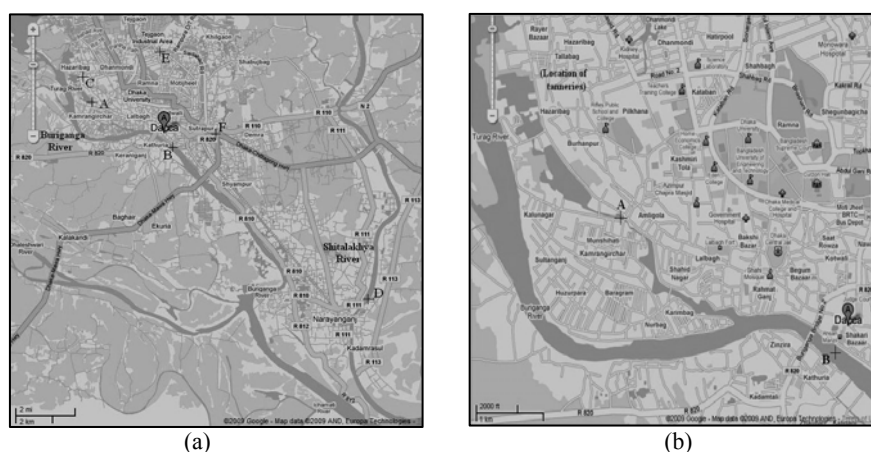


Fig. 2. Google maps of the area showing the sampling points (A, B, C, D, E and F). (a) shows the overall city of Dhaka and surroundings, and (b) shows the details near the tannery industries located in Hajaribag.



Many lines were found in the spectra that were identified using the NIST atomic line database<sup>(12)</sup>. Presence of Ca, Fe, K, Al, Mg, Ti, Na, Li were confirmed by the low resolution spectra. But no interesting heavy element was found in these spectra. Therefore high resolution LIBS experiments were performed with the 1200lines/mm grating, and lines of C, Si, Sr, Mn and Cr were confirmed (Figures 3 and 4). Emission lines of these elements were not observed in the low resolution spectra.

In these spectra, we identified six unambiguous lines of Cr which conclusively proves the existence of Cr in the suspended substance of the sample of Kamrangirchar. No other heavy metals could be identified. Table 1 summarizes the elements identified in the suspended substance of the samples of Kamrangirchar.

**Table 1.**  
**Elements found in the suspended substance of buriganga river water collected from kamrangirchar**

Elements Detected	Identifying Lines (nm)	Corresponding Lines from NIST Database (nm)
Li	670.77 (Li I)	670.78
C	247.86 (C I)	247.86
Na	588.94 (Na I)	588.99
	589.47 (Na I)	589.59
	818.21 (Na I)	818.33
	819.34 (Na I)	819.48
Mg	517.21 (Mg I)	517.29
	518.26 (Mg I)	518.36
Al	309.22 (Al I)	309.27
Si	251.63 (Si I)	251.61
K	766.3 (K I)	766.49
	769.79 (K I)	769.9
Ca	393.354 (Ca II)	393.37
	396.77 (Ca II)	396.85
	422.59 (Ca I)	422.67
	643.78 (Ca I)	643.9
	853.986 (Ca II)	854.2
	866.2 (Ca II)	866.21
Ti	335.05 (Ti II)	334.94
	453.3 (Ti I)	453.32
	520.7 (Ti I)	521.04
Cr	357.937 (Cr I)	357.87
	359.409 (Cr I)	359.35
	360.607 (Cr I)	360.53
	425.466 (Cr I)	425.43
	427.497 (Cr I)	427.48
	428.987 (Cr I)	428.97
Mn	403.104 (Mn I)	403.08
Fe	438.3 (Fe I)	238.20
Sr	407.805 (Sr II)	407.77

Next, the analysis of the dissolved substance of the sample of Kamrangirchar was performed. Emission lines of Li, C, Na, Mg, Al, Si, K, Ca and Sr were found in both low resolution and high resolution spectra. No evidence of Cr was found in those spectra.

ii) *Shoari Ghat*: Five liters of water was collected from Soari Ghat from which 150 mg of suspended substance was found. Both low resolution and high resolution experiments with suspended substance were performed. Overall, the findings with the suspended substance of the sample of Shoari Ghat were identical to that of Kamrangirchar, namely, the lines of Li, C, Na, Mg, Al, Si, K, Ca, Ti, Cr, Mn, Fe and Sr were observed and the presence of Cr was found conclusively in the sample. Similar analysis of dissolved substance of the samples of Shoari Ghat was performed. The result was identical to that of dissolved substance of Kamrangirchar i.e., lines of Li, C, Na, Mg, Al, Si, K, Ca, Sr were observed and the existence of Cr was not found.

iii) *Shitalakhya, Dholai Khal and Tejgaon Industrial Area (Hatir Jhil)*: Analyses of water samples from these places were performed as well. Similar results like Kamrangirchar (Table: 1) were found with the exception that no evidence of Cr was found.

The qualitative analysis shows the presence of Cr in the suspended substance of both the samples of Kamrangirchar and Shoari Ghat. But their intensities indicate that the concentration of Cr in Kamrangirchar is higher than that of Cr in Shoari Ghat. Thus to confirm it, quantitative analysis of those samples were performed.

The analytical measurements are generally done when a state of local thermal equilibrium (LTE) is achieved when the electron temperature is equal to the excitation temperature. At this equilibrium condition, the analyte intensity is proportional to the relative population of the level and follows the Boltzmann distribution. Under the LTE condition, the total intensity of a spectral line 'P' from an excited atom or ion in homogeneous and optically thin plasma for a transition from  $j \rightarrow i$  is given by<sup>(10)</sup>:

$$I_j = h\nu_{ji}A_{ji}Ng_jQ^{-1} \exp\left(-\frac{E_j}{kT}\right) \quad (1)$$

where,  $h$  is the Planck's constant,  $\nu_{ji}$  is the frequency of the transition from state  $j \rightarrow i$ ,  $A_{ji}$  is the Einstein transition probability,  $N$  is the ground level population density,  $g_j$  and  $E_j$  are statistical weight and energy of upper level  $j$ , respectively,  $Q$  is the partition of relevant species,  $k$  is the Boltzmann's constant and  $T$  is the electron temperature of the plasma.

Since  $I_j$  is proportional to the ground level population density, hence in practice, an empirical relationship can be sought that, the observed intensity ( $I$ ) is also proportional to the corresponding concentration ( $C$ ). However, the absolute intensity is dependent on plasma conditions. But from equation (1), if all the other parameters do not change,

$$\frac{C_j}{C_m} = \frac{N_j}{N_m} = \frac{I_j}{I_m} \quad (2)$$

where,  $C_j$ ,  $C_m$  are concentration of two elements  $j$  and  $m$ , in a sample,  $N_j$  and  $N_m$  are their ground level population densities and  $I_j$  and  $I_m$  are intensities of two particular lines of those elements, respectively. If all the other variables remain fixed, ratio of abundance of two elements in different samples is proportional to the ratio of spectral line intensities of two particular lines of those elements. This is the basis of quantitative analysis.

Since strong lines of Ca and Mg, which are extremely common elements in surface water were observed, we attempted to determine the ratio of Cr atoms to the sum of Ca and Mg atoms in the river samples. For this purpose, we mixed standard salts  $\text{Cr}_2(\text{SO}_4)_3$  and  $\text{CaCO}_3$ , and prepared samples containing 0.05%, 0.1%, 1%, 10%, 20% and 30% of Cr in Ca. LIBS spectrum was taken for each of the prepared samples, at a position centered at 425 nm that includes lines of both Cr and Ca at 425.43 nm and 422.67 nm, respectively. For instance, few spectra resulting from the samples with 0.1%, 1%, 10%, 30% Cr in Ca are shown in (Fig-5(a-d)). For each of the spectra intensity ratio (areas under the curves) of the spectral line of Cr to that of Ca was calculated. A calibration curve of '(Intensity ratio of Cr to Ca) Vs (Atomic ratio of Cr in Ca)' was drawn. Then LIBS spectrum was taken for each of the river samples at the same spectral window to determine the intensity ratio of the same spectral lines. Finally, from the calibration curve, the unknown atomic ratios of Cr to Ca in the river samples were found.

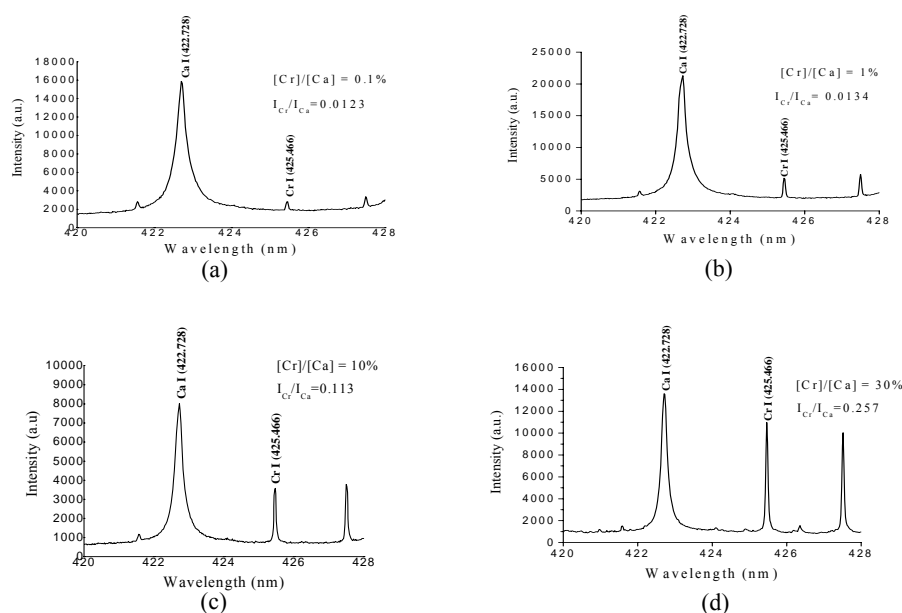


Fig. 5(a-d). LIBS Spectra showing increase in the spectral line intensity ratio of Cr ( $I_{\text{Cr}}$ ) to that of Ca ( $I_{\text{Ca}}$ ) with the increasing value of their atomic ratio.

Similarly the ratios of Mg to Ca in the river samples were calculated by making samples of Mg and Ca with 10%, 20%, 50%, 100%, 150% and 200% of Mg in Ca by mixing a standard salt of Mg,  $(\text{MgCO}_3)_4\text{Mg}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$  and a standard salt of  $\text{CaCO}_3$ . The resulting calibration curves are shown in (Fig: 6)

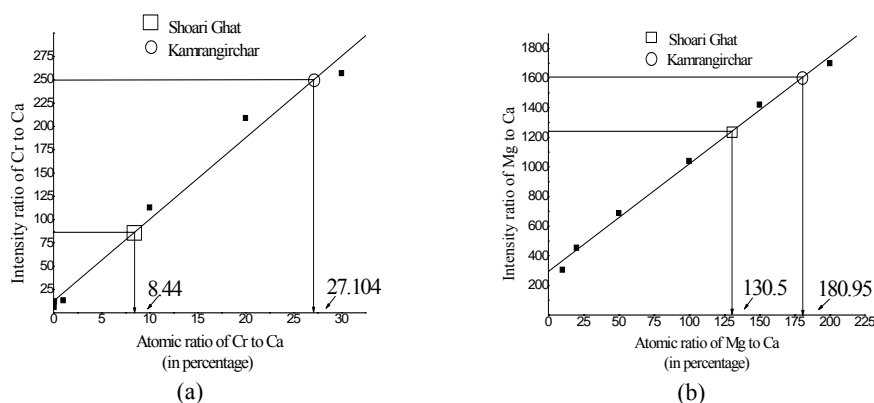


Fig. 6. Calibration curve to determine the atomic ratios of (a) Cr to Ca and (b) Mg to Ca in the suspended substance in river water samples

From the first calibration curve (Fig: 6(a)) atomic ratios of Cr to Ca were found to be 8.44 and 27.104 percent in Shoari Ghat and Kamrangirchar samples, respectively. From the second calibration curve (Fig: 6(b)) the atomic ratios of Mg to Ca were found to be 130.5 and 180.95 percent in those two samples, respectively.

Thus the atomic ratios of Cr to the sum of Ca and Mg were calculated for the river water suspended samples and presented in Table 2.

TABLE-2.

SEMI-QUANTITATIVE ANALYSIS OF CR IN THE SUSPENDED SUBSTANCE OF BURIGANGA RIVER WATER COLLECTED FROM KAMRANGIRCHAR AND SHOARI GHAT SITES

Sample location	From first calibration curve (Fig-6(a)), $\frac{[Cr]}{[Ca]} (= x)$	From second calibration curve (Fig-6(b)), $\frac{[Mg]}{[Ca]} (= y)$	In suspended contents, $\frac{Cr}{Ca + Mg} = \frac{x}{1 + y}$ (in percentage)
Kamrangirchar	0.271	1.8095	9.65
Shoari Ghat	0.0844	1.305	3.66

## DISCUSSION

In this paper, we analyzed the suspended and dissolved contents of the surface water (river water) around Dhaka City. We found the existence of many elements such as Li, C, Na, Mg, Al, Si, K, Ca, Ti, Mn, Fe, Sr in addition to Cr. The elements such as Mg, Al, Ca,



Ti, Fe, Sr are natural constituents of soil and may be expected to be present in surface water, and as such, their presence in the collected samples is hardly surprising. On the other hand, Cr is not usually present in soils and is hazardous if present in high concentrations<sup>(13)</sup>. This Cr must have come from the tanneries in Hajaribag area which is near the two sampling points of the river Buriganga ( Kamrangirchar and Shoari Ghat). Of these two locations, higher concentration of Cr was detected at Kamrangirchar. This can be due to the fact that Kamrangirchar is located nearer to the tanning industries compared to Shoari Ghat, and the effluent at the former location has less probability of dilution.

These tanneries might be using this Cr in the form of insoluble salts for tanning purposes which remain in suspended substance but not in dissolved substance. This might be the reason for which we could not detect Cr in the dissolved substance. Unfortunately we could not detect any other toxic elements like Pb, As, Cd, etc. in either of the suspended or dissolved substance in these samples. This is probably due to the limited sensitivity of the non-gated CCD system which is always open during the data accumulation and collects all the lights from plasma background and other noises. Therefore with this detection system, trace elements whose concentrations are less than roughly 1000 ppm can not be detected. Since only a small amount of sample was available we could not perform a full quantitative analysis.

The advantage of LIBS technique compared to the conventional chemical method lies in the fact that no chemical reagents are required in this case. In the LIBS method, analysis of multiple elements is possible at the same time and results can be obtained relatively quickly. To the best of our knowledge, it is the first application of LIBS to the analysis of surface water in Bangladesh. With the availability of a sensitive gated detector (ICCD), it should be possible to make a detailed study of all the toxic elements (some of which may be present in trace levels) in surface water around Dhaka City. This will give a clear idea about the dynamics of the flow and transport of harmful pollutants around the City of Dhaka which is essential for the proper management and control of the pollution.

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#### REFERENCES

1. D. A. CREMERS AND L. J. RADZIEMSKI (ed.), Handbook of Laser-Induced Breakdown Spectroscopy, John Wiley and Sons Ltd, 2006.
2. A. W. MIZIOLEK, V. P. PALLESCHI AND I. SCHECHTER (ed.), Laser-Induced Breakdown Spectroscopy (LIBS) Fundamentals and Applications, Cambridge University Press, 2006.
3. J. P. SINGH AND S. N. THAKUR (ed.) Laser-Induced Breakdown Spectroscopy, Elsevier, 2007.
4. MARTIN M. Z., S. D. WULLSCHLEGER, C. T. GARTEN JR. AND A. V. PALUMBO, *Appl. Opt.*, **42**, 2072, 2003.
5. ARCA.G. et al., *Appl. Physics B*, **63**, 185, 1996.

6. R. S. HARMON, F. C. DELUCIA, C. E. MCMANUS, N. J. MCMILLAN, T. F. JENKINS, M. E. WALSH, AND A. W. MIZIOLEK, *Appl. Geochemistry*, **21**, 730, 2006.
7. A. C. SAMUELS, F. C. DELUCIA JR., K. L. MCNESBY AND A. W. MIZIOLEK, *Appl. Opt.*, **42**, 6119, 2003.
8. L. J. RADZIEMSKI, T. R. LOREE, D. A. CREMERS AND N. M. HOFFMAN, *Anal Chem*, **55**, 1246, 1983.
9. N. K. RAI AND A. K. RAI, *Journal of Hazardous Material*, **150**, 835, 2007.
10. M. A. GONDAL AND T. HUSSAIN, *Talanta*, **71**, 73, 2007.
11. K. M. ABEDIN, S. F. U. FARHAD, A. F. M. YUSUF HAIDER AND M. R. ISLAM, *Dhaka Univ. J. Sci.*, **55**(2), 171, 2007.
12. [http://physics.nist.gov/PhysRefData/ASD/lines\\_form.html](http://physics.nist.gov/PhysRefData/ASD/lines_form.html)
13. F. BARUTHIO, *Biological Trace Element Research*, **32**, 1992.