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Elemental Investigation of River Ganga Water by LIBS

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Abstract An attempt has been made to investigate occurrence and bioaccumulation of metallic elements in river Ganga water at Allahabad using laser induced breakdown spectroscopy technique. The recorded spectrum shows the presence of atomic lines of the micronutrients (Ti, Si, Cr, Co, Br, Ba, Sr), macronutrients (H, N, Na, O, K, Ca, Mg, Cl, C) and toxic metals (Hg, Pb, Cd). The observed concentration of the detected elements in the river water shows the trend: Ti > H > N > Sr > Hg > Na > Si > O > Mg > Cl > Br > Ba > Cr > K > Cd > Ca > Pb > C > Co. The observation suggests that the use of such water for drinking may lead to potential health risk in long run.

Keywords LIBS technique · Elemental analysis · Ganga river · Bioaccumulation

Introduction

The river Ganga is one of the most important rivers of India. It has large drainage basin comprising an area of 861,404 km^2 encompassing a large part of various states. The water of this river possesses extra properties in comparison to the water of the other rivers due to presence of micronutrients and macronutrients. The river water is becoming polluted day by day due to industrialization, urbanization, sewage waste, increase in population, dead bodies burning ash and agricultural practices. In the modern civil society, people have a great faith in religious activities, a large quantity of the worship material like flower etc. are thrown into the river everyday. These wastes containing organic and inorganic chemicals and metallic elements are further deteriorating the quality of river water [1]. Metal ion derived from breakdown of rocks is controlled by several factors involving temperature, precipitation, water movement, soil movement, changes in redox potential and pH condition, absorption–desorption process, chemical complexation, hydrolysis, decay of vegetation and biochemical bacterial interactions. The accumulation of heavy metal in aquatic ecosystem has major problem of great concern in the river water [2]. The metallic elements have accumulation property like persistent, non-biodegradable and non-thermo degradable and cause sever impact on phytotoxicity of metals aquatic organism and human being without any visible sign possible intake through drinking water and aquatic food [3, 4]. These metallic elements cause serious health problem due to imbalance of concentration. Metals present in the river water in minute quantities become part of various food chains through irrigation and by biomagnifications process their concentration increases to such a level that cause toxic effect in human and other living organism [5–7]. Therefore detection of elements in river Ganga water is an urgent demand.

The quality of river Ganga water is determined by several earlier workers using various techniques such as atomic absorption spectroscopy (AAS), inductively coupled plasma optical emission spectroscopy (ICP-OES), mass spectroscopy (MS), inductively coupled plasma mass spectroscopy (ICP-MS), X-ray fluorescence (XRF) etc. [8, 9]. The techniques such as AAS, ICP-OES, ICP-MS, and MS work well for liquid samples. However some matrices can be difficult to get into solution like ceramics as well as for materials like graphite. Also for high purity copper and

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precious metals, the digestion needed to get the solid into solution, can dilute the sample beyond the detection limits of these techniques. Digestion steps also give rise the possibility of contamination of the acids and vessels used for the digestion process. On the other hand, laser induced breakdown spectroscopy (LIBS) is an emerging technique used for the detection and identification of elements in a variety of samples such as solid, liquid, gas, gel, slurry etc. [10]. This technique is very versatile because of its simplicity, rapid analysis, non-destructive, free from sample preparation and simultaneous multi-elemental analysis. In order to identify the latest status of the various elements and pollutants (toxic metals), we have applied LIBS technique to investigate the minerals present in the river Ganga water. The present manuscript describes our findings about the river Ganga water based on the observations of the recorded spectrum in the region 200–900 nm.

Experimental Details

Allahabad is an old and unique city of India where two big rivers of the country namely Ganga and Yamuna are carrying various industrial effluents, domestic sewage and waste with partial or no pretreatment. The water sample under investigation is collected from the surface water of river Ganga at Mori Nala, Daraganj, Allahabad.

The experimental set up used for the LIBS is shown in the Fig. 1. It consists of laser source, plasma collection optics, spectrometer and data acquisition system. The laser source used was a neodymium: yttrium–aluminum garnet (Nd: YAG) laser, operating at 532 nm wavelength and capable of delivering a maximum energy of 425 mJ over a pulse duration of 3–4 ns and a maximum pulse repetition rate 10 Hz. The laser beam was focused at the surface of water sample with the help of a quartz lens of focal length 15 cm. The experiment was performed by varying the laser energy and repetition rate of the laser pulse. Finally, a good signal to noise ratio was found at 100 mJ laser energy and 10 Hz repetition rate. The characteristic light emitted from the laser generated plasma was collected with an optical-fiber bundle and fed into the entrance slit of a grating spectrometer (Ocean Optics, LIBS 2000+ working in windows 2000 professional mode) equipped with a charge coupled device (CCD). The emission spectra of sample were been recorded by using a 1.5 μs gate delay with spectral resolution 0.1 nm in the spectral range 200–500 nm and a spectral resolution 0.75 nm in the spectral range 200–900 nm. Each LIBS spectrum is the average of 50 laser shot in order to reduce shot to shot variation and to enhance signal to noise ratio.

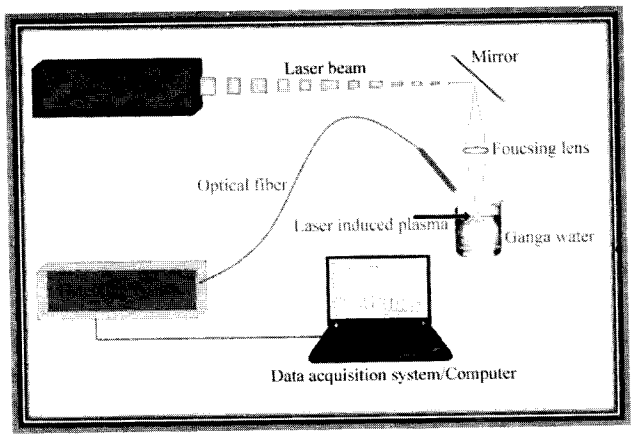

Fig. 1 Experimental set up used for the LIBS technique

Results and Discussion

The emission spectrum of river Ganga water has been recorded in the spectral region 200–900 nm using LIBS technique and is shown in Fig. 2. The recorded spectrum comprises of number of atomic lines of varying intensities. These spectrum lines have been identified using NIST spectral data [11]. The close scrutiny of the recorded spectrum shows presence of atomic lines of the macronutrients, (H, N, Na, O, K, Ca, Mg, Cl, C), micronutrients (Ti, Si, Cr, Co, Br, Ba, Sr), and toxic metals (Hg, Cd, Pb). The detected elements are presented in Table 1 with their wavelength. As the intensity of spectrum line is an indicative of concentration, therefore the order of the concentration of the detected elements is: Ti > H > N > Sr > Hg > Na > Si > O > Mg > Cl > Br > Ba > Cr > K > Cd > Ca > Pb > C > Co.

The detected macronutrients hydrogen, nitrogen, oxygen and carbon play an important role in the formation of tissues and organs while sodium, potassium, and chlorine have common electrolyte function in the body. Sodium regulates the total amount of water in the body and transmission of sodium into and out of individual cells and also plays a critical role in body functions. Potassium in the body regulates the heart beat and the function of muscle. The magnesium deficiency stimulates oxygen free radical. This damaging agent promotes secretion of mucus glycoprotein in the gallbladder, which contributes to the gallstone formation. In human body calcium is important for osteogenesis.

The micronutrients elements like chromium, silicon, titanium, cobalt, barium, strontium, and bromine are essential for the activation of some enzymes. But higher concentration of these is harmful for the human being. For instance chromium is activator of insulin, so it takes major role in glucose metabolism enzymes (phosphoglutamase). But chromium in excess quantity causes skin disease and cancer. In addition, chromium toxicity results from accidental acute

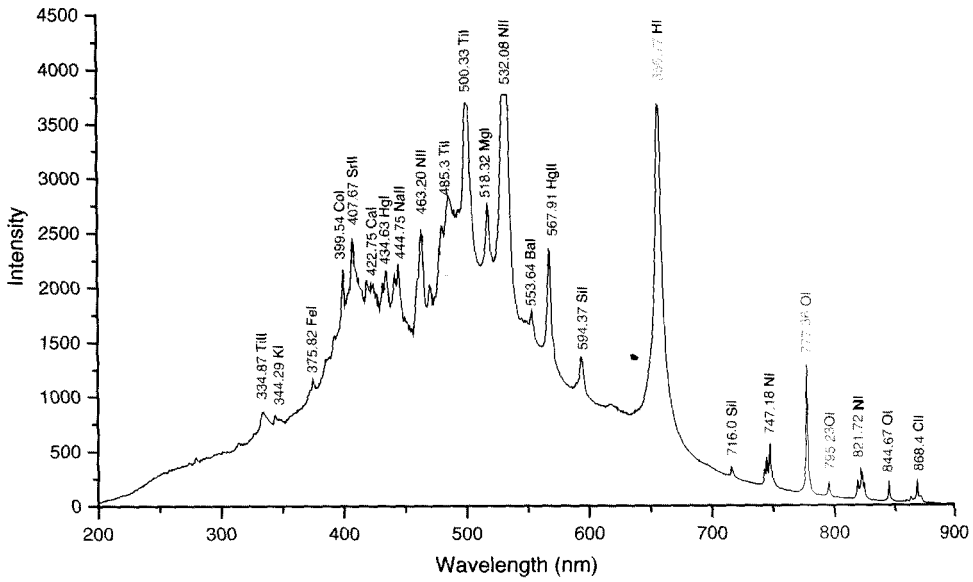

Fig. 2 Typical laser induced breakdown spectrum of river Ganga water in the spectral region 200–900 nm

Table 1 Detected elements in river Ganga water

Wavelength (nm)	Element	Wavelength (nm)	Element	Wavelength (nm)	Element
229.62	Co II	431.91	C II	518.32	Mg I
244.58	Co II	434.63	Hg I	532.08	N II
247.83	C I	441.57	Cd II	553.64	Ba I
279.48	Mg II	444.75	Na II	567.91	Hg II
333.94	Ti I	445.19	Na II	594.37	Si I
334.87	Ti II	455.37	Ba II	656.77	H I
344.29	K I	463.20	N II	716.00	Si I
375.82	Fe I	469.95	Cr II	747.18	N I
393.27	Ca II	470.62	Cr I	777.36	O I
399.54	Co I	480.41	K I	795.23	O I
407.44	Sr II	485.17	Ti I	821.72	N I
417.72	Cr I	487.15	Ca I	844.67	O I
422.75	Ca I	493.33	Ba II	868.40	Cl I
424.79	Pb II	500.33	Ti I		

poisoning or occupational exposures. Causalities due to chromium toxicity are usually preceded by nausea, vomiting, shock and coma. Silicon is essential for normal growth and bone development. But its excess amount is responsible for the gallstone formation. Gastrointestinal disturbance caused by barium. Cobalt is a component of vitamin B_{12} and protein. The strontium is beneficial in preventing the cavities, helpful in reducing loss of bone mineral in osteoporosis and reducing fracture. Bromine is important for the pituitary gland, whose hormones profoundly influence brain functioning and the production of hormone.

As the atomic lines of the elements cadmium, mercury, and lead are identified in the water sample therefore these elements are present in the river water sample. Since these elements belong to the nonessentials category and their large quantities will produce toxic or health hazardous effects. The accumulation of these elements can harm the organism itself or can be transmitted to the tropic level of the food chain, where a similar toxic process can take place. Ingested cadmium accumulates in the kidney. It causes toxicity owing to interaction with sulphydryl groups of essential enzymes. Cadmium induces hypertension and cirrhosis of liver. It has also been linked with pulmonary emphysema and lung cancer. Mercury combines with sulphydryl groups, which may be part of protein, such as an enzyme and becomes toxic to all the cells. Hence, mercury is a potent inhibitor of activities of enzyme containing sulphydryl group at their active site. Lead causes kidney damage while chronic exposure may lead to interstitial nephritis. It interferes at several steps in heme synthesis in the bone marrow by inhibiting the activities of enzymes ferrochelatase, α-amino laevulinate synthetase (ALAS) and α-amino laevulinate dehydrogenase (ALAD) and with the uptake of iron into mitochondria. Lead (Pb) also cause headache, neuropathy, encephalopathy, memory loss and CNS damage.

Conclusion

The present study demonstrates the capability of LIBS technique for the elemental analysis of water samples without sample treatment in short duration. The obtained results indicate that a constant monitoring of riverine system is needed before the level crosses its threshold and become toxic to the aquatic animals and human beings.

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