Detection of heavy (toxic) metals in water samples by Laser induced breakdown spectroscopy (LIBS)

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ABSTRACT

Laser Induced Breakdown Spectroscopy (LIBS) is used to analyze metal impurities in water samples. The experimental setup is equipped with a Nd:YAG pulsed laser, a sample viewing digital camera, a seven channel grating spectrometer and gated CCD detection system. Wavelength calibration of the spectrometer is done to ascertain resolution and proper identification of elements. Synthetic standard solutions containing 21 metal impurities were prepared for quantitative estimation of the impurities in the water samples. Minimum detection limits for all the elements were determined, a few parts per million (ppm) detection limits were obtained for most of the elemental standards. Water samples collected from different districts and localities of Jeddah city were analyzed. The analyses of samples were done against the calibrated standards. Analysis results show no contamination of highly toxic metals like As, Cd, Hg and Pb. Other elements were present in trace amounts. Some of the elements could not be detected due to poor sensitivity of the system for those elements.
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INTRODUCTION

Exposure to excessive concentrations of heavy elements produces adverse effects on human health and cause many diseases such as cancer, anaemia, kidney and liver damage etc. These elements enter our bodies via food, drinking water and air, and some of them remain inside for the lifetime of the individual. We need to monitor their intake and prevent inadvertent overdose by monitoring the quality of especially the drinking water. Minute concentration of some of the heavy elements is toxic and hence we need an analytical technique which can detect and quantify heavy elemental presence at trace level in drinking water.

Laser-induced breakdown spectroscopy (LIBS) also sometimes called laser-induced plasma spectroscopy (LIPS) or laser spark spectroscopy (LSS) has developed rapidly as an analytical technique over the last decade[1-4]. The technique employs a low-energy pulsed laser and a focusing lens to generate plasma that vaporizes a small amount of a sample. A portion of the plasma light is collected and a spectrometer disperses the light emitted by excited atomic and ionic species in the plasma, a detector records the emission signals, and electronics take over to digitize and display the emission spectrum. The spectra are used to determine the sample's elemental constituents. The initiation, formation and decay of the plasma are complex processes. The spectra observed change as the plasma evolves temporally. Soon after initiation, continuum and ionic

spectra are seen. As the plasma cools, these are followed by spectra from neutral atoms. Spectral analysis of the emissions will yield a fingerprint of the chemical and atomic species present. Quantitative estimation is usually done against standards of known concentrations. The LIBS technique has been demonstrated to have high sensitive, down to few parts-per-million concentrations, high elemental selectivity, needs no or little sample preparation and it takes very little time for sample analysis.

LIBS of liquids are a relatively new technique. The location of the plasma formation can be in the bulk solution (under the surface of the liquid), at the gas/liquid interface (on the surface of the liquid), or in a flowing sample. The emitting species are identified by spectrally and temporally resolving the plasma light[5-11].

Cremers, Radziemski, and Loree were the first to determine limits of detection (LOD) for Li, Na, K, Rb, Cs, Be, Mg, Ca, B, and Al in aqueous solutions[12]. With a Nd: YAG for excitation and a monochromator/PMT for detection, they concluded that the method was sufficient to excite the alkali metals and the technique could be useful to detect species in water at moderate to high concentrations. Some disadvantages they found were self-reversal at high concentrations, which causes a dip in the center of an emission line because the edges of the plasma are cooler than the core resulting in a stronger emission from the core than the edges, and noise may occur due to large particles or heterogeneous sample resulting in perturbations of the plasma characteristics. Another disadvantage of using a bulk solution is the plasma temperature is significantly lower than the temperature of plasma formed in a gas, resulting in lower excitation capabilities. Creamers and Watcher applied the LIBS of solutions technique to determining uranium in solution for possible use by nuclear fuel reprocessing facilities. The surface excitation where solution was placed in cylindrical glass vials to minimize handling of the toxic liquid, they observed plasma for times of order several μs[12].

Nakamura, et al. applied the LIBS of solutions technique to determining colloidal iron in water for possible use by electric power plants for controlling boiler water quality. Their experiment was based on forming the plasma in a flowing solution; this would allow electric power plants to save water and time by using an on-line monitoring technique during the flushing process used to check water quality. They reported LIBS detection of Fe concentrations less than 20 ppb[13,14]. The quick-freeze method for the quantitative analysis of trace metal ions in liquids was introduced. Using this procedure with calibrated samples, well-characterized linear working curves were determined for Na and Al water solutions over the 0.01-1% concentration range[15]. Fichet et al. used LIBS for the measurement of twelve elements in two liquids: water and oil[16, 17].

On the other hand, LIBS has been applied to the analysis of liquid samples using laminar flows of the liquid. In this case, the detection limits reported were insufficient for the direct application of the technique to environmental samples; pre-enrichment was required [18-20].

Pu et al. demonstrated two pulse laser-induced plasma spectroscopy for analysis of lead carbonate colloids. The lead emissions were much enhanced, while the background continuum interference was minimized. The detection limit for lead was shown to be 14.2 ppb, compared with 13 ppm achieved by conventional laser induced breakdown spectroscopy of lead ions in water and 210 ppb for lead aerosols[21]. Lead and sulphur were also analyzed in environmental samples by a two pulse technique by Burakov et al[22]. Lead in water samples was determined by Godwal et al.[23]. Using double pulse technique samples were also analyzed underwater by Giacomo et al.[24], whereas heavy metals in liquids were analyzed by Díaz Pace[25] by converting the liquids to solid samples.

Our research objectives in this work are detection of heavy metals in drinking water throughout old Jeddah water pipelines using laser induced break down spectroscopy (LIBS) and measure their concentrations along with the limit of detection of our system.

MATERIALS AND METHODS

With the objective of detecting heavy metal impurities in mind, a suitable LIBS spectrometer system from Ocean Optics, USA (model LIBS/3000) was selected and procured. The experimental system, Ocean Optics, USA (model LIBS/3000), consists of a Nd:YAG pulsed laser working at its fundamental wavelength 1064 nm, giving about 100 mJ/pulse energy in 5 nsec duration.

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TABLE 1: Observed wavelengths of prominent lines of Pure Aluminium, Copper and Nickel metals. Corresponding standard wavelengths of these lines from NIST database are also listed. A large number of lines are observed, however only a few are listed below

| S. no.	Element and ionization state	NIST Wavelengths (nm)	Observed Wavelengths (nm)	Error (nm) (NIST-OBSD)
1	Al II	281.6185	281.647	-0.0285
2	Al I	308.2153	308.36	-0.145
3	Al I	309.2710	309.377	-0.106
4	Al II	358.6557	358.709	-0.054
5	Al I	394.4006	394.384	0.0166
6	Al I	396.1520	396.117	0.035
7	Al II	466.3056	466.341	-0.036
8	Cu II	217.941	217.859	0.082
9	Cu II	219.2268	219.365	-0.139
10	Cu I	324.754	324.839	-0.085
11	Cu I	327.396	327.445	-0.049
12	Cu II	490.9734	490.895	0.078
13	Cu I	515.324	515.311	0.013
14	Cu I	521.82	521.777	0.043
15	Ni II	221.6482	221.6228	0.254
16	Ni I	341.4764	341.531	-0.0546
17	Ni I	345.8460	345.875	-0.029
18	Ni I	349.2956	349.297	-0.0014
19	Ni I	352.4536	352.461	-0.0074
20	Ni I	356.6372	356.638	-0.0008
21	Ni I	361.9391	361.927	0.0121
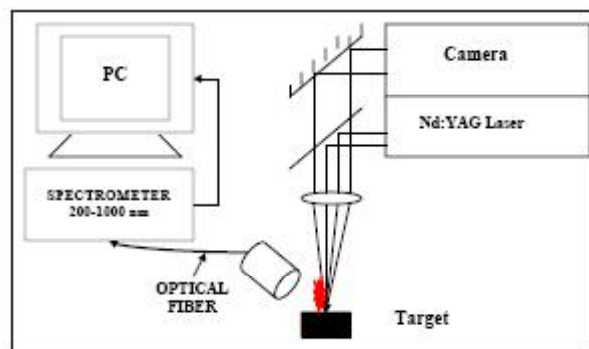
Figure 1: Schematic of the experimental setup

The laser beam is focussed onto the surface of the target via a 25 cm focal length plano convex lens. The system has an attached digital camera for viewing the sample, which uses the same focussing lens to ensure the laser gets focussed at the desired position on the sample. The plasma emission is collected by an optical fibre bundle. The system has a seven channel spectrometer covering a range of wavelengths from 200-1000 nm and CCD (charge coupled device) detection system. It has a resolution of 0.1 nm. The entire instrument is controlled by a computer programme and the software displays the spectra. The software also has the provision of identifying spectral lines with the help of a database. Figure 1 gives schematic diagram of the experimental setup.

High purity (99.9 % or higher, from Merc and Aldrich) salts of the metals are used for preparation of standards in double distilled and de-ionized water. The plastic bottle containers are thoroughly washed, rinsed with distilled water several times and dried. Master standards having 1000 parts per million (ppm) of the following elements are prepared and stored and then standards containing 500, 250, 100, 50, 20, 10, 5, 2 and 1 ppm were made from the master standards by successive dilution method. The elements included, Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Pb, Se, Sr, Tl, V and Zn. Apart from this a multi-element Perkin Elmer Interference Check Standard 18 which contained some of the above elements was also used in the studies.

Teflon sample holders that can accommodate 10 aqueous samples simultaneously were designed and fabricated. It is a block of Teflon with square cross section of 15x15 mm and length 115 mm consisting of 10 cylindrical pits of 6 mm diameter, 10 mm depth and separated by 5 mm along its length. About 0.3 mL of sample can be accommodated in each pit. They were thoroughly cleaned before use.

RESULTS AND DISCUSSION

We have carried out performance testing and wavelength calibration of the spectrometer, using pure solid metal samples of Al, Cu and Ni. Typical spectra obtained for Ni metal is shown in figure 2. TABLE 1 shows the wavelengths of some prominent lines of these elements taken from the National Institute of Standards and Technology (NIST), USA database. The wavelengths obtained with our spectrometer and the differences are also listed there.

We have also studied the variation of signal intensity by varying the laser power and delay time (between laser pulse and gating the detection system). As mentioned above, both these parameters play a very important role-in identifying the species and obtaining limits of detection of the experimental system. These
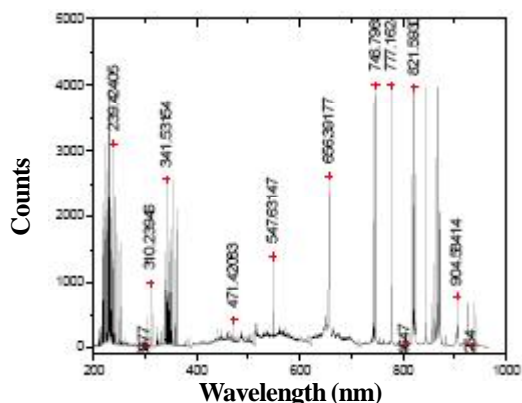
Figure 2: Spectrum of pure Nickle metal taken at low laser power, delay of 2.5 microseconds and averaged for 5 pulses. All the expected prominent lines of Ni are observed, besides some strong lines of nitrogen, oxygen and hydrogen are also seen
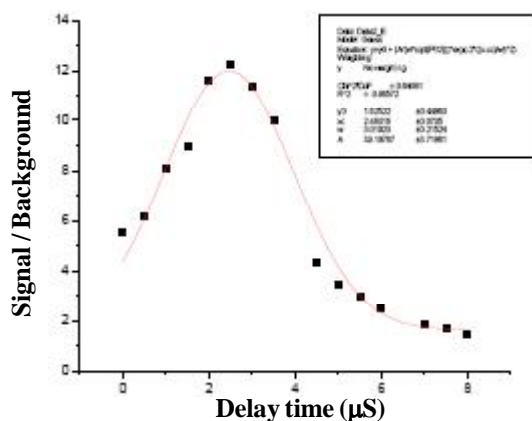

Figure 3: Signal-to-background ratio variation with delay time, for a typical spectral line. The laser power was kept constant. The solid line is a Gaussian fit through data points, showing a maximum at 2.5 μs
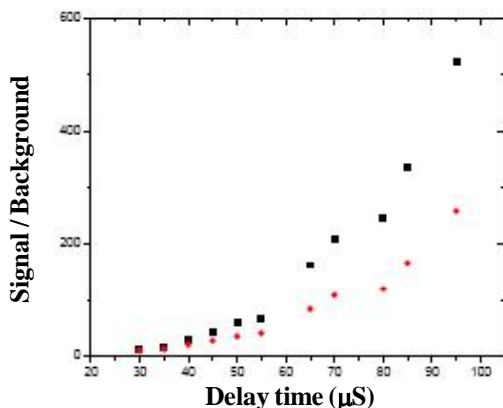

Figure 4: The signal intensity at various laser energies for two lines of Na impurity element at a concentration 100 ppm. The black squares represent 589.0 nm line variation while the red dots show variation for 589.6 nm line. The delay time was kept fixed at 2.5 μs
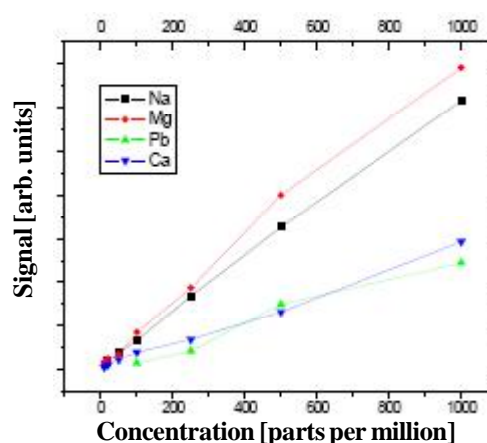

Figure 5: Intensity Calibration curves for some of the elements. The data points are average values for 5-8 measurements. The data was recorded at 40-70 % laser energies and a delay time of 2.5 μs

studies were conducted for all the elements under investigation, using standard samples of different concentrations, at various transitions and by varying delay time at several laser powers. However, only some typical results are shown in figures 3 and 4. The variation of signal to background ratio with delay times is shown in figure 3. One can clearly see that it shows a maximum at 2.5μs and the behaviour is more or less similar at different laser powers. However, some elements show an oscillatory behaviour showing gradually decreasing maxima at 2.5, 4 and 6μs. Variation of signal intensity with laser power for 589.0 nm and 589.6 nm transitions of Na is shown at constant delay time in figure 4. It follows almost a linear variation with powers. A similar behaviour is obtained for almost all other elements.

In order to get quantitative estimate of the heavy metal impurities, we ran the synthetic standards of various elements prepared as described in the previous section. The intensity calibration curves were obtained for all the elements of interest. Some typical curves are displayed in figure 5. These results are summarised in TABLE 2 for all the standards prepared. Quantification of the samples is carried out on the basis of the calibration curves by running each of the samples at least five times and mean and standard deviations are estimated for each of the samples. These results are presented in TABLE 3.

The spectrometer is the heart of the instrument as far as the correct identification of the constituents and quantitative analysis is concerned. Wavelength calibra-

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TABLE 2: Intensity calibration results and determination of lowest detection limit

Serial no.	Element	Wavelengths used [nm]	Range of conc. detected [ppm]	Lower limit of detection [ppm]
1	Aluminium, Al	281.6, 308.2, 309.2	1-1000	3
2	Arsenic, As	228.8	1-1000	5
3	Barium, Ba	553.5, 455.4	1-1000	3
4	Beryllium, Be	234.8	100-1000	65
5	Calcium, Ca	422.6, 443.5, 393.3, 396.8	1-1000	3
6	Cadmium, Cd	226.5, 231.2, 537.8	1-1000	3
7	Copper, Cu	324.7, 327.3, 510.5	50-1000	35
8	Iron, Fe	238.2, 248.3	1-1000	3
9	Mercury, Hg	253.6, 398.3	10-1000	5
10	Potassium, K	404.7, 766.4,769.8	1-1000	1
11	Magnesium, Mg	279.5, 280.2, 285.2	1-1000	1
12	Manganese, Mn	257.6, 403.7	1-1000	2
13	Sodium, Na	589.0, 589.6	1-1000	1
14	Lead, Pb	283.3, 287.3	10-1000	5
15	Strontium, Sr	407.7, 460.7	1-1000	3
16	Thallium, Tl	351.9	100-1000	75
17	Vanadium, V	290.8, 309.3, 437.9	100-1000	85
18	Zinc, Zn	213.8, 481.0	1-1000	1

tion and resolution of the spectrometer system plays the key role in proper identification of the constituents. These parameters need to be ascertained even before one proceeds with sample analysis. Our interest lies in elemental analysis where the spectral lines are quite well separated from each other for the same element and therefore a moderate resolution would suffice. However, there can be spectral interferences at some wavelengths from other species present in the sample due to rather limited resolution of the instrument. This may lead to wrong identification and erroneous quantitative estimate. Hence care must be exercised in choosing spectral lines which are free from spectral interference from other species. We carried out wavelength calibration of the spectrometer using pure metals in solid phase and also dissolved in solutions. We found that all the prominent lines are observed in the spectra of these pure metals and the error in wavelength calibration is within the resolution limit of the spectrometer. Hence the calibration of the spectrometer is established. TABLE 1

summarises the wavelength calibration results. However we found that the software provided does not correctly identify the elemental species. This was mainly due to limited resolution (0.1 nm) of the spectrometer and proximity of several lines of different elements within the resolvable wavelength interval.

The choice of lines was also based on the relative intensity of the transitions. Very strong lines would suffer from self reversal and lead to erroneous quantitative estimates and very weak lines would not be detectable at low concentrations. Based on these observations we have taken care to choose such spectral lines which have no interference from the expected impurities and have moderate transition strengths. The quantitative estimation was carried out at least on three different lines of each metallic impurity, in order to obtain a more reliable analysis.

LIBS technique for liquid samples poses some special problems. The density of aqueous solutions is relatively low as compared to solids. This leads to poor limits of detection for liquids. The second problem arises due to splashing of liquid sample out of the holder and into the chamber as droplets. This happens due to shock waves and acoustic waves generated by the focussed laser pulses at the surface. Some of the liquid gets condensed at the focussing lens, thereby reducing its transmission and lower laser power densities at the sample surface after a few laser shots. The focussing lens was therefore cleaned after every sample run. We also tried freezing the solutions into ice using liquid nitrogen. This helped in solving the problem of splashing, however we did not observe any increase in the signal intensity. This is expected, as the density of ice is almost the same as that of water, in fact a little lower. However we noticed a marked improvement in signal intensity for some weaker transitions of several elements. Using those lines we could obtain substantially improved (a factor of 10-35) lower limits of detection.

The intensity calibration of various impurities vs. their concentration was carried out very carefully for reliable quantitative estimation. This was done after optimizing the laser energy and pulse delay time parameters for each one of the impurities. The laser energy for a majority of the elements was kept around 60-70 % level. And the pulse delay time was kept fixed at 2.5 μs. The standards in the concentration range 1-1000 ppm were
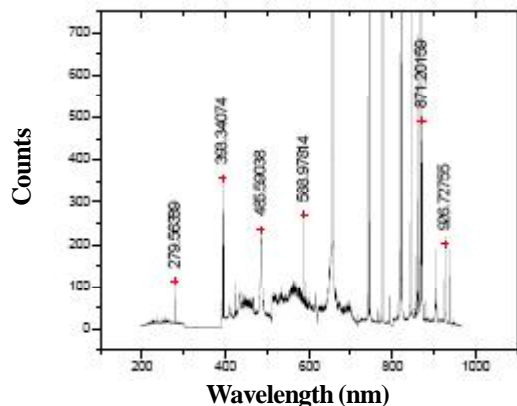
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Figure 6: Spectrum of a typical water sample collected from a locality in Jeddah. The spectrum was recorded at laser energy 50% and a delay time 2.5 μs

TABLE 3 : Summary of analysis of 165 water samples from different localities and districts of Jeddah city

Serial no.	Element	No. of samples containing it in total 165 samples	Mean conc. Observed [ppm]	Standard deviation %
1	Aluminium, Al	57	10	15
2	Arsenic, As	-	-	-
3	Barium, Ba	133	15	8
4	Beryllium, Be	-	-	-
5	Calcium, Ca	165	156	17
6	Cadmium, Cd	-	-	-
7	Copper, Cu	5	50	19
8	Iron, Fe	148	40	10
9	Mercury, Hg	-	-	-
10	Potassium, K	165	140	16
11	Magnesium, Mg	165	114	15
12	Manganese, Mn	48	25	23
13	Sodium, Na	165	188	10
14	Lead, Pb	-	-	-
15	Strontium, Sr	59	9	15
16	Thallium, Tl	-	-	-
17	Vanadium, V	-	-	-
18	Zinc, Zn	148	16	15

run. Some typical results are presented in figure 5. The limits of detection (LOD) for all the elements are determined based on these curves. The results are presented in TABLE 2, and as is evident from the table the LOD obtained are not very good for a number of heavy metal impurities which are toxic. This is mainly due to low density of the aqueous solutions, as mentioned above. Many other researchers have also faced this problem with liquid samples and a double pulse LIBS

technique is introduced to overcome this limitation in sensitivity. The sensitivity obtained by us is similar to those obtained by others in the literature with a single laser pulse LIBS technique. Our instrument does not have the facility of dual laser pulses.

Water samples from different localities and districts of Jeddah city were collected in cleaned plastic containers. Three to eight samples from each locality were taken on different days and in all 165 samples were analysed. One typical sample spectrum is shown in figure 6. The results of analysis are summarised in TABLE 3. It is clear from the data in the table that no samples contained highly toxic metal impurities like As, Cd, Pb and Hg. The amount of Ca, K, Na, Mg were found to be substantial in the 100-200 ppm range and while Fe, Zn and Mn were found to be 10-50 ppm in many samples. The detection limits for some elements like V, Be, B, Se are high and these elements were not detected in the samples for that reason, or one can say their concentration is lower than the respective detection limits.

CONCLUSION

In this work we have taken up analysis of water supplied through pipelines and tankers for domestic consumption. Laser Induced Breakdown Spectroscopy (LIBS) is used to detect presence of metallic impurities in water samples collected from different localities and districts of Jeddah city. We have carried out analysis of 165 samples. The analysis showed that alkali and alkaline earth elements are present in the samples, however these are not toxic at the concentration detected by us. No highly toxic impurities like As, Hg, Pb, Cd etc. could be detected during our research. This essentially means the water supplied through the pipelines contains acceptable concentrations of the elements, for the most toxic elements. However, the lowest detection limits for some elements are very high and those were not observed in the samples. The limits of detection could be improved by using a double pulse LIBS technique.

It must be mentioned that contamination of drinking water is not limited only to heavy metals seeping into it; there are a host of other chemical and biological contaminants that can make it unfit and unsafe for human consumption. Determination of these fall outside the

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scope of this work, and would require other techniques. The LIBS technique is best suited for and limited to determination of elemental and especially metallic impurities.

ACKNOWLEDGMENTS

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