

# A novel laser breakdown spectrometer for environmental monitoring

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## ABSTRACT

A novel experimental set-up using laser-induced breakdown spectroscopy (LIBS) for environmental analyses of heavy metals is described in this paper. It is based on state-of-the-art spectroscopic equipment, advanced detectors, and laser atomizers: a 0.75 m spectrometer ARC-750, intensified TE-cooled 256x1024 CCD camera, probe with fiber optic guide for signal transportation, and Nd:YAG laser plasma atomizers with two different methods for sample delivery. In the first method the liquid solution containing the atoms to be investigated is drawn into the chamber of the nebulizer. The mixture passes through the nozzle, accompanied by argon gas along with formed aerosol, and enters the plasma plume, which is generated by the laser spark in argon. The second method is based on direct generating of the plasma in the water jet of a continuously circulating sample. LIBS testing of samples containing Al, Cd, Cu, Fe, Pb, Zn, and Cr ions was compared with results using atomic absorption spectrophotometry. Initial indications showed good agreement between these two methods. Detection levels of less than 100 ppb were observed for copper and chromium. The described spectroscopic system exhibits high sensitivity, accumulation of luminescence spectrum in real time; and high dynamic range for concentrations detection from 100 ppb to 1000 ppm.

**Keywords:** Laser induced breakdown spectroscopy, Atomic fluorescence, Heavy metal atoms, Laser atomization.

## 1. INTRODUCTION

Laser induced breakdown spectroscopy (LIBS) is a simple, rapid, real-time analytical technique based on the analysis of the spectral emission from laser induced sparks or plasmas. Pulsed laser radiation is focused to a small spot on a sample material. A laser spark or microplasma with high temperature and electron density is formed for power densities in excess of hundreds of MW/cm<sup>2</sup>. The temperature of this plasma, initially, is very hot: 10<sup>4</sup>-10<sup>7</sup> °C. At such a high temperature, any sample material is decomposed ("broken down"), vaporized and ionized. At the early stages of plasma thermalization, as electrons interact and recombine with ions, energy will be released over a broad range of the energy spectrum, from soft X-rays through the visible to the near IR. These early stages of the plasma glowing are accompanied by the intense "bremsstrahlung" continuum emission that can be gated off by a detection system. After suitable time delays in detecting the emission spectra, the plasma cools down to the point when neutral atoms in excited states are formed. Time resolved spectral analysis of these atomic emissions yield a fingerprint of the atomic species present in the sample.

The basic features of LIBS are described in previous review papers<sup>1,2,3,4,5,6</sup>, while a variety of applications for alloy and metal surface analysis<sup>7,8</sup>, for gas<sup>9</sup>, liquid<sup>10,11,12</sup> and environmental sample analysis<sup>13,14</sup> have been reported. The greatest advantage of LIBS is that it provides simultaneous multi-element analysis, with no sample preparation in real time, within a minute or

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quicker. It can also be automated and does not require extensive operator training. Application of optical fiber techniques to this method enables the construction of a simple and compact device for real time remote sensing of solid, liquid and gaseous samples.

The purpose of this research is to demonstrate that by a proper optimization of experimental set-up in terms of laser pulse and sample delivery characteristics, sampling geometry, time-, spatially-, and spectrally-resolved detection system, a real time quantitative determinations of trace element concentrations in water by LIBS becomes feasible. In a previous publication, Cremers et al.<sup>10</sup> demonstrated direct LIBS detection of atomic species in water with detection limits of the order of several ppm for a number of atomic elements. Arca et al.<sup>11</sup> recently demonstrated the feasibility of quantitative determinations of trace elements in water by LIBS. However, the described experimental set-up utilized high energy (400 mJ) laser pulses focused on the free surface of the water sample. To avoid possible interference from bubbles formed by preceding spark, the system required a relatively low repetition rate (1Hz) and relatively long averaging acquisition time. Nakamura et al.<sup>12</sup> reported LIBS detection of Fe concentrations less than 20ppb using sequential laser pulses of two high rep rate (20Hz) Q-switched Nd:YAG lasers and continuous flow of water-purge gas aerosol.

The motivation of this study is to construct a simple, field operated LIBS instrument for fast in-situ analysis of heavy metals with a wide dynamic range of detection and sensitivity adequate for trace pollutant monitoring.

First, some of the specific problems will be discussed and the optimization of the experimental set-up will be described. Then, some results of actual analyses will be reported and suggestions for further improvements that are being planned, will be presented.

## 2. EXPERIMENTAL ARRANGEMENTS

- The overall system design is shown in Fig.1. The LIBS system consists of four principal components: laser breakdown

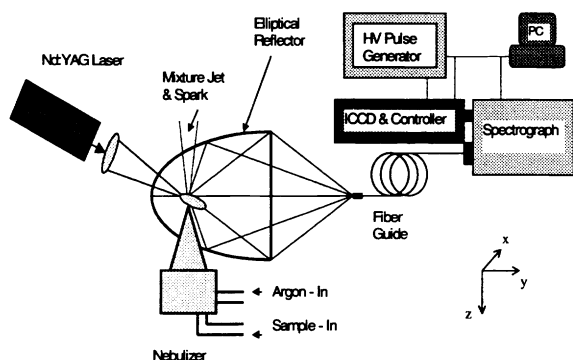


Fig.1a. LIBS System Design with argon-water aerosol sample delivery

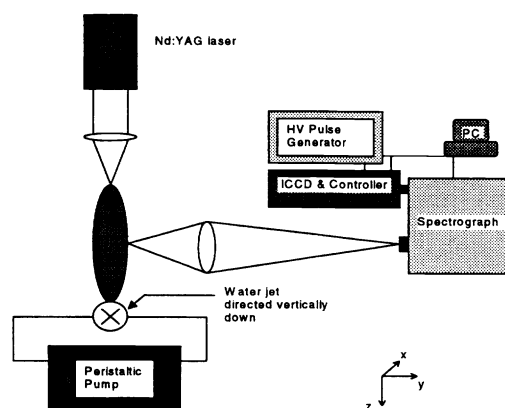


Fig.1b. LIBS System Design with direct generating plasma in the water jet of a continuously circulating sample

atomizing module, collection optics, spectrally selective, time resolved detection system - spectrograph-CCD detector (gated and intensified) combination, and data acquisition system (which is a controller- notebook computer combination). The operation principles are straightforward:

- The atomizing module serves as a reservoir of excited atoms. It includes a pulsed laser source and a system for sample delivery to the laser spark.
- Self-fluorescence of excited atoms is effectively collected and focused into the entrance slit of spectrograph.
- Fluorescence signal is spectrally selected there and acquired by a gated intensified CCD camera.
- The spectrograph and CCD camera are controlled by a personal notebook computer. The same computer is used to collect and analyze the experimental data. For greater flexibility in data acquisition and instrument control, we developed virtual instrument drivers based on the LabView<sup>®</sup> software for the Windows platform.
- A calibration curve for a particular instrument can be constructed from measurement of the amplitude or peak area of the fluorescence lines for different concentrations in a series of etalon samples.

The described experimental setup is based on a 0.75 m spectrometer ARC-750 (Acton Research Corp.), intensified TE-cooled 256x1024 CCD camera (Princeton Instruments), probe with fiber optic guide for signal transportation, and atomizer based on Nd:YAG laser (50-100 mJ @ 1.064 $\mu$ m, 7 ns pulse duration @ 10Hz, with injection seeding for temporally and spatially stable output pulse operation) generating plasma in the water jet of continuously circulating sample. In order to atomize the sample in the plasma plume we use two different methods for its delivery. In the first one (Fig. 1a.) the liquid solution containing the atoms to be investigated is drawn into the chamber of the nebulizer. It passes through the nozzle accompanied by argon gas along with formed aerosol and enters the plasma plume, which is generated by the laser spark in argon. The second approach (Fig. 1b.) is based on direct generating plasma in the water jet of a continuously circulating sample. Once in the plasma plume, the impurities are atomized and ionized and emit fluorescence that is collected by an elliptical mirror, directed through the fiber bundle to the slit of the spectrograph, and subsequently measured in real time with the multichannel detection system. Since the attainable signal is proportional to the fluorescence collection efficiency, it is important to optimize collection system. Our collection system uses an elliptical mirror, where the laser spark is generated near one of the focal points and the polished end of the multi-fiber bundle is placed into the second focal point. Elliptical mirror images atomic fluorescence into the polished end of the fiber bundle which transmits the collected fluorescence to the entrance slit of the spectrograph. The exit end of the fiber bundle is arranged to have a rectangular shape (4x0.1mm) to match it to the entrance slit. In our experiments, a TE-cooled 256x1024 CCD camera (Princeton Instruments), with a fiber-coupled intensifier was used for time-gated detection of fluorescence signal under pulsed laser excitation. Under normal conditions, the intensifier is "closed" and no photoelectrons reach the CCD detector. The pulse generator PG-200 (Princeton Instruments) produces a short high voltage (200 V) pulse to gate the detector for a 10-500  $\mu$ s exposure, 1-15  $\mu$ s after nanosecond laser pulse, allowing the continuum emission to decay. A single grating monochromator ARC-750 (Acton Research Corp.) with aperture ratio  $f/10$  and focal length 750 mm was operated as a spectrograph. The multichannel CCD detector was mounted at one of the output ports of the spectrometer. The spectral resolution of this system was estimated to be less than 0.04 nm at 633 nm for a 1200 g/mm grating measured with input slit width of 10  $\mu$ m. In our experiments, we used 2400 and 1200 g/mm gratings for UV and UV-VIS measurements, respectively.

As a preliminary test, we performed a series of measurements on various reference water samples, with the goal to find an optimum time delay from the laser pulse and the beginning of the LIBS spectra acquisition, as well as optimum gate duration. The importance of optimizing this time delay has been stressed in practically all the recent LIBS papers. Time evolution of the LIBS spectra of Cu (500 ppb)-contaminated water generated by the Nd:YAG laser radiation (1064 nm, 60 mJ) and measured at 1, 7, 15, and 25  $\mu$ s after the laser pulse is depicted in Fig.2.

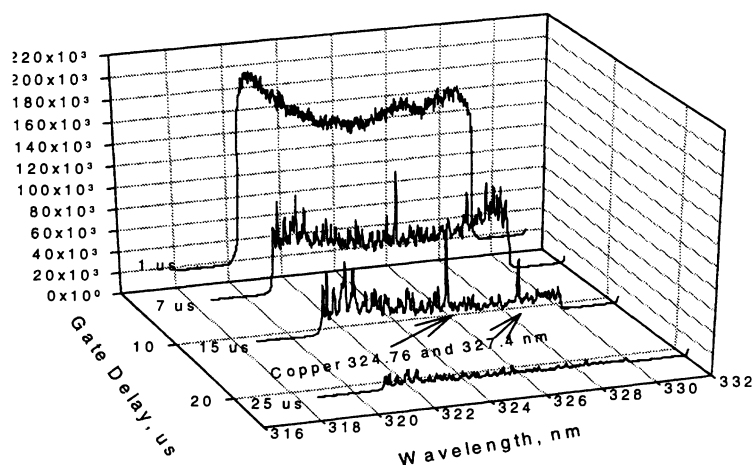


Fig.2. Time evolution of the LIBS spectrum for water containing 500 ppb Cu. Plasma is generated by Nd:YAG laser 1064 nm radiation in the water jet of continuously circulating sample. The spectra were obtained by averaging 30 acquisitions with a gate duration of 10  $\mu$ s.

Figure 2 demonstrates that the earlier stages of plasma discharge (gate delay <math> < 1\mu s </math>) are characterized by continuum emission. Only subsequent temporal stages of the plasma emission show gating off the continuum emission and appearance of the characteristic “fingerprint” line pattern of Cu atoms - 324.76 and 327.4 nm lines.

Recent work by Lee et. al<sup>6</sup> showed that the selection of the analytical location in the plasma is crucial for achieving the highest signal to background noise ratio of analytical atomic lines and to avoid self-absorption and line broadening. Fig.3 demonstrates our spatially resolved LIBS spectra of Cu (10 ppm)-contaminated water sample generated by the Nd:YAG laser and measured at distances of 5, 3, 2, 1, 0, and -1 mm from the continuously flowing water jet. These spectra were detected using the adjustable features of the atomizer (see Fig.1.b). Two XYZ mounts provided simultaneous and/or independent XYZ motion of the water jet and laser radiation focusing lens with respect to the fiber bundle or the input slit of the spectrograph.

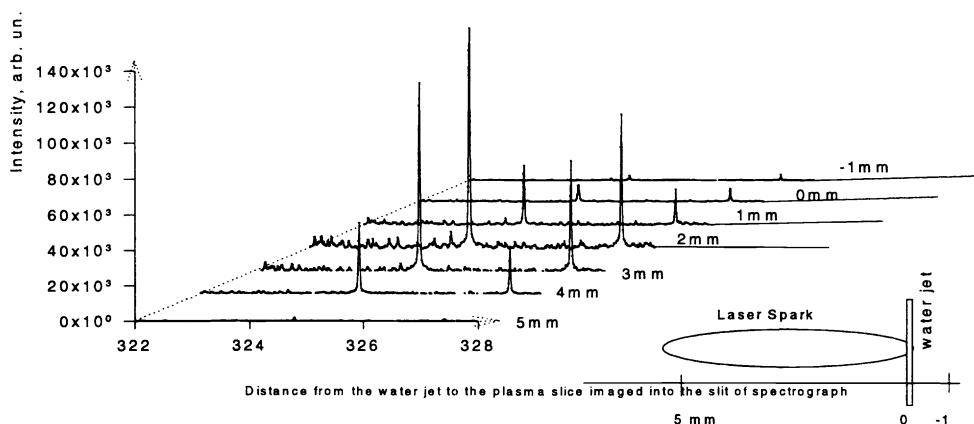


Fig.3. Spatially resolved LIBS spectrum of Cu (10-ppm) contaminated water sample generated by the Nd:YAG laser and measured at distances 5, 3, 2, 1, 0, and -1 mm from the continuous flowing water jet.

Fig3. clearly demonstrates that the highest signal to background noise ratio corresponds to the plasma slice located 2 mm in front of the water stream. This procedure has been repeated for different elements and we did not find any noticeable differences in spatial behavior of the optimal plasma locations.

## 2. RESULTS AND DISCUSSION

### 2.1. Water-argon gas aerosol LIBS measurements

LIBS testing of samples containing different concentrations of Al, Cd, Cu, Fe, Pb, and Zn, ions was performed. For quantitative analysis, additional reference water samples of known composition were measured with a Thermal Jarrell Ash AtomSPEC GF Workstation atomic absorption spectrophotometer (AAS). Actual concentrations of the heavy metals in samples were determined by comparison of the LIBS intensity of the characteristic lines of a given element to the corresponding intensities measured on the reference sample. Actual concentrations of the heavy metals in samples were also determined with the graphite furnace AAS.

The following is a summary of our results for the heavy metals tested in this experiment. Unless otherwise stated, the Nd:YAG laser was operated at an average power of 10 Hz with 100mJ energy per pulse. The resulting detection limits ranged from 2 ppm to 30 ppm. This is within the range of the TABLASER system delectability.<sup>15</sup> Sdorra and Niemax detected Mg samples as well as Zn samples at approximately the same wavelengths and intensities.<sup>16</sup> The results for each sample were graphed (concentration vs. relative intensity) to verify the validity of the experiment. Each element had a linear graph similar to that of Quentmeier, Sdorra, and Niemax.<sup>17</sup>

### 2.1.1. Aluminum (Al)

For Aluminum, the fluorescence signals at 394.4006 nm and 396.1520 nm were used. This emission transition was  ${}^2S_{1/2}(3s^24s) \rightarrow {}^2P^0_{1/2}(3s^23p)$  for 394.4006nm. The emission transition for 396.1520 nm was  ${}^2S_{1/2}(3s^24s) \rightarrow {}^2P^0_{3/2}(3s^23p)$ . The gate delay and width were optimized for best results to 15 $\mu$ s and 500 $\mu$ s, respectively. With the single laser system, the detection limit of Aluminum was approximately 30 ppm.

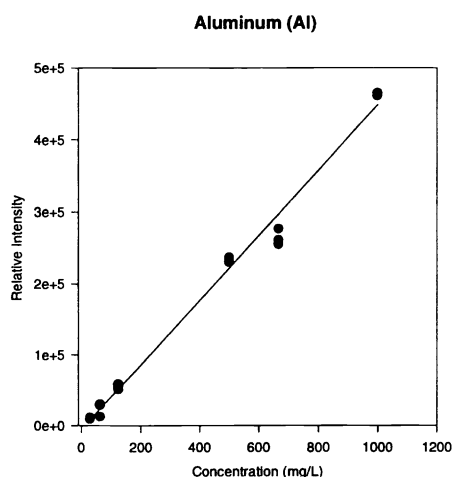


Fig.4. LIBS signal corresponding to Al line 394.4006 nm vs. LIBS determined concentration (mg/L)

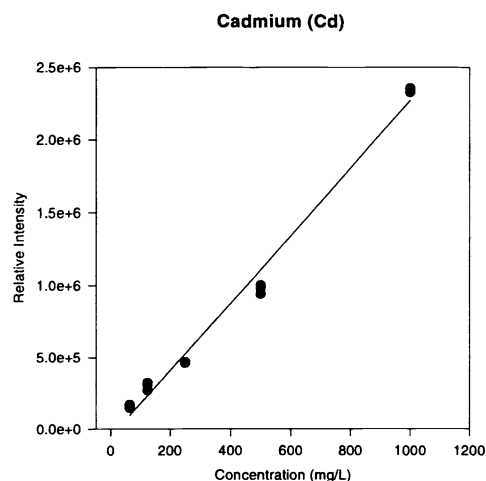


Fig.5. LIBS signal corresponding to Cd line at 228.8022 nm vs. LIBS determined concentration (mg/L)

### 2.1.2. Cadmium (Cd)

The optimum gate delay and width for Cadmium were 2 $\mu$ s and 250 $\mu$ s respectively. The fluorescence signal at 228.8022 nm was used. The limits of detection for Cadmium in this system were approximately 30 ppm.

### 2.1.3. Copper (Cu)

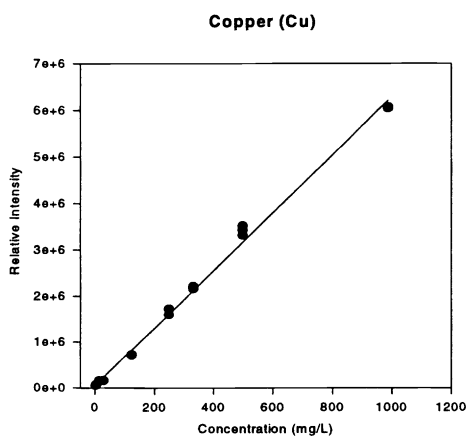


Fig.6. LIBS signal corresponding to Cu line at 324.754 nm vs. LIBS determined concentration (mg/L)

The copper fluorescence signals were detected at 327.3957 nm as well as 324.754 nm. The gate delay was optimized at 15 $\mu$ s and the gate width at 35 $\mu$ s. Copper had a detection limit of 3.25 ppm. The emission transition of copper detected at 324.754 nm was  ${}^2P^0_{3/2}(3d^{10}4p) \rightarrow {}^2S_{1/2}(3d^{10}4s)$ . The emission transition detected at 327.3957 nm was  ${}^2P^0_{1/2}(3d^{10}4p) \rightarrow {}^2S_{1/2}(3d^{10}4s)$ .

### 2.1.4 Iron (Fe)

Iron had an optimized gate delay and gate width of 24 $\mu$ s and 30 $\mu$ s respectively. Iron was detected at four wavelengths. Those wavelengths were 248.32718, 250.1132, 252.28505, and 256.6901 nm. Iron had a detection limit of approximately 30 ppm. The emission detected at 248.32718 nm was  ${}^5F^0_5 \rightarrow {}^5_aD_4(3d^64s^2)$ . The emission detected at 250.1132 nm was  ${}^7P^0_3 \rightarrow {}^5_aD_4(3d^64s^2)$ . The transition at 252.28505 nm was found to be  ${}^5_xD^0_3 \rightarrow {}^5_aD_4(3d^64s^2)$ . The last transition at 256.6901 was found to be  ${}^5_xD^0_4 \rightarrow {}^5_aD_4(3d^64s^2)$ .

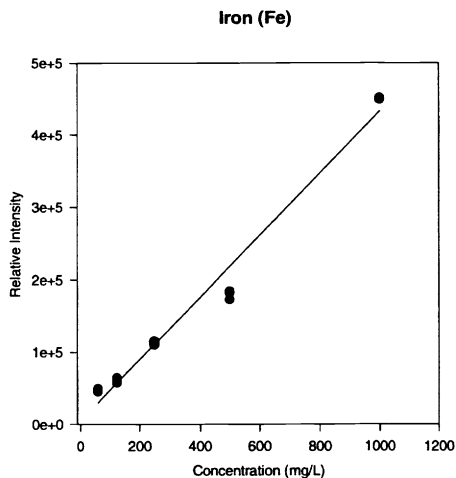


Fig.7. LIBS signal corresponding to Fe line at 248.327 nm vs. LIBS determined concentration (mg/L)

### 2.1.5 Lead (Pb)

Lead was detected at 405.7807 nm with a gate delay of 25 $\mu$ s and a gate width of 50 $\mu$ s. Once again, the delay and width were optimized to fit the element under investigation. Lead's limit of detection was found to be about 30 ppm. The transition of lead was shown to be  $^3P^0_1(6p7s) \rightarrow ^3P_2(6p^2)$ .

### 2.1.6 Zinc (Zn)

Zinc had an optimized gate delay and width of 10 $\mu$ s and 1 $\mu$ s respectively. Zinc was detected at 213.856 nm. This element had a detection limit of 30 ppm. Both clean and contaminated matrix samples of zinc were examined. They had approximately the same spectra and the same detection limits. This is especially important because it shows that the plasma generation system is not dependent on the sample's preparation.

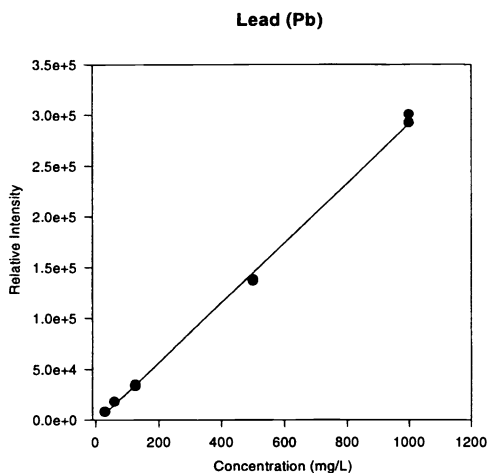


Fig.8. LIBS signal corresponding to Pb line at 405.78 nm vs. LIBS determined concentration (mg/L)

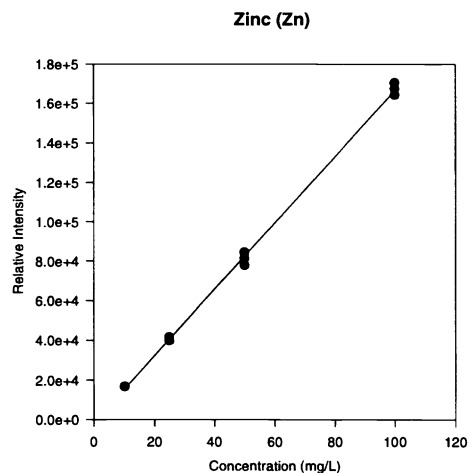


Fig.9. LIBS signal corresponding to Zn line at 213.856 nm vs. LIBS determined concentration (mg/L)

Our measurements confirmed the linearity of the LIBS signal vs. trace pollutant concentrations for samples containing Al, Cd, Cu, Fe, Pb, and Zn ions when compared with results using atomic absorption spectrophotometry. Initial indications showed good agreement (within 10%) between these two methods. The resulting detection limits (corresponding to S/N ratio of 3) ranged from 2 ppm to 30 ppm were not satisfactory for us. They can be improved by further optimization of sample delivery characteristics, sampling geometry, detection timing, and spectrograph throughput. The following results are related to optimization of sample delivery characteristics and substitution of Ar purge gas, featuring low ionization potential and small thermal conductivity, with an open air system. Our preliminary studies show that heavy metal atomic emission in Ar plasma is significantly suppressed with respect to atomic line emission in air or He plasma.

## 2.2. LIBS measurements when plasma is generated in the water jet of continuously circulating sample.

LIBS testing of samples containing known concentrations of Cu and Cr ions was also performed. For quantitative analysis, reference water samples were measured with a Thermal Jarrell Ash AtomSPEC GF Workstation atomic absorption spectrophotometer (AAS) with graphite furnace. Actual concentrations of the heavy metals were determined by comparison of the LIBS intensity of the characteristic lines of a given element to the corresponding intensities measured using the reference samples. All the samples were also characterized with AAS. The experimental results are depicted in Fig.10.

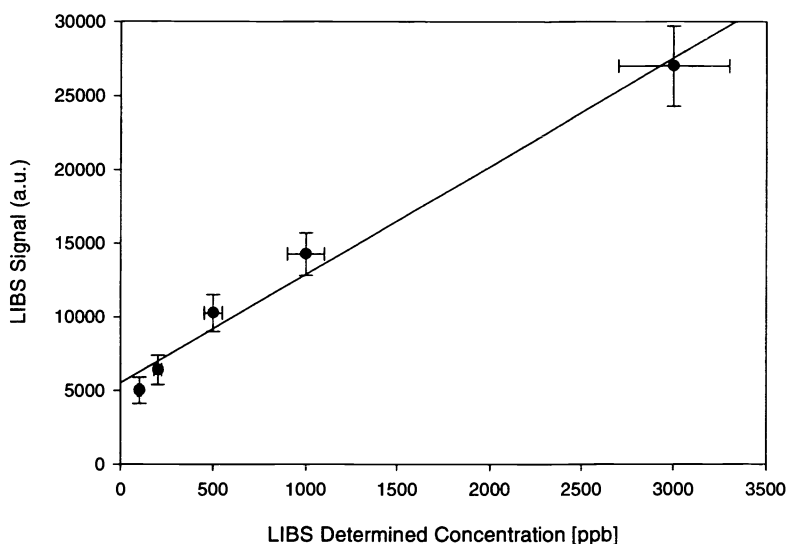


Fig.10. LIBS signal for Cu polluted water vs. LIBS determined concentration (ppb). The results correspond to Cu atomic line at 324.754 nm.

Results demonstrated in Fig.10 confirm the linearity of the LIBS signal vs. trace pollutant. The experimental error for Cu concentration measurements was found to be around 10%. Detection limits of 100 ppb for Cu and Cr atoms were achieved.

The US Environmental Protection Agency has established a primary drinking water goal for Cu (40 CFR D Subpart F 141.51) of 1.3 mg/L (ppm), and a secondary drinking water quality MCL (maximum contaminant limit) of 1.0 mg/L. The US EPA drinking water goal is 170 mg/L for  $\text{Cr}^{+3}$  and 50  $\mu\text{g/L}$  (ppb) for  $\text{Cr}^{+6}$ . The criteria for Cu for the protection of aquatic life is about 10 ppb, and for  $\text{Cr}^{+6}$  is about 200  $\mu\text{g/L}$ , for typical hardness levels. Therefore, the achieved detection limits for these metals are likely quite suitable for evaluations of drinking water safety and for the protection of aquatic life (especially after additional slight optimization). The LIBS results are therefore very important in view of applications for in-field continuous monitoring of water.

## 3. CONCLUSIONS

In conclusion, the results reported in this paper demonstrate the following:

- LIBS is a feasible technique for real time monitoring of trace element detection in water.
- The method described here provides direct and continuous determinations of Cu and Cr in water as low as 100 ppb, less than or close to the US EPA criteria for Cu and Cr in drinking water and for the protection of aquatic life.

- The wide dynamic range of LIBS detection makes it very attractive for in-field monitoring of water quality with different level of pollution without need for special sample preparation.
- Simple cell-less sample delivery results in easy handling.
- Continuously circulation or pumping of new sample water provides an opportunity for on-line measurements and suppresses interferences from bubbles formed by the preceding sparks.

The achieved detection limits gives promises for a new application of LIBS for sensing biological warfare agents. It is proposed to tie the detection of bioagents (e.g. anthrax spores) to the detection of heavy metal atoms that can be selectively attached to the spores. The method is pretty straightforward and is completely analogous to fluorescently labeled antibodies biosensing. Antibodies are substituted by special ligands featuring selective affinity to anthrax spores and instead of dye labeling, one may use heavy metal microspheres. The size of the metal microsphere (4 $\mu$ m) can be chosen to match the average size of the anthrax spores. So, in average, each spore will be bonded to one metal microsphere. Simple calculations show that each metal microsphere of 4  $\mu$ m size contains about  $10^{12}$  atoms of metal. A 100 ppb level of detectability of the method corresponds to  $\sim 10^{15}$  atoms/cm<sup>3</sup>, or 1000 spores per 1 cm<sup>3</sup> of water. For an ambient air intake volume of 10 m<sup>3</sup> forced through 10 cm<sup>3</sup> of water in the accumulation chamber, the final detectability of the proposed system turns out to be  $\sim 1000$  spores/m<sup>3</sup>, which is lower than health danger levels. The metal detection limits, and the corresponding detection limits of the bioagents, can be further significantly improved by the combined use of laser breakdown atomization with resonant laser excitation of metal atoms.

## REFERENCES

1. R.S. Adrain and J. Watson, "Laser microspectral analysis; a review of principles and applications" *J. Phys. D; Appl. Phys.*, **17**, 1915 (1984)
2. L.J. Radziemski and D.A. Cremers, *Laser-induced Plasmas and Applications*, Chapter 7, M. Dekker, New York, 1989.
3. L. Moenke-Blankenburg, *Laser Microanalysis*, J. Wiley & Sons, New York, 1989.
4. V. Majidi and M.R. Joseph " Spectroscopic applications of laser-induced plasmas", *Critical Review in Anal. Chem.*, **23**, 143 (1992)
5. D.A. Rusak, B. Castle, B.W. Smith, and J.D. Winefordner, "Fundamentals and applications of laser-induced breakdown spectroscopy", *Critical Review in Anal. Chem.*, **27**, 257, (1997).
6. Young-III Lee, Young-Jae Yoo, J. Sneddon, "Recent advances in laser-induced breakdown spectroscopy", *Spectroscopy* **13**, 14-21, 1998
7. D.A. Cremers, "The analysis of metals at a distance using laser-induced breakdown spectroscopy" *Appl. Spectrosc.*, **41**, 572-578, 1987.
8. K.J. Grant, G.L. Paul, J. O'Neill, "Quantitative elemental analysis of iron ore by laser-induced breakdown spectroscopy", *Appl. Spectrosc.*, **45**, 701, 1991.
9. D.K. Ottesen, J.C.F. Wang and L.J. Radziemski, "Real-time laser spark spectroscopy of particulates in combustion environments", *Appl. Spectrosc.*, **43**, 967-976, 1989.
10. D.A. Cremers and J.R. Wachter, "Determination of uranium in solution using laser-induced breakdown spectroscopy", *Appl. Spectrosc.*, **41**, 1042-1048, 1987.
11. G. Arca, A. Ciucci, V. Pallschi, S. Rastelli, and E. Tognoni, "Trace element analysis in water by the laser-induced breakdown spectroscopy technique", *Appl. Spectrosc.*, **51**, 1102-1105, 1997
12. S. Nakamura, Y. Ito, K. Sone, H. Hiraga, K. Kaneko, "Determination of an iron suspension in water by laser-induced breakdown spectroscopy with two sequential laser pulses", *Anal. Chem.*, **68**, 2981-2986, 1996.
13. K.Y. Yamamoto, D.A. Cremers, M.J. Ferris, and L.E. Foster, "Detection of metals in the environment using a portable laser-induced breakdown spectroscopy instrument", *Appl. Spectrosc.*, **50**, 222-233, 1996
14. A. Ciucci, V. Pallschi, S. Rastelli, R. Barbini, F. Colao, R. Fantoni, A. Palucci, S. Ribezzo, H.J.L. van der Steen, "Trace pollutants analysis in soil by a time-resolved laser-induced breakdown spectroscopy technique", *Appl. Phys. B*, **63**, 185-190, 1996
15. R.M. Measures and H.S. Kwong, "TABLASER: trace (element) analyzer based on laser ablation and selectively excited radiation," *Applied Optics* **18**, 281-286, 1979.
16. W. Sdorra and K. Niemax, "Temporal and spatial distribution of analyte atoms and ions in microplasmas produced by laser ablation of solid samples", *Spectrochimica Acta* **45B**, 917-926, 1990.
17. A. Quentmeier, W. Sdorra, and K. Niemax, "Internal Standardization in Laser induced Fluorescence Spectrometry of Microplasmas Produced by Laser Ablation of Solid Samples", *Spectrochimica Acta* **45B**, 537-546, 1990.