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Chapter 1

SPECTROSCOPIC TECHNIQUES FOR HIGH SENSITIVITY HEAVY METAL DETECTION IN THE LIQUID PHASE

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ABSTRACT

Heavy metal toxins and pollutants are a serious environmental and security concern affecting safe drinking water and public health in general. LIBS provides a powerful tool for detection of such threats but generally requires enhanced techniques in order to achieve the required ppb sensitivity levels for detection of such threats. A number of enhanced LIBS techniques have been developed recently and will be discussed in this chapter. These techniques include a dual laser pulse technique, Laser-Ablation Laser-Induced Fluorescence (LA-LIF), and sample pre-concentration techniques employing either absorbent sampling sticks or electrolytic deposition of species on metal electrodes. These techniques can be deployed using low energy laser pulses of the order of 4 μ J to 4 mJ which would be suitable for the development of portable systems using high efficiency diode pumped, high repetition rate lasers. In particular the detection of lead in water is discussed in detail and current resultant limits of detection (LOD) presented. The limits of detection of all three techniques were determined to be on the order of 7 to 30 ppb (3 sigma) allowing for the detection of lead contamination at the 15 ppb North American drinking water standard.

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1. INTRODUCTION

Heavy metals represent an important set of elements required for many processes and functions in modern society. However, at the same time they represent a significant risk to human health and environment [1-4]. In some cases they could also pose a security threat to our water supplies and systems. Thus it is important that simple, robust and preferably real time techniques be developed to both properly manage but also properly monitor these elements in our environment. The required levels of detection must be at a sensitivity level sufficient to measure these elements at the maximum safe threshold levels which are allowable in the environment, which typically are in the parts per billion (ppb) level [5-6].

Emission spectroscopy is a very powerful and sensitive technique for detecting any element in the periodic table. However, in general the species must be prepared in some manner in order to carry out the spectroscopic measurement. Laser ablation is one general method of vaporizing and atomizing samples from any starting state whether it be liquid, solid or gaseous. It requires no sample preparation and in principle allows any element to be easily measured by recording the emission spectrum from the excited atoms or ions in the vapour plume.

In general, the sensitivity of standard ablation spectroscopy techniques such as Laser Induced Breakdown Spectroscopy (LIBS) [7-11] is of the order of several parts per million (ppm) which is well above the parts per billion (ppb) sensitivity required for detecting hazardous heavy metals in the environment. Thus extra techniques must be employed in order to achieve the required sensitivities. These could include excitation at ultraviolet wavelengths, the use of resonant excitation of the atomic species or sample concentration techniques as outlined in this chapter. At the same time, ablation of liquid samples generally is more difficult than ablation of solid surfaces due to the high transmission of most liquid samples requiring high intensities to achieve breakdown. Additional complications can arise due to mechanical disruption of the fluid surface which can lead to splashing, difficulty in maintaining the focus at the surface of the sample and contamination of optical surfaces. Various means to mitigate such effects include the use of liquid jets, liquid droplets or microfluidic platforms.

With the aim of developing techniques which can be employed in field measurements it is also desirable to employ low energy microjoule to a few millijoule laser pulses which can be readily generated in compact, efficient, diode pumped laser systems. In order to improve the overall signal to noise one can take advantage of the potential repetition rates of such systems to achieve low limits of detection by averaging over thousands of shots. Such systems are currently available either in the form of microchip or fibre-optic lasers.

While detection of environmental contaminants at the part per billion level is still challenging and generally requires special techniques to enhance the spectroscopic signals, recent results have indicated that such detection is readily achievable. We have investigated three such techniques in detail: 1) using laser ablation followed by laser induced fluorescence (LA-LIF) [12]; 2) using absorbent wooden sampling sticks to concentrate the species on the surface after evaporation [13, 14] and; 3) using electrolytic sample concentration techniques [62, 64].

This chapter will review and outline the above approaches to measuring heavy metals in liquid samples and the limits of detection achieved to date with such techniques. It will

conclude with a comment on future directions and the possible practical implementation of these techniques to serve the needs of protecting our health and the environment.

2. PREVIOUS WORK

Optical spectroscopic techniques probing atomic transitions in atoms can readily be used to detect and identify individual atomic elements due to the unique energy transitions and spectral signatures of each atomic element. LIBS has been applied to the analysis of a number of contaminants in water as reported in several of studies in the past and outlined below. One particular species of interest is monitoring of lead in drinking water because of its prevalence in a number of city water systems with old metal distribution pipes. On-line real-time monitoring of hazardous contaminants in water is possible with LIBS but, in general, analysis of liquid samples is not as well studied as solid target samples because of increased difficulty in breaking down liquid samples. According to the United State Environmental Protection Agency, the action level (AL) for lead in drinking water is 15 ppb by weight [15]. Excessive ingestion of lead can result in physical or mental development delays for children and high blood pressure and kidney problems for adults [16]. Common techniques for measuring the lead content is by inductively coupled plasma mass spectrometry (ICPMS) or graphite furnace atomic absorption spectrometry (GFAAS). These techniques can achieve sensitivities ranging from 0.01 to 0.1 ppb [17,18]. However, the testing can only be conducted in a laboratory, which requires that samples be taken and sent to laboratories for testing, typically with inherent delays of several days before results are know. Fiddler *et al.* [19] has also described the different laser spectroscopy techniques to detect elements in solid, liquid, gases and aerosols. In contrast, LIBS is potentially a real-time portable technique which can be applied directly in the field.

There are a number of advantages of using water samples over solids such as, aqueous solutions do not suffer from spatial inhomogeneities caused by micron scale size precipitates and there is no permanent damage of the sample by the LIBS process. Thus, water samples provide good test cases for the investigation of the fundamental properties of LIBS. One drawback of using liquid as a target sample is that often the samples are somewhat transparent with little absorption at the entrance interface and thus higher fluences are normally required to achieve breakdown in liquids compared to solid surfaces. Detection of contaminants in water has been reported using LIBS in a variety of sampling geometries including water jets [20-25] and breakdown within a bulk water sample [26-27]. One of the earliest studies dealing with analysis of liquid solutions using LIBS was reported by Cremers *et al.* [28]. Using Nd:YAG laser pulses and detection of spectrally resolved light by a photomultiplier tube (PMT) they achieved a limit of detection for many trace elements at levels better than 1 $\mu\text{g/mL}$. The best LOD of 0.006 $\mu\text{g/mL}$ was achieved for Li. In this case the laser was focused inside the liquid samples. Arca *et al.* focused 1064 nm laser pulses on the surface of water and measured LOD's of few ppm for Ca, Mg and ~ 100 ppb for Cr [26]. P. Fichet *et al.* used a pulsed laser and focused with a tilted angle on the surface of the liquid to determine the concentration for twelve elements (Pb, Si, Ca, Na, Zn, Sn, Al, Cu, Ni, Fe, Mg and Cr) [29]. Two different liquid matrices were used such as water and oil. The detection

limits achieved were in the range of 0.3–120 $\mu\text{g/mL}$ with Ca having the best LOD of 0.3 $\mu\text{g/mL}$.

Typical limits of detection (LODs) for trace elements in water samples are in the ppm range well above the required sensitivities for monitoring drinking water and pollution in lakes and rivers. Also if one wants to employ lower energy pulses the LOD climbs higher. For example, a pulse energy of 260 μJ [30] gives an LOD of 75 ppm by weight whereas a pulse energy of 22 mJ gives 12.5 ppm [27]. In the latter report, using an excimer ($\lambda=308$ nm) pumped dye-laser system producing 28ns, 22 mJ pulses, Knopp *et al.* has achieved the best limit of detection (LOD) for lead in water using conventional LIBS to date of 12.5 ppm [27]. They also obtained LOD's for Li, Na, Ca, Ba and Cd in aqueous solutions of 0.0075 to 500 ppm. Another study using UV laser pulses by Lo *et al.* achieved an LOD as low as 300 ppb [25]. In this study, an ArF laser at 193 nm was used, and the LIBS signal was accumulated over 500 shots with 14 mJ laser energy per pulse. In their earlier study [31], it was found that the 193 nm laser pulses can enhance the atomic emission and reduce the continuum background in aqueous sample, compared with 532 nm pulses due to the very short absorption length of the order of 20 microns in the solution of this far UV wavelength [25]. Charfi *et al.* have reported LOD's of 1 and 2 ppm by weight for Mg and Na solutions respectively using 200 mJ, 7 ns laser pulses [32]. Loudyi *et al.* have obtained LOD values of 19 ppm for Pb and 37 ppm for Fe in their LIBS measurement by averaging over 100 laser shots [33]. Yuan Feng *et al.* demonstrated detection of Pb in a $\text{Pb}(\text{NO}_3)_2$ aqueous solutions with an LOD of 60 ppm when observing the Pb I emission line at 405.78 nm by using 532 nm, 10 ns laser pulses of 57 mJ energy [34].

Further enhancement of signals can be obtained using dual pulse LIBS. Rifai *et al.* have used dual pulse LIBS to detect Pb, Fe and Au where they showed that LOD's of 6 ppm could be obtained for Pb in water using 32 mJ energy for the first pulse and 200 mJ for the second pulse whereas, conventional single shot LIBS gave only 74 ppm using laser pulses of 32 mJ energy [35]. In their experiment the plasma was generated by using a UV (266 nm) frequency-quadrupled 7 ns Nd:YAG laser pulse and then reheated by a 7 ns 1064 Nd:YAG laser in a quasi-collinear geometrical configuration. In general, it is found that direct LIBS or dual pulse LIBS has a sensitivity level in the ppm range which is sufficient to monitor heavy metal contaminants in industrial processing situations or in the monitoring of direct effluent streams from such processing before dilution in the external environment. However, higher sensitivities are required for assessment of drinking water and environmental pollution levels.

One technique to obtain higher sensitivity is the direct excitation of a particular transition in the element of interest. In order to do this requires that the element be in an atomic state where excitation to an upper state from the ground state can be achieved. Fluorescent emission directly back to the ground state or to another lower excited state then can be detected as a signature of the transition. This process has been called Laser induced Fluorescence (LIF) [36] or Laser Excited Atomic Fluorescence Spectroscopy (LEAFS) [37-39]. One technique for preparation of the element in the atomic state is by means of laser ablation of a small sample spot and waiting until the ablation plume has cooled upon expansion but has not started to recombine into molecular species or clusters. At this optimum point in time the atoms can be excited by a narrow linewidth laser pulse tuned precisely to a resonant transition and the fluorescent emission observed promptly thereafter. This process which is closely related to LIBS has been called Laser Ablation Laser Excited Atomic Fluorescence Spectroscopy (LA-LEAFS) [12,40] or Laser Ablation Laser Induced

Fluorescence (LA-LIF) [13,41]. A limited number of previous studies have been reported to date using these techniques.

LA-LIF has proven to be an effective technique for measurement of trace elements in both solid and liquid samples. In one of the earliest reports, Kwong and Measures used the LA-LIF technique in the year 1979 to determine the concentration of chromium in metal alloys and organic substances at the ppm level [42]. After this initial work there have been a number of reports in literature that use the technique to improve the sensitivity over that of single pulse LIBS. Sdorra *et al.* carried out LA-LIF on steel samples [43] and Bondybey and English used the LA-LIF technique to study the spectroscopic and structural properties of metallic diatomic molecules [44]. Gornushkin *et al.* used this technique to determine concentrations of cobalt in soil, steel, and graphite samples in open air [45]. Detection of uranium in glass sample at a concentration of 462 ppm was demonstrated by Shen *et al.* [46]. In another publication they measured concentrations of lead in the range 0.15–750 ppm by weight in copper, brass, steel, and zinc by laser excited atomic fluorescence combined with UV laser ablation in a low-pressure (130 mbar) argon atmosphere [40]. The mass of the material ablated was determined by repetitive weighing of the target prior to and after approximately 10,000 ablating shots. A relative limit of detection of 72 ng/g was obtained for the determination of lead in copper, brass, steel, and zinc. The technique was also used to determine the concentration of lead in ultrafine aerosols by Neuhauser *et al.* [47].

For water samples, Koch *et al.* used the technique to measure the concentration of indium in bulk water samples [48] at a level of 10 ppm. Ho and Cheung demonstrated a sensitivity of 0.25 ppb for lead in colloid form, which propagated slower in the plume thus resulting in a more concentrated region in the expansion plume [20]. Atomic fluorescence from this region was emitted when excited by a 193 nm ArF laser. Loudyi *et al.* obtained LOD's of 39 ppb and 65 ppb for Pb and Fe respectively [33] using over 100 laser shots and laser energies of the order of 40 mJ for the ablation pulse and few ten's of μJ for the excitation pulse. In a different experiment determination of Pb concentration in water with an LOD of 4.3 ppm was achieved using 100 shots [30] and 35 ppb when 10,000 shots were employed [12]. LeBihan *et al.* have employed laser fluorescence with an optical parametric oscillator (OPO) to develop an analytical method for the direct determination of lead content in seawater by electrothermal atomization-laser-excited atomic fluorescence (ETA-LEAF) [49]. The best LOD for lead achieved by this technique was 0.3 ng/L by averaging 20 shots, which is the best reported laser induced fluorescence sensitivity for detection of Pb in water that we are aware of. It can be seen that the LA-LIF technique can achieve higher sensitivities into the ppb range as compared to LIBS itself and thus would be one approach to achieving sensitivities sufficient to assess the safety of drinking water directly.

In a related technique, Atsushi Kitano *et al.* demonstrated highly sensitive liquid electrode plasma atomic emission spectrometry (LEP-AES) by using a combination of a quartz glass microfluidic chip and sample flow system to investigate the LOD's for Cd and Pb [50]. In this process a sample solution is put into a microfluidic channel with a very narrow central space ($\sim 100 \mu\text{m}$ width) between two reservoirs. Two electrodes are in the two reservoirs at the ends of this channel. A high voltage, few millisecond pulse of $\sim 1500\text{V}$ was applied across the two electrodes heating the solution and creating a vapor bubble in the narrow channel region which ionizes and produces a discharge plasma. By analyzing the spectrum of that plasma they achieved LOD's of 0.52 $\mu\text{g/L}$ for Cd and 19.0 $\mu\text{g/L}$ for Pb under optimized conditions.

Another approach to achieving higher sensitivities with LIBS is to concentrate the analyte to be measured prior to carrying out the LIBS probing. In the past the results from a few such sample concentration techniques have been reported. These include the pre-concentration of analytes on a variety of porous substrates, such as paper [51-55], membranes [56-58], wood sampling sticks [14, 59], carbon disks [60] and bamboo charcoal [61]. In addition, electrolytic methods can be used to concentrate the metal cations from the aqueous sample to the surface of a metal [62-66]. Although the pre-concentration approach requires extra extraction steps before the LIBS analysis, it converts the liquid sample to a solid leading to an increase of the effective analyte density and avoids the water splashing and quenching of the plasma plume which can occur in the liquid sample.

Table 1. List of limits of detection (LODs) reported using different absorbent substrates (*Reported in mg/L, which is converted to ppm by weight in the aqueous sample)

| Substrate | Analyzed material and LOD (ppm) | Ref | Comments |
|-----------------------------|---|-----|--|
| Wood | Cr (0.034), Cu(0.029), Cd(0.59), Pb(0.076) | 59* | |
| Wood | Pb (0.113) | 14 | Different laser wavelengths were used |
| Paper | Ag(1), Al(4), Cd(4), Cr(12), Cu(1), Fe(3), Mn(3), Mo(5), Ni(20), Ti(5), V(2), Zn(2), Pb(3) | 51 | Oil samples. Double laser pulses LIBS |
| Ion Exchange Membranes | Ba(0.13), Cd(0.21), Cr(0.13), Cu(0.0042), Pb(1.1), Hg(2), Ni(3.1), Ag(0.43), Zn(0.85) | 56* | Filtration through a membrane |
| Membrane-based filter paper | Sm(1.3), Eu(1.9), Gd(2.3) | 52 | |
| Filter paper | Pb(0.075), Cr(0.018) | 53 | Totally evaporated a glass of water. Argon flow assisted |
| Paper | Ca(1.9), Mg(3.2) | 54* | |
| Filter paper | Na(0.9), Fe(0.5), Cu(0.4) | 55 | Oven assisted pre-concentration. Ethanol samples |
| PVC membrane | Cu(0.015) | 58* | pH 6.0 sodium acetate buffer solution |
| Amorphous graphite | Mg(0.01), Al(0.01), Si(0.01), Ca(0.01), Ti(0.01), Cr(0.1), Fe(0.01), Co(>0.1), Zn(1), As(5), Cd(0.1), Hg(10), Pb(2) | 60 | 75 Torr argon buffer gas |
| Bamboo charcoal | Pb(8.5) | 61* | |

Vander Wal *et al.* deposited the lead solution sample onto a carbon planchet and then evaporated the water. The residue left was probed by LIBS, and a sensitivity of 2 ppm for lead was obtained [67]. In a different approach, X. Hou *et al.* [68] used preconcentration of Cd, Ni, Cu, and Pb metals on a chelating solid-phase extraction disk and then determined the LOD by X-ray fluorescence spectrometry. The limits of detection for Cd, Ni, Cu, and Pb were 3.8, 0.6, 0.4, and 0.3 ng/mL, respectively. The concentration of samples by absorption in a porous medium such as paper or wood has been studied by a few groups and the reported LODs are in the ppm and sub-ppm. A summary of such studies is given in the Table 1. Among these studies, the best LOD of lead was found to be 0.075 ppm using filter paper by Y. Lee *et al.* [69]. In this work, a filter paper was placed at the bottom of a glass of sample solution, and the solution was totally evaporated to concentrate all the analyte on a filter

paper. In the other works, the absorbent substrates were placed in the aqueous sample to absorb some of the analyte, or in a few cases a few drops of sample were dropped on the substrate.

A second major technique for sample concentration is through electrolytic techniques which is particularly suitable for metal ions in solution. In this technique, two metal plates with a potential difference are placed in the solution; the metal ions can then be attracted and pre-concentrated on the surface of the cathode. In general, the electrolytic method has sensitivity in the ppb level, which is better than using absorbent substrate, according to the reported LODs as listed below. This is due to the fact that 1) the applied electric field can guide the metal ions actively to the surface and 2) the pre-concentrated ions stays mostly on the surface of the cathode, where the LIBS technique is suitable for surface analysis. It is also noteworthy that a sub-ppb LOD was achieved from the work of Z. Chen *et al.* [62] and F. Zhao *et al.* [65]. In their studies, the laser spot was slightly defocused to excite a larger amount of analyte for each shot. A summary of such studies is given in the Table 2.

Table 2. List of detection limits reported using electrolytic pre-concentration
(*Reported in ppb, which is converted to ppb by weight in aqueous sample)

| Analyzed material and LOD (ppb) | Ref | Comments |
|---|-----|---|
| Cr (0.57), Mn(0.37), Cu(0.083), Zn(5.6), Cd(0.53), Pb(0.52) | 62* | Laser pulse was slightly defocused to increase the excited area |
| Cu(16) | 63 | Compared ion replacement reaction with electric field guiding pre-concentration |
| Pb(6.4) | 64 | Microchip laser of 4 μ J and 8 kHz repetition rate was used |
| Cr(0.32), Mn(0.18), Cu(0.16), Zn(1.4), Cd(0.79), Pb(0.57) | 65* | Sample was prepared with tap water. Laser pulse was slightly defocused |
| Hg(11) | 66* | Circulation of liquid was applied |

Other attempts to convert the liquid sample to solid phase have also been reported. Pace *et al.* have converted aqueous solutions of Cr, Pb, Cd and Zn into solid pellets of calcium hydroxide by mixing with CaO. Therefore, liquid sample analysis was replaced by solid matrix analysis [70]. They used 160 mJ Nd:YAG laser pulses to obtain detection limits for Cr, Pb, Cd and Zn in the range of 1–120 ppm. Caceres *et al.* have carried out analysis of trace elements in frozen water samples using a quick freeze drying procedure [71], which shows the possibility of detection of Na and Al in water sample with the sensitivity limits of the order of a few ppm. According to Sorbal *et al.* [72], after converting the water sample to ice, the LIBS sensitivity can be improved by 3 to 9 times, and the LODs of Cd, Fe, Mg, Cr, Cu, Hg and Pb reached the 0.3-3.7 ppm level.

Overall past results have indicated that the detection of contaminants in water is possible at the ppb level. However, optimization of techniques and system parameters is required in order to achieve such results. In the following sections we present recent studies on the LA-LIF and sample concentration techniques with low energy laser pulses that would be feasible to carry into the field for real time, in-situ measurements.

3. LA-LIF TECHNIQUE

LA-LIF has been carried out with a variety of laser systems observing different emission lines in the past [12, 14, 40-48]. In the interest of developing field portable systems for measurement of water contamination in the future we have focused on an initial investigation of lead contamination in water with the use of low energy, 100 μJ to 300 μJ laser pulses, a regime referred to as microLIBS [73]. Such a technique should be amenable to the development of portable systems based on diode pumped high repetition rate lasers (either fiber or microchip based) together with precisely tuned excitation wavelength lasers based on current fiber optic wavelength division multiplexing techniques [74]. An initial goal is the reliable assessment of Pb contamination at the 15 ppb level which is a common standard in North America for allowed levels in drinking water.

To achieve such sensitivity accumulations of the order of 1,000 - 10,000 laser shots may be required. In the technique of Laser-Ablation Laser-Induced Fluorescence (LA-LIF) an ablation plume is created from the edge of a water jet sample containing a low concentration of Pb. After the plume has expanded in air for several hundred nanoseconds a second pulse tuned to a resonant absorption line of atomic lead at 283.3 nm is used to probe the plume with resultant fluorescence detected at 405.8 nm.

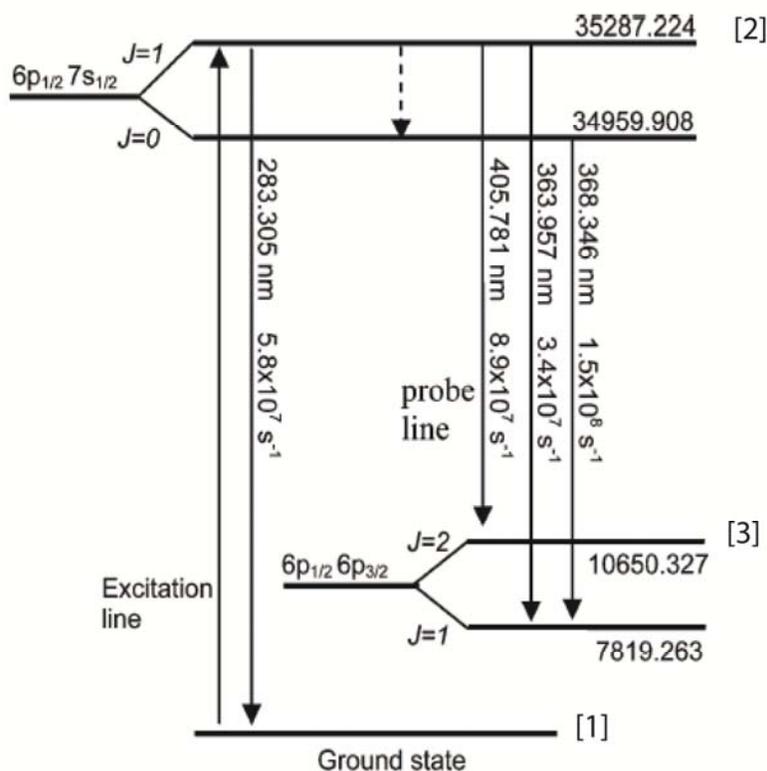


Figure 1. Energy levels of a Pb atom indicating the excitation at a wavelength of 283.305 nm and observation of emission at 405.781 nm [13].

The excitation scheme used for lead is shown in Figure 1 and is typical for excitation of species using the LA-LIF technique. In this case the excitation is at a wavelength of 283.305nm and emission is observed at the fluorescent transition at 405.871 nm. The excitation pulse was generated in a XeCl excimer laser pumped dye laser. The absorption cross sections are very strong for transitions from the ground state and thus it is relatively easy to excite the free atoms to the upper excited state with a few microjoules of energy and one can start to saturate the free atoms in the ablation plume with only 10 microjoules of excitation laser energy [13].

The experimental layout used for the LA-LIF experiments probing lead in water is shown in Figure 2. The laser ablation pulse was generated by a frequency-quadrupled flash lamp pumped Q-switched Nd:YAG laser (Big Sky Ultra CFR) at 266 nm with a pulse width of 10 ns. Typical pulse energies of 100 to 300 microjoules were used. The pulses were focused by a microscope objective lens (Optics For Research, 10x, 15 mm working distance, NA 0.25) to approximately a 10 micron spot on the water jet surface. The objective was protected by a microscope cover slip slide. It was found that this cover slip required cleaning on the order of every several 10,000's of shots. For longer experimental shot sequences it is expected that either a movable cover slip or a thin disposable plastic film cover could be employed instead. The liquid sample was flowed through a 1 mm nozzle and the laser focused onto the side of the liquid stream. The Pb was introduced into the water in the form of a lead salt, typically lead nitrate, The concentrations of solutions are given in ppm or ppb by weight and at low concentrations were checked by measuring the samples using Inductively Coupled Mass Spectroscopy (ICPMS) analysis.

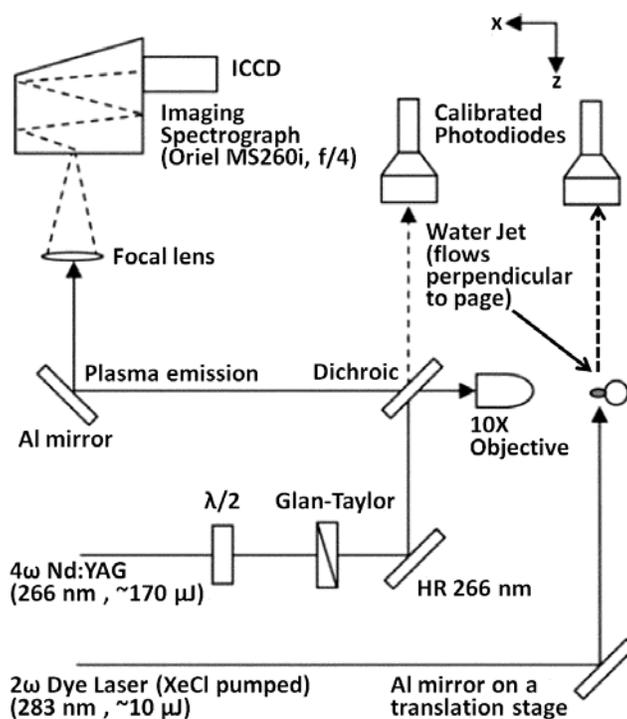


Figure 2. The experimental layout for the LA-LIF measurement [13].

An excitation probe pulse of the order of 10 μJ in energy was produced by frequency doubling the output of a XeCl pumped tunable dye laser (Lumonics HD-500, rhodamine 575 dye). This 9 ns probe pulse was focussed with a long focal length lens to a spot size of the order of 240 μm diameter at right angles through the ablation plume. The emission light was collected through the 10x objective and focused with a 20 cm focal length lens onto the entrance slit of a 0.25 m f/3.9 imaging spectrometer (Oriel MS260i) equipped with an intensified CCD (Andor iStar DH720). A grating of 2400 line mm^{-1} was used and the slit width was typically set at 300 μm , yielding a spectral resolution of the order of 0.45 nm. Precise tuning of the excitation pulse was obtained by observing the LIBS emission from the water sample at higher Pb concentrations where the three lines at 280.19 nm, 282.31 nm and 283.305 nm are observed as shown in Figure 3(a). The probe wavelength was then tuned to precisely overlap the third emission line. An example of the probe spectrum is shown in Figure 3(b). Since the ablation plume is still hot at the time of probing, the linewidth is expected to still be significantly broadened which reduces the requirement for a very narrow linewidth source and very precise frequency alignment. The temporal separation ΔT between the laser pulses was controlled by a delay generator (Stanford DG535) and the ICCD was also gated at slightly earlier time before the probe pulse with a 400 ns gate width to collect the emission.

Initial studies optimized the gate delay and width for the standard single pulse LIBS signal alone indicating a 3 sigma limit of detection ($3\sigma\text{-LOD}$) for a 100 shot accumulation of the order of 70 ppm by weight for a 260 μJ excitation pulse. The $3\sigma\text{-LOD}$ is defined as the sample concentration which would give an emission signal which is 3 times the standard deviation noise in the measured signal [13].

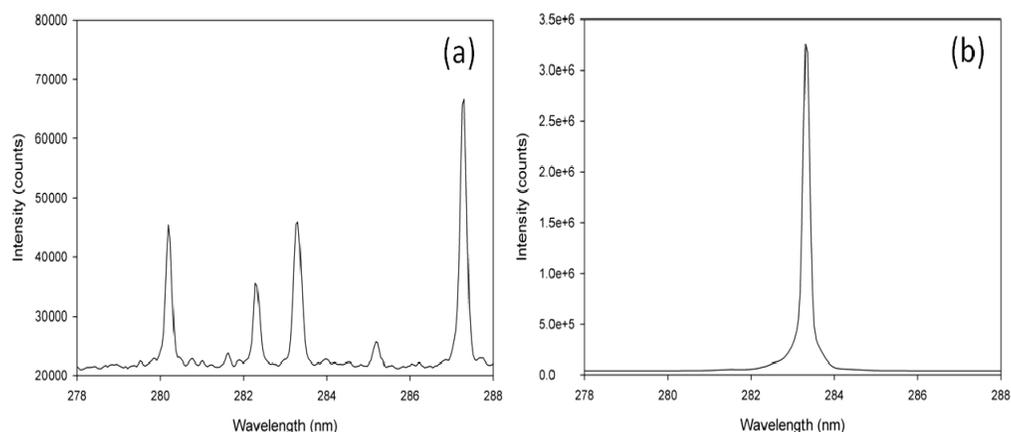


Figure 3. (a) The LIBS emission spectrum of Pb is shown. Three emission lines at 280.19 nm, 282.31 nm and 283.305 nm are observed from Pb. (b) The probe pulse spectrum from the dye laser at 283.305 nm is shown. A 2400 l/mm grating was used in both cases [13].

A number of measurements were taken to determine the $3\sigma\text{-LOD}$ for Pb in water. These include measuring the SNR for various concentrations of Pb in water over the range of 1 to 1000 ppm and taking 100 or 1000 shot accumulations. Also the SNR for a 5ppm sample of Pb was measured with accumulations of 100 to 10000 shots. The latter measurement demonstrated the $N^{1/2}$ scaling of SNR expected for statistical sampling with an increasing

number of shots, N , as shown in Figure 4. This scaling with number of shots is a critical result which can be exploited by using high repetition rate, low energy excitation lasers in the future. The LOD determined from three different experiments are given in Table 3 where it can be seen that a consistent value of the order of 35 ppb was obtained when scaled to 10,000 shot accumulations.

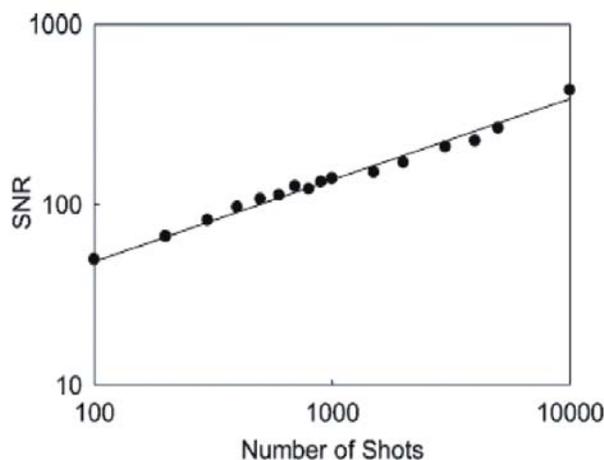


Figure 4. Relationship between number of accumulated shots and the S/N. Data were taken for a Pb concentration of 5 ppm and $\Delta T=300$ ns. The line is a least squares fit to an $N^{1/2}$ slope scaling law.

Table 3. Summary of the LODs from the measurements scaled to 10000 shot accumulations using a $N^{1/2}$ SNR scaling law with number of shots [12]

| Measurement Series | LOD scaled to $N = 10,000$ (ppb) |
|--------------------------------------|----------------------------------|
| 100 shot data | 35 ± 7 |
| 1000 shot data | 36 ± 7 |
| Scaling with $N_{\text{shot}}^{1/2}$ | 35 ± 8 |
| Average | 35 ± 7 |

A summary of typical sensitivities, both LIBS and our LA-LIF result, for measuring Pb in water by previous groups and ourselves is given in Table 4 when scaled to 100 shot accumulations. It can be seen that the use of LA-LIF has increased the sensitivity by the order of 200 times as compared to straight LIBS using our 260 μJ excitation energies. The use of a double pulse LIBS by Pu *et al.* also shows fairly high sensitivity and again is on the order of 3 times more sensitive than the single pulse LIBS results of Lo *et al.* at similar excitation pulse energies of 16 to 18 mJ. This double pulse sensitivity is slightly better than our LA-LIF result but with combined laser pulse energy of 74mJ which is 274 times our combined laser pulse energy of 270 μJ . Thus the LA-LIF technique allows ppb level sensitivity using 100 microjoule level laser pulses which otherwise would require 10 - 100 mJ level laser pulses which are not very compatible with portable kHz repetition rate systems.

Table 4. Summary of the LODs reported for Pb from literature including our results scaled to 100 shot accumulation

| Group | LOD | Laser Pulse Energy | Technique | Reference |
|--------------|-----------|--------------------------|-------------------|-----------|
| Present work | 75 ppm | 260 μ J | μ LIBS | 30 |
| Knopp | 13 ppm | 27 mJ | LIBS | 27 |
| Taschuk | 6 ppm | 45 mJ | LIBS | 73 |
| Arca | 100 ppm | 500 mJ | LIBS | 75 |
| Lo | 0.894 ppm | 16 mJ | LIBS | 25 |
| Pu | 0.304 ppm | 18 mJ +56 mJ | Double Pulse LIBS | 76 |
| Present work | 0.353 ppm | 260 μ J + 10 μ J | LA-LIF | 12 |

Further investigations were carried out using filtered photomultiplier and filtered avalanche photodiode array detectors. Since the LA-LIF technique is looking for one element at a time the use of a filtered single channel detector gives almost as much information as a spectrometer and is much simpler and less expensive to implement. In addition they allow the collection of light over a much larger solid angle and thus in principle can lead to higher signal to noise ratio with near single photon detectors.

The first system investigated was based on a standard (Hamamatsu R7518) photomultiplier tube (PMT) operated at a bias of 900V and an electron gain of $\sim 10^6$. A large collection angle, $f/0.8$, aspheric lens was used to collect the emitted light and image onto the PMT. A line filter with a center wavelength of 405.8 nm and a bandwidth of 2 nm was used to filter the incident light on the detector. A suitable delay time must be chosen so that both the self plasma emission has decayed away and the detector itself has recovered from the initial plasma emission. In the present case a delay time of 300 ns was employed for a 260 μ J excitation pulse. A 1 ppm solution of Pb was measured yielding a 100 shot accumulation SNR of 43 leading to a 3σ -LOD of 70 ppb. A typical signal is shown in Figure 5(a). In this case there is no limit to the potential repetition rate used since a fast gated integrator can be used to save the signal on every shot and summed in a second integrator system. Thus for a 10,000 shot accumulation a 3σ -LOD of 7 ppb could be achieved. In principle, a higher gain photomultiplier could be employed with a high voltage gating circuit to reduce sensitivity to the initial plasma emission, potentially yielding a more sensitive LOD.

The second detector investigated was a multi-pixel photon counter (MPPC) which basically is an avalanche photodiode (APD) array where single photon sensitivity could be obtained on each single photodiode element. The detector used had an array of 10 by 10 elements each 100 μ m square (Hamamatsu model S10362-100U). The same light collection system was employed for the MPPC as for the PMT detector but the MPPC has a much smaller active detection area of 1 mm² whereas the beam size of the imaged emission region was ~ 6 mm². Thus only a fraction of the photons imaged were detected in this case. One advantage with the MPPC is the high quantum efficiency (45%) which leads to a higher signal compared to the ICCD and the PMT. Another advantage in using the MPPC over the PMT is the lower power requirements for the MPPC for the same gain. Thus the MPPC would be ideal in a portable water monitoring system for Pb. A typical signal pulse measured by the MPPC detector is shown in Figure 5 (b). The measured 100 shot accumulation 3σ -LOD for a 1 ppm Pb solution was 103 ppb. If we had collected all the light onto the APD

surface then it would be expected that the measured 3σ -LOD would improve to 42 ppb for 100 shots making it potentially the most sensitive detector combination available. This would lead to a potential 10,000 shot 3σ -LOD of 4 ppb. Again, the detector would have no trouble measuring at high repetition rate as the measured recovery time for the array was on the order of 130 ns. This quick recovery time also allowed the recovery from the initial continuum emission from the plasma before the probe time which was set at a delay time of 300 ns after the initial plasma formation.

Overall, the results indicate that LA-LIF can meet the requirements for detection of heavy metals such as Pb in water at sensitivity levels below those for safe drinking water if high repetition rate lasers are employed.

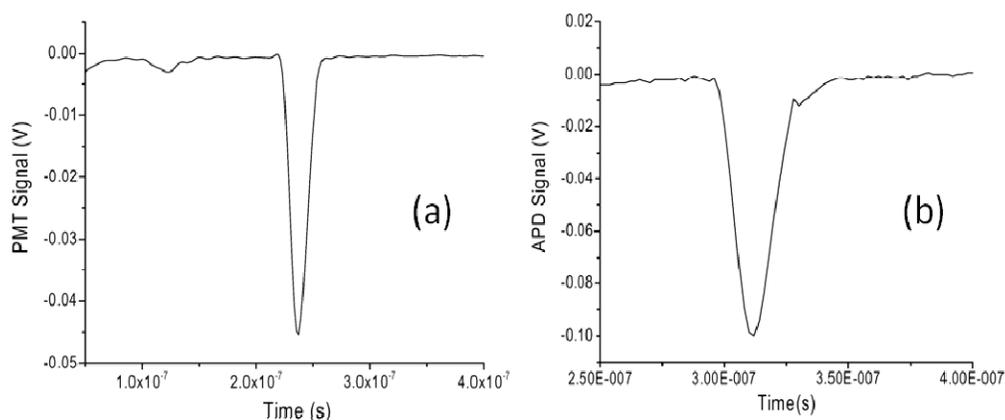


Figure 5. Measured laser induced fluorescence signals. (a) Pb emission signal measured using a PMT for an accumulation of 100 shots. The ablation laser energy was 260 μ J the probe laser energy was 8 μ J and (b) Pb emission signal measured using a MPPC for an accumulation of 100 shots. The ablation laser energy was 260 μ J the probe laser energy was 8 μ J. The interpulse separation was 300 ns in both cases.

4. SAMPLE CONCENTRATION ON POROUS SURFACES

A simple technique for concentration of aqueous samples is by dipping a porous absorbing sampling plate into the liquid sample and letting the sample plate dry. As it dries, the absorbed solution is wicked back to the surface concentrating any dissolved or suspended constituents back to the surface. This then leads to an enhanced concentration of such constituents on the surface with the advantage of carrying out measurements on solid surfaces, which is usually easier than on liquid surfaces. As discussed above this technique has already been investigated by a few groups with encouraging results. To date, wood slices, carbon substrates and paper absorbing filters have been explored. These are all relatively easy to handle and are capable of achieving a low LOD. For example, it has been reported that, by use of wood substrates, different types of heavy metal, such as lead, chromium, copper, and cadmium in water can be detected to an LOD at the sub-ppm level using single laser pulses of 1064nm with an energy of 100mJ [59]. In more recent work we have focused on investigating

this technique with lower laser pulse energies of $\sim 2\text{-}5$ mJ, which is more favorable for portable LIBS systems for in situ analysis

Measurements were carried out using small, 7 mm by 50 mm, wooden sampling sticks (coffee stirring sticks) which were immersed in the water solution for a period of 15 minutes and then dried for a period 10 to 20 minutes on a hotplate until the absorbed water evaporated, leading to enhanced concentration of any contaminants on the surface of the sticks due to the wicking of the water to the surface during drying. LIBS measurements were then performed on the surface of the sample using 2-4 mJ energy laser pulses of 10 ns duration with wavelengths of 266, 532 and 1064 nm. The whole procedure could be carried out in a period of approximately 30 minutes and could be sequenced for a continuous sequential stream of samples if working in the field.

The experimental layout for measuring the samples is illustrated in Figure 6. The emission from the plasma plume was imaged onto an ICCD spectrograph. Millijoule energies were required here to obtain consistent breakdown on the porous surface of the sampling sticks. Samples were prepared by dissolving lead nitrate in de-ionized water, and the solutions were homogenized by a magnetic stirrer before use. We prepared solutions with concentrations from 0.2 to 50 ppm for the measurements.

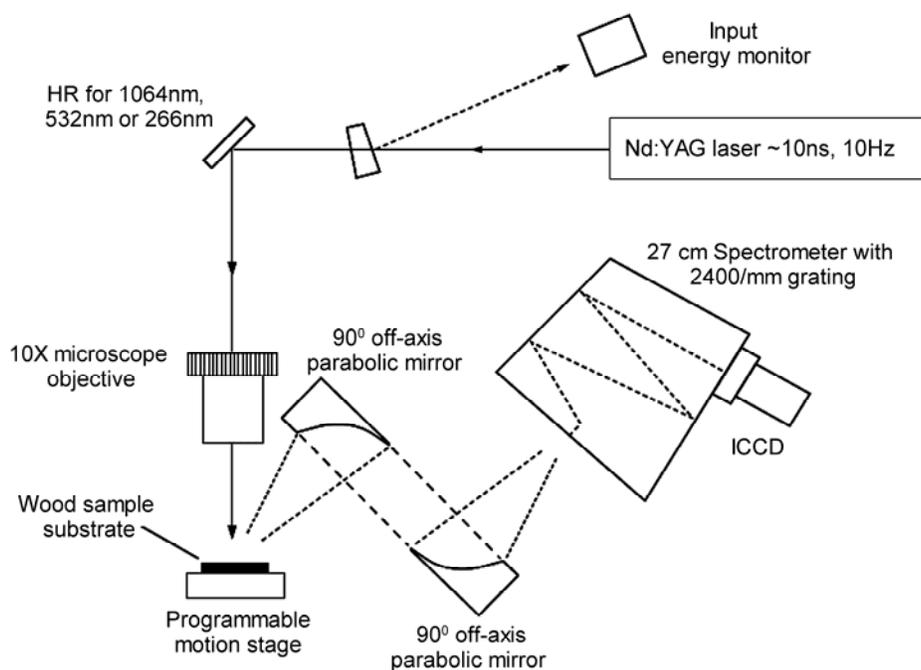


Figure 6. Illustration of the experimental setup for scanning the porous samples and measuring the LIBS spectra.

The laser pulses were focused with a 10 x microscope objective onto the sample surface with a focal spot of the order of $10\ \mu\text{m}$ in size on the surface with ablation spot size varying from 15 to $50\ \mu\text{m}$ depending on the energy and wavelength of laser pulses [14]. The samples were mounted on a motorized stage which was translated at $1.2\ \text{mm/s}$ leading to a separation of the order of $120\ \mu\text{m}$ between two consecutive spots to guarantee no overlap of spots. The

405.8 nm line of lead was measured with integration of the emission in a 0.75nm bandwidth line in the ICCD spectrometer detector.

For the three different wavelengths, 266, 532, and 1064 nm, the breakdown thresholds were determined to be $\sim 13 \mu\text{J}$ and $800 \mu\text{J}$ and 2 mJ respectively. For the 1064 nm wavelength there was approximately a 60% probability of breakdown at 2.2mJ pulse energies since the initiation of breakdown is more stochastic at longer wavelengths. After optimization of gate widths and sample times the LOD was found for the case of 100 shot accumulations as shown in Table 5. It can be seen that the best LODs obtained were for the case of 532 nm illumination with 3.5 mJ laser pulses where an LOD of 113 ppb was achieved which could lead to an LOD of 11.3 ppb if a 10,000 shot accumulation was used.

Table 5. Limits of detection measured for different wavelength excitation pulses with sample concentration on wooden sample sticks using 100 shot accumulations with sample concentrations ranging from 200 ppb to 50 ppm. Also, the LOD determined from a single sample of 20 ppm Pb taken with 1000 shots is given

| Wavelength (nm) | 266 | 532 | 1064 |
|---------------------------------------|-----|-----|------|
| 100 shot LOD (ppb) | 147 | 113 | 131 |
| Expected 1000 shot LOD (ppb) | 45 | 36 | 41 |
| 1000 shot LOD of 20 ppm samples (ppb) | 33 | 35 | 34 |

In order to confirm this sensitivity a sample of 200 ppb Pb, in water, was measured using the 532 nm excitation wavelength as shown in Figure 7.

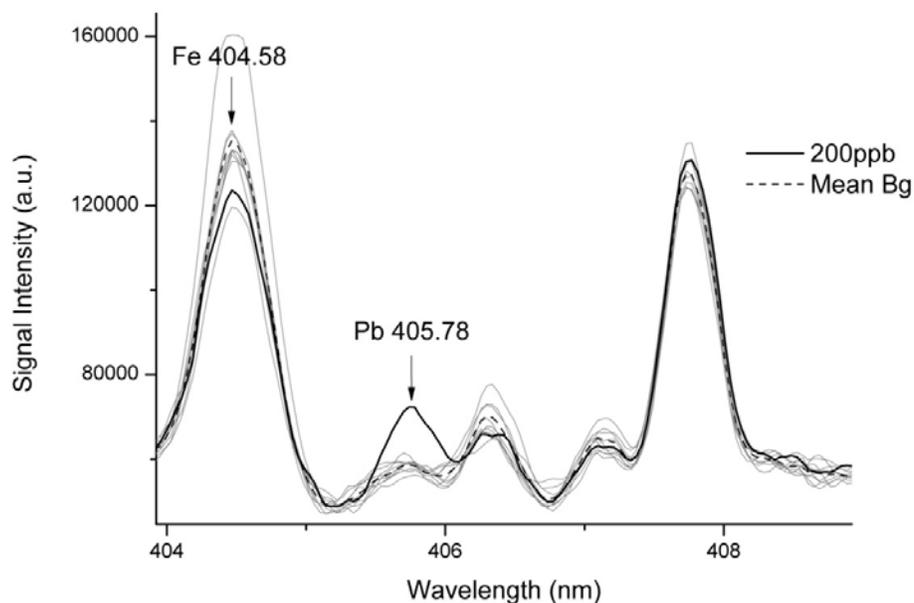


Figure 7. Measurement of the background emission of 10 different runs (light grey lines) and the emission from the wood substrate that has been dipped in 200 ppb lead solution (solid black line) by 100 shot accumulations with 532 nm pulses at an average energy of 3.5 mJ. The average of background signal is given by the black dashed line. An SNR of 6 is obtained.

The range of fluctuations in the background signal can be observed from the multiple samples of background taken. One can observe both the continuum emission (baseline) and line emission of other elements which lead to variations in the region of the 405.78 nm Pb line. However the Pb line is clearly much higher than the fluctuation level in this wavelength region. The background emission around the lead emission line (405.7 nm) also contains weak contributions possibly from the manganese lines at 405.55 and 405.89 nm. By subtracting the mean value of background emission from the lead line emission signal, the residual signal yields a SNR of 6 and a 100 shot 3σ -LOD of 100 ppb. If the wood chips would have no background line emission around 405.8 nm, the background fluctuations could be further minimized, and the SNR could be further improved.

The concentration by evaporation could lead to different response to species in dissolved form versus those in particle or nanoparticle form. It is conceivable that the latter species could be concentrated more on the surface than even the dissolved species. In addition, it is known that the use of femtosecond laser pulse LIBS leads to enhanced sensitivity to a thin surface layer [77] with little or no damage on the substrate [78], and thus might yield even higher sensitivity for the concentrated species on the surface. The results might also be improved further by use of artificial manmade porous surfaces that are finer in grain size, more uniform from batch to batch and with little background signal compared to wooden sampling sticks. Thus, it is expected that the sensitivity of this technique can be improved further. Additional studies in the future will be required in order to investigate these possibilities.

5. SAMPLE CONCENTRATION BY ELECTROLYTIC TECHNIQUES

The second technique for concentrating the elemental species dissolved in water is by means of electrolytic deposition on pure metal electrodes. This technique coupled with LIBS was demonstrated by Chen *et al.* [59] in 2008. They demonstrated sub-ppb LOD's for elements such as Cr, Cu, Mn, Zn, Cr and Pb. The trace metal atoms were electrically deposited on the surface of a high purity aluminium plate for a few minutes and quantitatively analyzed by LIBS using multi-mJ laser pulses. For ultrahigh purity testing this technique can be very effective as the preconcentration is very sensitive to the dissolved ions in the water.

In our recent investigation of this technique we have again focused on extending these results to the use of microjoule laser pulses at high repetition rate. The samples were collected by using two aluminum electrodes in water and passing current through the electrodes for a period of 15 minutes. A voltage of 6 V was applied across the electrodes in order to drive the current. It should be noted that the operating voltage and current depends on the conductivity of the solution and thus requires some adjustment and control if higher concentration or more conductive samples are measured.

After accumulation, the cathode electrode was dried and mounted on a spinning stage for LIBS analysis using an 8 kHz repetition rate microchip laser as shown in Figure 8. In this case the spinning stage was taken from a hard disk drive from a personal computer system and rotated at 5,400 rpm. The passively Q-switched Nd:YAG microchip laser delivered 4 μ J, 1.3 ns duration pulses at 1064 nm at a pulse repetition rate of 8 kHz. The signal was

integrated for 20 ms at a time and 1000 such signals added together giving an effective accumulation time of 20 seconds with no time gating using the ICCD spectrometer system. Thus the signal corresponded to an accumulation of 160,000 laser shots.

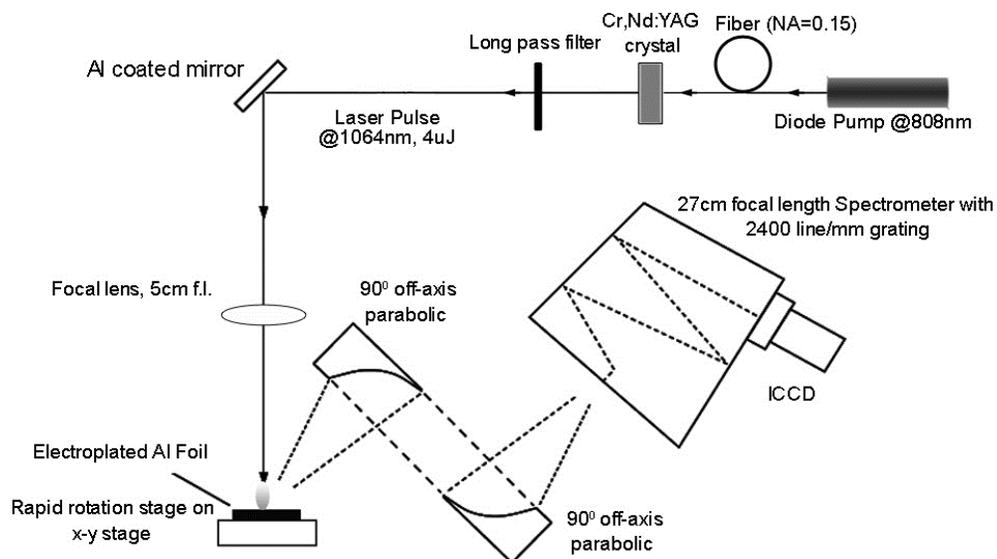


Figure 8. Experimental setup for μ LIBS using electrolytic pre-concentration. A microchip laser operating at 8 kHz repetition rate, 1064 nm and with 4 μ J pulse energy is also shown in the diagram.

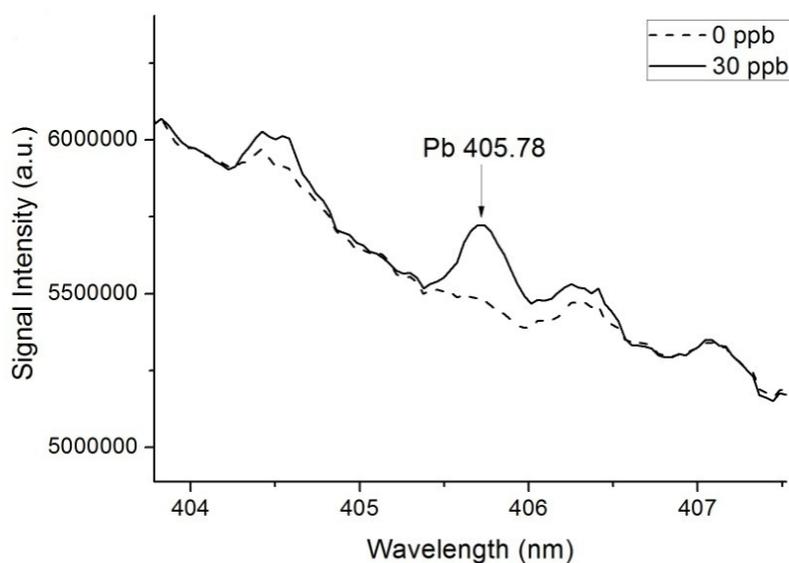


Figure 9. Measured signal and background using electrolytic concentration from a 30 ppb sample of Pb in water.

Figure 9 shows the measured signal and the background signal obtained using this setup for a sample containing 30 ppb Pb dissolved in water. The concentration of the sample was verified using ICP-MS. The SNR of this spectrum was 14 which correspond to a 3σ -LOD of 6.4 ppb. This initial result indicates this technique has great potential to increase the sensitivity of μ LIBS and make it a more widely acceptable technique. However during these measurements we observed that if the solution contained high concentrations of the heavy metals, more gas bubbles would be generated. These gas bubbles attached onto the surface of the aluminum plate and thus interfered with the further deposition of the metals. A similar observation was reported by [59]. In the study by Zhao *et al.* [65], tap water was used as background solution to simulate the actual condition of drinking water, and a rotational cathode was used to remove the bubbles during the pre-concentration efficiently. Their study also indicated that the hardness of the water can affect the sensitivity of this technique, and the calibration requires the knowledge of hardness of the aqueous sample. Further work is required in order to address these issues when implemented in real applications.

6. FUTURE DIRECTIONS

While the results discussed above already indicate the growing potential for enhanced LIBS techniques in the realtime analysis of heavy metals in water there is still considerable scope for further improvements in sensitivities obtained and to expand the scope of techniques employed.

One major area of investigation is the extension of the above measurements to other important metal samples such as Cr, Cu, Zn, Mo, Mn, Cd, Va and Hg and also to non-metallic contaminants such as As. The later is of particular importance for countries where arsenic is a significant contaminant in ground water. Thus suitable excitation and emission wavelengths must be chosen and studied for each element for the LA-LIF technique. For many species the upper state lifetimes are on the order of nanoseconds and thus it may be possible to re-excite the same atom several times in one ablation plume with longer excitation laser pulses of the order of 100 ns, leading to an increased number of detected photons and improved LOD. An optimization of the collection of light onto APD array detectors should also lead to improved signal to noise ratios and more sensitive detection of contaminants. In the experiments of Zhao *et al.*, trace heavy metal ions in tap water were measured by electrolytic deposition on the surface of a high purity aluminum rod and then analyzed with LIBS. The LOD's for Cr, Mn, Cu, Zn, Cd and Pb in tap water samples yielded sub ppm LODS [65].

Alternative techniques for delivering liquid samples for the LA-LIF measurement techniques are also under development. Droplet liquid sources have been used in many different laser ablation applications including laser driven high harmonic [79] and xuv radiation sources for next generation short wavelength EUV lithography [80]. Such sources can be timed to be synchronous with high repetition laser sources. Also the size of microdroplets can be as small as 20 microns allowing over 100,000 spectra to be accumulated per microliter of liquid sample if every droplet is irradiated. Our studies using a piezoelectrically driven microdroplet source [13] have indicated that the LA-LIF signal increases up to a droplet size of around 20 microns and then levels off for the conditions used for the LA-LIF experiments reported above.

Another delivery system of interest for micro samples is the use of microfluidic systems. While LIBS or laser ablation is difficult to carry out directly inside the channels it is possible to extrude droplets out of the channel under command similar to an inkjet printer nozzle. This can be done either using a piezoelectric pulser or a thermal heater. Initial experiments have been carried out to investigate this technique using a custom designed thermal heater to extrude droplets on demand out of an outlet hole on the top of the microfluidic chip and LIBS spectra were demonstrated on these extruded droplets [81]. It was determined that the droplet extrusion time was on the order of 25 μs and thus sampling rates of up to 10 kHz should be possible for systems. Just as for the piezo droplet source the actual amount of liquid sample required could be in the range of several microliters for data accumulations of 100,000 shots.

While microchip lasers and fiber lasers already are available as ablation pulses for the LA-LIF technique, the generation of suitable narrow linewidth 10 μJ class excitation pulses at the precise wavelengths required will require further development work. One potential architecture would be to employ diode seed laser sources which can be amplified and frequency converted to the required wavelengths. An initial demonstration of such a diode pumped fiber laser system has been developed with a frequency output at 386 nm, the 4th harmonic of 1544 nm, as illustrated in Figure 10. In this case, an ablation pulse energy of 50 μJ at 1550 nm and an excitation pulse energy of 1 μJ at 386 nm was obtained in 100 ns width pulses at a repetition rate of 10 kHz. The system was fabricated mainly from telecommunication type components which are relatively inexpensive and very robust. In future improvements the energies can be increased by a factor of 4 times by the addition of another large mode area fiber amplifier stage and the pulse width shortened by 10 to 100 times by the use of a faster pulsed DFB diode laser. The system illustrates that such systems are feasible and could easily be packaged in a portable battery powered system. The most difficult challenge is obtaining the laser source wavelengths such that the 4th harmonic will match the required excitation wavelength. For example to meet the requirement for the excitation of lead atoms at 283.3 nm requires a source laser at 1133.2 nm. This is just at the end of the possible tuning range for Yb: fiber lasers and might require mixing of one photon from a 1550 nm laser and 3 photons from an 1040 nm Yb: fiber laser (frequency summing and then frequency summing again). While this would require two narrow linewidth source lasers and associated amplifiers it is still readily achievable using current fiber laser technology. With current advances in laser technology we expect that such techniques could be employed in the near future for real time detection of heavy metal contamination in the environment and drinking water.

In the case of concentration of contaminants on porous sample collectors, a number of additional improvements can be envisaged. More uniform manmade porous substrates such as porous carbon. Ion exchange membranes [52, 56] may have better uniformity than natural substrates and perhaps could lead to lower background signals and more reproducible signals from shot to shot which could improve the measured signal to noise ratio. In addition the use of a dark surface for such collectors, which would have a lower breakdown threshold, would allow lower energy laser pulses to be used in such systems. Femtosecond lasers have demonstrated enhanced detection of surface contaminants due to their limited interaction depth and thus could prove valuable for both the porous sample and electrolytic sample concentration techniques since they both concentrate the analyte onto a solid surface.

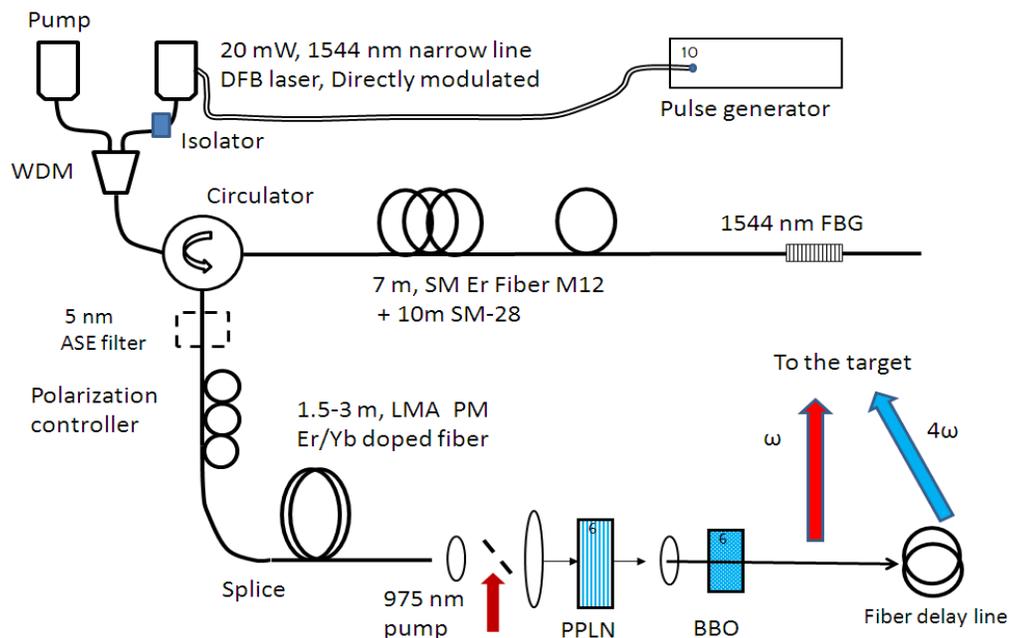


Figure 10. High repetition rate fiber laser based system as a prototype system for LA-LIF detection of heavy metals [74].

CONCLUSION

Studies of detection of heavy metals in water have been carried out using microjoule to few millijoule laser pulses suitable for future portable detector systems. Using the LA-LIF technique, measurements have been carried out at different concentrations of lead and it has been found that 3 sigma limits of detection of 35 ± 5 ppb, 7 ± 2 ppb and 10 ± 3 ppb could be obtained for the cases of ICCD, PMT and APD detectors respectively when scaled to 10,000 shots. Using sample concentration on the wooden sampling sticks, accumulated measurements of 100 shots were carried out leading to a 3 sigma LOD of 113 ppb which would scale to 11 ppb for accumulation of 10,000 shots. Finally, when using electrolytic concentration technique a signal was acquired at a repetition rate of 8 kHz for a period of 20 s with 3σ -LOD of 6 ppb. These results are consistent with previous work reported in the literature, mainly using much higher energy pulses.

It appears that enhanced LIBS and Laser induced emission spectroscopy techniques can be applied to the measurement of heavy metal contaminants in water at the ppb level. The development of portable measurement systems can now be envisaged in the near future for realtime detection of such heavy metal contamination in the environment and rapid analysis of liquid samples of all types from drinking water and environmental samples to clinical samples in medicine.

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