

Qualitative Analysis by Laser-Induced Breakdown in Aqueous Media

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Abstract

A pulsed, focused laser beam is used to induce dielectric breakdown (LIB) in various solid metallic targets and bulk aqueous samples. Emission from the breakdown plasma is investigated using a non time resolved technique with the feasibility of qualitative elemental analysis in mind. The results, whilst supporting the use of LIB for elemental analysis, highlight the complications present with bulk aqueous solutions. The study emphasises the need to discriminate continuum background radiation from elemental lines; pointing toward the need for more involved approaches to improve the sensitivity of LIBS when applied to aqueous solutions.

Introduction

The breakdown plasma produced when a laser beam is focused onto a sample can provide detailed analytic information about the sample. One can infer the presence of elements and their concentrations from spectral analysis of the plasma emission.

Breakdown occurs when a focused laser beam produces an electric field so strong that it exceeds the dielectric strength of the material at the focus, producing a laser spark [1]. Material at the focusing point is ablated. For short pulse exposures the breakdown is optical and the high irradiances present cause ionisation by inverse bremsstrahlung, multiphoton ionization, and impact electron ionisation [2-5], producing a visible flash. The breakdown produces a highly ionised, expanding atomic plasma which becomes opaque to the laser causing further absorption [1,5].

Analysis of plasma emission spectrum can be used as a diagnostic tool. Plasma spectroscopy has been used historically in astrophysics and plasma physics [6]. Measuring the characteristic emission spectrum from plasma can provide detail about the plasma structure. Properties such as the electron and ion temperatures and densities can be inferred from spectroscopic data [7-10].

The light emission during the early stages of the plasma is characterised by broadband continuum emission from the ultraviolet to the infrared with few spectral features [4]. Once the laser is off, the plasma expands and cools and ionic species begin to recombine and de-excite. This stage is characterised by emission of ionic and atomic spectral radiation due to electric transitions characterised by sharp peaks which rise above the fading continuum [11]. These spectral lines typically have decay lifetimes which persist long after the plasma, particularly for resonant lines [4,6]. The spectral lines and decay lifetimes are characteristic of the elemental composition of the sample material and hence qualitative spectral measurement of the fluorescence decay can be used to identify elemental species [4,12].

Laser induced breakdown spectroscopy (LIBS), describes emission spectroscopy using a laser spark and was first proposed by Loree and Radziemski in 1981 [13, 4]. LIBS has been used to quantitatively determine the composition of powdered coal in [14] and the detection of Pb in soil is highlighted in [15]. A feasibility study performed by the Woods Hole Oceanographic Institution [16] stated "LIBS is a promising analytical technique that can be used to detect analytes in high pressure, bulk aqueous solutions." The study also highlights the capability of LIBS to simultaneously detect multiple analytes, allowing for the analysis of deep sea sediments and ocean fluids, including hydrothermal vent fluids. LIBS spectrometers have the potential to be very small, highly portable devices, easily deployed in the field, and are able to perform real-time analysis [17-20]. However, several studies highlight complications and reduced sensitivity when applying LIBS to impurity analysis in bulk aqueous solutions compared to gaseous or solid samples [12, 21-24].

This study will investigate the differences in plasma spectra of solid metallic targets in air and aqueous solutions. This investigation will assist future studies aimed at improving the analytical power of LIBS when applied to bulk aqueous solutions.

The experimental method involves determining the best procedure within the limits of our equipment. The approach to the problem is critically analysed and solutions to improve spectral resolution and reduce experimental error are proposed. The results obtained will be discussed in relation to the feasibility of using plasma spectroscopy techniques for liquid sample identification, ionic concentration and impurity analysis.

Equipment

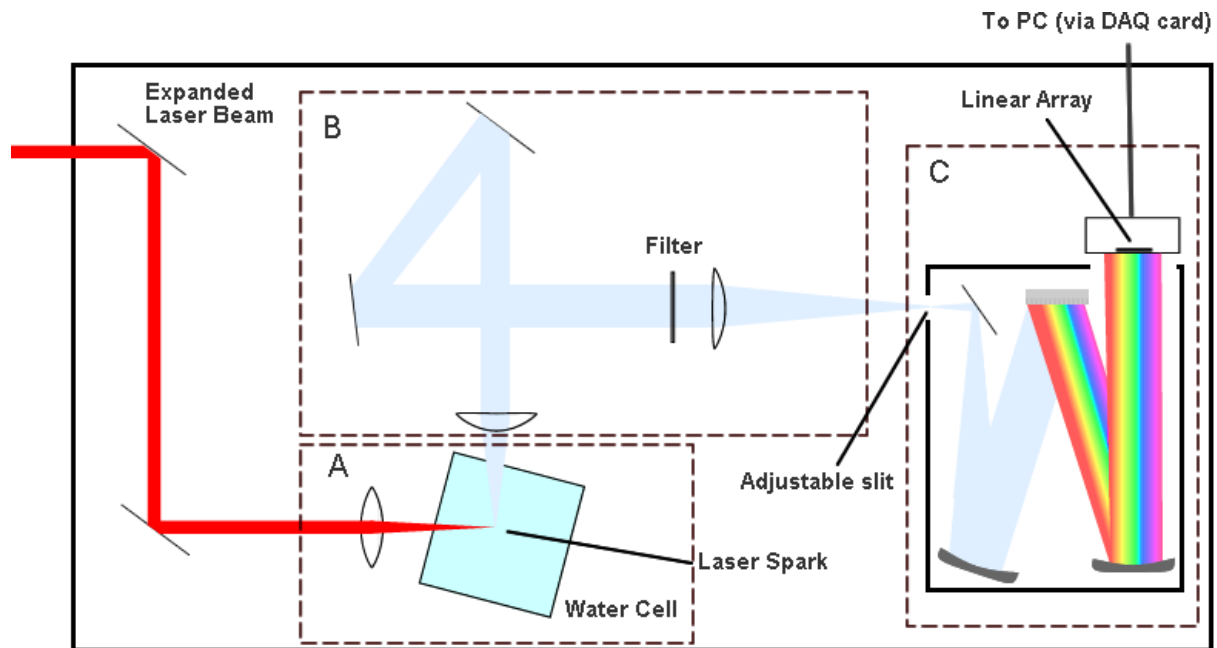


Figure 1: The experimental setup is split into sections: **A**, the beam focusing optics; **B**, the light collection optics; and **C**, spectral dispersion and detection. The water cell shown is used for the aqueous samples. In the case of solid targets the water cell would be removed and the sample mounted on a stand.

The Beam Focusing Optics

Referring to section A of Figure 1, the laser beam is expanded using a Galilean telescope to reduce divergence [25] before entering the experiment. The expanded beam is directed into the experiment by a series of mirrors, and focused onto either the surface of the solid or directly into the bulk of the liquid, depending on the type of sample in use. The focusing lens is mounted on a rail controlled by a micrometer gauge so the focal position can be modified.

In the case of aqueous solutions, a glass water cell is used to contain the sample. The cell is placed off-normal to the beam direction to prevent back reflections causing damage to the optics [26]. Solid samples are mounted on a stand and the focusing lens position is tweaked so that breakdown occurs at the sample surface.

The Light Collection Optics

The light from the plasma is collected perpendicular to the laser propagation direction by a plano-convex lens, producing a collimated beam (as can be seen in section B of Figure 1). A short focal length is used to maximise the light intensity collected by the lens. The beam is then focused onto the entrance slit of the monochromator using another plano-convex lens. Both lenses in the system are mounted on rails to allow good collimation for any sample.

Dispersion and Detection

A monochromator with interchangeable gratings is used to disperse the plasma light and can be manually driven throughout the wavelength range under study (400-800nm). The detector, a linear CCD sensor is placed at the exit aperture of the monochromator. The linear array is interfaced to an x86 PC using a data acquisition (DAQ) card. The readout signal is processed in *LabVIEW* using bespoke Virtual Instrument (VI).

Equipment

The laser is a *Continuum Minilite II* Q-Switched Nd:YAG system with a wavelength of 1064nm and a pulse duration of 5ns. At these settings the maximum output energy is 30mJ and when focused produces a power density of the order of $10^9 - 10^{11} \text{W.cm}^{-2}$ [3-5], which is sufficient to produce dielectric breakdown in pure water. Breakdown also occurs in impure water and solid targets since the threshold intensity is reduced in the presence of impurities for liquids [5,27], and the threshold intensity for solids is much lower than for pure water [28].

The monochromator is a Czerny-Turner type *Bentham M300* with a maximum spectral resolution of 0.5nm. Three interchangeable diffraction gratings are available (150, 500 and 1800 lines/mm).

The detector is a *Hamamatsu* NMOS linear image sensor (*S39093-512Q*). The array has 512 pixels and a pixel width of 25 μm . The sensor is self triggered by a *Hamamatsu C7884G* driver and pulse generator circuit. External triggering of the linear array is not possible when using the pulse generator circuit; it is constantly taking images and provides digital output to indicate the status of the signal. The pulse generator circuit allows discrete changes to the clock speed and integration time of the sensor.

VI Design

Preliminary work involved building a *LabVIEW* VI to enable the recording and processing of experimental data from the detector. *LabVIEW* is versatile solution and provides fine-grained control and signal manipulation abilities. The DAQ card integrates directly with *LabVIEW*, simplifying the VI development process. *LabVIEW* readily provides many functions for signal manipulation and analysis. Built in testing and debugging features speeded up the development process and there is the potential for extension to perform more operations on the data if required.

A *TekScope TDS7000* digital oscilloscope was used to look at the array output signals and their relationships. The high sample rate available provided sufficient resolution to observe in real-time the digital signals in full detail. From this work we gained full knowledge of the signal relationships and the effect of changing the integration time.

The VI converts the output signals from the linear array into a voltage-pixel plot, triggered by the start pulse. Additional functionality such as automatic averaging of successive read-outs and saving functionality is implemented.

Experiment

For qualitative spectral analysis, the critical parameter to be measured is the wavelength. For a quantitative analysis of impurity concentration, or plasma parameters, the detector intensity needs to be calibrated in addition to wavelength calibration.

There are several systematic sources of wavelength error – the most significant are concerned with the position of the linear array with respect to the exit aperture of the monochromator. Broadening of spectral lines due to errors or limitations with the optical system increase the uncertainty in the wavelength of the peak – this is known as instrument broadening.

Preliminary work and Calibration

The monochromator is calibrated against the linear array position using a low pressure Mercury pencil lamp. Data from *NIST Atomic Spectra Database* [29] is used for calibration. Low pressure is a requirement to improve accuracy by reducing line-broadening and shifting mechanisms [6]. Calibration ensures that the monochromator is linear in wavelength, and gives the dispersion relation. This dispersion relation is vital to produce a wavelength spectrum as needed for elemental analysis. To minimise instrument broadening the refocusing mirror of the monochromator was focused exactly onto the linear array at the zero order calibration line. A full calibration of the emission intensity is not important for qualitative analysis [6]. However, it is favourable to maximise intensity to allow resolution of small peaks over background noise inherent in the detector such as leakage current. To achieve this it is vital to have a well aligned optical path and a near perfectly collimated beam to ensure as much light as possible arrives at the monochromator allowing for reduction of the slit width.

Research shows that the most effective method of removing the background continuum is to use gated or time-resolved methods [30] since only the light emitted in the later stages of the plasma cycle is of interest for species identification. It is not possible to perform adequate time synchronisation of the laser, plasma and detector since the detector is not triggerable. Neither is it feasible to run the experiment by the clock of the linear array since the low integration times required for single plasma detection meant the laser shot rate would be too high. This limitation of the detector prevents temporal resolution and so the detector runs independently of the laser pulse with a large integration time. The averaging of many successive plasma emissions allows the resolution of atomic lines over the continuum background.

Optimisation of Parameters

The optimal integration time on the linear array is 5s. This allows the resolution of peaks over the continuum background without generating too much noise from the lab lighting and leakage currents in the detector. A laser shot rate of 10Hz provides sufficient pulses per integration to give peaks over the continuum. Higher shot rates bring minimal improvement and it is favourable to reduce the shot rate in order to improve the reproducibility of the plasma. However, another study by Castle *et al* [31] suggests that shot-to-shot pulse energy variance has a minimal effect on the LIBS signal.

Higher resolution gratings make the data acquisition process more difficult without giving extra information about the spectrum. The 150lines/mm (low resolution) grating is used. Increasing the width of the entrance slit improved the intensity and signal to noise ratio at the expense of increasing peak width. An optimal value of 0.86mm is used for aqueous samples; this is reduced further for solid targets in air.

Procedure

Particularly with aqueous samples the light collection optics needs to be tweaked for each sample. This is because the differing refractive indices of the solutions cause a change in the effective focal length of the focusing lens, changing the plasma position. This also affects the light collecting lens and the degree of collimation.

For each sample the presence of the zero order peak at the first pixel of the detector is ensured – if not the linear array needs to be recalibrated against the monochromator. This is done in an effort to reduce the wavelength error between datasets. Several snapshots are then captured with the VI starting in the low wavelength range with subsequent snapshots having a slight overlap so that no part of the spectrum is missed.

Samples

Distilled, de-ionised, and UV treated water is used as the solvent for all aqueous samples. Pure water, NaCl solution, and a solution containing 66% KCl and 33% NaCl is used.

The metallic samples are Lead, Copper, and Aluminium.

Results

Data for each sample was obtained by the addition of 10 snapshots each with an integration time of 5s. The laser pulse rate was 10Hz. Therefore, each spectrum is the cumulative emission of 500 full plasma cycles.

Individual snapshots of the entire spectrum were placed together using the dispersion relation. Using the dial reading of the start pixel of each snapshot, successive snapshots were placed together exactly to produce an extended intensity versus pixel plot. This was then converted into wavelength using the dispersion relation. Any significant overlap between the snapshots has been removed as it complicates the plots without providing useful information.

Intensities are in arbitrary units and are affected by many factors including the spectral response of the detector, integration time, and pulse rate. The data has thus been further processed to accurately represent the plasma emission. A simple Gaussian model of the linear array spectral response curve based on its typical profile at 25°C (as provided by the manufacturer) was applied (see [32]). A similar model of the typical grating response was built using a Spline of reference points. To apply these response functions it was necessary to create a Spline of the raw data.

The measured wavelength of the laser line was found to be within 1% of the actual value of 1064nm. This gives an upper limit of ± 10 nm due to error in calibration since all wavelengths of interest are below this value. The error in the wavelength is thus estimated to be ± 10 nm; this is mainly associated with the uncertainty in the position of the linear array with respect to the monochromator and errors in calibration. All quoted wavelength values hereon have a 10nm uncertainty.

It is important to consider the increased complications due the presence of ionic lines.

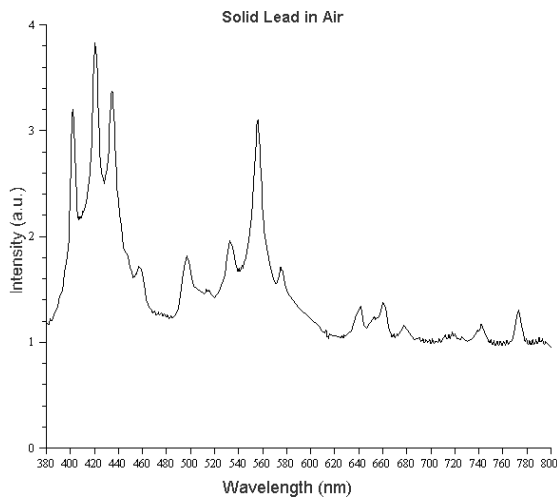


Figure 2: The emission after 500 plasma cycles of a Lead target in air. Detector and grating response has been accounted for.

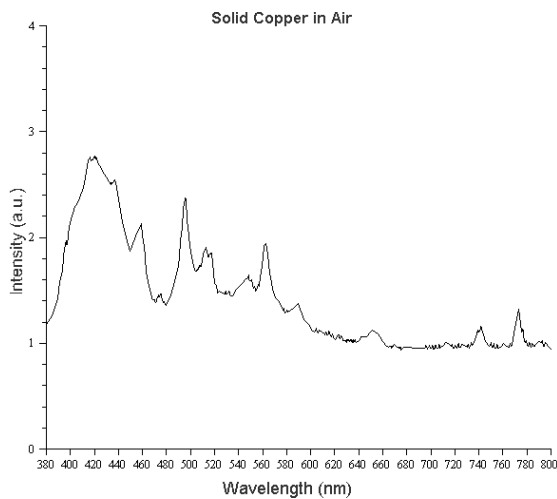


Figure 3: The emission after 500 plasma cycles of a Copper target in air. Detector and grating response has been accounted for.

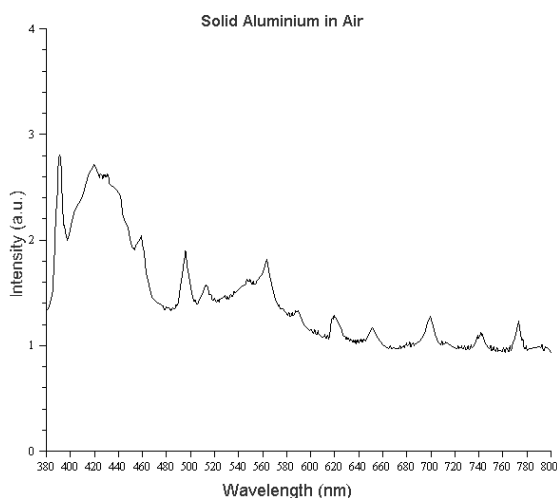


Figure 4: The emission after 500 plasma cycles of an Aluminium target in air. Detector and grating response has been accounted for.

Figure 2, the spectrum obtained with the Lead sample shows several sharply defined lines against background intensity stretching over the entire range observed. Strong peaks at 403nm, 420nm, 435nm, and 556nm are present.

Figure 3, the spectrum of Copper in air shows many similarities to that of Lead. In particular the high wavelength region has exactly the same characteristic. Well defined lines are present at 560nm, 496nm, 459nm, 438nm.

Figure 4, the spectrum obtained for Aluminium in air is again very similar to other metallic samples. Well defined peaks at 563nm, 496nm, 459nm, and 392nm.

All three spectra of the samples in air have similar characteristics. In particular, there is a very similar peak structure at the high wavelength range with little variation between all three. This suggests that there is ionisation of air around the ablated sample as highlighted in a similar study of metallic targets in air [40]. In this situation, photons emitted from the inner of the plasma, consisting of the ablated metal ions are absorbed by the outer ionised air. So, the spectrum, in the main, is characteristic of an air breakdown.

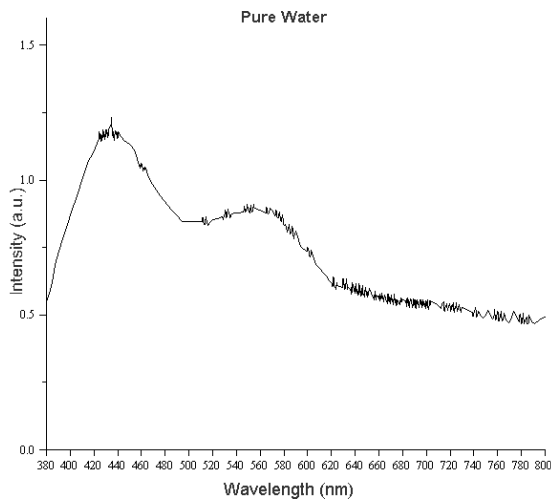


Figure 5: The spectrum obtained for pure water after 500 cycles. Grating and detector response have been applied.

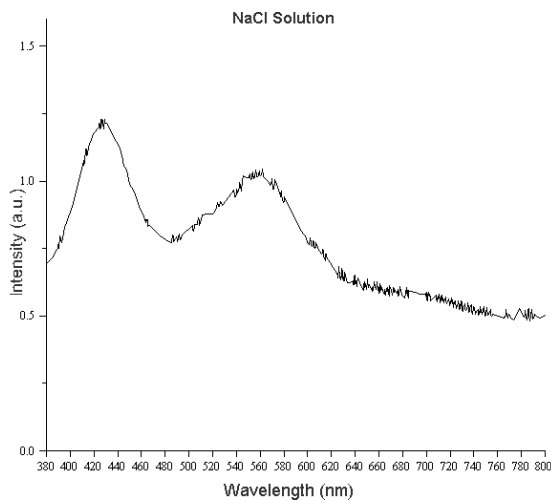


Figure 6: The spectrum of Sodium salt added to pure water after 500 cycles. Grating and detector response have been applied.

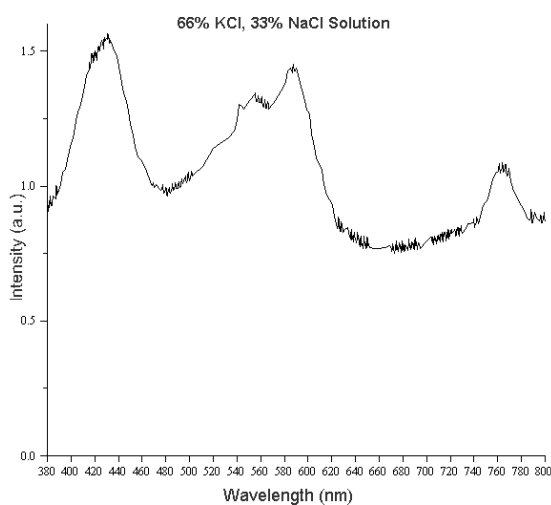


Figure 7: The spectrum obtained from a solution containing 66% KCl and 33% NaCl after 500 cycles. Grating and detector response have been applied.

Figure 5 shows the spectrum of pure water. The main profile is broadband continuum peaking at about 450nm. There are two very broad peaks at ~430nm and ~555nm.

Figure 6 is the spectrum obtained for NaCl solution, showing a similar profile to pure water with a sharper peak at 430nm and an improved peak at 555nm.

Figure 7 shows the spectrum obtained for the KCl/NaCl solution. The spectrum shows peaks at 430nm, 555nm, 587nm, and 765nm. It is interesting to note that the overall intensity is much greater compared to the other aqueous samples across the entire wavelength range observed and the peaks are typically better defined.

As with the metallic samples, all three spectra of aqueous solutions have similar profiles. All peaks are considerably broader than the spectra of the air samples and with many less features. The spectra is characterised by the broadband continuum. As expected there is a lack of characteristic lines of hydrogen and oxygen from water in the aqueous samples [4].

The intensity observed for the aqueous samples is much lower than that of the solid samples. This is in agreement with the larger breakdown threshold intensity of water and additional absorption of laser radiation by mechanical effects.

Particularly in the aqueous samples, additional peaks are present when adding more impurities, showing that the emission spectrum is dependent on the sample composition.

The background continuum has a similar profile for all samples, suggesting that its character is dependent largely upon the laser parameters. The continuum is more intense at shorter wavelengths for all samples and has a shape similar to a Planck blackbody radiation curve. It is valid to estimate the average plasma temperature by fitting a Planck radiation curve to the background continuum [3,4,33]. A rough estimate of the plasma temperature for the pure water result using the Wein displacement law with $\lambda_{max} = 450\text{nm}$ is:

$$T = \frac{2.898 \times 10^6}{\lambda_{max}} = 6440 \pm 150\text{K}$$

This represents the average plasma temperature over its lifetime; the value agrees within order of magnitude of more detailed calculations from similar studies [3,22,24].

Discussion of Results

The plasma emission spectrum is shown to depend on the sample composition in aqueous solutions. This sample-dependence of the spectral profile is evidence that the peaks are related to the presence of atomic species. It also provides support for using LIBS as a technique for elemental analysis in aqueous solutions. However, in this study very few spectral features were detected and the confirmation of the presence of particular species is not possible. The results for solid targets in air show that the plasma emission can produce a rich spectrum but more work needs to be done to obtain such detail for aqueous solutions.

Water and aqueous solutions show fewer spectral lines, broader peaks and weaker intensities compared with solid targets in air. There are many physical processes which can account for the additional broadening observed in aqueous solutions, but the primary source of broadening in the results is due to the instruments and the alignment of the optical path. This fact alone cannot account for the increase in broadening compared with air or the lack of spectral features.

Line Broadening Mechanisms

Photons can be partially re-absorbed as they travel through the plasma. This process is known as self absorption broadening [34] and can be reduced by ensuring the plasma is optically thin. This process also is responsible for the spectra obtained for the solid targets to be characteristic of the surrounding ionised air only.

Doppler broadening refers to the wavelength shift due to particle velocity of the atom during photon emission. This effect can both increase and decrease the observed wavelength resulting in a broadening of the spectral line. Here the effect is minimal since light was collected perpendicular to the laser and hence perpendicular to the direction of greatest plasma expansion [35, 36].

Stark broadening refers to the broadening of spectral lines due to the modification of quantum energy states in the presence of an electric field. Due to the nature of plasma this effect can contribute to spectral line width considerably, and is most apparent during the early stages where the plasma is dense and highly ionised [1,6,34]. It would be possible to reduce this effect considerably with time resolution techniques.

The surrounding bulk aqueous solution can also contribute to spectral line width due to collisions with boundary water clusters and quenching [3,12,27].

Lack of Spectral Features in Aqueous Solutions

In highly absorbing liquids, impurities in solution can scatter the plasma emission light, decreasing the efficiency of light collection [4]. Because the photons need to travel through a large volume of water to be detected it is possible that photons with energy corresponding to resonant lines are re-absorbed by other ground state atoms before leaving the cell thus reducing the intensity of the spectral line.

The Background Continuum and Plasma Temperature

The background continuum has the same shape over all samples and can be approximated as an ideal emitter. The general shape of the continuum correlates with the results given in a similar study on laser-induced breakdown at metal–air and metal–water interfaces [22]. The increase in continuum intensity at lower wavelength can be explained if one notes that the absorption coefficient for inverse bremsstrahlung is proportional to the square of the wavelength [33]. Thus the plasma is less opaque to low wavelength photons and are more likely to escape and be detected giving rise to a higher intensity.

More information about the validity of this approach can be found in [7]. A fuller investigation of the plasma temperature would require time resolution on the scale of the plasma lifetime to look at the variation of temperature in time and space [4]. To get an accurate value for the temperature, the intensity should be calibrated [6].

Critical Review of Approach

The results show that it is possible to observe spectral lines without time resolution but highlight limitations of the non-time-resolved approach. The background continuum is strong and will cover many of the weaker lines due to transitions occurring from short lived states. The presence of ionic lines complicates elemental analysis, particularly prevalent with aqueous samples.

The method simplified the process of interfacing the linear array with *LabVIEW* and effectively decoupled the different sections of the experiment (shown in *Figure 1*). It is known that laser plasmas have poor reproducibility and those produced in bulk water exhibit strong shot-to-shot intensity oscillations [2,4,27,37]. Our approach automatically compensated for this effect by averaging out the random variation. A time synchronised method would suffer from these problems unless additional steps to average successive snapshots were not taken. However, being unable to resolve the plasma in time severely limited the ability to perform an elemental analysis due to the strong continuum and presence of ionic lines.

It is vital to further reduce systematic errors in the experiment. Instrument broadening can be reduced by decreasing the slit width and integrating over more time to compensate. Greater optical precision would allow the slit width to be reduced further.

The post processing of results may be improved by considering the absorption spectrum of water in the visible region [3]. It would also be ideal to get experimental measurements of the grating and detectors response using a calibrated standard lamp instead of modelling the typical response. This additional effort would not be rewarded with anymore physical insight into the nature of the spectral emission without also improving the method and reducing uncertainties.

In future studies it would be ideal to use metallic samples in air and the same samples in water to make easier comparisons and clearer deductions of the effect of bulk water on the emission.

Time resolution could be achieved with the same equipment by gating the detector so that only light after a certain period in the plasma cycle is detected. This approach has the advantage that it would be relatively easy to integrate into the existing setup.

Future research

The study shows poor spectral sensitivity of bulk aqueous solutions compared with targets in air. It has been suggested that additional techniques are required for LIBS in aqueous solutions to produce spectra sufficiently detailed for elemental analysis. For example, double pulse LIBS [3] and gas buffering [38], both of which essentially aim to reproduce plasma conditions similar to those in air breakdown [39].

More accurate measurement of the plasma temperature can be realised by performing an absolute intensity calibration [6]. This would additionally allow diagnostics of plasma parameters, allowing identification of optimal laser and plasma parameters for aqueous LIBS [41].

Conclusion

The present study successfully interfaced a linear array with *LabVIEW* by creating a bespoke VI. This allowed the spectral measurement of breakdown plasma emission when used in conjunction with a monochromator.

Laser induced breakdown plasmas were studied to establish the feasibility of using such techniques for effective elemental analysis of aqueous samples. There is a particular interest in applying LIBS techniques to deep sea sediment analysis due to the potential of mobile, real-time quantitative elemental analysis in-situ.

It is shown that the application of LIBS to aqueous solutions suffers from increased complexities compared with solid targets in air. The results hint at the feasibility of this technique for quantitative analysis, but also show a requirement to refine and tweak the methodologies employed. In particular, the need to discriminate atomic emission lines from the continuum background radiation is essential and the study suggests methods to achieve this.

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