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Preliminary Investigation of Standoff Laser-Induced Breakdown Spectroscopy of Metallic Samples

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ABSTRACT

Analytical chemistry techniques with the ability to analyse objects of interest at significant standoff ranges are of great interest to defence and national security organisations. One analytical technique which has demonstrated standoff capability is Laser-Induced Breakdown Spectroscopy (LIBS). LIBS is performed by using a high-powered laser to ablate a small amount of a sample and to form a plasma. The high temperature of the plasma results in atomic emission of light, which is used to identify the type of atoms present and therefore the nature of the sample.

In simplistic terms, it is possible to perform LIBS at standoff distances by remotely irradiating the sample with a laser and collecting the radiation from the laser-induced plasma through a magnifying, large-aperture telescope. This report describes a series of experiments in which initial attempts to perform LIBS over moderate standoff distances were undertaken. Metallic samples were employed, as these materials represent readily available single element samples or simple alloy mixtures which simplify the initial investigation of an analytical technique. The ability of LIBS to identify these samples at a moderate standoff distance (approximately 3.5 m) is investigated, and the effects of laser focussing and pulse energy are examined. Finally, specific suggestions are provided for further development of a standoff LIBS system.

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Executive Summary

Analytical chemistry techniques with the ability to analyse objects of interest at significant standoff ranges are of great interest to defence and national security organisations. One analytical technique which has demonstrated standoff capability is Laser Induced Breakdown Spectroscopy (LIBS). LIBS is performed by using a laser to ablate a small amount of a sample and to form a plasma from this ablated material. The high temperature of the plasma results in atomic emission of light. The wavelength of this light is characteristic of the emitting atom, and can therefore be used to identify the type of atoms present and therefore the nature of the sample.

In simplistic terms, it is possible to perform LIBS at standoff distances by remotely irradiating the sample with a laser and collecting the radiation from the laser-induced plasma. However, the introduction of standoff distance complicates the technique due to laser focussing and diffraction, and laser-induced plasma radiation collection. It is potentially possible to overcome these difficulties by introducing laser focussing elements, a high-powered laser, and a magnifying telescope of large aperture for the collection of the radiation.

Experiments were conducted to investigate the ability of LIBS to identify metallic samples over moderate standoff distances (approximately 3.5 m). In order to simplify the experiments, the investigation was limited to metallic samples, as these provide readily available single element samples or simple alloy samples containing a low number of elements.

A lens was used to focus the high-energy laser pulses onto the sample, while a 6" aperture Newtonian telescope was used to collect the radiation from the laser-induced plasma. Differentiation of a range of metallic samples was trivial under these experimental conditions. Spectra obtained under these conditions clearly exhibit intense peaks which are characteristic of the elements present in the sample.

Further experiments focussed on characterising the effects of varying the laser pulse energy and removing the laser focussing lens. Both of these variations effectively vary the power density of the laser pulses impinging upon the sample. As expected, reducing the laser pulse energy or removing the laser focussing lens resulted in decreases in the absolute intensity of spectral peaks, and a decrease in the quality and signal to noise ratio of the spectra. This is believed to be due to the decrease in laser power density resulting in reduced sample ablation and plasma formation, and reduced plasma temperature resulting in lower emission intensity.

The results of these experiments provide clear guidance in further developing the LIBS system in order to improve and enhance the standoff capability.

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1 Introduction

Analytical chemistry techniques with the ability to analyse materials of interest at significant standoff ranges are of great interest to defence and national security organisations due to their potential ability to interrogate suspicious items and identify Improvised Explosive Devices (IEDs) whilst allowing personnel to remain outside the possible blast radius. A comprehensive review of available standoff techniques is available in a recent report by Dua and Hall [1]. One analytical technique which has demonstrated standoff capability is Laser-induced Breakdown Spectroscopy (LIBS).

Fundamentally, LIBS is performed by using a laser pulse to ablate a small amount of material from a sample surface. The laser pulse heats the ablated material, fragmenting the sample molecules into individual atoms and ions and forming a plasma. As the plasma cools, the thermally excited electrons of the atoms relax into lower energy states, which results in the emission of electromagnetic radiation at wavelengths which are characteristic of the type of atom present. Spectroscopic analysis of these wavelengths allows the types and relative abundance of the atoms in the sample to be identified. Comparison of the ratios of abundance of the atoms allows the sample to be identified as belonging to a certain class of materials, such as nitrates, which in certain operating environments or scenarios could be indicative of explosive material. Further technical information on the LIBS technique is available in several texts [2, 3].

Considering that the sample interaction and data collection processes in LIBS involve only interactions of electromagnetic radiation rather than physical manipulation, it is possible to perform LIBS at standoff distances by remotely irradiating the sample with a laser and collecting the radiation from the laser-induced plasma. A significant body of work has been undertaken in the last decade toward developing the ability to conduct LIBS at standoff distances up to and beyond 100 m. A thorough review of this research, and a technical analysis of the apparatus required, is available in a previous report [4].

It is useful to review previous work specifically related to standoff LIBS of metallic samples. Some of the earliest work in standoff LIBS was undertaken by researchers at the University of Málaga in Spain, with the aim of using standoff LIBS to analytically monitor the composition of molten steel during steelmaking operations. In a 2002 study the authors used a 230 mJ Q-switched Neodymium-doped Yttrium Aluminium Garnet (Nd:YAG) laser at the fundamental 1064 nm wavelength to perform LIBS on solid stainless steel samples at distances between 35 m and 45 m [5]. Q-switching is a technique used to enhance the power of a laser pulse. The authors were able to accurately monitor the composition of steel in real-time with this technique. The authors have also demonstrated that it is possible to characterise samples of steel moving at up to 24 cm min⁻¹ using standoff LIBS [6].

The University of Málaga group also experimented with the use of standoff LIBS for characterising metallic residues on other surfaces. In one study, the group successfully used standoff LIBS to detect iron and chromium contamination in the coastal environs surrounding an industrial area [7].

Sallé *et al.* experimented with a system incorporating a Q-switched Nd:YAG laser in order to achieve up to 12 m standoff when sampling metal and mineral mixtures [8]. The study was motivated by the possibility of implementing LIBS in scientific landing

probes to Mars, and the experiments were therefore conducted with the samples housed in a cell containing a low pressure mix of carbon dioxide, nitrogen and argon to simulate the atmosphere of Mars. The authors were able to successfully obtain LIBS spectra of aluminium and basalt samples at distances between 3 and 12 m, although the results of their study highlight the importance of good quality optics in conducting standoff experiments.

It is interesting to note that a LIBS system with a standoff capability of up to 7 m forms part of the scientific instrument package aboard the Mars Science Laboratory rover currently deployed on the surface of the planet Mars [9]. This system employs a focussed laser producing laser pulses of approximately 14 mJ with a duration of 5 ns. The plasma emission light is collected by a 110 mm telescope. The LIBS system will be used to remotely analyse the composition of martian rocks, with a predominant interest in the metallic elements present.

Researchers at the Lund Institute of Technology in Sweden have constructed a self contained, truck mounted standoff LIBS system, capable of travelling and operating independently through the use of a towed 40 kVa motor generator [10]. The system is designed to scan the laser beam, under computer control, over a target area in order to prepare a two-dimensional image of the target. In the image, different materials are represented by different colours. Using this system, a target composed of metal plates was imaged at 60 m, and remote LIBS spectra of copper and aluminium were obtained.

The introduction of standoff distance creates two main problems which complicate the technique:

1. The laser must interact with the sample in such a manner that sufficient laser power density is achieved on the sample surface to initiate ablation and plasma formation, but such that no air breakdown occurs in the laser beam prior to the sample surface.
2. Sufficient radiation from the relatively small laser-induced plasma must be collected at the standoff range to achieve accurate spectroscopic results with good signal to noise ratio.

1.1 Laser Interaction

Laser ablation and plasma formation typically requires laser power densities equal to or greater than $1 \times 10^9 \text{ Wcm}^{-2}$ [11]. However, upper limits to the power density of the laser are created by the potential breakdown of air into a high temperature, high density plasma. The formation of such a plasma between the irradiating laser and the sample surface will interfere with the laser beam and prevent it from interacting with the surface. Air breakdown occurs at laser power densities of approximately $1 \times 10^{11} \text{ Wcm}^{-2}$ [12]. Therefore, for LIBS to be conducted at standoff distances, the irradiating laser must not exceed this air breakdown threshold prior to reaching the sample, but must arrive at the sample with a power density greater than $1 \times 10^9 \text{ Wcm}^{-2}$.

A relatively powerful laser used for standoff LIBS measurements may produce 900 mJ pulses of 1064 nm radiation with a diameter of 9 mm at the aperture, with each pulse having a duration of 5 ns. Neglecting the typical Gaussian energy profile of a laser and

assuming uniform energy density within the beam, this equates to a beam area of 0.64 cm^2 , an energy density of 1.41 J cm^{-2} , and a power density of $2.83 \times 10^8 \text{ Wcm}^{-2}$ at the aperture. This power density is below that required for adequate laser ablation and plasma generation, and hence some degree of focussing of the laser is required in order to decrease the diameter of the laser beam at the sample and therefore increase the laser power density. It follows that, in order to achieve a power density of $1 \times 10^9 \text{ Wcm}^{-2}$ with this laser, the beam must be focussed to a diameter of 0.48 cm at the sample surface. Additionally, in order to prevent the breakdown of air, the laser beam must not be focussed to a diameter of less than 0.11 cm .

In theory, achieving a sufficiently small beam diameter is a simple process of passing the beam through a combination of a convex and a concave lens in an arrangement known as a Galilean telescope (Figure 1).

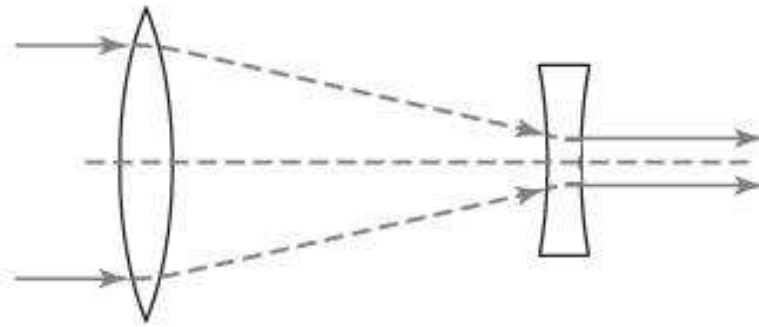


Figure 1: Schematic diagram of a Galilean telescope, showing the decrease in diameter of a laser beam passing firstly through the convex lens and then through the concave lens.

However, additional complexities in achieving adequate laser power densities at the sample surface are introduced by the unavoidable divergence of laser beams due to diffraction. For perfectly coherent light, a laser beam of diameter D will be diffraction limited to a divergence angle ϕ_{diff} , given by :

$$\phi_{diff} = \frac{2.44\lambda}{D} \tag{1}$$

where λ is the wavelength of the laser beam. Approximately 84% of the energy of the laser beam will be contained within this divergence angle. The beam diameter D_L at a range R is therefore given by :

$$D_L = R\phi_{diff} + D \tag{2}$$

Equation 1 indicates that a laser beam with a wavelength of 1064 nm and a diameter of 0.48 cm will be diffraction limited to a divergence angle of 0.54 mrad . At a distance of 10 m from the Galilean telescope, Equation 2 suggests that our initial beam diameter will have diverged to a diameter of 1.03 cm , consequently reducing the laser power density below that required for ablation and plasma formation. It is therefore necessary to compensate

for this divergence angle in the focussing of the laser beam in order to maintain adequate laser power density.

1.2 Radiation Collection for Spectroscopic Analysis

At small distances, sufficient light can be collected from a laser-induced plasma to perform spectroscopic analysis without magnification of the plasma. However, the intensity I of light observed from a light source decays with the square of the distance r from the light source, a property known as the inverse square law:

$$I \propto \frac{1}{r^2} \tag{3}$$

Therefore, as standoff distances are introduced into a LIBS system, the collection of sufficient atomic emission light from the laser induced plasma to perform accurate spectroscopy becomes increasingly difficult. The introduction of telescopic collection optics increases the amount of light collected due to the large aperture of the telescope, as a large aperture intercepts a greater flux area than a smaller collection area. The suitability of various designs of telescope to LIBS experimentation is discussed elsewhere [4]. In general, however, it is advantageous to employ the largest possible aperture which is practicable.

1.3 Initial Standoff Experimentation

As described above, the implementation of standoff into LIBS experiments introduces several additional aspects to the technique which increase the difficulty in obtaining spectra with good resolution and signal-to-noise ratios. In developing a standoff LIBS system, it is therefore advantageous to introduce standoff distances in small increments, so that these complicating aspects may be dealt with in regimes in which their deleterious effects do not dominate the obtained spectra to a prohibitive degree. This report describes a series of experiments in which initial attempts to perform LIBS over moderate standoff distances were undertaken.

2 Experimental

2.1 Experimental Arrangement

The principal LIBS apparatus consists of a Continuum Surelite III PIV system, incorporating two Q-switched Nd:YAG laser cavities producing 4-6 ns duration pulses of 1064 nm radiation with an energy of ~ 900 mJ at 10 Hz. The laser system allows the laser pulses from the two cavities to be fired simultaneously, or with a defined delay between them. Although this permits the use of dual pulses with a defined delay between the pulses, this mechanism was not utilised here as the current study represents an initial assessment of standoff capability. Dual pulse enhancement of standoff LIBS will be examined in detail in a future study. Simultaneous firing of the two cavities effectively results in a single

pulse with an energy of 1800 mJ. The system incorporates onboard optics to combine the two laser beams into a colinear arrangement. The power density of the laser light at the sample is increased by focussing the laser onto the sample with a Melles Griot 100 mm focal length, 1" diameter anti-reflective plano convex lens with high transmission at 1064 nm. This lens is placed approximately 8 cm from the sample. Spectral analysis is performed with an Andor ME 5000 echelle spectrometer, capable of analysing radiation between 200 nm and 975 nm with spectral continuity, coupled to an Andor DH 734 iStar intensified CCD camera. The laser, spectrometer and CCD are triggered via a Quantum Composers 9530 pulse generator capable of 250 ps resolution. Spectral data is analysed via Andor Solis software.

This LIBS system is undergoing development, and is currently primarily used for laboratory-based analysis. Typically, the distance between the sample and the fibre optic collection aperture of the spectrometer is less than 5 cm in order to maximise the plasma radiation collected by the spectrometer.

In order to achieve moderate standoff range, modifications were made to the system in order to improve the amount of plasma radiation collected. A schematic of the experimental arrangement is shown in Figure 2. The introduction of telescopic collection optics increases the amount of light collected due to the large aperture of the telescope. A Guan Sheng GS-500 Newtonian reflecting telescope with 6" aperture and 750 mm focal length, located approximately 3.5 m from the target sample, was therefore used to collect the light from the laser-induced plasma. An uncoated 30 mm focal length, 12.7 mm diameter Thorlabs UV fused silica plano convex was positioned approximately 300 mm from the eyepiece holder of the telescope, with the fibre optic collection aperture of the spectrometer positioned at the focal point of this lens. This arrangement provided a rudimentary method of coupling the spectrometer to the telescope. The implementation of appropriate optical coupling equipment would undoubtedly result in improved spectral performance, as the rudimentary coupling employed here was poorly aligned and optimised and would therefore have resulted in significant attenuation of the plasma radiation.

In short-range LIBS systems, the field of view of the light collection system is typically quite narrow. For such systems it is therefore often critical to ensure that the angle between the excitation laser and the light collection system is as small as possible in order to maximise the time that the evolving plasma remains within this field of view as it moves away from the sample surface. However, the relatively large field of view of the telescope used in the current standoff system enables it to capture the entire plasma evolution even when positioned orthogonally with respect to the axis of the excitation laser. Therefore, assuming that the luminescence of the plasma is approximately spherical, the angle between the excitation laser and light collection telescope should not be critical. The angle in the current system was approximately 15°.

The sample was located approximately 2.7 m from the laser source. The laser beam was focussed onto the sample with the 100 mm focal length lens, located approximately 8 cm from the sample, used in the typical experimental arrangement. This resulted in a laser impact region approximately 2 mm in diameter, corresponding to a beam area of 0.13 cm², an energy density of 7.16 J cm⁻¹, and a power density of 1.43 × 10⁹ W cm⁻² for a 900 mJ pulse of 5 ns duration. These values are doubled with the use of a single 1800 mJ laser pulse. As the laser focussing lens is in close proximity to the sample,

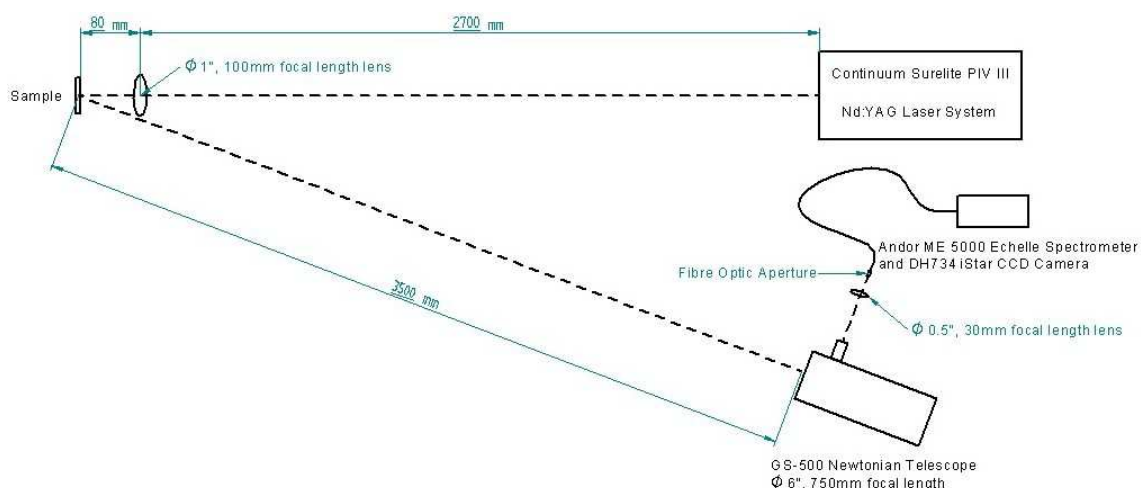


Figure 2: Schematic diagram of the experimental arrangement used in the standoff LIBS experiments.

irradiation of the sample was not achieved with true standoff. However, it is possible to replace this lens with a lens of much longer focal length, allowing the laser to be focussed onto the sample from a standoff distance. The technical details involved in this process are discussed in Section 1.1. The focussing of the laser beam, although by no means trivial, is therefore considered relatively easy to achieve in comparison to the complicated process of maximising light collection from the laser-induced plasma, and coupling this into the spectrometer with minimal attenuation. The distance between the sample and the telescope (3.5 m) is therefore considered to be the standoff distance implemented here, rather than the distance between the laser lens and the sample.

2.2 Samples

In order to simplify the experiments, the investigation was limited to metallic samples, as these provide readily available single element samples or simple alloy samples containing a low number of elements. The following samples were acquired from Goodfellow, United Kingdom:

- Zinc (1.0 mm thick, 25 mm square, 99.99+ % purity),
- Copper (1.0 mm thick, 25 mm square, 99.9+ % purity),
- Iron (1.0 mm thick, 25 mm square, 99.5 % purity),
- Magnesium (1.0 mm thick, 25 mm square, 99.9 % purity), and
- Aluminium foil (1.0 mm thick, 25 mm square, 99.999 % purity).

Copper beryllium alloy foil (0.13 mm thick, 150 mm by 200 mm, 98.1 % Cu, 1.9 % Be by weight) was obtained from Alfa Aesar, Massachusetts, USA. Lead samples were obtained by removing the acrylic coating from Acryflash lead roofing flashing supplied by Consolidated Alloys, Victoria, Australia.

2.3 Experimental Method

A gain setting of 230 and a temperature of -10°C was used for the iCCD. A delay of $20\ \mu\text{s}$ was used between the second laser pulse and the triggering of the spectrometer, and spectral integration was performed for $2\ \mu\text{s}$. For experiments in which a single $\sim 900\ \text{mJ}$ pulse was implemented, only a single cavity of the dual cavity Surelite III PIV laser system was energised. For high pulse energy experiments, a single $\sim 1800\ \text{mJ}$ pulse was generated by using a zero delay between the two laser pulses of the dual-cavity laser system, thereby effectively combining the two $\sim 900\ \text{mJ}$ pulses into a single $\sim 1800\ \text{mJ}$ pulse.

Accumulation spectra were obtained by repeatedly firing the laser at the same sample location, and collecting the spectral information after each shot. A summation of the spectra was then obtained via the Andor Solis software. In the current experimental arrangement, the rate at which spectra can be obtained is limited by the time required by the spectrometer to collect and record each spectrum. This is typically less than 1 second per spectrum, and hence an accumulation of 10 spectra can be collected in approximately 10 seconds.

Peak detection and element identification within the spectra was performed by the Andor Solis software used to operate the spectrometer and iCCD camera.

3 Results and Discussion

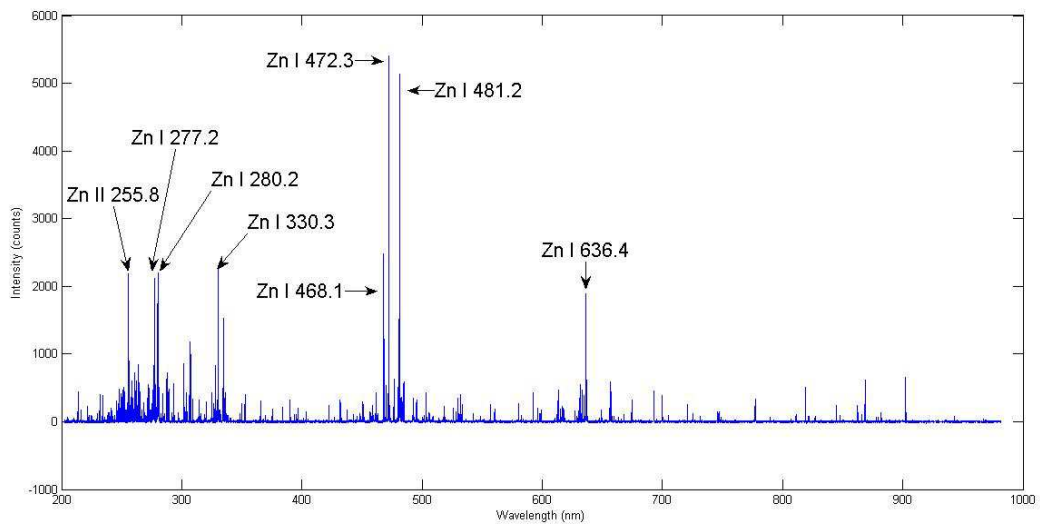
3.1 Identification of Metal Samples

A standoff LIBS spectrum of zinc metal collected using a single $1800\ \text{mJ}$ laser pulse (two simultaneous $900\ \text{mJ}$ pulses) is shown in Figure 3(a). Several spectral peaks which are characteristic of zinc metal are evident in the spectrum and are labelled accordingly. In this spectrum, and in all other spectra presented here, roman numerals following the element name represent the oxidation state of the element. The diminished intensity of the plasma radiation collected by the spectrometer in the standoff arrangement due to dispersion and atmospheric attenuation is evident in the relatively low count values of the spectral peaks. Despite this, however, the largest peaks of the spectrum (corresponding to the zinc peaks at $472\ \text{nm}$ and $481\ \text{nm}$) are clearly evident with signal-to-noise ratios of approximately 10:1.

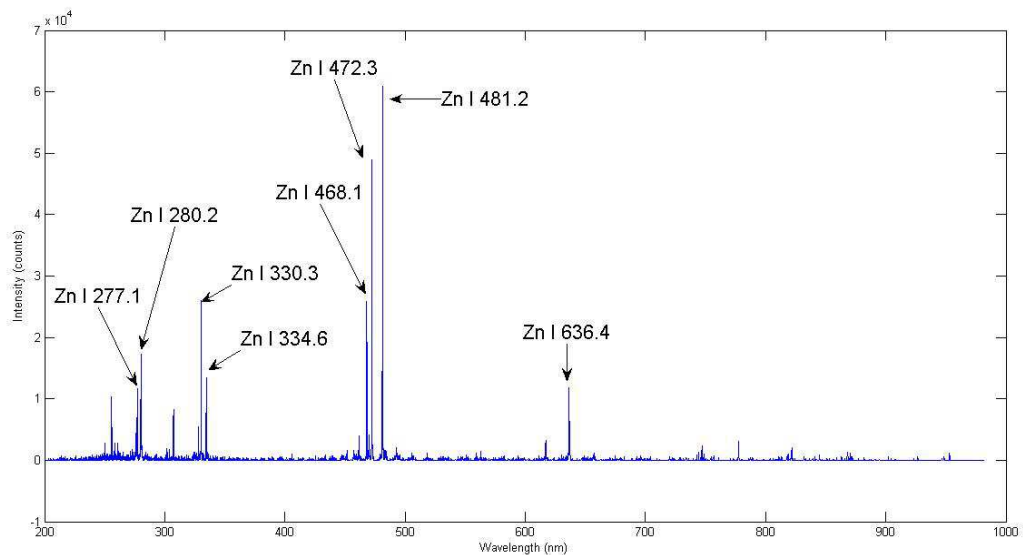
An accumulation of 10 spectra, each obtained with a single $1800\ \text{mJ}$ laser pulse, is shown in Figure 3(b). Emission peaks associated with zinc are labelled accordingly. A significant increase in the intensity of the peaks of the spectrum is evident, with an associated increase in the signal-to-noise ratio. The peaks associated with the zinc emission lines at $472\ \text{nm}$ and $481\ \text{nm}$ remain the highest peaks within the spectrum, with the vast majority of other prominent peaks also being associated with zinc emission lines.

Standoff LIBS spectra of aluminium (Figure 4), copper (Figure 5), and magnesium (Figure 6) metals show similar ratios of signal-to-noise in the single shot spectra, and similar increases in signal-to-noise ratio in 10 shot accumulation spectra, to the spectra obtained using zinc metal. In each case, the single shot spectra exhibit relatively low counts, reflecting losses due to atmospheric attenuation, standoff distance and instrumental

inefficiencies. However, the most prominent peaks of each spectrum are associated with the metal being analysed, and are labelled accordingly. An accumulation of 10 spectra of each metal results in a significant increase in the signal to noise ratios and an increase in the intensity counts of the prominent peaks. The most prominent peaks of each accumulated spectrum are associated with emission lines of the metal being analysed, and are labelled accordingly.

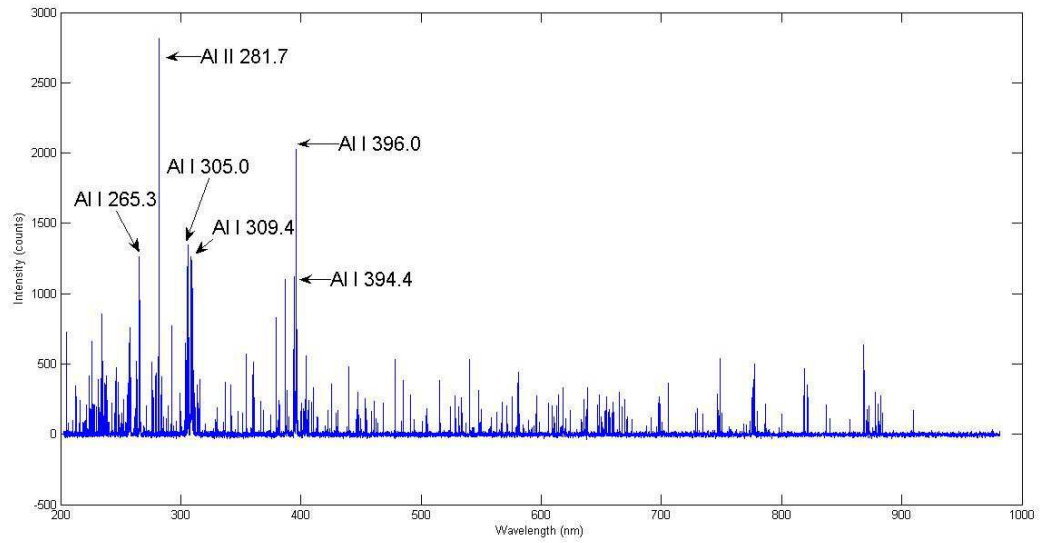


(a) Single spectrum obtained with a single 1800 mJ laser pulse.

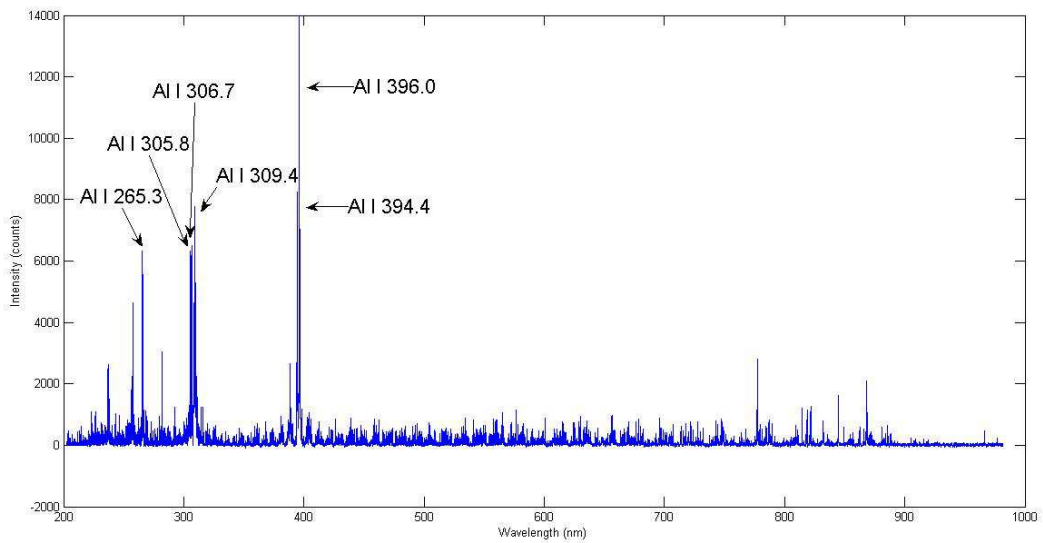


(b) Accumulation of 10 spectra.

Figure 3: LIBS spectra of zinc metal at a standoff distance of 3.5 m.

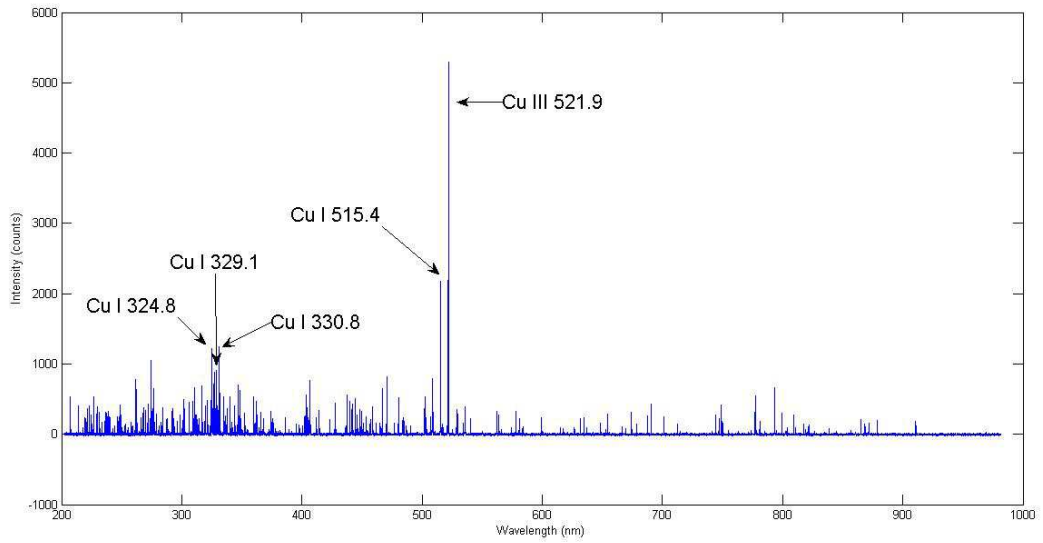


(a) Single spectrum obtained with a single 1800 mJ laser pulse.

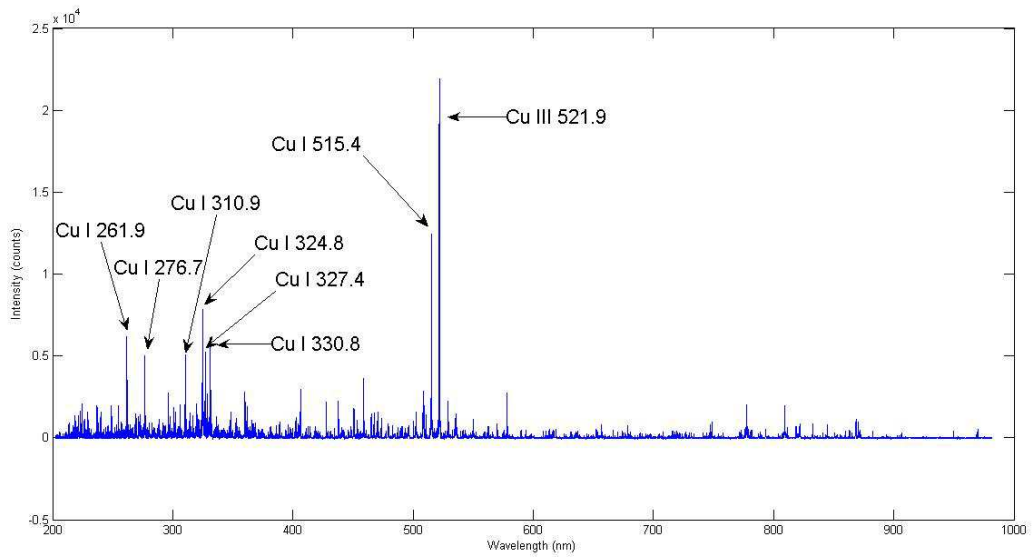


(b) Accumulation of 10 spectra.

Figure 4: LIBS spectra of aluminium metal at a standoff distance of 3.5 m.

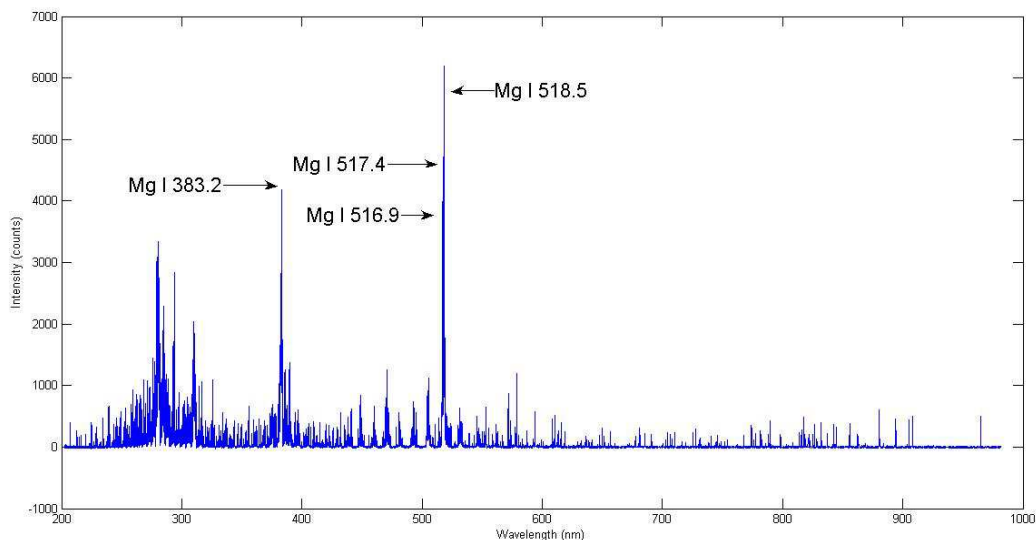


(a) Single spectrum obtained with a single 1800 mJ laser pulse.

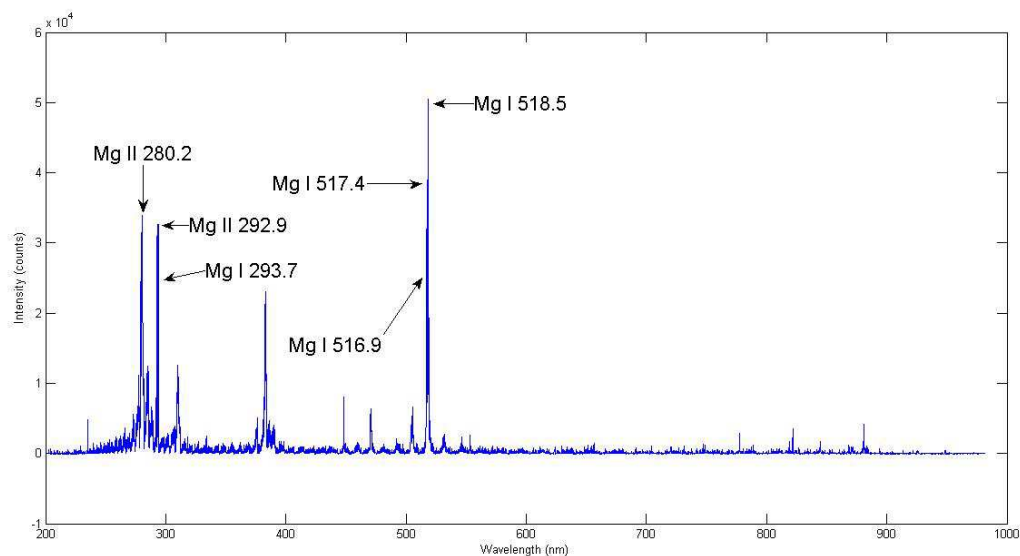


(b) Accumulation of 10 spectra.

Figure 5: LIBS spectra of copper metal at a standoff distance of 3.5 m.



(a) Single spectrum obtained with a single 1800 mJ laser pulse.



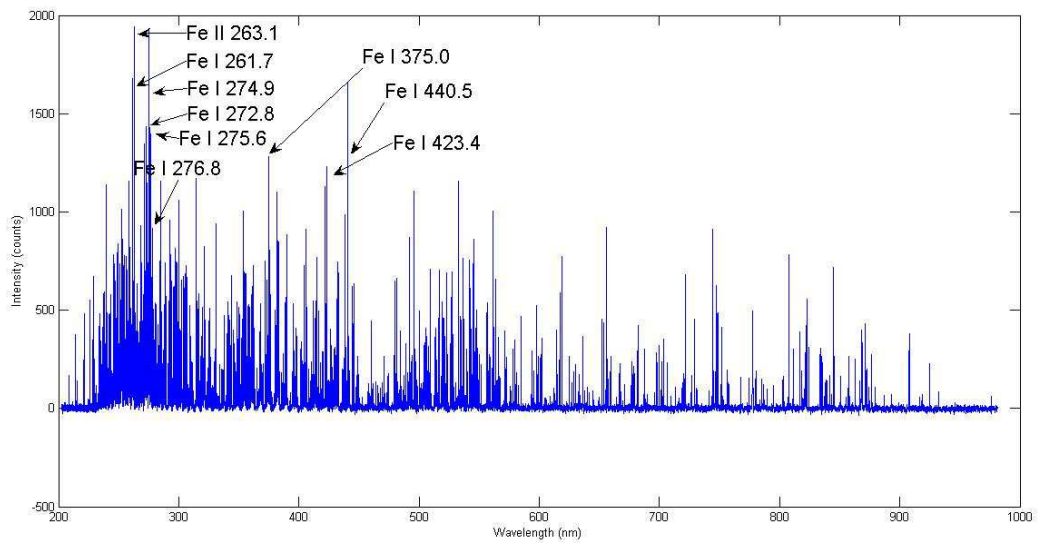
(b) Accumulation of 10 spectra.

Figure 6: LIBS Spectra of magnesium metal at a standoff distance of 3.5 m.

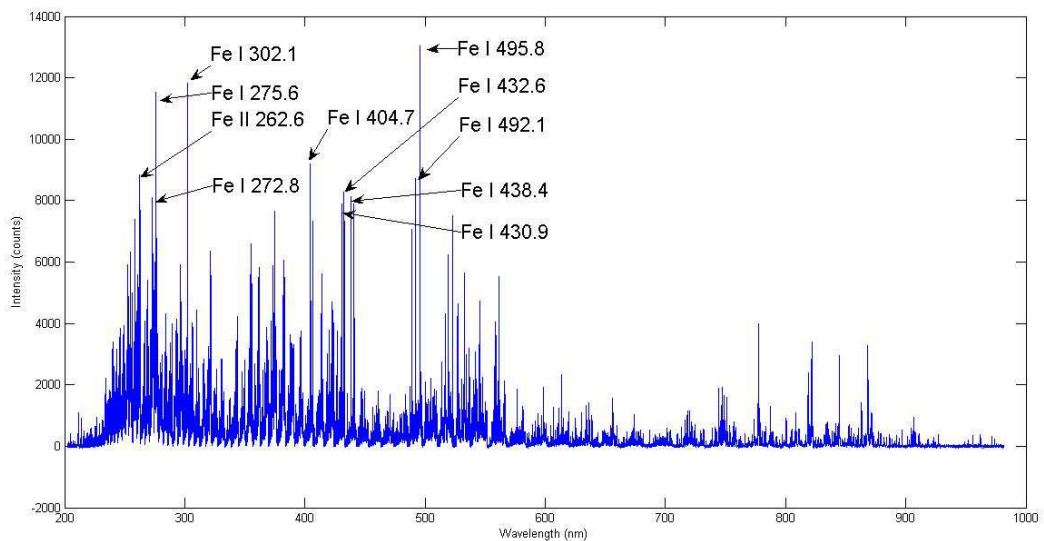
Single shot and 10 shot accumulation spectra for iron and lead are shown in Figures 7 and 8 respectively. These spectra are particularly notable as the signal-to-noise ratios are significantly lower than those exhibited in the spectra of the other pure metals examined here. Signal-to-noise ratios for both single shot and accumulated spectra are approximately 2:1 for both metals. The cause of the comparatively high levels of noise in these spectra is not yet known, although it is possible that it is due to significant differences in the laser-induced plasma lifetimes of these metals in comparison to the other metals examined here. This will be further investigated in future research. Despite the relatively high noise

levels, the highest peaks in each spectrum are associated with emission lines of each of the analysed metals in both the single shot and accumulated spectra.

Peaks associated with the emission lines of the metals being analysed are clearly evident and identifiable in all of the single shot spectra examined above, and in most cases the prominence of these peaks is significantly increased through the use of an accumulation of 10 spectra. These results validate the ability of LIBS to identify relatively pure metallic samples over moderate standoff distances.

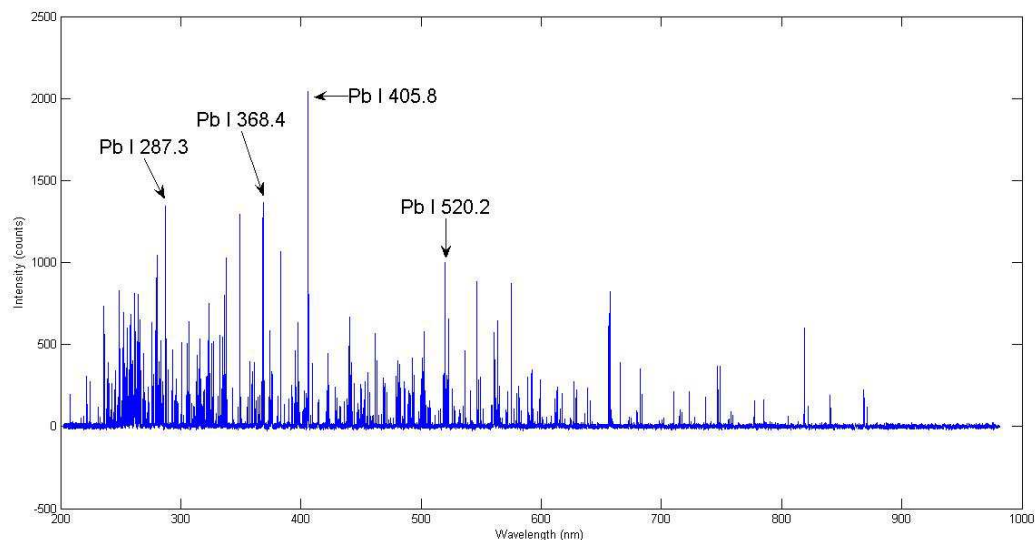


(a) Single spectrum obtained with a single 1800 mJ laser pulse.

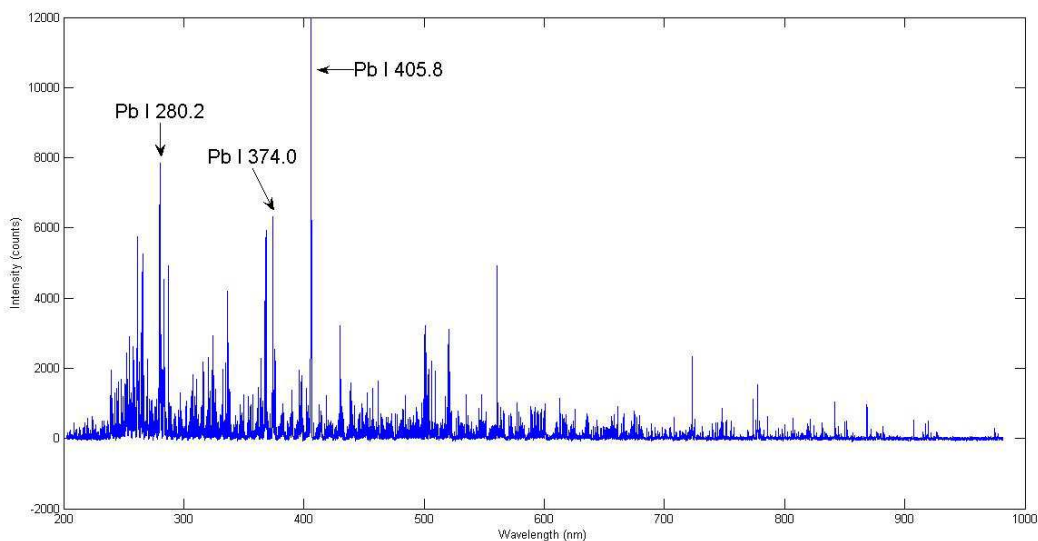


(b) Accumulation of 10 spectra.

Figure 7: LIBS spectra of iron metal at a standoff distance of 3.5 m.



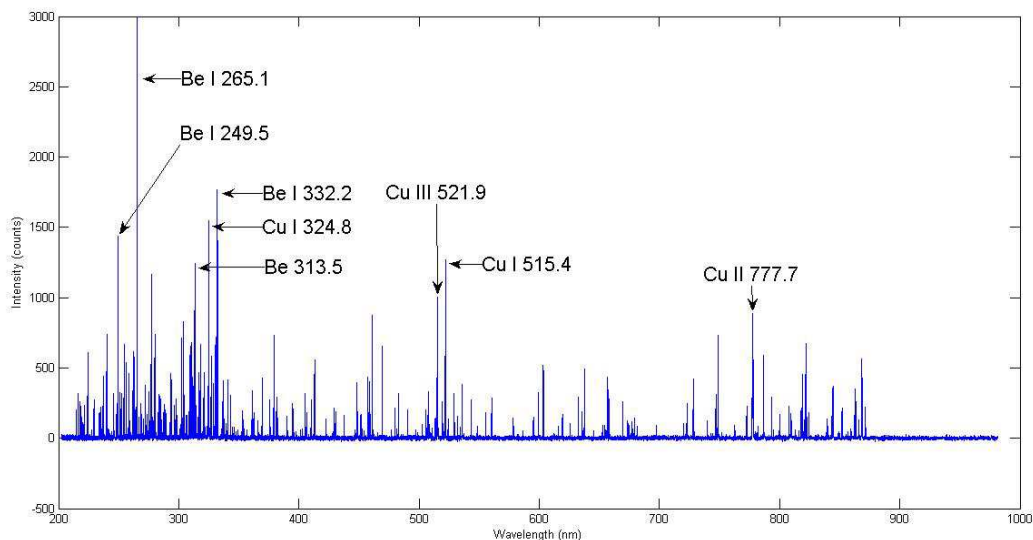
(a) Single spectrum obtained with a single 1800 mJ laser pulse.



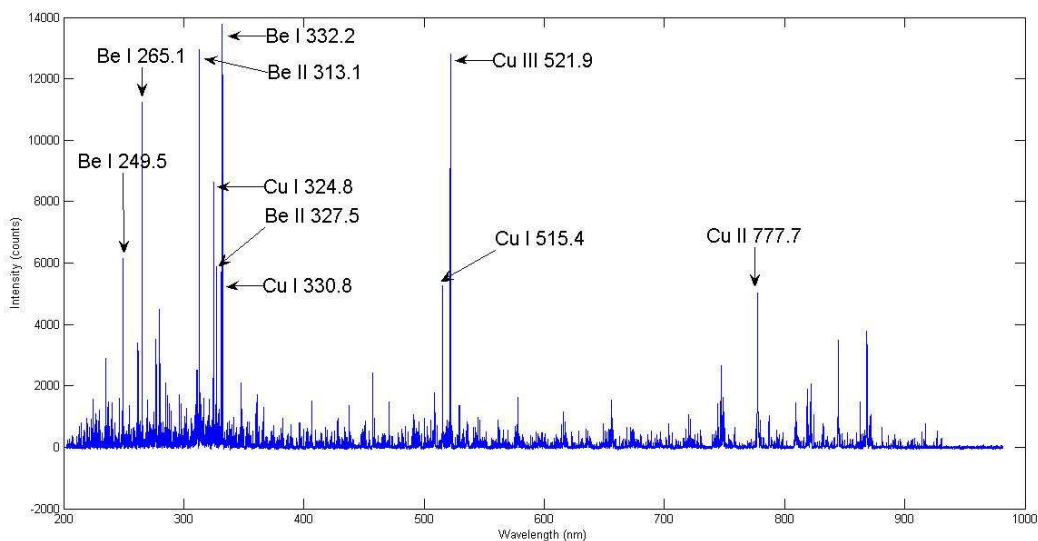
(b) Accumulation of 10 spectra.

Figure 8: LIBS spectra of lead metal at a standoff distance of 3.5 m.

Figure 9 shows single shot and 10 shot accumulated spectra of copper beryllium alloy. Although the signal-to-noise ratio of the single shot spectrum is quite low, at approximately 2:1, the prominent peaks of the spectrum are associated with emission peaks of copper and beryllium and are labelled accordingly. A tenfold accumulation results in a significant increase in intensity of the main peaks, and a corresponding increase in the signal to noise ratios. These results confirm that the constituents of a metallic alloy may be identified using standoff LIBS.



(a) Single spectrum obtained with a single 1800 mJ laser pulse.



(b) Accumulation of 10 spectra.

Figure 9: LIBS spectra of copper-beryllium alloy at a standoff distance of 3.5 m.

3.2 Effect of Laser Pulse Energy

A comparison of single standoff LIBS spectra of zinc metal obtained with two different laser pulse energies is shown in Figure 10. Although the largest peaks in the spectrum obtained using a single pulse of approximately 900 mJ (Figure 10(a)) are associated with atomic emission lines of zinc, several other strong spectral peaks are present which are not indicative of zinc. Specifically, the peaks identified at 233.8, 268.5, 468.4, 617.7, and 658.7 nm

are peaks of relatively high intensity which are not closely associated with atomic emission wavelengths of zinc. These peaks may represent emission lines from atmospheric species or minor contaminants on the sample surface. In addition, the intensities of the peaks present are significantly lower than that required for reliable and accurate identification of the species present, with the intensity of the highest peak within the spectrum being approximately 900 counts. Although the gross intensity of the peaks could be increased by increasing the gain on the iCCD detector, this would also result in the amplification of the noise present. Similarly, accumulation of spectra would result in an increase in the intensities of the zinc peaks, but would also increase the intensity of peaks associated with atmospheric species, and would therefore not result in improved spectra.

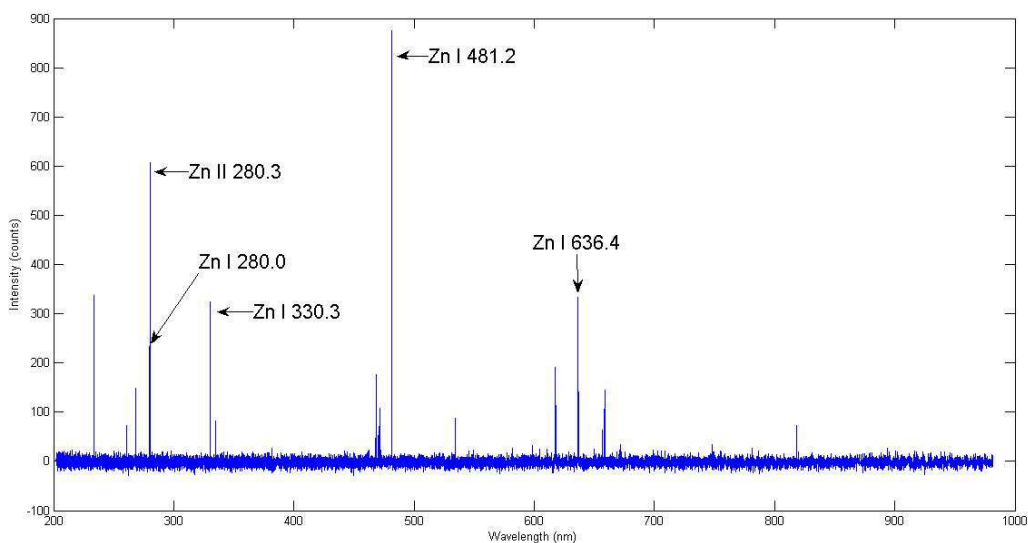
The spectrum of zinc metal obtained with a single laser pulse of approximately 1800 mJ (Figure 10(b)) exhibits comparatively few strong spectral peaks which are not associated with atomic emission lines of zinc metal. The intensities of the zinc peaks also significantly increase, with the strongest peaks being above 5000 counts in amplitude. Finally, a number of additional peaks which are associated with emission lines of zinc become evident with the increased laser pulse energy, in particular those at 255.8, 277.2, 468.1 and 472.3 nm. Intelligent spectral analysis software, with the capability of assessing the confidence of a particular elemental identification through the presence of multiple spectral peaks matching line emissions of the identified element, could use these additional peaks to improve the confidence with which zinc metal is identified as being present. Therefore, the identification of additional spectral peaks would be of great assistance in identifying the elements present in a sample.

3.3 Effect of Laser Focussing

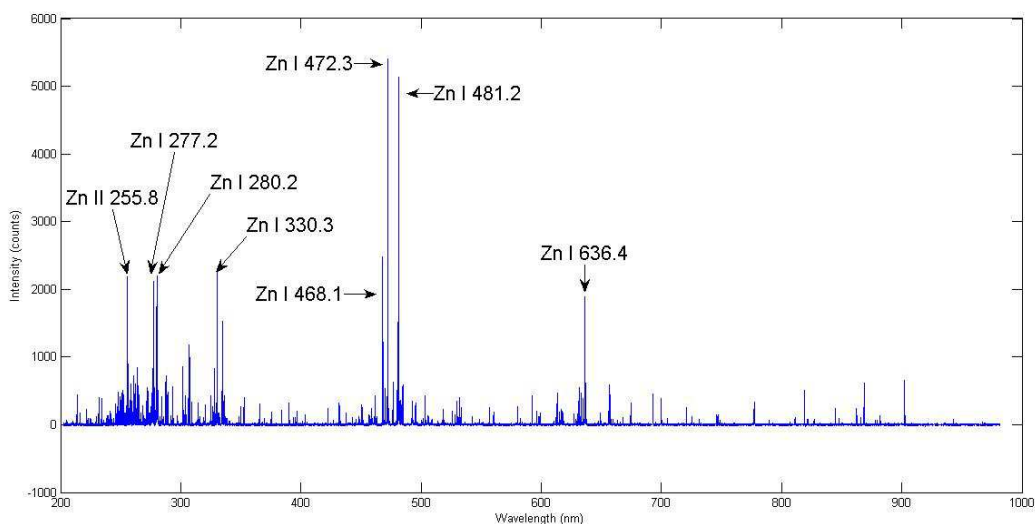
A comparison of LIBS spectra of zinc obtained using different laser focussing conditions is shown in Figure 11. A single laser pulse of approximately 1800 mJ was used to collect both spectra. Figure 11(a) was collected without focussing the excitation laser onto the sample. The spectrum was therefore obtained using relatively low laser power density, resulting in reduced material ablation and decreased plasma temperature. Consequently, the spectrum exhibits extremely low peak intensities. It is interesting to note, however, that the spectrum contains few peaks which are not characteristic of zinc emission. Unfortunately, the largest peak in the spectrum is not characteristic of a zinc emission wavelength, and the spectrum cannot therefore be considered adequate for identifying zinc metal.

In contrast, the spectrum shown in Figure 11(b) was collected using the experimental arrangement employed for all other experiments reported here, that is with the 100 mm focal length laser focussing lens approximately 8 cm from the sample. This resulted in a smaller laser impact region but a comparatively high laser power density within this region. This is expected to result in a greater degree of sample material ablation and subsequent heat transfer into the ablated material, forming a hotter plasma with greater atomic emission. These effects are evident in the higher intensities of the peaks present in the spectrum. In addition, the highest peaks in the spectrum are representative of zinc emission wavelengths. The spectrum does contain many more peaks that are not associated with zinc than the spectrum collected without focussing the laser, but these peaks are significantly lower in intensity than the primary zinc peaks and do not affect the

confidence with which zinc can be identified in the sample. These additional peaks may be due to increased atmospheric gas incorporation in the plasma as a result of increased laser power density and increased plasma temperature.

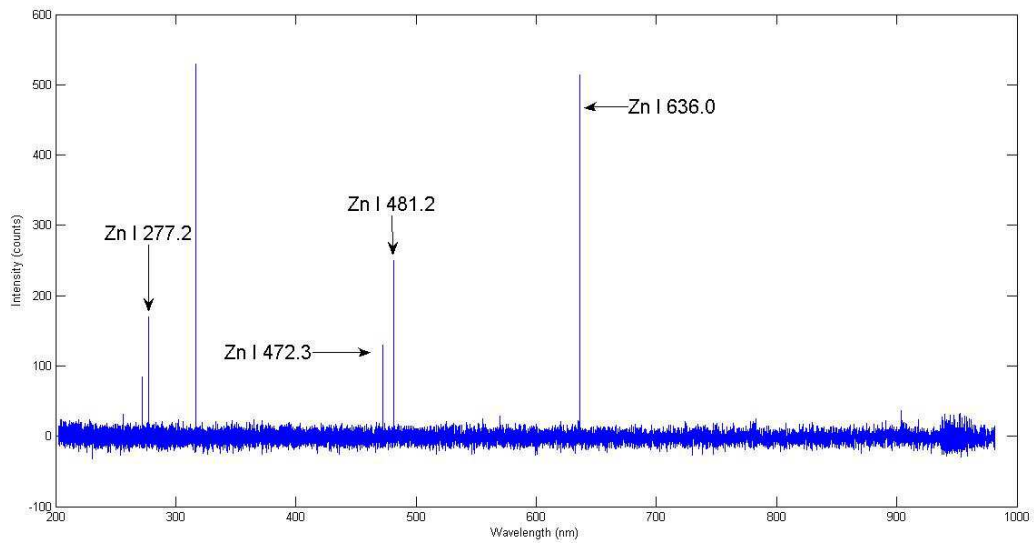


(a) Single spectrum obtained with a single 900 mJ laser pulse.

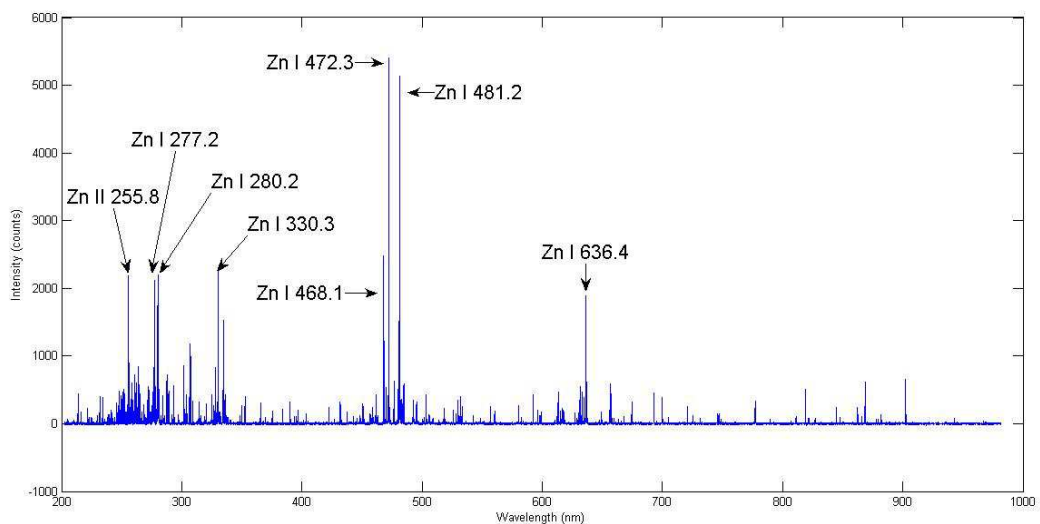


(b) Single spectrum obtained with a single 1800 mJ laser pulse.

Figure 10: Comparison of zinc LIBS spectra collected with different laser pulse energies at a standoff distance of 3.5 m.



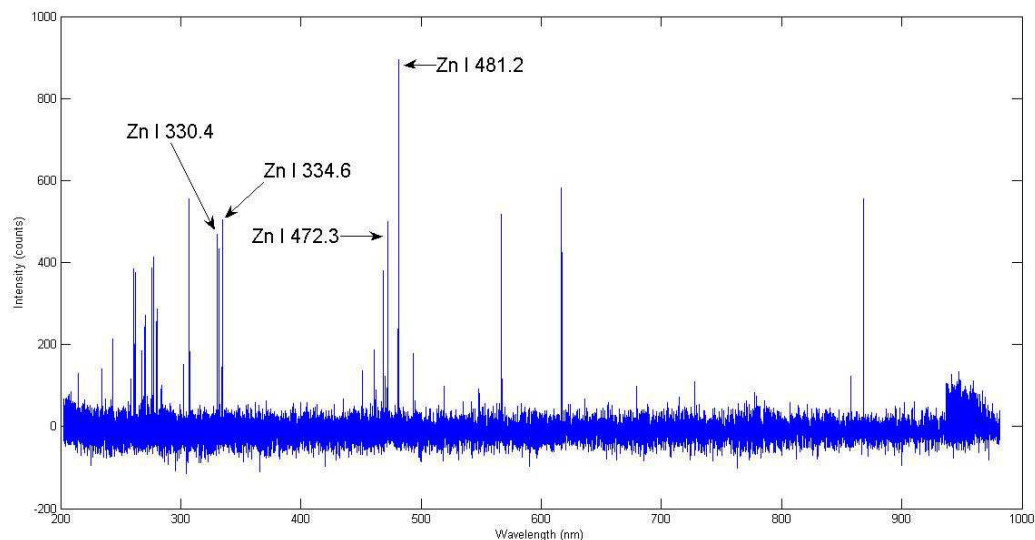
(a) Single spectrum obtained with a single non-focussed 1800 mJ laser pulse.



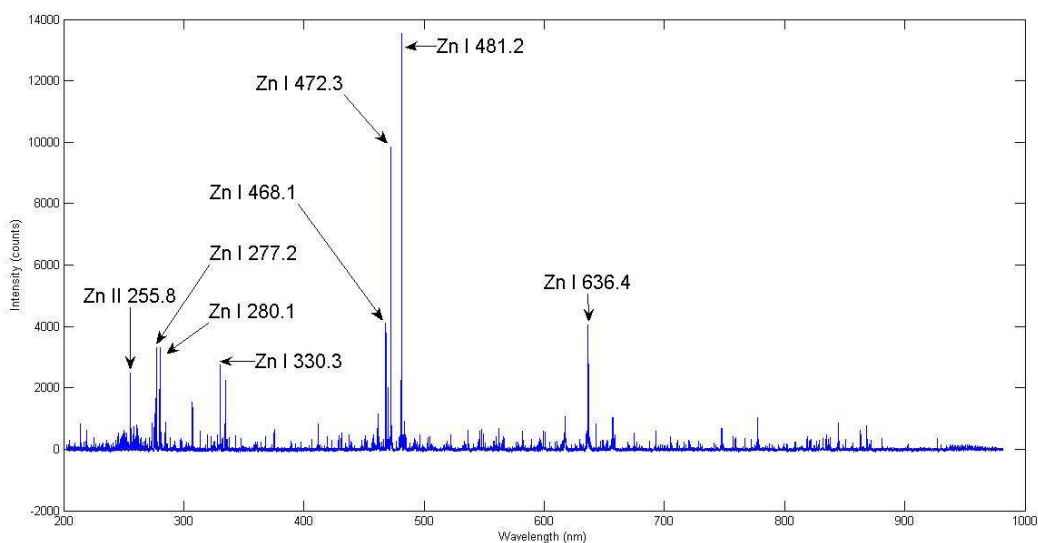
(b) Single spectrum obtained with a single focussed 1800 mJ laser pulse.

Figure 11: Comparison of single pulse zinc LIBS spectra collected with different laser focussing conditions at a standoff distance of 3.5 m.

The spectral improvements achieved by focussing the laser onto the sample become even more evident in spectra obtained by accumulating ten laser pulses, as shown in Figure 12. While the spectrum obtained using ten unfocussed pulses (Figure 12(a)) exhibits relatively low peak intensities and a large number of strong peaks not associated with zinc emission wavelengths, the spectrum obtained using ten focussed pulses (Figure 12(b)) shows high peak intensities and no significant peaks not associated with zinc emission.



(a) Accumulation spectrum obtained with ten non-focussed 1800 mJ laser pulses.



(b) Accumulation spectrum obtained with a ten focussed 1800 mJ laser pulses.

Figure 12: Comparison of 10-pulse accumulation spectra of zinc collected with different laser focussing conditions.

4 Conclusions

The implementation of standoff distance in LIBS introduces several effects which contribute to the difficulty of the technique, including management of the laser power density in the laser path and at the sample, and capturing sufficient radiation from the laser-induced

plasma to perform successful spectroscopic interrogation.

Despite the relatively rudimentary arrangement employed here, coupling between the spectrometer and the collection telescope was achieved with sufficient efficiency to enable spectroscopic analysis. In addition, although not performed in a true standoff fashion, the laser beam was able to be focussed onto the sample with sufficient laser power density to achieve adequate ablation and plasma formation. As a result, LIBS was able to be conducted at moderate standoff distances without prohibitive increases in signal-to-noise ratios. These results represent significant progress toward longer range standoff LIBS, as the increase in range is expected to be achievable by iterative increases in laser path management and light collection efficiency. As explained in Section 1.1, the process of focussing the laser onto the sample from a standoff range is well understood, and although not trivial, is expected to be achievable through the use of optical components arranged in the form of a Galilean telescope.

Differentiation of the metal and alloy samples was trivial with the implementation of high pulse energies and focussing of the laser, leading to maximised laser power density. Spectra acquired using a single laser pulse exhibited significant noise levels and low intensity spectral peaks for some metals, but the most intense peaks for all samples were characteristic of the elements present in the sample. Hence, even using a single laser pulse, the identity of the metal and alloy samples was easily ascertained. However, spectra obtained using an accumulation of ten laser pulses exhibited, in most cases, significantly lower levels of noise and spurious spectral peaks. Unfortunately, the spectra of lead and iron did not markedly improve with the use of accumulation techniques, possibly as a result of significantly different plasma lifetimes for these metals. Further research into the nature of the laser-induced plasmas of these metals may allow for optimised spectrometer delay periods to be incorporated to improve the spectra. However, it is important to note that even these comparatively noisy and poor spectra exhibited strong spectral peaks with sufficiently high signal-to-noise ratios to enable identification of the sample without difficulty.

The results presented here clearly demonstrate that, in order to maximise the signal-to-noise ratio and spectral performance of a standoff LIBS system, it is advantageous to employ high laser power densities equal to or in excess of $1 \times 10^9 \text{ Wcm}^{-2}$, as suggested by Russo [11]. This may be achieved, as in our experiments, through the implementation of a high initial laser pulse energy or by focussing a laser pulse of lesser energy into a small area. Both of these approaches result in an increased laser energy density, resulting in increased laser ablation and plasma formation, and improved spectral performance.

5 Future Development

Despite being performed using a relatively rudimentary experimental arrangement, the experiments discussed within this report clearly demonstrate that LIBS represents a viable standoff technique. However, the results of these experiments also emphasise methods by which the rudimentary experimental arrangement may be developed in order to achieve improved spectral performance. Specifically, the introduction of a variable focal length Galilean telescope for focussing the laser onto samples at a range of distances would allow

the energy density of the laser pulse to be maximised at the sample surface.

In addition, although not described here, observations made during the alignment of the rudimentary coupling between the telescope and fibre optic aperture of the spectrometer suggested that the accuracy of this alignment is critical to the efficiency of the light collection. Extremely small adjustments to the alignment of this coupling were found to result in large variations in the absolute amplitude and signal to noise ratios of the spectra. Therefore, the following additions to the experimental arrangement are also proposed :

- Introduce a rigid, accurately aligned coupling between the telescope and the fibre optic aperture of the spectrometer in order to reduce inefficiencies due to poor alignment.
- Introduce flip-mirror optical elements in the telescope-fibre optic coupling to allow for improved aiming and focussing of the telescope on the target area of the sample, in order to reduce inefficiencies due to poor aiming of the telescope.

An increase in the diameter of the collection telescope would result in a corresponding increase in the amount of light collected from the laser-induced plasma, and would be expected to result in increased signal-to-noise ratios and potentially a greater level of reproducibility in the collection of spectra. It would therefore be prudent to increase the aperture of the collection telescope to the maximum practicable diameter in future developments of the apparatus.

As reported elsewhere [4], the introduction of dual pulse lasing is expected to result in significant increases in the signal-to-noise ratio of spectra. This involves subjecting the sample to two successive laser pulses, separated by a period in the order of tens of microseconds, in order to achieve greater laser ablation, plasma formation, or plasma temperature. The mechanisms through which these improvements are achieved are not fully understood [13], however improvements in atomic emission intensity of up to 300 times have been reported [14]. It would therefore seem extremely prudent to implement the dual pulse capability of the Continuum Surelite III PIV system employed here in order to investigate and optimise the potential spectral improvements.

Finally, examination of the spectra within this report suggests that increased noise levels and the presence of peaks due to atmospheric species are potentially significant problems in standoff LIBS. It may be advantageous to employ advanced signal processing algorithms in order to reduce the impact of these problems and improve the accuracy of species identification. A large number of potential signal processing techniques exist, and identification of the optimal methods will be the subject of future research.

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19. ABSTRACT Analytical chemistry techniques with the ability to analyse objects of interest at significant standoff ranges are of great interest to defence and national security organisations. One analytical technique which has demonstrated standoff capability is Laser-Induced Breakdown Spectroscopy (LIBS). LIBS is performed by using a high-powered laser to ablate a small amount of a sample and to form a plasma. The high temperature of the plasma results in atomic emission of light, which is used to identify the type of atoms present and therefore the nature of the sample. In simplistic terms, it is possible to perform LIBS at standoff distances by remotely irradiating the sample with a laser and collecting the radiation from the laser-induced plasma through a magnifying, large-aperture telescope. This report describes a series of experiments in which initial attempts to perform LIBS over moderate standoff distances were undertaken. Metallic samples were employed, as these materials represent readily available single element samples or simple alloy mixtures which simplify the initial investigation of an analytical technique. The ability of LIBS to identify these samples at a moderate standoff distance (approximately 3.5 m) is investigated, and the effects of laser focussing and pulse energy are examined. Finally, specific suggestions are provided for further development of a standoff LIBS system.					