Chapter 8

Micro-LIBS

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1. INTRODUCTION

MicroLIBS (μLIBS) is a new growing area of Laser Induced Breakdown Spectroscopy which employs μJ energy laser pulses for excitation of plasma emission. Such μJ energy pulses are required to carry out 1D, 2D or 3D microanalysis of material surfaces with spatial resolutions approaching micron scale sizes laterally and nm scale sizes in depth. These pulses allow sampling of very small volumes (∼10–1000 μm³) and masses (∼10 pg–ng). μLIBS is also applicable where modest limits of detection, low cost or portable systems are required. The use of femtosecond pulses for LIBS over the past decade has in some cases also employed μJ laser pulses [1–4] and many of the advantages of μLIBS are also observed using such ultrashort pulses as described in Chapter 7 on femtosecond LIBS. In this chapter we will review the capabilities of LIBS as one scales to microjoule laser pulse energies and progress to date in the application of such systems.

The development of μLIBS has been driven by two factors:

1) the desire to obtain higher spatial resolution when carrying out 2D scans of material surfaces and
2) the development of high repetition rate compact microchip lasers leading to ideal sources for very low energy LIBS applications.

It has been found that the plasma and continuum emission decreases significantly with lower pulse energies and thus one can obtain reasonable performance without using temporal gating. The term μLIBS has also been used in the context of applications with ablation spots of micron scale size [5,6]. In most cases, the definitions based on μJ energy and micron resolution spot sizes are equivalent. This chapter will focus on those studies which have used pulse energies less than 1 mJ.

In the early 1990s Zayhowski developed the microchip laser [7–9] and he and other researchers started applying it to material analysis using both LIBS and laser-induced fluorescence detection [9–11]. Bloch et al. were able to achieve limits of detection...
(LOD) of the order of 100 to 1000 ppm without temporal gating for Pb, Cu and Fe in soils using pulse energies of several \( \mu \)J [10]. More recently \( \mu \)J fiber laser sources with pulse lengths of 10 ps [12] to several nanoseconds [13] have been developed.

By the mid 1990s several groups had started to investigate the application of \( \mu \)J pulses to LIBS in a variety of studies [9,14–17]. In 1996, Geertsen et al. demonstrated the use of 30–70\( \mu \)J pulses for the microanalysis of aluminum alloys [15]. The authors used 266 nm pulses for a variety of studies including LOD of minor elements down to 10 ppm, relative standard deviation (RSD) of \( \sim 10\% \) and lateral resolution to 6 \( \mu \)m. Sallé et al. [18,19] carried out studies of the crater diameters, ablation volumes and expansion plumes for the interaction of 248 nm and 266 nm pulses with energies of 65 to 130 \( \mu \)J and at 532 nm with energies of 10 \( \mu \)J to 4 mJ. Semerok et al. extended these studies to look at the scaling of ablation craters with pulse length for durations of femtoseconds, picoseconds and nanoseconds and energies down to 10 \( \mu \)J [20,21].

\( \mu \)LIBS has also been combined with scanning probe fiber tip microscopy to achieve micron scale size ablation spots by Kossakovski et al. [22]. However, in the later case the emission was not strong enough to give good species identification for submicron ablation spots using a non-gated and non-intensified camera. Rieger et al. [23] explored the scaling and optimization of measuring trace constituents in aluminum alloy for 50 to 300 \( \mu \)J laser pulses at 248 nm as a function of gate time. They achieved LODs of 2 to 450 ppm for elements of Mg to Fe for the case of optimized gate times and 200 \( \mu \)J pulses. Further studies by the same group [24] compared LIBS signals for picosecond versus nanosecond 248 nm pulses. Scaling of line emission, continuum emission and emission lifetime with pulse energy were characterized with reported energy thresholds for observable line emission of 1 \( \mu \)J for ns pulses and 0.1 \( \mu \)J for 50 ps pulses. Above energies of 3 \( \mu \)J the characteristics of the LIBS emission were reported to be comparable for both pulse lengths when identical laser and focusing conditions were used. In recent work by Gornushkin et al. [25], studies were carried out with a 7 \( \mu \)J 1064 nm microchip laser using a non-gated and non-intensified detector. The authors highlight many of the advantages of using microchip lasers, such as good mode quality of the beam, high shot-to-shot reproducibility, the high repetition rate, the low continuum emission and the possibility of using ungated detectors. Observation of line reversal in the emission spectra of Zn demonstrate that optically thick plasma conditions can exist for major constituents even for low energy microplasmas and observed signals and crater sizes for several metals were reported [25]. LODs of the order of a few percent were obtained for metallic samples but poorer sensitivity was observed for pelletized graphite samples.

Studies of surface mapping using \( \mu \)LIBS also began in the mid-1990s. Häkkänen et al. [14] used 200 \( \mu \)J 308 nm pulses to map Ca and Si concentrations in surface coatings of paper. They found good correlation with measurements of the surface using laser induced fluorescence. The group of Laserna et al. started their studies on surface mapping using \( \mu \)LIBS with the investigation of depth profiling of a TiO\(_2\) antireflection coating on silicon [16] and 2D mapping of carbon impurities [26] using 400 \( \mu \)J pulses at 337 nm. Further investigations indicated depth resolution of the order of 40 nm for carbon impurity and demonstrated 3D scans of carbon contamination with 70 \( \mu \)m lateral resolution and 160 nm depth resolution [27]. Recently Menut et al. [5] demonstrated 2D surface scans with 3 \( \mu \)m spatial resolution using 5 \( \mu \)J pulses at 266 nm and LODs in the percent range for mapping of the concentration of minor constituents on the surface of steel. They also reported that ablation probe spots down to 1 \( \mu \)m were possible but
that there was not sufficient signal to allow for measurements of the trace elements at the 1% level. Cravetchi et al. [28] studied crater size, line emission and RSD of signals from trace elements in aluminum demonstrating that μLIBS can resolve different types of micron scale size precipitates in aluminum. RSDs less than 10% were obtained with 7 μJ pulses at 266 nm. Full 2D scans mapping precipitate distribution in aluminum were subsequently demonstrated by the same group with a lateral resolution of 10 μm [29]. Redeposition of ablated material and cross contamination of a scanned surface has been noted by a number of different groups [15,19,22,25,27,29,30].

In the late 1990s, the analysis of elemental chemical content of liquid samples using μJ pulses with the goal of measuring the elemental contents of single cells was demonstrated by Ho and Cheung et al. [17,31]. Using 80–250 μJ pulses at wavelengths of 532 nm and 193 nm they demonstrated a LOD of 50 ppm for Na in water. An acoustic normalization which corrected for shot-to-shot variations in pulse energy and careful spatial sampling of the expansion plume improved sensitivity to the few ppm range.

During the first decade of work in the μJ energy regime many features of μLIBS have been identified and characterised as described in more detail below. In the following sections, microjoule laser sources and their application to μLIBS are briefly reviewed in Section 2, the scaling of LIBS to μJ pulse energies is discussed in Section 3, and finally, a review of the demonstrated applications of μLIBS to date is given in Section 4.

2. MICROJOULE LASER SOURCES

While traditional lasers can be operated in the microjoule range, one of the earliest sources specifically designed as a microjoule pulse source was the microchip laser developed by the group at MIT [7–9,11,32–35]. Additional sources for the μJ energy regime have also been developed by other groups [13,36–40]. At the same time femtosecond laser sources were developed, many of which also operate at microjoule energy levels. Studies of femtosecond LIBS are covered in Chapter 7 and thus femtosecond laser sources will not be discussed here. Recently, fiber optic oscillators and amplifiers have been developed to the point that μJ output energies are obtainable in pulsed operation mode and offer a potential new option for robust sources which can be used in field portable LIBS systems.

2.1. Microchip Lasers

In 1989 Zayhowski et al. reported on the development of a single frequency microchip laser in various different lasing materials [7]. Q-switched operation of the laser was developed using piezoelectric, electro-optic and passive techniques [8,33,34]. The output at the fundamental wavelength is polarized and frequency conversion of the output and Nd:YAG laser harmonics down to 213 nm have been demonstrated [9]. When using ~1 W pump power, output pulse energies of 8 μJ at the fundamental wavelength, 3.5 μJ at 532 nm and 0.7 μJ at 266 nm were reported. Higher pulse energies have since been reported with 10 W of diode pump power resulting in pulse energies of up to 250 μJ and 310 ps pulsewidths at the fundamental wavelength of 1064 nm and 12 μJ at 266 nm output with kHz repetition rates [11,35]. The layout of a low power harmonically
Fig. 1. Schematic of a UV harmonically converted passively Q-switched microchip laser. Entire device is about a cm across. (Reproduced with permission from Zayhowski [11]).

converted microchip laser is shown in Fig. 1. It is fabricated by bonding the gain medium to a saturable absorber and harmonic conversion crystals. In a typical configuration a 0.75 mm thick Nd:YAG gain medium is coupled to a 0.5 mm thick Cr:YAG saturable absorber [34]. Diode pump laser light of 1 W at 808 nm is coupled to the gain medium by a butt coupled fiber. The resonator is formed between a dichroic dielectric mirror at the fiber input face, with a high reflectivity at the laser wavelength and high transmissivity at the pump wavelength, and a partially transmitting mirror at the output face of the saturable absorber. KTP and BBO crystals ~5 mm long are butt coupled to the output face to generate 2nd and 4th harmonic output respectively. The laser output is a single frequency TEM$_{00}$ Gaussian mode with a diameter of the order of 50 $\mu$m. The short cavity length ensures single longitudinal mode operation since only one axial mode has sufficient gain to exceed the lasing threshold within the laser bandwidth.

Other groups have also developed similar microchip lasers with various gain media and geometries. Fluck et al. [41] passively modelocked an Er-Yb:Glass gain medium using a semiconductor saturable absorber mirror (SESAM) to achieve 4 $\mu$J pulses at 1535 nm with a repetition rate of 320 Hz. Spuhler et al. [42] applied a SESAM to a Yb:YAG laser, producing 1.1 $\mu$J pulses at 1030 nm with a repetition rate of 12 kHz. Feldman et al. [43] used a 4 mm Nd:YAG microchip crystal bonded to a 2 mm Cr:CaYAG saturable absorber crystal in a 31 mm external resonator to produce 50 $\mu$J pulses at 1064 nm. Karlsson et al. [44] have produced 12 $\mu$J at 1535 nm with a 1 mm Er-Yb:Glass microchip laser with an external acousto-optic Q-switch and cavity mirror. Druon et al. [45] achieved ~9 $\mu$J pulses at 1.06 $\mu$m and ~0.8 $\mu$J pulses at 355 nm with pulse durations of 300 ps using a Nd:YAG microchip laser together with a double-pass microchip amplifier. Higher repetition rate picosecond to subnanosecond pulsewidth microchip lasers with submicrojoule output energies have also been developed using SESAMs at 1.06 $\mu$m [46] and 1.34 $\mu$m [47]. Hansson et al. used a low voltage multiple quantum well electro-absorption Q-switch system applied to an Er-Yb:Glass laser to generate output pulses up to 470 nJ at a repetition rate of 10 kHz [48]. Further scaling in pump energy or addition of an amplifier chip should allow an increase in the output energy for some of these systems.
Microchip lasers have several attractive features for LIBS as pointed out by a number of authors [11,25]. They are compact, robust and relatively inexpensive. Because of the very short cavity length, the longitudinal mode spacing can be larger than the gain medium bandwidth and only a single narrow linewidth longitudinal mode will be generated. High repetition rates of 1 to 20 kHz can be obtained by passive Q-switching which can result in sub-nanosecond pulses making it easier to achieve the breakdown threshold for materials compared to several nanosecond pulses with the same energy. Active Q-switching can be used to set exact repetition rates and synchronize to external events at the cost of somewhat longer pulse durations. The pulse to pulse stability of microchip lasers is in the range of 0.05 to 0.5% [11,49]. Single transverse TEM$_{00}$ mode output is readily achieved via gain guiding and $M^2$ values of 1.0 to 1.3 have been obtained [32,35]. This leads to low divergence output which can be focused to diffraction limited spot diameters. Various output wavelengths in the range of 1030 nm to 1550 nm have been demonstrated. With low energy pulses, 1550 nm pulses can fall in the eye safe operation range which is an important advantage for system use in public areas.

There remain some disadvantages of microchip lasers with respect to their use for μLIBS. When converted to UV wavelengths microchip lasers still have limited energies, on the order of 1 to 10 μJ per pulse. Further, when the simplest technique of passive Q-switching is used the laser output is free running, making it difficult to synchronize gated detectors. Additionally, the repetition rates of passively modelocked microchip lasers may be too fast for some applications. It has been reported that in the case of graphite the damage from one pulse may modify the surface for the subsequent pulse, decreasing the reliability and sensitivity of the measurement [25]. Commercial versions of microchip lasers are currently available with output energies of the order of ten microjoules at 1064 nm. It is expected that output energies from commercially available microchip lasers will soon be sufficient to exploit the full capabilities of μLIBS. Such lasers should lead to the design of compact LIBS units.

2.2. Microjoule Fiber Lasers

High power modelocked fibre lasers offer another potential laser excitation source for μLIBS. Fiber lasers have undergone intense development for applications in communications and recently with the advent of cladding-pumped large mode area (LMA) fibers it is possible to achieve μJ to mJ pulse energies. Erbium doped fibers at 1550 nm are of particular interest since they are eye safe at low microjoule pulse energies. Recently, acousto-optic Q-switching of LMA Er-doped [37] and Yb-doped fibers [38] have demonstrated close to diffraction limited transverse mode quality output pulses with pulse durations of 100 ns, pulse energies of 500 μJ and 700 μJ, and repetition rates of 400 Hz and 2 kHz, with output wavelengths of approximately 1550 nm and 1060 nm respectively. Passive Q-switching of Er-Yb co-doped fiber has also been demonstrated yielding shorter 3.5 ns, 60 μJ output pulses at around 1550 nm with 0.6 to 6 kHz repetition rates [13]. Active seeding with a pulsed CW diode laser injected into a multi stage erbium fiber amplifier has led to 118 μJ 1550 nm pulses with a duration of few nanoseconds [36] and more recently seeding with a thin disk laser source yielded longer but higher energy diffraction limited pulses of 4 mJ and 50 ns duration at 1060 nm from LMA Yb-doped fiber [40]. In the latter case undoped plain fused silica end caps were fused onto the ends
of the fiber to allow the mode to expand before exiting to avoid damage on the fiber end faces. Harmonic conversion of the nanosecond output pulses from both acousto-optically modelocked and CW diode-laser-seeded Er-doped fiber systems has also been demonstrated using periodically poled Lithium Niobate crystals yielding peak 2\textsuperscript{nd} harmonic conversion efficiencies to 768 nm pulses of 83\% and 62\% respectively, a peak 2\textsuperscript{nd} harmonic energy of 80\(\mu\)J in 45 ns pulses and 3\textsuperscript{rd} harmonic conversion efficiencies of 15\% [50]. Generally the acousto-optically Q-switched systems have pulse lengths of tens of nanoseconds which is longer than the optimum pulse length of picoseconds to a nanosecond for \(\mu\)LIBS applications. The alternative approaches of passively modelocking and amplification of a short seed pulse allow much shorter pulses. However, the damage fluence levels of the fibers in the nanosecond regime scale with the 0.5 power of pulse length given by heat diffusion scaling. Thus, shorter pulses are limited to lower maximum energies. Even so, the amplification of 0.8 ns pulses to 1.2 mJ has been demonstrated in a high power chirped-pulse-amplification femtosecond laser system at 1055 nm [39] and 60\(\mu\)J pulses have been generated by passive modelocking at 1550 nm [13], indicating that sources with nanosecond duration are possible at the 100\(\mu\)J level. Recently work has started on the development of high-pulse-energy high-repetition-rate picosecond fiber sources with 0.6\(\mu\)J, 10 ps pulses at 1064 nm amplified at an 80 MHz repetition rate in a Yb-doped holey fiber system. These pulses were also frequency doubled with 50\% efficiency to 532 nm. It is expected that by using lower repetition rate seed sources the pulse energy should increase leading to 10 ps pulse sources with energies in the range of microjoules.

Recently a guide fiber has been employed for coupling light to micron scale size spots onto a sample for \(\mu\)LIBS analysis [22]. While fiber laser systems have not yet been applied to \(\mu\)LIBS studies it is expected that they will soon become useful in LIBS microanalysis.

3. SCALING LIBS TO MICROJOULE ENERGIES

Over the past decade a basic understanding has been developed of the scaling of the performance of LIBS systems to \(\mu\)J energies. It has been found that the duration of the line and continuum emission along with the relative amount of continuum radiation decreases as one goes below 1 mJ excitation energy. In many cases the signal to noise ratio (SNR) is a weak function of energy and thus it is still possible to obtain good sensitivity if care is taken in collecting the emission light. This means that working with ungated detectors becomes possible which greatly simplifies the detector requirements and reduces system cost. However, the highest sensitivities are achieved using gated systems. Due to the submillimeter size of the plasmas obtained in \(\mu\)LIBS a large fraction of the plasma emission can be coupled to the narrow input slit of grating spectrometer systems. As the pulse energy decreases, the craters produced in \(\mu\)LIBS decrease in diameter and depth. The smaller sample areas achieved allow the probing of much smaller features approaching a micron in size for microanalysis applications. However, there is a tradeoff between sensitivity and sample area that must be taken into account for any given application. In the following section the scaling of these properties is discussed in detail.
3.1. Plasma Emission and Lifetime

Many materials have been examined using μLIBS, including Si photovoltaic cells, paper and paper coatings, and various metals. These studies have been performed across a range of energies from 400 μJ [16] down to 0.1 μJ [24]. A spectrum typical of what can be obtained using μLIBS is given in Figure 2. This spectrum of aluminum was taken using a single 8 μJ pulse with zero gate delay and a gate width of 200 ns.

Emission scaling with energy has been studied using a photomultiplier with a bandpass filter centered at 289 nm and a collection angle of f/6. Single line emission has been detected from Si down to 1 μJ with 10 ns 248 nm pulses and down to 0.1 μJ with 50 ps 248 nm pulses [24]. The resultant signal strengths are shown in Fig. 3 as a function of pulse energy for these two pulse lengths. It is seen that above an energy of approximately 3 μJ the signals are of the same strength. Only as the breakdown threshold is approached does one see a difference in the emission. Emission is observed for shorter pulses at lower energies while emission disappears for longer pulses because the intensity is no longer sufficient to breakdown the target surface. Thus, above several microjoules the important variable appears to be energy fluence rather than intensity. The focal spot diameter was approximately 5 μm for these experiments leading to a fluence of approximately 5 J cm−2 for an energy of 1 μJ. The vertical scale units for Fig. 3 correspond approximately to photons per steradian except above ~3 × 10⁷ when the photomultiplier became weakly saturated. A more efficient optical collection system and more sensitive photomultiplier detector should be able to detect signals at even lower energies.

The scaling of peak emission time versus pulse energy has been studied by Häkkänen et al. [14] and Rieger et al. [24] for dielectric and metallic targets respectively. The scaling for the former case is shown in Fig. 4 indicating that optimum measurement

![Fig. 2. Background corrected spectrum of aluminum plasma emission using a single 50 ps, 8 μJ pulse at 248 nm, with a gate width of 200 ns and zero gate delay. The spectrum was obtained using a system for which an absolute calibration was performed. (Reproduced with permission from Rieger et al. [24]).](image-url)
Fig. 3. Filtered photomultiplier detection of silicon line emission at 288 nm as a function of laser pulse energy for 10 ns and 50 ps pulses at 248 nm. The focal spot diameter was approximately 5 μm, yielding a fluence of ∼5 J cm⁻² for 1 μJ pulse energies. The horizontal line represents the noise floor of the PMT. (Reproduced with permission from Rieger et al. [24]).

Fig. 4. (a) Smoothed and normalized time-resolved signal-to-background ratios of the silicon line at 251 nm at various excitation energies using a 308 nm laser. (b) Decay time for calcium and silicon signals at 422 nm and 251 nm respectively as a function of laser pulse energy. (Reproduced with permission from Häkkänen et al. [14]).

times for peak signal to background ratio decreases to about 100 ns for 200 μJ pulses in line with the decrease in plasma emission decay time with pulse energy. The results of Rieger et al. [24] shown in Fig. 5 indicate that the emission decay time reduces further to a few nanoseconds as the pulse energy is reduced below 2 μJ for 10 ns pulses and below 0.3 μJ for 50 ps pulses. For energies above 3 μJ an expanding spherical plasma with a lifetime of tens of ns is formed for both ps and ns pulses leading to similar decay time constants for the emission. Similar observations have been reported by other authors with plasma emission decay times of 8 ns [25] to 15 ns [10] for 10 μJ 1064 nm subnanosecond microchip laser pulses. Gornushkin et al. also observed a prompt emission which was only slightly longer than the subnanosecond laser pulse [25].
It has been observed that the decreasing decay time of the line emission is matched by an even faster decay of continuum emission. As a result, the ratio of line to continuum emission improves as one reduces pulse energy and thus one can detect the LIBS signal even in the absence of a gated detector [16,24,25].

3.2. Crater Size – Lateral and Depth Resolution

One of the important advantages of μLIBS for microanalysis is the size of the ablation spot as compared to conventional LIBS. Several groups have studied the scaling of crater diameter or crater volume as a function of pulse energy [15,18,19,21,25,27,28,51]. However, one must distinguish between the detection region, which is ionized sufficiently to yield emission signals, and the total region, which is ablated by the laser pulse. Much of the ablated material is removed after the laser pulse by the shock wave and melt wave propagating into the target. The crater size will therefore represent an upper bound to the actual region probed in composition measurements.

A careful test of the lateral resolution obtainable by μLIBS was performed by Geertsen et al. [15] using a specially fabricated test sample with a sharp Cu/Al interface. Using pulse energies in the range of 35–40 μJ at 266 nm, a series of shots were spaced at 2 μm intervals measured perpendicular to the interface. The sample was displaced parallel to the interface by 15 μm between each shot to prevent previously ablated material from being resampled. The data from the experiment is shown in Fig. 6. The reported lateral resolution was ~6 μm.

Kossakovski et al. [22] used 12.5 μJ pulses at 337 nm coupled to an etched fiber probe tip in a scanning probe microscope to investigate the surface of basalt and meteorite samples. They were able to produce submicron ablation spot diameters but noted that the corresponding emission signals were too weak to obtain useful LIBS signals using a
Fig. 6. μLIBS 1D scan using pulses in the range of 35–40 μJ at 266 nm across a Al-Cu interface for determination of lateral resolution. Special care was taken to prevent resampling of ablated material, and a lateral resolution of 6 μm was reported. (Reproduced with permission from Geertsen et al. [15]).

20X microscope objective and viewing the emission plasma from the side. Useful LIBS signals were obtained when using spots greater than a micron in diameter.

The scaling of crater size and volume is an important variable in μLIBS applications. Aluminum is one of the most thoroughly studied materials in the μLIBS literature, and probably represents the clearest dataset with which to investigate the scaling laws for sample volume. Measured crater diameters and volumes for aluminum using nanosecond μJ pulses are shown in Fig. 7 and Fig. 8. Given the different methods of defining crater

Fig. 7. Single-shot crater diameter as a function of energy for Al. Open circles represent shots using 248 nm pulses as described in [23]. Data from Cravetchi et al. [28], Geertsen et al. [15] and Sallé et al. [18] taken with ~10 ns pulses at 266 nm and data from Gornushkin et al. [25] taken with 1064 nm are shown as solid points.
Fig. 8. Single-shot crater volume as a function of energy for Al. Open circles represent shots using 248 nm pulses as described in [23]. Data from Geertsen et al. [15] and Sallé et al. [18] taken with $\sim$10 ns pulses at 266 nm. The line is a linear regression to the 248 nm data points which are above 25 $\mu$J and below 300 $\mu$J.

diameter and of measuring crater volume used in the literature the agreement between groups is quite good.

Ablation efficiency $[\mu m^3 \mu J^{-1}]$ has been measured for a variety of metals under different conditions. Results which used nanosecond pulses are given in Table 1, and picosecond results are given in Table 2. There are significant variations which may be due to the different focal geometries and intensities employed. While reasonable agreement for crater size scaling in the range applicable to $\mu$LIBS has been achieved in the literature between a number of groups, further work will be required to reach a consensus on the scaling of ablation efficiency.

The volume which actually contributes to LIBS emission is expected to be smaller and shallower than the final ablation crater. These effects will depend on the focal spot profile as well as the material characteristics. Redeposition both immediately surrounding the

<table>
<thead>
<tr>
<th>Author</th>
<th>(\lambda)</th>
<th>Pulse-width</th>
<th>Al</th>
<th>Cu</th>
<th>Fe</th>
<th>Ni</th>
<th>Pb</th>
<th>Mo</th>
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<td>30</td>
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<td>Semerok [20]</td>
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<td>29.3</td>
<td>6.5</td>
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<td></td>
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<td>6 ns</td>
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<td>6 ns</td>
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<td>0.55 ns</td>
<td></td>
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<td></td>
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<td></td>
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<tr>
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<td>6 ns</td>
<td>5</td>
<td>2</td>
<td>0.9</td>
<td>0.7</td>
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Table 2. Picosecond Ablation Efficiencies \( [\mu \text{m}^3 \mu \text{J}^{-1}] \)

<table>
<thead>
<tr>
<th>Author</th>
<th>( \lambda )</th>
<th>Pulse-width</th>
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<th>Cu</th>
<th>Fe</th>
<th>Ni</th>
<th>Pb</th>
<th>Mo</th>
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<td>0.9</td>
<td>21.3</td>
<td>0.5</td>
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<tr>
<td>Semerok [21]</td>
<td>532 nm</td>
<td>25 ps</td>
<td>4</td>
<td>0.9</td>
<td>0.4</td>
<td>0.7</td>
<td>12.5</td>
<td>0.7</td>
</tr>
<tr>
<td>Gornushkin [25]</td>
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<td>550 ps</td>
<td>1</td>
<td>0.4</td>
<td>0.45</td>
<td>0.6</td>
<td>2.0</td>
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<tr>
<td>Semerok [21]</td>
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<td>25 ps</td>
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<td>0.45</td>
<td>0.6</td>
<td>2.0</td>
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</tr>
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</table>

Crater and at further distances is an additional phenomenon which affects the effective lateral resolution that may be achieved by \( \mu \)LIBS. Under some conditions ablated material may redeposit and contaminate unsampled areas as discussed in Section 4.2 below. Further work will be required to ascertain the actual source volume contributing to the LIBS signal observed, and the ultimate spatial resolutions that will be possible in \( \mu \)LIBS.

3.3. Limits of Detection

Only a few studies have reported LODs for elements using \( \mu \)LIBS. Geertsen et al. used a frequency-quadrupled Nd:YAG with pulse energies of \( \sim 40 \mu \text{J} \) to measure LODs of minor elements in aluminum [15]. Specially prepared homogeneous aluminum targets were used for this work. In an alternative approach Rieger et al. [23] took advantage of the small probe spot size to probe only the matrix material in standard aluminum alloys for LOD measurements. The concentration of minor constituents in this matrix region was calibrated using electron probe microanalysis of the matrix region of the alloys. In the latter measurement the SNR was obtained by taking the peak line emission compared to the \( 3\sigma \) noise in nearby regions of the spectrum without line emission. For trace elements at concentrations below \( \sim 1\% \) it was assumed that the signal scales linearly with concentration. A comparison with the traditional technique for determining LOD was performed and reasonable agreement between the techniques was obtained. The SNR was measured versus gate delay times and the optimum gate delay found for the given plasma conditions for a number of trace elements.

An example of the \( 3\sigma \) LOD for Cu in aluminum alloy as a function of pulse energy and gate delay is given in Fig. 9. It is seen that the LOD and optimum gate time are weak functions of pulse energy. The optimum LODs for a number of elements were determined and are presented in Table 3 together with values reported by Geertsen et al. [15]. A typical set of values for mJ energy LIBS measurements from Sabsabi et al. [52] is also given for comparison. To compare values taken with different number of shots it was assumed that the LOD scales with the inverse square root of the number of shots. The values presented have all been scaled to single shot values using this scaling. It is seen that the optimized values are not greatly different from those reported for 60 mJ pulses, and single-shot LODs are mainly in the range of 20 to 400 ppm for 40 to 200 \( \mu \text{J} \) pulses, depending on the element and line observed. Using more shots improves the LODs that are possible, as in the case of Geertsen et al. who report a LOD of 3 ppm for Mg using an accumulation of 150 shots [15].

The detector used in Rieger et al. [23] and Sabsabi et al. [52] were both similar gated intensified photodiode arrays, with similar spectrometer characteristics, including...
Fig. 9. LOD as function of gate delay for Cu emission at 324.8 nm in Al 7075 alloy for 100 µJ (open squares) and 200 µJ (solid circles) laser pulse energy. (Reproduced with permission from Rieger et al. [23]).

Table 3. LOD for minor elements in aluminum alloys. All values are scaled to equivalent single shot acquisitions values, using an $N_{\text{shot}}^{-1/2}$ scaling.

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<tr>
<td>Cr</td>
<td>425.4 nm</td>
<td>204 ppm</td>
<td>22 ppm</td>
<td></td>
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<tr>
<td>Cu</td>
<td>324.8 nm</td>
<td>245 ppm</td>
<td>71 ppm</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>327.4 nm</td>
<td>245 ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>285.2 nm</td>
<td>37 ppm</td>
<td>2 ppm</td>
<td>14 ppm</td>
</tr>
<tr>
<td>Mn</td>
<td>279.5 nm</td>
<td>35 ppm</td>
<td>67 ppm</td>
<td>14 ppm</td>
</tr>
<tr>
<td>Si</td>
<td>251.6 nm</td>
<td>403.1 nm</td>
<td>67 ppm</td>
<td>14 ppm</td>
</tr>
<tr>
<td>Zn</td>
<td>334.5 nm</td>
<td>281 ppm</td>
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the slit widths. The only major difference in the experiments besides the energy is the laser wavelength used: Sabsabi et al. used 1064 nm whereas Rieger used 248 nm. The absorption will be better at 248 nm for metals, and plasma shielding will be a greater issue for the 1064 nm at higher energies which may affect the comparison somewhat. At still lower energies, Bloch et al. reported obtaining hundreds of ppm LODs for metals in soil [10].

In the case of a high energy LIBS emission plasma, the entrance slit of the spectrometer represents the limiting aperture for acceptance of light. The entrance slit and the collection optics limit the spatial region of the plasma plume that may be observed at any given time. In the case of µLIBS, the spatial expansion of the plasma is much
smaller with a size comparable to the slit widths used for spectral measurements. Thus, a larger fraction of the plasma emission can be collected by the spectrometer as compared to traditional mJ pulse energy LIBS. The result is that the LODs reported in the μLIBS literature are often comparable to those reported by more traditional LIBS systems using mJ pulse energies.

3.4. Signal Linearity with Concentration

An important issue in the application of LIBS to analytical measurements is the scaling of the signal with concentration. For a small, optically thin plasma it is expected that the line emission strength should scale linearly with concentration for minor constituents. This linear scaling is observed in the emission of Cu in aluminum targets for concentrations below 0.1% as seen in Fig. 10. For the dominant species self reversal, indicating strong optical opacity, can be observed at energies as low as 7 μJ as reported by Gornushkin et al. [25]. Signal linearity depends on the characteristics of the line under observation, the focal conditions of the laser and the observation time. However, it appears that for many elements at concentrations less than ~1000 ppm signal linearity can be assumed.

4. APPLICATIONS

To date, the main application areas of μLIBS have been in the analysis of very small sample volumes (~10–1000 μm³) and in the scanning microanalysis of surface composition. Microanalysis can be carried out in 2D or 3D with depth resolution by using repeated scans over the surface. Initial reported results in these areas are presented below.
4.1. Microanalysis of Small Volumes

Microanalysis of metallic samples has been reported by Geertsen et al. [15], Rieger et al. [23,24], Cravetchi et al. [28] and Gornushkin et al. [25]. Geertsen et al. demonstrated the use of μJ pulses for the microanalysis of aluminum alloys [15]. The authors used 30 to 70 μJ pulses at 266 nm focused onto the samples using a 25X reflective microscope objective. Due to the very small focal spot used in these experiments, the signals obtained were very sensitive to inhomogeneity on the μm scale size. In studies reported by Cravetchi et al. [28,29] it was shown that the small probe spot could be positioned on individual precipitate crystals and used to analyze the composition of individual precipitates. The placement of a probe spot either on the precipitate or in the surrounding homogeneous matrix region is illustrated in Fig. 11.

It was shown that statistically significant determination of precipitate type could be made with single shot spectra by detecting emission lines which were more than 3σ higher than the same line for the homogeneous matrix [29]. It is essential for any application on the micron scale that the analysis be obtained in a single shot since the features being measured may be ablated in a single shot.

Broadband LIBS signals, covering a large spectral range using μJ pulses have recently been demonstrated by Gornushkin et al. [25]. The use of broadband LIBS is seen as a major step forward for material analysis since one to two orders of magnitude more data can be obtained on each laser shot, thereby making optimum use of the limited photon emission from a single laser shot. Using an ungated detector, Gornushkin et al. measured the μLIBS spectra of a number of metals with clear observation of emission lines but with significant continuum for the 1064 nm 7 μJ probe pulses. The authors observed that a moving target was necessary since the melting from previous laser shots left a

![Fig. 11](image-url)

Fig. 11. (a) Scanning electron microscope image of precipitates on the surface of aluminum alloy and individual single-shot μLIBS craters produced with 7 μJ pulses at 266 nm. Matrix (dark area) shots are labeled M1 and M2, while μLIBS shots that sampled precipitates (bright areas) are labeled P1 and P2. (b) Representative single-shot spectra from matrix and precipitate regions of the aluminum surface. Clear differences are observed with a pulse energy of 7 μJ. (Reproduced with permission from Cravetchi et al. [28]).
more reflective surface and the LIBS signal would disappear after the first shot. This indicates that the use of 1064 nm wavelength is not optimum for measurements of many metals because of high reflectivity at this wavelength. For this reason many µLIBS investigations have been carried out using UV wavelength lasers to take advantage of the improved coupling.

Bloch et al. studied soil samples to detect Cu, Fe and Pb contamination using 10µJ pulses at 1064 nm from a microchip laser [10]. The plasma emission was measured using an ungated and unintensified compact diode-array based spectrometer. The authors noted that the plasma continuum radiation decays quite rapidly with a time constant of \( \sim 15 \text{ ns} \). As a result, they were able to measure concentrations at the hundreds of ppm level without the need for temporal gating. Kossakovski et al. probed a meteorite sample comparing probing with a focal spot from a 50 mm quartz lens with that through an etched fiber probe showing the signals were similar for similar power densities [22]. In both cases light was collected from the side with a 20X microscope objective and an ungated unintensified spectrometer was used. Good signals were obtained when higher energies per pulse were used leading to probe craters on the order of 2 µm in diameter or greater. Pelletized graphite targets impregnated with magnesium hydroxide powder were studied by Gornushkin et al. using 7µJ pulses with limited success [25]. They attributed the lack of success to the fragility and roughness of the target surface which eroded easily under the 5 kHz repetition rate laser. Due to the high repetition rate, the target was scanned in a spiral pattern in order to present a new spot to the sampling laser for every pulse.

4.2. Scanning Microanalysis of Material Surfaces

One main application of µLIBS is in the scanning microanalysis of material surfaces. To achieve high spatial resolution and small ablation depths, very small energies and small focal spots are desired. It has been reported that as the spot size approaches one micron, the signal becomes too weak for material composition analysis [5,22]. However, these observations were made for nanosecond pulses and without optical gating in one case. Using shorter picosecond or femtosecond pulses and better light collection efficiency it may be possible to obtain LIBS signals in cases where the ablation crater is less than 1 µm.

Häkkänen et al. have studied the application of µLIBS to the mapping of surface coatings on paper [14,30]. This work also represents one of the earliest uses of LIBS as a surface mapping tool. The LIBS results were compared with laser-induced fluorescence (LIF) and found to give good agreement. The results of the 2D µLIBS scan and 2D LIF scan are presented here in Fig. 12. 2µJ pulses at 308 nm were scanned over a 10 mm by 10 mm section of paperboard while monitoring the fluorescence signal at 422 nm. The same scan was performed after increasing the energy to 200µJ pulses at a fluence of \( \sim 10^9 \text{ W cm}^{-2} \), leading to plasma emission. This fluence was sufficient to remove the paper coating, and generated craters 30 µm in diameter, and 2 µm deep. The Si I 251 nm line was monitored using a PMT with a delayed boxcar integrator. 8 such shots, each displaced 32 µm, were averaged to generate a single data point corresponding to a pixel 30 µm \( \times \) 250 µm. 40 such pixels were taken to make a single row, and 40 such rows make up the entire image presented in Fig. 12b. The LIF and LIBS images are
expected to be negatives of each other since the Si line for the LIBS signal is sensitive to the coated regions of the paper while the fluorescence measurements are sensitive to organic compounds visible in the less coated regions.

Further improvements to the measurement technique were reported in a subsequent investigation [30]. Using a similar setup as previously the authors employed 80\(\mu\)J pulses at 308 nm and a 40 mm lens to generate focal spot sizes \(\sim 100\mu\)m in diameter. The resulting craters were also 100\(\mu\)m in diameter and 0.5\(\mu\)m deep. Using a series of 40 shots for each location on the target surface, the authors were able to measure the depth profile distribution of the pigment layers that make up the smooth surface of modern paper. A 2D depth resolved scan through the topcoat, precoat and into the base layer of paper, is shown in Fig. 13.

Scanning \(\mu\)LIBS of anti-reflection coated and uncoated silicon surfaces has been studied by Laserna’s group in several reports [16,26,27,53]. In the initial investigation of Hidalgo et al. TiO\(_2\) anti-reflection coatings for photovoltaic cells were studied using large, low fluence spots in order to achieve better depth resolution [16]. Using pulse energies of 400\(\mu\)J delivered to the target and focal spots of 160\(\mu\)m \(\times\) 40\(\mu\)m, depth profiling of the TiO\(_2\) coating was performed, and the coating was distinguishable from the Si substrate. However, a depth resolution was not estimated by the authors. One interesting feature noted by the authors was a dependence of the emission signal strength on the coating thickness which also correlated with the film reflectivity. The peak field

![Fig. 12. 2D scan of a 10 mm by 10 mm piece of coated paper board. (a) Laser-induced fluorescence of underlying paper at 422 nm and (b) \(\mu\)LIBS scan at 251 nm for Si in paper coating. (Reproduced with permission from Häkkänen et al. [14]).](image)

![Fig. 13. \(\mu\)LIBS 2D depth profile scan of the composition of paper using 80\(\mu\)J pulses at 308 nm. Gray indicates top coat, composed of a 50:50 mix of calcium carbonate:kaolin. Black indicates precoat, composed of a 80:20 mix of calcium carbonate:kaolin. White indicates the base paper. (Reproduced with permission from Häkkänen et al. [30]).](image)
strength in the coating which causes breakdown and emission depends on the interference between the reflected wave and incident wave and is a sensitive function of the layer thickness and thus a dependence on coating thickness is to be expected.

Using the same setup, Vadillo et al. applied μLIBS to a full 2D and 3D mapping of photovoltaic cell structures on silicon. The pulse energy was approximately 40 μJ [26]. Using these conditions, it was possible to produce a 2D surface map of carbon contamination distribution. By taking multiple shots to obtain depth profiling at each of the surface map locations, a 3D map was also produced, giving carbon distribution not only at the surface, but at layers further down.

The mapping work was extended to simultaneous monitoring of multiple wavelengths for mapping of Si photovoltaic cells in Romero et al. [27]. The setup was similar to that of Hidalgo et al. [16] where pulses of 100 to 400 μJ were used. Using this setup, the authors were able to generate a set of spectrally resolved images from their data, with a lateral resolution of about 80 μm. Moving on to a full three dimensional analysis of the photovoltaic cells Romero et al. studied the distribution of carbon in the solar cells, using a series of 2D scans over the same area [53]. The resulting lateral resolution obtained by Romero et al. was 70 μm, and the depth resolution was approximately 0.16 μm. In this work the goal was to achieve good depth resolution and thus the focal spot size was increased to give the low fluences necessary.

Menut et al. combined a LIBS system with an optical microscope and generated a 2D surface scanning instrument with a lateral resolution of 3 μm using an Ar buffer gas [5]. Crater sizes down to 1 μm are reported, though at such low energies the SNR was insufficient for analysis of minor constituents. The setup described by Menut et al. [5] detected signals at a pulse energy of 5 μJ, resulting in craters approximately 3 μm in diameter for their steel sample. The system was able to acquire signals at 20 Hz, and has been used to map the surface composition of various samples. In Fig. 14 a multi-elemental map of a single inclusion in a steel alloy is shown.

Cravetchi et al. reported 2D mapping of aluminum surfaces and identification of precipitates using 8 μJ pulses at 266 nm [29]. Particular attention was directed towards improving the statistical validity of the precipitate identification technique. A Gaussian function was fit to the signal intensity distribution of all shots in the mapped region to derive the average and standard deviation for signals corresponding to the background matrix. Only signals 3σ above this level were deemed to be regions of precipitates. Correlations between various elements in a given type of precipitate can easily be

Fig. 14. Scanning μLIBS image of a single inclusion on the surface of steel as seen in the emission of elements Mn, Fe, Ti and Ni. (Reproduced with permission from Menut et al. [5]).
Fig. 15. Correlation plots of peak intensity values for minor elements in aluminum alloys. (a) Mn vs Fe shows a positive correlation as they appear in the same precipitates, (b) Mn vs Mg yields a negative correlation in both lobes, as they do not appear in the same precipitates. Dashed lines are $3\sigma$ values from the nonlinear Gaussian fit to all available data. Solid lines are linear regressions within their respective quadrants. (Reproduced with permission from Cravetchi et al. [29]).

observed as shown in Fig. 15. The densely populated region in the lower left hand corner of the plots represents the matrix background. Based on the standard deviation of signals observed, it was possible to set detection thresholds for various trace elements and map out the two dominant precipitates in Al 2024 alloy with 10\(\mu\)m lateral resolution [29].

A few of the groups studying \(\mu\)LIBS have noted the issue of cross contamination from material redeposited onto the surface from previous ablation spots. Romero et al. [27] and Häkkänen et al. [30] measured the single-shot contamination range from an ablated location for silicon and paper targets using the LIBS signal itself, giving values of 80\(\mu\)m and 200\(\mu\)m respectively. Their results are shown in Fig. 16. Several other groups also refer to visible redeposition of target material on the sample surface [15,18,22,25].

Clear evidence of material redeposition was found in the 2D mapping of aluminum surfaces experiment of Cravetchi et al. [29]. Redeposition of Al\(_2\)O\(_3\) on the target surface was observed. The resulting coating of the target was quite pronounced when a large number of shots was taken, as can be seen in Fig. 17a. The left image is a SEM image which shows a smooth coating over the original aluminum surface. However, as can be seen in Fig. 17b, the redeposited layer ceases abruptly as one approaches the mapped area and around the isolated shots at the bottom of the images.

This can be understood by considering the blast wave in air and shock wave in the material created by the ablation plasma. As a LIBS plasma is created, it launches a shock wave that expands with a quasi-spherical symmetry and the force of this wave near the ablation spot is sufficient to remove the deposited material from the surface. The radius of this cleaned area is larger than the distance to the subsequent shot in the scanning analysis and thus the original target surface is probed by the scanning \(\mu\)LIBS measurement. The dynamics of material deposition and cleaning will depend on the sample being scanned and the conditions being employed. Redeposition may be reduced if one carries out the scans in vacuum but detailed studies need to be carried out to quantify the reduction.
Fig. 16. (a) Ratio of peak intensities of the Ti line measured at 626 nm from two adjacent points on the surface of a TiO$_2$ coated Si sample. A ratio of 1.0 indicates the second shot has sampled an undisturbed surface. (b) Silicon intensity of the first ablation layer of coated paper as a function of distance between sampling points and number of shots at each sampling point. In this case, Si is a contaminant from buried layers in a paper coating. (Reproduced with permission from (a) Romero et al. [27], and (b) Häkkänen et al. [30]).

Fig. 17. (a) Scanning electron microscopic image of macroscopic redeposition of Al$_2$O$_3$ and shock cleaning near the perimeter of a 2D µLIBS scan area 300 µm by 900 µm in size with probe spot separation of 10 µm. The edge of the scanned area is visible at the left edge of the image. (b) Isolated crater created using single 1.5 µJ pulses at 266 nm. (Reproduced with permission from Cravetchi et al. [29]).

In order to compare the various mapping experiments, we define a surface mapping rate (SMR) as the sample area per shot multiplied by the sample rate. In this case, the sample area per shot is defined by the crater diameter. These are plotted for published reports of µLIBS surface analysis in Fig. 18. Included for comparison is the use of line-focused beam scans with milli-joule energy pulses, as applied by Mateo et al. [55,56] and Rodolfo et al. [57]. In such line focused beams, the irradiance applied to the target can be in the same range as that of µLIBS. This plot demonstrates the current capabilities of µLIBS scanning rates for 2D multi-elemental surface mapping.
4.3. Liquid Samples

In the early 1990s a series of experiments applying LIBS to the detection of elements in water jet samples were performed by Cheung et al. [58,59]. This work has been extended to the \( \mu \)LIBS regime in more recent work by Ho and Cheung et al. [17,31] for detection of Na and K. One of the goals was to demonstrate sufficient sensitivity to measure the chemical content of single cells. 532 nm Nd-YAG and 193 nm ArF laser pulses were used as excitation sources, with both a photomultiplier tube and ICCD detection. To increase the absorption of the liquid water, a solution of 12 mM methyl violet was used. Using 240 \( \mu \)J pulses at 532 nm a detection limit of 50 ppm was achieved. The reported detection limit using the ArF excitation beam was 230 ppb. In further work by the same group, Cheung et al. note that the plasma generated by the ArF beam is significantly cooler than that generated by the 532 nm beam at short delay times. Plasma temperature and electron density were determined by line intensity ratios and line widths.

5. CONCLUSIONS

In the past decade there has been good initial progress in the development and understanding of \( \mu \)LIBS. Pulsed microchip laser sources with energies of 1 to 240 \( \mu \)J have been demonstrated and are beginning to be commercially available. The primary sources demonstrated to date are in the infrared region while the optimum wavelength for \( \mu \)LIBS is most likely in the UV region to give smaller, diffraction limited focal spots and better target absorption. The energy of harmonically converted UV sources is still limited to
less than $\sim 10\mu$J. However, at 1550 nm (erbium based lasers) one also has the advantage of eye safe sources at microjoule energy levels making practical systems easier to implement. More work needs to be done on the wavelength scaling issues to determine how effective these mid-infrared sources could be for $\mu$LIBS.

In microanalysis applications the ability to achieve single shot LODs of 10 to 100 ppm has been demonstrated with $\sim 100\mu$J energy pulses using gated detector systems and 100 to 10,000 ppm with $\sim 10\mu$J energy pulses using ungated detectors. The ability to analyze sample volumes of 10 to 1000 $\mu$m$^3$ has been demonstrated. 2D surface scans have been carried out with 3 $\mu$m lateral resolution on steel and 10 $\mu$m lateral resolution on aluminum. However, issues of determining the exact region of LIBS emission sensitivity within the ablation volume and cross contamination remain to be addressed in detail. It is likely that cross contamination is very much material and laser parameter dependent and particular attention should be paid to this issue in any scanning microanalysis system. Microanalysis of water samples has also been demonstrated achieving sub ppm sensitivities under optimized conditions.

While there is much that remains to be done in the study of $\mu$LIBS, particularly in the area of wavelength and pulselength scaling of LODs achievable, the use of $\mu$LIBS already appears as a promising new regime which should soon lead to cost effective portable systems.

REFERENCES