

Quality of open air, single-shot LIBS spectra from waste particles

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Abstract This work investigates the ability of LIBS to produce quality spectra from small particles of concrete demolition waste with single-shot spectra in open air. The 2 – 8 mm materials are rounded river gravel, green glass shards and plastic flakes. Considered are focal length, air, moisture, laser energy and laser angle of incidence. The research methodology is an experimental study using the observation depth and spectral abundance as quality indicators. The relation between ablation volume, breakdown threshold, signal strength and observation depth is captured in a simplified model to provide a better understanding of the dependence of the spectra on the laser incidence angle and material positioning in the laser beam. A 100 mm lens provided a compromise between spectral abundance, level of air interference and achievable observation depth. The study indicates LIBS can yield good quality data, even in cases of up to 3 mm surface roughness. Surface moisture did raise the percentage of bad spectra from an average 4 % to 18 %, but overall LIBS is still capable of providing quality data under challenging conditions.

1 Introduction

Laser-induced break down spectroscopy (LIBS) receives much attention from industry as a potential quality inspection technology [1]. Here, LIBS is under development for the inspection of particulate demolished concrete (2 – 32 mm) to ensure that the quality is suitable for recycling into new concrete. To that end LIBS must detect the number and type of quality degrading pollutants per ton, such as glass and plastic particles. In addition, inspection must take place while the material is in bulk

transport on a conveyor belt, i.e. the inspection may not interrupt the recycling process. These and additional environmental challenges (e.g. moisture, dust) posed to LIBS in an envisioned application must first be investigated under controlled conditions in the lab. Rounded river gravel is used to represent the concrete aggregates and shredded shards of glass and plastic flakes represent the pollutants. All materials are in the smallest range $2 - 8\text{ mm}$ that represents the highest challenge to LIBS.

LIBS is a plasma emission spectroscopic technique where the spectrum is representative for the elemental composition of the material and also highly characteristic for the material type in case of fingerprinting. LIBS employs high power laser pulses that exceed the material breakdown threshold of the material under inspection, typically in the range $10^9 - 10^{14}\text{ W/cm}^2$ [2]. The direct laser heat vaporizes a tiny amount of material into a hot plasma with electron density $10^{16} - 10^{19}\text{ cm}^{-3}$ and gas temperature of $10^3 - 10^5\text{ K}$ [3, 4]. After the laser shot the plasma keeps radiating and cools down until it delivers the elemental information as the atomic/ionic emission spectrum, where the photon energies correspond with the possible and specific electron transitions between atomic or ionic energy levels.

Particulate waste materials are complicated in shape, size and material composition, while the average environmental conditions in a recycling setting can be rather harsh. Both factors negatively affect the quality of the LIBS data and have to be understood and counteracted. Anomalous spectra arise as a result of off-target optical focusing, angled particle orientation, or poor surface conditions such as dust, a thick oxide layer or moisture. A solution could be to use two lasers or one with a higher shot rate to compensate for the loss of spectra, but this would render the LIBS inspection inefficient and considerably more expensive. It is therefore of paramount importance to investigate conditions and counter measures that can minimize the chance of anomalous spectra.

The objective of this work is to determine the conditions under which LIBS may still produce good quality spectra with single-shot spectra in open air. In detail, the influences of the open air, surface moisture, focal length, laser energy, and laser angle of incidence are taken into account. The research methodology is an experimental study employing the observation depth, which is the maximum distance range in which the target material spectrum can still be detected, and the spectral abundance, which is the number of identifiable emission lines.

2 Experimental

2.1 Setup and sample preparation

The beam from a diode pumped Q-switched Nd:YAG 1064 *nm* laser (6.9 *ns*, 11 – 18 *mJ*, max. 100 *Hz*) is directed downwards and focused on the sample surface. The incoming plasma emissions are guided anti-parallel to a spectrometer working at 250 – 820 *nm* range. The triggering of the laser unit and possible delayed spectrometer is performed by an external double pulse generator (Agilent 33500 series). The minimum integration time is set to 1 *ms*. Samples were mounted on a 2D motorized stage which height could be varied in steps of 0.5 *mm*. Three fused silica plano-convex lenses are available with focal lengths of 35 *mm*, 50 *mm* and 100 *mm*. This optical setup is relative robust and allows for the variations in plasma position and the possible plasma shielding effects from nearby particles. More details of the setup may be found in [5]. A polypropylene plate of 1 *mm* thick was shredded to flakes in the sieve size range 2 – 8 *mm*. Green glass bottles (varying thickness 1 – 3 *mm*) were smashed to produce shards in this range. Rounded river gravel was acquired from a concrete manufacturer and sieved to 2 – 8 *mm*. For the moist material tests the materials are wetted and left on a sieve until the free water has seeped out. Specifically for the observation height tests and laser angle tests the more flat particles were selected to minimize edge and surface curving effects.

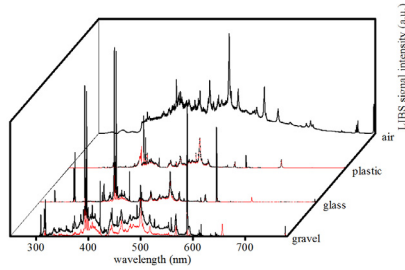


Figure 14.1: Averaged spectra from air and dry and moist (red dotted line) plastic, glass and gravel.

3 Results and discussion

As a reference Fig. 14.1 shows the averaged spectrum (10 shots at 11 mJ/shot) for a particle of plastic, glass and gravel, using the 35 mm focusing lens. The spectra for the moist material are shown in red. Note that the 10 shots are taken in different positions on the particle. These quality spectra are quite distinguishing in the three materials. The presence of moisture reduces the elemental intensity from the material and increases it for hydrogen ($H\alpha$), while the air emissions remain relatively constant. The air spectrum shows quite a few unresolvable emission/absorption bands that may add to the noise. Due to transparency of the green glass the emission lines of Si are rather weak. It is noted that gravel is rather heterogeneous in composition and therefore also its spectrum is subject to quite some variations.

To eliminate the undesired open air emission lines they must be classified w.r.t. to the targeted materials. To this end, a thousand spectra in air (i.e. without target material) were recorded and all emission lines that occur in more than 500 of them are identified as air emission lines. Fig. 14.2 (a) shows the abundance of the spectra in terms of the numbers of identified material and air emission lines using three focusing lenses. With increasing focal length, the material emission lines decrease while the air emissions remain relatively constant. To compare the spectrum quality for wet and dry materials we use some thousand particles of each type of material. Each type is put in a bucket which is manually

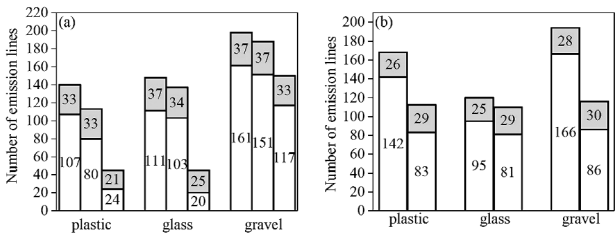


Figure 14.2: Number of emission lines from plastic, glass, gravel (white bars) and air (grey bar tops). Each material subgroup from left to right is related to (a) using 35, 50 and 100 mm lenses at 1 Hz diode frequency and (b) the dry and moist material at 100 Hz diode frequency, respectively.

moved/shaken continuously in horizontal directions as well as up and down (towards and away from the laser focus) while the laser acquires the spectra. In this fashion many different particles will be sampled. After elimination of the miss-shots a total of 5000 spectra are acquired for both dry and moist materials. The abundance of the spectra in terms of the number of identified air emission lines and material related emission lines are shown in Fig. 14.2 (b) for the dry and moist materials. It is noted that the shot rate was set to 100 Hz (18 mJ/shot). The output laser energy varies to some degree depending on the shot rate, optical oscillator, working temperature and diode pumping efficiency. Compared to the corresponding case in Fig. 14.2 (a) (dry case and 100 mm lens) considerably more emission lines are present from plastic and glass, but also for gravel it has increased. The abundance for air remained practically the same as for the lower laser energy setting, which indicates that using the highest energy is quite favourable. The abundance in the presence of surface moisture is lower, which may be attributed to a partial absorption of the laser energy.

This is due to the increase in Rayleigh length (cf. Fig. 14.3(a)) with focal length and decrease of the laser waist radius increases (cf. Fig. 14.3(b)) by which the power density decreases. Furthermore, the solid angle for plasma emission collection also decreases, and therefore the overall signal to noise ratio. The latter effect increases with the breakdown threshold of the material in question. A longer Rayleigh

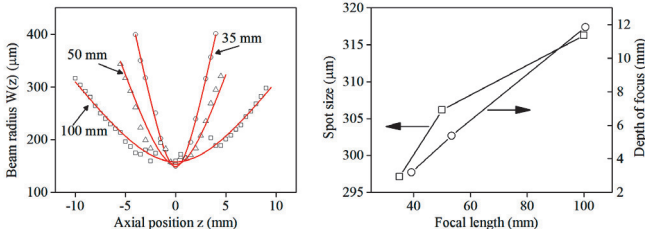


Figure 14.3: Laser profile for burn paper using three focal lengths. (a) Beam waist radius in axial direction; (b) Spot size (squares) and depth of focus (circles).

length facilitates the LIBS observation depth and should be determined in a compromise between focal length and spectral abundance.

The actual laser beam profile causing the ablation spot in a material is notoriously difficult to determine. However, it does play a crucial role in the whole process from material ablation to photon collection. To get a reasonable estimate, we determine the maximum laser beam profile using 0.5 mm thick burn paper, as it has a lower breakdown threshold than the target materials. The profile is determined from the burn hole diameter produced at different distances w.r.t. to the laser focus. Three focal lengths are tested and the holes are analyzed using microscopy image analysis. The Gaussian beam model which beam radius is given by:

$$W(z) = W_0 \cdot \sqrt{1 + (z/z_0)^2}, \quad (1)$$

where W_0 is the beam waist radius with spot size is $2W_0$, z_0 is the Rayleigh length with depth of focus $2z_0$. W_0 and z_0 are fitted for the burn paper in Fig. 14.3. The formula mostly used to calculate the (diffraction limited) spot size predicts 150 μm for the 100 mm lens, which proves to be a factor 2 smaller than the measured spot size. A probable cause is that the plasma disturbs/scatters the laser beam, resulting in a significantly larger spot. To a lesser but still measurable degree, also spherical and chromatic aberrations of refractive components like lenses result in a larger spot size.

Next task is to determine the observation depth (OD) from which the material dependent breakdown threshold can be estimated. Here we

define the observation threshold where material emissions disappear, by which it give an upper limit. The OD is determined as the average from multiple emission lines as shown in Table 14.1.

The air influence is noticeable in both the N and H lines in plastic, causing a larger OD than the average OD for carbon species. For glass and gravel, the OD for air is comparable with the OD for the material emission lines. Outside the range set by the material OD the air spectra dominate and degrade the quality of the spectrum. More abundant spectra can be acquired with 35 mm and 50 mm lenses, but the OD prove smaller. All subsequent tests will therefore be conducted with the 100 mm lens.

The influence of the laser incidence angle (LIA) is investigated in Table 14.2 for different species. Most emission lines are little sensitive to the LIA with the exception of those near the UV, such as Mg 279 nm and Si 288 nm. The OD identifies the preferable emission lines that carry robust information. The complex shapes of glass and gravel particles may have influenced the measured OD in Table 14.2, by which the average OD is more reliable. Using the average OD from Table 14.2 in Eq.(1), the breakdown thresholds are calculated as 1.6, 1.5 and 1.0 W/cm² for plastic, glass and gravel, respectively.

There is no observable monotonic trend in the dependence on LIA, as also reported in [6], and not even a common trend between the different materials. Main issue is that even for relatively large LIA there may still be sufficient signal strength, which is mandatory for application of LIBS to small granular materials. To better understand the dependence of the spectral amplitude and observation depth on the LIA (θ) we use a simplified model where the average spectrum is assumed directly proportional to the ablation hole volume $V_h = A_h \cdot z_h$ where A_h and z_h are the ablated surface $\pi \cdot W(z)^2 / \cos(\theta)$ and depth of the hole, respectively. The latter parameters may be estimated using the Beer-Lambert absorption law for fluence $F_b = F_{avg} \cdot \exp(-\alpha \cdot z_h)$, where the initial average fluence is defined as $F_{avg} = E_p / (A_h \cdot \tau_p)$ (E_p : pulse energy, τ_p : pulse width). Finally, the hole volume is described by:

$$V = \frac{A_h}{\alpha} \cdot \ln \left(\frac{F_{avg}}{F_B} \right). \quad (2)$$

The following discussion is restricted to plastic since those flat flakes offer the most reliable experimental LIA and sample distance dependence.

Table 14.1: Average OD [mm] of emission lines using a 35, 50 and 100 mm lens.

	air	wavelength [mm]	OD [mm]		
			35 mm	50 mm	100 mm
plastic		386, 387, 388 (CN), 516 (C ₂)	2.8	3.5	5.3
	Nitrogen	463, 500, 504, 568 (<i>N II</i>)	3.5	3.8	7.8
	Water	656 (<i>Hα</i>)	3.5	4.0	6.5
	Oxygen	777 (<i>O I</i>)	2.0	2.5	-
glass		279 (<i>Mg II</i>), 393&397 (<i>Ca I</i>) 589 (<i>Na I</i>)	3.0	3.8	7.8
	Nitrogen	463, 500, 504, 568 (<i>N II</i>)	3.3	4.5	6.0
	Water	656 (<i>Hα</i>)	3.0	4.0	-
	Oxygen	777 (<i>O I</i>)	3.0	3.5	0.5
gravel		279 (<i>Mg II</i>), 288, 385 & 390 (<i>Si I</i>) 634 (<i>Si II</i>), 393, 397, 422, 445, 616, 644 & 646 (<i>Ca I</i>), 309 (<i>Al I</i>), 455 & 493 (<i>Ba II</i>)	4.3	4.5	12.0
	Nitrogen	463, 500, 504, 568 (<i>N II</i>)	4.3	5.5	13.0
	Water	656 (<i>Hα</i>)	4.0	5.5	5.5
	Oxygen	777 (<i>O I</i>)	4.0	6.0	9.5

Table 14.2: OD [mm] for different laser incidence angles (LIA) and emission lines (100 mm lens).

LIA[°]	plastic		glass			gravel		
	CN 388	Ca 397	Na 589	Mg 279	Ca 318	Na 589	Al 309	Si 288
0	7.5	7.5	10.0	9.0	10.0	16.5	15.0	7.0
15	7.0	6.0	10.0	9.0	10.0	18.0	17.5	9.5
30	7.0	7.0	8.0	7.0	8.0	17.5	15.5	5.0
45	6.5	6.5	10.0	6.5	8.0	16.5	15.5	4.0
60	6.0	6.5	7.5	6.0	7.0	15.0	13.5	3.0

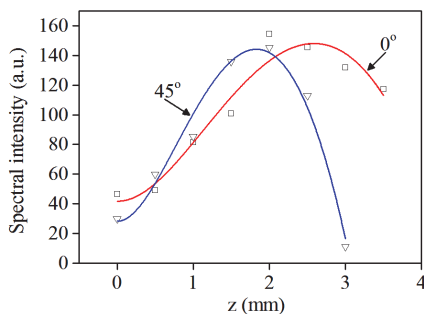


Figure 14.4: Experimental average intensities for plastic for 0 and 45 deg LIA as a function of plastic surface distance from the laser focus ($z=0$). The corresponding model fitted intensities are shown as continuous curves.

We explain how the signal strength depends on the position of the material in the laser beam. Fig. 14.4 shows the data points for the spectral intensity of plastic in the OD range for which the laser focus is on and below the flake surface. It also shows predicted curves for these two selected cases using the beam fitted with Eq.(1) and the fluence-ablation hole model in Eq.(2). The OD and maximum signal become smaller with larger laser angle, and the signal strength indeed increases with increased hole size (i.e. larger z and thus larger focus). More striking is that for the maximum signal the flake surface must be kept a few millimetres above the laser focus. It is noted that in reality the maximum signal may also be influenced by the laser angle through a dependency on the electric field polarization [7].

4 Summary

We investigated various factors that may affect the quality of LIBS spectra while inspecting small particles of gravel, glass and plastic using single-shot spectra in open air. The quality is inferred using the observation depth and spectral abundance. A long focal length lens of 100 mm provided a compromise between spectral abundance, air interference and achievable optical depth. The optical depth varied between

3–18 mm as the laser incidence angle varied from 0° – 60° . The actual value depends on the material type (i.e. the matrix) and the particular emission line under consideration. Nevertheless, the results indicate that in case for a surface roughness of up to 3 mm the inspection may still yield quality spectra. By fitting the experimentally determined laser beam profile, the breakdown thresholds are calculated as 1.6, 1.5 and 1.0 GW/cm^2 for plastic, glass and gravel, respectively. Based on the observation depth a threshold value can be determined to identify the anomalous spectra. For dry and moist materials the percentage of bad spectra is on average 4 % and 18 %, respectively. Moreover, the observation depth and abundance indicators provide a method to identify the reliable wavelengths that are suitable for either chemometric methods or classification algorithms.

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