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Double-pulse laser induced breakdown spectroscopy with ambient gas in the vacuum ultraviolet: Optimization of parameters for detection of carbon and sulfur in steel ☆

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ABSTRACT

Laser induced breakdown spectroscopy (LIBS) in the vacuum ultraviolet (VUV) has been applied to calibrated steel samples for the low concentration level detection of the light elements, carbon and sulfur in steel. Experimental optimization parameters, aimed at enhancing the sensitivity of the technique, included short wavelength spectral detection, double-pulse (DP) operation, variable focusing conditions and different ambient environments in terms of gas type and pressure. Two lasers were employed respectively as an ablation laser (Spectron: 1.06 μm/200 mJ/15 ns) and a reheating laser (Surelite: 1.06 μm/665 mJ/6 ns) in a collinear geometry. The results include insight into the most salient experimental variables and limits of detection in the parts per million range.

1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is relatively well developed as an elemental analytical technique. Advantages of LIBS often quoted include little or no sample preparation, fast data acquisition and processing, possibility for remote measurements and detection capability for nearly all elements in different sample states. However, as a micro-analytical technique, attaining low level detection limits with LIBS can often be challenging when compared to other analytical techniques [1–4]. To improve the analytical performance of LIBS in terms of limit of detection (LOD), a large number of systematic laboratory and industrial studies have been carried out and reported in the literature. Experiments often include exploitation of double/multiple laser pulses and the use of ambient gases.

After the early works of introducing the double-pulse LIBS enhancement, e.g., Cremers et al. [5], a range of double-pulse configurations were investigated in terms of the beam geometry [6–10], pulse energy and wavelength [7,11,12], inter-pulse delay [13–18] and the incorporation of femtosecond lasers [19–22]. The LIBS investigations generally examined multiple experimental parameters which were optimized individually for measurements with different elements or sample targets. Among these parameters, the inter-pulse delay is considered to be one of the most important variables when optimizing the double-pulse LIBS scheme. Some of the factors most often studied, such as the emission line intensity, the signal-to-background ratio and the ablated mass as well as the plasma temperature and electron density are often correlated and all are sensitive to the inter-pulse delay. The optimal inter-pulse delay time also differs from case to case and so it is necessary to optimize the inter-pulse separation for each individual LIBS setup.

As noted above, the ambient environment has proven to be another important factor determining LIBS performance. Early studies were often carried out in air at atmospheric pressure as it is the natural industrial environment. However, better analytical LIBS performances have been achieved by reducing the surrounding air pressure. For example, some investigations [11,23–25] on emission lines in the visible spectral regime emitted from a solid (often metallic) sample ablated by ns pulse duration lasers reported ambient pressures preferably under 200 mbar or even as low as 10 mbar. As an enhancement combination, the influence of ambient gas is often studied on single-pulse (SP) and double-pulse (DP) laser induced plasmas [26,27]. In both SP and DP cases, line intensities are enhanced with reduced ambient gas pressures (below atmospheric pressure). Some recent studies [22,28] using femtosecond pulse duration lasers on solid samples reported that lower ambient pressures between 840 and 133 mbar enhanced the observed emission line intensity and concentration detection sensitivity.

For most LIBS experiments, such as those outlined above, the observed spectral lines are in the visible or near ultraviolet spectral regions. Several efforts have also been made to exploit the shorter

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wavelength ultraviolet (UV) or vacuum ultraviolet (VUV) spectral regions. The potential of LIBS in the ultraviolet spectral region for steel analysis has been examined for terrestrial [29–32] and for space exploration applications [33–37]. The essential reason for choosing the short wavelength spectral range is that strong emission lines (often originating from charged ions rather than neutral atoms) are found in the short wavelength regions and higher emission intensities can lead to better ultimate detection limits.

For short wavelengths in the VUV region the natural environment is vacuum as ambient gases often exhibit large photo-absorption cross-sections at short wavelengths. The influence of the ambient gas pressure is studied by increasing the pressure of the ambient gas from vacuum [18,38,39]. Instead of reducing the ambient pressure from atmospheric pressure, low pressure ambient gas is introduced to the vacuum chamber. With appropriate gas type and pressures, the plasma expansion is buffered by the surrounding gas without excessive absorption of the emitted VUV spectral lines. The buffered plasma can result in increased temperature and electron density values leading to enhanced spectral line emission intensity. Furthermore the buffered plasma can change the interaction with the second incoming pulse in DP LIBS to provide an overall performance gain. Laser induced breakdown VUV spectroscopy has therefore become a valuable addition to the range of experiments aimed at obtaining ever better sensitivity, signal to background ratio and concomitantly lower limits of detection.

In a recent work [18], we have examined the applicability of the double-pulse LIBS technique combined with short wavelength vacuum ultraviolet emission line detection for sensitivity enhancement of LIBS detection of carbon in steel samples. Our results showed that there was a considerable variation in spectral line emission as a function of the inter-pulse time delay. A strong narrow peak was observed at a 100 ns inter-pulse delay setting, which was independent of the type of gas and pressure. A second much broader peak in the microsecond inter-pulse regime was not as strong and varied in height with the gas pressure.

In this paper, we combine VUV spectral line detection (from doubly ionized carbon and quadruply ionized sulfur) with optimization of the gas type and pressure, the inter-pulse time delay and the focusing conditions for both first and second laser pulses in a collinear geometry in order to provide an overall performance enhancement for carbon and sulfur determination in solid steel samples. The spectral line emission to background ratios are optimized by spatially resolving the emitted light from the plasma. Calibration curves are obtained leading to measurements of the corresponding limits of detection for carbon and sulfur. Enhancement factors arising from the ambient gas environment and the double-pulse inter-pulse delay optimizations are given.

2. Experimental

The experimental LIBS setup is shown in Fig. 1. It contains the laser pulse generation system (two synchronized lasers), the optical system (lenses, mirrors, polarizer and half-wave plate), an ablation chamber, spectrometer, detection system (CCD camera and computer), and finally the gas environment controls (needle valve, gauge, pressure meters).

Two Q-switched Nd:YAG lasers were used to create the plasmas in double-pulse mode. One was a Continuum Surelite (model III-10), operating at the fundamental wavelength of 1.06 μm with a pulse width of 6 ± 1 ns and maximum output energy of 800 mJ. The second laser was a Spectron SL404 laser, also operating at the 1.06 μm wavelength, with 400 mJ maximum pulse energy and 15 ns pulse width. The lasers were operated at a repetition rate of 10 Hz with the Spectron laser producing 200 mJ output energy pulses and the Surelite laser producing 665 mJ pulses for most of the experiments described in this work.

An optical combination of a half-wave plate and a polariser was inserted into the Surelite laser beam to vary the pulse energy incident on the sample. Both the Surelite and Spectron lasers produced

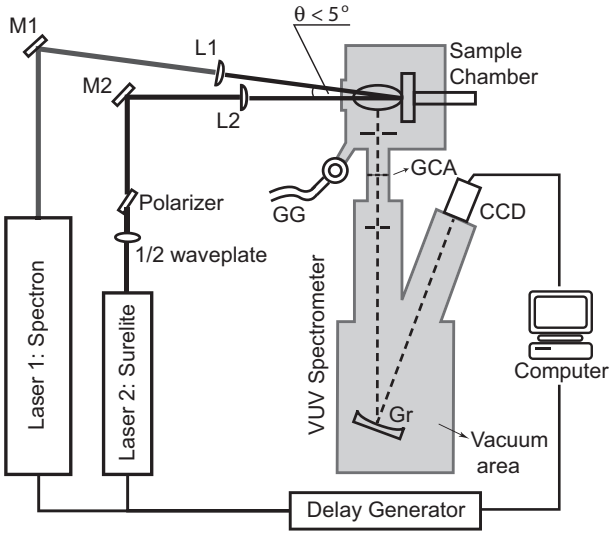

Fig. 1. Schematic of experimental apparatus. M1 and M2: Mirror 1 and mirror 2, L1 and L2: Lens 1 and lens 2, GG: gas gauge, Gr: grating, GCA: Glass Capillary Array, CCD: charge-coupled device.

approximately 10-mm-diameter beams which were focused onto the steel samples by plano-convex lenses of 125 mm and 150 mm focal lengths respectively.

The target chamber was an evacuated aluminum cube with a side length of 12.5 cm and a partially hollowed out interior. The base pressure in the chamber was maintained in the range of 10^{-6} mbar and was achieved using a combination of rotary and turbo-molecular pumps.

The spectrometer was a 1-m normal incidence Acton Research Corporation model VM-521 using a 1200 grooves/mm Bausch and Lomb Al + MgF_2 coated and holographically-ruled diffraction grating. The emitted plasma radiation was dispersed by the grating and the reciprocal linear dispersion was 0.83 nm per mm in the first order.

A Glass Capillary Array (GCA) was placed between the chamber and the spectrometer to maintain a stable vacuum environment ($\approx 10^{-6}$ mbar) in the spectrometer while the pressure in the chamber could be varied from vacuum to a few mbar (<10 mbar) in the ambient gas experiments.

A fore-slit was placed in the target chamber between the target and the entrance slit of the spectrometer and on the optical axis as defined by the spectrometer optics. The combination of the parallel fore-slit and spectrometer slits defined the plasma emission zone viewed by the spectrometer. The fore-slit was 250 μm wide and the spectrometer entrance slit width was set to 10 μm as determined by a compromise between signal strength and spectral resolution.

The radiation detection system was a back-illuminated, VUV-sensitive Andor Technology CCD camera, model number DV420-BN. The full frame CCD array contained 1024 × 256 pixels. To reduce the dark noise during the data acquisition time, the functioning temperature of CCD chip was cooled down to −30 °C. The CCD controller triggered the laser through a digital delay pulse generator so the plasma production and the data acquisition were synchronized.

The steel samples containing C and S of known concentrations employed in the study are listed in Table 1.

3. Results and discussion

3.1. Time-integrated spatial-resolved spectral analysis

The fore-slit was placed approximately 40 mm from the plasma and at a distance of 350 mm from the entrance slit of the spectrometer. The combination of both slits yielded a spatial resolution of the plasma