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Detection of lead in brass by Laser-Induced Breakdown Spectroscopy combined with Laser-Induced Fluorescence

Christian Goueguel^a, Stéphane Laville^{*b}, Hakim Loudyi^a, Mohamed Chaker^a,
Mohamad Sabsabi^b, François Vidal^a

^aInstitut National de la Recherche Scientifique – Énergie Matériaux Télécommunications,
1650 Lionel Boulet Blvd., Varennes, Qc, Canada J3X 1S2;

^bNational Research Council Canada – Industrial Materials Institute,
75 de Mortagne Blvd., Boucherville, Qc, Canada J4B 6Y4

ABSTRACT

Laser-Induced Breakdown Spectroscopy (LIBS) technique combined with Laser-Induced Fluorescence (LIF) is known to be a high sensitivity and high selectivity analytical technique. Although sub-ppm limits of detection (LoD) have already been demonstrated, there is still a constant and urgent need to reach lower LoDs. Here, we report results obtained for the detection of lead trace in brass samples. The plasma was produced by a Q-switched Nd:YAG laser at 1064 nm and then re-excited by a nanosecond optical parametric oscillator (OPO) laser tuned at 283.31 nm. Emission from Pb atoms was then observed at 405.78 nm. The experiments were performed in air at atmospheric pressure. We found out that the optimal conditions were obtained for an ablation fluence of 2-3 J/cm² and inter-pulse delay of 8-10 μs. Also, excitation energy of about 200 μJ was required to maximize the Pb(I) 405.78 nm emission. Using the LIBS-LIFS technique, the LoD was estimated to be about 180 ppb over 100 laser shots, which corresponds to an improvement of about two orders of magnitude with that obtained using conventional LIBS.

Keywords: Laser-Induced Breakdown Spectroscopy (LIBS), Laser-Induced Fluorescence (LIF), Trace metal analysis

1. INTRODUCTION

Laser-Induced Breakdown Spectroscopy (LIBS) has been proven to be a practical and versatile spectrochemical technique for a wide variety of materials [1]. The main advantages of LIBS over the other existing analytical techniques stem from its strictly optical nature. This makes LIBS suitable for rapid on-line analysis, without the requirement of sample preparation and only a small amount, in the order of a few micrograms to nanograms, is ablated from the surface of solid samples. However, there is constant demand for improving the detection limits (LoD) obtained by LIBS. It is generally in the part-per-million (ppm) range on solids, which is higher than more cumbersome analytical techniques such as, for instance, laser ablation coupled with inductively coupled plasma mass spectrometry (LA-ICP-MS) [2] or optical emission spectrometry (LA-ICP-OES) [3].

One promising avenue for improving the sensitivity of LIBS consists in using the LIBS-LIFS approach (LIBS combined with Laser-Induced Fluorescence Spectroscopy) [4]. It has already been shown for various trace elements that this approach can improve notably the LoD [5-10]. In the LIBS-LIFS scheme, the first laser pulse ablates the sample to produce plasma and then a second laser pulse, tuned at a specific wavelength, is used to excite the element of interest. The present paper deals with the use of the LIBS-LIFS technique for the detection of lead traces in brass samples. The intensity of the LIF signal emitted by lead was systematically studied to understand the influence of the main experimental parameters and to determine the plasma conditions to be achieved for optimizing the LIF signal.

*stephane.laville@imi.cnrc-nrc.gc.ca; phone 1 450 641-5230; fax 1 450 641-5106

2. EXPERIMENTAL

As shown on Fig.1, a Q-switched Nd:YAG laser (Continuum, Surelite II) was used to produce the LIBS plasma. It can deliver up to 600 mJ per pulse at a wavelength of 1064 nm. The pulse duration is 7 ns (FWHM) and the repetition rate was fixed to 2 Hz to prevail interaction between the laser and aerosols. The beam was focused onto a 2 mm diameter spot on the target using a BK7 lens (25.4 mm diameter, $f = 25$ cm focal length) at normal incidence. The experiments were performed in air at atmospheric pressure. Finally, the samples were translated using a double axis motorized stage (UTM 100 mm, Newport) controlled by a programmable controller (ESP300, Newport).

Fig. 1. Schematic of the LIBS-LIFS setup.

For LIFS probing, a Q-switched Nd:YAG laser (5 ns, 10 Hz), operating at its third harmonic wavelength (355 nm) with an energy limited to 250 mJ per pulse, pumped an Optical Parametric Oscillator (OPO) laser (Continuum, Panther 8000). Wavelengths available with the OPO laser were in the range of 215 nm to 2.7 μ m and the corresponding energy range was 10 μ J (at about 320 nm) to 70 mJ (at about 450 nm). A fused silica lens (25.4 mm diameter, $f = 20$ cm focal length) was used to focus the OPO laser beam into the plasma plume with an incidence angle of 80°, as shown on Fig. 1. The OPO spot was about 2 mm² onto the surface of the target. The OPO energy was varied from a few μ J to a few hundreds of μ J which corresponds to a maximum fluence of a few tens of mJ/cm², which is much lower than the damage threshold of our samples [11]. Both laser pulses were synchronized to each other by using a programmable pulse generator (PG200, Princeton Instruments). The detection system consisted of a Czerny-Turner spectrometer (VM504, Acton Research) with a 0.39 m focal length and a f-number of 5.4. It was equipped with a 1200 groove/mm grating blazed at 150 nm that leads to a reciprocal linear dispersion of 4.2 nm/mm. The output of the spectrometer was coupled with an intensified charge-coupled device (ICCD) (DH720-25H-05, Istar Andor) that contains 1024x256 pixels of 26 μ m² dimensions. The corresponding intensified spectral width was about 52 nm and the spectral resolution was about

0.12 nm. The plasma emission was then collected with a 600 μm core diameter optical fibre positioned close to the plasma plume and connected to the entrance slit of the spectrometer.

In this work, 10 certified brass samples were used with lead concentrations ranging from 30 ppm to 1100 ppm (the copper concentration ranges from 81.12 % to 99.7785 %). The samples were positioned in a motorized translation stage in order to sample at 4 positions that were spaced by 1 mm. At each position, 300 cleaning laser shots were first performed followed by 200 acquisition shots.

Partial atomic energy level diagram for lead is shown on Fig. 2 to illustrate the laser excitation and fluorescence decay scheme used in this work. Lead atoms from the ground state level were excited by the OPO laser tuned at 283.31 nm to the upper level $7s\ 3P^o_1$. The fluorescence emission was subsequently recorded at 405.78 nm. One also observes on Fig. 2 on-off LIF signals recorded after a delay time of 5 μs .

Fig. 2. Partial energy level diagram of lead atoms (left side) and LIBS-LIFS on-off resonance spectra averaged over 200 laser shots (right side). The spectra were offset vertically for clarity;
a: without OPO laser, b: off-resonance (282.85 nm) and c: on-resonance (283.31 nm).

3. RESULTS AND DISCUSSION

After the observation of the Pb(I) 405.78 nm LIF signal shown on Fig. 2, the influence of the main experimental parameters such as the excitation energy (E_{OPO}), the ablation fluence (F_{ABL}) and the delay between the ablation pulse and the excitation pulse (Δt_{IP}) were studied. The ICCD was gated at a time coincident to the OPO pulse ($t_d = \Delta t_{IP}$) and the gate width (t_g) was set to 40 ns to maximize the LIF signal and minimize the noise of the ICCD detector. The width of the slit of the spectrometer was fixed to 350 μm to maximize the LIF signal.

3.1 Influence of the excitation energy

On Fig. 3, the LIF signal as a function of the OPO laser energies is shown for three samples containing 30, 290 and 1100 ppm of lead.

Fig. 3. Pb(I) 405.78 nm LIF signal as a function of the OPO laser energy for three lead concentrations: 1100 ppm ($\square$), 290 ppm ($\bullet$) and 30 ppm (Δ).

As shown on Fig. 3, when the excitation energy delivered by the OPO laser is relatively weak, the LIF signal emitted by the Pb atoms at 405.78 nm evolves linearly with the OPO energy and the slope is about 1. As the excitation energy increases, the LIF signal becomes independent of the OPO energy, which corresponds to the so-called optical saturation regime. Fig. 3 also shows that the ratios of the saturation of the LIF signals for the three samples follow the lead concentration ratio, about 9 between lead concentrations of 30 and 290 ppm, and about 3.5 between 290 and 1100 ppm. However, below saturation the signal ratios appear to be smaller than concentration ratios.

When the excitation fluence F_{exc} is much smaller than the saturation fluence F_{sat} , the excitation probability of a single lead atom in the ground state is given by:

$$P_{exc} \approx \frac{\sigma_{02} F_{exc}}{h \nu_{02}} \quad (1)$$

Where σ_{02} is the absorption cross section for a transition from the ground state level to the excited level $7s \ ^3P_1^o$ given by Eq. (2) and $h \nu_{02}$ is the excitation photon energy.

$$\sigma_{02} = \frac{c^2 A_{20}}{8\pi \nu_{02}^2} \frac{g_2}{g_0} \frac{2}{\pi \Delta \nu_{1/2}} \quad (2)$$

Where g_0 and g_2 are the statistical weights, A_{20} is the spontaneous absorption coefficient between the excited level and the ground state, and $\Delta \nu_{1/2}$ is the FWHM of the line.

The LIF signal is proportional to $P_{exc} \cdot N_{Pb}$ (where N_{Pb} is the total number of lead atoms in the plasma) and thus to F_{exc} , as seen on Fig. 3. The transition from the linear regime to the saturation regime occurs when $P_{exc} \approx 1$. The corresponding fluence is given by:

$$F_{sat} \approx \frac{h\nu_{02}}{\sigma_{02}} \quad (3)$$

Estimation of σ_{02} using Eq. (2) yield $\sigma_{02} \approx 2 \cdot 10^{-14} \text{ cm}^2$ and thus $F_{sat} \approx 20 \text{ } \mu\text{J}/\text{cm}^2$. This leads to $E_{OPO} \approx 0.4 \text{ } \mu\text{J}$ which is not in contradiction with the saturation energy observed on Fig. 3 in the sample containing 30 ppm of Pb, since the deviation from the linear regime seems to occur below $1 \text{ } \mu\text{J}$. However, the saturation energy is obviously higher than $0.4 \text{ } \mu\text{J}$ in the 290 ppm case. The reason for this discrepancy is likely that Eq. (1) lies on the assumption that the Pb atoms are highly diluted in the plasma, a condition which is not verified in that case. Indeed, low coherence interferometry (LCI) measurements of the ablation craters indicates that a volume of about $6 \cdot 10^{-8} \text{ cm}^3$, or $\sim 0.5 \text{ } \mu\text{g}$ of the brass sample, is ablated per laser shot. This means that $N_{Pb} \approx 5 \cdot 10^{11}$ Pb atoms are ablated per laser shot in the 290 ppm case. The total Pb cross section is thus $\sigma_{02} \cdot N_{Pb} \approx 1 \text{ mm}^2$, which is comparable to the area of the side projection of the plasma, estimated as a few mm^2 . Therefore, the conditions underlying Eq. (1) are not respected in the 290 ppm case.

3.2 Influence of ablation fluence and inter-pulse delay

Fig. 4 shows the Pb(I) 405.78 nm LIF signal as a function of the inter-pulse delay Δt_{IP} for different ablation fluences F_{ABL} . The excitation energy was fixed to $200 \text{ } \mu\text{J}$, which ensures that the optical saturation regime was reached.

Fig. 4. LIF signal emitted by lead at 405.78 nm as a function of the delay between the ablation pulse and the excitation pulse. The experiments were performed for several ablation fluences: $1.6 \text{ J}/\text{cm}^2$ ($\blacktriangle$), $2 \text{ J}/\text{cm}^2$ ($\circ$), $2.6 \text{ J}/\text{cm}^2$ ($\star$), $2.7 \text{ J}/\text{cm}^2$ ($\bullet$), $3.3 \text{ J}/\text{cm}^2$ (∇) and $4.8 \text{ J}/\text{cm}^2$ ($\blacksquare$).

Fig. 4 shows that the LIF signal depends strongly of the ablation fluence and the inter-pulse delay. Indeed, for small inter-pulse delays the plasma temperature is high (typically a few eV), so that most lead atoms are ionized and the ground state level is weakly populated. Consequently, the excitation beam is marginally absorbed by the lead atoms.

When the inter-pulse delay increases, the plasma temperature decreases due to plasma cooling. The population of lead atoms in the ground state level increases, leading a higher LIF signal. However, as the inter-pulse delay (and so the acquisition delay) increases, the plasma volume becomes larger. The overlap between the plasma and the probe laser may also decrease. Therefore, fewer emitting lead atoms can be collected by the optical fibre, leading to the decrease of the LIF signal, as observed on Fig. 4.

3.3 Calibration curve

The signal-to-noise ratios of the Pb(I) 405.78 nm line as a function of the lead concentration obtained using LIBS and LIBS-LIFS are shown on Fig. 5. The calibration curves were based on 10 certified brass samples. For the LIBS-LIFS measurements, the ablation fluence was $F_{ABL} = 2.7 \text{ J/cm}^2$, the inter-pulse delay was $\Delta t_{IP} = 8 \mu\text{s}$ and the OPO energy was $E_{OPO} = 200 \mu\text{J}$. These conditions were previously found for optimizing the Pb(I) 405.78 nm LIF signal. For the LIBS technique, the ablation fluence was about 41 J/cm^2 , the acquisition delay was $t_d = 0.8 \mu\text{s}$, the gate delay was $t_g = 15 \mu\text{s}$, the spectrometer slit width was $50 \mu\text{m}$ and 100 acquisition shots were performed over 3 positions.

Fig. 5. Signal-to-noise ratio of lead at 405.78 nm as a function of lead concentration. The calibration curves of LIBS ($\circ$) and LIBS-LIFS ($\bullet$) are shown.

It can be seen from Fig. 5 that the LIBS-LIFS calibration curve displays a higher linearity (characterized by a correlation factor of $r^2 = 0.986$) than those using LIBS. Considering the standard 3σ -convention, where σ (defined as noise) is the standard deviation of the background intensity, the single-shot LoD obtained by LIBS was about 200 ppm. On the other hand, the LIBS-LIFS single-shot LoD was about 1.5 ppm while an accumulation over 100 laser shots leads to about 200 ppb. This corresponds to an improvement of about 2 orders of magnitude when compared with LIBS. These values are comparable to those available in literature with the same lead excitation-fluorescence scheme. For instance, in [9], Snyder *et al.* have demonstrated a LoD of 500 ppb accumulating over 50 laser shots while a LoD of 72 ppb was obtained by Gornushkin *et al.* [6].

4. CONCLUSION

Laser-Induced Breakdown Spectroscopy coupled with Laser-Induced Fluorescence (LIBS-LIFS) is a promising analytical technique for trace and ultra-trace elements in a wide variety of matrices. In this paper, the optimization of the detection of lead traces in a copper matrix was performed at atmospheric pressure. We investigated the influence and identified optimum conditions for the main experimental parameters (excitation energy, ablation fluence and inter-pulse delay) on the LIF signal emitted by lead. Using a set of 10 certified brass samples, a single-shot LoD of about 1.5 ppm was obtained and the LoD was about 200 ppb accumulating over 100 laser shots. These values are about 2 orders of magnitude lower than those obtained by conventional LIBS (200 ppm for the single-shot LoD). The achievable LoD strongly depends on the optical collection system and the background noise of the detector. In this context, it is likely that the spectrometer/ICCD combination could be replaced by an interferential filter and a photomultiplier (PMT) to reduce light losses and increase the photon conversion efficiency.

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