Influence of low-pressure glow discharge on laser-induced plasma spectra

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Abstract. A scheme is reported for spectrochemical analysis combining sample introduction by laser ablation and additional excitation of the ablated material by a hollow-cathode discharge. The optimal conditions allowing spatial separation of the two processes are determined. Under these conditions, enhancement of the analytical lines intensity in comparison with stand-alone laser-induced plasma is observed.

1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is widely applied for spectrochemical analysis due to its advantages [1]: ability to ablate a wide variety of samples – including non-conducting materials and liquids, lack of requirements to sample preparation, and capacity for fast microprobe analysis. In spite of these features, the laser ablation spectroscopy has some drawbacks in terms of analytical performance – matrix effects, limited depth resolution due to the need of ablating sufficient mass of material for producing visible plasma, difficulties in quantitative analysis, etc [2, 3]. This is why common techniques for spectrochemical analysis have been proposed combining a direct laser sampling method with an additional source of excitation of the ablated material – inductively-coupled plasma, arc/spark, etc. [4]. Such combined techniques, e.g. laser ablation-inductively coupled plasma-mass spectrometry, exhibit excellent characteristics but are economically demanding and experimentally sophisticated. Therefore, a more economically feasible alternative is needed.

The combination of a hollow-cathode discharge and laser ablation is a possible alternative because the hollow-cathode discharge is a proven spectroscopic source with narrow lines, high signal-to-background noise ratio and rich spectra [5]. The hollow-cathode discharge provides means for enhanced electron-atom excitation of the ablated material which gives the possibility to ablate less material per pulse and achieve better depth resolution. This has already been demonstrated for the conventional glow discharge [6]. Hence, the performance of the combined technique benefits from the micro-sampling capability of laser ablation, the enhanced excitation by the hollow-cathode glow discharge and the possibility to control each of them independently.

Four parameters play a key role for the performance of the technique: the laser source, the ambient gas environment, the cathode-sample gap length and the discharge current. The laser source governs the ablation mass per pulse and the plasma plume initiation. The presence of an ambient gas and its pressure strongly influences the expansion and the emission of the laser-induced plasma. The cathode-
sample gap length controls the time delay between the laser pulse and the discharge excitation and, accordingly, the state in which the ablated species enter the discharge. The current governs the excitation of the ablated material and the intensity of the analytical signal.

In this work, a laser-induced plasma hollow-cathode discharge (LIP-HCD) scheme is studied. The aim is to determine the conditions under which the processes of introduction and excitation can be separated and controlled independently. This is achieved by optimization of two of the key parameters: the ambient gas pressure and the cathode-sample gap length.

2. Experimental setup, conditions and procedure

The experimental LIP-HCD setup for spectrochemical analysis, shown in figure 1, consists of three main parts – a hollow-cathode discharge, a laser source and a registration system.

The laboratory-made neon hollow cathode, with a 3-mm inner diameter and a 20-mm length, is powered by a stabilized DC power supply. The cathode is made of aluminium, as this material has a low ion sputtering rate and a poor spectrum. Anode rods are placed at the two ends of the cathode. A disc-shaped copper sample is mounted at one of the anodes. The gap between the hollow-cathode plasma and the sample can be varied. The length of the gap defines the state in which the ablated species enter the discharge.

The laser is a pulsed nanosecond Q-switched Nd:YAG laser (Quanta Ray GCR3) lasing at 1064 nm at a repetition rate of 1÷20 Hz and a pulse energy up to 400 mJ. The spectra are recorded by a PC-controlled Digikröm 480 monochromator with a CCD camera.

![Figure 1. Experimental setup.](image-url)

The laser beam is directed to the hollow cathode by a mirror and is focused by a lens at the copper sample. The focused laser beam ablates the sample surface and laser-induced plasma is formed. The plasma expands in the space above the sample and into the hollow-cathode cavity. The laser-induced plasma interacts with the hollow-cathode discharge plasma in a variety of processes, including excitation and ionization of the ablated particles. The light emitted from the hollow-cathode volume is focused at the entrance slit of the monochromator and is registered by the CCD camera.
3. Experimental results

3.1. Influence of the ambient gas pressure on the laser-induced plasma spectra

As the spatial and energy distribution of the ablated material are very sensitive to the presence and nature of the ambient gas [7], its influence on the intensity of the emission lines is investigated. The emission spectra of laser-induced plasma in vacuum and in neon are measured. An increase of the copper lines intensity in the presence of the ambient gas is observed (figure 2).

The ablation threshold decreases significantly in the presence of the ambient gas compared to ablation in vacuum. The presence of gas next to the solid surface also increases the ablation rate due to thermal evaporation [8].

During its expansion, the laser-ablated plasma interacts with the neutral atoms of the ambient gas and excites them through different processes – electron-atom inelastic collisions, Penning ionization, etc. The atomic lines registered in the laser-induced spectra in neon, shown in figure 3, are an indication of the energy transfer from the laser-induced plasma to the ambient gas species. Hence, the expanding laser-induced plasma is dissipating its energy due to the ambient gas presence.

The influence of the ambient gas pressure on the plasma emission intensity is presented in figure 4. As it is seen, the copper lines intensity increases by an order of magnitude when the neon pressure is increased from 2 Torr to 25 Torr. This behavior of the emission is attributed to plasma contraction in a smaller volume with the pressure increase resulting in a higher species density, an increase in the collisional frequencies of plasma species, an enhancement of the electron cascade growth and stronger emission intensity [9]. A similar line intensity increase should be expected when a high repetition-rate laser is used for ablation due to the accumulation of ablated plasma above the surface of the solid target by successive pulses.

Figure 2. Laser-induced plasma emission spectra in vacuum (above) and in 4 Torr neon (below) at laser fluence 0.8 J cm⁻².

Figure 3. Laser-induced plasma spectra in neon at 4 Torr.

Figure 4. Laser-induced plasma emission spectra as a function of the neon pressure at a laser fluence of 0.8 J cm⁻².
3.2. Influence of the sample-cathode gap length on the LIP-HCD spectra

For the hollow cathode used with a 3-mm inner diameter and a 20-mm length, the hollow cathode effect is obtained at 4 Torr neon; the discharge is stable up to a 15-mA discharge current. The minimal laser fluence necessary for generation of laser-induced plasma in our experiments is 0.5 J cm\(^{-2}\).

Figure 5 compares the analytical copper lines 324.8 nm and 327.4 nm emitted from stand-alone laser-induced plasma and from LIP-HCD. As is seen, due to the additional excitation of the ablated material in the hollow-cathode discharge plasma, an enhancement of \(~30\%\) in the analytical signal is observed.

When the sample is close to the cathode, due to deposition of ablated material on the inner cathode surface and this material re-entering the discharge by ion cathode sputtering, copper lines are observed in the emission spectra of the discharge long after the end of the laser ablation pulse (up to few minutes depending on the number of laser ablation pulses performed). This means that the emission comes not only from hollow-cathode excitation of the ablated material, but also by cathode sputtering. Although this can be a positive effect when detecting trace elements, if depth analysis is performed, such an effect is undesired as it complicates the depth distribution analysis of the elements in the layer. In order to decrease the deposition of material on the inner cathode surface, the sample is moved away from the cathode. The translation of the sample results in both a lower amount of deposited material and a decrease of the analytical lines intensity. The experimentally determined minimal distance at which the signal from the deposited material is negligible, i.e. comparable to the background, is 12 mm. Figure 6 presents the emission spectra excited only by a hollow-cathode discharge (below), stand-alone laser-induced plasma (middle) and LIP-HCD (top) at a sample–cathode distance of 12 mm and a discharge current of 15 mA.

It is seen that the two copper lines (324.8 nm and 327.4 nm) are well-resolved only in the LIP-HCD spectrum. They are weak, as compared to the background noise, in the spectrum of the laser-induced plasma and are completely missing in the spectrum of the hollow-cathode discharge.

We assume that at this distance the analytical signal registered results from ablation caused by the laser pulses and excitation by the hollow-cathode discharge. Thus, separation of the processes of sample introduction and excitation of the ablated material is achieved. Increasing the distance leads to a further decrease in the analytical lines emission intensity.
4. Conclusions
It is shown that the presence of an ambient gas considerably affects the analytical lines intensity. The neon pressure increase leads to an increase in the intensity of the copper lines. When expanding, the laser ablation plasma interacts with atoms of the ambient gas which results in excitation of emission lines of the gas.

By optimizing the cathode-sample gap, the presented LIP-HCD scheme allows one to separate spatially the introduction and excitation of the ablated material and, hence, to control independently each of the two processes.

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