Emission characteristics of laser ablation-hollow cathode glow discharge spectral source

Abstract: The emission characteristics of a scheme combining laser ablation as sample introduction source and hollow cathode discharge as excitation source are presented. The spatial separation of the sample material introduction by laser ablation and hollow cathode excitation is achieved by optimizing the gas pressure and the sample-cathode gap length. At these conditions the discharge current is maximized to enhance the analytical lines intensity.

Keywords: glow discharge, laser ablation, LIBS

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1 Introduction

Laser-induced breakdown spectroscopy (LIBS) today is widely applied for spectrochemical analysis in scientific labs, industrial sites and even in space [1]. The large area of application of LIBS is due to the technique versatility – ability to perform microprobe elemental analysis of wide variety of samples with no preliminary sample preparation.

Though it can give a good estimate of the elements relative amount, the LIBS quantitative analysis is sensitive to the experimental factors – changes in the environment conditions (atmosphere and optical path) and matrix effects. The main difficulty arises from the matrix effects, which are defined as a strong dependence of the formation and emission of the laser-induced plasma on the type of material which is ablated. As a result of the matrix effects, it is necessary to use standard materials with known elemental composition and with a similar matrix in order to perform quantitative analysis, which can be very difficult and sometimes impossible. The qualitative analysis requires correct identification of the lines of a given element, which is difficult if the sample composition is not known and large number of lines is present.

One way to overcome these difficulties in quantitative and qualitative analysis is the combination of a direct laser sampling with an additional source of excitation of the ablated material. The most wide spread of these techniques is the combination of laser ablation with inductively coupled plasma (ICP) [2] or with arc/spark. Recently, investigations were done also on laser ablation in glow discharge [3,4]. These combined techniques consist of two steps: introduction by laser ablation, as it has the ability to preserve the sample stoichiometry [5] and excitation of the ablated sample species by the discharge. In this way, the matrix effects are minimized. The enhanced electron-atom excitation results in the possibility to ablate less material per laser pulse and achieve better depth resolution. For a conventional glow discharge such an improved depth resolution is demonstrated in [6]. The performance of the combined technique - laser-induced plasma in gas discharge, relies on the micro-sampling capability of laser ablation, the enhanced excitation of ablated species in the discharge and the possibility to control each of the two separately. The presence of background gas lines makes also the quantitative analysis easier as the buffer gas lines play the role of internal standard. In addition, the introduction of ablated species in the gas discharge plasma allows the opportunity to perform modification on the ablated species through plasma chemical reactions.

The hollow cathode discharge is a spectroscopic source of proved reliability with rich spectra, narrow lines and high signal-to-background noise ratio [7]. In this work, the study of a laser-induced plasma-hollow cathode discharge (LIP-HCD) scheme is reported. The aim is to achieve good separation of the processes of introduction and excitation of ablated sample material and optimization of the hollow cathode discharge as an excitation source for the ablated species. The key parameters of the technique – ambient gas pressure, cathode-sample gap length and discharge current, are optimized while the laser pulse energy and repetition rate are kept constant.
2 Experimental procedure

The scheme of the experimental setup is shown in Fig. 1. The sample is placed into a vacuum chamber and is ablated by a pulsed solid state laser. The ablated material is excited in a hollow cathode glow discharge and the spectral emission of the discharge is recorded and analyzed.

The laser source is a pulsed nanosecond Nd:YAG Quanta Ray GCR3 laser. It is operated at the fundamental wavelength 1064 nm, with repetition frequency of 10 Hz and pulse energy 30 mJ.

The glass vacuum chamber is connected to a high vacuum pump system AV 63 Lavat a.s. (<10^{-5} Torr). Inside the glass chamber is the laboratory made hollow cathode, with 3 mm inner diameter and 20 mm length. The cathode is made from aluminium, as this material has low ion sputtering rate and poor spectrum. The sample is a movable pure copper disc – 22 mm diameter and 3 mm thick, which is mounted at the anode. The gap between the hollow cathode and the sample can be varied between 2÷20 mm. The discharge is powered by a stabilized DC power supply with DC voltage between 0-300 V. The registration system is a Digikröm 480 monochromator equipped with SBIG ST-6A CCD camera, controlled by KestrelSpec 5.14 Lite software.

Before each experiment, the vacuum chamber is pumped up to 10^{-5} Torr and then it is filled with spectrally pure neon 99.99% (neon N40 L’Air Liquide S.A.). The laser beam is focused on the sample by a lens with 25 cm focal distance. The focused laser beam ablates the sample and laser-induced plasma plume is formed. The plasma expands in the space above the sample in the environment of the ambient gas, enters into the cavity of the hollow cathode where it interacts with the glow discharge plasma. The emission from the discharge cavity is focused onto the entrance slit of the monochromator. Each emission spectrum is recorded with time integration of 1 s at laser repetition frequency of 10 Hz, thus each spectrum is averaged over 10 laser pulses.

3 Results and discussion

The proposed system - LIP-HCD consists of two plasma sources - laser-induced plasma and hollow cathode plasma. Laser ablation is sensitive to laser pulse parameters, ambient gas environment and the sample material and structure [8, 9]. The excitation in the hollow cathode discharge is a function of the pressure and the type of the buffer gas and of the discharge current [10].

3.1 Influence of background gas pressure on the laser-induced plasma spectral emission alone

A typical spectrum of copper sample laser-induced plasma emission in air at atmospheric pressure and 4 Torr neon is shown in Fig. 2. In vacuum, the laser-induced plasma expands adiabatically [12] and it is seen that at low pressure value there are narrow, weak and well-resolved analytical spectral lines; a large number of strong spectral lines of the ambient gas and low background emission. Characteristic for the low-pressure region is the fast expansion of the laser-induced plasma, formation of a large plasma plume,
weak spectral emission and weak broadening, due to the predominant dissipation of the ablated particles energy in directed kinetic movement. This results in appearance of the observed weak but well-resolved analytical spectra lines.

In ambient gas environment, the expansion of the laser-induced plasma compresses the gas environment and shock waves are created [13]. In this case the laser-induced plasma interacts actively with the gas phase and the expanding plume consists of atoms and ions of the ablated sample and of the ambient gas. In the spectrum at atmospheric pressure, there is strong background emission, stronger copper analytical lines intensity by a factor of 3-5 and presence of a number of spectral lines of the ambient air. The plasma species are confined in smaller spatial volume than in the low-pressure case, stimulating the dissipation of energy in collisions rather than in kinetic movement of the plasma plume. This leads to enhancement of the collisional frequencies and to rise in emission lines intensity respectively. Additional enhancement of the emission takes place due to the strong plasma shielding effect that occurs in the higher pressure region [8]. At the same time the increase of pressure and the shielding effect lead also to decrease in the laser ablated mass per pulse [9].

In Fig. 3 the pressure dependence of the intensity of the copper lines – 510.5 nm, 515.3 nm and 521.8 nm, emitted by laser-induced plasma, is shown in the pressure range 0.1÷135 Torr. It is seen that there is strong increase of line intensity at 10 Torr. This increase is ascribed to the confinement effect that the ambient gas imposes on the expanding laser-induced plasma leading to transfer of energy from kinetic particle movement to collisions within the laser-induced plasma and with the background gas particles. The confinement is responsible for the trapping of absorbed laser energy and its transfer into emission. Simultaneously, decrease in the ablated mass per pulse with increasing the pressure is possible [9] but the trapping of the ablated species results in enhanced emission than the one from the free expanding material in the low-pressure region. It can be seen in the figure that lowering the pressure below 10 Torr results in very low emission. The used cathode works at a pressure of few Torr where the behaviour of the expanding laser-induced plasma is near to free expansion. Thus, the combination LIP-HCD operates at conditions where low laser ablated plasma emission is observed.

3.2 Influence of cathode-sample gap length on the LIP–HCD emission

The cathode sample gap length is the important parameter allowing the spatial separation of the laser introduction from the glow discharge excitation. The gap length also defines the velocity of ablated particles and their density and energy state at entering the discharge.
For the used cathode with 3 mm inner diameter and 20 mm length stable glow discharge and confinement of the discharge glow in the cavity is observed between 3-13 Torr. The influence of the cathode sample distance on the analytical signal is investigated at three cathode-sample distances: 2 mm, 10 mm and 20 mm at fixed pressure of 4 Torr and discharge current 15 mA. The results show that at 2 mm deposition of ablated material on the inner hollow cathode surface takes place. This is detected by observation of copper atom lines in the spectra long after the end of the laser ablation pulse up to few minutes depending on the number of laser ablation pulses and discharge current. It is assumed that this is due to emission from deposited copper target material in the hollow cathode cavity. The deposited material is re-introduced in the discharge by ion sputtering. The re-introduced material is excited and emits lines of the target till the deposited amount diffuses out of the cathode.

The laser ablation deposition effect could be used as a method for preliminary sample preparation when the hollow cathode is used as a stand alone spectroscopic source. On the other hand, depth analysis is done this effect should be avoided as it leads to superposition of optical emission from different layers and thus it makes the layer discrimination more difficult. At the other extreme – 20 mm sample-cathode gap, very weak signal from the sample lines is obtained.

At 10 mm gap the emission signal of the deposited material is negligible, i.e., comparable to the background and at the same time strong well-resolved lines of the target are observed. It is important to note that the optimal cathode-sample length depends on the ambient gas pressure. In general, the change of background pressure should be followed accordingly with change in the cathode-sample gap length. The expected trend is that the increase of pressure will require decrease of the gap length and vice versa, lowering the pressure will require increasing of the gap length. In the narrow pressure range 3-13 Torr, where the used cathode works – the 10 mm gap length is applicable.

### 3.3 Hollow cathode excitation in the LIP-HCD technique

#### 3.3.1 Hollow cathode excitation in the LIP-HCD technique as a function of pressure

Next step is to determine the influence of the pressure on the analytical signal from the LIP-HCD system. Results for the intensity of the Cu I line - 510.5 nm as a function of the buffer gas pressure at 40 mA discharge current are shown in Fig. 4.

It is seen in the figure that decreasing pressure from 13 to 3 Torr gives rise to increase in the Cu I line intensity. At 13 Torr the Cu I line intensity is detectable but relatively weak. At 3 Torr the intensity of the spectral line is much stronger but there is also an increase of the background signal. From these results it can be concluded that the optimal pressure is between 4 Torr and 7 Torr.

The trend of sample emission line intensity to increase with decreasing the pressure of the hollow cathode discharge is opposite to the trend observed in Fig. 3 where the laser-induced plasma emission increases as a function of raising the ambient gas pressure. This proves that the LIP-HCD emission spectrum is not strongly influenced by the laser-induced plasma emission.
3.3.2 Hollow cathode excitation in the LIP-HCD technique as a function of current

In Fig. 5 the CuI emission line intensity is presented as a function of the current at pressure of 7 Torr. It is seen in the figure that, there is a linear increase in the CuI emission line intensity with raising the current. This behaviour of the copper emission line is explained with the increased electron concentration at higher currents leading to better excitation of the copper atoms. The CuI line is completely missing in the hollow cathode spectrum without laser ablation, which shows that copper is introduced only by the laser ablation and not from sputtering of deposited target material on the cathode wall or of cathode material.

Here the current is not increased above 40 mA as considerable heating of the cathode takes place which results in fast degredation of the cathode. Of course providing cooling of the cathode, further increase of current can be done in order to enhance even more sample emission lines, thus leading to better sensitivity of the technique.

4 Conclusions

The described technique allows independent control of the processes of laser ablation and hollow cathode plasma excitation. The spatial separation of the sample material introduction by laser ablation and hollow cathode excitation is achieved by optimizing the background gas pressure and choosing the optimal sample-cathode gap length for which no deposition of target material on the
cathode walls takes place. The experimental results show that the optimal pressure for this system is 4-7 Torr and the optimal sample-cathode distance is about 10 mm. The increase of discharge current leads to enhancement of the analytical lines intensity. The dependence of sample emission line intensity on buffer gas pressure in the LIP-HCD system is opposite to the trend of laser-induced plasma emission on ambient gas pressure.

The scheme combining laser ablation as sample introduction source and hollow cathode discharge as excitation source presented here can be applied for local elemental analysis of solid samples including non-conducting ones. By using laser energy as low as the one required solely for laser ablation of the sample surface, the depth resolution can be improved. The future work will be focused on time-resolved investigation of the emission characteristics of the proposed technique.

**References**