

## A novel device for spectrochemical analysis based on a combination of LIBS and a hollow cathode discharge

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**Abstract.** A new modified analytical scheme of laser ablation-hollow cathode discharge (LA- HCD) for elemental analysis is reported. The novelty is the use of a hollow cathode with a longitudinal slit. This slit enables registration of the axial species distribution in the discharge and decoupling of the laser and the analytical signals. In this paper preliminary experiments on the modified LA-HCD set-up are reported. The improved analytical performance of the new LA-HCD scheme is demonstrated by comparing it to stand-alone laser induced breakdown spectroscopy. The results of the modified LA-HCD technique show enhancement of the excitation efficiency.

### 1. Introduction

Spectrochemical analysis is a powerful instrumental method for the determination of the elemental composition of various materials. From the variety of methods for spectrochemical analysis, one that is being widely applied in recent years is laser induced breakdown spectroscopy (LIBS) [1]. The LIBS technique offers the opportunity to analyze any material and to detect all elements in the periodic table, requiring at the same time no or minimal sample preparation. These features enable the technique to perform analysis of multi-component samples in the laboratory or in-situ in a fast automated measurement process. The main drawbacks of the technique are the matrix effects and the lower sensitivity compared to other techniques [2]. One of the possible ways to overcome these drawbacks is to combine the LIBS technique with a gas discharge [3]. In such a combined technique the laser provides ablation and atomization of the sample and the gas discharge provides excitation and/or ionization of the ablated atoms. Such hybrid laser-gas discharge schemes employ a variety of different discharges - ICP, microwave discharge, spark/arc discharge, DC plasma devices, hollow cathode discharge (HCD). One hybrid technique that is being reported in recent years is laser ablation-hollow cathode discharge (LA- HCD) technique [4-7]. In the existing realizations of the technique, the HCD is operated in different electrical regimes - DC, RF and pulse mode and the registration of the discharge emission is done on-axis.

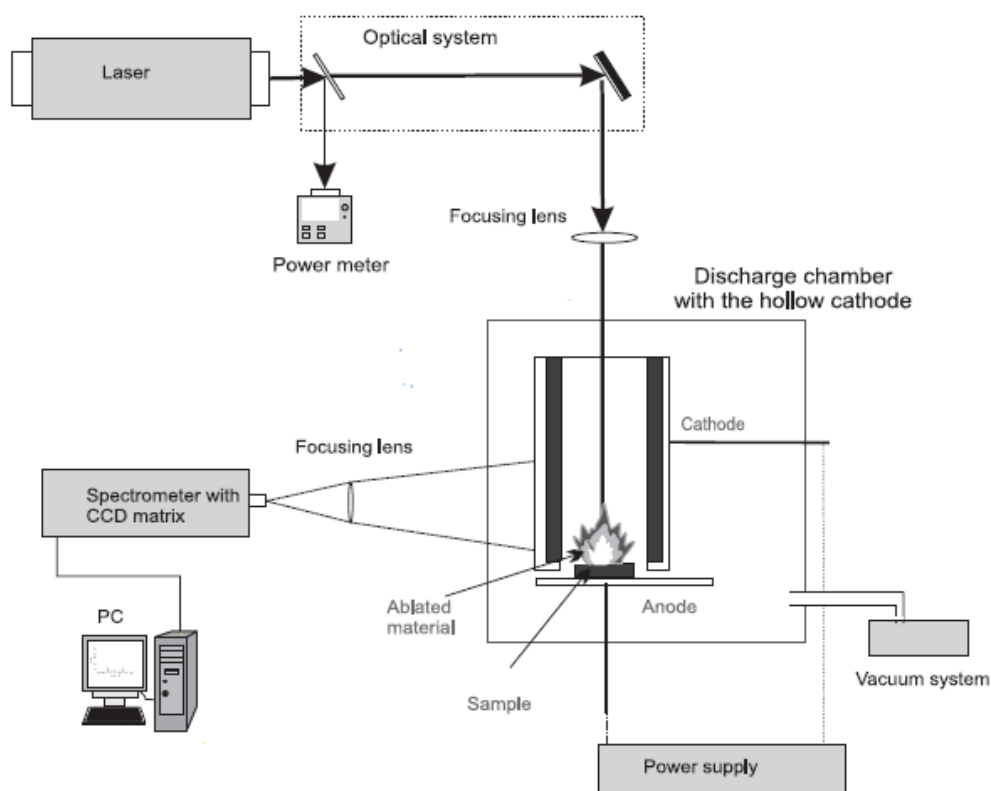
In this work a novel modification of the LA-HCD technique is presented, allowing also observation of the side emission from the discharge. This is made possible by the use of a hollow cathode (HC) with a slit cut along the axis. The capabilities of the modified LA-HCD are demonstrated by comparing its results with those of stand-alone LIBS.



## 2. Experimental setup and conditions

The experimental setup of the modified LA-HCD technique is shown in figure 1. It consists of three main parts: HCD, laser and signal registration.

The modified HC is a hollow cylinder with a longitudinal slit. The slit enables registration of the discharge side emission. Such registration gives opportunity for obtaining the species axial distribution and the evolution of this distribution in time. Apart from that, this slit allows the decoupling of the laser excitation and the analytical signal acquisition. In this way this novel LA-HCD scheme widens the scope of applications of the LA-HCD technique and makes it easier to perform.



**Figure 1.** Experimental setup of the LA-HCD technique.

The discharge part of the set-up consists of the discharge chamber, the HC, the power supply and the vacuum system. The dimensions of the HC are inner radius 4 mm and length 20 mm. These dimensions are chosen according to results from PLASIMO's MD2D model for homogeneous electron density distribution [8-10]. The HC is made from duralumin because this material has small sputtering yield. The anode is a disc. The sample is standing on top of the anode or can be the anode itself, if the sample is made from conducting material. HC is in a chamber with controlled pressure and gas composition. For the first experiments helium is chosen as buffer gas, as it causes low sputtering of the cathode wall. The discharge is excited by DC power supply.

The laser source is Quanta Ray GCR3 pulsed Nd:YAG laser. The pulse repetition rate of the laser can be changed from 1 to 30 Hz, the pulse duration for the primary wavelength 1064 nm is 8 ns and the laser pulse energy is between 10 ÷ 450 mJ. The spectroscopic part of the system consists of a Digikrom 240 spectrometer controlled by a PC.

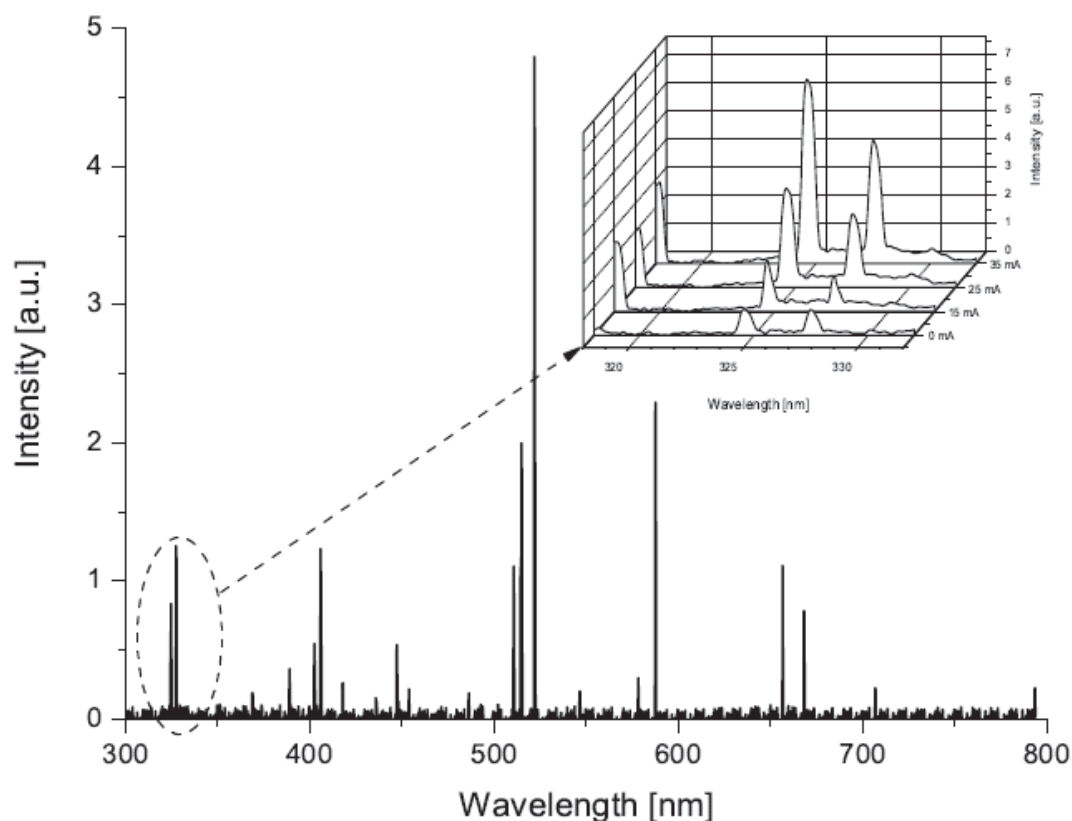
The laser beam is directed to the HC by a set of mirrors and through a lens is focused onto the sample material, which is placed on the anode. The focused laser beam ablates atoms from the surface of the material. The ablated atoms enter the HCD and there they are excited and/or ionized. The optical emission from these atoms is then registered through the longitudinal slit of the HC and focused by the collective lens on the entrance slit of the spectrometer.

The experiments are performed with the fundamental wavelength of the Nd:YAG laser, that is 1064 nm, with laser repetition rate of 10 Hz and with laser pulse energy of 80 mJ. The buffer gas is helium with pressure of 4.2 Torr. The discharge current is varied from 10 to 40 mA.

### 3. Experimental results

The first experiment performed on this setup is the comparison of the modified LA-HCD scheme to stand-alone LIBS. The investigated sample is the copper anode. The anode is made with radius bigger than that of the HC and it can be rotated, so that the laser beam does not hit each time at the same point on the anode. The spectra obtained under different excitation and conditions are compared.

Figure 2 shows the obtained spectrum of the investigated copper sample. The main figure shows the full spectrum obtained by stand-alone LIBS in helium atmosphere (4.2 Torr) over the wavelength range 300÷800nm.



**Figure 2.** The full spectrum obtained by LIBS on a copper sample. The subfigure shows the intensity of two analytical copper lines (324.75 nm and 327.4 nm) at four different values of the discharge current.

In this spectrum the characteristic lines of copper - 324.75 nm, 327.4 nm, 510.55 nm, 515.32 nm, 522.01 nm, 578.21 nm and those of helium - 447.15 nm, 587.56 nm, 667.81 nm and 706.52 nm are

found. A section of this spectrum, from 318 to 332 nm, is plotted in the sub-figure against the spectra obtained from LA-HCD technique at discharge currents of 15, 25 and 35 mA. This plot allows observing the behavior of the copper analytical lines 324.75 and 327.4 nm as a function of discharge current. The stand-alone LIBS plot is marked as 0 mA and the others are accordingly 15, 25 and 35 mA.

The sub-figure shows a well-pronounced enhancement of intensity of the copper analytical lines with discharge current. As it is seen both copper analytical lines increase about five times when changing the discharge current from 15 mA to 35 mA. So the analytical line intensity obtained by LA-HCD is proportional to the value of the discharge current and the enhancement of the intensity is proportional to the discharge input power. Such a behavior of the analytical lines is explained by taking into account the additional excitation of the ablated copper atoms which they undergo in the HCD. This excitation is due to the larger number of excitation collisions between the ablated atoms and the discharge species - electrons, excited atoms and ions. Hence the ablated atoms gain more energy in these collisions and dissipate more energy in radiation processes causing higher intensity of the corresponding analytical lines. This shows that under identical conditions the LA-HCD technique can provide better excitation efficiency than the stand-alone LIBS. This results in more intense analytical signal which leads to better sensitivity.

#### 4. Conclusions

A novel design of a LA-HCD technique is presented. The new features can be observed due to the slit along the HC that allows registration of the longitudinal distribution of the optical signal and its decoupling from the laser excitation. Preliminary results of the modified LA-HCD scheme are presented. Comparison between these results and results from stand-alone LIBS is done. Enhanced analytical performance of the LA-HCD technique is observed. This improvement is attributed to more efficient excitation of the ablated atoms in the HCD. The future work on the modified LA-HCD technique includes: additional optimization of the operational parameters, recording of the temporal evolution of axial species distribution and use of buffer gases other than helium - argon, neon and mixtures of them.

#### Acknowledgments

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