

Optimization of Plasma Parameters for Preliminary Analysis of Chromium Containing Tablet by Laser Induced Breakdown Spectroscopy

M. Hornáčková, Z. Grolmusová, J. Rakovský, J. Plavčan, P. Veis

Department of experimental physics, Faculty of mathematics physics and informatics, Comenius University in Bratislava, Mlynská dolina, 842 48, Bratislava, Slovakia.

J. Heitz, J. D. Pedarnig

Christian Doppler Laboratory Laser Assisted Diagnostics, Institute of Applied Physics, Johannes Kepler University, Altenbergerstr. 69, 4040 Linz, Austria.

Abstract. Laser induced breakdown spectroscopy was used for preliminary elemental analysis of chromium containing tablet. Plasma was generated by 532 nm Q-switched Nd:YAG laser. To collect the plasma emission, lens in the body tube was used. This lens focused emission in the optical fiber linked with the entrance slit of an Echelle spectrometer. The emission beam was recorded with an intensified charge-coupled device (iCCD), finally. Laser induced plasma parameters like electron temperature and concentration were determined for the analysis of tablet containing 0,03 mg of chromium in the form of chromium(III) picolinate. A Saha-Boltzmann plot method was used for determination of electron temperature, assuming the local thermodynamic equilibrium. Electron concentration was estimated by Stark broadening mechanism of H α line (656 nm). Time evolution of electron temperature and concentration were estimated and dependency of intensity on delay was found out for some spectral lines for reaching optimal experimental conditions. Also elemental analysis of the sample was realized. Laser induced breakdown spectroscopy is a suitable technique for qualitative and quantitative analysis of pharmaceutical samples and can provide fast and simple analysis with minimal or no sample preparation.

Introduction

Laser induced breakdown spectroscopy is an analytical method for determination of qualitative and quantitative composition of sample. One of the main advantages of LIBS is the possibility to perform non-contact measurements without significant requirements for sample preparation. LIBS is a versatile method for fast and accurate multi-element analysis of solid, liquid and gaseous samples. In the last few years LIBS has become a popular tool for determination of sample composition and has found versatility in many fields, including environmental [1], biomedical [2,7], art [3], pharmaceutical [4], steel industry [5], botanical and agricultural [6] or nuclear power [8].

As sources for material ablation and simultaneous plasma generation from ablated material Q-switched Nd:YAG lasers are commonly used. Intensive laser pulse is focused on the sample surface to produce plasma or laser spark. Emission from the plasma is collected by fiber optic and analyzed by spectrograph or photodiode. When optimal experimental conditions are obtained, LIBS can provide accurate analysis of examined samples.

The purpose of this work is to find out optimal experimental conditions for analysis of chromium containing tablet, determine time evolution of plasma parameters and make elemental analysis of examined sample.

Experimental

The experimental setup of LIBS for solid samples is depicted in Figure 1. Laser beam generated by Q-switched Nd:YAG laser (Brilliant Eazy, Quantel) delivering energy of about 165 mJ within a pulse of 5 ns duration at second harmonic frequency (532 nm) is focused on the sample surface by lens with focal length 40 mm. The sample was placed on X-Y-Z stage, where position could be changed in all directions. The plasma emission was collected by lens set in the body tube. Collected beam was focused into the optical fiber bundled with the entrance slit of an Echelle spectrometer (Mechelle ME 5000, Andor) and recorded by intensified charge coupled device camera iStar (Andor). Data from measurements were acquired and analyzed by personal computer.

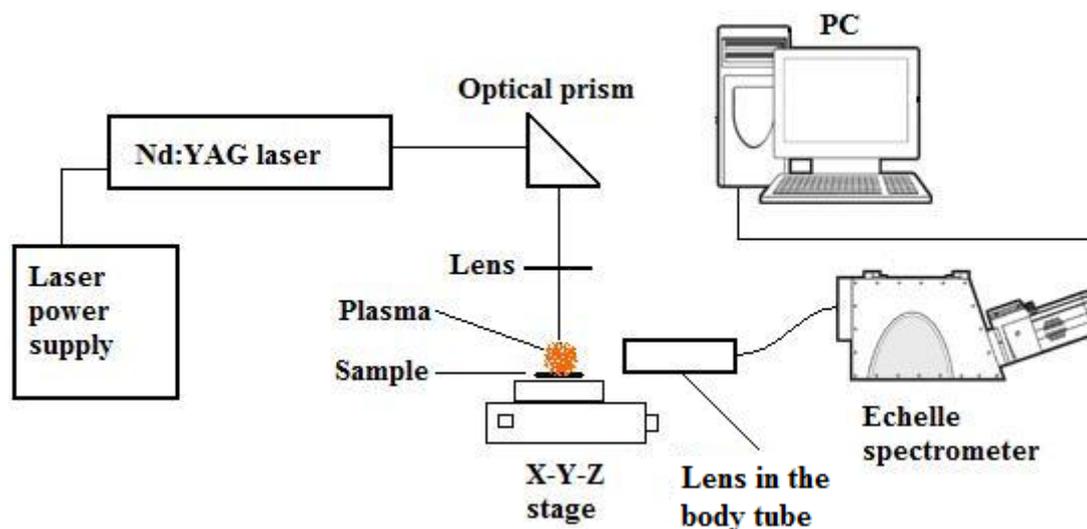


Figure 1. Scheme of the experimental apparatus.

Sample

Classical nutritional supplement “CHRÓM” (Salviafarm- Vitae) available freely at the market of pharmaceuticals was used as the sample for our LIBS analysis. Because LIBS is an optical method, which claims only optical approach to the sample, these analyses required no sample preparation.

Sample composition (1 tablet): 0,03 mg of chromium (in the form of picolinate), 9 mg of zinc (in the form gluconate), 1,2 mg of vitamin B6, inactive ingredients: microcrystalline cellulose, mannitol-E421, talc- E553b, sodium salt- E466, magnesium stearate-E572.

Results and discussion

When an intensive laser beam is focused on the sample surface, small amount of the sample, typically few micrograms, is ablated after each pulse[13]. Ablated material is dissociated into ionic and atomic particles and consequently plasma is created. In time of duration of the laser pulse the sample surface is exposed up to 1 GW/cm^2 energy density. Plasma thus created has a short lifetime, but reaches a temperature in excess of 10 000 K. During this short time, plasma cools very quickly and spreads into the surrounding at supersonic speeds. Excited atoms and ions revert to the lower energy states by light radiation at wavelengths from VUV to NIR region. Wavelength of emitted lines is characteristic for different elements.

Determination of elemental components of the sample

For identification of spectral lines obtained in measured spectra, NIST atomic lines database [9] implemented into the Labview program was used. Spectra of the sample were recorded in the wavelength range 200–950 nm. All measurements were carried out in air at atmospheric pressure and all analyzed LIBS spectra were normalized using the measured response function. Each spectrum is sum of accumulation of 20 laser shots. Typical spectrum of the sample at delay 1 μs and gate width 10 μs illustrates Figure 2.

Our interest was focused on the element chromium. Nine lines of chromium Cr I and four of chromium Cr II were detected in acquired spectra. List of chromium lines detected in the sample is summarized in Table 1.

Some other elements like magnesium, zinc, potassium, sodium, silicon, carbon and calcium were found in obtained spectra. Spectral lines of nitrogen, oxygen and hydrogen were also noticed in spectra, because measurements were carrying out in air at atmospheric pressure.

Determination of electron temperature

Saha- Boltzmann plot method is multi line approach for determination of electron temperature based on the Saha and Boltzmann equations. This method allows plotting both neutrals and ions on the

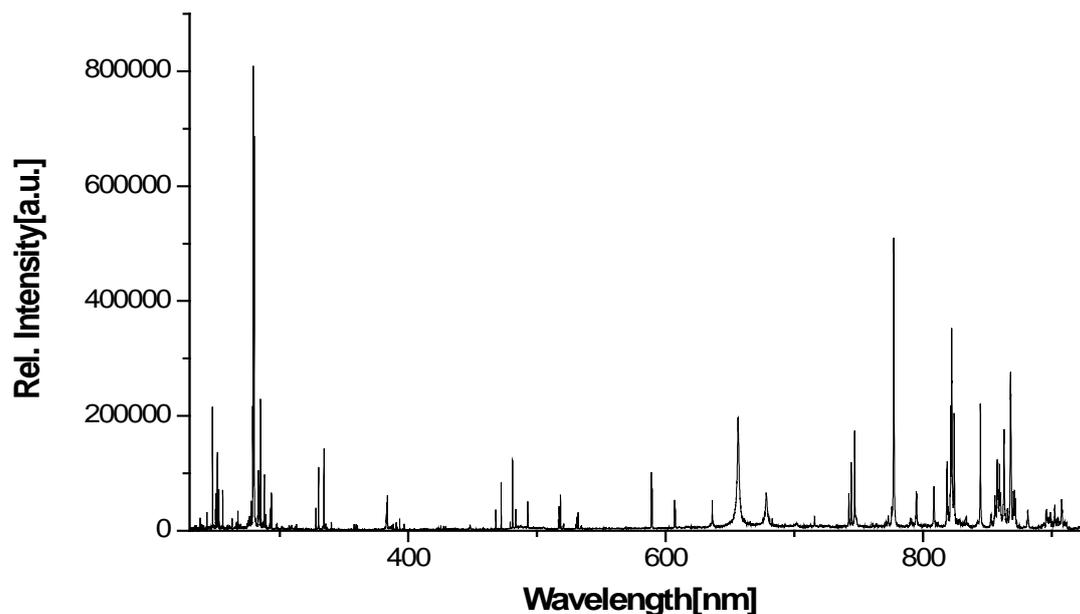


Figure 2. Typical spectrum of chromium containing tablet in wavelength range 230–930 nm, delay 1 μ s and gate width 10 μ s.

Table 1. List of chromium lines detected in the sample by LIBS.

Element	Degree of ionization	$\lambda_{\text{NIST}}(\text{nm})$ [9]
Cr	I	357,869
Cr	I	359,349
Cr	I	360,533
Cr	I	425,435
Cr	I	427,48
Cr	I	428,972
Cr	I	520,452
Cr	I	520,604
Cr	I	520,844
Cr	II	266,602
Cr	II	267,716
Cr	II	283,563
Cr	II	284,325

same plot. Saha-Boltzmann equation (1) relates relative emissivities of lines from subsequent ionization stages of the same element to the temperature T and the electron density N_e [10]:

$$\ln\left(\frac{y_2}{y_1}\right) = -\frac{1}{kT}(E_2 - E_1 + E_\infty - \Delta E_\infty) + \ln\left[\frac{2(2\pi mk)^{\frac{3}{2}} T^{\frac{3}{2}}}{h^3 N_e}\right] \quad (1)$$

X- and Y- coordinates for Saha- Boltzmann plots are determined from equations (2- 5)[11]:

$$x = E_k \quad \text{for neutral lines (2)}$$

$$x = E_j + E_{\text{ION}} \quad \text{for ionized lines (3)}$$

$$y = \ln\left(\frac{I_{ki}}{A_k g_k}\right) \quad \text{for neutral lines (4)}$$

$$y = \ln\left(\frac{I_{jh}}{A_{jh}g_j}\right) - \ln\left(\frac{2(2\pi m_e)^{3/2}(k_B T)^{3/2}}{n_e h^3}\right) \quad \text{for ionized lines (5)}$$

Electron temperatures were determined both from chromium Cr I, Cr II and magnesium Mg I and Mg II lines. Time evolutions of electron temperature for different gate widths (10 – 40 μs) were obtained. Figure 3 illustrates time evolution of electron temperature at gate width 10 μs, where electron temperature is in the range 0,92 - 1eV (±0,043eV) and was determined from magnesium lines.

Figure 4 illustrates time evolution of electron temperature at gate width 10 μs, where electron temperature is in the range 0.85–1.1 eV (±0.048 eV) and was determined from chromium lines. Both evolutions of electron temperature determined from chromium and magnesium lines have linearly decreasing character as it was expected, because plasma cools down very quickly.

Determination of electron concentration

Analyses of lines broadened by Stark effect are commonly used for determination of plasma parameters. The shape of a line depends on the concentration of charged particles surrounding the emitter. For the hydrogen, Stark effect is linear and therefore this dependence is very important. For

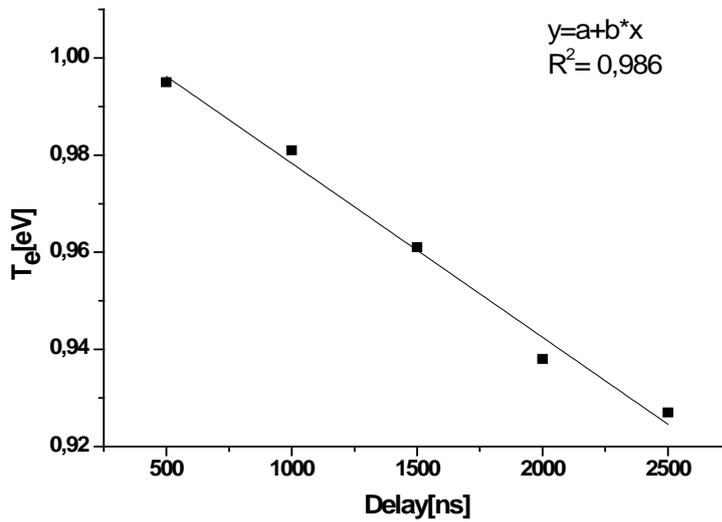


Figure 3. Time evolution of electron temperature determined from magnesium Mg I and Mg II lines, gate width 10 μs.

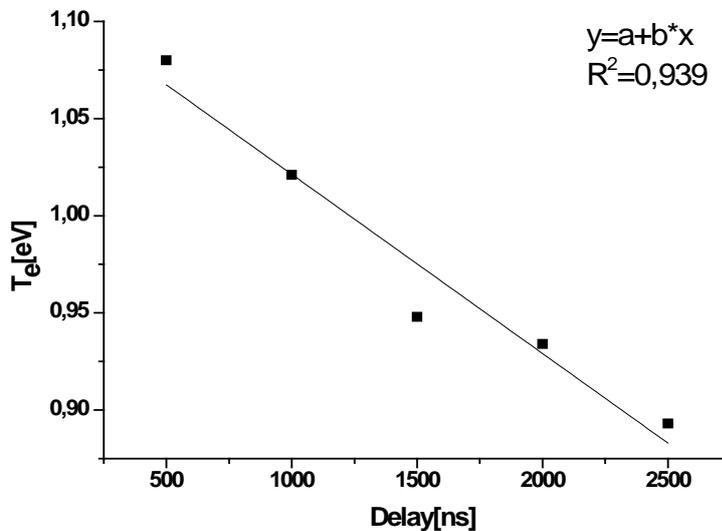


Figure 4. Time evolution of electron temperature determined from chromium Cr I and Cr II lines, gate width 10 μs.

determination of electron concentration full width at half maxima parameter (FWHM) is used generally. But full width at half area (FWHA) parameter is much less sensitive to ion dynamics effects than the FWHM parameter [12]. Account on that, electron concentration was determined from equation (6) [12], for Stark broadening mechanism of hydrogen H α (656 nm) line by means of FWHA parameter.

$$FWHA = 0,549nm \times \left(\frac{N_e}{10^{23} m^{-3}} \right)^{0,67965} \quad (6)$$

Figure 5 depicts time evolution of electron concentration at gate width 30 μ s. Time evolutions of electron concentration were also determined for different gate width (10–40 μ s). All of these evolutions have exponentially decreasing character.

Optimization of experimental conditions

Determination of optimal delay time between gate duration from the laser pulse and the collection of spectra is very important for LIBS analysis, taking into account facts, that in the first nanoseconds continuum radiation is dominant and plasma cools down very quickly. To find optimal conditions spectra were recorded at different delay times. Figure 6 illustrates three spectral lines of chromium observed in spectra recorded at different delay times from 500 ns to 2500 ns. The highest intensity for these spectral lines was observed at delay time 1000 ns.

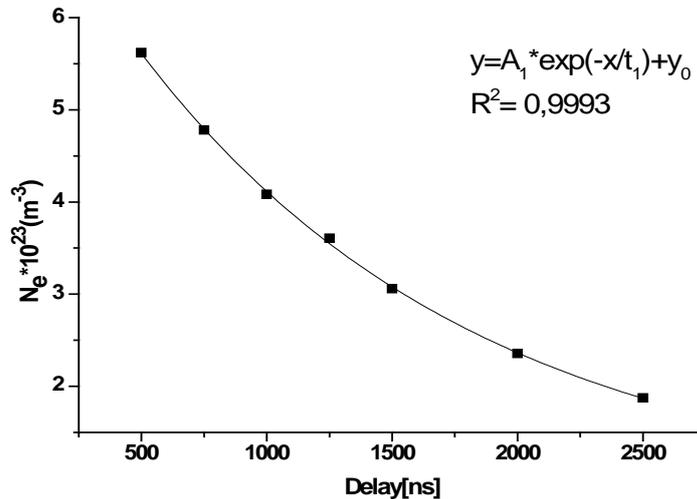


Figure 5. Time evolution of electron concentration, gate width 30 μ s.

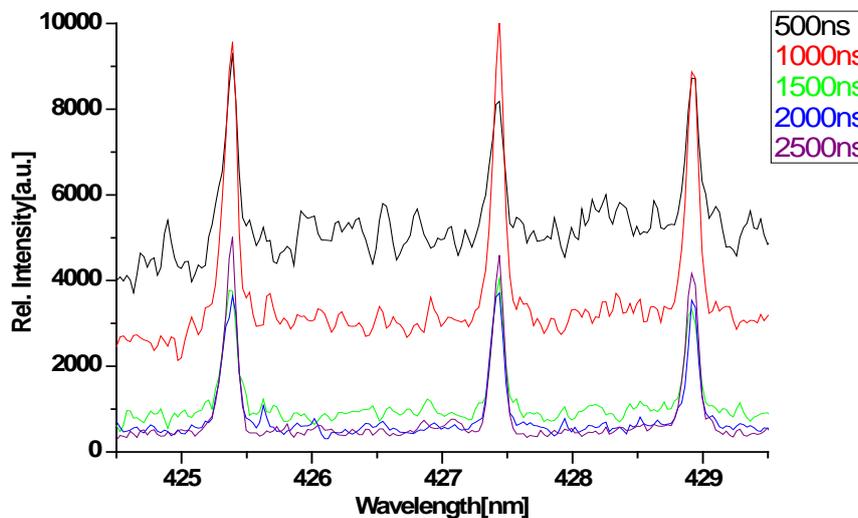


Figure 6. Intensity comparison of three chromium spectral lines detected in the sample at different delays, gate width 10 μ s.

Conclusion

Laser induced breakdown spectroscopy was used for analysis of chromium containing tablet. Complete elemental analysis was realized and optimal experimental conditions were found for the next step of our research, calibration free laser induced breakdown spectroscopy. Several spectral lines of chromium were detected in obtained spectra and found optimal experimental conditions are suitable for both neutral and ionic spectral lines of elements of our interest. No surface contaminants were detected, because of pure treatment with samples. We can conclude that LIBS is a suitable method for detection of minor elements in samples of pharmaceuticals and have great potential for application in the process of pharmaceuticals production. Some other elements like magnesium, zinc, potassium, sodium, silicon, calcium and carbon were also identified in the sample.

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