

LASER INDUCED OPTICAL EMISSION SPECTROSCOPY

M. Trtica¹, M. Kuzmanovic², M. Momcilovic¹, J. Ciganovic¹, D. Rankovic²,
J. Savovic¹

¹Vinča Institute of Nuclear Sciences, University of Belgrade,
POB 522, 11001 Belgrade, Serbia, etrtica@vinca.rs

²Faculty of Physical Chemistry, University of Belgrade, POB 276, 11001 Belgrade, Serbia

A brief review of Laser Induced Optical Emission Spectroscopy (LIOES) along with some experimental results obtained at VINCA Institute will be given. LIOES is a relatively new spectroscopy method/technique which attracts attention and shows good prospects. It is a contemporary physical and chemical or physico-chemical method, applied for various purposes, primarily for qualitative and quantitative analysis. In some cases, it can be used for monitoring of the reactions. Basically, the LIOES is an emission spectroscopy technique in which a plasma is initiated by a laser in front of a target. Plasma is generated at typical laser intensities of about 10^8 W/cm², simultaneously with target ablation. The ablated material is vaporized and then partially atomized, or excited and ionized within a plasma plume formed above the surface. Initially, plasma emits a continuum radiation, but in a short time it expands and cools /1,2/. During this stage characteristic atomic lines of the target elements can be emitted, thus the plasma can give information about the target composition.

A contemporary apparatus for LIOES includes: (i) a pulsed laser; (ii) a set of optics for directing the laser beam onto the target; (iii) a set of optics for collection the plasma emission and directing it into dispersive system; (iv) spectrometer with a detection system and, (v) data processing system. Today, various systems are used as pulsed lasers. With respect to the pulse duration the femto-, pico or nano- second lasers are used. Laser active mediums are also diverse in different types of lasers: solid state lasers (Nd:YAG, Ti:sapphire), gas lasers (N₂, TEA CO₂, excimer), etc.

LIOE Spectroscopy method/technique possess some advantages with respect to other spectroscopy methods such as: (i) this method can be applied to solid, gaseous or liquid samples. Focusing only on the solid the method can be employed on metal, nonmetal, semiconductor, bio-materials, etc.; (ii) LIOES is a non-destructive technique. A typical quantity of the material which is removed during ablation process per pulse is extra-low, of the order of ng or pg. This practically means that the mass of the target/sample can be minimal (e.g. order of milligrams); (iii) LIOES is a non-contact technique; (iv) sample preparation time (SPT) for LIOES is minimal, of the order of seconds. For comparison – the SPT of Inductively Coupled Plasma (ICP) spectroscopy is typically several hours; (v) detection rate of the LIOES method is short; and (vi) LIOES has a

relatively high sensitivity. Beside these superior characteristics, LIOES has some disadvantages, such as relatively poorer sensitivity compared to e.g. ICP and mass-spectrometry. The accuracy and precision of the measurements are about 10 and 5%, respectively /3/.

Historically, if the first laser, i.e. ruby system, was realized 1961 then the first observation of plasma produced by laser dates from 1962 /4/. The first analytical usage, the first optically induced breakdown studies in gases and initial observation of the induced shock wave plasma by laser dates from 1963, 1964 and 1967, respectively. The period from 1964 to 1967 is a period of appearance of the first commercial systems. Two companies, C. Zeiss and J. Ash, were the pioneers in this area. The period of intensive development and studying of LIOES is between the 80-ties of the last century and present. Commonly, LIOE Spectroscopy can be classified in relation to several parameters like operational pressure, the site of detection, resolution, etc. In today's literature, different terms can be found which are complementary with Laser Induced Optical Emission Spectroscopy, such as Laser Induced Breakdown Spectroscopy (LIBS), Laser Induced Plasma (emission) Spectroscopy (LIPS), Optical Emission Spectroscopy (OES), Laser Induced Shock Wave Plasma Spectroscopy, Laser Micro-analysis, etc.

Nowadays, Laser Induced Optical Emission Spectroscopy, as a superior spectroscopy method, can be applied in manifold applications, like: (i) environmental monitoring; (ii) material analysis; (iii) forensic and biomedical studies; (iv) industry; (v) art restoration/conservation area; (v) safety and military needs and (vi) specific purposes (e.g. geology; Space exploration; nuclear complex; isotope analysis).

Within the VINCA Institute the initial activity in Laser Induced Optical Emission Spectroscopy was focused only on copper. The development of instrumentation capable of sensitive and quantitative measurements of elemental composition of copper based materials is of considerable interest for industry. For many purposes, it is important to control the concentration of trace impurities in copper and its alloys, because today they are one of the major groups of commercial metals.

Considering the laser-copper interaction, the physical processes on the surface depend on the laser pulse duration used. Some results obtained using a nanosecond TEA CO₂ laser will be presented. Generally, the emphasis will be on the plasma spectral emission at low pressure. The experimental apparatus used for this measurement is described elsewhere /5/. Commonly, the energy absorbed from the TEA CO₂ laser beam is converted into thermal energy, which causes melting, vaporization of the molten material, dissociation and/or ionization of the vaporized material, shock waves in the vapor and solid, etc. If the laser energy/intensity is sufficient, the plasma will be created in front of the target surface. This plasma generation generally depends also on the laser output

parameters (pulse energy density (fluence), intensity, wavelength, optical/laser pulse duration, etc.), as well as on the target characteristics (e.g. its absorptivity) and also on irradiation conditions (e.g. working atmosphere – vacuum, air, etc.). The role of the plasma in energy coupling between the laser and the metal surface can be essential. Depending on the surrounding gas pressure [6] three different laser plasma modes exist. Our experiments are conducted at an air pressure of about 0.1 mbar, thus the shock wave plasma/mode is present. This mode is known as “laser-induced shock wave plasma”.

Plasma characteristics

Irradiation of Cu-target at low laser fluence ($\sim 6 \text{ J/cm}^2$) resulted in the appearance of plasma whose shape, size and colour depended on the working conditions. The changes of plasma as a function of the air pressure are shown in Figure 1. The plasma shape was changed from the semi-spherical (intensive green colour) at an air pressure of $\sim 0.1 \text{ mbar}$ (Fig. 1a) to the cone shape (intensive bright-whitish colour) at an air pressure of 1013 mbars (Fig. 1b). At the pressures below 10 mbar the plasma consisted of two distinctly separated regions, Fig. 1a. The first region, close to the target, was characterized by a whitish colour, known as primary plasma. This region is confined to a relatively low volume and it generates intense continuous emission spectrum in a short time. The second region (Fig. 1a) is larger in volume, coloured green, and known as secondary plasma. This region typically emits atomic spectral lines with low background.

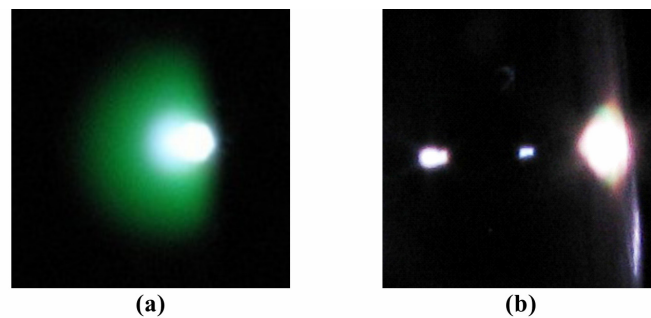


Figure 1. The view of the Cu-plasma at air pressure of $\sim 0.1 \text{ mbar}$ (a) and, 1013 mbar (b).

The spectral emission of Cu-plasma

Spectral emission of Cu-plasma initiated by CO_2 laser is presented in Figure 2. This figure shows a limited spectral region (250 - 400 nm) although the measurements were conducted in a wider range, from 225 to 700 nm. Spectral emission was observed at two locations/distances above the target, corresponding to primary and secondary plasma regions. Emission from primary plasma (Fig. 2b) resulted in numerous lines (146 lines). These lines have ionic or atomic origin. Emission from secondary plasma (Fig. 2c) resulted in lower number of spectral lines (44 lines) as well as in a lower number of ionic species. Such behavior can probably be attributed to the lower temperature in this plasma

region. In all plasma regions the ultimate Cu-lines at 324.75, 327.39, 510.55, 515.32 and 521.82 nm were recorded. The strongest lines were always the ones at 324.75 and 327.39 nm. All spectral ultimate lines have a very good signal-to-background ratio, especially from the secondary plasma region. The ratio in this region is estimated to be higher than 300:1.

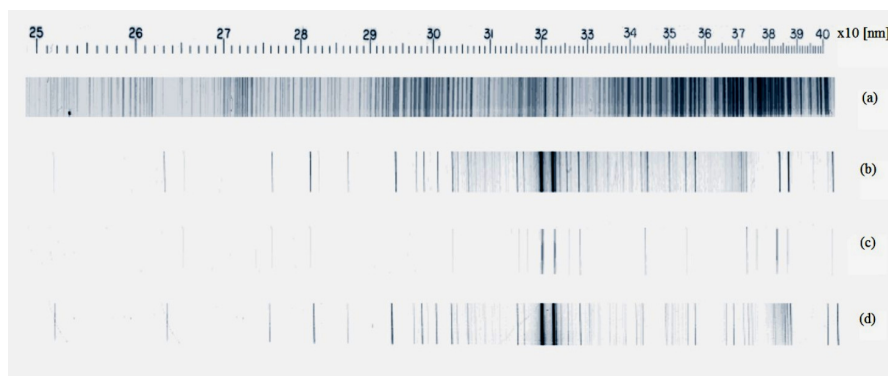


Figure 2. UV/VIS spectral lines of Cu-plasma induced by laser. ((a), (d) Calibration spectrum of Fe- and Cu- arc, respectively; (b), (c) plasma emission from primary and secondary plasma, respectively).

Preliminary observation of the time evolution/history of the individual Cu-spectral lines was carried out, too. FWHM of the neutral spectral line (324.75 nm) in the primary and secondary plasma regions was of the order of μs , whereas for the ionic line ((Cu II), 271.35 nm; primary plasma) the FWHM was $\sim 0.5 \mu\text{s}$.

A brief review on the contemporary spectroscopic method/technique, i.e. the Laser Induced Optical Emission Spectroscopy, is provided. In the same manner, some research conducted at the VINCA Institute is presented. Based on these studies it can be concluded that the method can be effectively applied for analytical purposes.

References

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