

LIBS TECHNIQUE BASED ON TEA CO₂ LASER FOR ELEMENTAL ANALYSIS OF IMPURITIES IN GRAPHITE

J. PETROVIC^{1*}, M. KUZMANOVIC², D. RANKOVIC², M. TRTICA¹ and J. SAVOVIC¹

¹*Department of Physical Chemistry, VINCA Institute of Nuclear Sciences - National Institute of the Republic of Serbia, University of Belgrade, Mike Alasa 12-14, 11001 Belgrade, Serbia
E-mail jpetrovic@vin.bg.ac.rs*

²*Faculty of Physical Chemistry, University of Belgrade, Studentski trg 12-16, 11158 Belgrade, 118, PAC 105305, Serbia*

Abstract. Optical emission spectroscopy investigation of plasma induced in air at atmospheric pressure by a transversely excited atmospheric carbon dioxide laser (TEA CO₂) on a pressed graphite (with soil as impurity) target is presented. Despite the softness of the sample, bright and voluminous plasma was obtained, with intensive and well defined spectral emission of atomic and single charge ionic lines of elements contained in the target material. Strong molecular emission bands of CN and C₂ were recorded as well. Good signal to noise ratio provided low values of limits of detection (LODs) for metal elements; in the range of 10 to 100 ppm. Plasma temperature was estimated using a Boltzmann plot method (Fe I and Fe II lines) and rotational structure of the 0-0 band of CN violet system. The obtained temperatures characterize the plasma zones where maximal emission of iron atomic and ionic lines (8200 and 13800 K, respectively), and CN molecular bands (6200 K) could be expected.

1. INTRODUCTION

Laser induced breakdown spectroscopy (LIBS) is a popular analytical technique for rapid and sensitive analysis of most elements, including the ones with low atomic number. Some of the advantages of LIBS are minimal destructiveness and sample preparation, possibility of surface and depth profiling of the chemical composition, remote analysis. A typical LIBS system uses a robust and compact nanosecond Nd:YAG laser, with pulse energy usually less than 200 mJ. However, CO₂ gas lasers were also successfully applied for LIBS analysis of various sample types, with some advantages like eyesight safety and transparency in the air atmosphere. Graphite is very important material in modern technology and there is an interest for rapid and sensitive elemental analysis of its impurities that are usually in the

form of the soil aluminosilicate. In this work, applicability of the LIBS system based on TEA CO₂ laser with low pulse energy, for elemental analysis of pelleted graphite samples was demonstrated.

2. EXPERIMENTAL

A compact, laboratory made IR gas laser was applied to create plasma on pressed graphite sample. The maximal pulse energy of laser was 160 mJ (in multimode), with a cross section of the focused beam of 0.015 cm², providing maximal fluence and peak intensity of 10.7 J/cm² and 37 MW/cm², respectively. The initial peak of the laser pulse contains approximately 35% of total energy (full width at half maximum of 100 ns), followed by a 2 μs long tail. Samples for LIBS analysis were obtained as follows: spectrochemical pure graphite powder was carefully mixed with a powder sample of soil of known composition, and then pelleted under a pressure of 10 tons per cm², for 30 min.

Optimal condition to obtain the best signal to noise ratio for metal elements lines was: laser beam focused 5 mm behind the target and plasma observation zone of 1 mm from the target surface. Instead, commonly used time-gated detection, an alternative detection technique was applied; plasma image of the selected plasma slice was focused on the entrance slit of a Cherny-Turner spectrograph (2 m) and recorded in a time-integrated regime using back thinned CCD detector (Apogee Alta F1007).

3. RESULTS AND DISCUSSION

Graphite and coal samples have high absorption in mid-IR spectral range, thus, it was possible to obtain analytically usable plasma and spectral emission by focusing the laser behind the target. The recorded spectra consist of narrow lines with favorable signal to background ratio, without usually very broad O and N lines from air. LODs were estimated as the concentration of analyte that gives a signal that is equal to three times standard deviation of the background intensity. By taking into account known concentration of the elements in graphite pastille, we derived minimal detectable concentration for several elements: Fe II 9.2 ppm, Fe I 67 ppm, Ti I 90 ppm, Ti II 70 ppm, Mn II 10.5 ppm, Mg II 4.5 ppm and Si I 22 ppm. Additionally, improvement of detectability could be obtained by optimization of the experimental conditions and by selecting the optimal spectral line for each element. As an example of typical spectra, spectral intervals containing Fe I and Fe II lines are shown in Figure 1.

Integral intensities of iron spectral lines (Figure 1) were used for Boltzmann plot method, i.e. for estimation of the excitation temperature. As shown in Figure 2a, the estimated temperature was 8200 ± 400 K. Temperature derived from iron ionic lines (Figure 2b) was 13800 ± 500 K. Considering that time-integrated spectral intensities of a plasma slice parallel to the target surface were detected, it is clear that ionic and atomic lines were emitted from different plasma zones and at different time interval during plasma temporal evolution. However, knowledge of

these temperatures is important for estimating the excitation conditions for the observed element and its spectral line, as well as for comparing the line intensities of different elements.

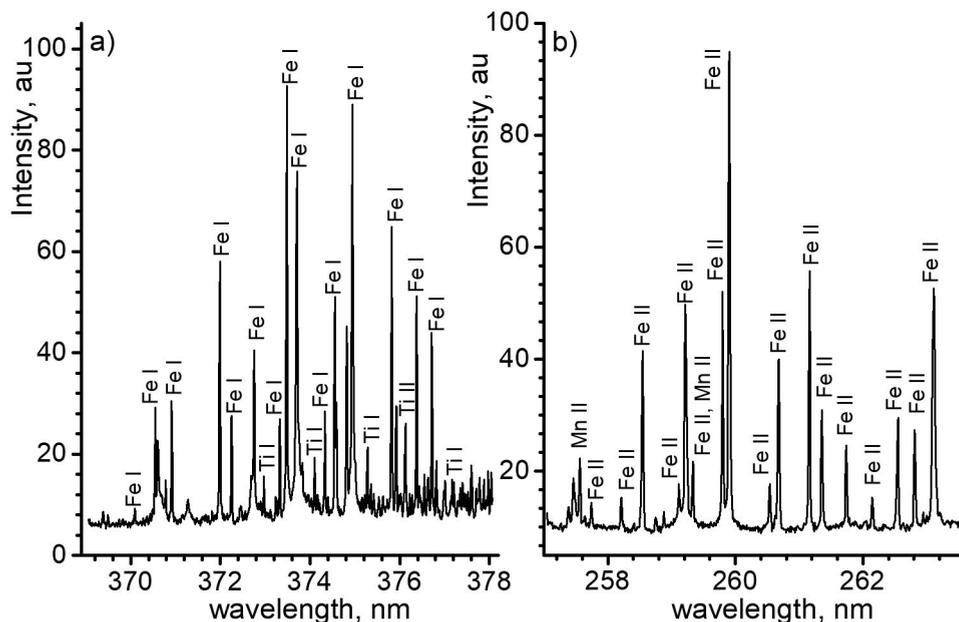


Figure 1: Example of LIBS spectra of pressed graphite with 5% soil.

CN bands of violet system have strong emission even for lower carbon concentration in plasma, especially the 0-0 band. That's why this band could be used for determination of low level carbon content in samples. In case of high carbon concentration in plasma, this band suffers from self-absorption that also reduces its applicability for rotation temperature determination (close to gas temperature). For moderate spectral resolution, rotational structure of 0-0 CN band is unresolved and cannot be used for rotational temperature estimation. In this work, temperature determination by using part of 0-0 band near 1-1 band head, obtained with higher spectral resolution (0.0052 nm FWHM of instrumental profile): as is shown in figure 2b) was demonstrated. The intensity ratios of adjacent components of P and R branches are very temperature sensitive. On the other hand, these rotational components have much lower intensities than band heads, and they are much less perturbed by self-absorption. Experimental and synthetic spectra are normalized with intensities of R components and then fitted to obtain best matching. Best fitting was obtained for $T_{\text{rot}} = 6200$ K, and this result is independent on T_{vib} . The difference in the intensity of the 1-1 band head could be the consequence of two different effects: self-absorption of experimental spectrum and lower value of T_{vib} in comparison with T_{rot} .

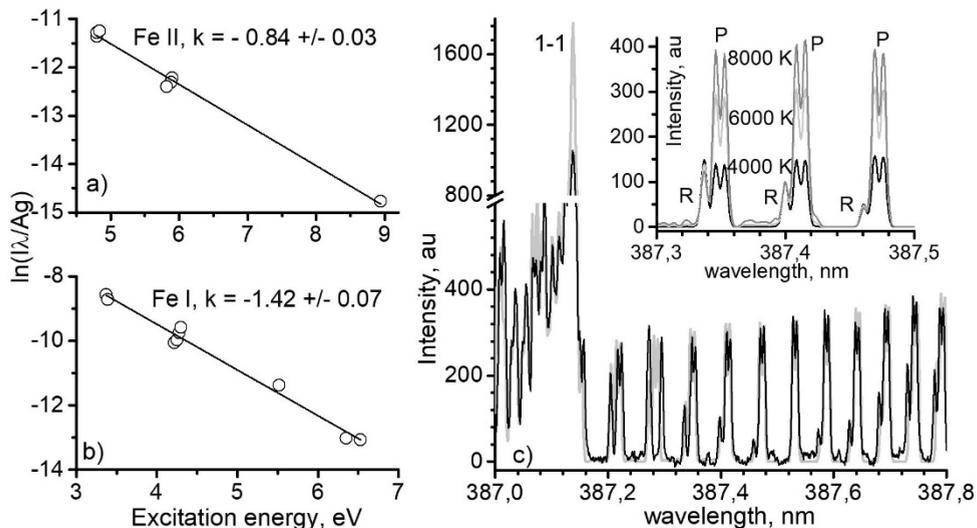


Figure 2: a) and b) Boltzmann plot of ionic and atomic iron lines; c) part of high resolution spectra of 0-0 and 1-1 bands of CN violet system. Grey curve represents a synthetic spectra for $T_{rot} = T_{vib} = 6200$ K. Small graph in figure c) illustrates temperature sensitivity of rotational components of CN band.

4. CONCLUSION

Optical spectroscopy investigation of plasma induced by TEA CO₂ laser on the graphite target was performed to check the applicability of the LIBS technique for elemental chemical analysis of graphite impurities. Low LOD values (in the range of 10 – 100 ppm) were obtained for metal elements from the soil. Plasma temperatures were estimated using a Boltzmann plot method and by analysing CN emission spectral bands. The obtained temperatures are related to the optimal emission zones of different species: 13800 and 8200 K for ionic and atomic emission of iron, and 6200 K for CN molecular emission.

Acknowledgements: The research was funded by the Ministry of Education, Science and Technological Development of the Republic of Serbia (contract numbers: 451-03-68/2020-14/200146; 451-03-68/2020-14/200017).

References

- Kuzmanović, M., Ranković, D., Trtica, M., Ciganović, J., Petrović, J., Savović, J.: 2019, *Spectrochim. Acta*, **157B**, 37.
- Luque, J., Crosley, D. R.: 1999, *SRI Int. Rep. MP*, **99**, 9.
- Savović, J., Stoilković, M., Kuzmanović, M., Momčilović, M., Ciganović, J., Ranković, D., Živković, S., Trtica, M.: 2016, *Spectrochim. Acta*, **118B**, 127.