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# DIAGNOSTICS OF PLASMA PRODUCED BY LASER ABLATION OF CARBON-BASED POLYMER MATERIAL

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**Abstract.** Carbon-based polymer materials such as fluoroplastic (Teflon) are commonly used as the inert substrate in laser-induced breakdown spectroscopy (LIBS) analysis of dry residues of liquid samples whether they are inorganic, organic or biological materials. Alongside the emission of analyte atoms, the induced plasma often involves the emission from the substrate material. Strong atomic and ionic carbon lines as well as $C_2$ and CN molecular bands emitted from Teflon plasma are suitable for plasma diagnostics. In this work, optical emission spectroscopy of TEA $CO_2$ laser-induced plasma on a Teflon target was applied for the estimation of plasma parameters, temperature, and electron number density. Estimated plasma parameters may be used to correct shot-to-shot variations of the measured intensities of analyte emission.

## 1. INTRODUCTION

Applications of LIBS for quantitative analysis of liquid solutions are still challenging and suffer from low sensitivity and poor repeatability of measurements. One of the available methods for improvement of analytical performance is to convert liquid to a solid matrix, for example by depositing micro-drops of analyte solutions on a substrate and drying. Commonly, inert material is chosen as a substrate in order to reduce a portion of the laser energy that is spent on substrate vaporization, i.e. to ensure that the induced plasma mainly involves the deposited material. Carbon-based polymer materials such as Teflon are often used

for this purpose: see De Giacomo et al. 2016. Teflon molecules contain only carbon and fluorine and because of the low excitation efficiency of fluorine, the spectral contribution from the substrate is practically limited to carbon. In case the LIBS analysis is carried out in the ambience air, along with carbon atomic and ionic lines molecular bands of diatomic species such as CN and $C_2$ could be registered in the plasma. In this work, emission from the laser-induced Teflon plasma was utilized for diagnostics of plasma, i.e. estimation of plasma temperature and electron number density. Estimated plasma parameters may be used for correction of the measured intensities of analyte lines whose variations are caused by fluctuations of signal intensities (shot-to-shot variations).

## 2. EXPERIMENTAL

The experimental setup was based on the Transversely Excited Atmospheric pressure carbon dioxide (TEA $CO_2$) laser. The laser simultaneously operates at two wavelengths, 10.5709 and 10.5909 μm, with pulse repetition rate up to 2 Hz, in a multimode regime. Laser pulse has initial peak (~100 ns) followed by a decaying tail (~2 μs), with approximately 35% of total pulse energy in the initial spike. The laser beam was focused by ZnSe lens on the target. In most measurements, the laser pulse energy of 150 mJ was used and the beam was focused 5 mm in front of the target. The corresponding fluence and intensity were 10 J/cm$^2$ and 35 MW/cm$^2$, respectively. Image of plasma was projected on the entrance slit of a Carl Zeiss PGS2 spectrograph by an achromatic quartz lens. Spatially resolved measurements were provided by moving the target along the laser beam direction. Spectral emission was time-integrated using a scientific grade deep cooled CCD camera, with high quantum efficiency in the UV and VIS spectral region. A Czerny Turner spectrograph was equipped with two plane reflective diffraction gratings with 650 rules/mm blazed at 330 and 590 nm. Linear dispersion in the first spectral order was about 0.7 nm/mm, and the FWHM of the instrumental profile was 0.027 nm for the entrance slit of 25 μm. For the applied spectral dispersion, spectral region captured by a CCD was about 9 nm.

## 3. RESULTS AND DISCUSSION

When the TEA $CO_2$ laser beam was focused on the Teflon target surface reproducible plasma could not be obtained even with the highest attainable laser pulse energy of 170 mJ. On the contrary, spectrochemically usable plasma was obtained by focusing the laser beam 5 mm in front of the target. In that case the threshold energy for plasma creation on the Teflon was 130 mJ. Teflon plasma emits strong atomic and ionic carbon lines and $C_2$ and CN molecular bands, suitable for plasma diagnostics.

The electron number density was determined from Stark width of carbon ionic C II 283.67 nm line. Figure 1a shows the profiles of C II spectral lines obtained using laser pulse energy of 150 mJ focused 5 mm in front of the Teflon target, emitted from a part of the plasma 1 mm from the target surface. The estimated

electron number density was in the range $1.9 \cdot 10^{17}$ to $9.4 \cdot 10^{17}$ $cm^{-3}$, depending on the plasma observation zone (1 to 3 mm from the target). The carbon lines, C II 250.91 nm and C I 247.86 nm (Figure 1b) were used for determination of the ionization temperature using the ion-to-atom spectral line integral intensities ratios. The estimated plasma temperature was in the range of 16500 K (0.9 mm) to 20500 K (0.3 mm).

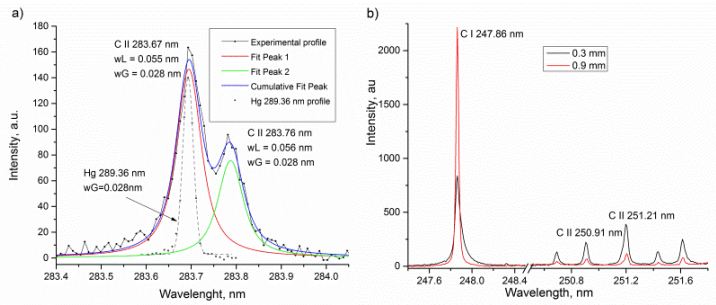


Figure 1: (a) Profile of C II 283.67 nm line used for determination of $n_e$; (b) Part of LIBS spectra recorded at 0.3 and 0.9 mm from target surface.

The emission spectra of $C_2$ and CN molecules were used for determination of the rotational ($T_{rot}$) and vibrational ($T_{vib}$) temperatures, by comparing the experimentally obtained and synthetic molecular spectra. Because of high dissociation energy of these molecules, relatively low excitation energy of the first excited electronic state, and the favorable value of the transition probabilities their emission intensities are high and suitable for plasma diagnostics: see Kuzmanovic et al. 2019. The emission of the Swan system of $C_2$ molecules could be obtained only from the plasma region close to the target surface, Figure 2.

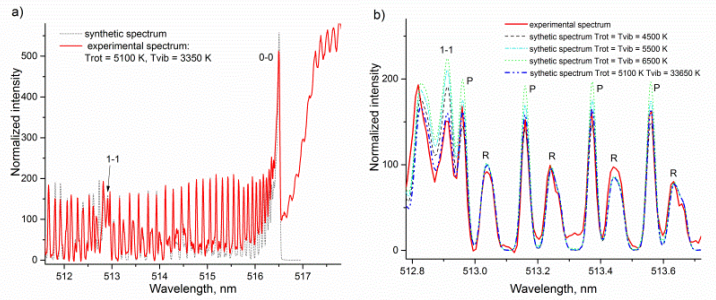


Figure 2: (a) Part of spectrum of sequence $\Delta v=0$ of $C_2$ Swan system. The spectrum was recorded at a distance of 0.3 mm from the target; (b) the P and R components of the 0-0 band spectrum.

On the contrary, the intensive emission of the $\Delta v = 0$ sequence of B-X violet system of CN molecule could be detected at distances up to 2 mm from the target surface, Figure 3. This is understandable as the CN molecule is formed by the reaction of carbon ablated from the target and nitrogen from the air.

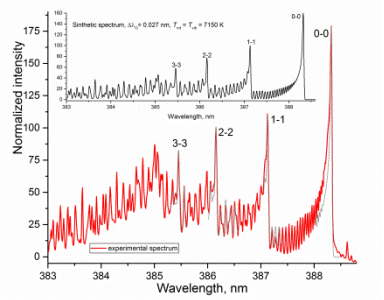


Figure 3: The spectrum of Δv=0 sequence of CN B-X violet system. Laser pulse energy 150 mJ, laser beam focused 5 mm in front of the target. The spectrum was recorded from a slice of plasma parallel to the target, at a distance of 0.3 mm from the target.

From the $C_2$ spectra, the best matching was obtained for $T_{vib}$ = 3350 K, and the $T_{rot}$ = 5100 K, while from the CN bands, $T_{rot}$ = $T_{vib}$ = 7150 K. The most intense band of the CN violet system showed strong self-absorption and led to overestimated temperature values.

## 4. CONCLUSIONS

Diagnostics of the TEA $CO_2$ laser induced Teflon plasma was performed using the emission spectroscopy. The plasma parameters, electron density and temperature, were estimated using emission spectra of neutral and singly charged carbon atoms. Depending on the plasma observation zone, the electron number density and temperature were in the range $1.9 \cdot 10^{17}$ to $9.4 \cdot 10^{17}$ $cm^{-3}$, and 16500 to 20500 K, respectively. Additional information was obtained from the rotational-vibrational structure of $C_2$ and CN band intensities. The most intense bands of $C_2$ emission spectra had more distinct band heads and a better resolved rotational structure than bands of CN violet system, thus, they were more convenient for determination of temperature.

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