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The effect of the duration of laser pulses on the spectral-temporal characteristics of laser plasma in femtosecond laser-induced breakdown spectroscopy of human hair

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The effect of the duration of laser pulses of 40 and 650 fs with an energy of 1.1 mJ at a wavelength of 800 nm on the spectral-temporal characteristics of plasma during femtosecond laser-induced breakdown spectroscopy of human hair has been studied. The time dependences of the radiation line intensities of Ca I 422.6 nm, C I 193.1 nm, C I 247.8 nm, Ca II 396.8 nm, Mg II 279.5 nm, Zn II 206.2 nm and the continuous plasma spectrum in the range from 0 to 1 μ s are obtained

Keywords: emission spectrum, laser plasma, human hair.

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Further development of personalized medicine is one of the key current strategic goals. According to the estimates of experts from the World Health Organization, 25–33% of reportable diseases are attributable to adverse environmental factors [1]. Human hair is a fine biomarker for health assessment and monitoring of environmental risks that is done by determining the elemental composition and may complement traditional diagnostics techniques [2–4] (specifically, in estimating trace concentrations of elements and persistent organic pollutants [5,6] and identifying osteoporosis [7]). Human hair grows at a rate of ~ 1 cm per month. Microelements are introduced into hair in the process of growth and characterize the microelemental composition of blood plasma at the time of formation [8,9]. This allows one to perform a retrospective analysis and provides an advantage over blood or urine tests, which yield a microelemental pattern that is relevant only to the moment of sampling.

Laser-induced breakdown spectroscopy (LIBS) is often applied at present in the analysis of biological objects [10]. Although it has a number of advantages, a relatively low sensitivity is one of its disadvantages that cannot be overlooked. The technique of temporal signal selection is used to enhance the LIBS sensitivity. Time delay t_d of spectrum recording relative to a laser pulse and exposure time t_g are important parameters of this procedure [10]. Although nanosecond laser pulses are used in most LIBS applications [10,11], recent studies have demonstrated that femtosecond pulses provide such advantages as minimization of thermal bulk damage to biological samples, identification of the molecular composition of biomaterials, minimization of the influence of atmospheric nitrogen and oxygen lines, and lowering of detection thresholds [12–14].

In the present study, the temporal evolution of intensity of a continuous plasma spectrum and emission lines of elements in laser plasma, which is generated on the surface of a single degreased human hair fiber by femtosecond pulses, is examined in order to determine the optimum parameters of temporal signal selection. Plasma was generated on the hair surface by focusing laser pulses with a duration of 40 and 650 fs, a center wavelength of 800 nm, an energy of 1.1 mJ, and a repetition rate of 100 Hz (Spitfire Pro 40F laser, Spectra-Physics) by a lens with a focal distance of 50 mm at a distance of 0.1 mm from the exit aperture of the sample transfer unit. The plasma emission was collected at an angle of 90° to the laser beam by an LA4380 (Thorlabs) quartz lens and was fed to the entrance slit of a spectrograph via a CVH100-COL (Thorlabs) collimator along a P600-2-SR (Ocean Optics) light guide. The rate of hair sample transfer to the focusing region was 0.008 mm/s; given that the hair growth rate is 1 cm per month, this allows one to monitor changes in the hair composition with a resolution of ~ 6 h. Emission spectra were recorded by an ICCD camera (PicoStar HR, Lavisision) coupled with a spectrograph (SpectraPro 2500i, Princeton Instruments) that had a grating with 1200 lines/mm. Figure 1 shows example spectra of plasma, which was generated by 40-fs-long pulses on the hair surface, recorded with a delay of 20, 40, and 60 ns (lines C I 193.1 nm, Zn II 202.5 nm, Zn II 206.2 nm, and Zn I 213.8 nm [15]). Figure 2 presents the temporal dependences of the sum of intensities of emission lines C I 193.1 nm, C I 247.8 nm, Zn II 206.2 nm, Mg II 279.5 nm, Ca II 396.8 nm, and Ca I 422.6 nm and the continuous spectrum (peak height) and the intensity of the continuous spectrum of plasma (height of the approximated continuous spectrum at the emission line wavelength) generated on the surface of human hair under excitation with 40- and

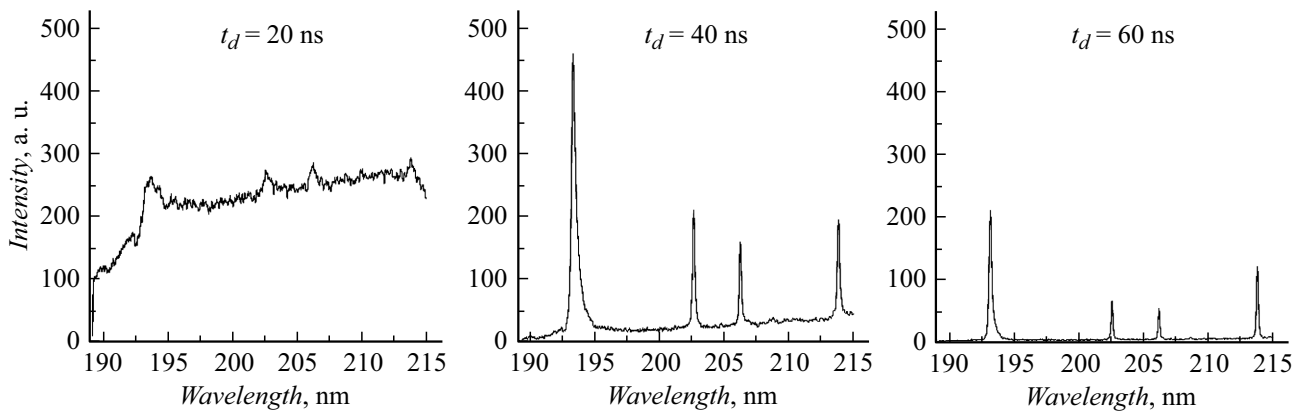


Figure 1. Plasma spectra in the 190–215 nm wavelength range.

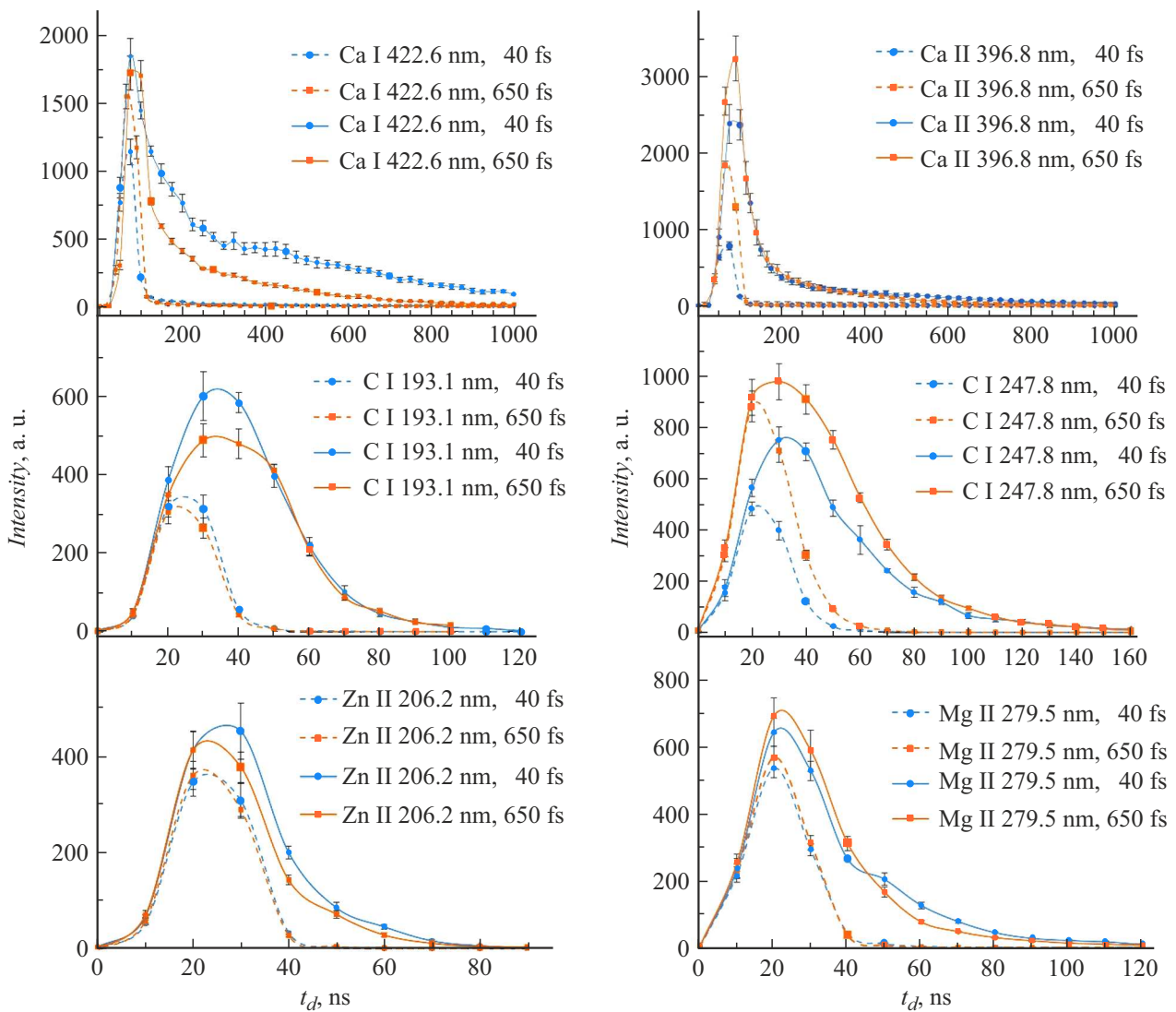


Figure 2. Dependences of the sum of intensities of emission lines and the continuous spectrum below them (solid curves) and the intensity of the continuous spectrum (dashed curves) on detection delay t_d at a laser pulse duration of 40 and 650 fs.

650-fs-long laser pulses. The exposure time for a single laser pulse was $t_g = 50$ ns for Ca lines and $t_g = 20$ ns for Mg, Zn, and C lines. The overall recording time in a single ICCD-camera measurement was 4 s (thus, signal was integrated over 400 laser pulses at a repetition rate of 100 Hz). Averaging at each point in Fig. 2 was performed over seven measurements carried out under continuous hair sample transfer at a rate of 0.008 mm/s. The presented dependences reveal that the intensities of Mg, Zn, and C emission lines remain low within 20 ns of exposure to a laser pulse; in contrast, the intensity of the continuous spectrum is high.

These lines reach their maximum intensity at a delay of $t_d = 40$ ns, while the continuous spectrum becomes considerably less intense at this point (the sole exception here is line C I 247.8 nm at a pulse duration of 650 fs, which has $t_d = 50$ ns). The emission lines of atoms and single-charged ions of calcium persist for a time that is an order of magnitude longer ($\sim 1 \mu\text{s}$). These lines reach their maximum intensity at $t_d \sim 100$ ns, and a substantial reduction in the intensity of the continuous spectrum is observed at $t_d \sim 100$ –110 ns. Notably, the intensity of line Ca II 396.8 nm remains higher than the intensity of the continuous plasma spectrum throughout the entire time interval.

Thus, the obtained experimental data on temporal dynamics of emission spectra excited on the hair surface by femtosecond (40 and 650 fs) pulses demonstrated that the optimum time delay of signal recording relative to a laser pulse is ~ 40 ns in most cases of detection of the widest possible range of chemical elements. The results of examination may be refined by setting a time delay differing from $t_d = 40$ ns for specific elements (e.g., $t_d = 50$ ns for line C I 247.8 nm or $t_d = 100$ ns for lines Ca I 422.6 nm and Ca II 396.8 nm). If measurements are performed without temporal selection of emission lines Ca I 422.6 nm, Ca II 396.8 nm, and C I 247.8 nm, it is advantageous to use shorter laser pulses, since the intensity of the continuous plasma spectrum is lower in this case.

Compliance with ethical standards

All procedures performed in studies involving human participants were in accordance with the ethical standards of the institutional and national research committee and with the 1964 Helsinki Declaration and its later amendments or comparable ethical standards. Informed voluntary consent was obtained from each study participant.

Conflict of interest

The authors declare that they have no conflict of interest.

References

- [1] A. Pruss-Ustun, C. Corvalan, *Preventing disease through healthy environments. Towards an estimate of the environmental burden of disease* (WHO, Geneva, 2006).
- [2] J.J. Miranda, A. Taype-Rondan, J.C. Tapia, M.G. Gastanadui-Gonzalez, R. Roman-Carpio, *Med. Hypotheses*, **95**, 39 (2016). DOI: 10.1016/j.mehy.2016.08.009
- [3] I. Cherni, H. Ghalila, S. Hamzaoui, I. Rachdi, F. Daoued, *Appl. Opt.*, **59**, 6774 (2020). DOI: 10.1364/AO.393646
- [4] I. Cherni, H. Ghalila, S. Hamzaoui, I. Rachdi, F. Daoued, N. Jaidane, *OSA Continuum*, **4**, 2053 (2021). DOI: 10.1364/OSAC.430740
- [5] N.A. Agadzhanyan, A.V. Skalny, *Chemical elements in the habitat and ecological portrait of a person* (KMK, M., 2001).
- [6] B. Appenzeller, M. Tsatsakis, *Toxicol. Lett.*, **210**, 119 (2011). DOI: 10.1016/j.toxlet.2011.10.021
- [7] I. Cherni, R. Nouir, F. Daoud, S. Hamzaoui, H. Ghalila, *Med. Eng. Phys.*, **103**, 133798 (2022). DOI: 10.1016/j.medengphy.2022.103798
- [8] B.A. Benner, B.C. Levin, in *Hair in toxicology: an important bio-monitor*, ed. by D.J. Tobin (RSC, Cambridge, 2005), p. 127–159.
- [9] M. Yukawa, M. Suzuki-Yasumoto, S. Tanaka, *Sci. Total Environ*, **38**, 41 (1984). DOI: 10.1016/0048-9697(84)90206-7
- [10] G. Galbács, *Laser-induced breakdown spectroscopy in biological, forensic and materials sciences* (Springer, Cham, 2022).
- [11] D.A. Cremers, L.J. Radziemski, *Handbook of laser-induced breakdown spectroscopy* (Wiley, 2013).
- [12] S.S. Golik, O.A. Bukin, A.A. Il'in, E.B. Sokolova, A.V. Kolesnikov, M.Yu. Babi, Yu.N. Kul'chin, A.A. Gal'chenko, *J. Appl. Spectrosc.*, **79**, 471 (2012). DOI: 10.1007/s10812-012-9625-z.
- [13] T.A. Labutin, V.N. Lednev, A.A. Ilyin, A.M. Popov, *J. Anal. At. Spectrom.*, **31**, 90 (2016). DOI: 10.1039/C5JA00301F
- [14] M. Baudalet, L. Guyon, J. Yu, J.-P. Wolf, *J. Appl. Phys.*, **99**, 084701 (2006). DOI: 10.1063/1.2187107
- [15] NIST LIBS database [Electronic source]. <https://physics.nist.gov/PhysRefData/ASD/LIBS/lib-form.html>