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Dynamics of emission lines under laser plasma generation in aqueous aerosol

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Spectra of plasma generated in aqueous aerosol under different focusing conditions (NA = 0.008, 0.02, 0.044) by short (8 ns) laser pulses with energies of 12.5, 25, 50 mJ have been studied. Time dependences of the signal−to−noise ratio for the emission lines of Ca II (393.4 nm), Ba II (455.4 nm), Na I (589 nm), and Al I (396.2 nm) in the time range from 0 to 6 μs were obtained.

Keywords: emission spectrum, laser plasma, aqueous aerosol.

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Laser-Induced Breakdown Spectroscopy (LIBS) is a rapidly developing method for multi-element analysis that does not require sample pretreatment and does not generate toxic waste [1–3]. Over the last time, more and more researchers use LSS for fast detection of air pollutants [4,5] including volatile organic compounds, heavy metals, and other hazardous substances [6]. The presence of those air pollutants can become a serious threat to the ecological environment and human health [7,8]. Since the concentration of aqueous aerosols varies continuously, promotion of the reliability of measurements needs high rate of analysis, which is a great problem for conventional methods (ICP-OES, ICP-MS) [9].

The modern progress in developing remotely controllable unmanned vehicles (RCUVs) and small-size air-cooled pulsed lasers integrated into a single module has made it possible to jointly apply RCUVs and laser spark spectroscopy methods in monitoring remote environmental objects [10–12]. Our ambient atmosphere contains aerosols of both natural and anthropogenic origin; therefore, monitoring of atmospheric aerosols is one of the priority issues of environmental control. In this work we have studied the dynamics of chemical elementsémission lines of laser plasma excited in aqueous aerosols at low pulse energies of up to 50 mJ with different focusing acuities (with the design aperture (NA) ranging from 0.008 to 0.04); the goal of the study was to evolve the integration of RCUV and LSS methods. The signal−to−noise ratio (SNR) is more informative for assessing the LSS analytical capabilities for detecting elements than intensities of the emission lines and background; thus, here we consider the SNR results [13].

The experiments were performed on the setup of the Institute of Automation and Control Processes (RAS Far Eastern Branch) whose layout is presented in Fig. 1. Plasma was excited with laser Quantel Brilliant B (*1* in Fig. 1) at the radiation wavelength of 1064 nm, laser pulse repetition rate of up to 10 Hz, laser pulse length of 8 ns, pulse energy of up to 550 mJ, and beam diameter of 8 mm at the $1/e^2$ level. Using mirror splitter *2*, the energy was reduced to 50, 25 or 12.5 mJ; then, radiation was directed with dielectric mirrors *3* to the plano-convex lens with the focal length of 500, 200 or 100 mm mounted on a rail so as to enable correction of distance between the focal point and aerosol front. Laser radiation was blocked by absorber *7*. As the aerosol source (with the droplet size distribution from 0.8 to 2 *mu*m), compressor nebulizer Flaem Nuova Boreal F400 (*5* in Fig. 1) was used. Exhaust hood *8* with nebulizer *5* created a uniform aerosol flow inside chamber *6*.

The receiving system comprised spectrograph Acton SP2300 (*11* in Fig. 1) with ICCD camera PI-MAX3 (Prinston Instrument, USA) (*12* in Fig. 1); the minimum exposure time was 3 ns. Plasma radiation was collected by quartz collimator *9* (74-UV, Ocean Optics) with filter BG-39 and then directed to the spectrometer entrance slit via multifiber lightguide *10*. The setup parameters were controlled by using personal computer *13*. The average laser power was monitored by a power meter (SOLO2, Gentec) (not shown in the figure). Focusing with lenses with focal lengths of 500, 200 and 100 mm corresponded to NA = 0.008, 0.02 and 0.04 designed for the given setup. The measurements were carried out at the following test substance concentrations in aerosol: calcium — 0.8 to 2.4 mg/m^3, barium — 0.6 to 1.2 mg/m^3, sodium — 4.8 to 24 mg/m^3, aluminum — 0.8 to 48 mg/m^3.

In this study we examined under various focusing conditions and pulse energies the dynamics of the signal−to−noise ratio for the emission lines of calcium, barium, sodium and aluminum: Ca II (393.4 nm), Ba II (455.4 nm), Na I (589 nm), Al I (396.2 nm). Fig. 2 presents the results for the barium ion emission line at 455.4 nm; the

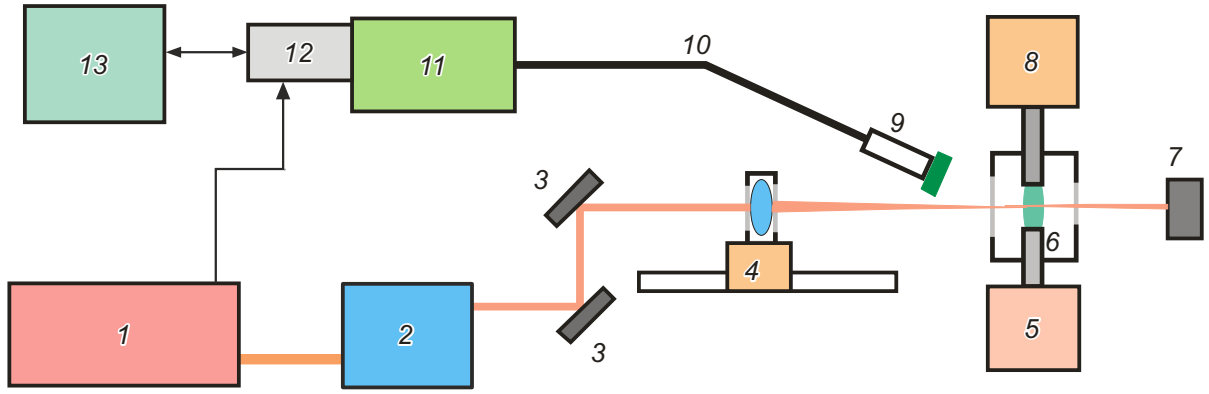

Figure 1. Experimental setup diagram. Relevant comments are given in the text.

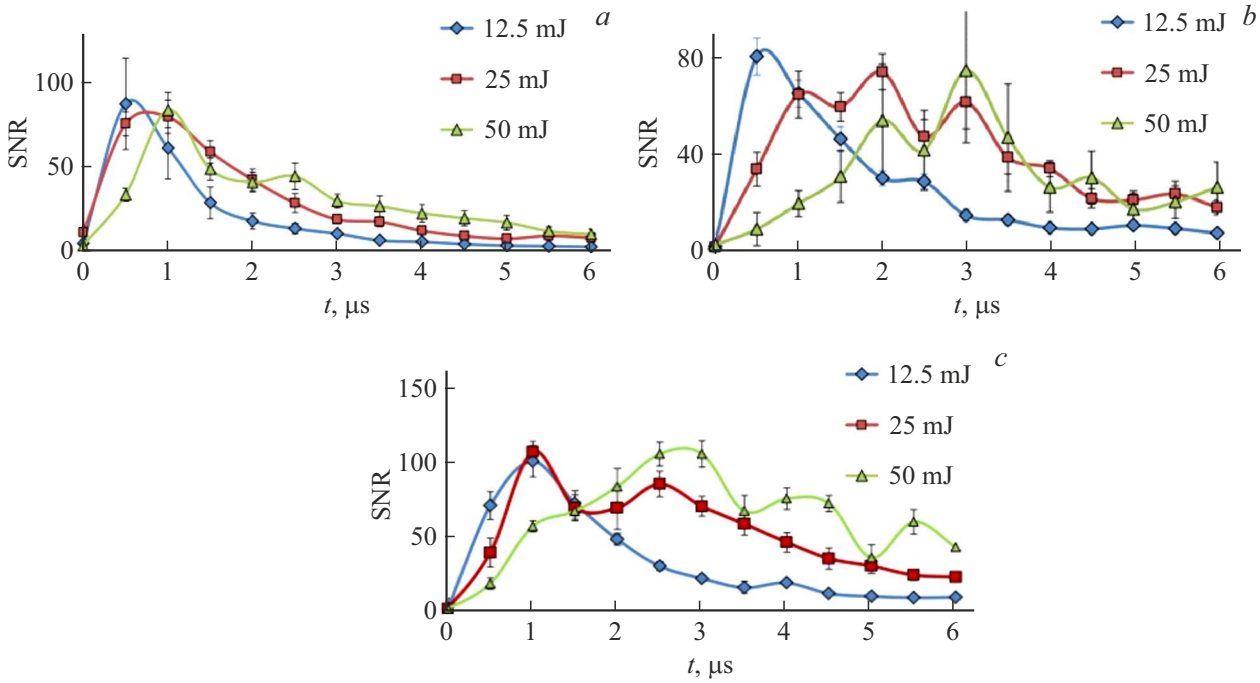

Figure 2. SNR dynamics for the line of Ba II (455.4 nm) (normalized to the maximum intensity) for the pulse energies of 12.5, 25 and 50 mJ. NA = 0.008 (*a*), 0.02 (*b*), 0.04 (*c*).

results were normalized to the maximum. The spectra were measured with the 10 s exposure to 100 laser pulses. The spectra were recorded with the exposure delay (t_d) from the laser pulse of 0 to 6 μs with the step of 0.5 μs and exposure of 0.5 μs. First, the spectrum of the distillate aerosol was recorded; after that, the spectrum of aerosol of the test-substance salt solution was measured. The presented results were obtained by averaging over ten measurements of the laser plasma spectra; the measurement was followed by median three-point filtering with subsequent smoothing by five-point moving average. The resulting emission lines spectrum from which their intensities were determined was the difference between the solution and distillate spectra. The noise intensity was determined as the standard deviation of the aligned distillate spectrum in the region where the elements emission line was recorded. The Table presents for all the elements the detection delays from the laser pulse in accordance with the SNR maxima (SNR_{max}).

The t_d values at SNR_{max} (relative to the laser pulse) obtained for aerosol and aqueous solutions are close to each other under similar plasma excitation conditions [14]. When the pulse energy is 12.5 mJ, those values weakly depended on focusing conditions, while at constant NA t_d at SNR_{max} increased, as expected, with increasing pulse energy for all the elements; the only exception was calcium (at NA = 0.008, t_d was constant). At the same energy density in the beam waist (NA = 0.02 at 50 mJ and NA = 0.04 at 12.5 mJ), t_d at SNR_{max} increased with increasing pulse energy by 2–3 times.

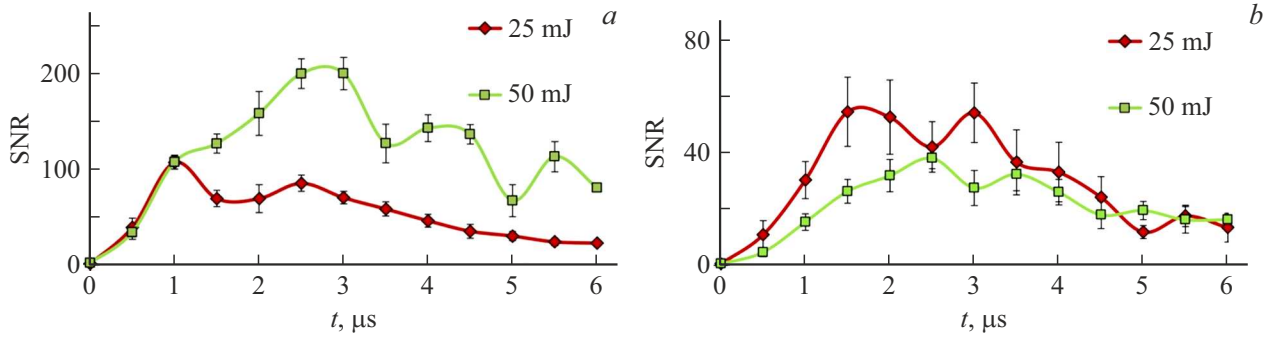

Figure 3. SNR versus the detection delay at the exciting pulse energies of 25 and 50 mJ. *a* — Ba, NA = 0.02; *b* — Al, NA = 0.04.

Detection delays from the laser pulse at SNR_{max} for the studied lines of Ca, Ba, Na, Al

Element (emission line)	Energy, mJ	Delay at SNR_{max}, μs		
		NA = 0.008	NA = 0.02	NA = 0.04
Ca II (393.4 nm)	12.5	1	1	1
	25	1	1.5	1
	50	1	2	2
Ba II (455.4 nm)	12.5	0.5	0.5	1
	25	1	1.5	1
	50	1	3	2.5
Na I (589 nm)	12.5	0.5	0.5	0.5
	25	1	1	1.5
	50	1	1	4
Al I (396.2 nm)	12.5	1	1	1
	25	1.5	1.5	1.5
	50	1.5	2.5	2.5

Examination of the SNR value showed that at NA = 0.008 its dependence on the pulse energy is linear for all the elements. As NA increases, in the case of barium (Fig. 3, *a*) and sodium this dependence is preserved; for aluminum (Fig. 3, *b*) and calcium at NA = 0.02, SNR at the pulse energy of 25 mJ is higher than that at 50 mJ; at NA = 0.04, they become approximately equal within the error.

The results obtained from studying the spectra of plasma excited in aqueous aerosol by pulses with low energies of up to 50 mJ showed that the optimal signal-detection delay from the laser pulse ranges from 0.5 to 4 μs. It has been shown that the laser pulse energy increase does not always entail an improvement in the signal contrast; beginning from a certain energy level, the rate of signal dispersion increase exceeds the rate of increase in the intensity of the elementś emission line. One of the reasons for this may be a decrease in the aerosol content in the plasma formation region due to the aerosol removal by a shock sound wave. When the energy was 50 mJ at NA = 0.04, droplets from splashes became visible on the chamber walls. If the optimal focusing conditions are chosen, it becomes possible to lower the requirements for the pulse energy, which is important in the case of using the LSS method jointly with remotely controllable uninhabited vehicles; nevertheless, this issue needs further research.

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Conflict of interests

The authors declare that they have no conflict of interests.

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