DETERMINATION OF SEA WATER MACROCOMPOSITION BY THE METHOD OF LASER SPARK SPECTROSCOPY

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Received May 19, 1992

Some results of experiments on determining minimum detectable concentration of some elements in water using the laser spark spectroscopy on a liquid surface are presented. It is shown that the two–pulse excitation technique decreases the minimum detectable concentration by a factor of three.

Possibilities of determining the element composition of sea water were investigated using the spectroscopy of a laser spark emission spectrum on a liquid surface.[1,2,3] The minimum detectable concentration (MDC) of Na as well as the spectral ranges of emission spectrum feasible for separately recording elements of sea water macrocomposition were determined.[1]

Lower MDC of elements are required for solving many problems in which the element composition of sea water is needed (in particular, the problems of water pollutions). In this connection we have carried out the experiments using the technique of signal accumulation and the method providing the sensitivity increase owing to preliminary treatment of water surface.

The experiments were performed using the instrumentation[1] where a Princeton Applied Research optical multichannel analyzer was used as a radiation detector.

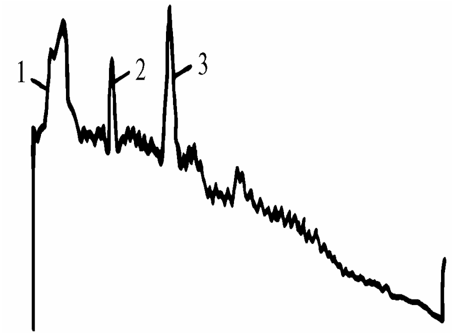

FIG. 1. Emission lines of calcium.

The intensity of spectral components of a laser spark emission initiated on the surface of sea water samples was measured to determine the MDC level of different elements of the sea water macrostructure by the accumulation technique. Depicted in Figs. 1–3 are the examples of spark emission spectra excited on the surface of a sea water sample within different spectral ranges. The interval of the recorded wavelengths in a shortwave range was limited by 3800 Å due to the use of glass optical components. The shortest wavelengths currently reliably recorded were the lines of Ca (3933.6 and 3968.5 Å). These lines were most conveniently recorded in the second order of diffraction. Figure 1 presents the Ca lines 3933.6 (curve *1*) and 3968.5 Å (*2*) and the band 3998 Å (*3*) which are observed on the background of a broadband emission. Depicted in Fig. 2 are strong lines of the yellow doublet of Na 5886 (curve *1*) and 5890 Å (*2*). In the same figure the spectrum of mercury lines at 5460 Ð and the doublet 5770 and 5790 Å is given as reference wavelengths and for the dispersion determination. The lines of potassium doublet recorded with accumulation are shown in Fig. 3 (wavelengths 7665 and 7699 Å). In all of these cases the lines were observed on the background of a broadband fluorescence of water and organic matter dissolved in sea water.

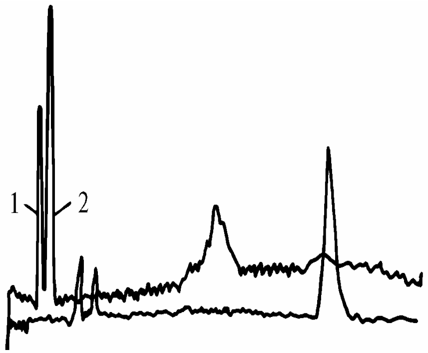

FIG. 2. The sodium doublet and calibration mercury emission lines.

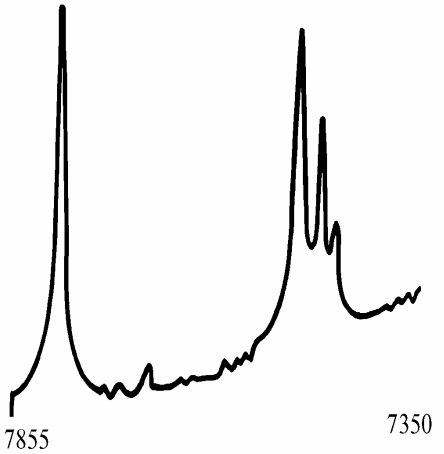

FIG. 3. The potassium emission line doublet.

The broadband fluorescence background is the basic factor which increases the MDC of elements occurring in

0235-6880/92/11 780-03 \$02.00

sea waters. The values of the MDC were found for Na, Ca, and K using the signal accumulation technique. A series of intensity measurements were made for the elements under study in solutions with different concentrations of elements in distilled water. The broadband fluorescence background intensity obtained in the vicinity of a measured line in sea water was taken as a noise value. Accumulation was carried out over a series of laser shots and was limited by the conditions of a sea expedition. The MDC (the signal–to–noise ratio equal to 3) for potassium was of the order of 10^{-2} g/L and for calcium and sodium it was of the order of 10^{-3} g/L.

The obtained MDC values were quite sufficient for conducting a routine analysis of sea waters macrocomposition and for determining pollutants in water with concentrations of the same value. However, further increase of the method sensitivity can be reached by employing the technique of multipulse excitation of a laser spark on the surface of liquid. Such a possibility has been pointed out in Ref. 4 and the results obtained by the double–pulse technique of spark excitation for a solid body are discussed in Ref. 5. An increase of the signal–to–noise ratio in recording the emission spectral lines of a laser spark can be achieved in two ways, i.e., by increasing either relative concentrations of elements under study in the vicinity of a spark or the temperature of a laser spark plasma. In the first case the concentration is increased due to preliminary heating of the liquid surface by a laser pulse with the power density not exceeding the explosive boiling threshold. The second way of increasing the emission line strengths is performed by formation of a laser spark using two laser pulses with the power density exceeding the optical breakdown threshold. Below we give the results of the experiments aimed at increasing the line strengths by the preliminary heating of the liquid surface with the free–running pulsed laser. The experimental setup is shown in Fig. 4.

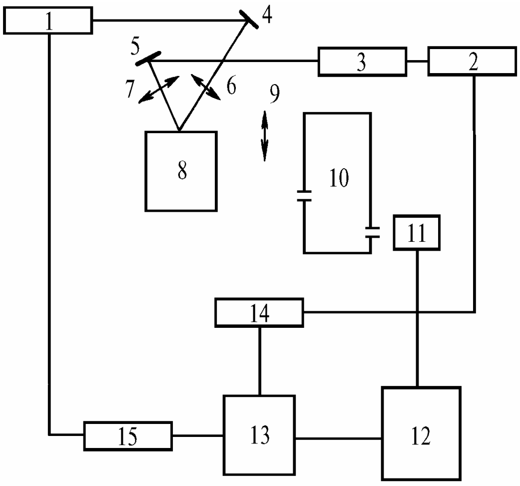

FIG. 4. Experimental setup: 1) free–running laser, 2) Q–switching laser, 3) amplifier, 4) and 5) mirrors, 6, 7, and 9) lenses, 8) cell, 10) monochromator, 11) recorder, 12) computer, 13) delay pulse generator, and 14 and 15) power supply units.

A free–running aluminate laser was used for preliminary heating of liquid and creating the regime of evaporation. The radiation pulse full duration was 300 μs and the radiation energy per pulse was of the order of 3 J. The radiation was focused on the liquid surface onto a spot 1 mm in radius. The energy density on the liquid surface was much lower than the explosive boiling threshold so that a purely linear mechanism of liquid heating was accomplished. Synchronization of a Q–switched laser (Nd : YAG laser) with respect to the free–running laser was changed with a specially designed delay generator. The parameters of the YAG laser used in the study were the following: the energy per pulse up to 0.4 J, pulse duration 12 ns, the focal spot on the liquid surface 0.2 mm in radius.

The experimental setup was arranged so that the focal spot of the Nd : YAG–laser emission was at the center of the focal spot of the free–running laser. The delay (ΔT) between the laser pulses changed discretely so that the Q–switched laser pulse could be moved in time along the free–running laser pulse as shown in Fig. 5*b*. The Na doublet line strength was measured as a function of delay ΔT between the pulses. The characteristic delay dependence of the normalized doublet intensity is given in Fig. 5*a*.

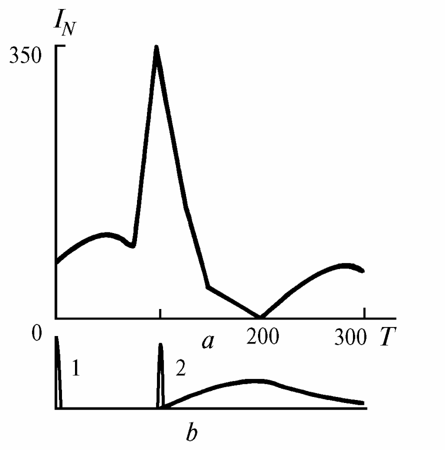

FIG. 5. Dependence of the sodium emission line doublet on the time delay T(a) and relative position of pulses (b).

The value $T = 0$ was relevant to the position of a giant pulse before a free–running pulse and the values of the Na doublet intensity corresponded to the values of signals for conventional single–pulse excitation of a spark on the liquid surface(in Fig. 5*b* figure 1 denotes the pulse position). For $T = 75$ μs the Na doublet intensity sharply increased, these delays were relevant to the giant–pulse position for the onset of the free–running pulse (position 2 in Fig. 5*b*), the delay of the order of 100 μs corresponded to the giant–pulse position at the maximum of free–running pulse. The Na doublet line intensity increased by a factor of three for $T = 75$ μs due to the increase of Na atom concentration in the region of a plasma flare caused by free–running pulse evaporation.

Based on the equation of thermal conductivity it is possible to estimate the time of boiling up of a thin water layer under the action of a free–running pulse. The equation of thermal conductivity for the thin water layer can be written in the form

$$\rho c \frac{\partial T}{\partial T} = \mu \frac{4E}{\pi d^2} \sqrt{\frac{\alpha}{\pi}} \int_0^t e^{-\alpha(t'-\tau)^2} \, dt' , \qquad (1)$$

where ρ is the density, C is the thermal conductivity, T is the temperature, E is the laser pulse energy, d is the spot diameter on the water surface, $\sqrt{a} = 2 \cdot 10^4 \ \mathrm{s}^{-1}$, $\tau = 100$ μs, and $\mu = 5 \ \mathrm{cm}^{-1}$ is the absorption coefficient at the 1.06 μm wavelength. In the approach from Ref. 1 Eq. (1) gives the time of boiling up the surface water layer equal to 6 μs. As can be seen from Fig. 5, the maximum intensity of the Na doublet is observed if the *Q*–switching is done close to the moment of water boiling up. A discrete of regulation of a delay between two laser pulses is 10 μs. Further increase in the *T* values results in a decrease of the Na doublet intensity. This is connected with the appearance of water vapors over the liquid surface during evaporation which screen the surface from laser radiation and decrease the laser power density stimulating a spark. At a later time as the free–running pulse passes, the concentration of water vapors screening the surface decreases, and the doublet intensity increases.

Thus, the two–pulse technique of laser spark excitation in which the first pulse serves for preliminary heating of the surface makes it possible to decrease the MDC values by a factor of three. The sensitivity of this method with respect to element detection in liquid can be increased with further improvement of the technique of two–pulse excitation of a laser spark. From our point of view, it must consist in the increase of power density of the first pulse (at the transition to preliminary heating of liquid in the mode of explosive boiling up or dielectric breakdown).

REFERENCES

1. O.A. Bukin, A.N. Pavlov, N.V. Sushilov, and S.L. Eduardov, Zh. Prikl. Spektrosk. **52**, No. 5, 736–738 (1990).
2. A.M. Prokhorov, D.V. Vlasov, D.Yu. Tsipenyuk, and V.S. Bukreev, Zh. Prikl. Spektrosk. **55**, No. 2, 313–314 (1991).
3. D.V. Vlasov, A.M. Prokhorov, D.Yu. Tsipenyuk, and V.S. Bukreev, Atm. Opt. **4**, No. 4, 337–338 (1991).
4. A.Yu. Bukharov and S.M. Pershin, Zh. Prikl. Spektrosk. **51**, No. 4, 564–571 (1989).