Article

The Ultrasound Action on the Laser– Induced Breakdown and Spectral Elemental Analyzes of Seawater

Alexey V. Bulanov[1*], Vladimir A.Krikun[1] and Ivan G. Nagorny[2]

[1] V.I. Il'ichev Pacific Oceanological Institute, Far East Branch of Russian Academy of Sciences, 43, Baltiyskaya Street, Vladivostok, 690041, Russia
[2] Institute of Automation and Control Processes, Far East Branch, Russian Academy of Sciences, 5, Radio Street, Vladivostok, 690041, Russia
* Correspondence: bulanov2009@gmail.com, kv99@mail.ru

Abstract: This paper develops the study of the effect of powerful ultrasound on the laser breakdown of liquids and a comparative study of the possibilities of acoustic and optical diagnostics of breakdown. The method of laser-induced breakdown spectroscopy (LIBS) for elemental analysis of liquids, along with high efficiency, continues to be less sensitive compared to traditional chemical methods. The paper develops a method of using additional ultrasound irradiation of the laser breakdown area in order to increase the efficiency of LIBS. Using the developed technique, spectral lines of chemical elements such as potassium, manganese, sodium, calcium, etc. were obtained for the first time depending on the frequency and power of ultrasound. It is shown that a sharp increase in the intensity of spectral lines of elements in water during laser breakdown is observed in the field of high-power ultrasound. It indicates an increase in the sensitivity of the combined method of ultrasonic LIBS. Along with the optical spectrum, the spectral and energy characteristics of acoustic emission were studied. An automated complex for hydrophysical and spectral studies is described, which was tested in the Sea of Japan during the voyage No. 81 of the research vessel RV "Professor Gagarinsky" in August 2022.

Keywords: laser–induced breakdown; ultrasound; spectroscopy; sea water

1. Introduction

Laser-induced breakdown spectroscopy is a widely used technology and is used in industry and in scientific research [1-3] mainly in relation to solid objects. It seems important and relevant to use this method for the analysis of liquid media [2,3]. The relevance of studying the mechanisms of optical breakdown generation in a liquid is associated with the development of new opto–acoustic sound sources and methods of opto–acoustic diagnostics of media [1], as well as with the use of laser-induced breakdown spectroscopy for elemental analysis of liquids [2-7]. At the same time, the mechanism of optical breakdown when irradiated with powerful laser radiation of water targets has been studied much weaker than the mechanism of interaction of laser radiation with metals and other solids. Spectroscopic analysis of liquids is difficult due to the fact that, as a rule, a breakdown is used on the surface of liquids, where, in turn, lines of atmospheric gases make a powerful contribution. The solution is to use a breakdown within the thickness of the liquid, since in this case the extraneous effect of the gas is excluded [7-9]. However, in this case there is an additional difficulty associated with the weakening of the excited weak lines of the elements due to absorption in the liquid. Therefore, it is important to increase the intensity of the lines at the breakdown. It would seem obvious to increase the power of laser irradiation could be a way to overcome this difficulty. However, a number of experiments [7-9] indicate the opposite paradoxical effect – starting from certain thresholds, an increase in the irradiation power does not lead to an increase in

 doi:10.20944/preprints202211.0214.v1

the intensity of the illuminated lines of elements.

The development of sensors for in situ elemental analysis in seawater is very important for modern expeditionary oceanography. At the same time, the problem of high spatial and temporal resolution remains significant when registering the distribution of elements in the ocean. The articles [8, 9] present the results of laboratory studies to verify the use of LIBS for the detection of chemical elements in large volumes of water at oceanic pressures. Intensive lines of sodium, manganese, calcium, potassium, and lithium in dissolved solutions at pressures of 27.6 MPa were studied by the LIBS method. The effects of pressure, laser pulse energy, pulse delay, temperature and NaCl concentration on the optical spectrum were investigated. The authors found the optimal range of laser pulse energies for detecting chemical elements in aqueous solutions at low and high pressure. It turned out that the effect of improving the intensity of the calcium and sodium line with an increase in pressure was not detected. However, such an effect was present for manganese. It turned out that the presence of NaCl increased the emission intensity for Ca, but had no effect on the peak intensity of Mn or K. According to the results of the research, the authors concluded that LIBS is a viable method for detecting chemical elements in situ when measured in an environment with high static pressure, such as at great depths of the World Ocean.

It seems important to us to try to replace the static effect with an acoustic effect, which also looks quasi-static in relation to the rapid processes of plasma expansion during optical breakdown. In this case, it would be possible to try to implement LIBS in focused acoustic fields in order to identify the effectiveness of such an improvement in the method for the rapid detection of chemical elements in liquid media.

Important works were related to the study of the combined effects of laser radiation and ultrasound [10-12]. It turned out that ultrasound strongly affects the dynamics of bubbles formed as a result of laser breakdown in water. So for a bubble in the absence of sound, the maximum size is ~ 30 x 55 microns, the collapse time is 2.2 microseconds. It is important that the dynamics of the bubble in the ultrasound field depend on the phase of the field. In the stretching phases, the greatest influence of ultrasound was observed. The maximum size turned out to be significantly higher compared to the case of bubbles without sound: the radius is ~ 100 microns, the collapse time is 15 microseconds. The influence of the sound amplitude was also analyzed. As a rule, an increase in the maximum radius of the bubble was observed with an increase in the amplitude of ultrasound.

In [13] the efficiency of optoacoustic transformation in dilute suspensions under the action of a nanosecond laser pulse were presented. It has been shown that competition between thermo-optical and cavitation sound transformations is observed in micro-inhomogeneous media, leading to significant fluctuations in the acoustic response from one laser pulse to another. As a result, it was concluded that histograms of the amplitudes of acoustic signals can be used to discriminate the mechanisms of optoacoustic transformation, and can also be used as the basis for a method for diagnosing a small content of insoluble phase in liquids. Similar results were obtained in [14]. In [15], the spectral features of acoustic signals generated during optical cavitation due to the action of laser radiation were used as the basis for studying the resonant frequencies of the formed bubbles and the attenuation of their oscillations over time. In the review [16], the mechanism of thermocavitation was studied, which is associated with local overheating of the liquid above the spinodal, the formation of vapor bubbles and the emission of acoustic signals during their formation and collapse. The dynamics of the growth and collapse of bubbles with the emission of acoustic signals has also been studied in [17, 18]. In the works LIBS above, it was shown that, along with the method of laser spectroscopy in the optical domain, information about acoustic signals accompanying the interaction of laser radiation with the medium, which increases especially strongly in the presence of microparticles, can be very significantly used for the diagnosis of media.

 doi:10.20944/preprints202211.0214.v1

In this regard, it is interesting to study the dependence of the characteristics of the breakdown of the liquid on the energy of the laser pulse and its focusing in the liquid, as well as on the combined action of acoustic and laser radiation. The basis of this work is the study of the effect of additional acoustic radiation on the process of laser breakdown in order to identify the possibility of its influence on increasing the intensity of the lines of elements excited by such a combined breakdown of the liquid. Previously, we proposed to replace the static effect with an acoustic effect [19, 20], which also looks quasi-static with respect to the rapid processes of plasma dispersion during optical breakdown. Important works were related to the study of the combined effects of laser radiation and ultrasound [21-23]. In this article, the study of this issue and the results obtained allowed us to form the possibilities for creating a device for rapid assessment of the characteristics of aquatic environments.

Experimental methods associated with the simultaneous use of laser breakdown and ultrasonic radiation, as well as equipment used for the practical implementation of elemental analysis in a liquid by the combined method of ultrasonic LIBS are described in section 2. Also, section 2 describes an automated installation that allows using ultrasound to implement spectroscopy of elements in aerosol droplets. The installation has been tested in studies of the state of the near-surface waters of the Sea of Japan along the routes with a length of about 1000 km. The main experimental results are presented in Section 3. The effect of ultrasound power and phase on the intensity of sodium and calcium spectral lines is shown. An analysis of the delay in optical breakdown by laser radiation was carried out for optimal registration of the spectra of Na, N, Ca, Mg, Mn, Al, K in accordance with the database [24]. The delay on average turned out to be about 700 ns. The dependence of the intensity of the spectral lines of manganese, potassium, oxygen during optical breakdown in the liquid column under the influence of ultrasound was revealed depending on the concentration of elements and on the power of acoustic radiation at different delay times. The discussion of the obtained results is presented in section 4, which shows the possibility of using the combined LIBS method to improve the capabilities of elemental analysis of elements in liquids, including seawater.

2. Materials and Methods

2.1. Experimental complex for combined ultrasonic LIBS

For the practical implementation of elemental analysis in a liquid by the combined ultrasonic LIBS method , experimental complexes based on Nd:YAG "Brilliant" lasers with the following radiation parameters were assembled: wavelength 532 nm, pulse duration 10 ns, pulse energy up to 180 MJ, varying in the modulated Q–factor mode, pulse repetition rate 1- 15 Hz. A typical scheme of the experimental setup is shown in Figure 1. The laser provided a pulsed mode of plasma generation on the surface of aqueous solutions. The power density of the laser radiation was further increased due to the sharp focusing of the radiation in the desired location (in the liquid, on the surface or near the surface of the liquid) using lenses with different focal lengths F = 40 mm, 75 mm and 125 mm. Optical breakdown was recorded using an optical multichannel spectrum analyzer Flame Vision PRO System, with a time resolution of 3 ns. Usually the optical breakdown occurred in the focusing area, the radiation of which was directed using a quartz lens or a light guide to the entrance slit of the Spectra Pro spectrograph connected to a CCD camera with strobing. This scheme provided a delay in recording the pulse relative to the beginning of the optical breakdown and varying the exposure time of the signal from 10 ns to 50 microseconds from the beginning of the laser breakdown. Taking into account the variation of delays and exposures, the necessary optimal conditions for recording optical breakdown inside the liquid were found.

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 11 November 2022 doi:10.20944/preprints202211.0214.v1

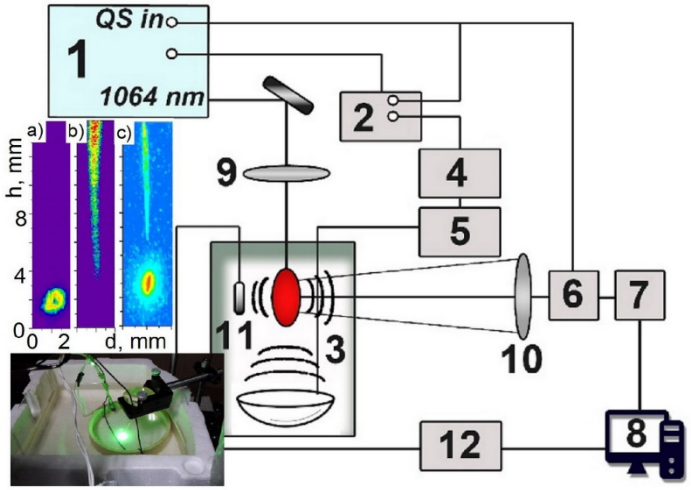


Figure 1. Experiment diagram and photo with acoustic emitter: 1 – laser, 2 – delay generator, 3 – ultrasonic emitter, 4 – pulse generator of arbitrary shape GSPF 053, 5 – power amplifier U7– 5 or Phonic for the emitter, 6 – CCD camera, 7 – monochromator, 8 – computer, 9 – rotary mirror and lens, 10 – lens, 11 – Brüel&Kjær hydrophone, 12 – ADC board. In the photo: a yellow cylinder is a piezoceramic radiator with a resonant frequency of 29 kHz, a black cylinder near the inner surface of the radiator is a type 8103 Brüel&Kjær hydrophone.

Table 1. Main parameters of experimental equipment

Type	Main Characteristics
Ultrasound radiation equipment	1. Digital signal generator GSPF-053: 12 digits, frequency up to 10 MHz, voltage 5 V. 2. Broadband power amplifier U7-5: frequency up to 3 MHz, power 20 W, voltage 20 V 3. Pioneer power amplifier (Japan): frequency up to 100 kHz, power 600 W, voltage up to 200 V
Equipment for receiving acoustic signals	1. Selective filters for individual frequencies (TOI), with the possibility of frequency adjustment, Q factor 10. 2. Brüel&Kjær type 2605 pre-amplifier: frequency up to 200 kHz, LF and HF filters: 30 kHz and 2 kHz, maximum gain 100
Equipment for recording acoustic signals	1. La2 USB ADC (Rudnev and Shilyaev): quantization frequency up to 400 kHz, 14 digits, 16 channels, maximum gain 1000 2. ADC E20-10 (L-Card): quantization frequency up to 10 MHz, 12 digits, 4 channels, maximum gain 100 3. Raspberry pi3 microcomputer

In addition to the standard LIBS schemes, acoustic radiation at ultrasonic frequencies of sufficiently high power was used. Ultrasound radiation was controlled using a digital arbitrary waveform generator GSPF_053 (Rudnev and Shilyaev, Russia) and a broadband amplifier with an ultrasound amplitude of up to 105 kPa. The choice of the frequency range, ultrasound power and their practical implementation in ultrasonic emitters of various configurations (spherical, annular and cylindrical resonators) took place depending on the degree of ultrasound exposure for each LIBS experiment. Thus, Figure 1 schematically shows a focusing acoustic emitter 3 in the form of a sphere segment, at the

 doi:10.20944/preprints202211.0214.v1

same time, the same Figure 1 in the photo shows a cylindrical resonator, which was also used in experiments. Sea or fresh water was poured into the cells, acoustic emission was recorded using a type 8103 hydrophone from Brüel&Kjær (Denmark). Analog signals were recorded on a personal computer using an E20–10 ADC of the L–card company with a quantization frequency from 1 to 5 MHz. The main parameters of the elements of the experimental setup are presented in Table 1.

2.2. Automated experimental complex for spectral and hydrophysical measurements

In order to detect chemical elements in seawater under expedition conditions, a compact automated experimental complex was created using the LIBS method, which also allows simultaneous measurement of other hydrophysical parameters important for oceanographic measurements. The schematic diagram is shown in Figure2. Water was delivered from the sea or other body of water to a special cuvette by a pump. There are two possible options. The first was when the laser provided a pulsed mode of plasma generation on the surface of water and an aerosol dispersed cloud created by ultrasound. The second is the most practical when emission spectra in dispersed droplets arise under the action of a high-voltage spark discharge. Ultrasonic radiation using piezoceramic emitters of various configurations (spherical, annular and cylindrical resonators) was carried out to create an aerosol dispersed cloud. A microcomputer is installed inside the complex, which allows not only data registration, but also their preliminary processing. The presence in the complex of an autonomous power source based on a lithium-ion battery with a capacity of 10000 mAh allows it to be used in places completely devoid of electrical energy, and in the presence of a shelter protected from precipitation, the complex is able to operate without human intervention for two days.

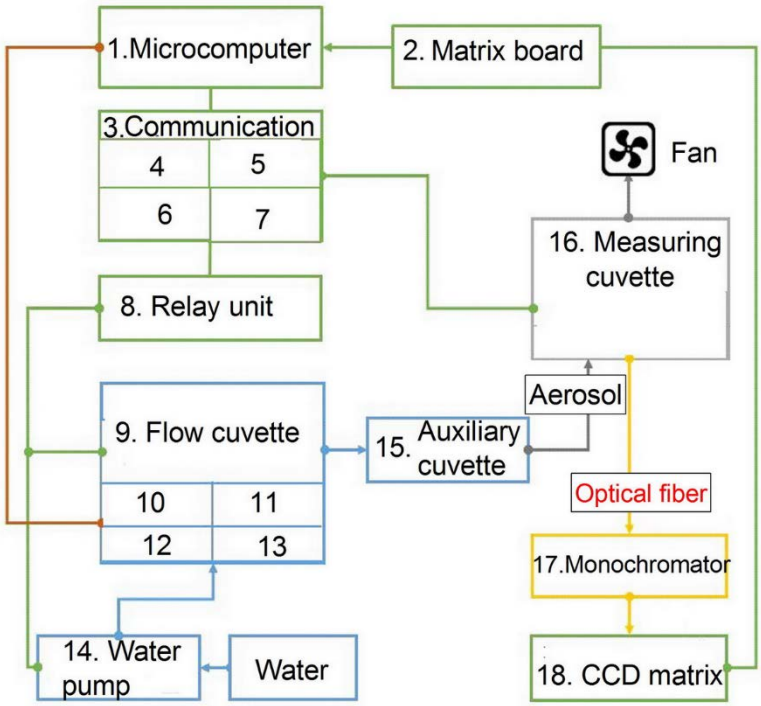


Figure 2. Schematic diagram of an automated experimental complex that allows, along with the spectral characteristics of water, to simultaneously measure other hydrophysical parameters important for oceanographic measurements. 1. Microcomputer; 2. Matrix control board; 3. Communication board with sensors: 4. Tilt sensor, 5. Compass, 6. Atmosphere pressure sensor, 7. GPS; 8. Relay unit; 9. Flow cuvette with sensors: 10 Solution, 11 –

 doi:10.20944/preprints202211.0214.v1

Temperature, 12 - Salinity, 13 – Turbidity; 14 – Water pump; 15 Auxiliary cuvette; 16 – Measuring cuvette; 17 – Monochromator; 18 CCD matrix

Table 2 shows the main technical characteristics of the complex. The dimensions and weight of the complex allow it to be carried by one person, since all devices are installed inside a plastic expedition box with external dimensions of 600 x 400 x 420mm.

Table 2. The main technical characteristics of the complex

Parameter	Value
External dimensions	L600 x W400 x H420mm
The weight of the complex	11 kg
Built-in battery capacity	10000 mAh
Battery life in measurement mode	48 hours
Characteristics of microcomputer processor	ARM Cortex A53 4 x 1.2 GHz
Microcomputer RAM/ROM Capacity	1 GB RAM / 32 GB ROM
The recorded parameters of the studied liquid	Emission spectra, turbidity, salinity, temperature, concentration of dissolved oxygen.
The recorded auxiliary parameters	Roll, pitch, direction, geographical coordinates, atmospheric pressure
The recorded spectral range	300 – 800 nm
Spectral resolution	0.125 nm
Spectral sensitivity	160 V*Lx/ Cp

2.3. Methods of conducting LIBS experiments using ultrasound

The optical part of the experiments is traditional and were carried out according to the following scheme [17, 18]. Laser radiation (1) was focused into a liquid using a rotary mirror and a lens (9). The radiation of the optical breakdown plasma was projected by a lens (10) onto the input slit of a monochromator (7) coupled to a CCD camera. The control was carried out by a computer (8). Various types of breakdown in water were achieved by focusing laser radiation using various lenses. The breakdown occurred either in the depth of the water, or in the near-surface layers, or in a combination of these two types, as shown in Figure1. Depending on the types of breakdown, different resolution of spectral lines is realized.

To analyze the breakdown dynamics and study the parameters of the acoustic wave initiated by optical breakdown, a Brüel &Kjær type 8103 hydrophone was used as a broadband acoustic receiver, the information from which was digitized and recorded using a multichannel I/O board from L–Card with a maximum digitization frequency of ~ 5 MHz. To control ultrasound, an arbitrary pulse generator GSPF 053, a power amplifier

 doi:10.20944/preprints202211.0214.v1

and a resonant cylindrical radiator [19, 20] were used, inside which a liquid breakdown occurred in a converging ultrasound field.

To study the energy and frequency characteristics of the impact of ultrasound on LIBS, a technique was created that allows the use of intensive ultrasonic irradiation of the breakdown area using piezoceramic emitters with different resonant frequencies. It was important to solve the problem of synchronization of acoustic and optical pulses, for which the method of synchronization and study of acoustic emission by a specialized measuring hydrophone with simultaneous registration of breakdown in the optical region of the spectrum was worked out. By changing the delay duration of the control pulses, it was possible to synchronize the moment of maximum stretching or compression of the liquid by acoustic pulses and the beginning of optical breakdown. A delay generator was used to synchronize acoustic and optical pulses.

Synchronization and measurement of acoustic emission was carried out by a measuring hydrophone with simultaneous recording of breakdown in the optical region of the spectrum. By changing the delay duration of the control pulses, the researcher could synchronize the moment of maximum stretching or compression of the liquid by acoustic pulses and the beginning of optical breakdown. The solution of this problem made it possible to effectively use ultrasound sources of small power (at the threshold of cavitation), which predetermined a decrease in the breakdown threshold in the liquid thickness. Ultrasonic irradiation of the breakdown area was carried out using piezoceramic acoustic emitters with different resonant frequencies.

Since absorption in a liquid can significantly weaken the intensity of the lines, a number of measures have been taken to reduce this effect. For this purpose, we used an oblique drop of laser radiation into the liquid. Near the target, the angle between the surface and the direction of propagation of laser radiation was different from 900, while its magnitude was such that the breakdown plasma propagated towards the laser beam, and the erosion torch was mainly perpendicular to the breakdown surface.

A distinctive feature of this method is to reduce the dependence of the increasing undesirable effect of explosive boiling and instability of the surface of aqueous solutions on an increase in energy. This allows the use of more intense laser pulses to improve detection limits. Using the technique described above, spectral lines of chemical elements such as potassium, manganese were obtained for the first time depending on the frequency and power of ultrasound. It should be noted that the lifetime of the lines was about 60 microseconds, which is more than 50 times longer than the lifetime for the case of a breakdown inside the liquid. Figure 3 shows a typical liquid breakdown using the technique described above:

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 11 November 2022 doi:10.20944/preprints202211.0214.v1

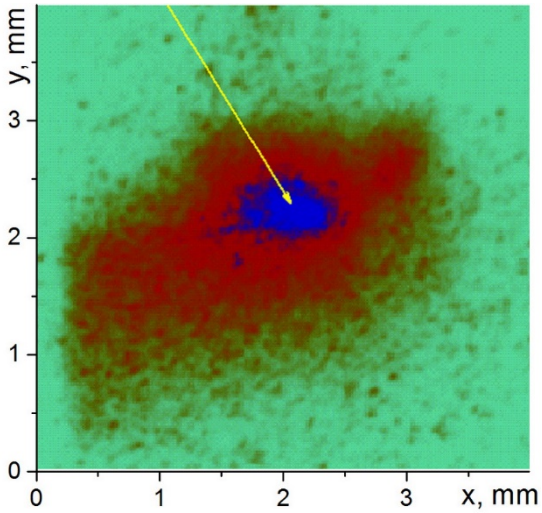


Figure 3. Breakdown of a liquid with an oblique incidence of laser radiation with the formation of a cavity (blue color) with an apparent size of 0.7 x 0.4 mm and a perturbation of the density of a liquid with an apparent size of 1.5 x 2.9 mm

2.4. Main characteristics and methods of operation of the automated complex for spectral measurements

Let's consider the possibilities and some characteristics of the automated spectral complex, the scheme of which is shown in Figure2. Due to the presence of a large number of sensors, the complex, along with emission spectra, records a large number of parameters describing the composition of the pumped liquid under study. The complex also allows recording auxiliary data necessary for the correct interpretation of experimental results in expedition conditions.

After starting the program, the microcomputer 1, using a specially designed communication board 3 controlling the relay unit 8, sends a command to start the pump 14, which begins continuous pumping of liquid through the flow cell 9, in which temperature, salinity, turbidity and dissolved oxygen are recorded using sensors 10, 11, 12, 13. From the flow cuvette, the liquid under study is pumped into an auxiliary cuvette 15, where, with the help of an ultrasonic emitter, it is converted into a fine aerosol and, by means of an exhaust fan, is fed into a measuring cuvette 16, in which a high-voltage spark gap is installed, activated by a special command fed from a microcomputer. Under the action of a spark discharge, emission spectra characterizing the chemical composition of the liquid under study arise in the cuvette, which are recorded and recorded into the microcomputer data storage device using the MI-44 17 monochromator, the TCD1304 CCD 18 and the control board 2 with the CCD matrix 2 built on the basis of STM32.

Additionally, the following sensors are mounted on the communication board: MPU-6050 tilt sensor, which allows you to monitor changes in the roll and pitch of the trim of the vessel; digital compass; atmospheric pressure sensor and GPS module NEO-7m, which allows you to record the geographical coordinates of the vessel.

3. Results

3.1. Spectroscopy of elements during laser breakdown of liquid in the ultrasound field

Studies of spectroscopic parameters of laser water breakdown were carried out in the presence and absence of an ultrasound field with a frequency of 29 kHz at various salt concentrations.

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 11 November 2022 doi:10.20944/preprints202211.0214.v1

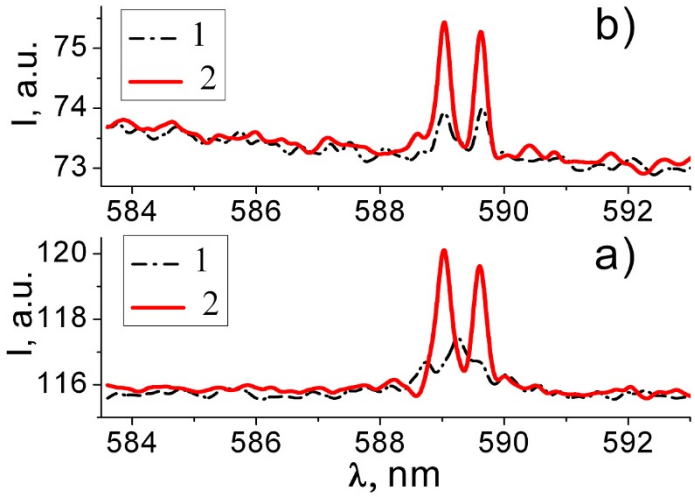


Figure 4. Intensity of sodium I lines without ultrasound (1) and using ultrasound with a frequency of 29 kHz (2) at different concentrations of NaCl aqueous solution: a) 10%; b) 3.5 %

To process and visualize the results, a free multi-paradigm and object-oriented programming language python was used with the addition of scientific libraries Numpy (for simultaneous processing of large data arrays) and Matplotlib (for visualization of results). Figure 4 shows sodium lines at laser breakdown with additional use of ultrasound and without ultrasound at different concentrations of NaCl – for 10% and 3.5% NaCl solution. The latter, in particular, corresponds to the typical concentration of salt in ocean water. It should be noted that the laser radiation was the threshold for the breakdown of the liquid and the effect of line amplification was manifested most vividly in the ultrasound field. It should also be noted at the same time that a different breakdown pattern was revealed at different concentrations of dissolved salt in water. Experimental confirmation of this was the detection of an increase in the intensity of sodium lines at different concentrations of NaCl salt, which are shown in Figure2a and Figure2b.

Using modulation and synchronization of acoustic and optical radiation according to the method described in section 2, an increase in the intensity of the line of another element, calcium, was determined at different amplitudes of ultrasonic irradiation.

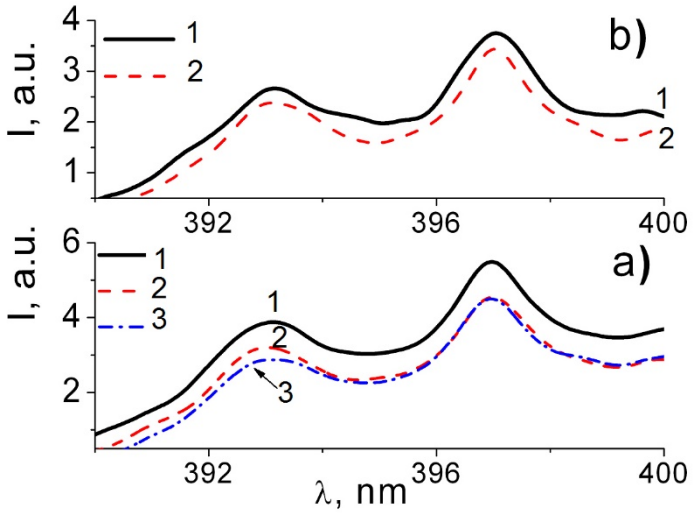


Figure 5. Intensity enhancement of the I lines of a single ionized calcium doublet (Ca II): a) depending on the amplitude

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 11 November 2022 doi:10.20944/preprints202211.0214.v1

of the ultrasonic radiation P: 1 – P =25 kPa, 2 – P=12 kPa, 3 – P=0 kPa (laser radiation is constant and corresponds to the liquid breakdown threshold); b) depending on the phase of the acoustic field (1 – φ = – stretching phase, 2 – φ=0 is the phase in which the effect of ultrasound is insignificant).

Figure 5a shows the intensities of the calcium line at different acoustic radiation power at threshold laser radiation. It can be seen that with an increase in the power of acoustic radiation, the intensity of the line increases with threshold laser radiation. Figure 5b shows an increase in the intensity of the calcium ion line at wavelengths of 393.4 and 396.8 nm in the compression phase compared with the intensity in the zero phase, when the influence of the ultrasonic wave is insignificant. Thus, it can be seen that in the phase of maximum ultrasonic exposure (compression of the breakdown cavity), the intensity of the calcium ion line increases compared to the absence of ultrasound.

It is important to note the result showing the paradoxical dependence of the intensity of the lines on the energy of laser radiation. Figure 6 shows the dependence of the intensity of the Na line at 589 nm on the radiation energy. It can be seen that the effect of increasing the intensity of the line in a liquid differs from the case of a breakdown in air in that with a significant increase in the energy of laser radiation at a certain energy (about 100 MJ), a weakening of the intensity of the line begins, most likely caused by a powerful nonlinear absorption of light in the liquid.

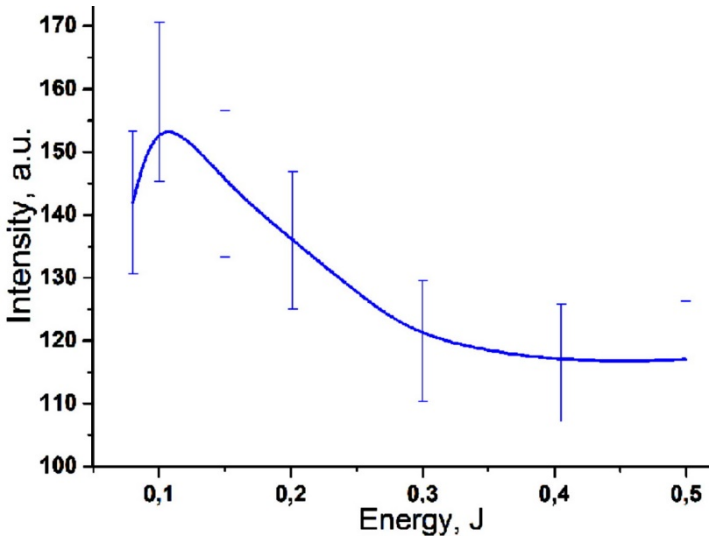


Figure 6. Dependence of the sodium line intensity on the laser radiation energy

It should be noted that with an increase in the power of laser radiation, a strong broadening of the line occurs. The above suggests that the study of lines of chemical elements at high laser radiation powers should be carried out not only taking into account the intensity of the line, but also taking into account the entire area of the spectrum in the vicinity of the spectral line.

The obtained result indicates the possibility of using relatively small capacities for spectral studies by the laser breakdown method. Consequently, there is no need to use large laser radiation powers to improve the sensitivity of laser-induced breakdown spectroscopy in the ultrasound field, which in practice can significantly simplify the implementation of this combined LIBS method.

It is important to study the dependence of the intensity of the lines of chemical elements on the time of development

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 11 November 2022 doi:10.20944/preprints202211.0214.v1

of laser breakdown in the presence and absence of ultrasound in order to solve the issues of the use of ultrasound in LIBS tasks. Under these conditions, the relationship between the intensity of spectral lines of chemical elements, such as potassium and manganese, arising from an optical breakdown in the liquid thickness under the influence of ultrasound, with the concentration of chemical elements and with the power of acoustic radiation at different delay times was studied. An aqueous solution of KCl was used to analyze the spectral lines of potassium during laser breakdown. Data were obtained on the spectral lines of the atomic potassium doublet at wavelengths of 766.4 and 769.8 nm, as well as the spectral emission line of atomic oxygen at a wavelength of 777 nm and the nitrogen triplet line at wavelengths of 742, 744 and 746 nm, which are shown in Figure 7.

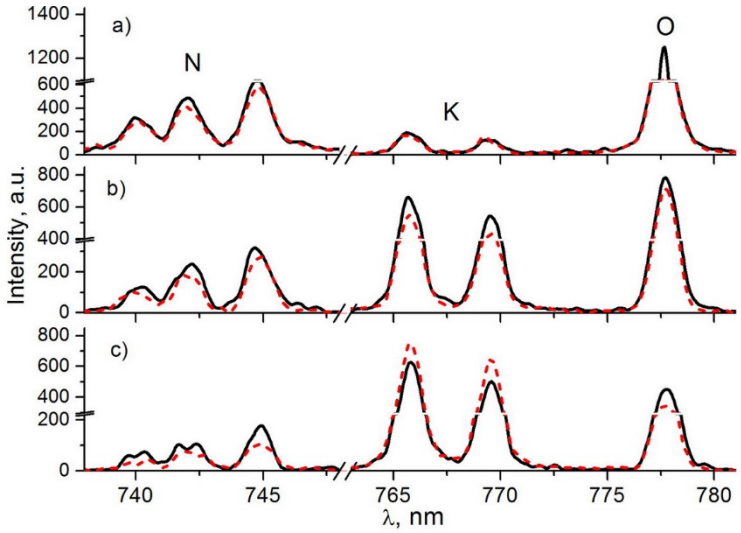


Figure 7. The intensities of the spectral lines of nitrogen, potassium, oxygen at different times: a) at t = 800 ns, b) at t = 1300 ns, c) at t = 2800 ns under conditions of irradiation with ultrasound frequency 220 kHz (solid curves) and without ultrasound (dashed curves).

Additionally, an aqueous solution of K2S04 was used to analyze the dynamics of potassium spectral lines during laser breakdown. Figure 8 shows the dependences of spectral lines of atomic potassium doublet at wavelengths of 766.4 and 769.8 nm on ultrasound parameters. Simultaneously with the potassium line, a spectral emission line of atomic oxygen at a wavelength of 777 nm was recorded.

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 11 November 2022 doi:10.20944/preprints202211.0214.v1

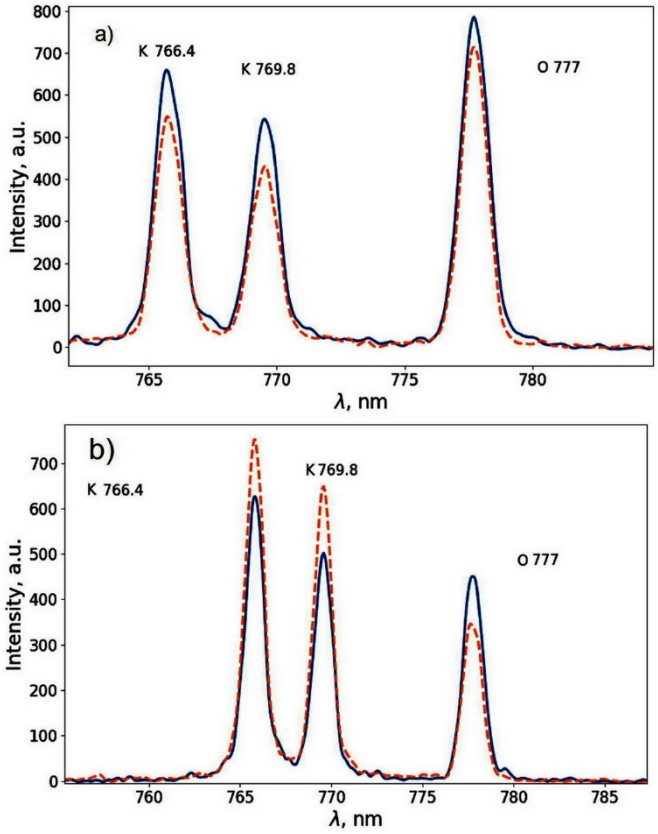
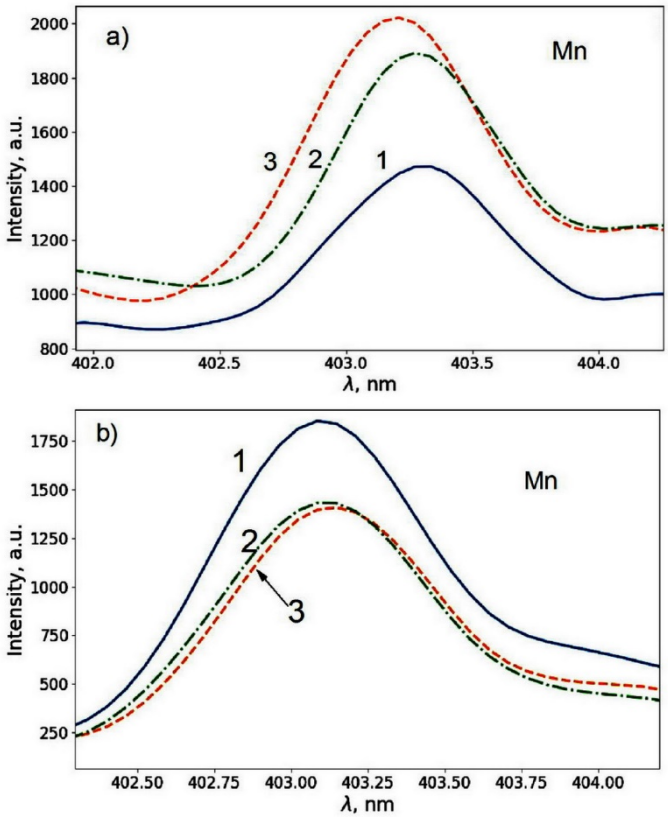


Figure 8. Spectral lines of potassium and oxygen under the influence of 220 kHz ultrasound (P=40 kPa - solid curves) and without ultrasound (P=0 kPa - dashed curves) at various delays relative to the laser pulse: a) 1.3 microseconds; b) 1.8 microseconds



Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 11 November 2022 doi:10.20944/preprints202211.0214.v1

Figure 9. Spectral lines of manganese at different amplitudes of ultrasound P: 1 – P=25 kPa, 2 – P=12 kPa, 3 – P=0 kPa at a frequency of 220 kHz with different delays relative to the laser pulse: a) 0.8 microseconds; b) 1.3 microseconds

In a number of experiments, an ambiguous effect of ultrasound on the expected increase in the intensity of the spectral lines of oxygen and potassium was obtained. In the studying the dynamics of optical breakdown spectra relative to the moment of the beginning of the interaction of laser pulses, it was experimentally shown that with varying delay and exposure, a different contribution of ultrasound to the change in the intensity of the spectral lines of oxygen and potassium is recorded, leading to both an increase and a decrease in the intensity of the spectral lines. This, in particular, is shown in Figure 8, which shows the ambiguous behavior of the spectral lines of oxygen and potassium in the ultrasound field at different delays of 1300 ns and 1800 ns from the beginning of the breakdown with the same exposure time of 500 ns in all cases.

It was also shown that ultrasound affects the change in the intensity of the spectral atomic lines of manganese in an aqueous solution of MnCl2 (at a length of 403 nm) similarly to the effect on the lines of oxygen and potassium and differs significantly at different times of development of optical breakdown, as shown in Figure 9.

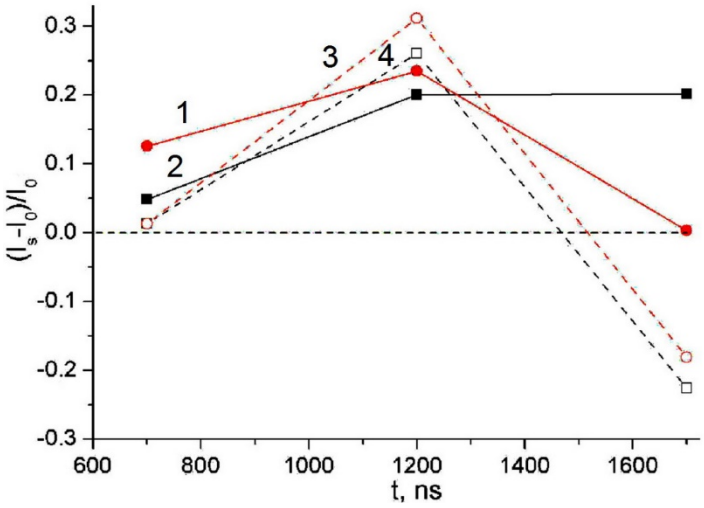


Figure 10. Dependence of the relative intensity ($I-I_0/I_0$) of potassium spectral lines at a wavelength of 766 nm (curves 1 and 2) and 769 nm (curves 3 and 4) when exposed to ultrasound at a frequency of 220 kHz with different amplitudes (curves 1, 3 – P =40 kPa; curves 2, 4 – P = 20 kPa;) from the time of the breakdown registration

A more detailed picture of the evolution of relative intensity ($I-I_0/I_0$) of the spectral lines K at a wavelength of 766 nm and 769 nm from the time of the breakdown detection when exposed to ultrasound with different amplitudes is shown in Figure 10. Here I_0 is the intensity of the line in the absence of ultrasound.

In the cases presented above, it can be seen that the effect of ultrasound on the intensity of the lines of chemical elements varies depending on the time of evolution of the laser breakdown. Therefore, it is important to choose a characteristic delay time from the beginning of the breakdown and then the effect of ultrasound is manifested to the maximum extent. In general, it is shown that ultrasound, even at low power, leads to an increase in the intensity of spectral lines. The reason for this effect should presumably be sought in different conditions of the appearance of bubbles nucleus in a standing wave when exposed to ultrasound on a liquid during an optical breakdown. Descriptions

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 11 November 2022 doi:10.20944/preprints202211.0214.v1

of the results related to the dynamics of the lines of various elements during the development of laser breakdown in the ultrasound field are partially contained in [21-23]. The spectral data base (Atomic Spectra Database) was used everywhere when analyzing the results [24].

3.2. Experimental results of ultrasonic LIBS with heterogeneous breakdown

To further study the possibility of increasing the efficiency of LIBS in the ultrasound field, experiments were conducted on heterogeneous breakdown in the presence of an aluminum plate near the water surface, which are shown in Figure 11.

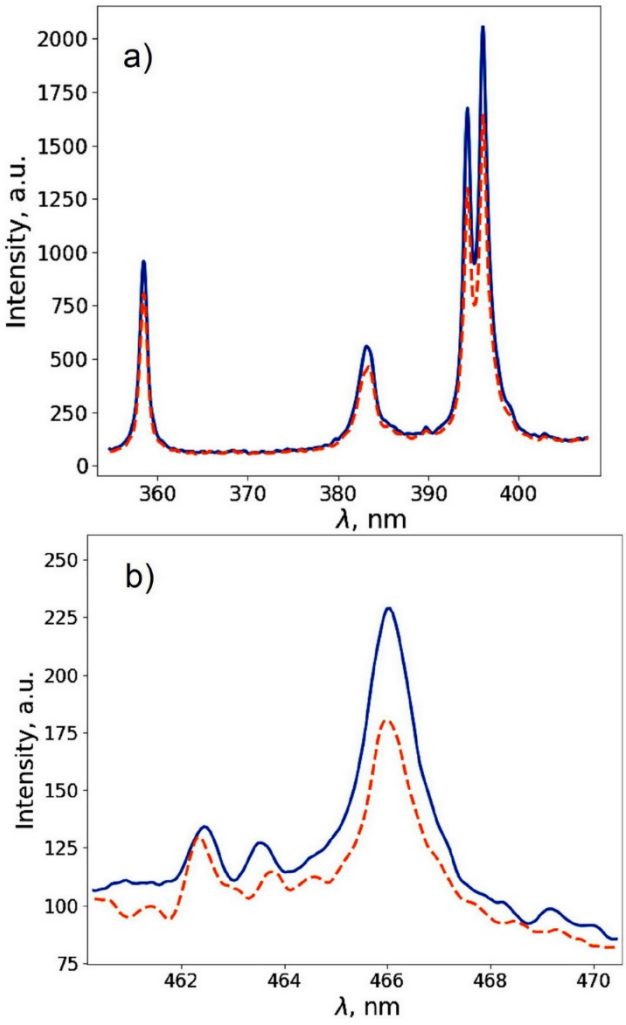


Figure 11. Spectral lines with heterogeneous breakdown of water near the aluminum plate under the influence of ultrasound frequency 220 kHz (P= 40 kPa - solid curves) and without ultrasound (P=0 kPa - dashed curves): a) atomic line of aluminum Al I doublet (394.4 and 396 nm); b) aluminum Al II ion line (466.3 nm)

Presumably, the effects described above for various elements in the liquid thickness should have been observed. It can be seen that the behavior of the atomic and ionic lines of aluminum, depending on ultrasound, is quite different. So, for the ion line, the excess in the ultrasound field is about 25%, while for atomic lines, the excess of the lines in the ultrasound field is less than 20%.

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 11 November 2022 doi:10.20944/preprints202211.0214.v1

The reason for this difference, in our opinion, lies in the significantly different effect of the ultrasonic field on the breakdown in the liquid column and near the free boundary. In the latter case, the magnitude of the acoustic pressure is minimal in the presence of large values of particle velocities in the ultrasound field, while in the liquid column (especially in the standing wave field), the reverse pattern is observed, the pressure in the antinode is maximum, and the velocities are minimal. Therefore, to increase the effectiveness of the effect of ultrasound on spectroscopy, it is important to choose the configuration of the experiment. To increase the efficiency of the LIBS of atomic lines in the ultrasound field, a place in the liquid column near the maximum pressure in the ultrasound field should be chosen as the focus point of laser radiation.

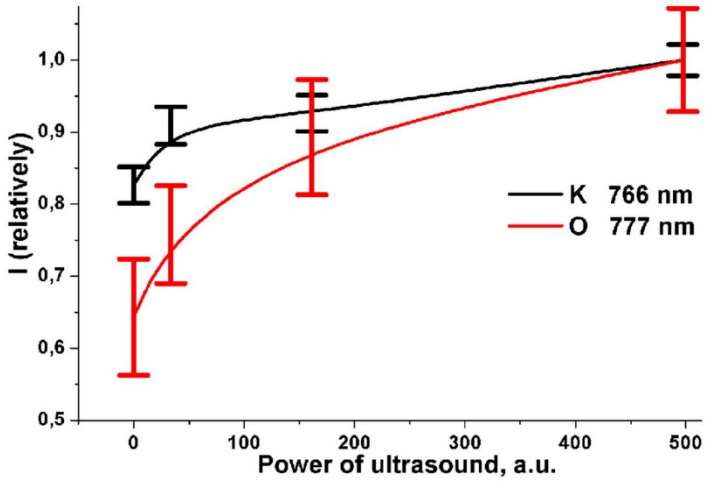


Figure 12. Dependence of the relative intensity of the spectral lines of potassium (766 nm) and oxygen (777 nm) on the power of ultrasound with a frequency of 220 kHz at optical breakdown in water

Along with the ambiguous effect of laser irradiation power on the intensity of spectral lines, it was natural to raise the question of the effect of acoustic radiation power on the intensity of spectral lines of various chemical elements during optical breakdown in a liquid. Figure 12 shows a significant dependence of the intensity of the spectral lines of potassium and oxygen on the power of ultrasound during laser breakdown in water. Ultrasound has a strong effect on the intensity of spectral lines, while its effect increases with power. An increase in the intensity of the potassium and oxygen spectral lines from the ultrasound power was recorded during an optical breakdown using ultrasound with a frequency of 220 kHz. Figure 16 shows the dependence of the relative intensity (i.e. normalized to the maximum value of the line intensity in experiments) under the influence of ultrasound from the power of ultrasound. It should be noted a certain edge, beyond which, according to Figure12, the effect of increasing ultrasound power slows down and saturation occurs.

3.3. Features of acoustic spectroscopy of laser breakdown of liquid

Along with the registration of radiation from the breakdown site in the optical region of the spectrum, the spectral and energy characteristics of acoustic emission were studied.

The effect of ultrasound at various frequencies on spectral acoustic emission at breakdown is shown in Figure 13. From Figure 13 it can be seen that the use of an ultrasound source in a certain frequency band above

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 11 November 2022 doi:10.20944/preprints202211.0214.v1

200 kHz practically does not affect the change in the spectral density of acoustic emission from breakdown. Thus, there is a characteristic range of ultrasound frequencies, limited from above, which can be the basis for application in the LIBS method.

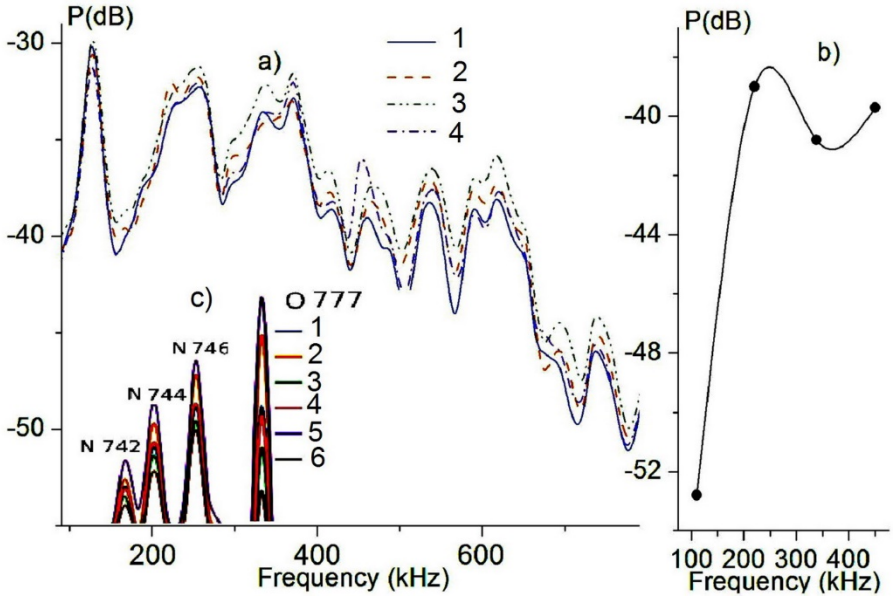
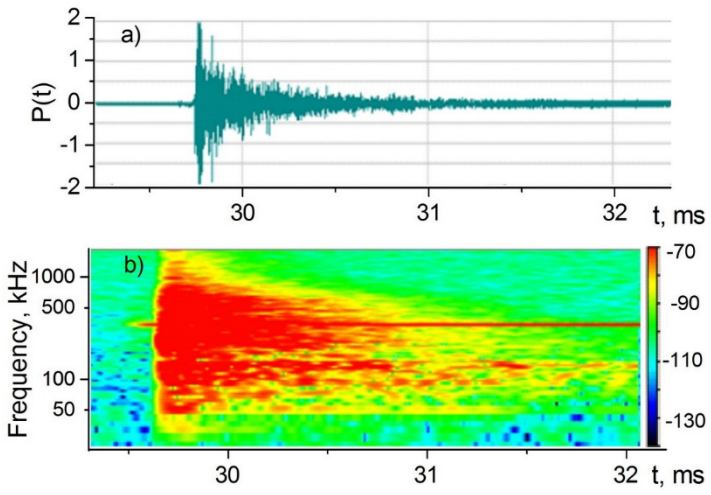


Figure 13. The effect of ultrasound frequency on the spectral composition (a) and the integral amplitude of acoustic emission (b), as well as on the spectral lines of nitrogen and oxygen at optical breakdown of water (c): 1 – 110 kHz, P = 4 kPa; : 2 – 220 kHz, P = 20 kPa; : 3 – 338 kHz, P=16 kPa; : 4 – 450 kHz, P=18 kPa; 5 – 450 kHz, P=40 kPa; 6 – without ultrasound, P=0 kPa

Figure 14 a shows a typical acoustic pulse, the spectrogram of which is shown in Figure 14 b. It can be seen that in the early stages of breakdown, the acoustic emission associated with the expansion of the cavity is so large that it significantly overlaps the pressure in the external acoustic field with a frequency of 450 kHz.



Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 11 November 2022 doi:10.20944/preprints202211.0214.v1

Figure 14. Time scan and spectrogram of acoustic emission from optical breakdown

This is shown in more detail in Figure 15. The upper graph of Figure15a is the spectrum of the signal at long breakout evolution times of about 1.35 ms, which is marked with a horizontal line in Figure15b. The side graph of Figure15c shows the dynamics of the spectral component of the acoustic emission of 225 kHz (sub-harmonics of the frequency of the external field), which is marked in Figure 15b is a vertical line. It can be seen that the level of the re-emitted signal from the external field becomes noticeable only at times greater than 400-500 microseconds. However, already at times of about 1.35 ms, the spectral line at a frequency of 450 kHz becomes at least 10 dB larger than any spectral component of the presented signal. A significant drop of 60 dB of the signal at a frequency of 225 kHz, which is not associated with an external field, also occurs very quickly, in about 1.9 ms. Consequently, acoustic emission at the early stages of less than 1 ms is mainly associated with acoustic excitation of the environment during the expansion of the laser breakdown plasma. Thus, despite the presence of an acoustic field, it is possible to restore the dynamics of the expansion of the cavity at an early stage, without resorting to solving the problem of the dynamics of the cavity in the external field.

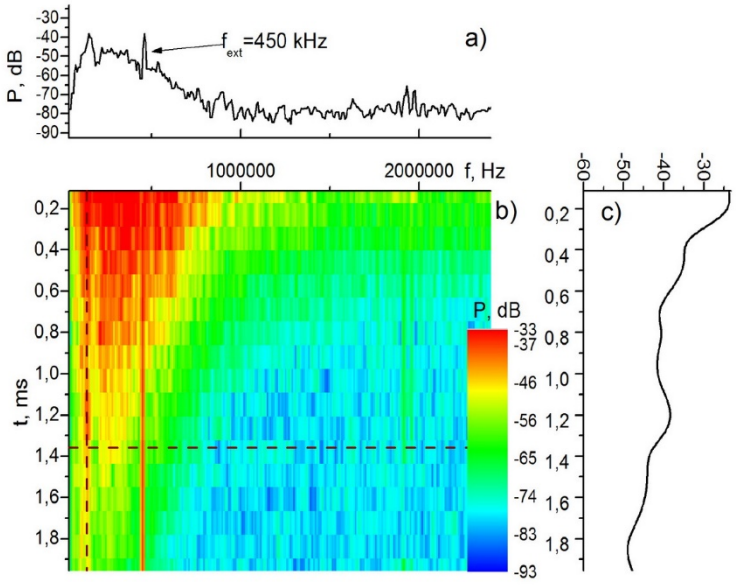


Figure 15. The change in the spectral components of the acoustic signal from the laser breakdown in time in the presence of ultrasound with a frequency f = 450 kHz: a) the spectrum of the signal over long breakout evolution times of about 1.35 ms; b) 2D graph of the acoustic signal – functions *P(f,t);* c) the dynamics of the spectral component of the acoustic emission f=225 kHz

In this paper, an attempt was made to obtain data on the dynamics of the breakdown cavity using acoustic emission data by solving the inverse problem based on Rayleigh type equations [10]. The theoretical basis is

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 11 November 2022 doi:10.20944/preprints202211.0214.v1

a formula for the distribution of pressure $P_r(t-r/c)$ in the radiated wave from a pulsating spherical bubble of radius $R(t) = R_0 + \delta R(t)$ as a source of monopole radiation. The formula can be written as [25]

$$P_r(t-r/c) = \rho\left[R\frac{d^2R}{dt^2} + 2\left(\frac{dR}{dt}\right)^2\right]_{t-r/c} \frac{R(t-r/c)}{r}. \quad (1)$$

The nonlinear differential equation (1) was solved by the Runge-Kutta method with respect to the function *R(t)*, using the time variable pressure function known from experimental data at a fixed distance r from the center of the bubble. As a result, it was possible to calculate both the function and the velocity of the liquid on the surface of the bubble and the amount of pressure on the wall of the cavity.

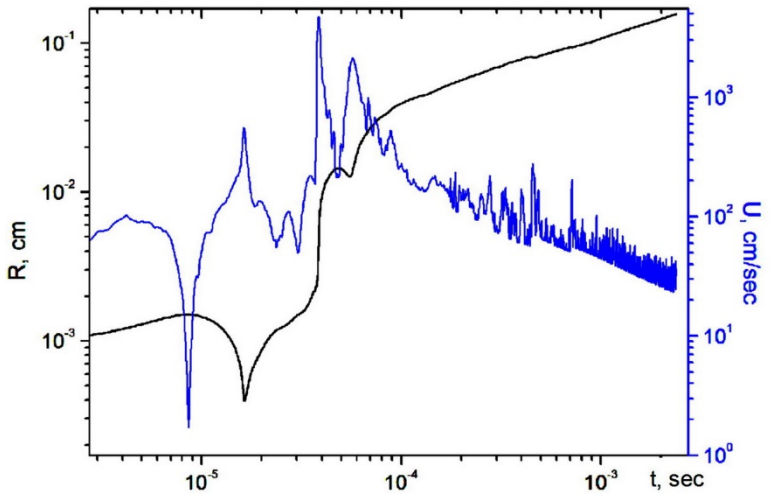
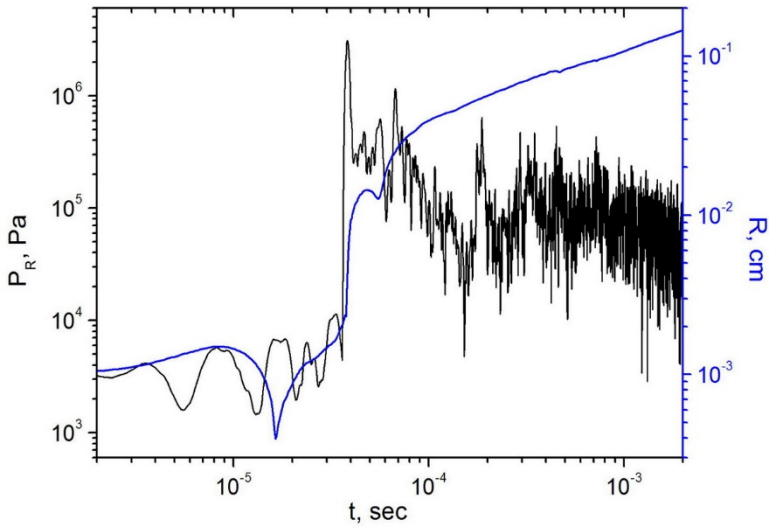


Figure 16. The function of *R(t)* and the velocity of expansion of the walls of the cavity *U(t)*



Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 11 November 2022 doi:10.20944/preprints202211.0214.v1

Figure 17. The pressure function on the cavity wall $P_R(t)$ and the function $R(t)$ during the expansion of the cavity

Figures 16 and 17 show these dependences for $R(t)$, $P_R(t)$ and the rate of expansion of the walls of the cavity $U(t)$, which show that according to acoustic data it is possible to reproduce the function $R(t)$, which is consistent with the characteristic dependences $R(t)$ obtained from direct measurements of optical images breakdown in the later stages of its evolution.

In conclusion, we present some results of modeling resonant vibrations of cavities under the influence of ultrasound with an amplitude typical of the experiments carried out. Figure 18 shows the dependences for $R(t)$, $P_R(t)$ and the oscillation rate of the cavity walls $U(t)$. This Figure shows that at a frequency of 60.4 kHz for cavities with radii of 54 microns, the effect of ultrasound with an amplitude of 25 kPa leads to the swinging such cavities by non-stationary nonlinear processes. These are manifested in the spectra of the re-emitted acoustic fields (unsteady scattering of ultrasonic pulses), shown in Figure19.

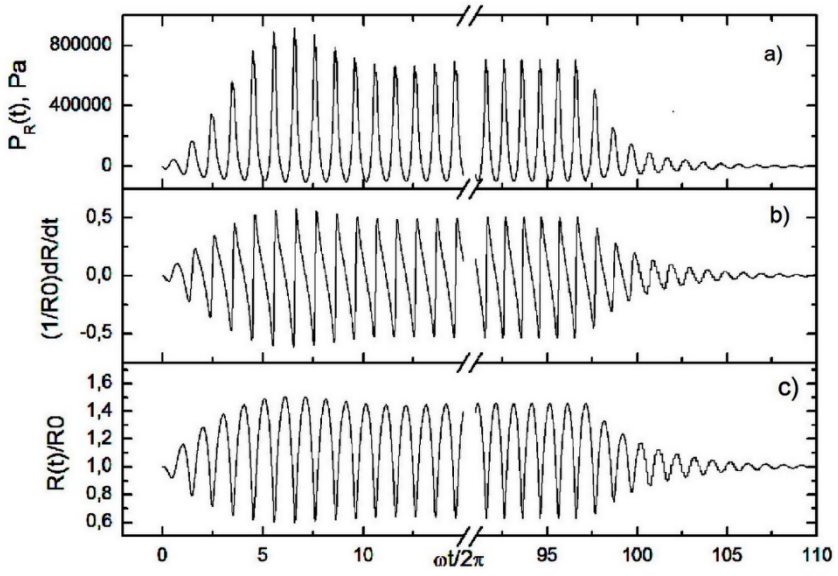


Figure 18. Dependences for $R(t)$, $P_R(t)$ and the oscillation rate of the walls of the cavity $U(t)$

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 11 November 2022 doi:10.20944/preprints202211.0214.v1

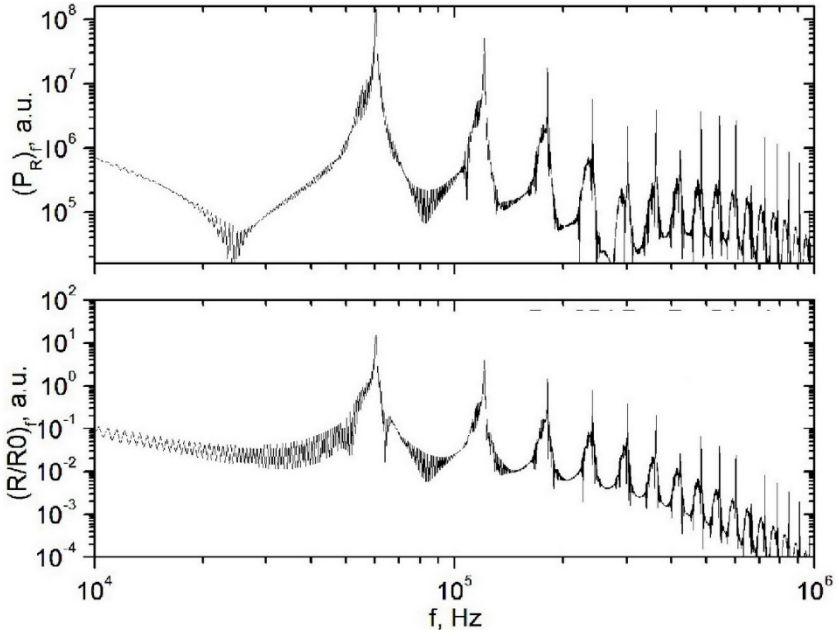


Figure 19. The spectrum of vibrations of the cavity and the re-emitted pressure under the influence of an ultrasound pulse with a frequency of 60.4 kHz.

3.4. Spectroscopy of elements in an aerosol cloud of seawater created by ultrasound

The automated spectral complex described in section 2 above made it possible to carry out operational measurements of spectral and hydrophysical characteristics of seawater. It was used in field research in the expedition in the Sea of Japan and the Tatar Strait in route No. 81 of the research vessel RV "Professor Gagarinsky" from August 1 to August 14, 2022. As an example, Figure 20 shows the distribution of air and water temperature and electrical conductivity of water with high spatial resolution depending on the time and coordinates that were simultaneously recorded by the complex. The shaded area in Figure 20b corresponds to the anchorage of the ship near the port of Chekhov on the western part of Sakhalin Island (the northernmost point of the route).

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 11 November 2022 doi:10.20944/preprints202211.0214.v1

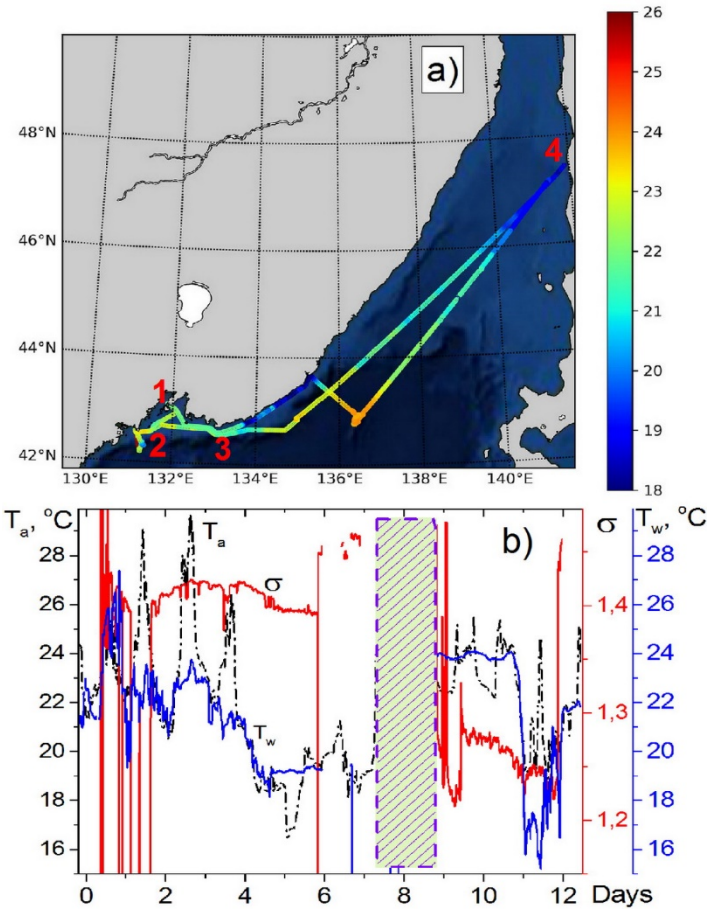


Figure 20. The route map of the RV "Professor Gagarinsky" (a) and the distribution of air temperature T_a , water temperature T_w and electrical conductivity σ of water (b) in the near-surface layer at a depth of 4 m. The color in Figure 20a shows the water temperature T_w, the shaded area in Figure 20b corresponds to the anchorage of the vessel at the northernmost point of the route.

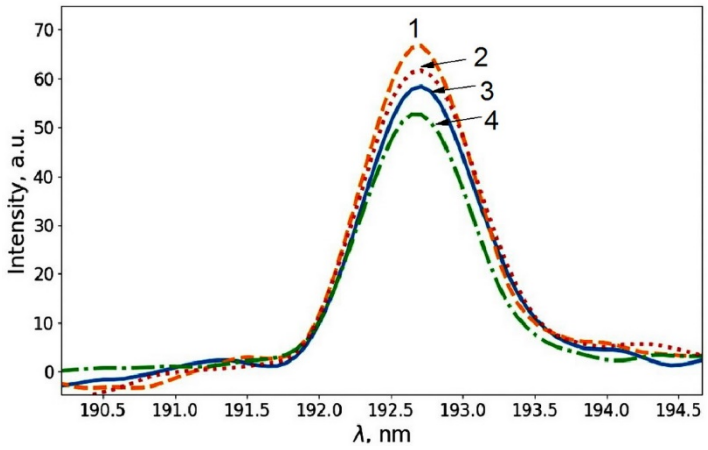


Figure 21. The intensities of carbon lines obtained at various coordinate points 1, 2, 3, 4 along the trace (see Figure 20a) in the upper layer of the Sea of Japan.

An important difference in the operation of the automated complex with a flow cell was the use of ultrasound to

 doi:10.20944/preprints202211.0214.v1

create an aerosol cloud. It is essential that the spectral data were obtained using an electric discharge not in a liquid volume, but in an aerosol cloud. Thus, here the breakdown of the liquid and the creation of plasma for spectral measurements took place using an electric discharge in finely dispersed water droplets. Emission spectra arising under the action of a spark discharge in a cuvette characterize the chemical composition of the liquid under study. Then they were analyzed using a monochromator and a CCD matrix, recorded and recorded in a microcomputer data storage device.

An automated complex with a flow cell was used to register various elements in the near-surface layer of the sea, including carbon registration in situ conditions along the course of the vessel with high spatial resolution. As known, such a task is very relevant in connection with measurements within carbon polygons. As an example of a typical registration by an automated complex, Figure 21 shows the intensities of carbon lines obtained at various coordinate points along the trace, which demonstrate the variability of the data obtained inside the polygon. The results obtained prove the possibility of using the method for monitoring carbon polygons.

4. Discussion

The results obtained indicate that a technique has been created that allows the use of ultrasonic irradiation of the breakdown area using piezoceramic acoustic emitters with different resonant frequencies in order to increase the sensitivity of the LIBS method. It was important to solve the problem of synchronization of acoustic and optical pulses, for which the method of synchronization and study of acoustic emission by a specialized measuring hydrophone with simultaneous registration of breakdown in the optical region of the spectrum was worked out. The solution of this problem made it possible to use ultrasound sources with extremely low power (at the cavitation boundary), which predetermined a decrease in the breakdown threshold in the liquid thickness.

Studies of the spectroscopic parameters of the laser breakdown were carried out in the presence and absence of an ultrasound field at different salt concentrations. This made it possible to increase the intensity of individual spectral lines (and some lines were resolved), which allows us to talk about a new combined method of laser and ultrasonic spark spectroscopy.

As can be seen from Figure 4, 5, 8, 10, the amplification of the line under the influence of ultrasound is observed at all concentrations of the solutions used, which indicates an increase in spectroscopic excitation of the liquid by ultrasound. The results in Figure 5 clearly show that the intensity of the calcium ion line increases during the phase of maximum ultrasonic exposure (compression of the breakdown cavity) compared with the absence of ultrasound.

Attention should be paid to the results presented in Figure6, from which it can be seen that with a significant increase in the power of laser radiation, the line intensity begins to weaken, most likely caused by the absorption of the medium. This effect indicates the possibility of using small power to study optoacoustic effects and spectroscopic properties of the medium when using LIBS in the ultrasound field. At the same time, it should be noted that with a significant increase in the power of laser radiation, a strong broadening of the line occurs. It can be assumed that the study of lines at high laser radiation powers should be carried out not only in the amplitude region, i.e. when studying the intensity of the line, but also take into account the area of the spectral line.

A detailed study of the dependence of the intensity of the lines of chemical elements on the time of evolution of the laser breakdown in the presence and absence of ultrasound has shown that with varying delay and

 doi:10.20944/preprints202211.0214.v1

exposure, a different contribution of ultrasound to the intensity of the spectral lines of oxygen and potassium is recorded, leading to both an increase and a decrease in the intensity of the spectral lines. The delay range from 800 ns to 1500 ns has been revealed, in which there is an unambiguous gain in the intensity of spectral lines. As can be seen from Figure 14 in the specified range, the relative intensity of spectral lines when using ultrasound significantly exceeds background values.

The mechanism of the influence of ultrasound on the amplification of the intensity of the lines is not completely clear. It seems to us that the amplification effect is associated with the manifestation of the features of the laser breakdown on the wall of the cavitated bubble from ultrasound. The atoms of the dissolved substance located on the surface of the bubble easily fall into the breakdown area, which is located near the surface. Essentially, the bubble collects the atoms of the dissolved substance from a volume of liquid approximately equal to its own volume. In the absence of a bubble with its free surface, the contribution to the emission of lines gives a smaller number of atoms, their number is determined by the size of the region in the initial stage of laser breakdown in the liquid. A certain role in lowering the breakdown threshold can also be played by the mechanism of joint electroacoustic interaction in a conductive solution. The latter can lead to additional energy dissipation in the focal region of the interaction of laser radiation with the solution, resulting in additional overheating and facilitating the formation of cavities in the liquid.

Conclusion

The features of laser breakdown of liquids in the field of high-power ultrasound and a comparative study of the possibilities of acoustic and optical diagnostics of breakdown were studied. The study of the laser breakdown was carried out in the nanosecond region and at later stages. The use of ultrasonic irradiation of the breakdown area at various frequencies was new. Along with the registration of radiation from the breakdown site in the optical region of the spectrum, the spectral and energy characteristics of acoustic emission were studied.

An important effect found in experiments with laser breakdown of water and aqueous solutions was the effect of a sharp increase in the intensity of the spectral lines of dissolved elements for aqueous solutions with an increase in the concentration of the solution. It was found that at different phases of the acoustic field (stretching and compression phases), the intensity of the lines of a single ionized calcium doublet changes. It is shown that, in general, there is a sharp increase in the intensity of the spectral lines of elements in water during laser breakdown in the field of high-power ultrasound, which indicates an increase in the sensitivity of the standard method of laser-induced breakdown spectroscopy when using the combined method of ultrasonic LIBS.

Using the developed technique, spectral lines of chemical elements such as potassium, manganese and sodium were obtained for the first time depending on the frequency and power of ultrasound. A significant dependence of the intensity of the spectral lines of various chemical elements during an optical breakdown in a liquid on the power of acoustic radiation was revealed. The results obtained show that the developed technique avoids the effect of explosive boiling and instability of the surface of aqueous solutions, which expands the possibilities of using the technique for the technique for LIBS in liquid.

An automated complex for spectral and hydrophysical studies, which has been tested in expedition conditions, is described. With its help, new data were obtained on the distribution of dissolved elements, including carbon, and the state of seawater with high spatial resolution in the carbon landfill in the Sea of Japan and the Tatar Strait during flight No. 81 of the RV "Professor Gagarinsky" in August 2022. The complex can be recommended for in-situ studies of the state of natural waters.

Author's contribution: Conceptualization, AB; Methodology, AB and IN; Software, AB and VK; Validation, AB, IN and VK; Formal Analysis, AB and VK; Investigation, AB and IN; Resources, AB; Data Curation, AB and IN; Writing – Original Draft Preparation, AB.; Writing – Review & Editing, AB; Visualization, AB and VK, Supervision, AB; Project Administration, AB; Funding Acquisition, AB and VK.

AB – A.V. Bulanov, VK– V.A. Krikun**,** IN -I.G. Nagorny

Funding: The work was carried out with the support of the Russian Science Foundation, project No. 22-22-20075.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Davies, C.M.; Telle, H.H.; Montgomery, D.J.; Corbett, R.E. Quantitative analysis using remote laser-induced breakdown spectroscopy (LIBS). *Spectrochem. Acta Part B*. **1995**, *50*, 1059 – 1075.
2. Cremers, D.A.; Radziemski, L. J. *Handbook of Laser– Induced Breakdown Spectroscopy*, John Wiley& Sons: New York, USA, 2006, 282 p.
3. Musazzi, S.; Perini, U. *Laser-Induced Breakdown Spectroscopy*, Springer-Verlag: Berlin Heidelberg, 2014, 575 p.
4. De Giacomo, A.; Dell'Aglio, M.; Gaudiuso, R.; Amoruso, S.; De Pascale, O. Effects of the background environment on formation, evolution and emission spectra of laser-induced plasmas. *Spectrochim. Acta*, *Part B*. **2012**. *78*, 1-19.
5. Xue, B.; Tian, Y.; Lu, Y.; Li, Y.; Zheng, R. Characteristics of the secondary breakdown of DP-LIBS in bulk water with different axial focusing arrangements and laser energies. *Spectrochim. Acta Part B: Atomic Spectroscopy*, **2019**. *151*, 20-25.
6. Xue, B.; Li, N.; Lu, Y.; Li, Y.; Zheng, R. Emission enhancement of underwater collinear dual-pulse laser-induced breakdown spectroscopy with the second pulse defocused. *Appl. Phys. Lett*. **2017**. *110*, 101102.
7. Noll, R. *Laser-Induced Breakdown Spectroscopy: Fundamentals and Applications*, Springer: Berlin, 2012. 543 p.
8. Lawrence-Snyder, M.; Scaffidi, J.; Angel, S.M.; Michel, A.P.M.; Chave, A.D. Sequential-Pulse Laser-Induced Breakdown Spectroscopy of High-Pressure Bulk Aqueous Solutions. *Appl. Spectroscopy*, **2007**, *61*, 171– 176.
9. Michel, A.P.M.; Michel, A.P.M.; Lawrence-Snyder, M.; Angel, S.M.; Chave, A.D. Laser– induced breakdown spectroscopy of bulk aqueous solutions at oceanic pressures: evaluation of key measurement parameters. *Appl. Optics*. **2007**, *46*, 2507–2515.
10. Lauterborn, W.; Kurz, T. Physics of bubble oscillations. *Rep. Prog. Phys*. **2010**, *73*, 106501.
11. Kurz, T.; Kroninger, D.; Geisler, R.; Lauterborn, W. Optic cavitation in an ultrasonic field. *Phys. Rev.E.* **2006.** 74. 066307;
12. Kurz, T.; Wilken, T.; Kroninger, D.; Wimann, L.; Lauterborn, W. Transient dynamics of laser–induced bubbles in an ultrasonic field, *AIP Conf. Proc*. **2008**, *1022*, 221–224
13. Egerev, S.V.; Ovchinnikov, O.B.; Fokin. A.V. Optoacoustic conversion in suspensions: the competition of

mechanisms and statistical characteristics. *Acoust. Phys.*, **2005**, *51*, 160–166.

14. Lina, C.P.; Kelly, M.W. Cavitation and acoustic emission around laser– heated microparticles. *Appl. Phys. Lett*. **1998**, *72*, 2800-2802.
15. Kudryashov, S.I.; Lyon, K.; Allen, S.D. Photoacoustic study of relaxation dynamics in multibubbles systems in laser–superheated water. *Phys. Rev. E*. **2006,** *73*, 055301
16. Padilla–Martinez, J. P.; Berrospe–Rodriguez, C.; Aguilar, G.; Ramirez-San-Juan, J.C.; Ramos–Garcia, R. Optic cavitation with CW lasers: A review. *Phys.Fluids*. **2014**, *26*, 122007.
17. Taylor, R.S.; Hnatovsky, C. Growth and decay dynamics of a stable microbubble produced at the end of a near–field scanning optical microscopy fiber probe. *J. Appl. Phys*. **2004**, *95*, 8444
18. Byun, K.T.; Kwak, H.Y.; Karng, S.W. Bubble Evolution and Radiation Mechanism for Laser–Induced Collapsing Bubble in Water. *Japanese Journ. Appl. Phys.* **2004**, *43*, 6364–6370
19. Bulanov, A.V. Acoustic emission and optics of bubbles originated by laser breakdown of salt water. *Proc. Mtgs. Acoust*. **2015**, *24*, 070014, 1– 7.
20. Bulanov, A.V.; Nagorny, I.G. Acoustic emission and magnification of atomic lines intensity originated by laser breakdown of salt water. *Proc. SPIE*. **2016,** 10176;
21. Bulanov, A.V.; Nagorny, I. G.; Sosedko, E.V. Spectroscopic features of laser-induced breakdown in water and aqueous solutions in ultrasonic field. *Tech. Phys. Lett.* **2017**, *43*, 753-755.
22. Bulanov, A.V., Nagorny, I. G.; Sosedko, E.V. A study of the optical and acoustic spectral characteristics by laser breakdown of water in an ultrasonic field. *Tech. Phys. Lett.* **2019**, *45*, 1200-1203.
23. Bulanov, A.V.; Sosedko, E.V. Opto-acoustic effects by laser breakdown of seawater in an ultrasonic field. *Doklady Earth Sciences*. **2020**, *491*, 183–186.
24. Atomic Spectra Database. Available online: URL: https://dx.doi.org/10.18434/T4W30F (accessed on 18.05.2021)