Colloidal selenium solutions prepared by laser ablation and ultrasonic dispersion

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Abstract. On the basis of nonequilibrium processes production technologies of aqueous colloidal systems of chemical elements not soluble in water, in particular, selenium were developed. Selenium is a trace element with unique biological functions, which has a wide range of effects on living organisms. The aim of this work is to obtain an aqueous colloidal selenium solution, suitable for biological researches, by laser ablation and ultrasonic dispersion. The method of laser ablation allows to obtain an aqueous colloidal solution of selenium with a concentration of up to 5.6 mg/l, Zeta potential up to -14.1 mV and pH = 4.92. Using an ultrasonic homogenizer, aqueous colloidal solutions of amorphous selenium with a concentration of 9.8 mg/l, Zeta potential of 26.3 mV and pH = 6.47 were obtained. Ultrasonic dispersion method using a waveguide is more preferable for the preparation of colloidal solutions of selenium for biological research due to the higher concentration and stability at pH values close to neutral.

1. Introduction
The use of highly nonequilibrium processes in extreme technologies opens up fundamentally new possibilities for obtaining materials with preset controlled properties [1]. On the basis of nonequilibrium processes, technologies have been developed for the production of aqueous colloidal systems of water-insoluble chemical elements, selenium in particular [2].

Selenium is a microelement with unique biological functions, possessing a wide spectrum of action on living organisms. Selenium and its compounds are included into a number of enzymes involved in the maintenance of peroxide homeostasis [3], which play a key role in the formation of the organism’s response to stress factors. Increasing the bioavailability and efficiency of selenium-bearing new-generation compounds is achieved through the use of nano-sized selenium particles. The literature data of domestic [4] and foreign researchers [5] indicate a lower toxicity of nano-sized selenium, which means the "zero-valent" state of selenium is less toxic. In Stavropol State Agrarian University it was found out that with intraperitoneal admission of nano-sized selenium, the average dose of a substance that causes the death of half of the members of the test group of mice (LD₅₀) is 32.9 mg/kg [6]. For comparison, the corresponding indicator for sodium selenite is 10 mg/kg. Chinese researchers have shown that LD₅₀ for nano-sized selenium is 113.0 mg/kg, while LD₅₀ of sodium selenite is 15.7 mg/kg [5]. Thus, the acute toxicity of selenium in nanosized form is 7 times lower than sodium selenite.

The aim of this work is to use highly nonequilibrium processes to develop methods for the preparation of an aqueous colloidal solution of selenium suitable for biological research.
2. Materials and methods
As a target, elemental selenium of the grade OSCH (GOST 5.1489-72) was used in the work. Spraying medium was bidistilled water (TU 6-09-2502-77), and the fluid was not forced to mix.

For the preparation of colloidal solutions of selenium, a solid-state laser with a radiation wavelength of 1064 nm, a pulse energy of 2.50 J with a pulse duration of 12 ns was used. The pulse repetition rate is 1 Hz.

Ultrasonic resources were ultrasonic bath UZV-1.3 ("Sapphire", Russia) with an operating frequency of 35 kHz and a generator power of 50 W, and an ultrasonic homogenizer UP200S (Hielscher, Germany) with an operating frequency of 24 kHz and a power of 200 W. In the second case, a waveguide with a diameter of 12 mm was used. The concentration of selenium in the aqueous solution was measured by atomic-emission spectroscopy with inductively coupled plasma (AES with ICP) on a ULTIMA 2 instrument (Horiba Jobin-Yvon, France). The particle size distribution in the aqueous dispersion and the zeta potential of the selenium particles were estimated by the Dynamic Light Scattering (DLS) method using a ZetasizerNano ZS device (Malvern, UK). The hydrogen index was measured using a S220-Kit pH meter (Mettler Toledo, Switzerland).

3. Result and discussion
Laser ablation of a solid target in a liquid is a nonequilibrium process involving local pulsed heating of matter at the solid-liquid interface, the formation of a melt zone of the target material and the vapor-gas cloud of ablation products, their sublimation and crystallization. In this process aqueous colloidal solutions with a selenium concentration of about 9 mg/l were obtained, with particle distribution shown in Fig. 1. The solution has pH = 4.92, ζ-potential -12.3 mV. In Table. 1 shows the dependence of the concentration of the colloidal solution and the electrokinetic potential on the number of pulses of laser irradiation. The colloidal solution turns red, which indicates the formation of amorphous selenium.

![Figure 1. Distribution of selenium particles in size.](image)

| Number of pulses | Concentration of Se, mg/l | ζ-potential, mV |
|------------------|---------------------------|----------------|
| 60               | 1.7                       | -7.6           |
| 100              | 2.6                       | -8.2           |
| 240              | 3.8                       | -12.3          |
| 2000             | 5.6                       | -14.1          |

The ultrasonic bath allows to remove from the surface a thin layer of material the order of 1.5 - 2 μm. Colloidal solutions of selenium depend on the material of the vessel they were obtained in [7]. Thus, in a quartz vessel, the particles have a bimodal distribution with a number-average size $d_n$ of about 40 and 100 nm, and particles with $d_n \approx 200$ nm are formed in a glass vessel. The particle size distribution in a glass vessel corresponds approximately to the distribution in systems obtained by
laser ablation. In a quartz vessel, pH = 6.14, the ζ potential is -14.5 mV, and in the glass vessel pH = 5.29, the ζ potential is -1.97 mV. Solutions were obtained within 13 hours.

If the evaporation of matter during laser ablation takes place and the nano-sized particles are generated from the right phase [8], a completely different process during the ultrasonic dispersion is observed - the destruction of the polycrystalline material [9]. A colloidal solution of selenium at a preparation temperature of 40°C gets gray, indicating the presence of selenium particles with a polycrystalline structure.

Figure 2. Distribution of selenium particles obtained in a quartz vessel (a) and a glass vessel (b), in size.

Ultrasonic dispersing (UD) using an ultrasonic homogenizer also made it possible to obtain aqueous colloidal solutions of selenium. UD is based on the phenomenon of acoustic cavitation - the formation and collapse of cavities in a liquid under the influence of sound [9]. As a result of the pulsation of cavitation bubbles, the low energy density of the sound wave is concentrated into high-density energy. In the phase of rarefaction of an acoustic wave in a liquid, a gap is formed in the form of a cavity that is filled up with a saturated vapor of a given liquid. In the compression phase under the influence of increased pressure and surface tension forces, the cavity collapses, and the vapor condenses at the interface. Gas dissolved in the liquid diffuses into the cavity through its walls, and then undergoes strong adiabatic compression. After the collapse of the cavity a rapidly damped spherical shock wave propagates in the surrounding liquid. The explosion time lasts several nanoseconds, during which the cooling rate exceeds 1011 K/s and flows with the velocity up to 150 m/s occur. Such a cooling rate prevents the appearance of crystalline reaction products. Under the influence of ultrasound, amorphous nanoparticles are formed. In addition, the process of grinding by collision of powder particles, which arises during their disordered motion under the action of ultrasound is also possible.

The distribution of selenium particles after ultrasound irradiation for 30, 45 and 60 minutes is shown in figure 3.

Figure 3. Distribution of the number of selenium particles in size after 30 min (a), 45 min (b) and 60 min (c) of irradiation.

Initially, a significant amount of particles with an average size of ≈100 nm appears (Fig. 3a). During the irradiation of the colloidal solution, the particles are destroyed. The number of particles with an average size below 100 nm increases (Fig. 3b). Then a separate peak with a number average size of ≈35 nm appears.

The solution has the following characteristics: concentration is 9.8 mg/l, electrokinetic potential is 26.3 mV, pH is 6.47. In the process of processing by an ultrasonic homogenizer, the solution turns red.
The red aqueous colloidal solution of selenium obtained by laser ablation was used for treating the seeds of garden and flower crops after a period of one month. It is established that it has a growth-stimulating effect. Feeds for broiler chickens also included colloidal selenium. Solutions of selenium were added to feed in variants of concentration of nano-sized selenium: 0.001 mg/l, 0.01 mg/l and 1 mg/l. The results of the studies showed that the optimal concentration of the solution of nanosized selenium is 0.01 mg/l [10]. This concentration corresponds to the content of selenium in the feed equal to 0.016 mg/t. The established rate of introduction of selenium in nanosized form for chickens is significantly lower than the traditional norm for selenium salts – 200 mg/t. Selenium is also widely used in cosmeceuticals. The absence of toxicity of the nanoselenium substance was established in concentrations of less than 0.14 mg/l [11].

4. Conclusion
As a result of the investigation, it was established that the laser ablation method makes it possible to obtain an aqueous colloidal solution of selenium with a concentration up to 5.6 mg/L, ζ-potential up to -14.1 mV and pH = 4.92. Using an ultrasonic homogenizer, aqueous colloidal solutions of amorphous selenium with a concentration of 9.8 mg/l, ζ-potential of -26.3 mV and pH = 6.47 were obtained. The ultrasonic dispersion method with a waveguide used is more preferable for the preparation of colloidal selenium solutions for biological studies due to higher concentration and stability at pH values close to neutral.

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5. References
[1] Balankin A S, Bannykh O A and Ivanova V S 1991 Synergetics of extreme technologies of metal materials production with self-organizing structures. Coll. New technologies and properties of metal materials (Moscow, Science) (in Russian)
[2] Roldugin V I, Fedotov M A, Folmanis G E, Kovalenko L V and Tananaev I G 2015 Formation of aqueous colloidal solutions of selenium and silicon by laser ablation Doklady Physical Chemistry 463, 1 pp. 161-164 DOI: 10.1134/S0012501615070064
[3] Golubkina N A and Papazyan T T 2006 Selenium in nutrition. Plants, animals, humans (Moscow, Print city) (in Russian)
[4] Karpova E A, Demidenko O K and Iлина O P 2014 To the question of the toxicity of nanoselenium-based substances Newsletter of KSAU 4, pp. 207-210 (in Russian)
[5] Khramtsov A G, Serov V A, Timchenko V P and Miroshnichenko M V 2010 New biologically active substance based on selenium nanoparticles Newsletter of NKSTU 4, pp. 122-125 (in Russian)
[6] Zhang J, Wang X and Xu T 2008 Elemental selenium at Nano Size (Nano-Se) as a potential chemopreventive Agent with reduced risk of selenium toxicity: comparison with Se-Methylenocysteine in mice Toxicological sciences 10, 1 22-30 DOI: 10.1093/toxsci/kfm221
[7] Folmanis G E, Fedotov M A, Kovalenko L V, Roldugin V I and Tananaev I G 2018 Influence of the vessel wall material on the dispersion of selenium in an ultrasonic bath Physics and chemistry of materials treatment 1 88-92 (in Russian)
[8] Simakin A V, Voronov V V and Shafeev G A 2004 Formation of nanoparticles by laser ablation of solids in liquids Proc. of Prokhorov General Physics Institute 60 83-107 (in Russian)
[9] Novik A A 2010 The use of ultrasound in the production of nanomaterials Proc. of the XXII session of the Russian acoustic society pp. 276-278 (in Russian)
[10] Nikonov I N, Folmanis J G, Kovalenko L V, Laptev G Y, Folmanis G E, Egorov I A, Fisinin V I and Tananaev I G 2012 Biological activity of nanoscale colloidal selenium Doklady Biochemistry and Biophysics 447 1 297-299 DOI: 10.1134/S1607672912060075
[11] Gelyakhov I M, Kompantsev D V, Privalov I M and Stepanova E F 2017 The production and study of cosmeceuticals agent with biologically active compositions of nanoselenium Electronic scientific J. Modern problems of science and education 5 (in Russian)