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The obtaining of biologically active substance by mechanical dispersion of selenium particles in water

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Abstract. Selenium colloidal solutions with particles ranging from 20 to 100 nm were obtained by mechanical dispersion of selenium pellets in water at frequency of 100 Hz. It is shown that the properties of selenium colloidal solutions prepared by mechanical dispersion depend on the material of the vessel in which they are obtained. The selenium solutions obtained in plastic vessels have acidic properties, while in glass vessels they are alkaline. Upon evaporation of colloidal solutions, highly anisotropic dendritic structures are formed, which may indicate anisotropy of the formed nanoparticles. The aqueous colloidal system of nanoscale selenium obtained by mechanical dispersion in concentrations physiologically significant for plants has a positive effect on the seeds of agricultural crops. Selenium colloidal solutions have greater antioxidant activity compared to sodium selenite with lower toxicity values.

1. Introduction

In the early 60s of the 20th century, the establishment of the antioxidant properties of selenium made it possible to consider it as a trace element for human and animal life. One of the main functions of selenium is to enhance the immune defense of the body [1]. Selenium basically enters the body with plant origin food. The use of inorganic selenium compounds for the preparation of functional foods is undesirable, since its particles are highly toxic [2]. The use of selenium nanoparticles has proven to be a promising process. Unlike ionic forms, selenium nanoparticles are less toxic, are easily absorbed by the body, and have a prolonged effect [3]. Selenium also plays an important role in the regulation of plant life [4].

Medications generally are prepared on the basis of colloidal solutions of biologically active substances [5]. For the preparation of colloidal solutions, various methods of dispersion are used, allowing one way or another to grind up the initial material to a nanoscale state. The laser ablation method turned out to be very effective, making it possible to obtain Se nanoparticles [6, 7]. However, this technique is still expensive, which limits its widespread use. An alternative is the method of mechanical dispersion in distilled water as an environmentally friendly dispersion medium [8]. The preparation of a substance in a nanoscale state in mechanical plants occurs by the shock interaction between macroscopic particles of a substance.

The aim of the work is to obtain an aqueous colloidal solution of biologically active selenium by mechanically dispersion its granules at a sufficiently low frequency (100 Hz).



2. Materials and Methods

Chemical glass vessels and clear polystyrene vessels were installed on a vibrating polishing machine Metapolan-2 with a vibration frequency of 100 Hz. Bidistilled water with pH value of 6.32 and pellets of high-purity selenium was poured into the vessels. Mechanical dispersion was carried out for 25–30 hours at a temperature of 300 K. After dispersion, the aqueous solution was settled together with the granules until clarification.

The concentration of selenium in the solution was determined on an atomic emission spectrometer with inductively coupled plasma ULTIMA-2 instrument (Horiba Jobin-Yvon, France). The size distribution and ζ -potential of selenium particles was measured on a Zetasizer Nano ZS instrument (Malvern, United Kingdom). It is known that as a result of the thermal motion the particles of the dispersed phase in colloidal systems perform random motions, changing the direction about 10^{14} times per second, therefore several successive measurements were on the instrument. Determination of the solution pH was carried out on a S220 Seven Compact device (Mettler Toledo, Switzerland).

The clarified selenium solution was evaporated at a temperature of 50–70 °C in glass vessels with a volume of 20–30 ml (figure 1). The upper narrow glass plate with size 1.5x15x50 mm prevented the entrainment of selenium particles with water vapor when the vessel was heated. The lower glass plate with a size of 1.5x10x25 mm was used to control the precipitation of selenium particles from a colloidal solution on its front and back sides. The face side was considered the side of the plate facing the solution in the vessel. The solution was evaporated on an electric heater. The surface temperature of the heater was controlled by a copper-constantan thermocouple. At the temperature of 60–70 °C, the process of complete evaporation of the solution in air lasted about 60 hours. After the solution was completely evaporated, the glass plates were taken out for investigation on an optical microscope LENOVO (Germany).

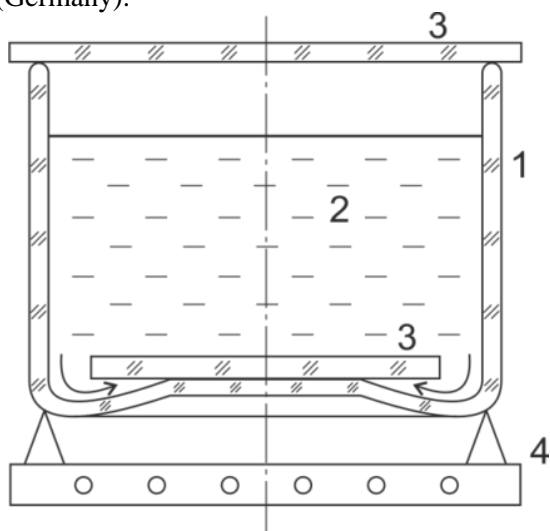


Figure 1. Evaporation process scheme:
1 – glass vessel; 2 – selenium solution;
3 – glass plate; 4 – electric heater.

3. Results

The figure 2 shows the distribution of selenium particles by size and zeta potential in a solution obtained by mechanical dispersion in a plastic vessel for 27 hours. The sample was taken with a syringe from the upper layer of liquid, which was settled in the vessel with selenium pellets for more than five days until complete clarification at 300 K. The selenium concentration was 1.8 mg/l.

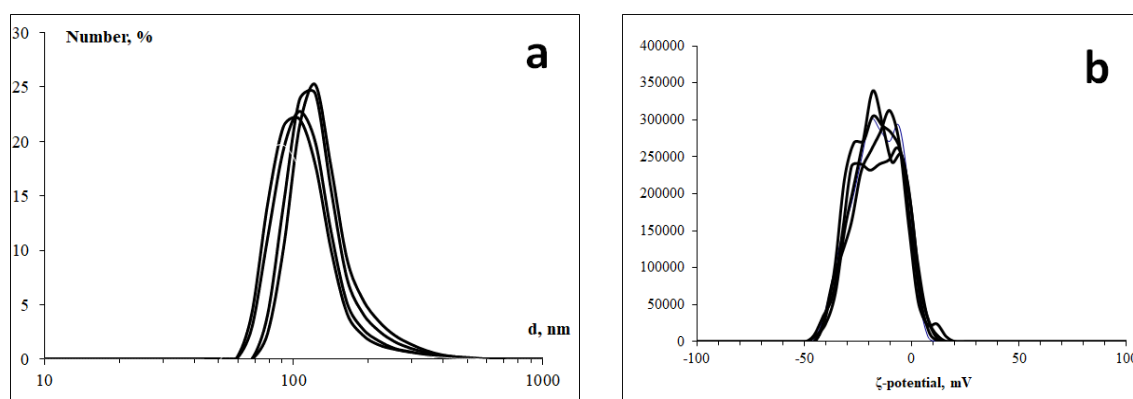


Figure 2. Selenium particle size distribution (a) and particles ζ -potential (b) in an aqueous solution in a plastic vessel after mechanical dispersion of the granules for 27 h. Particle distribution was measured with a time interval of 2 minutes.

The figure 2 shows that the maximum of the particle size distribution is in the region of about 100 nm. The average value of the particles ζ -potential in the solution obtained in the plastic vessel is in the range from -15.4 to -17.0 mV.

The distribution of selenium particles and the ζ -potential of a solution in a glass vessel are shown on figure 3, the dispersion time is ~27 h. Sampling was carried out with a syringe near the surface of the granules. The concentration of selenium in the solution was 10 mg/l. As it is shown on figure 3, particle sizes are grouped around discrete values of ~40, 100, and 500 nm. Thus, a system with a multimodal particle size distribution is formed. Unlike the solution obtained in a plastic vessel, in a glass vessel the particles ζ -potential can be both positive and negative. Its value changes from negative values of about -5 mV to positive +20 mV. In this case, significant changes in time are observed, both in the size distribution of particles and in the values of the ζ -potential.

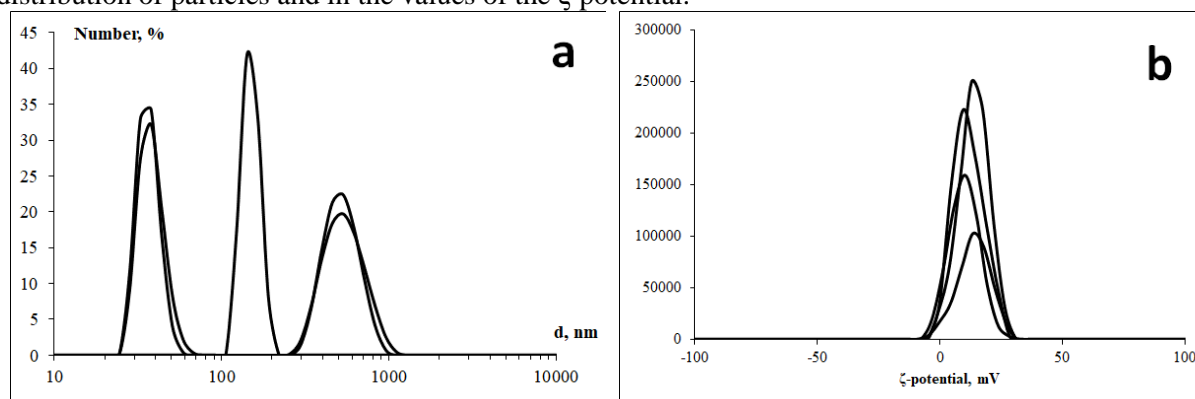


Figure 3. Selenium particle size distribution (a) and particles ζ -potential (b) in an aqueous solution in a glass vessel after mechanical dispersion of the granules for 27 h. Particle distribution was measured with a time interval of 2 minutes.

The results indicate that the process of dispersing the selenium granules proceeds differently in the plastic and glass vessels. This fact is confirmed by the formation of a red strip of amorphous selenium on the wall of the plastic vessel, equal in height to the thickness of the layer of selenium pellets; this strip is not observed on the wall of the glass tube. This can be explained by the difference in the charge of particles formed in the glass and plastic vessels, and the charging of the surface of the plastic wall. When large granules of selenium collide with the wall of a plastic container, a positive charge accumulates on the surface, which binds small particles of amorphous selenium. On the surface of glass wall, the charge does not accumulate, possibly because of its rather high electrical conductivity. In

addition, it is noticed that in the plastic vessel the granules of gray selenium become shiny during the dispersion process, and in the glass vessel the surface of the granules remains matt gray. On the surface of the granules, there is always a gray selenium oxide – SeO_2 , which is formed in air at the melting point of selenium, when the granules are obtained by the drip method. In water, selenium oxide dissolves to form weak selenous acid H_2SeO_3 . It is possible that negative SeO_3^- ions are bound by positive charges on the wall of the plastic container. In this case, SeO_2 is carried away from the surface, and it becomes shiny since pure selenium is practically insoluble in water. It is possible that there are other mechanisms in the plastic vessel that prevent the formation of an oxide film on the surface of the granules. If the solution is removed from the plastic vessel, then after a while the granules will become gray in the air again. In the glass vessel selenium granules always remain gray under the same experimental conditions.

After settling of selenium solution with granules for a long time (several months), the other particle distributions and their ζ -potential values were observed. Thus, the concentration of selenium in the upper layers of the solution decreases, and increases above the surface of the granules. Under the same conditions of preparation process, the selenium concentration above the surface of the granules in colloidal solution in a glass vessel reaches 8–10 mg/l, and in the plastic vessel the concentration of selenium is 2 mg/l.

Depending on the material of the vessel, the colloidal solution may be acidic or alkaline. In glass vessels, the alkaline nature of the solutions increases with time (from 6.94 to 7.23). In plastic vessels, an acidic environment is usually observed, the acidity of which also increases with time (from 6.28 to 5.96). The increase in acidity can be explained by the fact that some of the SeO_2 can enter the colloidal solution from the surface of the plastic wall over time. The other part of SeO_2 probably comes from selenium granules located in the inner layers of the granulate backfill. In our case, the height of the granule layer was 8–10 mm. As for the glass vessel, here it can be assumed that in the presence of weak selenous acid alkali metal atoms contained in glass are transferred into the solution. An excess of alkali metal ions leads to the alkaline nature of the solutions in glass vessels.

Figure 4 shows the distribution of particles in the selenium solution obtained in a plastic vessel with mechanical dispersion for 27 h and clarified during the year without granules. The data on the ζ -potential of the particles are also presented here. It can be seen that the relative proportion of small nanoparticles with a size of 20–40 nm has increased, but the solution is not stable: significant changes in the spectrum are observed during the measurement time. This may be due to a significant decrease in the concentration of particles due to the Ostwald ripening.

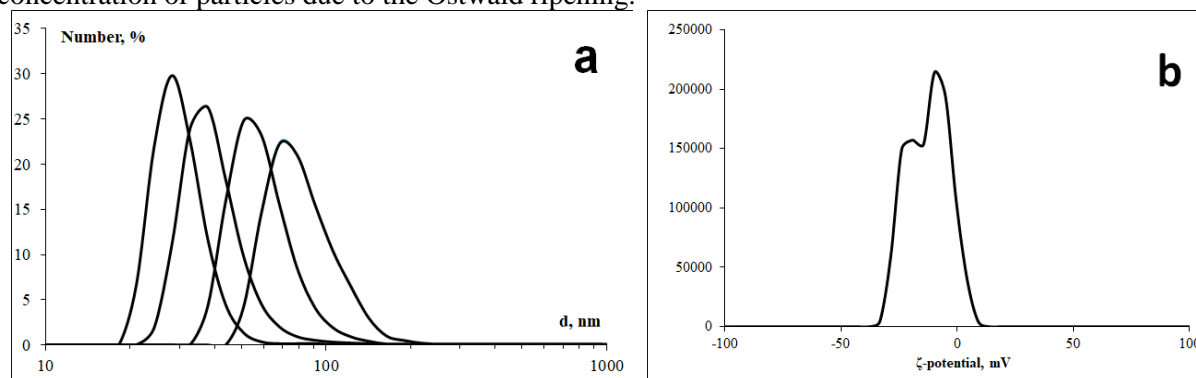


Figure 4. Selenium particle size distribution (a) and particles ζ -potential (b) in an aqueous solution obtained in a plastic vessel by mechanical dispersion for 27 h. Clarification of the solution - 1 year. The concentration of selenium in the solution is 0.17 mg/l. Particle distribution was measured with a time interval of 2 minutes.

When the selenium solutions is evaporate on glass plates, the structures of a dendritic type are also formed, whose dimensions and structure depend on the concentration of selenium in the solution. Figure 5 shows some of the characteristic types of structures observed on the surface of a glass plate turned to the bottom of the vessel. The concentration of selenium in the solution was 0.25 mg/l.

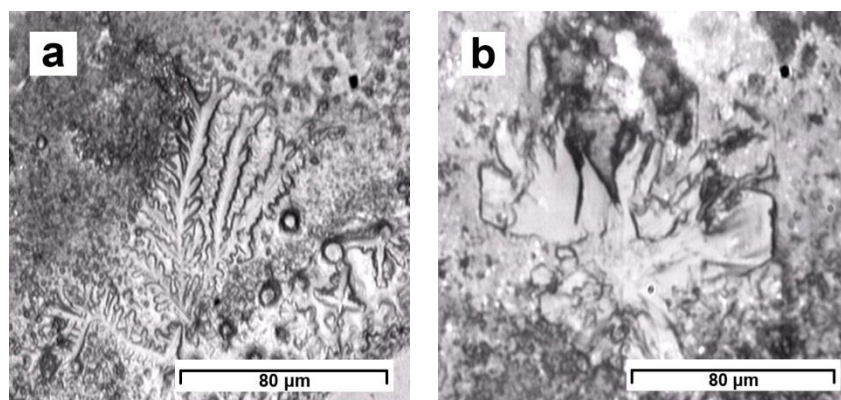


Figure 5. Fractal structures on a glass plate turned with the front surface to the bottom of the vessel (a) and on the front side (b). The concentration of selenium in the solution was 0.25 mg/l. The evaporation temperature of the solution was 60 °C.

It was established that when the solution is evaporated on the upper plate (position 3, figure 1), small accumulations of selenium particles are observed, i.e. there is an entrainment of selenium particles with water vapor.

The obtained colloidal selenium solutions were used to treat the seeds of garden crops. It is established that it has a growth-promoting effect. When comparing the obtained suspension with selenium salts, it was noted that the content of ascorbic acid in radish seedling seedlings is reduced from 35.3 mg/100 g (control sample) to 20.1 mg/100 g in the case of sodium selenite and to 15.3 mg/100 g in the case of colloidal selenium. Selenium colloidal solutions have an antioxidant effect. Antioxidant activity is expressed in mg-equivalents of gallic acid per gram of dry mass (mg-eq. GK/g d.m.) Seeds treated with colloidal selenium have values of 20.1 mg-eq. GK/g d.m., while for sodium selenite this value is 6.9 mg-eq. GK/g d.m. Antioxidant activity of the control sample was 16.3 mg-eq. GK/g d.m.

4. Discussions

By mechanical dispersion of selenium granules in water at a low frequency (100 Hz), colloidal solutions of selenium nanoparticles 20–100 nm in size can be obtained; however, their relative fraction is small compared to larger particles (500 nm or more). With a sufficiently long exposure of colloidal aqueous solutions with selenium granules at 300 K, it is possible to increase the concentration of selenium in the solution near the surface of the granules to 10 mg/l. However, during long-term storage of solutions in the absence of granules, a decrease in selenium concentration to values of 0.1 mg/l or less is observed. At the same time, a precipitate of red amorphous selenium is observed at the bottom of the vessel, which indicates that the nanoparticles interact with each other to form large particles.

When the selenium solutions are evaporated, different fractal structures form on the surface of the glass plates, which indicates the more complex nature of the colloidal solution with selenium nanoparticles than just water and a suspension of particles. It can be assumed that the colloidal solution contains a weak selenous acid, which is formed when the selenium dioxide is dissolved in water. It is known that selenium granules are always covered with a thin layer of SeO_2 , which is highly soluble in water. The mechanical dispersion of the granules of the selenium in glass and plastic vessels showed that the material of the vessel significantly affects the chemical composition of the solutions and their pH. This means that upon receipt of selenium solutions, it is necessary to select carefully the vessel material. Preliminary studies have shown that pure quartz is the most suitable material. An interesting feature of the mechanical dispersion of selenium granules is the change in the optical properties of the surface of the granules depending on the material of the vessel. In a plastic vessel, selenium granules in the solution become shiny, while in a glass vessel the surface of the granules remains matt gray. This indicates that we are dealing with a different chemical environment in the studied solutions, the nature of which is currently not clear. It also follows from the presented results that a part of selenium atoms

are included in various molecular compounds, therefore measuring the concentration as a whole does not give a true distribution of selenium nanoparticles in solution. For example, in a glass vessel, part of the selenium may be bound in the form of alkali metal selenates. Therefore, the given concentration values cannot be attributed only to nanoparticles. It follows from the above that the known antioxidant and immune effect of colloidal solutions of selenium nanoparticles may also be due to various molecular compounds.

5. Conclusion

By mechanical dispersion of selenium granules at a frequency of 100 Hz, colloidal solutions of selenium nanoparticles ranging in size from 20 to 100 nm were obtained. The concentration of selenium in colloidal solutions depends on the material of the vessel. The selenium solutions obtained in plastic vessels have acidic properties, while in glass vessels they are alkaline. Upon evaporation of colloidal solutions, highly anisotropic dendritic structures are formed, which may indicate anisotropy of the formed nanoparticles. Selenium colloidal solutions have greater antioxidant activity compared to sodium selenite with lower toxicity values.

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