

Investigation of the influence of the molecular weight of polyethyleneglycols on the optical properties and dispersed characteristics of sols of Au nanoparticles used in medicine

Abstract

The synthesis of Au nanoparticles stabilized with polyethyleneglycols with different molecular weights from 200 to 8000 Da was carried out. The synthesis was carried out by the method of chemical reduction in an aqueous medium using sodium citrate as a reducing agent. The dependence of the optical properties on the concentration and molar mass of polyethyleneglycol was studied in the obtained samples of Au nanoparticles. The absorption spectra were recorded using an SF-56 optical spectrometer. The studies were carried out in the visible range of the spectrum from 400 to 800 nm. It was found that the type of spectrum, the position of the surface plasmon resonance band and the optical density of the samples of Au nanoparticles stabilized with PEG-8000 with a concentration of 10 and 20% did not undergo significant changes during storage, which characterizes the high aggregate stability of these sols. The dispersed characteristics of these samples of sols of Au nanoparticles were also studied. The studies were carried out using photon-correlation spectroscopy by the method of dynamic light scattering. It is established that an increase in the concentration of the stabilizer leads to an increase in the average hydrodynamic radius of the particles. This fact is associated with an increase in the thickness of the stabilizer layer and with the "stitching" of the polymer layer of Au nanoparticles with the formation of aggregates.

Key words: *Au nanoparticles, polyethyleneglycol, spectrophotometry, plasmon resonance.*

Introduction

Recently, Au nanoparticles have found wide practical application in various fields of science and technology. Au nanoparticles are used in optics to enhance polar-sensitive optical processes (1,2), in biomedicine, as a means of targeted drug delivery (3–7), as a means for the treatment and diagnosis of bacterial infections (8–10), in biosensorics for the detection of oncological diseases, where it acts as an immobilizer of the probe surface (11–13), as heterogeneous catalysts (14–16), in photoelectronics (17).

There are many methods that allow synthesizing Au nanoparticles of various sizes and shapes. The synthesis of Au nanoparticles with a controlled size using condensation in an inert gas is known (18), short Au nanorods (19), monodisperse Au nanoparticles with a tunable size and frequency of surface plasmon resonance (20). Variants of the Turkevich – Frans synthesis method have been frequently used in recent years (21–26). A "green" method for obtaining Au nanoparticles is known, proposed by Raveendran P. (27). In (28), a method for obtaining Au nanoparticles by the electrochemical method is presented. The authors of (29) obtained anisotropic Au nanostructures by photochemical reduction of $HAuCl_4$.

The issue of stabilization of nanoparticles, in particular Au nanoparticles, is relevant (30–37). In (30), the stabilization of Au nanoparticles in aqueous solutions by mononucleotides is considered. It is known that polyethyleneglycol dendrimers are used to stabilize Au nanoparticles (38,39). Chitosan (40–42) and albumin (43) can be used as a stabilizer. In (44), a method for stabilizing Au nanoparticles with pink-blueberry hibiscus extract was described, the presence of Au nanoparticles with a diameter of 16 to 30 nm was confirmed using optical spectroscopy and transmission electron

microscopy. In (45), he reports on the study of stabilized Au nanoparticles from chlorogenic acid using lentinan.

The purpose of this work is to synthesize and optimize the method for obtaining Au nanoparticles, as well as to study the optical properties and stability of the obtained samples.

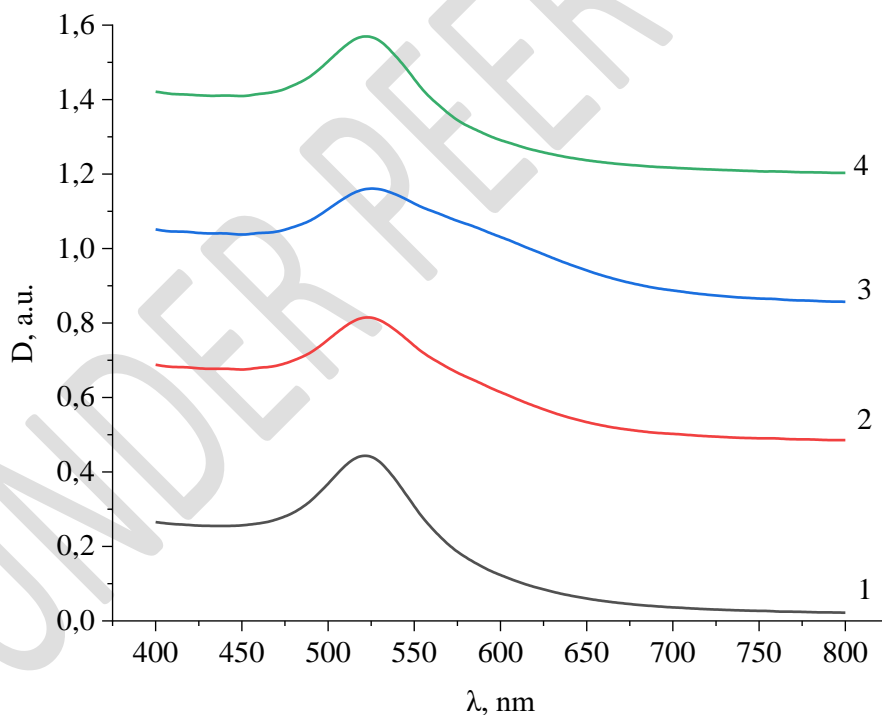
Materials and Methods

In this work, sols of Au nanoparticles were synthesized by the citrate method. Hydrochloric acid was used as a precursor, sodium citrate was used as a reducing agent. Polyethyleneglycol (PEG) with different molecular weights was used to stabilize Au nanoparticles. The concentration of the stabilizer was varied from 1 to 20 wt.%.

The obtained samples of sols of Au nanoparticles stabilized by PEG were studied by the method of dynamic light scattering at the Photocor-Complex installation (Antek-97 LLC, Russia) (46). Computer processing of the results was carried out using the DynaLS computer software.

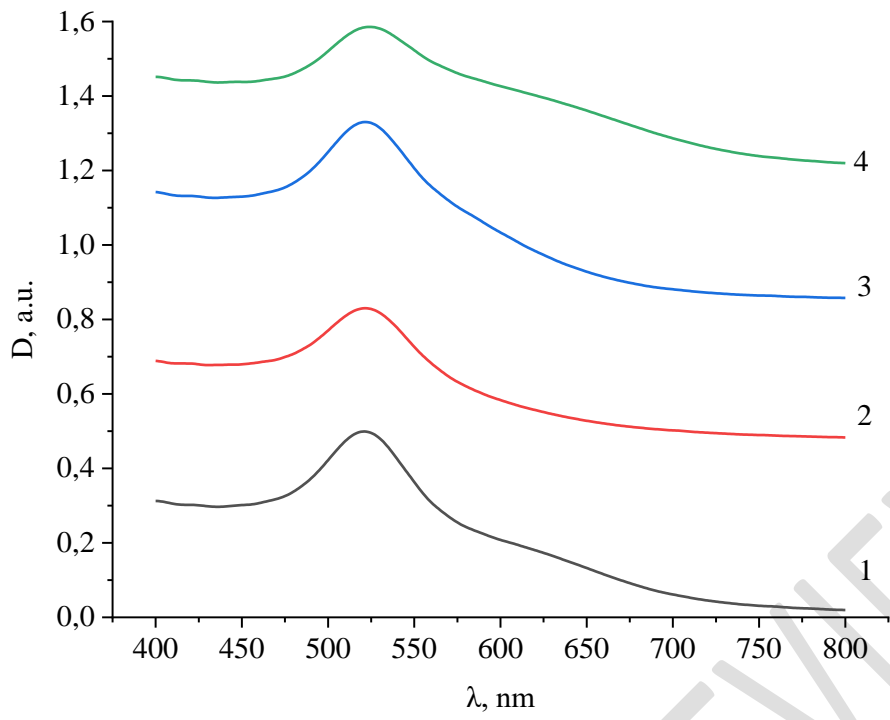
The optical characteristics of sols of Au nanoparticles were studied by optical spectroscopy on the SF-56 spectrophotometer. The studies were carried out in the visible range of the spectrum from 400 to 800 nm (47).

At the first stage, sols of Au nanoparticles stabilized with polyethyleneglycol with a molecular weight from 200 to 8000 Da were studied immediately after production. The obtained results are presented in Figures 1-5.



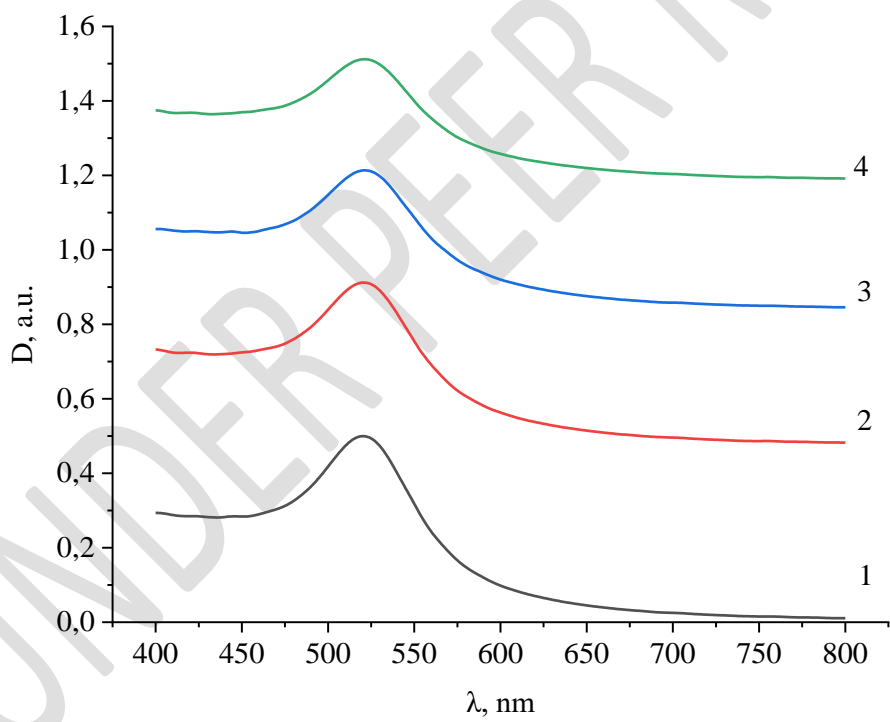
1 – 1 mac. %; 2 – 5 %; 3 – 10 %; 4 – 20 %

Figure 1. Absorption spectrum of Au nanoparticles stabilized by PEG-200



1 – 1 %; 2 – 5 %; 3 – 10 %; 4 – 20 %

Figure 2. Absorption spectrum of Au nanoparticles stabilized by PEG-400



1 – 1 %; 2 – 5 %; 3 – 10 %; 4 – 20 %

Figure 3. Absorption spectrum of Au nanoparticles stabilized by PEG-1500

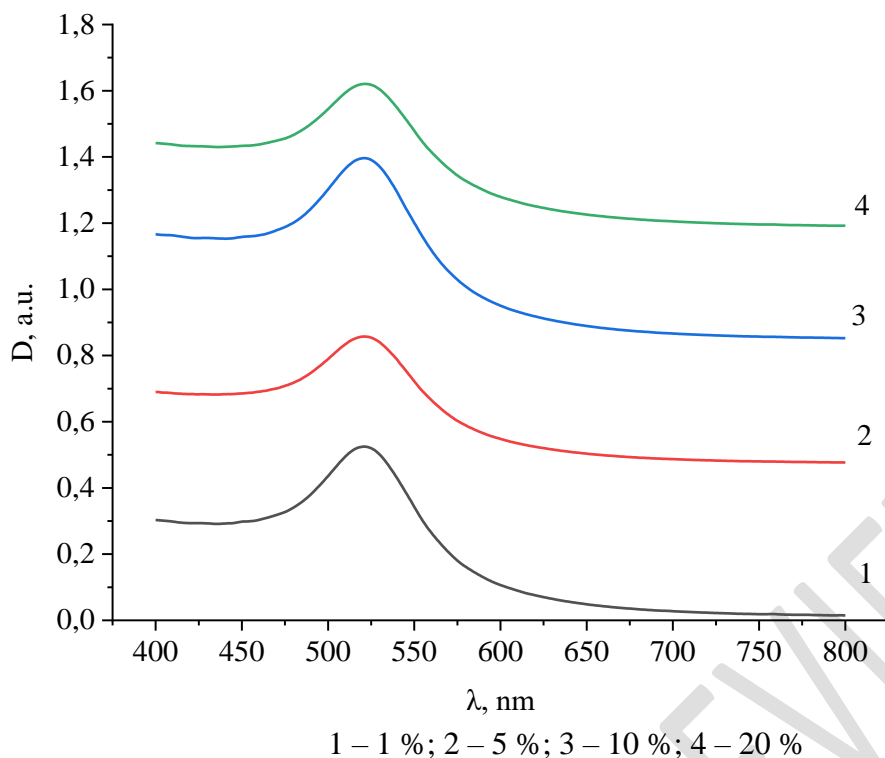


Figure 4. Absorption spectrum of Au nanoparticles stabilized by PEG-4000

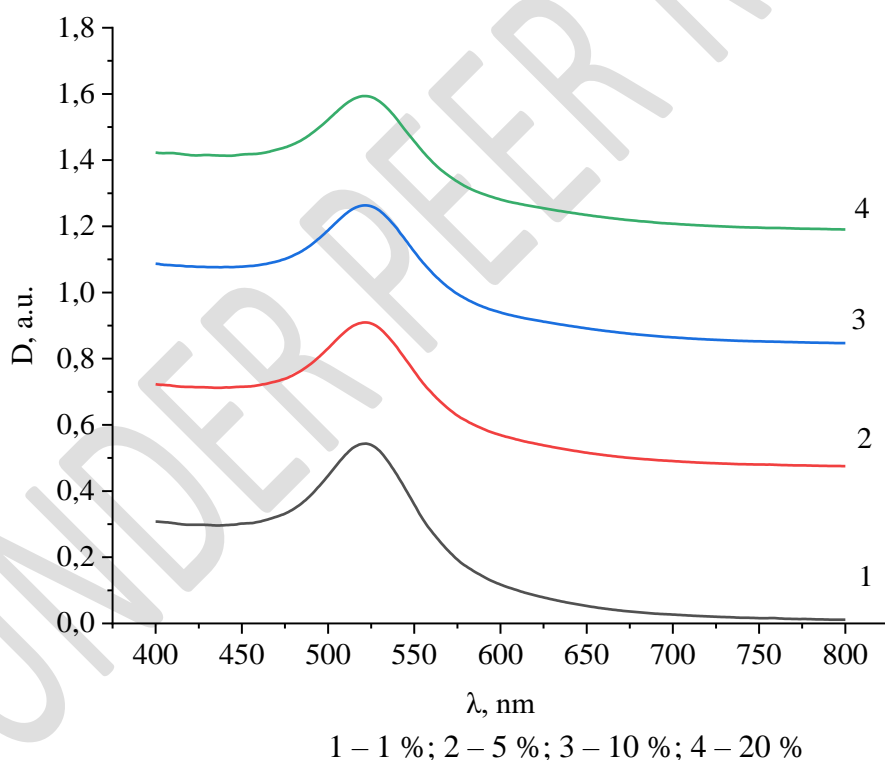


Figure 5. Absorption spectrum of Au nanoparticles stabilized by PEG-6000

As a result of the analysis of the obtained absorption spectra, it can be concluded that Au nanoparticles are present in all samples stabilized with polyethyleneglycol, as evidenced by the presence of bands at 520 – 526 nm in the spectrum, which correspond to the surface plasmon resonance of Au nanoparticles.

Then the sols of Au nanoparticles were re-examined a month later. The obtained absorption spectra are shown in Figures 6-10. Table 1 shows a comparison of the

spectra obtained immediately after synthesis and the spectra obtained a month after synthesis.

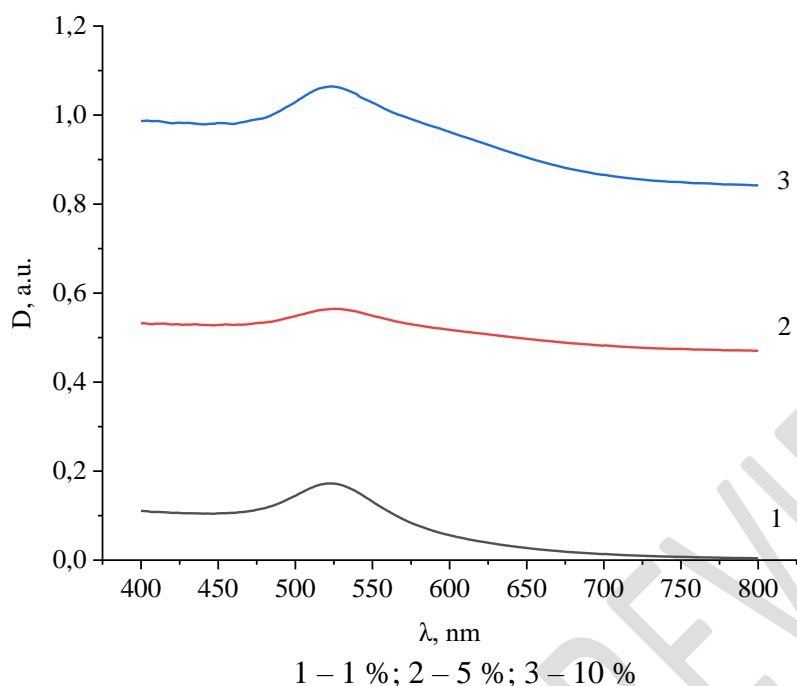


Figure 6. Absorption spectrum of Au nanoparticles stabilized with PEG-200 after 30 days of storage at room temperature

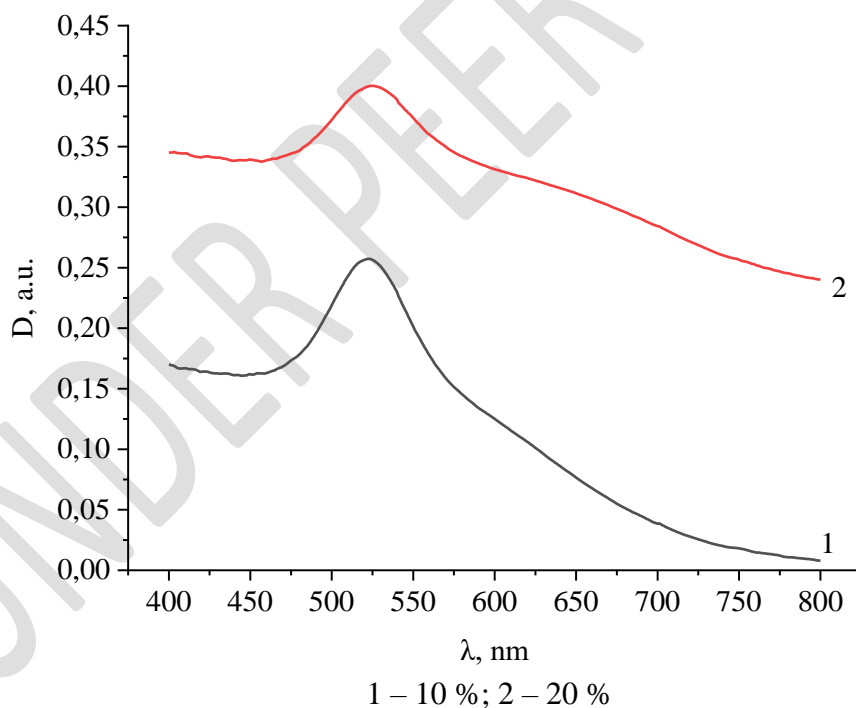


Figure 7. Absorption spectrum of Au nanoparticles stabilized with PEG-400 after 30 days of storage at room temperature

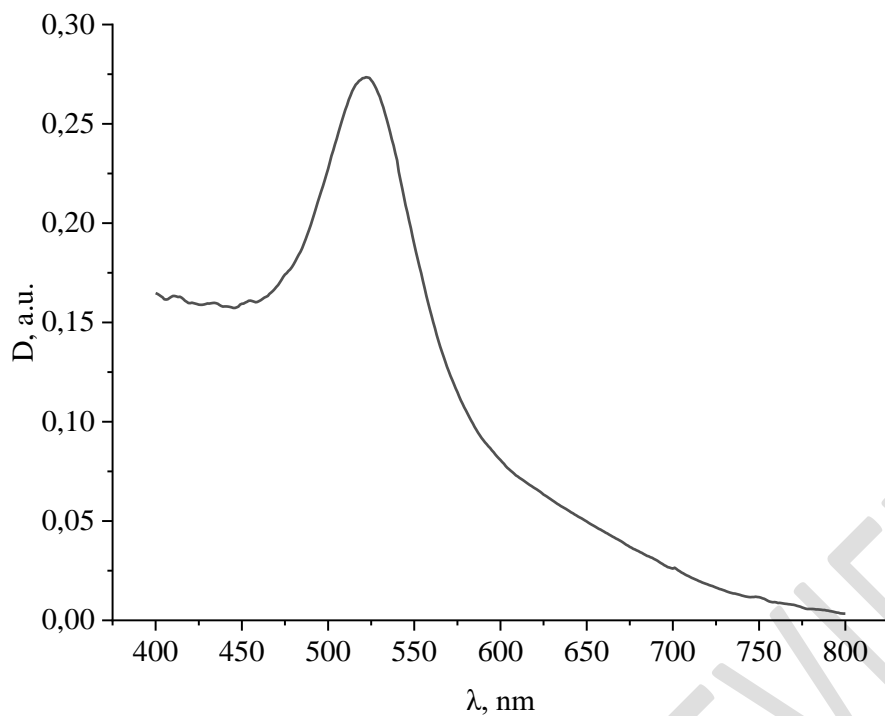
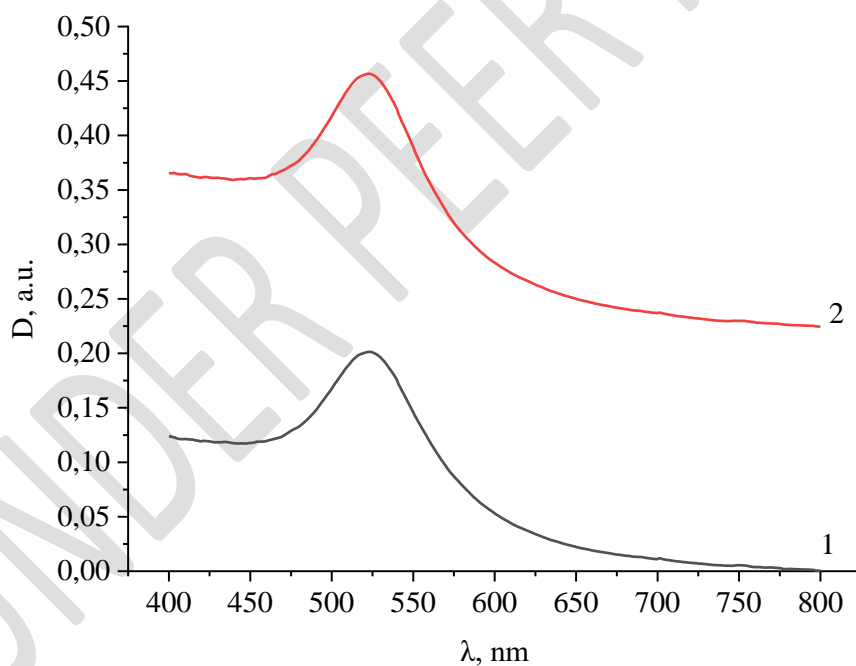
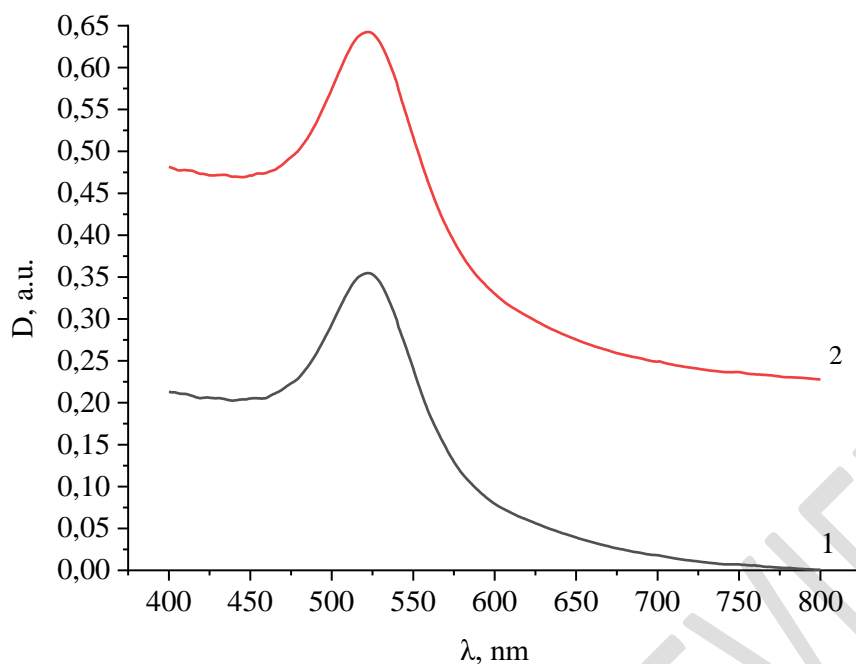


Figure 8. Absorption spectrum of Au nanoparticles stabilized with PEG-1500 after 30 days of storage at room temperature (20% content)



1 – 10 %; 2 – 20 %

Figure 9. Absorption spectrum of Au nanoparticles stabilized with PEG-4000 after 30 days of storage at room temperature



1 – 10 %; 2 – 20 %

Figure 10. Absorption spectrum of Au nanoparticles stabilized with PEG-6000 after 30 days of storage at room temperature

Table 1. Optical properties of Au nanoparticles stabilized by PEG with different molecular weight and concentration

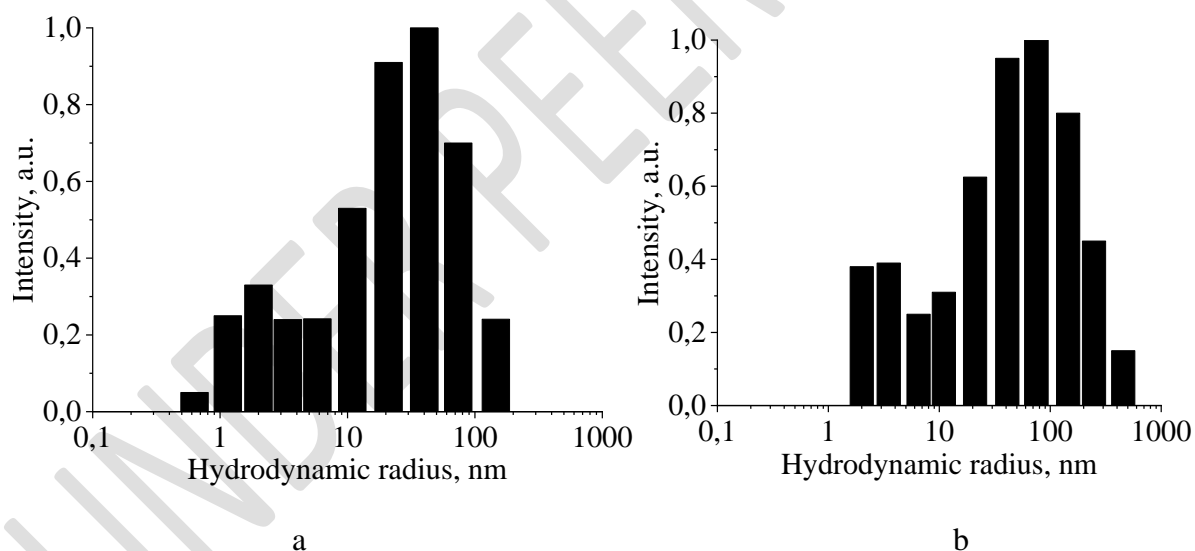
PEG brand	PEG concentration, %	The position of the band at the initial time, nm	The position of the peak λ in a month, nm	D, a u. at the initial moment of time	<i>D, a u.</i> in a month, nm
PEG 200	1	522	470	0,4433	0,1099
	5	523	524	0,3473	0,0971
	10	526	524	0,3259	0,2292
	20	522	0	0,3932	0
PEG 400	1	521	0	0,4991	0
	5	522	0	0,3625	0
	10	522	522	0,4951	0,2573
	20	524	524	0,4093	0,1755
PEG 1500	1	520	0	0,499732	0
	5	521	0	0,4447	0
	10	521	0	0,3784	0
	20	521	522	0,3355	0,2735
PEG 4000	1	521	0	0,5248	0
	5	521	0	0,3898	0
	10	521	523	0,5614	0,2014
	20	522	522	0,4443	0,2318

PEG 8000	1	522	0	0,5433	0
	5	522	0	0,4418	0
	10	522	522	0,4283	0,3548
	20	521	522	0,4173	0,4176

As a result of the analysis of the obtained data, it was revealed that the molecular weight and concentration of polyethyleneglycol significantly affect the stability of sols of Au nanoparticles. The second band is observed in the PEG-400 sample with concentrations of 1 and 20%, which indicates the content of an anisotropic form in the samples. In samples stabilized with PEG-200 with a concentration of 20 %, PEG-400 (1 %, 5 %), PEG-1500 (1 %, 5 %, 10 %), PEG-4000 (1 %, 5 %) and PEG-8000 (1 %, 5 %), a significant decrease in the intensity of the surface plasmon resonance band was found during repeated examination, which indicates the formation of large agglomerates.

The best result was found in PEG-8000 samples with concentrations of 10 and 20%, since the type of spectrum, the position of the surface plasmon resonance band and the optical density did not undergo significant changes. Based on the data obtained, it can be concluded that the best stabilizer for Au nanoparticles obtained by the citrate method is PEG-8000 with a concentration of at least 10 %.

Then, the average hydrodynamic radius of the sols of Au nanoparticles, stabilized polyethyleneglycols with a molecular weight of 8000 Da, was determined by the method of dynamic light scattering. The results are shown in Figure 11 and in Table 2.



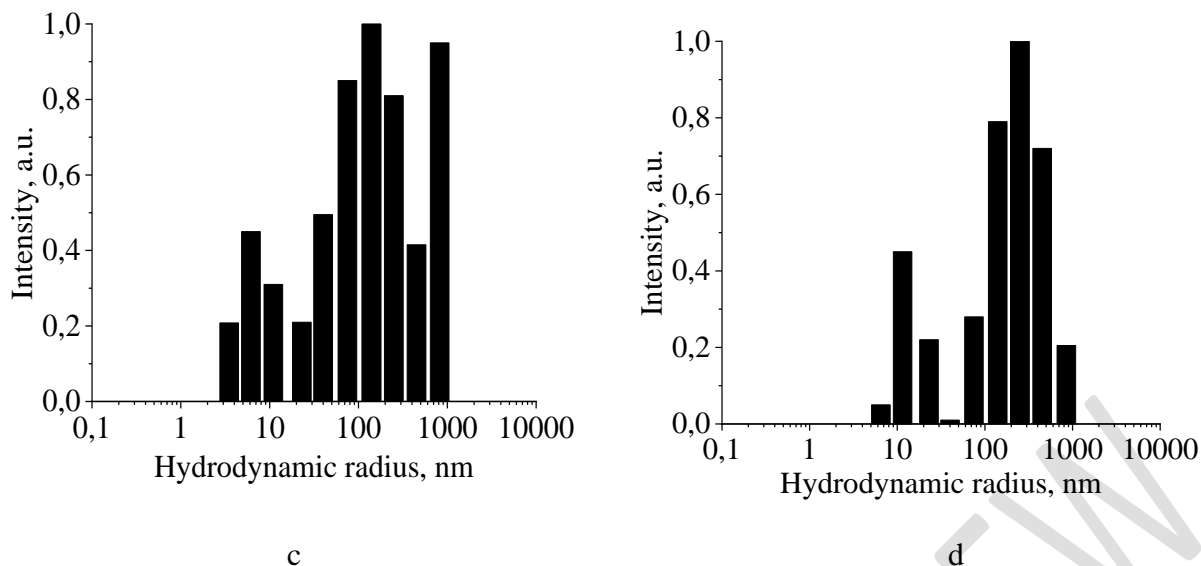


Figure 11. Histograms of the distribution of hydrodynamic radii of Au nanoparticles stabilized with PEG 8000: a-1%; b-5%; c-10%;d-20%

Table 2. Results of the study of Au nanoparticle samples by dynamic light scattering

	PEG 8000 1%	PEG 8000 5%	PEG 8000 10%	PEG 8000 20%
1 st fraction	5 HM	7 HM	10 HM	13 HM
2 nd fraction	75 HM	90 HM	120 HM	200 HM

As a result of the analysis of the data obtained by the method of dynamic light scattering, it was found that in each sample of sols of Au nanoparticles stabilized by PEG-8000, there are 2 fractions: 1 fraction - from 5 to 13 nm, 2 fraction - from 75 to 200 nm. It is important to note that with an increase in the concentration of the stabilizer, the average hydrodynamic radius of the particles increases. This fact is associated with an increase in the thickness of the stabilizer layer and with the "stitching" of Au nanoparticles.

Conclusion

Thus, we can conclude that the best result was found in PEG-8000 samples with concentrations of 10 and 20%, since the type of spectrum, the position of the surface plasmon resonance band and the optical density did not undergo significant changes. Based on the data obtained, it can be concluded that the best stabilizer for Au nanoparticles obtained by the citrate method is PEG-8000 with a concentration of at least 10 %. It is important to note that with an increase in the concentration of the stabilizer, the average hydrodynamic radius of the particles increases. This fact is associated with an increase in the thickness of the stabilizer layer and with the "stitching" of Au nanoparticles.

COMPETING INTERESTS DISCLAIMER:

Authors have declared that no competing interests exist. The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to

use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

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