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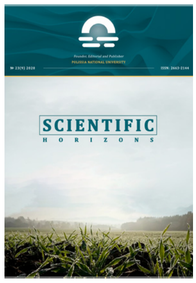

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OPTICAL PROPERTIES OF COLLOIDAL SOLUTIONS OF METAL NANOPARTICLES

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Abstract. Nanoparticles are finding more practical applications in various fields of human activity, including veterinary and medicine. Due to the fact that the effectiveness of colloidal solutions of nanoparticles is directly related to their aggregate state, convenient methods for assessing the physicochemical characteristics of such preparations is of high priority. Nanoparticles have unique optical properties that depend on their size and shape. They can be determined by the refractive index of light on the surface of nanoparticles in a phenomenon known as plasmon resonance, which makes the UV-Vis spectroscopy a valuable tool for studying and evaluating the properties of nanomaterials. Optical characteristics of NPs colloidal solutions of noble metals (silver) or bioelements (copper, silicon dioxide) were determined at various wavelengths (nm): 300–800 nm. The surface plasmon resonance has been found in all test preparations, while all of them exhibited obvious nonlinear optical properties. The most pronounced plasmon resonance peak was found in the colloidal solution of silver NPs within a wavelength of 420 nm. In the case of a colloidal solution of copper NPs, the peak of plasmon resonance was less pronounced and had a red shift (peak at 560 nm). In the colloidal solution of silicon dioxide, the plasmon resonance was less pronounced than in other test preparations, being shifted to the blue side of the spectrum (360 nm). UV-Vis spectroscopy of metal NPs requires further studies to assess their stability and influence of various external factors on their activity

Keywords: nanoparticles, spectroscopy, light absorption, plasmon, plasmon resonance

ОПТИЧНІ ВЛАСТИВОСТІ КОЛОЇДНИХ РОЗЧИНІВ НАНОЧАСТИНОК МЕТАЛІВ

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Анотація. Наночастинки знаходять усе більш практичне застосування в різноманітних сферах діяльності людини, зокрема ветеринарній медицині. У зв'язку з тим, що ефективність дії колоїдних розчинів наночастинок безпосередньо пов'язана зі станом агрегації нанорозмірних частинок, зручні методи оцінки фізико-хімічних характеристик таких препаратів є пріоритетними. Наночастинки мають унікальні оптичні властивості, які залежать від їх розміру та форми. Їх можна визначити за коефіцієнтом заломлення світла на поверхні наночастинок у явищі, відомому як плазмонний резонанс, що робить УФ-візоспектроскопію цінним інструментом для вивчення та оцінки характеристик наноматеріалів. Оптичні характеристики колоїдних розчинів благородних металів (срібло) або біоелементів (мідь, діоксид кремнію) розчинів наночастинок визначали при різних довжинах хвиль (нм): 300–800 нм. Поверхневий резонанс плазмону був знайдений у всіх тестових препаратах, тоді як усі вони виявляли очевидні нелінійні оптичні властивості. Найбільш виражений пік плазмонного резонансу виявляється в колоїдному розчині наночастинок срібла на довжині хвилі 420 нм. У випадку колоїдного розчину наночастинок міді пік плазмонного резонансу був менш вираженим і мав червоний зсув (пік при 560 нм). У колоїдному розчині діоксиду кремнію плазмонний резонанс був менш вираженим, ніж інші тестові препарати, і був зміщений на синю сторону спектра (360 нм). Ультрафіолетова спектроскопія наночастинок металів вимагає подальших досліджень для оцінки їх стійкості та впливу на їх активність різних зовнішніх факторів

Ключові слова: наночастинки, спектроскопія, поглинання світла, плазмон, плазмонний резонанс

INTRODUCTION

Prevention and treatment of infectious diseases in animals is still a serious challenge, despite the obvious achievements of the veterinary pharmacology. Practicing veterinarians are dealing with pathogens that have multidrug resistance. The treatment of such pathologies requires the use of broad-spectrum antibiotics, which are more toxic, more expensive and often less effective than that of a narrow spectrum. In addition, the participation of multidrug-resistant pathogens in the pathogenesis increases the recovery period of a sick animal or the course of its treatment. One of the effective alternatives to the use of classical antibiotics is the introduction of compounds based on colloidal solutions of metal nanoparticles [1; 2]. Their therapeutic effect is always multilateral, but more often it is based on the release of free ions, which are known to have bactericidal properties against a wide group of various pathogens, including viruses and bacteria. Silver NPs, which are considered the most effective among the drugs of this group, are active against more than 150 bacterial species, including methicillin-resistant *Staphylococcus aureus* (MRSA), bacteria of the genera *Acinetobacter*, *Klebsiella* and *Pseudomonas* which comprise the ESKAPE group of microorganisms with pronounced antibacterial resistance.

On the other hand, nanostructures are also much stronger than bulk materials and therefore are widely used in the fields of structural engineering, energy, and chemistry [3]. Silver NPs are of particular interest due to many useful properties. They have high electrical and thermal conductivity and have high optical reflectivity [4]. In addition to commercial use, due to their optical properties, nanoparticles are also used in the popular research area of plasmonics. Silver NPs exhibit pronounced and wide surface plasmon resonances in ultraviolet and visible light due to the strong coherent oscillation of free surface electrons in the nanoparticles [5], which leads to strong absorption and scattering of light. The unique plasmon resonant characteristics in NPs facilitated their introduction into various branches of chemistry and organic synthesis, for example, in the reactions of epoxidation of ethylene and oxidation of carbon monoxide [6].

UV-Vis spectroscopy (Ultraviolet/Visible Light) is a powerful analytical research tool for several reasons. It allows to quickly and accurately compare the properties of a large number of samples without prior knowledge of their nature. By comparing the spectroscopic characteristics of several samples, it is easy to determine whether their electronic structures differ [7; 8]. Due to the fact that the spectroscopic properties of colloidal solutions of nanoparticles very much depend on their homogeneity [9], UV-Vis spectroscopy can quickly and reliably determine their qualitative characteristics [10].

In fact, UV-Vis spectroscopy is based on measuring the amount of ultraviolet and visible light that is absorbed by a sample. From a physics perspective, after the absorption of photons by the test sample, the electrons become excited in the material and transit to a high-energy state, creating a spectral characteristic at the given wavelength. UV-Vis spectroscopy is a recognised method for assessing colloidal aggregation of substances, especially for particle of microscopic size. Despite its undeniable advantages, this method has certain limitations. In particular, due to the fact that the measured light signal varies both depending on the volume fraction and size of the particles, and only if both parameters are changed simultaneously, the qualitative characteristics of the sample can be reliably evaluated. For plasmon NPs exhibiting strong light absorption, UV-Vis absorption spectroscopy overcomes this limitation, since absorption is closely related to the physical properties of the nanoparticle itself [11].

The aim of the work was to study the optical characteristics of colloidal samples of nanoparticles based on noble metal (silver) and bioelements (copper, silicon dioxide) in order to determine the possibility of further application of UV-Vis spectroscopy to assess the activity and stability of NPs colloidal solutions.

MATERIALS AND METHODS

The optical characteristics of colloidal solutions of metal and bioelements nanoparticles were assessed by the presence of plasmon resonance peaks in the absorption spectra of colloids. Plasmon resonance is a resonant oscillation of free electrons on the surface of nanoparticles under the influence of a time-varying external electromagnetic field created by electromagnetic waves. This phenomenon is a strong indicator that the material under examination is nanosized in its physical parameters. It is believed that the width of the plasmon resonance peak indicates a greater heterogeneity in the NPs size in the test sample, and the absorption intensity of plasmon resonance (peak height) decreases with decreasing nanoparticle size [10]. In some papers [12] it was shown that the position of the plasmon resonance band shows an exceptional dependence on the size of nanoparticles.

The rate of light absorption at a specific wavelength (λ) is determined by the equation (1):

$$\alpha_{\lambda} = log_{10} (I_0/I_1) \quad (1)$$

where I_0 – impinging light intensity; I_1 – light intensity transmitted through the sample.

The table 1 shows the correspondence of the absorption index to the numerical values of the percentage of light absorption by the sample.

Table 1. *Correspondences of the light absorption to the optical characteristics of the sample*

Light absorption (α_{λ})	Light absorption intensity (%)	Intensity of light transmitted through a sample (%)	I_0/I_1
0	0	100	1
0.25	43.7	56.23	1.778410101
0.5	68.38	31.62	3.162555345
1	90	10	10
2	99	1	100
3	99.9	0.1	1000
4	99.99	0.01	10000

To study the optical characteristics of colloidal solutions, commercial formulations based on nanoparticles of noble metal (silver) and bioelements (copper, silicon dioxide) in the recommended dilutions were used. The size of the nanoparticles, according to the manufacturer, was in the range of 10–40 nm. At the time of the experiment, all preparations had an unexpired shelf life (manufacture date within 2–4 months), met the physicochemical parameters declared by the manufacturers. After the solutions were added to the cells, the samples were allowed to stand for 10 minutes at room temperature to free them from gas bubbles.

The optical density and absorption spectra were determined with the Hanon I3 spectrophotometer (manufactured in China) at the following wavelengths (nm): 300, 320, 340, 360, 380, 400, 405, 410, 415, 420, 425, 430, 440, 460, 480, 500, 520, 540, 560, 580, 600, 650, 700, 750, 800. The uneven reading of the absorption indexes (α_λ) was determined by the expected plasmon resonance peak of colloids lying in the electromagnetic wavelength range of 300–600 nm. Before analysing the samples, the basic measurements of the solvent (distilled water) used as the zero sample were recorded.

RESULTS AND DISCUSSION

In the course of spectrophotometric analysis of the tested samples of the nanoparticle colloids, indexes of light absorption at different wavelengths were obtained, which are listed in Table 2.

The numerical data from Table 2 was used to draw graphs for visual detection of the plasmon resonance peaks in the considered samples of NPs colloidal solutions (Figs. 1–3).

***Table 2**. Light absorption indexes of NPs colloidal*

Wavelength (λ)	Light absorption (α_λ)		
	Silver nanoparticles	Copper nanoparticles	Silicon dioxide nanoparticles
300	0.548	1.297	0.475
320	0.344	1.262	0.398
340	0.669	1.237	0.407
360	1.42	1.221	0.380
380	2.284	1.199	0.360
400	2.722	1.182	0.348
405	2.725	1.175	0.341
410	2.728	1.168	0.335
415	2.735	1.164	0.330
420	2.756	1.156	0.324
425	2.655	1.148	0.321
430	2.616	1.137	0.316
440	2.261	1.126	0.311
460	1.108	1.101	0.306
480	0.574	1.072	0.289
500	0.345	0.962	0.280
520	0.287	0.934	0.271
540	0.247	0.915	0.263
560	0.220	0.952	0.256
580	0.154	0.827	0.248
600	0.089	0.742	0.243
650	0.064	0.347	0.231
700	0.045	0.213	0.224
750	0.036	0.178	0.219
800	0.026	0.073	0.209

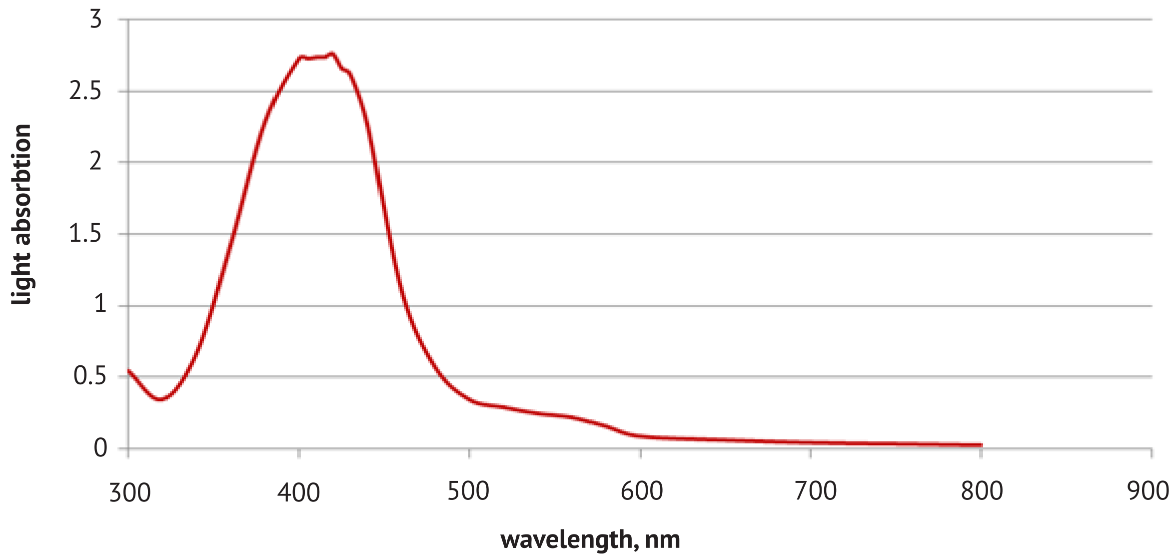

Figure 1*. Spectrophotometric characteristics of a colloidal solution of silver nanoparticles*

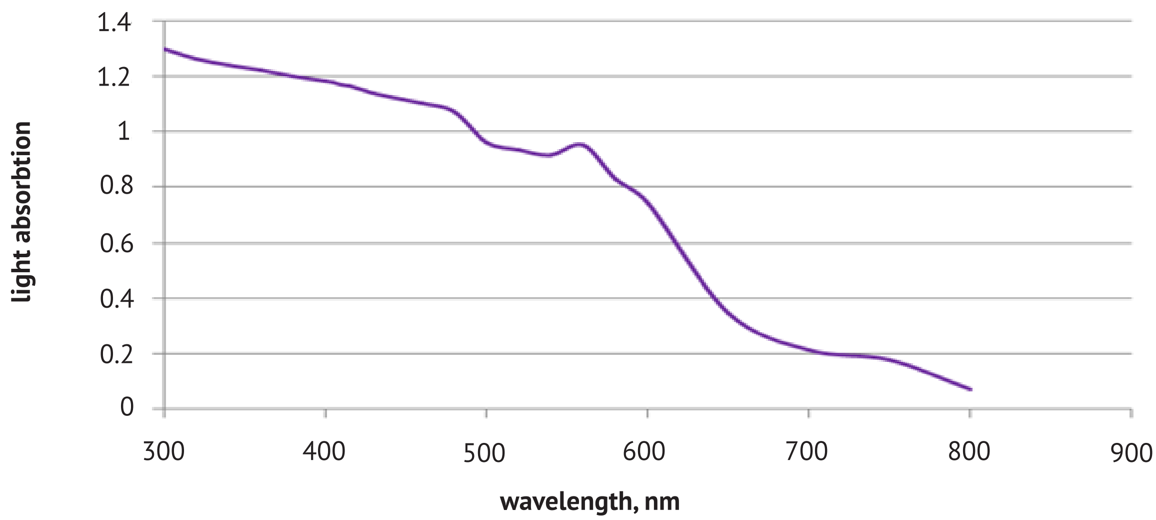

Figure 2*. Spectrophotometric characteristics of a colloidal solution of copper nanoparticles*

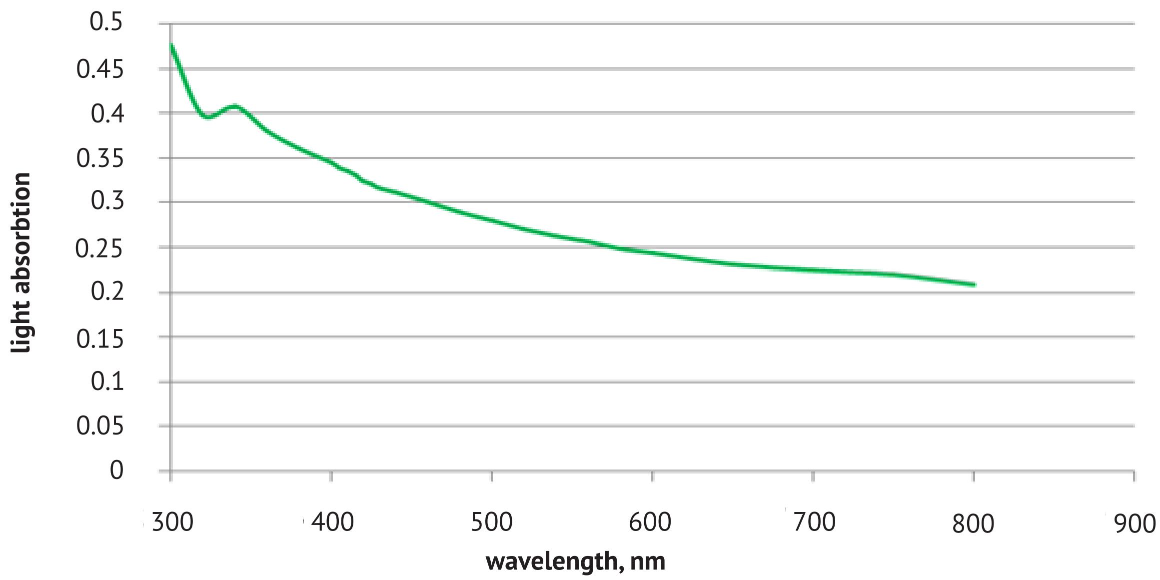

Figure 3*. Spectrophotometric characteristics of a colloidal solution of silicon dioxide nanoparticles*

The constructed graphs (Figs. 1–3) demonstrate the presence of surface plasmon resonance in all tested preparations, due to which they all exhibit obvious nonlinear optical properties. The most pronounced peak of plasmon resonance is present in the colloidal solution of silver nanoparticles, which lies within the wavelength of 420 nm. In the case of the colloidal solution of copper nanoparticles, the peak of plasmon resonance turned out to be less pronounced and, moreover, the red shift was noted (its peak falls on the length of 560 nm). In the colloidal solution of silicon dioxide nanoparticles, plasmon resonance was less pronounced compared to the other tested preparations, being shifted to the blue side of the spectrum (360 nm).

In connection with the above matter, among the studied samples, a much more pronounced plasmon resonance was observed in a colloidal solution of noble metal (silver) nanoparticles, since the strong light absorption is due to its surface plasmon resonance properties. In addition, according to some authors [13], noble metal NPs exhibit light absorption peaks that strongly depend on the size, shape, ratio, composition of the nanoparticles and their antibacterial activity [14; 15]. This opens a possibility to subsequently conduct a series of additional experiments to evaluate the stability and activity of colloidal solutions of nanoparticles by their spectrophotometric analysis.

CONCLUSIONS

The performed research allows to draw the following conclusions and outline the following prospects for further inquiry:

1) colloidal solutions of nanosized metal particles have consistently uniform optical characteristics, which accessibly can be determined by conducting the UV-Vis spectroscopy;

2) peaks in the intensity of light absorption due to the plasmon resonance on the surface of metal NPs have the most pronounced characteristics in the noble metal (silver) nanoparticles compared to nanoparticles of bioelements (copper and silicon dioxide);

3) the method of UV-Vis spectroscopy of nanosized particles of noble metals and bioelements requires further research to assess their stability, safety and the impact of various external factors on their activity.

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