

Metals Hydrosols Universal Extinction Spectrum of 0.2 Micrometer Wavelength Ultrafine Component

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Abstract: The results of comparative experiments on hydrosol of metals and weak metal saline solution with 0.2 micrometer wavelength spectroscopy have been presented. Quality identity of the spectrum for all examined metals such as Ag, Cu, Na, Ni, Fe, has been defined. In conclusion based upon the similarities between metal colloid solutions and salt solutions with 0.2 micrometre wavelength ($\lambda = 0.2$ mkm) extinction spectra, a metal corpuscular and atomic component, as well as low level clusters were found in the solutions.

Keywords: Hydrosol of Metals, The Spectrum for Metals, Atomic Component in the Solutions, Metals Skin Layer, Spectrum of Absorption, Silver Hydrosol Solution, Absorbent Material Busofit, Silver Crystals

1. Introduction

The purpose of this work was to attempt to explain the phenomenon of extinction band in metal colloidal solutions, acquired through Electrical Discharge Technology in the area of 0.2 micrometer wavelength. The obtained results can be used for direct measurement of an atomic component presence in metal colloid solutions. This method compared with chemical methods [16] gives significant advantages. The development of the methods of estimation of atomic component concentration in these solutions is presented, i.e. the component obtained by the water existing single atoms and their low level clusters were found. The existence of this component in hydrosols of metals acquired by electrical impulse charge in liquids [1] has resulted from the existence of power emission in the area of the discharge, which is significantly increased the power evaporation needs. So, firstly, the metal appears in the water as single atoms' component. In the discharge zone, energy emission is significantly bigger than the energy evaporation needs. So firstly, the metal appears in the water as single atoms.

Particularly, there are multiple evidences of biological

activity increase while the size of silver particles in the solutions is being decreased. Therefore, the development of ultra-dispersed measurement test method for colloid solution components gives promising opportunities.

2. Colloid Solutions Spectroscopy Background; Problem Definition

The electrical discharge treatment of metal colloidal water solutions obtain technology has been detailed described in reference [1]. According to the mentioned above technology, multiple repeated milliseconds short-term, high-voltage (2-3 kV) (electric pulsed corona discharge PCD) is being carried out between two metal electrodes which are submerged in distilled water. This method to get colloid solution has significant advantages over the traditional chemical method [13, 14], as it enables to reduce the amount of impurities. The direct measurement of discharge parameters has shown that the energy released in the colloid spot area where the shock cord is being concentrated and then the erosive crater has

been formed, at least, much exceeds the energy necessary for crater volume size metal evaporation. On this basis, the conclusion has been made [1] that in the process of in-water discharge a flow of water metal steam, i.e. the flow of single high-speed metal atoms, is being injected.

Owing (insert indent) to high concentration of metal atoms in each separate portion of steam and high speeds of atoms move, the frequency of interatomic collisions ranges high as well. Therefore, by the time the steam cools, a significant number of atoms are being formed into particles, which size in case of silver made 20-60 nanometers. However, it seems quite obvious that due to a probability nature of the process, some atoms remain single. Moreover, after being cooled the speed of their motion is decreased and (OH) complexes are being formed due to their hydration. The probability of the formation of particles from the "cold" hydrated atoms of metal is (extremely insignificant). The mentioned above clearly explains the atomic component existence in metal colloid solutions, which was firstly published in [3].

The spectrogram extinction analysis based method of colloidal solution research is considered the most widespread method.[7-10].

The characteristic of hydrosols of metals spectra of extinction (absorption + scattering) is the existence of intensive absorption spectra which is caused by Surface Plasmon Resonance (SPR) with its maximum at the frequency of the metal [11] valence electron plasma oscillations.[11].

$$\omega = \left(\frac{4\pi e^2}{m} N_e \right)^{1/2} \quad (1)$$

where: e and m - charge and electronic mass respectively, N_e - concentration of valence electrons.

Some single properties of hydrosol of metals can be easily diagnosed by the shape of extinction spectrum SPR. For example, for silver and gold these maximums are located at 0.4 μm for silver, and at 0.55 μm for gold. The SPR caused explicit extinction is being observed in the limited band of metal particle sizes

$$\delta \leq d \leq \lambda \quad (2)$$

Where: δ - metal skin-layer thickness

λ - the wavelength of the probing radiation.

For the majority of metals skin layer thickness for optical range ≈ 0.01 microns, that is about 10 nano meters. If the particle size is less than δ , the electromagnetic wave of the probing radiation extends through it practically without indignation; if the particle size considerably exceeds the wavelength of the probing radiation, the wavelength not connected geometrical shadow effect becomes essential.

Aforesaid has been fully confirmed by experimental data. The silver hydrosol with particle size of 20-60 nanometers has firmly expressed extinction maximum on about 0,4 microns wavelength. When the particles being grinded to 3 nanometers, which is less than the skin-layer thickness at the wavelength of 0, 4 microns, [6] the extinction has decreased to the background values. A research of an experimental test

of the second restriction for SPR, hasn't been carried out as the size of the formed particles did not exceed 100 nanometers and short-wave border of the probing radiation was 195 nanometers, that is in all experiments $d < \lambda$ equaled.

In hydrosol of silver, for the first time [3], attention has been paid to the existence of the second, additional to SPR spectrum, spectra in the vicinity $\lambda = 0, 2$ microns.

It should be noted that in different studies on metal optics [7] as well as experiments on colloidal solutions spectroscopy [8-10], the growth of extinction while the wavelength is less than 0,3 microns reduced, is shown. However, in none of these studies either a short-wave range border of the increase or the nature of short-wave absorption is specified. The situation is also being complicated by the fact that SPR maxima of extinction of metals (Fe, Ni, Cr) is located in a range of 0,22 - 0,28 microns.

The experiments in which the particles were grinded into the sizes smaller than the thickness of skin layer [6] and soaked in distilled water with massive metal samples [3] have shown no spectra of extinction band formed by SPR, but at the same time the spectra of extinction in the vicinity $\lambda = 0,2$ microns remained, and it was identical to all metals (Ag, Cr, Fe, Ni, Zn, Cu) studied. This basis enables the authors to consider extinction in the vicinity $\lambda = 0,2$ microns a consequence of the presence of metals in the form of single atoms or their clusters of the lowest orders in the water.

In this research an attempt has been made, firstly, to define the criteria range for the spectrum of extinction appearing in water and metal mixes at an extinction spectrum in the vicinity of wavelength $\lambda = 0,2$ microns; secondly, to analyze the nature of absorption of radiation on lengths of waves vicinities $\lambda = 0,2$ microns; and, thirdly to estimate the possibility of absorption usage on this wavelength for water- and metal- mixes diagnostics in particular for determination of atomic components concentration of metals.

3. Materials and Methods

Using spectrometer WTW Photolab 6600UV, the extinction spectra, such as absorption and dispersion spectra in weak metal salt solution of Ag, Cu, Na, Ni, Fe metals, metal colloid solutions and water solutions mixtures, which were obtained by the distillate water infusion of cuprum, stainless steel, and silver plated component, have been recorded. A typical salt and colloid silver solutions spectrograms are shown in Fig. 1- Fig. 3.

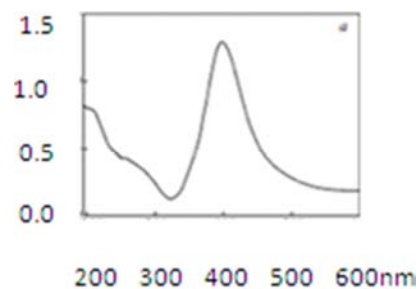


Figure 1. Spectrum of absorption of colloid silver solution.

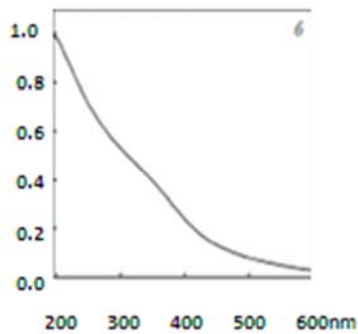


Figure 2. Spectrum of absorption of weak salt Na_2CO_3 solution.

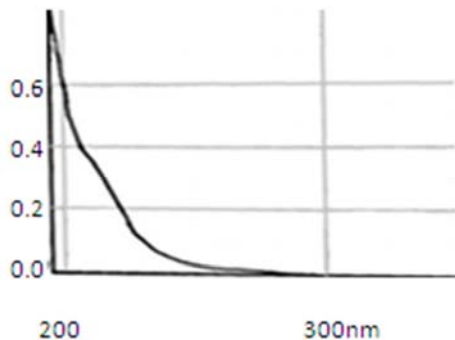


Figure 3. Spectrum of absorption of iron colloid solution.

In order to prove the possibility of interconverting of a corpuscular based component into an atomic component of colloid solutions, the spectra of extinction have been registered in THE COLD solutions at standard room temperature; as well as THE HEATED, heated up to 80°C (Fig. 4).

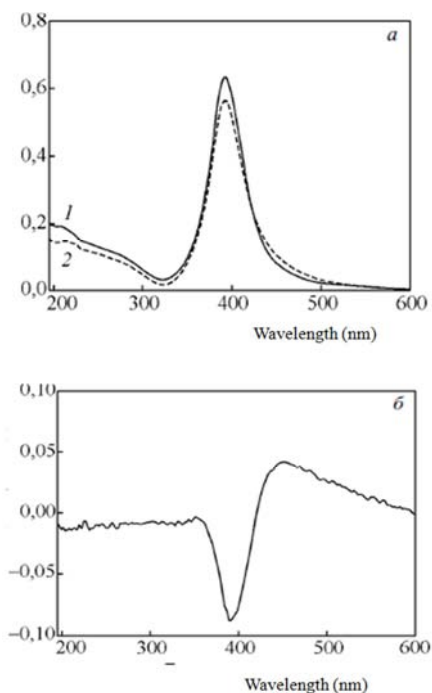


Figure 4. Silver hydrosol solution in standard room temperature experiment (1), Silver hydrosol solution in 80°C heated experiment (a), Differential spectrograms of silver hydrosol in $t=80^\circ\text{C}$ (spectrogram at 20°C is considered as ZERO).

For the high quality comparison, salt solution spectrum with the spectrum of 0.2 micrometer wavelength Ag colloid solution, the normalized spectrograms of the values proportional to the K indexes of extinction were laid one on another. (Figure 5).

Value K was calculated according to the equation:

$$K = \ln[1/(1-A)] \quad (3)$$

where A is the sample registered absorptivity.

In Figure 5, for each sample K ($\lambda=0.2$ micrometers) the wavelength is considered as 1, where as the correlation $K(\lambda)/K(0.2 \text{ micrometer})$ is used for the others wavelength. Extinction spectrum match for the all examined samples, including Ag hydrosol, which have been normalized by the described methods, seems evident.

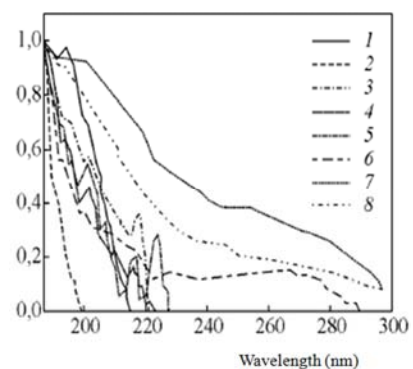


Figure 5. Normalized by 1, spectra extinction of distilled water mixture, which contains singular metal atoms, where.

- 1 –AgNO₃ salt solution (m=6.1 mg. in 640 ml of water Amax=0.099);
- 2 –NiSO₄ (m=7.2 mg. in 100 ml of distilled water, Amax=0.064);
- 3 –CuCl₂ (m=1 mg in 100 ml of distilled water, Amax=0.043);
- 4 –copper laid soaked in distilled water with in 8 days (Amax=0.018);
- 5 –stainless steel laid soaked in distilled water 8 days (Amax=0.012);
- 6 –silver block laid soaked in distilled water 8 days (Amax=0.1);
- 7 –a part of a silver hydrosol 0.2 micrometer wavelength spectrum (Amax= 0.85);
- 8 –curve $\ln[1/(1-A)]$ for curve 7.

Detailed comparison of the spectra of extinction of different metals shows that spectra are not absolutely identical. In particular, for different metals the lengths of waves of the maxima of the absorption (spectra centers) do not match, for example, absorption maximum wavelength ~ 0.205 microns stands for silver, and it is less than 0.195 microns for Na, that is less than short-wave border of spectral range of sensitivity absorbed in work of the spectrometer. In the experiments for the metals similar to Na only the decreasing, long-wave, part of the spectrum was registered.

The resolution for the spectrometer which was used in this research does not allow us to prove experimentally the thesis that the examined spectrum is formed by the families of the spectra caused by the exaltation of the bonds in the $\text{Men}(\text{OH})_m$ complexes, though some signs of existence of these spectra as the local maxima on the received spectrograms can be seen.

To prove the possibility of interconversion of corpuscular

based component into an atomic component of a colloid solution, the experiments with silver hydrosol were conducted. During the experiment, busofit viz. absorbent fabric of carbon fiber /3/, existed approximately during 10 hours with silver hydrosol (in silver hydrosol solution), which had been heated up to 80°C, yet, in the other experiments the temperature of the samples was standard room temperature.

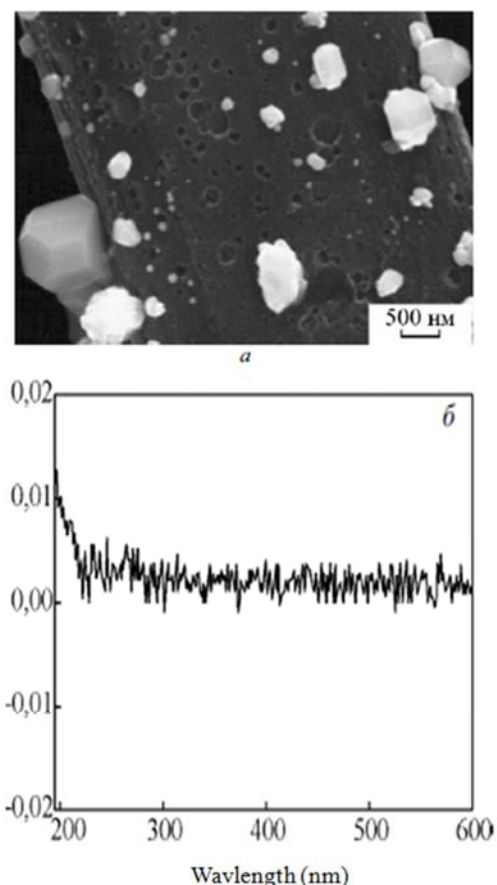


Figure 6. spectrograms of hydrosol extinction for the busofit(b) and heated hydrosol stayed in the solution. are presented and Busofit fiber micro photo (a).

4. Results

Quality identity of weak metal salt solutions and a part of silver hydrosol sector of extinction in the vicinity of $\lambda=0.2$ the wavelength indicates the existence of silver in the solution as single atoms or their low level clusters, i.e. They exist in the same state as metals exist in their weak salt solutions. Existing in that state metal builds atomic component in colloid solution, along with a well-known corpuscular one viz. metal nano-particles, extinction band, in case of silver existence in $\lambda=0.4$ mcm.

In the process of colloid solution preparation, its atomic component appears as a combination of silver atoms evaporated from electrodes' /1 / erosion craters, yet non-formed nucleus of metal nano-particles condensed phase. In the solutions of salts the atomic component is formed by the hydrated ions of metal arising at the salt molecular

decomposition. Having massive samples of metal soaking in water the emission of single atoms of metal from the sample surface is being stimulated by the molecules of water. Thus, the atomic component of metal in water - metal mixes arises in all the cases where a contact of metal with water time is provided for the sufficient time. Then dynamic equilibrium is established between the corpuscular and the atomic component of the hydrosol, which is characterized by the equality of atom streams emitted by the surface of nano-particles in (hydrosol) solution, and atomic component atoms flow backward from the volume per particles surface, adsorbed by the last ones into a crystal cell.

The direct confirmation of the existence of the emission of atoms from the surface of metal into water is spectrograms of water mixtures obtained by infusing big amount of metal into water.

The spectrogram of a solution in which absorbent material Busofit /3/ viz. carbon fiber fabric, was soaked for 10 hours, proves directly the existence of silver atoms emission from the Nano-particles surface into water. The photo of carbon fiber absorbed nano-particles and perfectly formed silver crystals shown in Fig. 4a, also indicates the lack of a band in the epitaxy spectrum near $\lambda=0.2$ micrometer wavelength, although being significantly reduced it is not disappeared completely. According to the authors, such a reduction of absorption namely due to final concentration, or which also means the flux of silver atoms, passing into the solution from the surface of the absorbent particles, while most of the atomic components of the parent solution has been absorbed by the carbon fiber, along with the particles.

Spectrum extinction change, once the solution has been heated, can be adequately explained by the processes occurring as a result of velocity increase of the particles thermal motion, as well as individual atoms and the collision frequency, including the merger of the colliding objects, in particular atoms absorption of atomic component as well as the fine part of a corpuscular one, and the concentration growth of large-scale particles concentration. Even the solution composition change corresponds to the change in the spectrum which is shown in Fig. 4. Moreover, Fig. 3 also shows the differential spectrogram high sensitivity to solution conditions.

Special attention should be paid to the fact of the relatively intense absorption band in water (aqueous) mixtures, containing metals as single atoms (ions) or their low clusters in the vicinity of $\lambda=0.2$ microns, viz. in the vacuum ultraviolet area. Such absorption could be associated with a relatively rigid bond Me-(H₂O), formed in the hydration of the metal atoms. As a possible analogue of such a bond, unbalanced oxygen atoms bond in a molecule of ozone can be taken, which provides a well-known intensive UV absorption by ozone at less than 0.29 microns wavelength.

5. Conclusions

1. The existence of the unified spectra of extinction for all metals, with maximum in the vicinity of wavelength $\lambda = 0.2$

microns in of water - metal mixes as well as in colloidal solutions was experimentally proved.

2. On the basis of comparative experiments it is shown that the spectra of extinction in the vicinity $\lambda = 0.2$ microns in water as well as in water metal mixes are caused by the existence of single atoms or /and their clusters in metal mixes in the form of the lowest level clusters which size does not exceed the thickness of the skin metal layer.

3. The unambiguous connection of the existence of an atomic metal components in water metal solutions and the extinction of mixes on wavelength $\lambda = 0.2$ microns provides an opportunity to determine the concentration of the atomic metal component by the intensity of the absorption on wavelength $\lambda = 0.2$ microns.

4. According to the authors, the most probable cause of the rather strong absorption existence, initial for different metals, in the vacuum ultraviolet ($\lambda \sim 0, 2$ microns) with high values of hydration energy of atoms and nuclear and ionic clusters high values of hydration energy of atoms as well as nuclear or ionic clusters of metals with the formation of the complexes as $[Men (H_2O)_m]$ [12]. High hydration energy (Cr, Fe, Ne ~ 700 kcal/mol [12]) provides the hard, high rigid bond formation inside the complexes as well as the high frequencies, being stimulated by the radiation.

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