*Досліджено проблему використання тетраетоксисилану різного терміну зберігання при виробництві фотонних кристалів. Синтезовані суспензії досліджені методом седиментационного аналізу. Встановлено, що граничний термін зберігання очищеного тетраетоксисилану становить 96 годин. Перевищення цього терміну призводить до утворення частинок з коефіцієнтом варіації їх діаметра більше 6 %. Останнє неприпустимо в виробництві фотонних кристалів*

*Ключові слова: фотонний кристал, тетраетоксисилан, седиментація, торсіонні ваги, сферичні частинки, метод Штобера*

*Исследована проблема использования тетраэтоксисилана различного срока хранения при производстве фотонных кристаллов. Синтезированные суспензии исследованы методом седиментационного анализа. Установлено, что граничный срок хранения очищенного тетраэтоксисилана составляет 96 часов. Превышение этого срока приводит к образованию частиц с коэффициентом вариации их диаметра более 6 %. Последнее недопустимо в производстве фотонных кристаллов*

*Ключевые слова: фотонный кристалл, тетраэтоксисилан, седиментация, торсионные весы, сферические частицы, метод Штобера*

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# EXAMINING QUALITY OF MATERIAL FOR THE SYNTHESIS OF PHOTONIC CRYSTALS BY THE METHOD OF SEDIMENTATION ANALYSIS

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## 1. Introduction

Under conditions of industrial fabrication of photonic crystals (FC), there arises a problem of economic efficiency of the production. At present, this problem is not solved. Among the existing methods of FC manufacturing, the most profitable one is the self-assembly of particles. This method makes it possible to create photonic crystals of unlimited dimensions; however, their defectiveness depends on the dispersed characteristics of particles [1]. Only particles of spherical shape with the coefficient of variation in size less that 5 % are suitable for the formation of FC [2]. Synthesis of the $SiO_2$ particles, uniform in dimensions, is most frequently carried out by the hydrolysis of tetraethoxysilane (TEOS) by the Stцber method in aqueous-alcohol-ammoniacal medium. However, TEOS, due to their significant reactivity, when stored, reacts with the moisture of air, which leads to its partial polymerization. Particles that are synthesized from such reagent display considerable deviation in size from the average value. An increase in the TEOS cleanliness is typically achieved by its distillation into fractions. This technological operation is one of the most expensive elements in the fabrication of $SiO_2$ particles by the Stöber method. In view of this, there is an issue of permissible storage period of the purified tetraethoxysilane.

The relevance of conducting present study is in determining the optimum between the cost of FC production and their quality. Since the basic expenditure is the TEOS fractional distillation, then increasing the period between conducting the given operations will lead to a reduction in the cost of FC fabrication.

## 2. Literature review and problem statement

The hydrolysis of tetraethoxysilane (TEOS) by the Stцber method in the aqueous-alcohol-ammoniacal medium makes it possible to obtain nano- and sub-micron spherical particles of $SiO_2$ [3]. The problem of synthesis of quality material for the formation of photonic crystals has been examined repeatedly. The size of $SiO_2$ particles that are synthesized by the hydrolysis of TEOS to a large degree depends on the concentration of TEOS, ammonia and temperature of reaction [4]. Extended studies demonstrated essential effect of the concentrations of water, ammonia and TEOS on the diameter of particles and their uniformity by dimensions [5]. Particles with a coefficient of variation lower than 5 % were synthesized by the modified method. A special feature of the method is mixing two prepared stock solutions. The formulation of one solution contained a solution of ammonia and water with the fixed molar ratio. The second solution comprised ethanol and TEOS. The ratio in the concentrations of reagents of the second solution was determined by the end properties of synthesized particles [6]. A possibility of obtaining particles, uniform in size, at high concentrations of TEOS was examined [7]. Authors of later studies

established influence of the volume of ethanol on the characteristics of silica particles [8]. An analysis of periodicals on the synthesis of $SiO_2$ particles to form photonic crystals reveals that the direction, related to the variation in conditions for conducting the synthesis of particles, is thoroughly explored. The purity of reagents has a significant effect on the uniformity of dimensions in the synthesized particles. The use of ammonium hydroxide and ethanol of the "p. a." brand, as well as distilled water, is commonly accepted in studies of different authors and by means is a bottleneck in the technology. At the same time, the application of TEOS as a key component, and its quality instability, is the main object under consideration in the specialized literature [9]. Traditionally, an increase in the TEOS purity is achieved by its fractional distillation in a rectifying column at atmospheric pressure. A finer purification is carried out in several stages. First, chemical treatment of the purified TEOS is performed by the 0.3–1,5 % aqueous solution of ammonia. Next, a rectification of the treated TEOS is carried out, and at the completing stage, a distillation at surface evaporation without boiling [10]. By other method [11], TEOS after fractional distillation is treated with ammonia and only then it is used for the synthesis. There is a combined method of purification. Its special feature is the fractionation of TEOS with its subsequent treatment by ammonia and water [12].

In the methods for TEOS purification examined above, its storage period is either not indicated or the need for conducting this operation directly before its usage is indicated. We did not find any information regarding a dependence of the dispersed composition of suspension on the period of TEOS storage. Thus, it is expedient to establish final terms for the application of purified TEOS in the synthesis of photonic crystals, which will make it possible to avoid manufacturing poor quality products.

## 3. The aim and tasks of the study

The aim of present work was the substantiation of final term for using TEOS after its fractional distillation for the synthesis of photonic crystals.

To achieve the set aim, the following tasks were to be solved:

– to devise a procedure for sedimentation analysis of the dispersed composition of suspension in the fabrication of photonic crystals;

– to substantiate the applicability of sedimentation analysis;

– to conduct experimental studies and to compare results of the synthesis of materials for photonic crystals from TEOS with different storage period.

## 4. Materials and methods of examining the suspensions, synthesized by the alkaline hydrolysis of TEOS with different fractional composition

### 4. 1. Materials and equipment that were used during experiment

Reagents that are used in the course of the study: distilled water, 96 % ethyl alcohol of the "p. a." brand, 25 % aqueous solution of ammonia of the "p. a." brand, tetraethoxysilane of the "p. a." brand. TEOS was additionally purified by the fractional distillation at atmospheric pressure, using for the synthesis the fraction, separated at temperature from 167 to 170 °C.

Manufacturing section for the synthesis of $SiO_2$ particles by the hydrolysis of TEOS with different periods of storage (Fig. 1) consists of reactor 1 with capacity 50 ml and mixer 3, which is set in action by electric motor 4. The assigned temperature in the reaction medium was maintained automatically with the help of electrical heating. The heating element is designed in the form of reactor body's winding by tungsten wire 2. Reactor temperature control system is realized based on thermistor 5 and regulator 6.

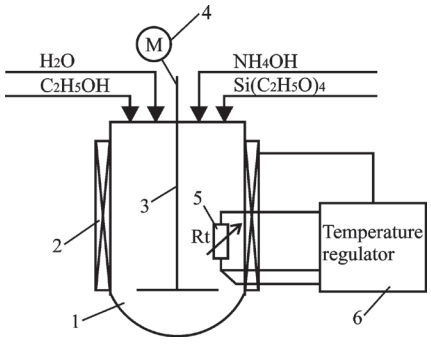



Fig. 1. Manufacturing section for the synthesis of $SiO_2$ particles by the hydrolysis of TEOS with different storage period: 1 — reactor; 2 — heating element; 3 — mixer; 4 — electric motor; 5 — thermistor; 6 — regulator

Study of the synthesized particles was conducted by the scanning electron microscopy method using the microscope REM 106I (made in Ukraine), as well as by sedimentation curves, constructed with the help of measurements at the torsion scales VT-500 (made in Ukraine).

### 4. 2. Devising a procedure for determining particle distribution by size

Let us examine photonic crystals, designed to operate in the visible region of spectrum (wavelength 400–700 nm). According to the Wulff-Bragg's law [13], such materials must consist of monodispersed $SiO_2$ particles with diameter from 210 to 380 nm.

Determining a dispersed composition of suspensions, which contain the above-indicated range of particle diameters is possible by the electronic scanning microscopy method, by nephelometric or sedimentation analysis. Electronic scanning microscopy provides for an analysis only of small selected sample of the synthesized suspension and does not yield full information about fractional composition of the entire suspension. In this case, an instrument error in the measurements of particle diameters reaches ±40 nm. A magnitude of error indicated does not make it possible to predict properties of photonic crystal with the accuracy required for their practical application. Deficiencies in the method of scanning electron microscopy necessitate a search for the more precise methods of quality control of material for the synthesis of photonic crystals.

Implementation of nephelometric method to analyze the whole suspension is a complicated technical problem, related to the development of a nonstandard nephelometer. And this method does not provide information about particle distribution by their size. A sedimentation analysis is easily realized and yields information about the particle dispersion in the whole synthesized suspension, it makes it

possible to conduct objective studies in line with the goal stated in the work.

In the sedimentation analysis, a characteristic of dispersiveness is the sedimentation velocity of particles. This process is described by the Stokes's formula under the following conditions:

a) incompressibility of medium and its infinite extent;

b) infinitely low speed of the motion of medium at the particle surface;

c) particles possess ideal spherical shape;

d) absence of the mutual influence of particles on each other.

The settling velocity of spherical particles V is determined by formula:

$$V = \frac{2}{9} \cdot \frac{\rho_r - \rho_s}{\mu_s} \cdot g \cdot r^2, \quad (1)$$

where r is the radius of particles, $\mu_s$ is the dynamic viscosity of medium, $\rho_s$ is the medium density, $\rho_r$ is the particle density, g is the acceleration of gravity.

Dependence (1) adequately describes the sedimentation of particles at low volumetric concentration of dispersed phase; however, it requires the use of highly sensitive instruments for determining the velocity or time of particle settling. Furthermore, against the background of low useful signal, there appear significant errors in the analysis, caused by the convection flows, the Brownian motion or other factors.

An increase in the concentration of the analyzed suspension leads to the decrease in the distance between particles of the dispersed phase. As a result, the influence of particles on each other directly or through the dispersion medium becomes essential. In this case, the dependences that link settling velocity of particles to their size get complicated.

An increase in the concentration of solid phase in the suspension causes an increase in density and viscosity of the whole disperse system. At significant volumetric concentrations of solid phase (larger than 0.05), the displacement of dispersion medium by the settling particles starts to manifest itself.

Let us examine physical laws governing the process of sedimentation under these conditions and we shall obtain a formula for settling velocity of particles in the suspension dependent on their size. Expression for the suspension viscosity can be written down by using simplified dependence [14].

$$\mu_s = \mu_p \cdot (1 - \nu)^{-2,8}, \quad (2)$$

where $\nu$ is the volumetric concentration of suspension; $\mu_p$ is the dynamic viscosity of dispersion medium.

Let us write down expression for suspension density $\rho_s$:

$$\rho_s = \rho_p \cdot (1 - \nu) + \rho_r \cdot \nu, \quad (3)$$

where $\rho_p$ is the density of dispersion medium. After substituting (1) into dependences (2) and (3), we shall obtain:

$$V_r = \frac{2}{9} \cdot \frac{(\rho_r - \rho_p) \cdot g \cdot r^2}{\mu_p} \cdot (1 - \nu)^{3,8}, \quad (4)$$

where $V_r$ is the velocity of particles relative to liquid.

The real settling velocity of particles V is lower than the relative speed by the magnitude of countercurrent of dispersion medium $V_p$

$$V = V_r - V_p. \quad (5)$$

Dependence is valid for the mono-disperse suspension:

$$V_p = \frac{V \cdot \nu}{1 - \nu}. \quad (6)$$

Let us write down formula for calculating true velocity of mono-disperse particles, based on expressions (4)–(6):

$$V = \frac{2}{9} \cdot \frac{(\rho_r - \rho_p) \cdot g \cdot r^2}{\mu_p} \cdot (1 - \nu)^{4,8}. \quad (7)$$

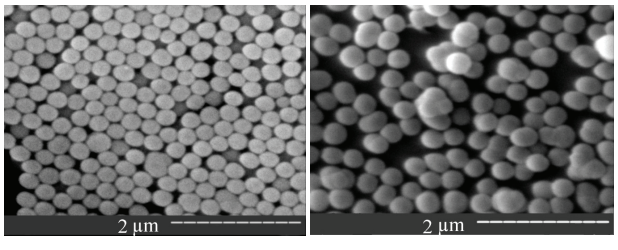
The dependence obtained (7) considers the countercurrent of dispersion medium, caused by its displacement by the particles which are settled. This technique makes it possible to carry out sedimentation analysis of the higher concentrated suspensions and to decrease their volume. This leads to a decrease in the level of the examined liquid and consequently to shortening the duration of sedimentation analysis.

The choice of method for the realization of sedimentation analysis is conducted based on the characteristics of the examined suspensions, which are synthesized by the TEOS hydrolysis. Density of dispersion medium by the indications of areometer is 0.88 g/cm$^3$. Kinematic viscosity μ' is measured using the capillary viscometer VPZh-1. Subsequently, it was recalculated into dynamic viscosity by dependence $\mu_r = \mu' \cdot \rho_p$. The result obtained is $\mu_r = 1{,}1 \cdot 10^{-3}$ Pa·s. All the described measurements are carried out under standard conditions. Density of the photonic crystal formed from the $SiO_2$ particles $SiO_2$ synthesized by the Stцber method is 1.27–1.28 g/cm$^3$ [15]. Since the particles occupy 74 % of the volume of opal matrix, we assume $SiO_2$ particle density to equal 1.72–1.73 g/cm$^3$. As was already mentioned above, the examined suspension contains particles of diameter from 210 to 380 nm. Particle concentration was calculated taking into account the equation of reaction of the TEOS hydrolysis, amount of the reagents used and considering that the whole TEOS reacted and was used to form $SiO_2$, which composes the dispersed phase of the obtained suspension. Mass concentration of particles in the examined suspensions is from 6 g/l to 12 g/l, depending on the amount, used for the TEOS synthesis. Volume of the examined suspension is 280 ml.

Sedimentation quality control of material for the synthesis of photonic crystals can be realized by the sedimentation of particles in the gravitational or centrifugal fields. When using the centrifugal fields, it is technologically complicated to conduct repeated measurements; therefore, the accuracy of measurement is insufficient to compare results of the synthesis of materials for the photonic crystals from TEOS with different storage period to solve the problem presented in present work. In order to obtain a curve of sedimentation in the gravitational field, different methods are used. Because of simplicity in realization, attractive is a pipette method. However, labor-consuming nature of the method related to taking the samples of suspension from a specific height over equal time intervals and low accuracy do not allow using it in the fabrication of photonic crystals. Low accuracy of measurements is inherent in the methods, based on measuring the pressure of suspension pole. Promising is a sedimentation particle analysis by the vibration frequency method. Applying the laboratory vibration density gauge VIP-2MR will provide for the indirect measurement of particle weight in the suspension with error not exceeding ±60 mg. Sedimen-

tation analysis, realized by the gravimetric method with the application of torsion scales VT-500, ensures error ±1 mg. It is obvious that the gravimetric method is more preferable at the sedimentation quality control of material for the synthesis of photonic crystals.

Let us determine a possibility of applying dependence (7) by solving inverse problem – prediction of sedimentation curve by the known dispersed composition of suspension. For this purpose, we shall investigate two suspensions synthesized by the TEOS hydrolysis. Quality photonic crystal was formed from the particles of one suspension. It was impossible to form photonic crystal from the second one. The sediment obtained as a result did not display iridescence. The shape of the synthesized $SiO_2$ particles, their size and polydispersity index were determined using a scanning electron microscope (Fig. 2, *a, b*).




*a* *b*

Fig. 2. Micrographs of the synthesized particles: *a* — suitable for the formation of photonic crystal; *b* — not forming photonic crystal

Fig. 2, *a* shows that the synthesized particles mostly have a spherical shape; the coagulation of particles or their coalescence as a result of synthesis is rarely observed. An analysis of micrograph of the synthesized particles allowed us to obtain a number of generalizing parameters: mean diameter $d_m$=258 nm, mean surface radius $r_s$=129.9 nm, mean volumetric radius $r_m$=130.2 nm, polydispersity index k=0.993295, variation coefficient is 4,7 %. Particle distribution by size is better visualized by histogram (Fig. 3, *a*). As can be seen from the histogram, particle distribution is close to normal law. Defined parameters of the particles allow us to argue about possibility of their application for the formation of photonic crystals.

Synthesized particles in Fig. 2, *b*, in comparison with Fig. 2, *a*, are more heterogeneous. Generalizing parameters of the particles depicted in micrograph Fig. 2, *b* are as follows: mean diameter $d_m$=315 nm, mean surface radius $r_s$=162.3 nm, mean volumetric radius $r_m$=165.6 nm, polydispersity index k=0.95, variation coefficient 11.5 %. Since the determined variation coefficient exceeds 5 %, the use of such particles for the formation of photonic crystals is unacceptable.

The corresponding histogram of particle distribution by size is shown in Fig. 3, *b*.

The calculations reveal that the volumetric concentration of $SiO_2$ particles whose micrograph is shown in Fig. 2, *a, b* in the suspension is 0.0035.

By the determined parameters of suspension, for the particle distribution given in histograms Fig. 3, *a, b* we modelled the appropriate sedimentation curves (Fig. 4, curve 1). Measurements by the micrographs, obtained at scanning electron microscope, are performed with a significant error, which is connected to the quality of preparation of the sample, tuning and the microscope features. The permissible error in this case for all particles in the same image is identical (in Fig. 4, curves 2 and 3); hence, the ratio of their size is close to the real value. Thus, the bends in sedimentation curve 1 reflect the non linearity of change in the weight of sediment during sedimentation. Experimental measurements carried out on the torsion scales VT-500 yield a similar dependence of the weight of sediment on the time of sedimentation (curve 4 in Fig. 4, *a, b*). Measurements were taken at placing the cup of torsion scales at a distance of 6 mm from walls of the vessel. This made it possible to eliminate the influence of near-wall effects on the process of sedimentation of particles. At such position of cup of the torsion scales, part of the sediment was not considered because some particles penetrated through the left gap between a wall of the vessel and the cup of scales. To construct charts, the measured weight of sediment was brought to the calculated amount of synthesized $SiO_2$.

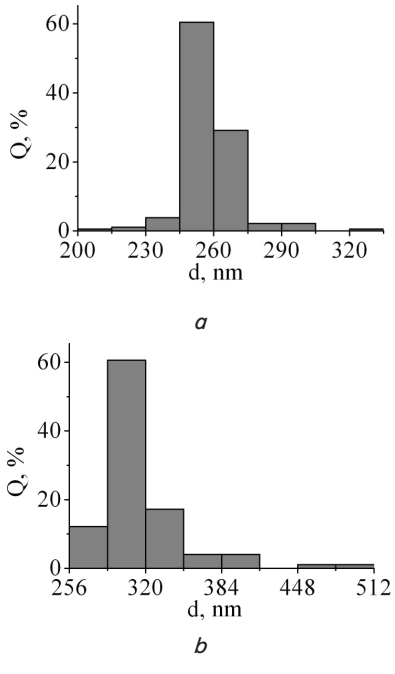


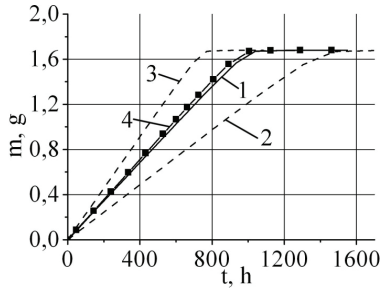

Fig. 3. Histogram of diameter distribution of synthesized particles d depending on the relative amount of particles in the interval of column of in histogram Q: *a* — particles, suitable for the formation of photonic crystal; *b* — particles that do not form photonic crystal

Fig. 4, *a* shows that sedimentation curve 1 practically does not have transition sections. That is why, when processing it, it will be natural to conclude that there is a monodispersity of the synthesized particles. On sedimentation curve 1 in Fig. 4, *b*, it is possible to highlight 3–4 sections where individual fractions are settled. As a result of determining the dispersed composition by such a curve, we obtain variation coefficient in the particle size equal to 10 %. This indicates unsuitability of the synthesized particles to formation FC. The obtained value of variation coefficient is different by 1.5 % from the initial data, accepted for its modeling. The defined accuracy is sufficient to control quality of the material at FC synthesis.

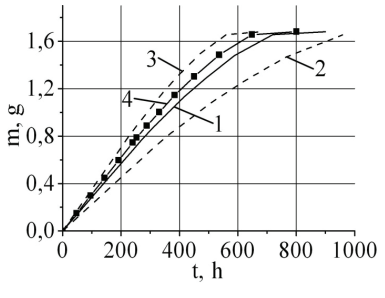
Preliminary estimation of the possibility of applying sedimentation analysis for determining the fractional composition of suspension under the assigned conditions demonstrated its feasibility. However, small diameter of particles in the examined suspensions leads to a significant duration of the sedimentation process (1000–1500 hours). Acceleration of the process of settling the particles is achieved by

the replacement of dispersion medium with methanol whose dynamic viscosity is $0.58 \cdot 10^{-3}$ Pa·s, which is 2 times lower than that in the dispersion medium obtained after synthesis. Thus, particle deposition velocity will increase by 2 times.

The replacement of dispersion medium with methanol was carried out by settling the particles with the help of centrifuge, then the dispersion medium was discharged and methanol was added, restoring the volume of suspension. The dispersion of suspension was conducted at the last stage.




*a*




*b*

Fig. 4. Sedimentation curves, built in the coordinates of particle settling t and sediment mass m: *a* — suspension with the particles capable of forming a photonic crystal; *b* — suspension with the particles not suitable for the formation of a photonic crystal; 1 — result of modeling the settling of particles; 2 and 3 — boundaries of the modeling uncertainty; 4 — experimental curve of measurement at the torsion scales VT-500

## 5. Experimental studies of the dispersed composition of suspensions synthesized by alkaline hydrolysis of TEOS with different storage periods

In order to conduct reaction of the TEOS hydrolysis, we added, constantly stirring, 6.2 ml of TEOS into the mixture of alcohol (198 ml), water (10 ml) and ammonia (65 ml), put in advance to the reactor and brought to temperature 20 °C. In 2 hours after adding TEOS, we obtained the suspension of $SiO_2$ particles whose dispersed composition was investigated by the sedimentation method.

Fig. 5 shows results of sedimentation studies of the suspensions synthesized from tetraethoxysilane with different storage periods.

Fig. 5 displays insignificant deviation in the speed of sediment accumulation in the process of sedimentation. This phenomenon is explained by the uncertainties in the results of measuring volumes of the reagents, applied in the synthesis and insignificant deviations in the regulation of reactor temperature mode in the process of obtaining the particles.

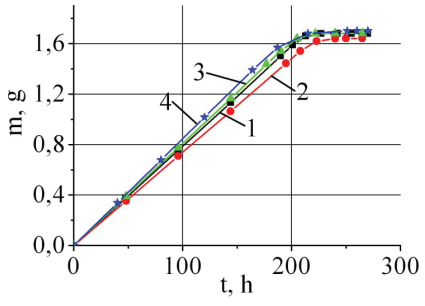



Fig. 5. Sedimentation curves of suspensions (dependence of sediment mass m on the settling time t) synthesized from tetraethoxysilane with different storage periods: 1 — immediately after fractional distillation; 2 — in 48 hours after TEOS purification; 3 — in 96 hours after TEOS purification; 4 — in 144 hours after TEOS purification

## 6. Discussion of results of examining dispersed composition of the suspensions synthesized by alkaline hydrolysis of TEOS with different storage periods

Sedimentation analysis of suspensions (Fig. 5), obtained by the hydrolysis of TEOS with different storage periods, provides information about particle distribution by size. A difference in the dispersed composition of suspensions manifests itself more vividly after double differentiation in time of sedimentation curves, given in Fig. 5. Results of differentiation are represented in Fig. 6.

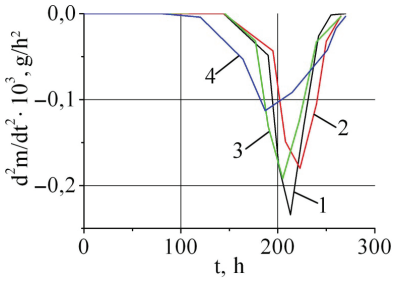



Fig. 6. Increase in the sediment mass in the sedimentation process of $SiO_2$ particles synthesized from TEOS with different storage periods: 1 — immediately after fractional distillation; 2 — in 48 hours after TEOS purification; 3 — in 96 hours after TEOS purification; 4 — in 144 hours after TEOS purification

As is evident from Fig. 6, periods of the acceleration of increment in the mass for each sedimentation curve are different. Changes in the acceleration of increment are related to the end of settling by one of the fractions of dispersion medium. Thus, the larger the period of acceleration of increment in mass, the more heterogeneous the dimensions of the settled particles are.

By analyzing Fig. 6, it is possible to draw a conclusion that the $SiO_2$ particles synthesized from TEOS immediately after fractional distillation have the most uniform dimensions (curve 1, Fig. 6). The worst characteristics for the formation of FK are displayed by particles, synthesized

from TEOS that was stored for 144 hours after purification (curve 4, Fig. 6).

According to data, given in Fig. 5, it is easy to define such parameters as the mean diameter and variation coefficient in the diameter of synthesized particles; results of calculations are in Table 1.

Table 1

Results of sedimentation analysis of the synthesized suspensions

| TEOS storage period, hours | 0 | 48 | 96 | 144 |
|---|---|---|---|---|
| Variation coefficient, % | 4,2 | 4,3 | 4,8 | 6,2 |
| Mean diameter, nm | 411 | 405 | 422 | 426 |

As can be seen from data in Table 1, an increase in the period of storage leads to the growth in variation coefficient in the diameter of particles and their standard deviation. In the synthesis of particles from TEOS with storage period after fractional distillation of 6 days, variation coefficient reaches 6 %, which exceeds permissible value for obtaining a photonic crystal.

Thus, effective use of tetraethoxysilane in the production of photonic crystals is provided by the application of purified TEOS during 96 hours from the moment of its fractional distillation.

## 7. Conclusions

1. A proposed procedure of sedimentation analysis of the dispersed composition of suspension in the fabrication of photonic crystals considers the countercurrent of dispersion medium, caused by its displacement with particles, which are settled. This procedure makes it possible to carry out sedimentation analysis of higher concentrated suspensions and to decrease their volume. This leads to the decrease in the level of analyzed liquid and, as a consequence, to shortening the duration of sedimentation analysis.

2. By comparing the results of modeling and experimental data, we substantiated the feasibility of sedimentation quality control of material for the synthesis of photonic crystals. It is established that error in variation coefficient in the diameters of particles, determined by the method of sedimentation analysis, reaches 1.5 %. Such accuracy is sufficient to control quality of the material in the FC synthesis.

3. Conducted experimental studies on the synthesis of materials for photonic crystals from TEOS with different storage periods demonstrated that variation coefficient in the diameters of synthesized particles is different. It is established that the boundary period of storing purified tetraethoxysilane is 96 hours. Exceeding this period leads to the formation of particles with variation coefficient in their diameter larger than 6 %. The latter is unacceptable in the production of photonic crystals.

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