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ХИМИЯ ҒЫЛЫМДАРЫ ИНСТИТУТЫ»
АКЦИОНЕРЛІК ҚОҒАМЫ

# ҚАЗАҚСТАННЫҢ ХИМИЯ ЖУРНАЛЫ

# ХИМИЧЕСКИЙ ЖУРНАЛ КАЗАХСТАНА

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«ИНСТИТУТ ХИМИЧЕСКИХ НАУК
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**Туған жер! Осы сөзді естігенде құлаққа жағымды, жүрекке жылы тиіп, бойыңды бір тәтті сезім билейді. «Туған жердей жер болмас, туған елдей ел болмас» демекші, қай жерде жүрмесін әр адамның туған жерге деген сағынышы бір бөлек.**

# ТУҒАН ЖЕРГЕ ТАҒЗЫМ

Сол себептен химия ғылымдарының докторы, академик **Еділ Ерғожаұлы** өзінің туған жерге деген құрметін, сезімін, сағынышын білдіре отырып, жаңа оқу жылының басталуына орай, Ескелді ауданындағы Титов атындағы орта мектебіне өз кітаптарын мектеп ұстаздарына және оқушыларға тарту етті. Бұл тарту мектеп ұжымына ұмытылмас әсер қалдырды.

«Адамның ісі қандай болса, өзі де сондай» деген екен неміс философы Гегель. Адамның ең асыл қасиеттері қашанда күндей жарқырып көрініп тұрады.

Халқымыз Еділ Ерғожаұлын ғылым жолындағы табанды ізденістермен абырой биігіне көтерілген көрнекті ғалым, академик, ұлағатты ұстаз, белгілі мемлекет және қоғам қайраткері тұрғысында біледі және де құрметтейді.

Отандық химия ғылымы саласының қарқынды дамуына жол ашқан білікті маман ретінде сіңірген еңбегі, екі жүзден аса авторлық куәлікпен потенттері Қазақстанның келешегі үшін аса маңызды.

Өмірдегі мақсат-мұратына адамдар да ақ адал маңдай терімен атқарылған игілікті істері арқылы ғана жетіп отырған. Соған орай абырой да, атақ та бастарына бақыт құсындай қонып тұрған. Университеттің бірінші проректорының жұмсақ креслосына отырғаннан бері Еділ Ерғожиннің есіне ұстазының «Сенің алтын тағың - ғылым, ұшатын қанатың - білім» дейтін ұлағатты сөзі жиі есіне түсетін болатын. Тәлімгер ұстазы құлағына қорғасындай құйған-ақ екен. Өмірлік асыл арманына айналған ғылым жолынан бір сәт те ажыраса алар емес. Өз жұмысын біле отырып, жұмысқа деген құштарлығы аса зор күйінде адал еңбек етуде. Академик Еділ Ерғожаұлы игерген істері мен қол жеткізген табыстарының көпе-көрнеу бағасы төмендеп, бағының жанбауына намыстанбай тұра алмады. Қолда барда алтынның қадірін білместіктің арты өкініш екенін ескермеу естілік емес еді. Ол отандық ғалымдар тағдырына немқұрайлы қарай алмады. Үкімет алдына ғылымды тығырықтан алып шығудың ғылыми жобаларын ұсынып, оның қажеттілігін батыл дәлелдеумен болды.

«Туған жерге туың тік» демекші, әр перзент өз еңбектерін, ізгі істерін туған жерден бастауы керек. Соған дәлел химия ғылымдарының докторы, профессор, ҚР ҒА-ның академигі, ҚазССР ғылымына еңбегі сіңген қайраткер Еділ Ерғожаұлының есімін келер ұрпаққа мақтанышпен айта аламыз.

**Әлия СҰЛТАНОВА,**
**Титов атындағы орта мектеп қазақ тілі мен әдебиет пәнінің мұғалімі.**

УДК 547. 62-278. 54-114

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# TRACK MEMBRANES: METHODS OF PREPARATION AND AREA OF THEIR APPLICATION

**Abstract.** The article summarizes the results of theoretical and experimental research in the field of synthesis and application of track membranes, as the main component of modern waste-free environmentally friendly technologies. The features of formation of track membranes from various types synthesized by polymerization or polycondensation of various monomers and chemical modification of the finished membranes are discussed. The results of studies on increasing their selective permeability, physico-mechanical and electrochemical properties are presented.

Perspective directions of their practical application for solving urgent problems of water treatment, processing of industrial effluent by extraction valuable components, separation of gas and liquid mixtures at high pressures and intensive regimes of mass transfer are determined.

**Keywords:** tracks, track membranes, accelerated ions, nuclear filters, pore diameter.

Track (nuclear) membranes are made of polymer films with a thickness of 12-23 microns by bombarding them with high-energy krypton ions piercing through the film. In the places of passage of individual ions, channels of destructed material (tracks) are formed, differing in their physico-chemical properties from the material intact by ions. The selective dissolution of the ion-destructed material transforms the original film into a microfiltration membrane with through-pores of cylindrical shape, that is, when the ion-treated material is subsequently etched in to alkali solution, and strictly identical through-holes are formed in place of the tracks.

The diameter of these pores can be varied in the range from 0.05 to 5µm, depending on the etching conditions (figures 1, 2). For the mass production of track membranes (TM), used the U-400 ion accelerator of the Nuclear Reaction Laboratory of the Joint Institute for Nuclear Research (JINR, Dubna, Russia), producing up to $10^{12}$ ions per second, which made it possible to produce TM with a pore density in the range $1\cdot10^5$–$3\cdot10^9$ pores/cm². Their porosity is about 10-15%. The main property of TM, distinguishing from other types, is high selectivity (all single pores have the same diameter with deviations of not more than 5%). Therefore, depending on the functional purpose (filtration of mechanical impurities, bacterial or virus suspensions, etc.), a corresponding TM rating, optimal for a specific microfiltration process can be selected.

The porous of TM system formed as a result of irradiation of thin polymer films by a beam of high-energy heavy ions with subsequent etching of ion tracks to the formation of uniform through holes (figure 3). Small pore sizes (from 10 nm

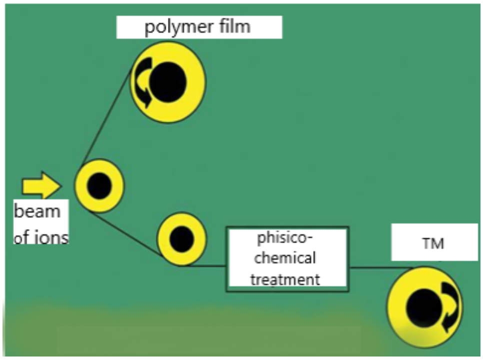


Figure 1 – Scheme of obtaining TM

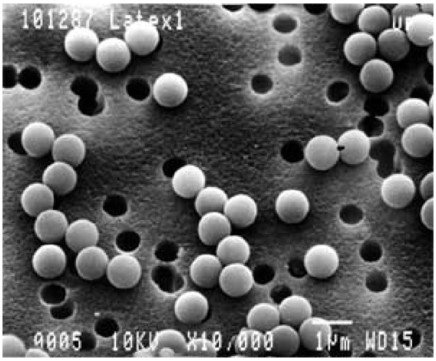


Figure 2 – Latex (control balls) on TM

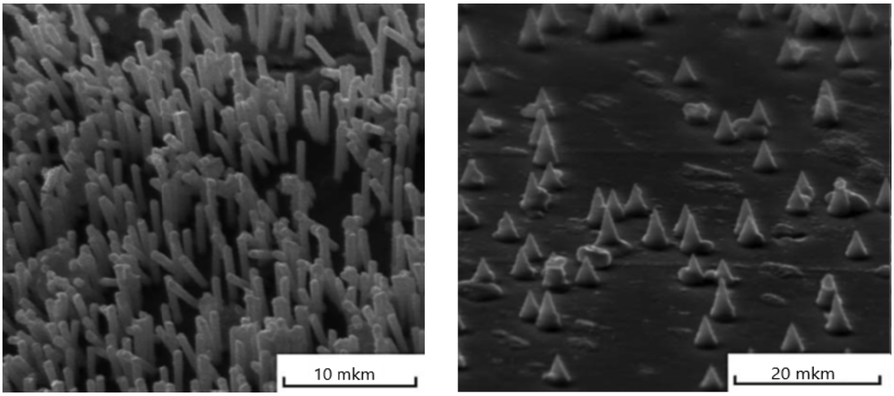


Figure 3 – Microphotographs (SEM TESLA BS-340) of metal structures based on TM

to several microns), their calibration, the possibility of modifying the geometry of pores and their intersections make TM a unique material used both in the separation of liquid and gaseous media, and for many other tasks.

For example, on the basis of TM as templates, secondary metal structures are grown that are promising for use in optics and as auto-emission (cold) cathodes [1].

The specific productivity of TM is better, the higher the density of pores. However, an increase in the density of the pores leads to a decrease in strength. During the filtration process, the membrane may break down. Therefore, mechanical properties are an important performance characteristic of TM. The dependence of their strength on the strength of the matrix material, on porosity, and on the concentration of stress on the pores considered in [2-4]. It was also found that the strength characteristics of TM in some cases depend on the interaction of the elastic fields near the pores (it is known that if the distance between the pores is less than 5 diameters, then the elastic stresses around these pores interact [5]).

The pore geometry in the standard TM is an ensemble of cylindrical holes of the same size. TM have found wide application in scientific research and in various manufacturing processes associated with the purification and separation of liquid and gas media [6]. There are also works devoted to their use as templates for the formation of tip nanostructures. In particular, the possibility of fabricating a metallized structure with a developed TM-based surface by electrolytic deposition has been shown [7]. The formation of needle microcrystals in pores of TM from polyethylene terephthalate was studied [8] upon filtration of a supersaturated aqueous solution of $HIO_3$. It was found that the transverse dimensions and directions of the predominant growth of the formed faceted microcrystals correspond to the configuration of the pores of the TM.

A technology has been developed for cleaning oil-containing toxic liquid waste from maps of land fills of their disposal [9]. A compact unit including four modules: separation the oil fraction by thin-bed sedimentation with preliminary aeration, flotating purification of water using coagulation, membrane filtration by TM, and oxidation [10].

TM (nuclear filters) widely used for analytical purposes (including for testing the bacterial contamination of water [11, 12], for the separation of blood components [13, 14], in the purification of drinking water [15], in recent years have been used in the purification of natural water – rivers, canals, lakes, ground and rain water, sea water [16-19]. Besides it, there were some reports on the use of TM for wastewater treatment [20-23].

As shown in [17, 18], for purification of water with high turbidity and chromaticity using the membrane (including TM), the efficiencyis significantly increased when combining the processes of coagulation and microfiltration.

Membrane filtration is one of the most widespread laboratory and industrial processes for cleaning liquids from colloidal contaminants [24]. The process of cleaning technological media, based on membrane processes, is intensively developing, the processes of such filtration and the devices created in this process are being improved. One such method is pressure filtration, which allows for higher performance. TM are characterized by high productivity, selectivity of media separation (pore size dispersion is not more than ±2%), the possibility of regeneration and a number of other advantages. At present, membrane filtration processes using TM are involved in many technological schemes, and the scope of their application is expanding.

The term dynamic polarization of nuclei is understood as the process of achieving a high degree of polarization of electron spins in matter under the action of high-frequency magnetic fields, and the transfer of this polarization to a nuclear spin system [25]. Obtaining objects (targets) with high nuclear polarization is of great interest for elementary particle physics, since it is an instrument for studying spin interactions in experiments on scattering of particles by extracted beams of accelerators. The polarized target used in these experiments, the main part of which is the working substance, is a technically complex device.It combines several main parts necessary for the realization in the process of the dynamic polarization of nuclei, such as a magnet with a strong permanent magnetic field (2.5-5.0 T), cryogenic systems providing ultra-low temperatures (T <0.5K), a source ultrahigh frequency. The main requirements for the working substances of the target are: a high content of polarizable nuclei in the material. In experiments with a polarized target, an important problem is also the effective cooling of the working substance. In order to avoid heating of the substance, especially from the heat release of the superhigh frequency and the consequent reduction in the degree of polarization of the nuclei, it is preferable to have a developed surface in the working substance. For this purpose, for example, working substances, which are liquids, are used as frozen droplets in liquid nitrogen with a diameter of several millimeters.

In recent years, polymers have become increasingly used as the material of the working substance in the creation of targets with polarized hydrogen nuclei (protons or deuterons) [26]. These materials are solids, which greatly simplifies their use as targets and opens up new experimental possibilities. Polymers with the general formula $(–CH_2–)_n$ and $(–CD_2–)_n$ are especially interesting because of the maximum content of hydrogen atoms among solid organic substances. For some experiments in nuclear physics, a thin (film) target is especially needed based on these materials.

To impart paramagnetic properties to polymers, compounds exhibiting magnetic properties are introduced into their composition. As a substance with magnetic properties, a highly stable, volatile nitroxide radical 2,2,6,6-tetramethyl-piperidine-1-oxyl (TEMPO) with the general formula $C_9H_{18}NO$. is often used. Radical pairs have the ability to diffuse into amorphous parts of polymers, which leads to the formation of a paramagnetic system necessary for the creation of polarization of nuclei in matter by dynamic methods.

As a working substance of the polarized target, it is proposed to use a new material − polypropylene TM, obtained by irradiating polypropylene films with a beam of high-energy heavy ions followed by chemical etching of latent tracks of these particles [25]. To impart the paramagnetic properties necessary for the dynamic polarization of nuclei to membranes, a nitroxide radical TEMPO was introduced into the samples by thermal diffusion. Using the EPR method, information was obtained on the paramagnetic centers in the polymer matrix of membranes, the concentration of the nitroxide radical and the rotational mobility of the spin probe in them was determined.

In most cases, the process of surface hydrophilizationis used to impart a greater polarity to polymer materials. This means a steady significant increase in polarity, which is achieved by radical interference in the nature of the surface layer of the polymer. The chemical composition of surface macromolecules varies significantly. In [27] various methods of hydrophilization of polymeric materials based on physical and chemical influences are considered. The most frequently using methods include the treatment of polymers by herbal solutions or reagent pairs, thermal treatment (in particular, laser chemical) treatment, as well as in plasma or flame.One of the simplest and most frequently used methods of surface hydrophilization is etching with chemical reagents, which leads to the formation of a thin surface modified layer with a large number of functional groups [27]. During the hydrophilization process, a suitable etching solution and optimal etching conditions selected for each polymer. In the case of polypropylene, for example, various solutions of mixtures of chromic and sulfuric acids, as well as concentrated nitric acid or used solutions containing persulfates. The processing of polymeric materials by elevating temperatures used both for hydrophilizing the surface of products and for modifying their volume. When the hydrophilizing surface of polymers exposure to high temperature, other factors also simultaneously used: chemically active solutions, various particles, irradiation.

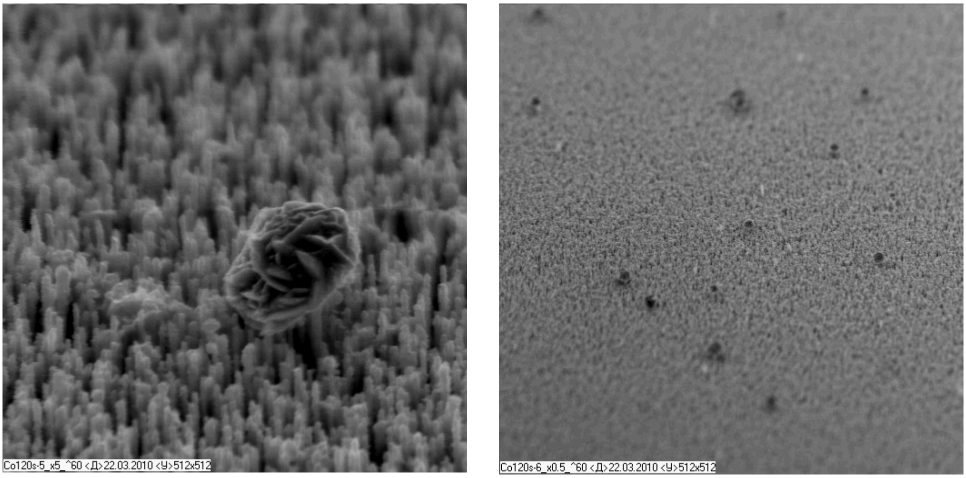
One of the methods for modifying the surface of polymer materials is the method of radiation graft polymerization, which is based on the generation of active radical and ionic sites under the action of ionizing radiation followed by the grafting variety of polymers from the gas phase or from solutions of monomers. Radiation graft polymerization is mainly carried out by two methods. One of them is the irradiation of polymers in the presence of a monomer which is the method of direct grafting. In another method, the polymer is grafted by contacting the previously irradiated polymer with the monomer. The most common way to produce polymers with a modified surface is radiation graft polymerization by the method of preconditioning using low-energy electron accelerators. This method used to modify a wide range of industrial polymers: polyolefins, fluorine-containing polymers, polyamides, etc. Disadvantage of radiation graft polymerization is the need to use expensive sources of ionizing radiation.

From the physical methods of action for hydrophilizing the surface of polymers, the most widely used method is plasma processing, the advantage of which is the change in the thin surface layer of the material due to the small depth of penetration of active plasma particles into its volume. The bulk of the polymer does not change, which is extremely important from the point of view of preserving the mechanical and physico-chemical properties of the materials being modified. In this connection, in a number of works published recently, a study of the effect of plasma on polymer membranes [28-30], including track [31-33], has been carried out to modify the properties. The results of the research show that the effect of low-temperature plasma of both unpolymerized and polymerized gases under different conditions by the nature of the membrane leads to a change in a number of properties: adsorption, selective, and transport [34, 35]. The study of these processes, depending on the parameters of the discharge and the composition of the plasma-forming gas, in order to improve the surface properties of membranes, is dictated by practical and scientific tasks. In this connection, it is of great interest to study the process of hydrophilization of the surface of polypropylene TM having hydrophobic properties, which inhibits their use in microfiltration of aqueous solutions.

The surface and electrochemical properties of polypropylene TM, processed in nitrogen, air and oxygen plasma have been studied[36]. The influence of the composition of the plasma-forming gas on the morphology of its surface was studied. It has been established that the surface microrelief of membranes formed in the process of gas-discharge etching is changing. The effect of the plasma of nonpolymerizing gases, in addition, causing oxidation of the surface layer of the membrane, leads to the formation of oxygen-containing functional, mainly carbonyl and carboxyl groups. It is shown that an increase in the surface roughness of the membrane and its hydrophilization cause an improvement in wettability. The presence of polar groups in the surface layer of the membrane, in addition, causes a change in its hydrodynamic and electrochemical properties − the permeability and electrical conductivity of the modified materials are increased.

One the way of producing micro- and nanostructured metals is the matrix synthesis method, which consists in filling the pores of a matrix with the desired material. Pore parameters in the "parent" matrix can usually be adjusted: set their orientation in space, shape, and size and location density. Polymeric TM most often used as a porous material, and pore characteristics in which are specified both during ion irradiation of the initial polymer film and during its subsequent etching. The obtained pores are filled with various metals by electrodeposition. This method, called "replication" ("template synthesis") develops in many countries [37-40], replicas from a number of metals received. However, the properties of metal replicas obtained by different authors are very different. The study of the electrochemical process of metal deposition in pores will allow us to determine the effect of electrodeposition conditions on the resulting metallic replicas, and then control the structure and properties of these replicas (figure 4).

Electrochemical processes of metal deposition are well studied and used in practice; for nanoscale structure in pores of TM. Nanowires made from cobalt have many potential applications due to the magnetic properties of this metal [41]. The process of producing micro- and nanostructured cobalt [42] was studied by



a b

Figure 4 – Microphotographs of pore replicas with a diameter of 200 nm, growth conditions potentiostatic (E = -580 mV). The side of the frame is 30.5 μm (a), 325 μm (b)

electrochemical filling of the pore channels of TM. Dependencies of the course of the process on the geometric (pore diameter) and electrochemical (potential, current density) parameters are shown.

Sulphated lignin is a composite non-uniform network organic copolymer formed as a by-product from the most common sulfate cooking of wood [43]. It is a valuable organic raw material for the chemical industry. The comparatively low molecular weight and the presence of reactive groups in combination with solubility in alkaline solutions make it possible to use sulfate lignin in the production of both polymers (as fillers and modifiers in the manufacture of plastics, rubbers and rubbers) and phenol-formaldehyde oligomers of the resol type, dimethylsulfoxide. It is also used in ceramic production as a plasticizer and as a binding agent in the production of paper plates and the like. In the future, it can become one of the significant sources of both low-molecular and polymeric valuable organic products.

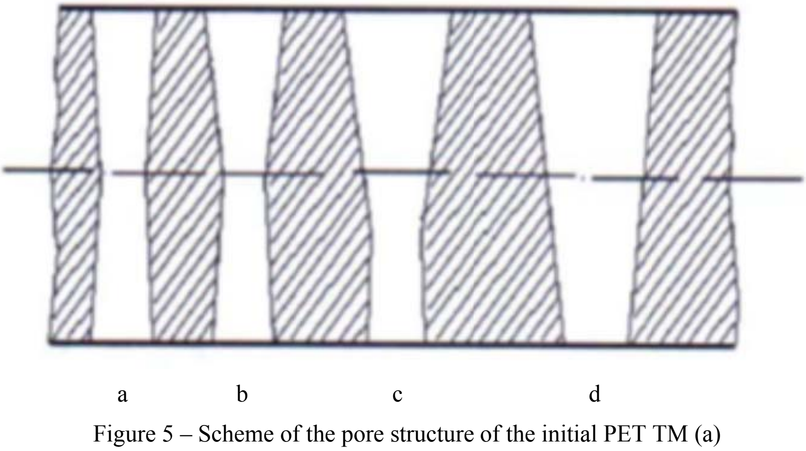
To date, great progress has been made in studying the structure and application of sulphate lignin, but the questions related to the study of its colloidal chemical properties continue to remain relevant. This is primarily due to the fact that this information is important not only for the development of the theory of sulphate delignification of wood [44], but also for solving a number of applied problems of the pulp and paper industry, for example, finding new more economical ways of using sulfate lignin [45] and optimizing work of systems for local purification of lignin-containing wastewater. In connection with this, it is of interest to study the aggregation of sulfate lignin dispersions in solutions of electrolytes and, in the first place, the patterns of their coagulation.

The filtration through TM, differing in the diameter of the capillaries (from 50 to 2500 nm), studied the aggregate stability of dilute (10 mg/L) aqueous dispersions of sulfate lignin in solutions of NaCl and $CaCl_2$ ($0\text{-}10^{-1}$ mol/L) in the pH range 9.5-2.0 [46]. It is shown, that in the absence of salts, the liberation of sulphate lignin on the filters increases with decreasing pH and approaching the isoelectric point of sulfate lignin (pH 2.0). The introduction of salts leads to an increase in the delay efficiency of sulfate lignin, which becomes significantly higher in the case of $CaCl_2$. Based on the data obtained, the sizes of aggregates of sulfate lignin formed in solutions of different composition are determined.

One of the ways to clean natural and waste water from coarse, colloidal and other contaminants is the method of coagulation. In practice, aluminum salts are widely used as such materials, during the hydrolysis of which polynuclearhydroxocomplexes and hydroxides are formed. The formation and coarsening of particles in the dispersed phase and, consequently, the efficiency of the water purification process depend on their parameters [47]. Therefore, it is of undoubted interest to investigate the effect of $AlCl_3$ on the aggregate stability and particle size of aqueous dispersions of sulfate lignin, one of the specific pollutants of sewage generated by the use of a widespread and water-intensive sulfate method for the production of commercial pulp. The features of aggregative stability of dispersions of sulfate lignin and the sizes of their particles in solutions of various electrolytes in a wide range of their concentrations and pH are established [46, 48, 49].

The effect of $AlCl_3$ ($0-10^{-3}$ M) and pH (9.5-2.0) on the aggregation of dilute (10 mg/L) aqueous dispersions of sulfate lignin was studied by filtration through a series of TMs with capillary diameters from 50 to 2500 nm [50]. It is shown that $AlCl_3$ has a significantly higher coagulating ability than NaCl and $CaCl_2$. In the pH range 4.1-7.0, which corresponds to a significant hydrolysis of $AlCl_3$, a concentration inversion of the coagulating ability of $AlCl_3$ occurs in the transition from $10^{-4}$ to $10^{-3}$ M due to charge exchange of negatively charged sulphate lignin particles by $AlCl_3$ hydrolysis products.

One of the urgent problems in ophthalmology is the surgical treatment of refractory glaucoma. Refractory glaucoma includes both primary glaucoma surgery, requiring repeated surgical procedures, as well as congenital, juvenile and some types of secondary glaucoma. Unsuccessful attempts of antiglaucomatousoperations, as a rule, are the result of proliferation of connective tissue and blockage of surgically formed ways of outflow of intraocular fluid. Due to the resistance of refractory glaucoma to traditional treatment, the long-term preservation of the hypotensive effect is ensured by the implantation of various drains. Presented are [51] the results of the formation and use of polymeric TM from polyethylene terephthalate (PET) with a nanostructured surface as explant drainage in the surgical treatment of refractory glaucoma. For nanostructuring of the surface layer of membranes, treatment in an oxygen-containing plasma was applied (figure 5).



a b c d

Figure 5 – Scheme of the pore structure of the initial PET TM (a) and membranes modified in air plasma (b-d)

Lithographic and chemical methods usually use for the synthesis of nanostructures. The essence of the method of matrix synthesis is the filling of pores of small size in a porous matrix (template) [1]. Interest in this method of synthesis is due to its sufficient simplicity, as well as the ability to manufacture micro- and nanowires from various materials.

The matrices can be manufactured by ion-track technology (irradiation of the polymer with heavy ions and subsequent etching of latent tracks), which gives a unique opportunity to create matrices with through or blind pores of cylindrical and conical shape. Then the pores in the resulting patterns are galvanically filled with various metals: copper, nickel, silver. Choose the conditions for uniform filling of pores with metal. The micro- and nanowires produced in the matrix can be used either in a growth matrix (metal/polymer composite material) or the polymer can be removed and individual micro- and nanowires are obtained. If metal is additionally deposited on one of the surfaces of the polymer in the process of galvanic filling of pores with metal, then after removal of the polymer, a "brush" made of micro- or nanowires on a metal base is formed.

Earlier in [52], showed the possibility of using such brushes for electron emission. The possibility of ion emission from such substrates in mass spectrometry has been demonstrated [53].

Matrix (template) synthesis in the pores of TM produces micro- and nanowires of cylindrical and conical shape [1]. The technique of filling the pores of the matrix with metal (copper, nickel and silver) has been worked out. Since the polymer templates are dielectrics, they were first dusted on the one side with the metal that was being adsorbed. For galvanic deposition of metal in the pores of the template, a circuit consisting of a power source, a digital milliammeter and a special Teflon cell was used. The processes of desorption/ionization of biological molecules from metallic micro wires have been studied experimentally.

The relationship between the growth conditions and the morphological changes that accompany the electrodeposition of copper in the etched channels of TM from PET has been studied [54]. TM was used with a diameter of etched channels from 5 μm to 50 nm. The experiments were carried out under potentiostatic conditions at different cathode potentials without forced mixing. The electrodeposition of the copper precipitate was carried out at temperatures 20 or 60°C. The morphology and crystallinity of copper nanostructures were studied using raster (JSM-840) and transmission (EM-125K) electron microscopy. It is found that an increase in overvoltage stimulates the formation of a polycrystalline structure of a micro wire, and a reduction in overvoltage stimulates the formation of a single-crystal structure of a micro wire. At the same time, the determining effect of the magnitude of the overvoltage on the features of the crystal structure of nanometer-sized wires was not observed.

During the micro- and ultrafiltration of process fluids, a layer of gel deposits forms on the surface of the membrane, which inevitably leads to a decrease in the specific rate of the process (membrane permeability), down to its complete stop. To restore the transmissivity of the membrane it is necessary to carry out its periodic regeneration, which is an integral element in the implementation of any membrane process. Moreover, we are talking about restoring the percentage of permeability that decreases due to plugging, clogging of the pores of membranes, the formation of deposits of different nature on their surface, in contrast to the reduction in the capacity of membranes due to irreversible shrinkage of the pores under the action of the pressure gradient. Ultimately, the efficiency of regeneration determines the service life in micro- and ultrafiltration plants, and, consequently, the economic component of the membrane process used [55].

Since the used TM for microfiltration of beer had very low mechanical stability, the only and effective method of regenerating the membranes remains mechanical cleaning in combination with combined washing and disinfecting agents.

The applicability of countercurrent washes inevitably led to the rupture of TM due to its separation from the drainage substrate. The use of spongy bodies with a diameter from5 to 7 mm in combination with the operating agitator has shown successful results in restoring the permeability of TM. In this case, membrane regeneration is carried out without excess pressure applied to the film, and the intensity of the exposure to it was determined mainly by the level of detergent solutions on the surface of the membrane, their concentration, temperature, duration of action and the speed of rotation of the mixing device.

Methods of regeneration of various types of membranes in the process of micro- and ultrafiltration of technological liquids in food production using pilot plants are considered [55]. Algorithms for regeneration and washing of track, hollow fiber and ceramic membranes are given, the regime parameters (temperature, duration, concentration, method and direction of feeding) are indicated, the kind of reagents used for micro- and ultrafiltration of technological liquids of food production, for example, the beer of unfiltered unpasteurized, enzyme preparation inulinase, water tap and curd whey.

Today, one of the urgent problems in the field of ecology is the purification of drinking water from bacteria, viruses and parasites, and alsoair purification. The most effective means for filtering drinking water are TM, as well as the most needed application of TM have been found in the processes of fine air cleaning and as respirators.

At present, there are a lot of enterprises in our republic in this area, namely, in the Institute of Nuclear Physics of the National Nuclear Center of the Republic of Kazakhstan in the city of Astana, tests are conducted on irradiation and etching of the PET film, which is later used as a filtration means [56]. The Institute is one of the 18 member states of the Dubna Joint Institute for Nuclear Research.

The main functional feature of membranes is a high selectivity of filtration, which ensures high quality of the filtrate. The guarantee of high filtration quality is ensured by the advantage of the TM structure: a smooth surface. In contrast to fine air filters based on glass paper, in which the capture of particles is mainly due to the mechanisms of contact (particles of 0.3-1.0μm in size) and diffusion (particles smaller than 0.3 μm), in TM the capture of particles occurs in a single sieve effect (a special case of the touch effect). Sieve is the effect that occurs when the particle size is larger than the pore size. The field of application of TM is determined by the functional ability to ensure that particles with dimensions exceeding the nominal diameter of the membrane pores are guaranteed to be retained on the surface.

At the branch of the Institute of Nuclear Physics (Astana), work was carried out on irradiation of a 19.41 μm PET film [56]. Three films with a length of 200 meters were irradiated, with various modes of operation of the isochronous cyclotron DC-60 providing the given density of track pores. After irradiation, samples were taken from each film to control the correspondence of the irradiation parameters to the specified properties.

Depending on the size of the particles, which must be retarded or separated, the diameters of the pores TM D must correspond to the task assigned to them [57]. Accordingly, as the pore size decreases, the membranes are divided into microfiltration (0.05 μm <D <5μm), ultrafiltration (0.005 μm <D <0.05 μm), nanofiltration (0.001 μm <D <0.005 μm) and reverse osmosis (D <0.001 μm). Membranes of the latter kind can be considered an artificial analogue of biological membranes capable of separating ionized atoms and molecules.

TM formed in two main stages. First, the original non-porous materials are irradiated with high-energy particles (accelerated heavy multiply charged ions at the accelerator or fission fragments of heavy nuclei in a nuclear reactor) or through a mask by a synchrotron radiation beam. As a result, in the material, zones of destruction (material structure disturbances) are formed along the rectilinear trajectories of the bombarding particles, latent tracks. Then the tracks are chemically etched until the formation of through pores of a given diameter, the value of which is set by irradiation and etching modes. The nature of the etchant is determined by the material of the irradiated film. For example, for etching tracks in the most common polyethylene terephthalate for the production of TM alkaline solutions are used. This stage of the transformation of the irradiated film into a membrane and gave the term track membrane.

The features of the porous structure of TM make them in the fundamental field an almost ideal model for studying the physicochemical mechanism of membrane filtration, and in practice they provide them with a selectivity that is record-breaking compared to other types of membranes. The pore sizes of TM lie in the range from several units to several hundred nanometers (track nano-, ultra- and microfiltration membranes). Thus, according to modern classification, TM is typical nanomaterials [57].

In 1972, at JINR (Dubna) under the leadership of Academician G.N. Flerov began work on the creation of method obtaining TM based on using accelerated heavy ions [58]. Methods have been developed for the production of PET-based TM with a porous structure that is comparable to TM produced using fission fragments. As a result, in 1974, both methods of obtaining TMhad been realized. In the first method, irradiation of the polymer film is performed by $^{235}$U fission fragments, in the second method, multiply-charged ions of the accelerator are used to create the tracks.

On the basis of the SSC RF-IPPE (Obninsk), studies have begun to develop a reactor technology for the production of PET-based TM using the BR-10 reactor as an irradiator [59]. In the development of this technology, it was assumed that reactor TMs would have better selectivity values than those obtained with the accelerator method. The basis for this assumption was the following circumstances.

When irradiation takes place at the accelerator, ions enter to the film at the same angle. Due to the stochastic nature of the radiation, the resulting tracks are randomly distributed relative to one another. As a result, the distance between individual tracks may be so small that after etching several pores can overlap. As a result, a through channel is formed of a larger size than the size of a single pore. The dispersion of pores along the diameter worsens the quality of the membrane. Therefore, in order to reduce the effect of this factor, it is necessary to introduce additional devices that help to change the angles of the entry of ions into the film in order to exclude the overlapping of pores over the entire thickness of the film.

When the film is irradiated on an accelerator, ions enter to the film at the same angle. Due to the nature of the fission, the emission angles of the fission fragments from the source have an isotropic distribution. Therefore, the fission fragments enter the film at different angles in the range of values determined by the design of the collimator. The overlap of pores, which retains the depth of the membrane, becomes unlikely. In the reactor production method, a much more uniform irradiation of the polymer film web is achieved than in the accelerator method, where a narrow scanning ion beam is used. The advantages of the reactor method include the simplicity of the device for forming a beam of fission fragments. At the same time, the reactor method is not devoid of shortcomings. The main drawback is the possibility of radioactive contamination of the membrane due to the braking of a number of fragments within the thickness of the film [59].

Track membranes are widely used as filters for fine purification of gases and liquids, for medical purposes (plasmapheresis, bacteriological and viral control, etc.), as spectral-selective diffraction filters, as well as for the creation of secondary micro- and nanostructures (tips, debris). The advantages of using TM are in the small pore sizes, their calibration, the possibility of modifying the pore geometry and their intersections. Membranes made on the basis of PET with a variation in porosity and pore diameters and their orientation relative to the TM surface were investigated [4].

When using any materials, its mechanical properties are always important. The strength of TM with different porosity and pore orientation with respect to the surface was investigated [4]. Three main factors influencing the destruction of TM have been identified and analyzed; the influence of the stress concentration on the pores and the role of their interaction in the destruction are demonstrated.

The formation of pores in polycarbonate films exposed to accelerated ions during their treatment with an alkaline solution containing a surface-active agent was studied [60]. It was found that the shape of the pores is determined both by the structure of the initial film and by the features of the interaction of the surface active agent with the surface of the polymer and its transfer to the track. Due to the inhomogeneity of the starting material, the cross-section of the pore track varies along the length of the pore. The presence of a surface-active agent leads to an additional effect. Being adsorbed to the surface of the film and to the inputs of

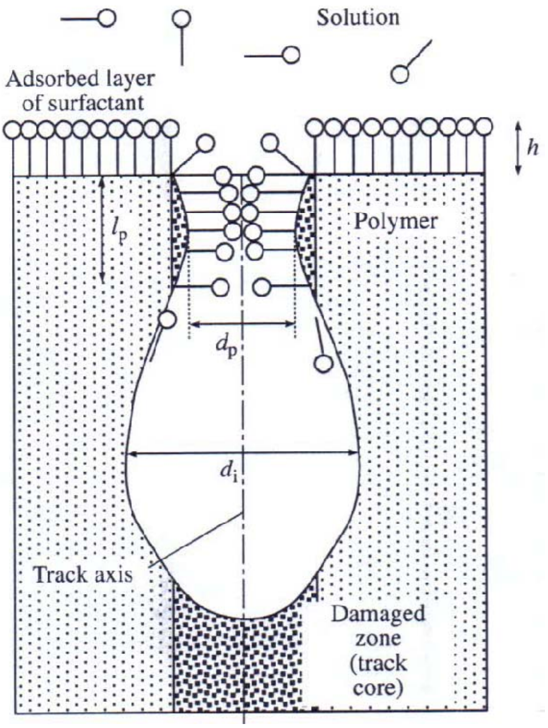


Figure 6 – Schematic diagram illustrating the initial stage of etching of heavy ion tracks in a polymer in the presence of a surfactant

etched heavy ion tracks, the surface-active agent molecules tend to reduce the etch rate, resulting in "roll-like" pores (figure 6).

The use of a surface-active agent as a component of a chemical etching solution makes it possible to vary the shape of the pores of the TM with respect to direction, optimizing their efficiency and selectivity.

Investigation of the properties of polyethylene terephthalate TM modified by the polymerization of dimethylaniline in the discharge of direct current showed that membrane treatment on the anode provides polymer precipitation both on the membrane surfaces and on the pore walls [61]. The polymer obtained from dimethylaniline by plasma polymerization can swell in aqueous solutions, and the degree of swelling depends on a large extent of the pH solution. This process is associated with the formation of a positive charge on nitrogen atoms. The swelling of a layer of plasma-polymerized dimethylaniline on the surface of the pores causes a reduction in the pore diameter of the membrane. In membranes with a deposited polymer layer, partial reduction of pores is observed, leading to a decrease in water permeability in solutions at pH 1.2. At pH 4.6 there is no formation of charge on nitrogen atoms, and the polymer swells to a much lesser degree, thus leading to an increase in the permeability of the membrane. The introduction of iodine into the polymer layer leads to the formation of poly-electrolyte, the swelling of which in the acid medium leads to a complete reduction of the pores within certain pressure limits. As the pressure increases, the gel collapses due to the transition of the coil-globule, as a result, the permeability of the membrane increases sharply. The results indicate that PET-TM, modified in dimethylaniline plasma, is capable of reversibly changing its permeability depending on the pH of the solution and the applied pressure.

The dependence on the electrical conductivity of KClaqueoussolutions in the pores of polyethylene terephthalate and polyimide track etched membranes on the solution concentration and pore diameter was studied by impedance spectroscopy [62]. It was found that the electrical conductivity values, calculated from the experimental results, significantly exceed the standard values in the case of small pore diameters and low solution concentrations, and this difference is more pronounced in the case of PET-TM. As the solution concentration and pore diameter increase, the electrical conductivity of the solution in the pores tends to approach the standard values. The observed effect is explained by the presence of a free layer on the walls of the pores, which appears as a result of decomposition of the polymer caused by irradiation with high-energy ions. The contact of this layer with the solution leads to the formation of a gel layer filled with electrolyte and shortening the measured resistance of the membrane.

A plasma-chemical process was developed for the production of composite TM with an electrically conductive coating of nitride-titanium particles having a complex hierarchical structure [63]. Due to the deposition of nitride oxide on the surface of PET-TM, the membrane channels become asymmetric, and the film power is enhanced. The size of the pore openings in the composite membranes can vary over a wide range by changing the synthesis parameters. The possibilities of direct use of composite TM in electron microscopy for qualitative and quantitative fractionation by the size of microelements in natural waters by means of ultrafiltration have been demonstrated by the example of a number of macro- (C, Al, Si, Mg, Fe, P) and macroelements (Sr, U, Th).

Improved TM was used for the first time to study the distribution of elements between particles of different sizes and other water components. The properties of strengthened membranes are considered [64]. Factors affecting the quality of water in the Volga River near the water intake near the city of Dubna in the Moscow region and drinking water in various parts of the city are characterized by the fractional composition of macro and micro components.

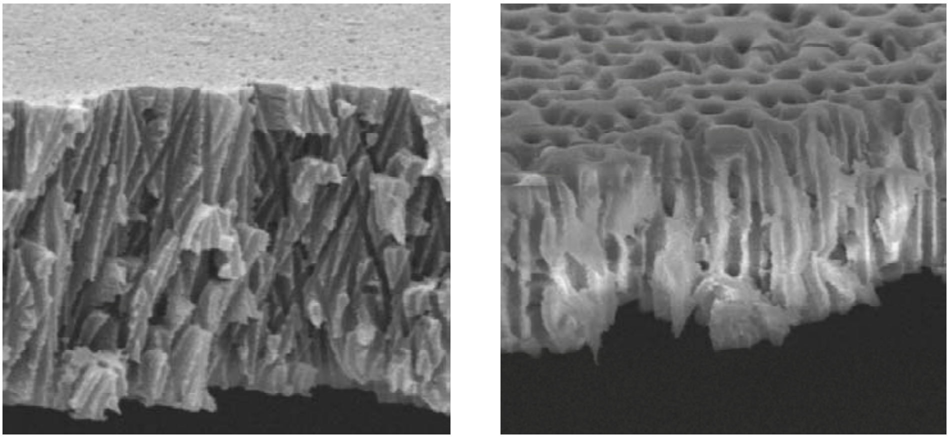
The key problem of nanometrology is the development of relatively simple and reliable methods for measuring the geometric parameters of nanoobjects. Such measurements are usually made using scanning electron (SEM) and scanning probe microscopes (SPM). The ability of SPM to perform a 3D survey of nanoobjects requires the presence of three-dimensional reference materials, among which, for example, step structures obtained by anisotropic etching of (100) -oriented silicon wafers can be mentioned. Three-dimensional silicon stepped nanostructures are currently used for calibration and verification of SEM and SPM along with such traditional reference materials as the islet of gold for SEM and oriented graphite for SPM. The potential of etched polymeric membranes with a conductive coating of titanium nitride for calibration and verification of SEM, as well as SPM operating in the scanning tunnel microscope and ACM modes, was demonstrated [65]. This universal reference material can be used both in ultrahigh vacuum and in environmental conditions.

The sorption of polyethylene glycol with a molecular weight of 3 and 40 kDa on TM at different pH has been studied [66]. Sorption of polyethylene glycol and the selectivity of its sorption increase by decreasing pH. The contact angles of the water with the membrane measured for both intact TM and for polyethylene glycol modified ones. Sorption of polyethylene glycol on TM reduces the contact angle of the film, which indicates an increased hydrophilicity of its surface. The fibers of human membrane aqueous albumin and the membrane aqueous insulin adhesive show that, unlike insulin, human serum albumin makes TM more hydrophilic than polyethylene glycol. Due to the relatively low surface tension, 5% by weight of human aqueous albumin completely displaces polyethylene glycol from the surface of the modified TM.

The ultrafiltration of aqueous solutions of sodium lignosulfonate through TM with pores of 30 nm was studied [67]. Their selectivity was studied depending on the concentration of sodium lignosulfonate (10, 20, 50 and 100 mg/dm$^3$) and electrolyte NaCl ($10^{-3}$, $10^{-2}$ and $10^{-1}$ M). It was shown that ultrafiltration of solutions of lignosulfonates is associated with the mechanism of "membrane-selective permeability-related" charge. Selectivity of membranes decreases with increasing concentrations of lignosulfonate and NaCl, as well as the degree of filtrate extraction.

Compared with proteins and water-soluble dyes, the adsorption properties of metal-ceramic and etched PET-TM are compared [68]. It is shown that metal-ceramic membranes have a noticeably higher adsorption capacity (calculated per unit surface area) than PET-TM. In this case, the nature of the adsorption of these substances on both types of membranes is very similar and is determined by the combination of ionic and hydrophobic interactions. The adsorption values of the main dyes are much higher than those of the acid dyes, because of the negative charge on the surfaces of the membrane. The isotherm of adsorption of the main dye of rhodamine 6G on PET-TM from the aqueous solution is characterized by growth in the concentration range below 1 μmol/l due to the presence of highly active adsorption sites on the surface. Adsorption of dyes is significantly reduced when isopropanol is added to the aqueous solution. Using as an example the base protein cytochrome C, it has been found that its adsorption on cermet membranes can be prevented by increasing the ionic strength of the solution.

The possibility of obtaining fracture discontinuities of trace membranes based on polyethylene naphthalate was investigated by electron microscopic studies [69]. These splittings make it possible to study the structure of the pore canal over the entire length of pores from one surface to the other (figure 7).



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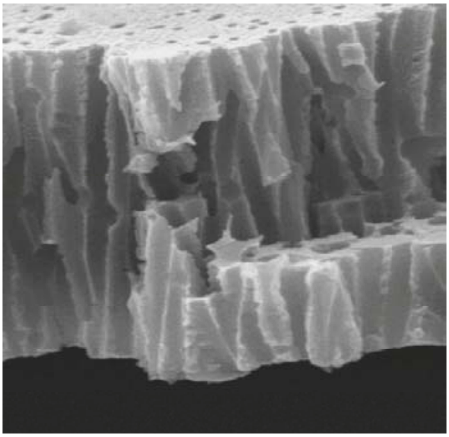

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Figure 7 –
Electronic microphotographs
of membrane cracks based
on polyethylene naphthalate obtained after
a) UV irradiation with a LE-30 lamp for 7 days,
b) after exposure to high-energy protons
with a dose of 107 Gy,
c) after exposure to nitric acid vapor

Because of the high radiation and thermal stability of polyethylene naphthalate films, thermal, ultraviolet and radiation treatment methods used for the production of brittle films of polymers such as PET, polycarbonate and polypropylene are unsuitable for them. Processing samples with concentrated nitric acid vapor for 1.5 months makes them brittle. It is possible to obtain a good cross-section.

Based on the results of the study, samples of chemically resistant TM were obtained [23]. The structure of the porous membrane was formed by bombarding a polyvinylidene fluoride film (PVDF) with 41 MeV argon ions followed by thermal treatment and chemical etching. Ion-track membrane PVDF can be used for the production of a proton exchange membrane.

The surface diameter of the pores is approximately 250 nm. This value confirms that the heat treatment and composition of the etchant accelerated the growth of the pores during etching compared to the results reported previously.

Conducting research confirmed the values of pore diameters. The results of this study and the use of thermal treatment of irradiated PVDF allowed to reduce the etching temperature of the through pores and increase the etching rate of the PVDF track. Thus, it can be expected that the technology of making membranes resistant to aggressive media will be developed in the foreseeable future, and PVDF membranes after appropriate grafting to change their surface properties will find application in fuel cells.

The possibility of using TM for subsequent treatment of biologically purified domestic effluents from individual buildings was investigated [70]. The dependence of pressure on the productivity of distilled water and the process of filtering of effluents for TM prepared from Russian and imported films, the dependence of the efficiency of the process and the efficiency of purification on the pore size of the membrane in the dead-end and transverse flow modes, the efficiency of traditional methods of regenerating TM using citric acid and the influence of the reverse washing to restore the efficiency of filtration of biologically treated domestic sewage.

Oxidative polymerization of pyrrole and N-methylpyrrole was studied using matrix synthesis on PET TM [71]. By scanning electron microscopy, it was found that a polymer film was formed on the surface of membranes and on the walls of membrane pores. The polymerization rates on the surface of membranes and pore walls, as well as the yield and structure of the polymer film, depend on the membrane parameters (pore length, diameter and porosity), the chemical structure of the monomer, the diffusion of polymerized solutions through the pores of the template and temperature.Methods for obtaining samples of a porous polymer for studying its structure using scanning electron microscopy are described. The technique for preparing cracks is supplemented by preliminary treatment of the polymer with radiation, photo- or thermo-oxidative degradation to make it brittle. The advantages of this method have been demonstrated with Mylar, polycarbonate and polypropylene TM [72].

The kinetics of isothermal evaporation of distilled water, which was in remote (10-15 mm) contact with porous TM, was studied by microgravimetry (derivatograph). When the $H_2O$-TM system contained a dispersed medium, the supramolecular structure of the water changed, and the number of clusters (coherent domains) decreased sharply. Extraction of the light phase from liquid water correlated with the chemisorption of $H_2O$ molecules containing a hydrogen para-isomer, which predominantly form coherent water domains [73].

The flow potential method implemented in a slot device using KCl solutions of $10^{-4}$-$10^{-2}$ mol/L was used to study the electro- surface characteristics of PET films, both initial and irradiated with heavy ions, and also in the form of TM with pore sizes of 50 and 210 nm, made of these films [74]. Their potentials and surface charges are calculated. The obtained data indicate that irradiation of polymer films with heavy ions reduces the $\zeta$ potential and the surface charge. However, as a result of film etching, when preparing a TM, the potential and surface charge increase and exceed the corresponding values for the original film.

The processes of electric current flow through metal-covered TMs in air and in vacuum are consistent with the traditional concepts of the current dependence on the voltage in the dielectric [75]. The reversible change in the current-voltage characteristic during the transition from vacuum to air (and vice versa) can be explained by reversible processes of adsorption-desorption of atmospheric moisture on TM. The same sorption processes can explain the time dependence of the intensity of the current when the voltage is applied. In this regard, the identified effects should be taken into account when choosing the operational conditions of field emission nanostructures based on metal-coated TM in future technical applications.

The results of a structural study of conductive polymer coatings deposited on TM from PET by matrix synthesis are reported [76]. The following aspects of the quality of polymer coatings were studied: the ratio between the film and the granulated polymers, the polymer distribution over the surface, and the thickness of the polymer layers on opposite sides of the TM. The fraction of granular polypyrrole on the surface and in the pores of the film increased with the pore diameter. The decrease in the polymerization temperature reduced the amount of granular polypyrrole on the surface of the membranes, while its effect on water permeability of TM remained unchanged. A more uniform distribution of polypyrrole over the TM surface can be achieved by equalizing the density of the reacting solutions; but the fraction of granular polypyrrole on the surface of the membrane increased in this case. It turned out that the polymer coatings on both sides of the surface of the membrane matrix have different thicknesses. Poly-N-methylpyrrole completely covered only one side of the TM facing the monomer solution.

The features of etching of latent heavy ion tracks in PET prior to pore formation were studied [77]. It turned out that the etching process includes the following steps: 1) penetration of the electrolyte into the pores due to capillary forces and removal of products of monomeric radiolysis; 2) swelling of cross-linked (due to secondary electrons) polymer regions around the tracks to form a gel layer; 3) removal of the gel layer and the formation of TM with a pore radius of 40-50 Å. Radiation-chemical processes in polymers affect the physicochemical properties of the resulting membranes. The microrelief of their surface was studied by the AFM method.

Surface-active substances are used to etch TM to form pores of specific geometry, for example, to obtain membranes with improved characteristics. Knowledge of the state of the molecules of surface-active substances in technological solutions, in particular, the patterns of their aggregation, is important for understanding the mechanisms of the action of surface-active substances on the etching of tracks. Data on the micellization of dodecyl (sulfophenoxy) benzenesulfonate and nonylbenzene deca (ethylene oxide) in neutral and alkaline electrolyte solutions of various concentrations presented in [78]. The measurements carried out using small-angle neutron scattering. It is shown that cylindrical (ellipsoidal) micelles formed in solutions. The characteristic sizes of micelles as function of the surfactant and electrolyte concentration are determined. The correlation of the obtained data versus the geometry of track nanopores and the dynamics of their etching in surface-active solutions is discussed.

The structural and electrokinetic characteristics of microfilters versusof track coating with a pore radius of 1 μm and microfilters modified with a perfluorinated sulfocationite ionomer, depending on the pH and the concentration of KCl solutionswere studied [79]. The colloidal properties of the modified microfilters and the perfluorinated sulfo-cation exchanger membrane MF-4SK were compared.

Time-of-flight spectra of ions formed during the extraction of negative ions from the KI solution in a water-glycerin mixture by high-speed electric field pulses are analyzed using a source with a polymer-based interface. It is shown that the ions formed in the secondary processes of bombardment of the membrane surface contribute significantly to the observed spectra. It was found that the peaks of negative hydrogen ions have the highest intensity in the spectrum, which indicates the effective emission of these ions upon bombardment of PET by secondary ions with an energy of about 6 keV. The main directions of modification of the membrane interface are described to reduce the fraction of secondary ions in the ion beam [80].

The properties of asymmetric nanopores obtained by chemical etching of tracks by accelerated heavy ions have been studied [81]. Procedures have been developed to control the size and shape of pores over a wide range. The presence of charged functional groups on the walls of pores is an intrinsic property of TM, which makes them a convenient object for studying electrokinetic phenomena in nanocapillaries. In electrolyte solutions, asymmetric "road" membranes exhibit a diode effect. Two methods of manufacturing asymmetric nanopores in PET films have been proposed and introduced into practice. The features of both methods, their advantages and disadvantages are considered.

The possibility of performing an energy-efficient irradiation of 20-μm PET films for the production of TM is considered[82]. Irradiation carried out on both sides of the film by an $Ar^{8+}$ ion beam with an energy of 53.4 MeV, the energy of which was insufficient to form a through track. The characteristics of the obtained TM samples were studied. It has been found that these membranes can be used in some cases as a basis for manufacturing composite gas separation membranes.

The iron and cobalt-iron nanostructures synthesized in polymer ion-track membranes were studied by Mossbauer spectroscopy in combination with scanning electron microscopy, energy dispersive analysis, and X-ray diffraction data [83]. The nanostructures obtained are single-phase $Fe_{1-x}Co_x$ nanotubes with a high degree of polycrystallinity, the length of which is 12 μm; their diameter is 110 ± 3 nm, and the wall thickness is 21 ± 2 nm. $Fe^{2+}$ and $Fe^{3+}$ cations were found in nanotubes, which belong to the iron salts used and are formed by electrochemical deposition. The Fe nanotubes show the distribution of the directions of the magnetic moment along the directions of the Fe atoms, while the Fe/Co nanotubes have a partial magnetic structure along the axis with an average angle between the magnetic moment and the nanotube axis of 34° ± 2°. Substitution of the Fe and Co atoms in the nearest medium of the Fe atom in the structure of Fe/Co nanotubes leads to a significant increase in the hyperfine magnetic field on $^{57}$Fe nuclei (by 8.7 ± 0.4 kOe) and to a slight decrease in the Mossbauer line shift (by 0.005 ± 0.004 mm /s).

The results of an investigation of the friction process of a metal-polymer pair on a disc-scheme are presented[84]. The material for the study was TM from PET and had pores with a diameter of 0.4 and 0.8 μm. The influence of sliding velocity for membranes with pores of 0.8 μm is determined. It was shown that an increase in the pore diameter leads to decrease the coefficient of friction and its amplitude oscillations. The study showed that TM has sufficient resistance to wear and can be successfully used in surgical procedures in the layers of the cornea.

PET-containing etched membranes with an average pore size of 400 nm underwent UV grafting of polyacrylic acid after oxidation of internal surfaces by the $H_2O_2$/UV system [85]. Carboxylate groups of chains of grafted polyacrylic acid readily interacted with $Cu^{2+}$ ions in aqueous solutions. These ions were converted into metallic copper nanoparticles by radiation-induced reduction of copper ions in a water-alcohol solution by gamma rays in a dose range of 46-250 kGy. Copper ions chelating with COOH groups of polyacrylic acid chains grafted onto PET form an ion-polymer complex that prevents the formation of agglomerates during the reduction of copper ions to metallic nanoparticles. Detailed analysis by X-ray diffraction, transmission electron microscopy, scanning electron microscopy and energy-dispersive X-ray spectroscopy confirmed the superposition of copper nanoparticles with an average size of 70 nm on the inner surface of PET nanocannels. Samples were also examined by EPR spectroscopy for the subsequent reduction of copper ions.

Track membranes based on PET, activated by low-temperature plasma, were modified using a solution of N-isopropylacrylamide in an organic solvent [86]. The filtration efficiency of the modified membranes was 2.5 times higher than that of the original TM.

On the basis of TM as templates, secondary metal structures are grown, which are promising for use in optics and as auto-emission (cold) cathodes. Four methods for analyzing the distribution of pores over the surface of TM (nuclear filters) are considered [87]. It is shown that on some TM samples the pore distribution function is Poisson, on the majority there is clearly a deviation from the Poisson distribution. The fractal dimension of the pore distribution in the TM does not describe the distribution law, but characterizes the interaction between the fields of mechanical stress near the pores.

Experimental studies carried out to obtain TM samples by irradiating a monolithic PET film accelerated on the pre-fermentation section of the Kharkov Linear Heavy Ion Accelerator LUMZI by $Ar^{12+}$ ions with an energy of 1 MeV/nucleus [88]. And the subsequent physicochemical treatment of the irradiated film to form pores of a given size and density. Electron-microscopic studies of pore etching in a polymer film were performed. Samples of TM with a pore diameter

$\geq 0.05$ μm prepared for the development of membranes with bacteriostatic action in water treatment systems.

X-ray microscopy as a method of observing hidden details, opaque in the visible range of polymeric materials, and biological objects with variable penetration depth and micron or submicron resolution increasingly attracts the attention of researchers [89]. One of the reasons for this interest is due (for bioobjects) to the need to observe the processes occurring in biological tissues in vivo at the cell and whole organs level with submillimeter, and sometimes submicron resolution.

One of the main reasons restraining the widespread development of X-ray microscopy of these systems is as follows. In the short-wave part of the X-ray spectrum the absorption coefficients of many substances are small and very close. With increasing wavelength the difference in the absorption coefficients increases, but with it absorption also increases.

The possibility of obtaining enlarged images of objects with a micron resolution is shown [89]. An image of a number of objects with an increase of ~ 20 has been obtained. It was possible to register enlarged images of holes in shock TM with a minimum diameter of about $2\times10^4$ nm.

The problem of creating optical filters for soft X-ray and hard ultraviolet spectral regions with a high level of blocking of ultraviolet and visible background radiation is discussed in Ref. [90]. Unlike traditional thin-film systems, filters based on TM-porous polymeric films with micron and submicron pores are investigated. For the production of filters it is proposed to use membranes of polyethylene naphthalate and polyimide, the ultraviolet absorption edge of which lies near the boundary of the visible region. A comparison is made of membranes from polyethylene naphthalate and polyimide with known porous PET-TM obtained by etching ion tracks. The spectral characteristics of polyethylene naphthalate and polyimide films are analyzed, the process of formation of track tracks during the serial processing of samples by accelerated heavy ions and chemical reagents is analyzed, the main parameters of the resulting porous structures are determined. polyethylenenaphthalate and polyimide TM can be used in x-ray astronomy as filters detectors of solar telescopes and in optical experiments with laboratory plasma.

In this review the state and properties of track membranes for baromembrane processes (micro, ultra and nanofiltration) are considered. One of the way to increase the productivity of membrane modules and their selectivity is to modify their porous structure.They are porous materials that are designed to purify liquid and gas mixtures from unwanted particles, to isolate specific components of the mixture.

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## Резюме

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## ТРЕКТІК МЕМБРАНАЛАР: АЛУ ЖОЛДАРЫ ЖӘНЕ ҚОЛДАНЫЛУЫ

Мақалада заманауи қалдықсыз экологиялық таза технологиялардың негізгі құрамдас бөлігі ретінде тректік мембраналардың алынуы мен қолданылуы салаларындағы теориялық және экспериментальдық зерттеулердің нәтижелеріне шолу жасалынған. Түрлі мономерлерді полимеризациялау мен поликонденсациялау және дайын мембраналаларды модификациялау әдістерімен алынған әртүрлі тректік мембраналардың алынулары мен түзілу жағдайлары қарастырылған. Олардың селективтілігін арттыру жолындағы, физикалық-механикалық және электрхимиялық қасиеттерін зерттеу нәтиежелері келтірілген.

Су дайындау, өнеркәсіп өндірістерінің қалдықтары құрамындағы бағалы бөліктерін бөліп алу үшін қайта өңдеу, жоғары қысымда және масса тасымалдаудың интенсивті режимінде газды және сұйық қоспаларды айыру сияқты өзекті мәселелерді шешу үшін олардың қолданылу бағыттары анықталды.

**Түйін сөздер:** мембраналар, тректер, үдетілген иондар, ядролық фильтрлер, кеуек диаметрі.

## Резюме

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## ТРЕКОВЫЕ МЕМБРАНЫ: СПОСОБЫ ПОЛУЧЕНИЯ И ОБЛАСТЬ ИХ ПРИМЕНЕНИЯ

В статье обобщены результаты теоретических и экспериментальных исследований в области синтеза и применения трековых мембран, как главной составляющей современных безотходных экологически чистых технологий. Обсуждены особенности условий образования трековых мембран различных типов, синтезированных методами полимеризации или поликонденсации различных мономеров и химической модификацией готовых мембран. Представлены результаты исследований по повышению их селективной проницаемости, физико-механических и электрохимических свойств.

Определены перспективные направления их практического применения для решения актуальных проблем водоподготовки, переработки стоков промышленных производств с извлечением ценных компонентов, разделения газовых и жидких смесей при высоких давлениях и интенсивных режимах массопереноса.

**Ключевые слова:** мембраны, треки, ускоренные ионы, ядерные фильтры, диаметр пор.

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# APPLICATION OF MODIFIED HUMIC COMPOUNDS FOR RESTORATION OF DESERTIFICATION IN MANGISTAUS REGION

**Abstract.** In this article considered agrochemical experiments of modified humic preparations in the field conditions which carried out in the Mangistau region (Senek, Ushtagan, Tushchykadyk) on the black saxaul and zhuzgen crops. It is established that their use allows obtaining a high yield of saxaul seedlings of black and zhuzgen in nurseries. It has been revealed that the application of modified humic preparations contributes to the formation of a more branched and powerful root system, to an increase in the coefficient of soil moisture use by plants, to regulate the yield of nutrients and to improve the mineral nutrition of plants, to shorten the periods of their vegetation (by 10-15 days), to enhance the protective action of plants adverse factors. The survival rate of black saxaul and zhuzgen saplings transplanted from the nursery to mobile sand (over 2000 pieces each) was 94-98% and 67-72% in control variant in the absence of irrigation. The tests carried out over three years have shown that the application of modified composite humic preparations leads to an increase in the areas occupied by saxaul and zhuzgen (total forest area is more than 250 ha), stopping mobile barkhans and fixing sand.

**Keywords:** modified humic materials,growth stimulants,desertification, saxaul, zhuzgen, field tests.

One of the most acute problems at present is the problem of land degradation and desertification. The scale and intensity of this phenomenon are becoming more and more threatening [1-5]. About 75% of the territory of Kazakhstan is subject to degradation processes. In the Mangistau region the process of desertification has been intensifing and brings about economic and social losses. The main causes of land degradation are: erosion terrain, arid climate, alkalinity, salinity, etc. Natural soil conditions create natural background to the instability of soil covering to man-made impacts. The development of oil and gas industry and irrational use of natural resources have intensified the process of desertification of soils. There are different ways to restore desertified and degraded lands, however, the work performed does not lead to high results. Therefore, the development of innovative ways to restore degraded and deserted grounds is an important task. The use of composite humic materials makes it possible to solve the problems described above with a minimum of costs, since the chemical composition of humic compounds is compatible with organic ground substances by genetic characteristics, and humic materials also have structure-forming and moisture-retaining properties. Modification of their phosphogypsum and polymeric compounds enhances this ability, and also imparts new properties.

In mobile sands, the bulk of sands should be mastered by blocking barkhans and fixing sands, i.e. cultivation of saxaul, zhuzgen, salsola, etc. The experiments were laid by the Mangistau and Karakian regions, where mobile sand dunes are observed. Seeds and saplings of black saxaul and zhuzgen (figure 1) are taken as test crops. Before planting, furrows were prepared, modified composite humic preparations were introduced by spreading into the furrow, the expenditure was about 10-15 g.

Figure 1 – Humic growth-stimulants experiments layout in Mangistau and Karakiya regions

Modified compositional humic preparations have been applied in the following settlements in the Mangistau region:

1. Senek village
2. Usthagan village
3. Tuschykydyk village

Experiments have been carried out in the nursery, as well as on a fenced and sand-covered area.

In the nursery of Senek village modified humic preparations mixed with the ground and prepared grooves 5 m in long, 12 m in wide and 30-35 cm in deep, holes made on both sides of the groove, and planted zhuzgen seedlings (height 15-32 cm), just 500 pieces. From phenological observations it follows that the use of humic materials leads to an increase in the survival of the tested crops, their better growth and development throughout the growing season.

Agrochemical experiments carried out for three years. During the conducted works it was established that the application of modified humic preparations helps to obtain a stable and rather high yield of seedlings in the nurseries of the Mangistau region. In the course of work, seedlings of black saxaul and zhuzgen were already obtained from the first years, which were used to create protective plantations. The main way to create plantings of saxaul and zhuzgen in the region is planting seedlings. So, in 2015 black saxaul and zhuzgen seedlings - 100 pcs, and in 2016 - 300 pcs are transplanted to bare sandy soil from the nursery. It is shown that the application of modified humic preparations makes a positive effect on the plant from the beginning of the period of its growth and vegetation, in particular, improving such parameters as survival rate, growth, stem thickness, number of leaves. The survival rate of the tested crops was about 97-100%, and in control variants - 80-87%. At the same time, the vegetation period of the test plants reduced by 10-15 days.

Cultivated in the nursery in Ushtagan using modified humic preparations black saxaul seedlings (2000 pcs.) and zhuzgen (2000 pcs.) are landed on the sand in Ushtagan and Tushchykydyk villages in the fall of 2015. When calculating the number of plants that have risen, it turned out that humic preparations increase the habits of black saxaul and zhuzgen. As shown by phenological observations, after their transplantation, there was a noticeable advance in the growth and development of plants with the application of modified humic preparations.

During the vegetative period the experimental plants were externally noticeably distinguished by more intense color of leaves and by total power of their development in comparison with plants of the control variant. In experimental variants, plants grew by an average of 90-95%. Thus, the height of tested black saxaul was about 68-73 cm (the highest), in control variant about - 39-47 cm, experimental zhuzgen about - 81-89 cm, and control one from 42 to 48 cm.

It is known that irrigation is mandatory in the cultivation of saxaul and zhuzgen seedlings. However, in the conducted experiments the plants were not watered, and irrigation was carried out by sprinkling. As noted above, the weather conditions of the field season 2015-2017 were characterized by dry and hot weather. It was established that the experimental plants, in contrast to the control ones, were more resistant to a lack of moisture during their growth and development. With a lack of water, the stems of the experimental plants remained strong, and the leaf surface was saturated green and smooth, and in the control variant leaves turned yellow, the stem of the plants weakened and dried out, i.e. the use of modified humic preparations lowers the intensity of transpiration. This means that when processing plants with modified humic preparations, they use less water.

Effectiveness of the assimilation of nutrients from the environment depends on the volume and quality of their root system. In the course of the experiments it was established that the application of modified humic preparations promotes the formation of a more branched and powerful root system. The developed root system promotes the intensive intake of nutrients and the best growth of saxaul and zhuzgen.

The effectiveness of the assimilation of nutrients from the environment depends on the volume and quality of their root system. In the course of the experiments it was established that the use of modified humic preparations promotes the formation of a more branched and powerful root system. The developed root system promotes the intensive intake of nutrients and the best growth of saxaul and zhuzgen. It should be noted that in the absence of watering and loosening of the soil in experimental variants for 3 years, the black saxaul and zhuzgen plants grew by 2.2-3.1 m on average, their trunks were strong and branched, average trunk diameter was 15-26 cm (figure 2). Survival rate of the experimental crops was 94-98%, and in the control variant - 67-72%, the plants on average grew by 20-30%.

Figure 2 – Influence of modified humic preparations on the plants growth and development

**Conclusions.** Thus, as a result of use of modified humic preparations from the transplanted from the nursery to the sand black saxaul and zhuzgen appeared a forest which led to the stopping of mobile dunes. In addition, when using them the soil is enriched with nutrients, its agrotechnical properties are improved. This allows us to return the soil to a productive state and solve the problem of desertification of ground. The use of humic preparations also helped to regulate the nutrient yield during the entire growing season of development of experimental crops and improve the mineral nutrition of plants, and helped to better growth and development of black saxaul and zhuzgen.

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## Резюме

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### ТҮРЛЕНДІРІЛГЕН ГУМИНДІ ҚОСЫЛЫСТАРЫН МАҢҒЫСТАУ ОБЛЫСЫНДА ШӨЛЕЙТТЕНГЕН ТОПЫРАҚТЫ ҚАЛПЫНА КЕЛТІРУГЕ ҚОЛДАНУ

Түрлендірілген гуминді материалдарға Маңғыстау обл. (Сенек, Ұштаған, Тұщықұдық а.) егістік жағдайында қара сексеуіл мен жүзгенге қолдану арқылы агрохимиялық сынақтар жүргізілді. Бұларды қолдану қара сексеуіл мен жүзгеннің биотикалық мен абиотиктік стрестерге тұрақтылығын арттыратындығы, құмды бекітіп және жылжымалы құмды тоқтататындығы анықталды.

**Түйін сөздер:** түрлендірілген гуминді материалдар, өсімдіктің өсуін тездеткіштер, шөлейттену, сексеуіл, жүзген, егістік сынақтар.

## Резюме

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### ИСПОЛЬЗОВАНИЕ МОДИФИЦИРОВАННЫХ ГУМИНОВЫХ СОЕДИНЕНИЙ ДЛЯ ВОССТАНОВЛЕНИЯ ОПУСТЫНЕННЫХ ПОЧВ В МАНГИСТАУСКОЙ ОБЛАСТИ

Проведены агрохимические опыты модифицированных гуминовых препаратов в полевых условиях Мангистауской обл. (с. Сенек, Уштаган, Тущыкудык) на культурах черного саксаула и жузгена. Установлено, что их применение повышает устойчивость саксаула черного и жузгена к биотическим и абиотическим стрессам, приводит к остановке подвижных барханов и закреплению песка.

**Ключевые слова:** модифицированные гуминовые материалы, ростостимуляторы, опустынивание, саксаул, жузген, полевые испытания.

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# CHARACTERISTICS OF MICROWAVES, SOME ASPECTS THEORY OF MICROWAVE HEATING AND THE FIELD OF APPLICATION OF MICROWAVES IN ORGANIC CHEMISTRY AND CHEMISTRY OF NATURAL COMPOUNDS

**Abstract.** The review considers the characteristics of microwaves, the theory of microwave heating in a comparative analysis with the features of thermal heating. The presented material shows the areas of use of the microwave radiation in organic chemistry and chemistry of natural compounds.

**Key words:** microwave radiation, microwave heating.

The problem of complex processing of plant raw materials and the creation of new highly effective methods for obtaining biologically active substances (BAS) are among the priority directions in the development of chemical science. At the same time, an important aspect in the development and use of new chemical, physico-chemical, physical and biological approaches is the following principles of «green chemistry» [1, 2].

Currently, studies are underway to modify and improve these processes, which include such areas as: improvements in the technical equipment of the process, replacement of the conditions for carrying out the reaction and extraction, including the solvents used, the use of various factors of physical impact, including ultrasonic and microwave treatment [3-7].

**Microwave radiation and its characteristics.** Microwaves are electromagnetic waves, consisting of two oscillating perpendicular fields: electric and magnetic (figure 1).

The microwave radiation is electromagnetic radiation, which includes a decimeter, centimeter and millimeter wave ranges. Quantum energy, frequency ($\nu$) and wavelength of their waves ($\lambda$) are joined by rigid dependencies (figure 2). In accordance with them, the electromagnetic spectrum is conventionally divided into partially overlapping bands, depending in part on the source of the radiation. Microwave is usually called the spectral region in the frequency range 300 GHz – 300 MHz (wavelength from 1 mm to 1 m). It is located in the interval between the infrared and radio frequency ranges [8-10].

Microwaves are used as information carriers or as energy vectors. Microwave radiation of low intensity is used in communications, mostly portable, and microwave radiation of high intensity is used for contactless heating of bodies. The second direction is related to the direct action of waves on a material that is

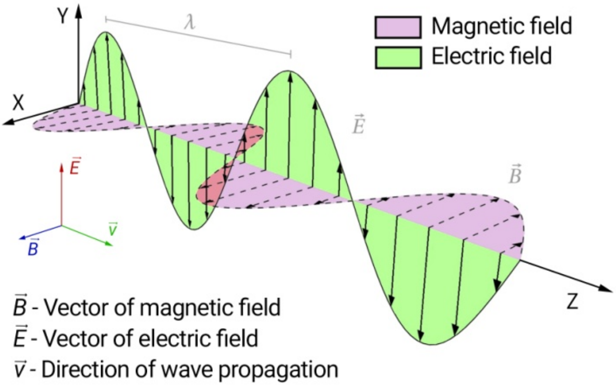


Figure 1 – Schematic description of the electromagnetic wave

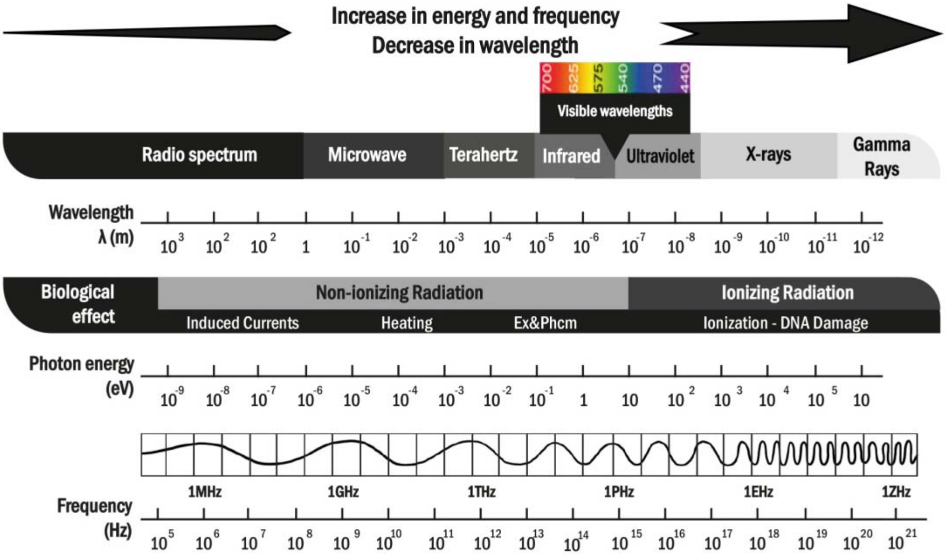


Figure 2 – The scale of electromagnetic radiation

capable of absorbing some of the electromagnetic energy and turning it into heat and used for heating [8, 9].

In most microwave installations, including household microwave ovens, a frequency of 2,450 MHz is used, which can only cause the rotation of molecules. This frequency was chosen to avoid interference with radar and telecommunications systems. The wavelength and frequency are related by the relation: $\lambda = c/\nu$, where $\lambda$ - wavelength, c - wave propagation velocity, $\nu$ – frequency. Knowing that electromagnetic waves propagate at a speed of light equal to 300,000 km/s, it is not difficult to calculate what the wavelength of the microwave radiation of a given frequency is equal to: $\lambda = c/\nu = 12.25$ cm.

**Features of thermal and microwave heating.** An important factor affecting the extraction process and the reaction in solutions and heterogeneous systems is the increase in temperature. The traditional (thermal) method of heating is characterized by the transfer of heat from the surface to the volume of matter by means of thermal conductivity and convection (figure 3). However, with a slow transfer of thermal energy from the source to the sample and inside it, obstacles are created that do not allow significantly accelerating the course of the processes. In the case of the low thermal conductivity of the object, heating proceeds slowly and is complicated by local overheating on the surface [10].

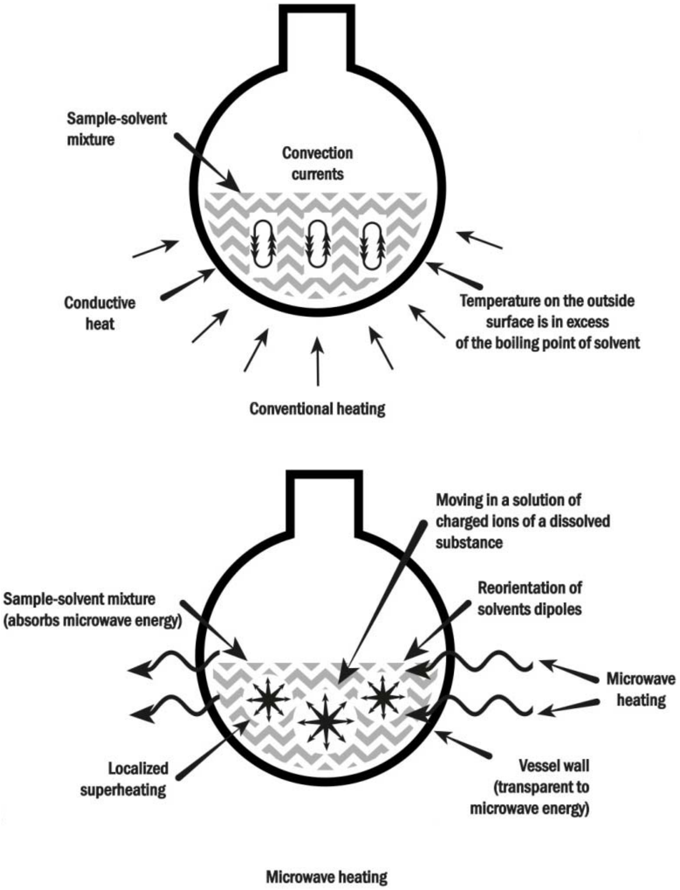


Figure 3 – Schematic representation of specificity thermal and microwave heating [12]

Microwave heating is an alternative way to increase the temperature. When microwave radiation is used, the mechanism of interaction with matter consists in absorbing the energy of electromagnetic radiation and scattering it in the form of heat. In this case, heating occurs from within the entire volume of the sample due to the creation of the effect of dielectric losses. Microwave heating differs from the traditional method by a high volume and time gradient, and also by the unequal ability of solutions and components of a heterogeneous system that differ in composition to absorb radiation energy [11].

There are two main mechanisms for the interaction of microwave radiation with matter. The transformation of electromagnetic energy into thermal energy is due to two mechanisms: ionic conductivity and dipole rotation. Ionic conductivity generates heat due to resistance. Migration of dissolved ions causes collisions between molecules because the direction of ions varies as many times as the field changes sign. Dipole rotation is associated with an alternative motion of polar molecules which is caused by the continuously changing direction of the vector of the electrical component of the radiation. Multiple collisions associated with such a movement of molecules generate energy and, consequently, an increase in temperature. The frequency of microwave radiation corresponds to the rotational motion of molecules (figure 4), and in the condensed state, in which there is no free rotation, the absorption of energy leads to its redistribution between molecules and homogeneous heating.

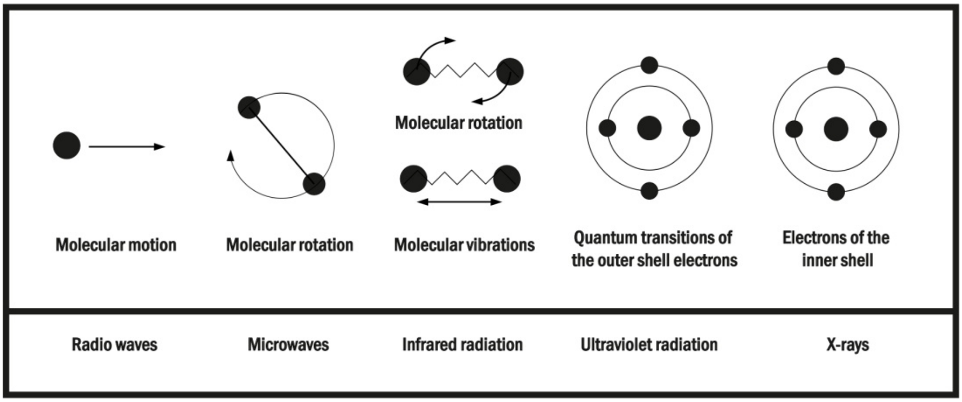
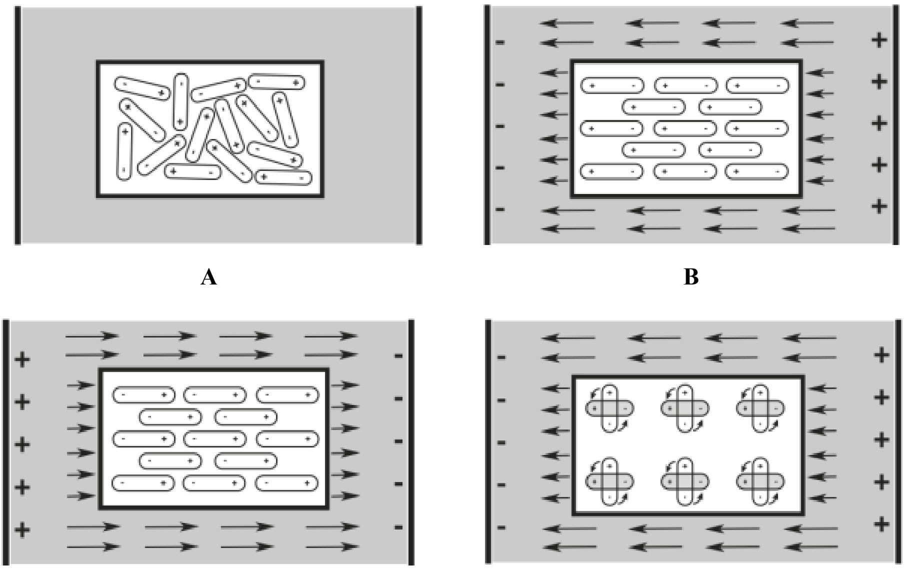


Figure 4 – Motion of molecules at different frequencies electromagnetic radiation [13]

Since the frequency of microwaves used is 2,450 MHz, and one hertz is one oscillation per second, the megahertz is one million oscillations per second. During one period of the wave, the field changes its direction twice, hence, the field in which the molecules are located changes the polarity 4,900,000,000 times per second. The change in the electrical component of the wave $4.9\times10^9$ times per second contributes to the generation of unorganized motion of polar molecules, which when irradiated by microwaves and produce heat [4, 5]. This heating is a consequence of the interaction of the electrical component of the electromagnetic wave with charged or polar particles. In the absence of an external electric field effect, such particles have random chaotic motion or oscillate with respect to the equilibrium state (figure 5A). When an external electric field is imposed, such



A B

C D

Figure 5 – Schematic representation of interaction microwave radiation with polar particles

particles are ordered, electrostatic forces will tend to orient the dipole moments of the molecules along the field lines (figures 5B and 5C), and if the field is ascending, their orientation will change with each oscillation (figure 5D). Thus, the reorientation of particles, which is activated by an alternating electric field, and causes intense internal heating.

Thus, the effect of the electromagnetic wave on the substance of the microwave band leads to a continuous reorientation of the polar molecules, due to the continuously changing direction of the vector of the electric component of the radiation, which, as a result of intermolecular interactions, leads to the release of heat.

In the case of a condensed phase in which free charged particles exist, these particles will move in accordance with a change in the electric field and generate an electric current. This situation is typical for metals, where electrons act as mobile charged particles, and for solutions of electrolytes in which charge carriers are ions. If microwave radiation is used for a phase containing polar molecules, then these molecules will orientate themselves in the applied electric field and reorient themselves with its oscillations. Such a motion and collisions of molecules in the condensed phase will cause heating, thus conditioning «from within». Another property of the microwave heating is that it does not affect nonpolar molecules and materials such as quartz, ceramics and glass that do not contain water, Teflon, polyethylene, alkanes. This allows them to be used (quartz, ceramics, glass, teflon) as dishes for chemical reactions, as well as (non-polar solvents) as a specific reaction medium. As a rule, in the microwave treatment the polar solvents are used, because they effectively absorbing microwave radiation.

**Some aspects of the theory of the microwave heating and effects of microwaves on solutions.** Discussing the feature of microwave heating it should be noted that in contrast to thermal heating when it is used there is a so-called dielectric heating. In this case, the total heating is made up of the electrical conductivity losses that occur when in a dielectric or a reaction mixture there are free ions capable of moving in an electric field and which, when moving and colliding with the molecules of the substance, transform some of the electrical energy into thermal energy, as well as to relaxation losses, which are due to the orientation of the dipole molecules in the direction of the lines of force of the electric field [10]. At the frequency that is used at 2450 MHz, the electric field strength vector changes its direction $4.9 \cdot 10^9$ times/s. Because of it the vibrational vibrations of the dipole moments of the molecules occur, which contributes to the transfer of some of the energy of the electromagnetic field, and accordingly to the temperature increase which occurs uniformly throughout volume, taking into account the depth of penetration of microwave radiation (table 1).

Table 1 – Data on penetration depth microwave radiation (20-25 °C) [10 (p.16), 14]

| Substance | Depth of penetration (cm) microwave radiation at different frequencies | | |
|---|---|---|---|
| | 433 MHz | 915 MHz | 2450 MHz |
| Water | 70,5 | 23,4 | 3,5 |
| Methanol | 33,0 | 7,8 | 1,4 |
| Glass | 4600 | 2180 | 840 |

In the superposition of a high-frequency electromagnetic field, in addition to dielectric polarization, atomic, electronic, and structural polarization are also observed. The first is due to the displacement of the atoms relative to each other because of the nonuniformity of the charge distribution, the second is due to the displacement of electrons relative to the atomic nucleus. The contribution of structural polarization, which is observed at the interface of inhomogeneous media, is relatively small [9, 10].

The release of heat is observed merely when the materials have dielectric losses during microwave irradiation. The ability of a substance to store potential energy under the action of an electric field is characterized by a dielectric constant, denoted by ε'. The coefficient of dielectric loss ε'' determines the efficiency of conversion of electromagnetic energy into heat. The absorbed energy depends on the defined coefficient as the tangent of the dielectric loss angle:

$$\tan \delta = \varepsilon'' / \varepsilon' \qquad (1)$$

where ε'' is the coefficient of dielectric losses, which characterizes the efficiency with which the energy of the electromagnetic field is converted into heat, and ε' is the dielectric constant.

Thus, the value of the tangent of the dielectric loss angle characterizes the ability of a given material at a fixed temperature to absorb MB radiation of a certain frequency and convert this energy into energy of thermal motion. The values of ε 'and ε" depend on the nature and state of the substance, the frequency of electromagnetic radiation and temperature. Compounds that have high dielec-tric losses are mainly polar compounds. The dielectric constants of some solvents are given in table 2.

Table 2 – Values of the dielectric constant and coefficient
the dielectric losses of some solvents [9]

| Solvent | Frequency | | | | | |
|---|---|---|---|---|---|---|
| | $3\cdot10^{8}$ Hz | | $3\cdot10^{9}$ Hz | | $1\cdot10^{10}$ Hz | |
| | ε' | ε" | ε' | ε" | ε' | ε" |
| Water (t=25 ºC) | 77,5 | 1,2 | 76,7 | 12,0 | 55,0 | 29,7 |
| Aquatic NaCl (0,1 M) | 76,0 | 59,0 | 75,5 | 18,1 | 54,0 | 30,0 |
| Heptane | 1,97 | | 1,97 | $2\cdot10^{-4}$ | 1,97 | $3\cdot10^{-3}$ |
| Methanol | 30,9 | 2,5 | 23,9 | 15,3 | 8,9 | 7,2 |
| Ethanol | 22,3 | 6,0 | 6,5 | 1,6 | 1,7 | 0,11 |
| n-Propanol | 16,0 | 6,7 | 3,7 | 2,5 | 2,3 | 0,20 |
| n-Butanol | 11,5 | 6,3 | 3,5 | 1,6 | 0,2 | |
| Ethylene glycol | 39,0 | 6,2 | 12,0 | 12,0 | 7,0 | 5,5 |
| Carbon tetrachloride | 2,2 | | 2,2 | $9\cdot10^{-4}$ | 2,2 | $3\cdot10^{-3}$ |

The rate of temperature rise due to the electric field of microwave radiation is determined by the following equation:

$$\frac{dT}{dt} = \frac{const\cdot\varepsilon'\cdot f\cdot E^{2}}{\rho\cdot C_{\rho}}$$

where f is the frequency of the radiation (Hz); E is the field strength (V/cm); ρ – density of the substance (kg/cm$^3$); $C_p$ is the heat capacity of the substance (kJ/kg·K).

It follows from the equation that at a constant radiation frequency, the heating rate depends on the electro-physical properties of the substance and the power of the electromagnetic radiation.

The value of the thermal energy (Q, W/cm$^3$), which is released per unit of time per unit volume, can be determined from the equation (2) below, from which it follows the amount of energy released depends on the dielectric properties of the object, the frequency and the electric field strength [ 10]:

$$Q = 0{,}055\cdot10^{-14}\cdot\varepsilon'\cdot f\cdot E^{2}\cdot tg\,\delta = 0{,}555\cdot10^{-14}\cdot\varepsilon''\cdot f\cdot E^{2} \qquad (2)$$

where f is the radiation frequency, Hz; E is the intensity of the electrical component of the electromagnetic field, V/cm, ε ' is the dielectric constant, tg δ is the tangent of the dielectric loss angle, ε '' is the coefficient of dielectric losses.

The last expression shows that the amount of thermal energy released in the material depends only on the electrical characteristics of the material and the field parameters and does not depend on the thermal conductivity of the material. This feature obtain the primary advantage of microwave heating, which allows to significantly intensify the process of material heating in comparison with any other traditional type of heating, where the main role in the heating speed is played by thermal conductivity.

As a result of the interaction of radiation with matter, its intensity decreases exponentially as it passes through matter. The distance from the material surface at which the energy flux density decreases by "e" times (where, e is the basis of natural logarithms) in comparison with its value on the surface is called the depth of penetration. The depth of penetration of the electromagnetic field into matter decreases with increasing ε ', tg *δ*, f, and the released thermal energy increases.

Because of the decrease in the radiation intensity, the thermal power released per unit volume of the material falls off exponentially. It is therefore natural to expect a decrease in temperature from the surface to the center of the volume of the material. This occurs when the depth of penetration is much less than the thickness of the heated object. In the opposite case, when the depth of penetration is comparable or exceeds the dimensions of the object, there is a reverse, or inversion, temperature profile, i.e. the temperature inside the material is higher than on the surface. This is explained by thermal radiation from the surface and by convection cooling of the outer layers of the material with ambient air. The volume, and not only the surface nature of the heating of the irradiated samples, in the case of the usual thermal action, is an important feature of the action of microwaves.

From the foregoing it follows that microwave heating has a completely different nature than convection heating. In the case of convection heating, diffusive heat transfer from the coolant to the heated substance occurs. In the microwave heating, the increase in the internal energy of a substance occurs as a result of the dissipation in the substance itself of some part of the absorbed electromagnetic energy. From this follows the following significant advantages and peculiarities of microwave heating: heating occurs throughout the volume of the material, and the thermal conductivity of the material does not play a role; the temperature change of the heated material occurs without inertia in accordance with the change in the input power; the possibility of dynamic temperature control during the experiment; possibility of rapid temperature rise of the material up to the set values; the absence of heat transfer agent eliminates the possibility of burning the material.

An important factor to consider when using microwave heating is the thermal and electrical strength of the object, which is the limit for increasing the strength of the electric field. In this case, it is necessary to take into account that as the frequency increases, the depth of penetration of microwave radiation into the dielectric decreases (table 1).

In the case of microwave heating of solutions, the conversion of electromagnetic energy into thermal energy takes place due to two mechanisms: due to the reorientation of the dipoles of the solvent in an alternating electric field and as a result of directed migration of the dissolved ions present in the solution under the action of an external field, that is, due to dipole polarization and ionic conductivity [10-12].

The second factor is especially important for the release of heat during microwave exposure to solutions. Its mechanism of microwave heating is associated with conductivity effects, which can be caused by electrophoretic migration of ions in a solution when an electromagnetic field is applied. Such migration of ions is actually an electric current flowing through the solution. The passage of current I through a conductor with resistance R leads to the release of heat. Moreover, the higher the concentration and mobility of ions, the more intense the heating. Ionic conductivity is the conductive migration of dissolved ions that occurs when an electromagnetic field is applied, which leads to a loss of I2R (where I denotes the current intensity and R is the resistance) through the resistance to ion flow. Since the resistance R increases with increasing temperature, and the strength of the current carried by the ions I with increasing their concentration, both these factors significantly affect the tangent of the losses of microwave radiation in solutions. The contribution of the mechanism of ionic conductivity in solutions is determined by the dimensions, charges and specific electric conductivity of ions, and also by the interaction of ions with solvent molecules. Ionic conductivity depends on the concentration, mobility of ions and temperature of the solution [11].

In the case of microwave heating of water and other solvents, in which the degree of dissociation is low, the mechanism of dipole polarization will be the main one. The rate of heating will depend on the initial temperature, the frequency of the radiation and on the properties of the solvent, in particular its dielectric constant. The contribution of dipole polarization or ionic conductivity is largely determined by the temperature. For water molecules and other solvents, the dielectric losses due to the contribution of dipole rotation decrease with increasing temperature, and the dielectric loss due to ionic conductivity, on the contrary, increases with increasing sample temperature [11, 15].

With thermal heating, the number of boiling points in the solution volume is much less than that of the surface. In microwave treatment, heating is carried out from within throughout the entire volume, as a result of which the temperature of the solution is higher than the temperature of its environment (the walls of the vessel and the gas phase above the surface of the solution, etc.). In addition to the bulk thermal effect, the advantage of microwave heating is the rate at which such heating takes place. When using microwaves, the effect of overheating is possible, since the temperature, which is reached, can be higher than their theoretical boiling point. Thus, the rate of heating of the sample using microwaves depends on the dielectric characteristics, heat capacity, volume and power of the radiator.

Table 3 – Boiling temperatures ($T_b$, ºC) and temperatures under microwave heating of some organic solvents of 50 ml volume after microwave for 1 minute at 560 W, 2450 MHz [9]

| Solvent | Conventional heating | Microwave heating |
|---|---|---|
| | Boiling temperature $T_b$, ºC | Heating temperature $T_h$, ºC |
| Water | 100 | 81 |
| Methanol | 65 | 65 |
| Ethanol | 78 | 78 |
| n-Propanol | 97 | 97 |
| n-Butanol | 117 | 109 |
| 1-Pentanol | 137 | 106 |
| 1-Hexanol | 158 | 92 |
| Dimethylformamide | 153 | 131 |
| Hexane | 68 | 25 |
| Heptane | 98 | 26 |
| Ethyl acetate | 77 | 73 |
| Chloroform | 61 | 49 |
| Acetone | 56 | 56 |
| Diethyl ether | 35 | 32 |
| $CCl_4$ | 77 | 28 |
| Acetic acid | 119 | 110 |

Thus, table 3 gives data on the temperature values that are reached by microwave heating of some solvents.

The variety of factors influencing the microwave heating makes it difficult to model this process, although the literature suggests a physical model that allows calculations of the temperature change in an open system, analysis of the mechanisms for obtaining and energy losses in solution, and theoretical aspects of microwave heating of solids [16, 12]. The review [17] discusses the theories underlying microwave dielectric heating and presents dielectric data for various organic solvents used in microwave synthesis.

**Areas of use of microwave treatment in organic chemistry and chemistry of natural compounds.** Microwaves have found application in various fields of science, as shown in figure 6. As can be seen from the presented data, microwave radiation has found the greatest application in chemistry (42.4%), chemical engineering (14.5%) and materials science (9.3%).

The first use of microwave treatment in chemistry was described in 1975 by Adu-Samra et al. [19] who used a microwave oven for laboratory analysis of trace amounts of metals in biological media. Since that time, the number of scientific publications devoted to the effects of microwaves and their use in chemistry has

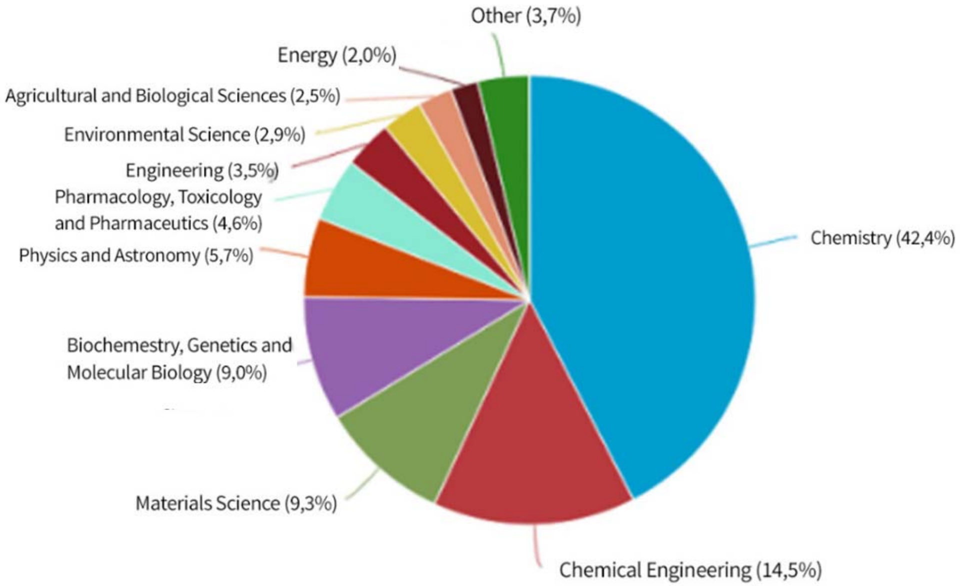


Figure 6 – Application of microwaves in various fields of science [18]

been increasing every year. Thus, according to the data of [18], there is a steady interest of researchers in the use of microwave radiation, which is confirmed by the number of publications presented on the histogram (figure 6).

At present, microwave radiation has found practical application in sample preparation [11, 20], for extraction [21-34], drying of plant objects [35], thermal

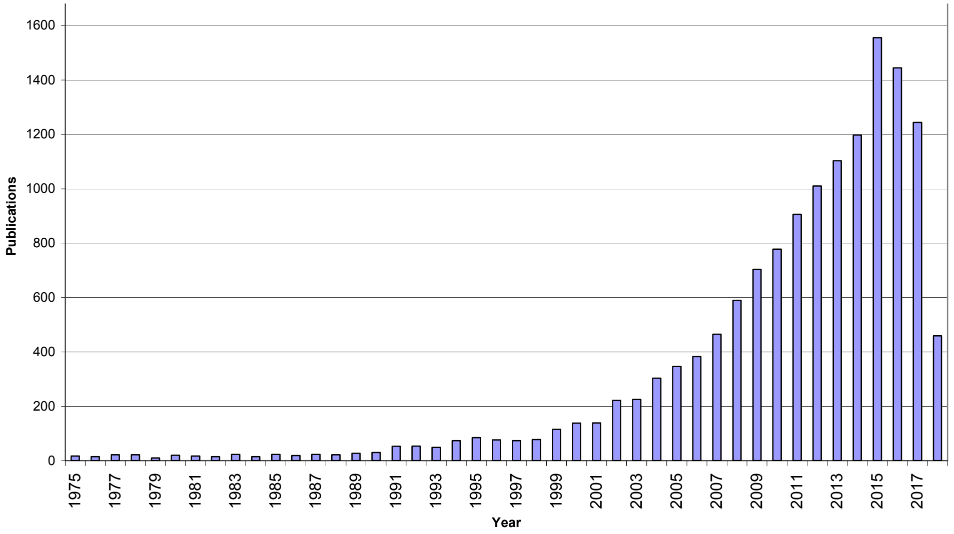


Figure 7 – Number of publications on use microwave radiation in chemistry [18]

decomposition of plant biomass [36], in particular hydrolysis of plant biomass for biofuel production (bioethanol), as well as for enzymatic [37] and acid hydrolysis [38,39], pyrolysis of wood [40], delignification, for example rice hull [41] and beech wood [42], and after the appearance of the first works on the use of microwave radiation in organic synthesis, which by appeared in 1986 [43,44], intensive studies of the influence of microwave treatment on the course of chemical reactions and chemical modification of plant raw materials began. Thus, the accumulated experimental material indicates the acceleration of many chemical reactions under the action of microwave treatment: elimination, esterification, cycloaddition, isomerization, condensation, substitution, hydrolysis, oxidation, etc. [10, 45-51]. The reaction conditions are extremely diverse, and the final effect depends on the nature of the process, the nature of the reacting particles, the type of solvent and the power of the microwave radiation.

Microwave radiation is used to dry food materials, as well as plant objects. Overview of the latest microwave technologies, including microwave drying, heating and sterilizing fruits (bananas, apples, olives, blueberries, kiwi, strawberries, etc.), vegetables (potatoes, onions, beans, pumpkin, eggplant, garlic, cabbage, tomato, cassava, lentils, chickpeas, broccoli, brussels sprouts, cauliflower, etc.), fish (sardine, carp, salmon, cod, etc.) and meat products (beef, etc.) are discussed in detail in [52, 53]. Data on the use of microwaves for drying grain of wheat after its treatment with aqueous solutions of disinfectants, protective equipment, etc. are described in [54], and the application of microwave radiation for wood drying is presented in [55].

Hydrolysis under the influence of microwave radiation was used to synthesize a number of organic derivatives [56, 57], was used for the cleavage of proteins in order to establish their amino acid composition [58, 59] and in the analysis of the composition of some natural compounds [59, 60]. Thus, the authors of the study [39] used acid hydrolysis to convert carbohydrates derived from biomass into sugars such as glucose, mannose and fructose, which are important universal products that are easily processed into biofuel. The highest yield of mannose (92.11%) was achieved under optimal conditions: 148 °C, 0.75 N $H_2SO_4$, time 10 min and substrate to solvent ratio (w/v) 1: 49.69.

Hydrolysis should take into account the fact that under severe conditions with the use of concentrated acids and increasing the temperature, the process will promote the cleavage of most of the hydrolysable bonds in organic compounds, which may affect the course of side processes and the destruction of the starting compounds.

The results of studies on the microwave oxidation of individual organic substances, such as amino acids, monosaccharides and stearic acid, whose structures are the basis of such natural compounds as proteins, carbohydrates and fats, are reported in Refs [61, 62].

As an example of chemical modification of plant raw materials, reviews [63, 64], which describe methods for modifying polysaccharides under the action of microwave irradiation, are given. In [65] the process of cellulose treatment with crosslinking reagents is presented, and the authors of the study [66] indicated the possibility of esterification of cellulose from marine herbaceous plants *Posidonia oceanica* with succinic, maleic and phthalic anhydride. The results of studies on carboxymethylation of cellulose under the influence of microwave treatment are summarized in the reviews [67, 68], the results on carboxymethylation of cotton stems are presented in [69], and in the article [70] - cassava starch.

Of particular interest are papers aimed at investigating the selective extraction of organic compounds by solvents under the action of microwave radiation [21-34]. To date, the microwave-assisted extraction (MAE) technique has been developed to extract soluble components from plant, ecological, biological, geological and metallic matrices. Simultaneously, technology and technology were developed with the creation of commercial reactors for laboratory microwave extraction technology both in closed reactors and in systems communicating with the atmosphere [30, 31, 71]. Thus, in [27], methods for extracting organic toxic substances are described, and the review [72] presents a material on the use of microwave radiation for the separation of polychlorinated biphenyls, pesticides, phenols, organometallic compounds and dioxins. Great prospects are associated with the use of microwave extraction in the chemistry of natural compounds to extract components of plant raw materials [29-34].

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## Резюме

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## МИКРОТОЛҚЫНДАР СИПАТТАМАСЫ, СОНЫМЕН БІРГЕ МИКРОТОЛҚЫНДЫҚ ҚЫЗДЫРУ ТЕОРИЯЛАРЫНЫҢ КЕЙБІР АСПЕКТІЛЕРІ МЕН ОРГАНИКАЛЫҚ ХИМИЯДА ЖӘНЕ ТАБИҒИ ҚОСЫЛЫСТАР ХИМИЯСЫНДА МИКРОТОЛҚЫНДЫҚ СӘУЛЕЛЕНУДІҢ ҚОЛДАНЫЛУЫ

Өсімдік материалдарын кешенді өңдеу мәселесі мен биологиялық активті заттарды алудың жоғары эффективті әдістерін жасау химия ғылымын дамытудың басым бағыттарының ішіне кіреді. Осы процестерді жақсарту үшін маңызды жағдайы «жасыл химия» принциптерін сақтау болып табылады. Шолуда микротолқындар сипаттамалары, сонымен бірге микротолқындық қыздыру жылулық қыздыру ерекшеліктерімен салыстырмалы сараптамасы және еріткіштерге микротолқындардың кейбір әсер ету мәселелері қарастырылған. Микротолқындық сәулелендірудің органикалық химияда және табиғи қосылыстар химиясында микротолқындық сәулеленудің қолданылу аймақтары қарастырылған.

**Түйін сөздер:** микротолқындық сәулелендіру, микротолқындар.

## Резюме

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## ХАРАКТЕРИСТИКИ МИКРОВОЛН, А ТАКЖЕ НЕКОТОРЫЕ АСПЕКТЫ ТЕОРИИ МИКРОВОЛНОВОГО НАГРЕВА И ПРИМЕНЕНИЕ МИКРОВОЛНОВОГО ИЗЛУЧЕНИЯ В ОРГАНИЧЕСКОЙ ХИМИИ И ХИМИИ ПРИРОДНЫХ СОЕДИНЕНИЙ

Проблема комплексной переработки растительных материалов и создание высокоэффективных методов получения биологически активных веществ входят в число приоритетных направлений развития химической науки. Важным условием для улучшения этих процессов является соблюдение принципов «зеленой химии». В обзоре рассматриваются характеристики микроволн, а также теория микроволнового нагрева в сравнительном анализе с особенностями теплового нагрева и некоторые вопросы влияния микроволн на растворы. Рассмотрены области использования микроволнового излучения в органической химии и химии природных соединений.

**Ключевые слова:** микроволновое излучение, микроволны.

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# THERMODYNAMIC PROPERTIES OF ITTRIUM-MAGNESIUM BISMUTHITE

**Abstract.** The possibility of obtaining bismuthite of yttrium with an s-element in a solid-phase method from yttrium (III) oxides, bismuth (III) and magnesium carbonate is shown. Using X-ray diffraction analysis determined that yttrium-magnesium bismuthite crystallizes in cubic syngony, and also the parameters of primitive cell, X-ray and pycnometric densities. To investigate the isobaric heat capacity of the compound used dynamic calorimetry in the interval from 298.15 to 673 K. The λ-shaped jump at 473 K on the curve of the temperature dependence of the heat capacity of the compound indicates a second-order phase transition due to valuable electrophysical properties

**Keywords:** yttrium-magnesium bismuthite, calorimetry, heat capacity, second-order phase transition, thermodynamic functions.

The study of systems consisting of alkaline-earth oxides, bismuth and rare-earth elements is of great importance for inorganic materials science. The new bismuthites formed in these systems can possess both original and unique properties.

The paper presents the results of the synthesis and calorimetric study of the heat capacity of yttrium-magnesium bismuthite. The synthesis was carried out by a solid-phase method. The stoichiometric amounts of yttrium oxide, bismuth and magnesium carbonate were mixed and thoroughly rubbed in an agate mortar [1]. The heat treatment of the mixture was carried out in an alundum crucible in a selitic furnace in 3 stages in the temperature range 600 – 1200°C for 30 hours. After each step, the mixture was blended and grinded in an agate mortar.

The formation of the equilibrium composition of the compound was monitored by X-ray diffraction analysis using a DRON-2.0 setup and $CuK_\alpha$ – radiation filtered by a Ni-filter ($U = 30$ kV, $I = 10$ mA, pulse counter scale 1000 pulses per second, counter rotation rate 2 grad/min, rotation speed of 1000 pulses per second, time constant $\tau = 5$ seconds, angular interval $2\theta$ from 10 to 90°). The intensity of the diffraction peaks was estimated from the hundred-point scale. The X-ray powder diffraction patterns of the research compound were determined by the homology method [2].

The reliability of the results of the X-ray display indicates a satisfactory agreement between the experimental and theoretical values of the reciprocals of the squares of the interplanar distances (table 1).

The density of the resulting compound was determined by a pycnometric method [3]. It is established that the compound under consideration crystallizes in a cubic system with the following parameters of a primitive cell: $a = 10.84$ Å, $V^0 = 1272$ Å$^3$, $Z = 16$, $V_{primit.\ cell} = 79.5$ Å$^3$, $\rho_{x\text{-}ray} = 8.06$, $\rho_{pycn} = 7.98$ g/cm$^3$.

Table 1 – X-ray indication of $YMgBiO_4$

| $I/I_0$ | d, Å | $10^4/d^2_{exp.}$ | hkl | $10^4/d^2_{teor.}$ |
|---|---|---|---|---|
| 100 | 3.1212 | 1026 | 222 | 1022 |
| 43 | 2.7054 | 1366 | 400 | 1363 |
| 6 | 2.0934 | 2292 | 333 | 2300 |
| 45 | 1.9141 | 2729 | 440 | 2726 |
| 37 | 1.6323 | 3753 | 622 | 3748 |
| 9 | 1.5629 | 4094 | 444 | 4089 |
| 3 | 1.4885 | 4513 | 641, 720 | 4515, 4514 |
| 5 | 1.3537 | 5457 | 800 | 5451 |
| 11 | 1.2429 | 6473 | 662 | 6474 |
| 9 | 1.2113 | 6815 | 840 | 6815 |

The heat capacity of the synthesized substance was investigated on a serial ITC-400 calorimeter [4, 5]. From the experimental values, the molar heat capacities of YMgBiO4 were calculated (table 2).

Table 2 – Experimental values of the heat capacities $YMgBiO_4$

| T, K | $C_p \pm \overline{\delta}$, J/(g·K) | $C_p^0 \pm \overset{0}{\Delta}$, J/(mol·K) |
|---|---|---|
| 298.15 | 0.2063 ± 0.0064 | 80 ± 7 |
| 323 | 0.2527 ± 0.0055 | 98 ± 6 |
| 348 | 0.2931 ± 0.0087 | 113 ± 9 |
| 373 | 0.3121 ± 0.0055 | 120 ± 6 |
| 398 | 0.3293 ± 0.0075 | 127 ± 8 |
| 423 | 0.3416 ± 0.0069 | 132 ± 7 |
| 448 | 0.4010 ± 0.0086 | 156 ± 9 |
| 473 | 0.4582 ± 0.0072 | 177 ± 8 |
| 498 | 0.4036 ± 0.0121 | 156 ± 13 |
| 523 | 0.3781 ± 0.0099 | 146 ± 11 |
| 548 | 0.3736 ± 0.0119 | 144 ± 13 |
| 573 | 0.3689±0.0067 | 142 ± 7 |
| 598 | 0.3707±0.0097 | 143 ± 10 |
| 623 | 0.3790±0.0062 | 146 ± 7 |
| 648 | 0.3844±0.0087 | 148 ± 9 |
| 673 | 0.3908±0.0103 | 151 ± 11 |

When researching the dependence of the heat capacity of $YMgBiO_4$ on the temperature at 473 K, a sharp anomalous jump was observed, probably connected with a second-order phase transition. These transitions can be associated with cation redistributions, with changes in the coefficients of thermal expansion and changes in the magnetic moments of the synthesized compound. In connection with the presence of a phase transition, the dependence $C_p^0 \sim f(T)$ was described by several equations (table 3).

Table 3 – Equations of the temperature dependence of the heat capacities $YMgBiO_4$ in the interval 298.15 – 673K

| ΔT, K | The coefficients of equation $C_p^0 = a + bT + cT^{-2}$, J/(mol·K) | | |
|---|---|---|---|
| | a | $b \cdot 10^{-3}$ | $c \cdot 10^{5}$ |
| 298 – 473 | -101.25 ± 6.65 | 581.78 ± 38.20 | 6.70 ± 0.44 |
| 473 – 573 | -332.53 ± 21.84 | 515.83 ± 33.90 | 590.00 ± 38.80 |
| 573 – 673 | -133.87 ± 8.79 | 319.95 ± 21.02 | 310.00 ± 20.40 |

Table 4 – Thermodynamic functions of yttrium-magnesium bismuthite

| T, K | $C_p^0(T) \pm \overset{0}{\Delta}$, J/(mol·K) | $S^0(T) \pm \overset{0}{\Delta}$, J/(mol·K) | $H^0(T) - H^0(298{,}15) \pm \overset{0}{\Delta}$, J/mol | $\Phi^{xx}(T) \pm \overset{0}{\Delta}$, J/(mol·K) |
|---|---|---|---|---|
| 298.15 | 80 ± 5 | 147 ± 4 | – | 147 ± 4 |
| 300 | 81 ± 5 | 147 ± 14 | 160 ± 10 | 147 ± 14 |
| 325 | 94 ± 6 | 154 ± 15 | 2350 ± 150 | 147 ± 14 |
| 350 | 108 ± 7 | 162 ± 15 | 4870 ± 320 | 148 ± 14 |
| 375 | 122 ±8 | 170 ± 16 | 7740 ± 510 | 149 ± 14 |
| 400 | 136 ± 9 | 178 ± 17 | 10960 ± 720 | 151 ± 14 |
| 425 | 150 ± 10 | 187 ± 18 | 14520 ± 950 | 152 ± 14 |
| 450 | 164 ± 11 | 196 ± 19 | 18440 ± 1210 | 155 ± 15 |
| 475 | 178 ± 12 | 205 ± 20 | 22720 ± 1490 | 157 ± 15 |
| 500 | 161 ± 10 | 213 ± 20 | 26900 ± 1770 | 160 ± 15 |
| 525 | 152 ± 10 | 221 ± 21 | 30820 ± 2020 | 162 ± 15 |
| 550 | 146 ± 9 | 228 ± 22 | 34540 ± 2270 | 165 ± 16 |
| 575 | 142 ± 9 | 234 ± 22 | 38150 ± 2510 | 168 ± 26 |
| 600 | 144 ± 9 | 241 ± 23 | 41750 ± 2740 | 171 ± 16 |
| 625 | 145 ± 9 | 246 ± 23 | 45370 ± 2980 | 174 ± 17 |
| 650 | 147 ± 10 | 252 ± 24 | 49030 ± 3220 | 177 ± 17 |
| 675 | 150 ± 10 | 258 ± 25 | 52740 ± 3470 | 180 ± 17 |

Based on the known relationships and the values of the coefficients, the thermodynamic functions S°(T), H°(T) – H°(298.15) и $\Phi^{xx}$(T). were calculated from the equations for the temperature dependence on the heat capacity of the compound in question. The obtained results are given in table 4. For all values of the heat capacity and enthalpy, the average random components of the error were estimated over the whole temperature range, and for entropy values and the reduced thermodynamic potential, the accuracy of calculating the entropy (± 3%) is included in the error estimate.

The results are of definite theoretical and practical interest for the directed synthesis of compounds with valuable physicochemical properties.

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## Резюме

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### ТЕРМОДИНАМИЧЕСКИЕ СВОЙСТВА ВИСМУТИТА ИТТРИЯ-МАГНИЯ

Твердофазным способом получен двойной висмутит иттрия-магния. Результаты рентгенофазового анализа показывают, что соединение кристаллизуется в кубической сингонии. Параметры элементарной ячейки: a = 10.84 Å, $V^0$ = 1272 Å$^3$, Z = 16, $V_{эл.ячейки}$ = 79.5 Å$^3$, $\rho_{рентг}$ = 8.06, $\rho_{пикн}$ = 7.98 г/см$^3$. Методом динамической калориметрии исследована изобарная теплоемкость висмутита, на основе которой выведены уравнения зависимости $C_p^o$~f(T) и определены термодинамические функции.

**Ключевые слова:** висмутит иттрия-магния, калориметрия, теплоемкость, фазовый переход II рода, термодинамические функции.

## Резюме

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### ИТТРИЙ-МАГНИЙ ВИСМУТИТТІҢ ТЕРМОДИНАМИКАЛЫҚ ҚАСИЕТТЕРІ

Қатты фазалық синтез әдісімен иттрий-магний висмутиті алынды. Рентгенфазалық анализ нәтижелері бойынша жаңа қосылыс кубты сингонияда кристалданатыны анықталды. Элементарлы ұяшық параметрлері: a = 10.84 Å, $V^0$ = 1272 Å$^3$, Z = 16, $V_{эл.ұяшық}$ = 79.5 Å$^3$, $\rho_{рентг}$ = 8.06, $\rho_{пикн}$ = 7.98 г/см$^3$. Динамикалық калориметрия әдісімен висмутиттің изобаралық жылусыйымдылығы зерттеліп, $C_p^o$ ~ f(T) тәуелділіктің теңдеулері шығарылып, термодинамикалық функциялары анықталды.

**Түйін сөздер:** иттрий-магний висмутиті, калориметрия, жылусыйымдылық, II текті фазалық ауысу, термодинамикалық функциялар.

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# CATALYTIC PROPERTIES OF MODIFIED IRON-CHROMIUM-POTASSIUM SYSTEMS IN THE THERMOCATALYTIC DEHYDROGENATION OF ETHYLBENZENE

**Abstract.** The comparison of the efficiency of iron oxide catalytic systems modified with additions of cerium and zirconium oxides in the dehydrogenation of ethylbenzene to styrene was considered. According to the yield of the desired product (styrene), cerium- and zirconium-containing contacts exceed the unmodified Fe-K-Cr-O catalyst. Styrene is obtained about the yield of 79 % at 630 °C, ethylbenzene load of 150 g per liter of catalyst per hour and a molar ratio of water:ethylbenzene = 17,4.

**Key words:** dehydrogenation, ethylbenzene, styrene, catalysts.

**Introduction.** Styrene is one of the most important petrochemical product, which use as raw material for polymer production (polystyrene, synthetic rubber) and copolymers (impact-resistant polystyrene based on acrylonitrile and butadiene). The styrene production is a large-tonnage, the volume of styrene production is over 30 million tons per year [1]. There has been a recovery in styrene production in Russia over the last three years. In 2017, Russia produced 69 1748 tons of styrene [2], which is 1.3% more than the previous year.

About 90 % of the world styrene production (ST) is realized by the dehydrogenation of ethylbenzene (EB). The process is carried out at the presence of an iron oxide catalyst in the gas phase at 580-630 °C. The producers of iron oxide catalysts in Russia are OJSC "Kauchuk" (Sterlitamak), OJSC "SRI Yarsintez" (Yaroslavl) and OJSC "Nizhnekamskneftekhim", and foreing overseas – companies such as Shell, Sud Chemie, BASF and others [3,4]. The main component of all catalysts of the listed companies is iron oxide, promoted by compounds of alkali, alkaline-earth, transition and rare-earth metals. The efficiency of the catalyst depends on the content and nature of the catalytically active component, the presence of modifying additives and the technology for manufacturing the catalyst.

Additives to iron oxide take a special role in the formation of the catalysts properties. For example, in its work D.V. Kachalov [5] showed that the compounds of cerium and molybdenum significantly increase the electron-exchange rate, etween of $Fe^{2+}/Fe^{3+}$, thereby contributing to the oxidation-reduction mechanism of catalysis. When studying the influence of cerium oxide on the formation of the active phase, it was noted by Dementieva E.V. that cerium oxide interferes with the formation of potassium polyferrites, and in the topochemical reaction of hematite with potassium carbonate, potassium monoferrites are mainly formed. The author assumes that the introduction of cerium compounds leads to the dispersion of the polyferritic phase and the secondary particles (agglomerates) of the catalyst, accompanied by an increase of the specific surface [6]. The authors of the work [7] showed that the modification of aluminum oxide with additives of $ZrO_2$ and/or $CeO_2$ resulted in a significant increase in the activity of Cr-containing catalysts.

A.A. Emekeyev with contributors [8] investigated the effect of iron oxide compounds, as well as alkali metals, rare-earth elements and transition metals with several common oxidation states on the catalytic activity in the ethylbenzene dehydrogenation reaction to styrene. The introduction of cerium or molybdenum compounds into the catalyst composition leads to an increase in the selectivity of the process up to 88.0-90.7 % and a relatively small increase in the conversion of ethylbenzene with the iron- cerium-oxide (Fe-Ce-O) system.

Analysis of literature data showed that, despite the fact that iron oxide contacts have long been used in industry, research continues on the nature of their catalytic activity and the effect of promoters on activity.

This article is devoted the development of modified iron oxide catalysts for dehydrogenation of ethylbenzene in order to improve their catalytic properties.

## EXPERIMENTAL PART

Experimental researches of catalytic dehydrogenation ethylbenzene (EB) were carried out on a flow reactor with a fixed-bed catalyst at the presence of water vapor.

In our work we used freshly distilled ethylbenzene (boiling temperature 136 °C), obtained at the Aktau Plastics Plant by catalytic alkylation of benzene with ethylene. Experiments of dehydrogenation ethylbenzene were carried out on the flow reactor (300 mm in length and an internal diameter of 8 mm). The catalysts were prepared by mixing the calculated amounts of iron oxides, chromium (III) and potassium carbonate, which had been pre-ground thoroughly in a mortar. The resulting charge was compressed into tablets, which were dried for 2 hours at 150 °C and calcined at 800 °C for 2 hours. The calcined tablets were ground to particles of 1-3 mm in size. 10 ml of catalyst was charged into the reactor.

To test the synthesized catalysts, the operating mode of the K-24 catalyst used in industry was adopted as a basis.

Turning on the nitrogen supply ($20 L\cdot h^{-1}$), heating furnace and evaporator, at 350 °C, water is supplied to the evaporator at rate of $174\ g\cdot h^{-1}$. The nitrogen supply is stopped. The reactor is heated to 650 °C and the catalyst is maintained in a stream of steam for 2 hours. At the end of the exposure, the temperature is lowered to 550 °C and the ethylbenzene supply starts at a rate of $10\text{-}14\ g\cdot h^{-1}$. After 30 minutes the supply is increased to $24\text{-}30\ g\cdot h^{-1}$, the temperature - up to 570 °C. After another 60 minutes the supply is increased to $40\ g\cdot h^{-1}$ and the temperature - up to 600 °C. The catalyst test is started after 120 minutes.

The reaction products were captured in scrubbers of airlift type irrigated with acetone. Gas chromatographic analysis of the reaction products were carried out by chromatograph "Color-106" with a flame ionization detector; a glass column 1000 × 4 mm in size, filled with a fixed phase of 25% PEGA + 2% $H_3PO_4$ on an INZ-600 carrier. Gas carrier- Argon, and column temperature is 90 $^{o}$C.

## RESULTS AND DISCUSSION

The process of thermocatalytic dehydrogenation of ethylbenzene to styrene is widely considered in the literature, and a lot of catalysts are described. One of the main component is $Fe_2O_3$, which initial presence is 55-85 %. However, in many cases, the conversion of the initial product is only 50-75 %. According to this, the search for the new efficient catalytic systems continues.

Catalytic activity and selectivity of dehydrogenation catalysts are due to their chemical composition, crystal lattice structure and surface size.

The active components of iron-oxide systems in the dehydrogenation reaction are potassium ferrites, which formation occurs during the preparation and activation of the catalyst.

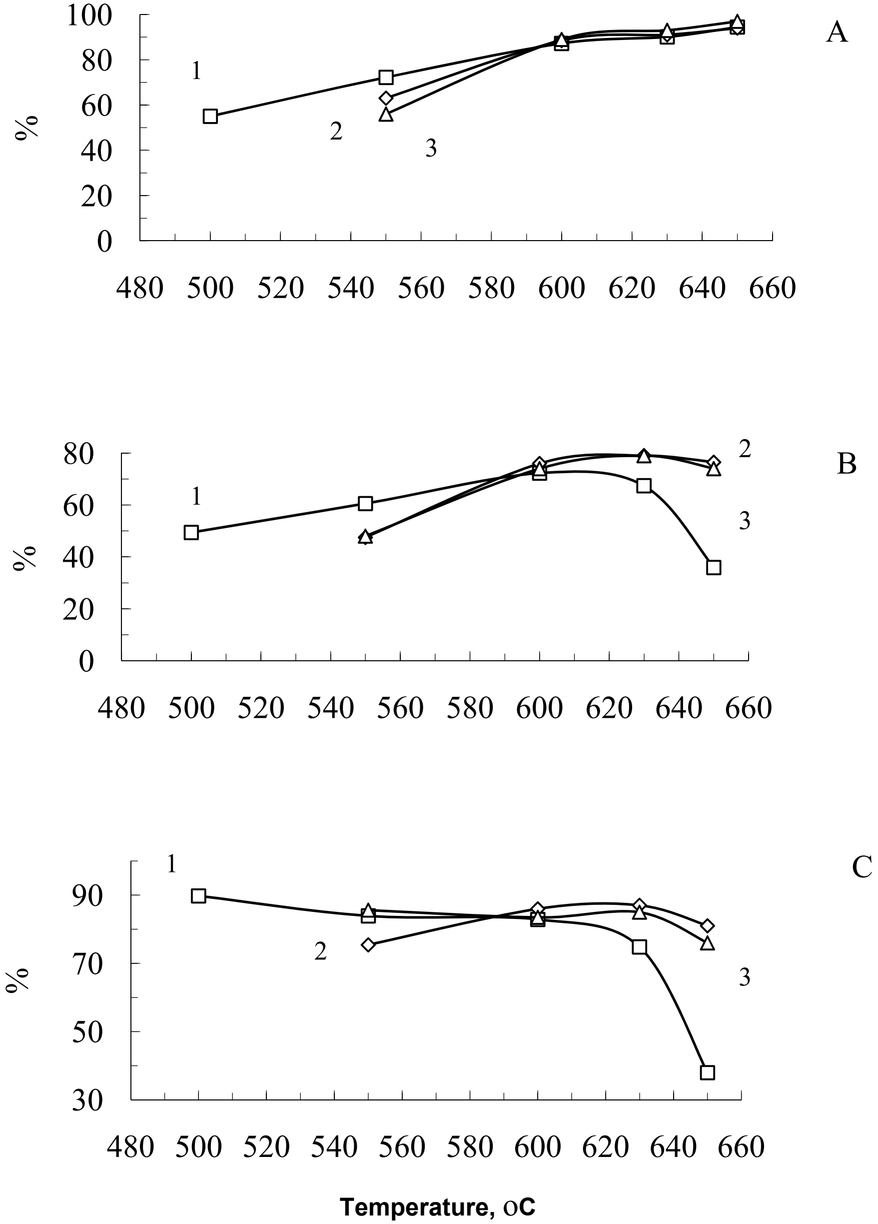
It is possible to change the catalyst properties at various stages of preparation in order to create highly effective connections.

In chemical technology the technological conditions of the process are of great importance, therefore, the dependence of the EB conversion, the styrene (ST) yield and the selectivity of its formation on the dehydrogenation temperature, the supply rate of EB and the ratio of dilution on the dehydrogenation process have been studied.

There are side processes in the process of dehydrogenation of ethylbenzene along with the main reaction, such as: coking, isomerization and cracking. Cracking and isomerization reduce the selectivity of the process, and coking has an effect on catalyst deactivation. If we want the catalyst work for a longer-term period, it is necessary to carry out periodic oxidative regeneration, as a result of which coke is burnt off from the catalyst surface.

Initially, a triple Fe-Cr-K-oxide system of 85 % $Fe_2O_3$-10 % $K_2O$-5 % $Cr_2O_3$, which is the basis of industrial catalysts, was tested in the thermocatalytic dehydrogenation of ethylbenzene. The conversion of ethylbenzene on this sample at 600 °C was 87.2 %, at the maximum yield of styrene 72 %.

Further, the catalytic activity of iron-chromium-potassium catalysts modified with additives of zirconium and aluminum oxides were investigated. When testing catalyst samples, the ethylbenzene supply rate was 153 g., water - 450 g. per 1 lt. of catalyst per an hour, which corresponded to a molar ratio of ethylbenzene: $H_2O$ = 1:17.4. Dehydrogenation of ethylbenzene was carried out at the range temperature from 550 to 650 °C. The obtained results showed that the introduction of zirconium dioxide and aluminum oxide in the compound of iron-chromium-potassium catalyst increased its catalytic activity: an increase in the conversion of the initial product up to 94% was observed. Styrene was obtained with the highest yield (69-72 %) on the unmodified Fe-Cr-K-O catalyst prepared by the dry oxide tableting method. On the catalyst with the addition of zirconium dioxide, the yield



Influence of temperature on conversion of ethylbenzene (A), yield (B) and selectivity of styrene formation (C) on modified catalysts.

The supply rate of ethylbenzene - 1.53 g, water - 4.5 g., nitrogen 12.4 L. per hour. The molar ratio of ethylbenzene:$H_2O$ = 1: 17.4. Catalysts:1- 85 % $Fe_2O_3$ -10 % $K_2O$ - 5 % $Cr_2O_3$; 2 - 45,87 % $Fe_2O_3$ - 20,29 % $K_2O$ - 5,46 % $Cr_2O_3$ - 6,53 % $V_2O_5$ -12,36 % $CeO_2$; 3 – 47,54 % $Fe_2O_3$ - 21,03 % $K_2O$ - 5,66 % $Cr_2O_3$ - 6,77 % $V_2O_5$ - 9,17 % $ZrO_2$.

of styrene at 600 °C reached 69 %, andat the somtime it was 42-46 % on the iron-chromium-potassium catalyst modified with aluminum oxide.

Next step is that catalyst samples containing vanadium pentoxide were synthesized by the method of mixing dry components. The number of main components varied within the limits: $Fe_2O_3$ - 45-85 %, $K_2O$ - 10-21 %, $Cr_2O_3$ - 5-6 %, $V_2O_5$ - 6.5-6.8 %. Additionally, cerium and zirconium oxides were introduced in these catalysts. Influence of the temperature, contacting time and amount of nitrogen and water vapor supplied to the catalysis zone on the yield of the main reaction products (styrene, toluene, benzene, unreacted ethylbenzene) were studied.

As part of experimental studies it was found that the dehydrogenation of EB on catalysts modified with cerium and zirconium oxides in the presence of water, the general regularities of the influence of dehydrogenation conditions on the process parameters are preserved, while achieving a higher yield of ST at the temperature of the dehydrogenation process - 630 °C. The figure shows the dependence of the conversion of the initial ethylbenzene, the yield and the selectivity of the desired product formation versus of temperature on Fe-Cr-K-V-Ce-O and Fe-Cr-K-V-Zr-O contact. The maximum conversion of ethylbenzene has been achieved on a Fe-Cr-K-V-Zr-O catalyst and was 97 % at 650 °C. As it is seen from the figure that on both tested catalysts styrene was obtained about yield of 79 % at 630 °C, ethylbenzene load of 150 g. per liter of catalyst per hour and a molar ratio of water:ethylbenzene = 17.4.

**Conclusion.** The obtained results indicate that these catalysts are sufficiently effective for thermocatalytic dehydrogenation of ethylbenzene to styrene. Apparently, the additions of zirconium and cerium oxides influence the formation of potassium ferrites, determining the activity of the tested catalytic systems in the ethylbenzene dehydrogenation reaction. Adding vanadium and/or cerium, zirconium oxides to the three-component Fe-K-Cr-O catalyst resulted in an increase in the yield of styrene from 72 to 79 %. The selectivity of styrene formation on the iron-oxide catalyst modified by $ZrO_2$ in the temperature range of 550-600 °C was 85.6-83.5 %, and on Fe-Cr-K-V-Ce-O connection - 86-87 % (600-630 °C).

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## Резюме

*Т. П. Михайловская, П. Б. Воробьев, О. К. Югай, Қ. А. Кадирбеков*

## МОДИФИЦИРЛЕНГЕН ТЕМІР-ХРОМ КАТАЛИЗАТОРЛАРЫНДА ЭТИЛБЕНЗОЛДЫҢ ТЕРМОКАТАЛИТИКАЛЫҚ ДЕГИДРЛЕНУІН ЗЕРТТЕУ

Этилбензолды церий және цирконий оксидтерімен модифицирленген темір-хром оксидті катализаторларында дегидрлеуді зерттеу.

**Түйін сөздер:** дегидрирлеу, этилбензол, стирол, катализаторлар

## Резюме

*Т. П. Михайловская, П. Б. Воробьев, О. К. Югай, К. А. Кадирбеков*

## КАТАЛИТИЧЕСКИЕ СВОЙСТВА МОДИФИЦИРОВАННЫХ ЖЕЛЕЗОХРОМКАЛИЕВЫХ СИСТЕМ В ТЕРМОКАТАЛИТИЧЕСКОМ ДЕГИДРИРОВАНИИ ЭТИЛБЕНЗОЛА

Обсуждено влияние оксидов церия и циркония на каталитические свойства железооксидного контакта в термокаталитическом дегидрировании этилбензола.

**Ключевые слова:** дегидрирование, этилбензол, стирол, катализаторы.

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# COMPARISON OF ETHYL ALCOHOL AND NITRIC ACID AS DESORBENTS FOR LANTHANUM IONS FROM MATRIX OF RARE-CROSSLINKED POLYMER HYDROGELS OF ACID AND BASIC NATURE

**Abstract.** Desorption process of lanthanum ions by 95 ethyl alcohol and 2M nitric acid from matrix of polymer hydrogels of polyacrylic acid (hPAA), polymethacrylic acid (hPMAA), poly-4-vinylpyridine (hP4VP), poly-2-methyl-5-vinylpyridine (hP2M5VP) was studied. For desorption hydrogels in the ratio: 33%hPAA:67%hP4VP, 17%hPMAA:83%hP4VP, 67%hPAA:33%hP2M5VP and 50%hPMAA:50%hP2M5VP were taken. Extraction degree of lanthanum ions at these ratios after 48 hours is 94.05; 90.34; 91.09; 89.65 respectively. Total desorption degree with ethyl alcohol is( %) 85.46; 82.26; 80/17; 77.27 respectively. Total desorption degree by nitric acid is( %) 96.27; 94.43; 92.55; 93.09 respectively. Such difference is due to the nature of the desorbents (as known, ethyl alcohol is a polar organic solvent, nitric acid – strong mineral acid).

**Key words:** intergel systems, desorption, $La^{3+}$ ions, hydrogels, polyacrylic acid, polymethacrylic acid, poly-4-vinylpyridine, poly-2-methyl-5-vinylpyridine.

**Introdaction.** Previous studies were devoted to investigation of sorption properties of intergel systems based on rare-crosslinked hydrogels in relation to ions of rare-earth metals [1-9]. In result of these studies it was found that there is significant increase of sorption properties of initial macromolecules due to their mutual activation. Sorption properties increase on 25-30% comparatively to individual hydrogels.

For desorption of lanthanum ions after its sorption by ion-exchangers polar organic compounds and mineral acids can be used [10, 11].

The goal of this work is study desorption properties of ethyl alcohol and nitric acid in relation to lanthanum ions.

## EXPERIMENTAL PART

*Equipment.* Measurements of optical density of solutions for further calculation of $La^{3+}$ions concentration were carried out by spectrophotometer Jenway-6305 (UK).

*Materials.* Studies carried out in 95% solution of ethyl alcohol and 2M solution of nitric acid. Hydrogels of polyacrylic (PAA) and polymethacrylic (PMAA) acids were synthetized at the presence of crosslinking agent N,N-methylene-bis-acrylamide and redox system $K_2S_2O_8$–$Na_2S_2O_3$. Hydrogel of poly-4-vinylpyridine (hP4VP) was synthetized by “Sigma Aldrich” company (2% of crosslinking agent). Hydrogel of poly-2-methyl-5-vinylpyridine was synthetized in medium of dimethylformamide at the presence of crosslinking agent epichlorohydrine. From synthetized hydrogels intergel pairs were created. Swelling degrees of the hydrogels are: $\alpha_{(hPAA)}$=27.93 g/g, $\alpha_{(hPMAA)}$=20.65 g/g; $\alpha_{(hP4VP)}$=3.27 g/g, and $\alpha_{(hP2M5VP)}$=3.20 g/g.

*Experiment.* Experiments were carried out at a room temperature. Study of desorption of lanthanum ions was made as follows: calculated amount of each hydrogel in dry initial state were put in special glass filters, pores of which is permeable for low-molecular ions and molecules, but impermeable for hydrogels dispersion. After that intergel pairs in the relation 33%hPAA:67%hP4VP, 17%hPMAA:83%hP4VP, 67%hPAA:33%hP2M5VP, 50%hPMAA:50%hP2M5VP were put into 0.005M solution of lanthanum nitrate and were left for sorption during 48 hours. After that filters with hydrogels undergo desorption by ethyl alcohol and nitric acid for separating from each other.

*Methodology of determination lanthanum ions.* Determination of lanthanum ions in solution is based on formation of colored complex compound of organic analytical reagent arsenazo III with ions of rare-earth metals [12].

Lanthanum ions extraction degree was calculated in accordance following equation:

$$\eta = \frac{C_{\text{initial}} - C_{\text{residual}}}{C_{\text{initial}}} \cdot 100\%$$

where $C_{initial}$ – initial concentration of lanthanum in solution, g/L; $C_{residual}$ is residual concentration of lanthanum in solution, g/L.

Desorption degree of lanthanum ions was calculated by formula:

$$R = \frac{m_{\text{desorbed}}}{m_{\text{sorbed}}} \cdot 100\%$$

where $m_{desorbed}$ is mass of desorbed lanthanum, g; $m_{sorbed}$ is mass of sorbed lanthanum, g.

## RESULTS AND DISCUSSION

For desorption of the rare-earth element, which was sorbed in a form of hydrophobic complex, strong mineral acids or polar organic solvents can be used. For the desorption the hydrogels from the following ratios 33%hPAA:67%hP4VP, 17%hPMAA:83%hP4VP, 67%hPAA:33%hP2M5VP, 50%hPMAA:50%hP2M5VP were taken. Extraction degree of lanthanum ions at these ratios after 48 hours is 94.05%; 90.34%; 91.09%; 89.65%.

***Features of lanthanum ions desorption by ethyl alcohol.*** Dependence of lanthanum ions desorption degree by ethyl alcohol from matrix of hydrogels of polyacrylic acid and poly-4-vinylpyridine from time is presented on figure 1. Strong increase of the metal ions desorption is observed during 6 hours as for acid as for basic hydrogels. After this time desorption degree is 47.64% for hPAA and 15.52% for hP4VP.

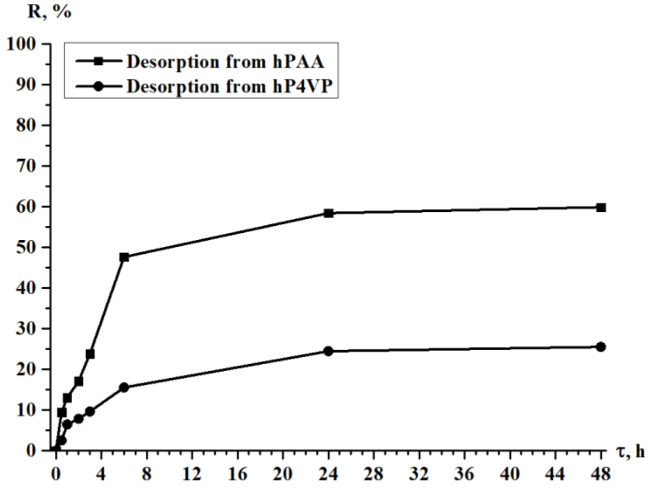

Figure 1 – Dependence of lanthanum ions desorption degree versus of duration of the time by ethyl alcohol from PAA and P4VP hydrogels from time

Further increase of lanthanum ions desorption degree is not so intensive, after 24 hours of interaction of the hydrogels with elthyl alcohol desorption degree from hPAA is 59.92%, from hP4VP – 24.46%. Consequent interaction of the hydrogels with the desorbent provides slight increase of lanthanum ions concentration in solution, what indicates that equilibrium is almost achieved. Total desorption degree from matrix of both hydrogels at 48 hours is 85.46%.

Figure 2 represents dependence on desorption degree of lanthanum ions versus duration by ethyl alcohol from matrix of hPMAA and hP4VP from time.

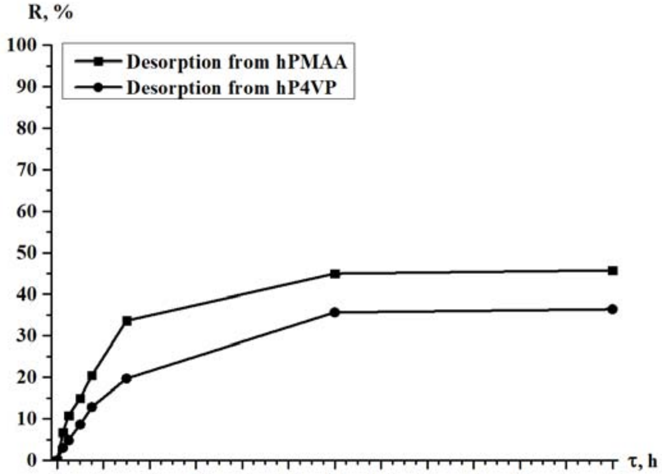

Figure 2 – Dependence of lanthanum ions desorption degree versus of duration of the time by ethyl alcohol from PMAA and P4VP hydrogels

Overwhelming majority of lanthanum is released during 6 hours. Obtained results show that better part of lanthanum during its sorption was sorbed by the polyacid. Further desorption occurs more slightly for both hydrogels. Total desorption degree at 48 hours is 82.26%.

Curves of dependence of lanthanum desorption by ethyl alcohol from time from matrix of hydrogels of polyacrylic acid and poly-2-methyl-5-vinylpyridine are presented on figure 3. As seen from the figure, the most of lanthanum was sorbed by the polyacid. Strong increase of desorption degree is observed during 6 hours, at this time 50.20% of lanthanum is desorbed from hPAA, 13.44% – from hP2M5VP. After 2 days (48 hours) total desorption degree of lanthanum is 80.17%.

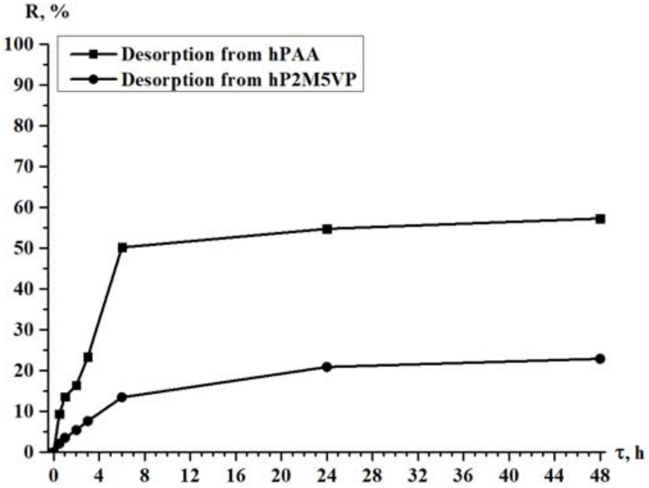

Figure 3 – Dependence on lanthanum ions desorption degree versus of duration of the time by ethyl alcohol from PAA and P2M5VP hydrogels from time

Figure 4 represents dependence of lanthanum desorption by ethyl alcohol from time. Similarly to previous cases (fig. 1-3), intensive desorption occurs during 6 hours, at this time 31.58% of the metal is desorbed from hPMAA, 17.83% – from hP2M5VP. Total desorption degree of lanthanum ions from hPMAA and hP2M5VP after 2 days is 77.27%.

Comparative analysis of total desorption degree of lanthanum ions by ethyl alcohol from hydrogels of PAA, PMAA, P4VP and P2M5VP at 48 hours is presented in table 1.

As seen from the obtained data, are represented in table 1 not high (~77-85%) desorption degree is in direct dependence from the nature of the desorbent (as known, ethyl alcohol is polar solvent). Due to this fact not full desorption of lanthanum ions from hydrogels matrix occurs.

*Features of lanthanum ions desorption by nitric acid.* Dependence on lanthanum ions desorption degree by nitric acid from matrix of polymer hydrogels of polyacrylic acid and poly-4-vinylpyridine is shown on figure 5.

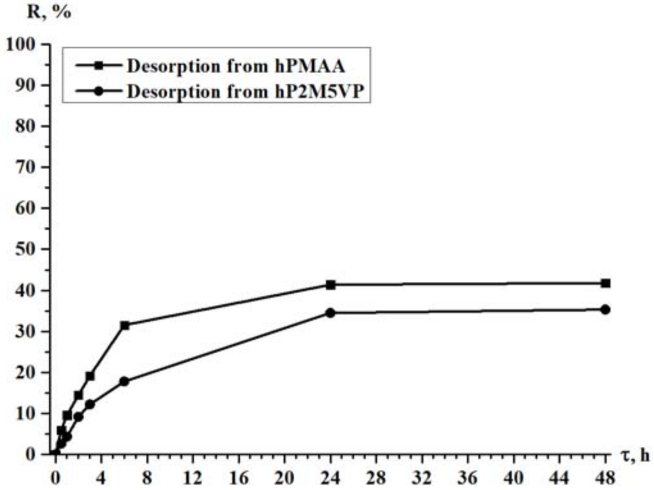

Figure 4 – Dependence on lanthanum ions desorption degree versus of duration of time by ethyl alcohol from PMAA and P2M5VP hydrogels

Table 1 – Total desorption degree of lanthanum ions by ethyl alcohol from intergel systems

| Intergel system | hPAA-hP4VP | hPMAA-hP4VP | hPAA-hP2M5VP | hPMAA-hP2M5VP |
|---|---|---|---|---|
| Hydrogels ratio | 33%hPAA:<br>67%hP4VP | 17%hPMAA:<br>83%hP4VP | 67%hPAA:<br>33%hP2M5VP | 50%hPMAA:<br>50%hP2M5VP |
| Total desorption degree, % | 85.46 | 82.26 | 80.17 | 77.27 |

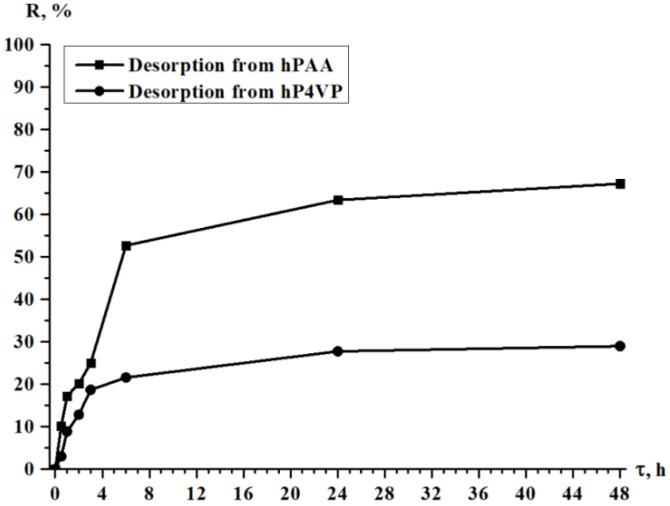

Figure 5 – Dependence on lanthanum ions desorption degree versus of duration of time by nitric acid from PAA and P4VP hydrogels

The most intensive desorption occurs at first 6 hours: at this time 52.70% of lanthanum is desorbed from hPAA, 21.56% – from hP4VP. Subsequent desorption provide increase of the parameter, at 24 hours 63.41% of the metal is released from hPAA and 27.75% – from hP4VP. Further increase is very slight, what indicates that system is almost reaches equilibrium state. Total desorption degree from the polymers at 48 hours is 96.27%.

Desorption process of lanthanum ions from polymer hydrogels of polymethacrylic acid and poly-4-vinylpyridine in time is presented on figure 6. Similarly to the previous system (figure 5), first six hours – area of high desorption of lanthanum ions from the macromolecules during their contact with desorbing agent. From all amount of sorbed lanthanum 36.55% is released from hydrogel of PMAA and 20.96% is released from hydrogel of P4VP. After end of the experiment (48 hours) total desorption degree from the macromolecules is 94.43%.

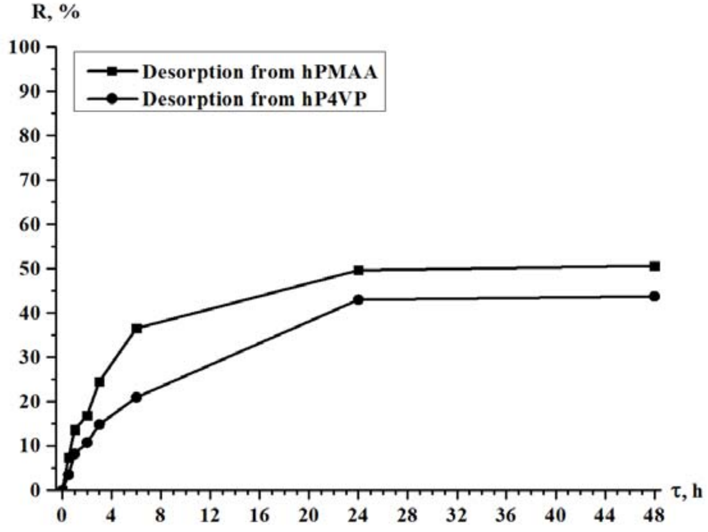

Figure 6 – Dependence on lanthanum ions desorption degree versus of duration of time by nitric acid from PMAA and P4VP hydrogels

Figure 7 represents dependence of desorption degree of lanthanum ions by nitric acid from matrix of the hydrogels of PAA and P2M5VP from time. After 6 hours after beginning of interaction of the desorbent with the hydrogels there is a release of main amount of lanthanum. As seen from the figure, polyacid sorbes 2 times more lanthanum than polybasis. Total desorption degree of lanthanum from hydrogels of PMAA and P4VP is 92.55% at 48 hours.

As seen from figure 8, intensive desorption is observed during 24 hours. During 6 first hours 31.94% of lanthanum is desorbed from hPMAA and 20.04% from hP2M5VP. Total desorption degree is 93.09% for 48 hours.

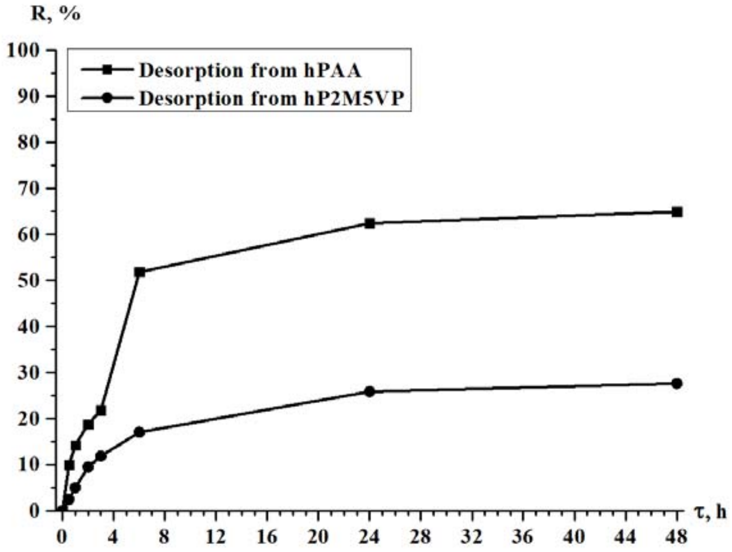

Figure 7 – Dependence on lanthanum ions desorption degree versus duration of time by nitric acid from PAA and P2M5VP hydrogels

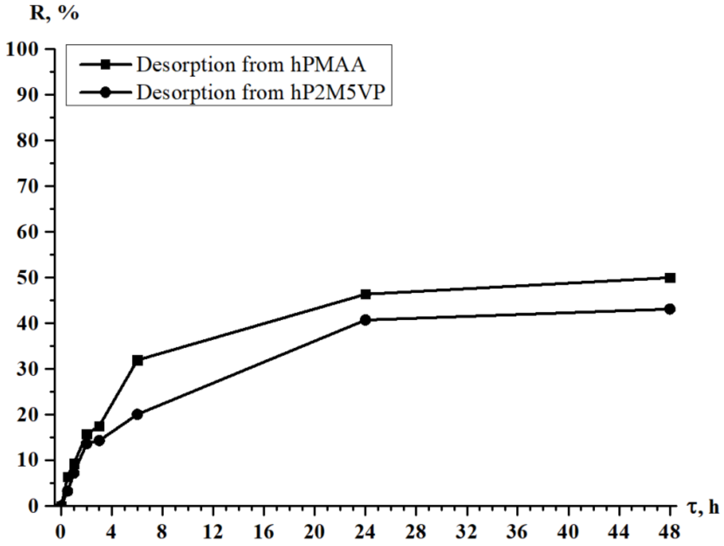

Figure 8 – Dependence of lanthanum ions desorption degree by nitric acid from PMAA and P2M5VP hydrogels from time

Table 2 shows comparison of total desorption degree of lanthanum ions by nitric acid from hydrogels of PAA, PMAA, P4VP and P2M5VP at 48 hours.

Table 2 – Total desorption degree of lanthanum by nitric acid from intergel systems

| Intergel system | hPAA-hP4VP | hPMAA-hP4VP | hPAA-hP2M5VP | hPMAA-hP2M5VP |
|---|---|---|---|---|
| Hydrogels ratio | 33%hPAA:<br>67%hP4VP | 17%hPMAA:<br>83%hP4VP | 67%hPAA:<br>33%hP2M5VP | 50%hPMAA:<br>50%hP2M5VP |
| Total desorption degree, % | 96.27 | 94.43 | 92.55 | 93.09 |

The obtained results indicate that nitric acid, being a strong mineral acid, interacts sufficiently with polymer hydrogels, what is evidenced by higher (~92-96%) desorption degree comparatively with ethyl alcohol.

**Conclusions.**

1. Obtained results point to the fact, that 95% ethyl alcohol and 2M nitric acid can be used for desorption of lanthanum ions from PAA, PMAA, P4VP, P2M5VP polymer hydrogels matrix.
2. Desorption degree of lanthanum ions from polymer hydrogels matrix by ethyl alcohol do not have high values (not more than 85%) what is due to nature of polar solvent.
3. High values of desorption degree are achieved at desorption of the metal by nitric acid. Due to the fact that mineral acid is strong by its nature, and desorption degree have high (over 95%) values.

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## Резюме

*Т. Қ. Жұмаділов, Р. Г. Кондауров*

## ТАБИҒИ НЕГІЗДІК ЖӘНЕ ҚЫШҚЫЛДЫҚ СИРЕК ТОРЛАНҒАН ГИДРОГЕЛЬ МАТРИЦАСЫНАН ЛАНТАН ИОНДАРЫН ДЕСОРБЦИЯЛАУДА ЭТИЛ СПИРТІ МЕН АЗОТ ҚЫШҚЫЛЫН ДЕСОРБЕНТ РЕТІНДЕ САЛЫСТЫРУ

Полиакрил қышқылы (ПАҚг), полиметакрил қышқылы (ПМАКг), поли-4-винилпиридин (П4ВПг) және поли-2-метил-5-винилпиридин (П2М5ВПг) гидрогельдерінің полимерлік матрицасынан лантан ионын 95% этанолда және 2М азот қышқылында десорбциялау процесі жүргізілді. Десорбциялау үшін интергелді жүйелеріндегі гидрогельдер мынадай қатынастарда алынды: 33%ПАҚг:67%П4ВПг, 17%ПМАҚг:83%П4ВПг, 67%ПАҚг:33%П2М5ВПг, 50%ПМАҚг:50%П2М5ВПг. Осы қатынастарда 48 сағаттық десорбциядан кейінгі лантан иондарын бөліп алу дәрежесі келесідей: 94,05; 90,34; 91,09; 89,65%: Этил спиртіндегі десорбцияның жалпы бөліп алу дәрежесі 85,46; 82,26; 80,17; 77,27% құрайды. Азот қышқылындағы десорбцияның жалпы бөліп алу дәрежесі 96,27; 94,43; 92,55; 93,09% құрайды. Бұндай айырмашылық десорбенттердің табиғатының ерекшеліктеріне байланысты (белгілі, этил спирті – полярлық органикалық еріткіш, ал азот қышқылы - күшті минералды қышқылы) болып табылады.

**Түйін сөздер:** интергелді жүйе, десорбция, La$^{3+}$ иондары, гидрогель, полиакрил қышқылы, полиметакрил қышқылы, поли-4-винилпиридин, поли-2-метил-5-винилпиридин.

## Резюме

*Т. К. Джумадилов, Р. Г. Кондауров*

# СРАВНЕНИЕ ЭТИЛОВОГО СПИРТА И АЗОТНОЙ КИСЛОТЫ В КАЧЕСТВЕ ДЕСОРБЕНТОВ ДЛЯ ИОНОВ ЛАНТАНА ИЗ МАТРИЦЫ РЕДКОСШИТЫХ ПОЛИМЕРНЫХ ГИДРОГЕЛЕЙ КИСЛОТНОЙ И ОСНОВНОЙ ПРИРОДЫ

Исследован процесс десорбции ионов лантана 95% этиловым спиртом и 2М азотной кислотой из матрицы полимерных гидрогелей полиакриловой кислоты (гПАК), полиметакриловой кислоты (гПМАК), поли-4-винилпиридина (гП4ВП) и поли-2-метил-5-винилпиридина (гП2М5ВП). Для десорбции были взяты следующие соотношения гидрогелей в интергелевых системах 33%гПАК:67%гП4ВП, 17%гПМАК:83%гП4ВП, 67%гПАК:33%гП2М5ВП, 50%гПМАК:50%гП2М5ВП. Степень извлечения ионов лантана при этих соотношениях по истечении 48 ч составляет 94,05; 90,34; 91,09; 89,65%. Суммарная степень десорбции этиловым спиртом составляет 85,46; 82,26; 80,17; 77,27%. Суммарная степень десорбции азотной кислотой составляет 96,27; 94,43; 92,55; 93,09%. Подобная разница обусловлена природой десорбентов (как известно, этиловый спирт – полярный органический растворитель, азотная кислота – сильная минеральная кислота).

**Ключевые слова:** интергелевые системы, десорбция, ионы $La^{3+}$, гидрогели, полиакриловая кислота, полиметакриловая кислота, поли-4-винилпиридин, поли-2-метил-5-винилпиридин.

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# SYNTHESIS DIACETYLENIC GLYCOLS BASED ON 1,5-DI(PROP-2-INILOXY)NAPHTHALINE

**Abstract.** Conditions of synthesis of new potentially biologically active diacetylenic glycols were developed. The reaction of nucleophilic addition 1,5-di (prop-2-ynyloxy)naphthalene at the carbonyl group of the cyclic ketones (cyclohexanone and N-substituted piperidones) was studied. Structure of new compounds were established based on the analysis by $^{1}$H and $^{13}$C NMR spectral data.

**Keywords:** 1,5-di(prop-2-ynyloxy)naphthalene, ethynylation, diacetylenic glycols, cyclohexanone, N-substituted piperidones.

**Introduction.** At the beginning of the 20-th century A. E. Favorsky showed that in the presence of strong bases the carbonyl compounds react with acetylene and its monosubstituted derivatives formed the corresponding acetylenic alcohols. The ethynylation reaction successfully used such strong bases such as hydroxides of K, Na, Rb, Mg, alkaline amides and alkaline earth metal alkoxides, and quaternary ammonium ion exchange resins [1]. The condensation of ketones with acetylenes are widely used for the synthesis of structurally simplest acetylenic alcoholic of complex analogues of natural physiologically active compounds which are used in the development of anticancer drugs, hemorheologic agents [2], plant growth regulators [3] and fungicides [4, 5].

**Results and Discussion.** The reaction of nucleophilic addition 1,5-di(prop-2-ynyloxy)naphthalene at the carbonyl group of cyclic ketones of cyclohexanone, 1-methylpiperidin-4-one, 1-propylpiperidin-4-one and 1-benzyl-4-piperidone were studied in order to synthesize of new potentially biologically active compounds in the series of diproparpylic ethers of naphthols. The reaction was carried out in the presence of a 4-fold excess of technical KOH at room temperature in diethyl ether. As a result of ethinylation of cyclohexanone and N-substituted piperidoneswith 1,5-di (prop-2-ynyloxy) naphthalene, were obtained the corresponding tertiary diacetylenic glycols.

After appropriate treatment of the reaction mixture the following diacetylenic glycols were obtained in individual state:1,1'-(3,3'-(naphthalene-1,5-diylbis(oxy))bis(prop-1-yne-3,1-diyl))dicyclohexanol1, 4,4'-(3,3'-(naphthalene-1,5-diylbis(oxy))bis(prop-1-yne-3,1-diyl))bis(1-methylpiperidin-4-ol)2, 4,4'-(3,3'-(naphthalene-1,5-diylbis(oxy))bis(prop-1-yne-3,1-diyl))bis(1-propylpiperidin-4-

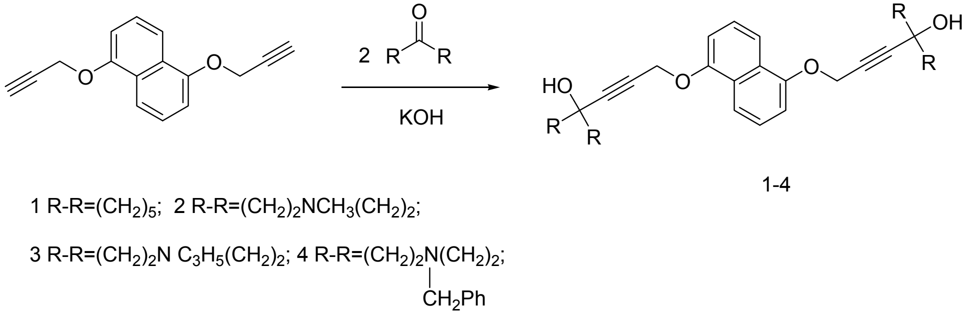

Figure 1 – Scheme of the nucleophilic addition reaction of 1,5-di(prop-2-ynyloxy)naphthalene

ol)3 and 4,4'-3,3'-(naphthalene-1,5-diylbis(oxy))-bis(prop-1-yn-3,1-diyl))bis(1-benzylpiperidin-4-ol) 4 in yield 50, 82, 75, 87%, respectively.

The structure of synthesized compounds 1-4 was confirmed by IR spectra and NMR $^1$H, $^{13}$C, COZY ($^1$H–$^1$H) and HMQC ($^1$H–$^{13}$C) spectroscopy. The data of $^1$H and $^{13}$C NMR spectra are given in the tables 1 and 2.

In IR spectra, diacetylenic glycols 1–4 are characterized by the presence of broadened absorption bands in the 3400–3500 cm$^{-1}$ region, characteristic for valence vibrations of hydroxyl groups, weak intensity peaks in the region of 2100 cm$^{-1}$ indicate the presence of a triple acetylenic bond.

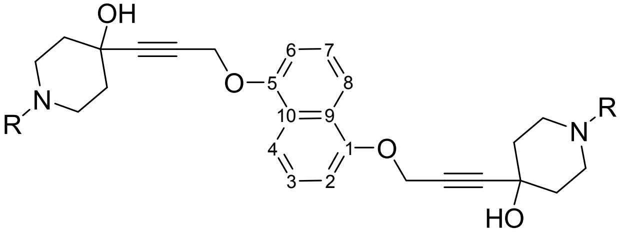

Table 1 – $^1$H NMR(δ, ppm) spectral data for compounds 1 – 4

| Comp. | A type spectrum | PMR,δ, ppm | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | O–CH$_2$ | N–R (CH$_3$, CH$_2$CH$_2$CH$_3$, CH$_2$Ph) | CH$_2$(cycle) | OH | Protons of naphthalene cycle | | |
| | | | | | | C$^{2,6}$H | C$^{3,7}$H | C$^{4,8}$H |
| 1 | e$^1$ | 4,97 | – | 1,38-2,22 | 3,56 | 7,07 д | 7,4 т | 7,74 д |
| | c$^2$ | 4,91 | – | 1,34-2,15 | 3,58 | 6,94 | 7,20 | 7,80 |
| 2 | e$^1$ | 5,0 | 2,03 | 1,59-2,32 | 2,46 | 7,06 д | 7,4 т | 7,72 д |
| | c$^2$ | 4,91 | 2,31 | 1,99-2,10 | 2,92 | 6,94 | 7,20 | 7,80 |
| 3 | e$^1$ | 4,94 | 0,71;1,25;2,01 | 1,52-2,41 | 3,40 | 7,01д | 7,33т | 7,65д |
| | c$^2$ | 4,91 | 0,86;1,47;2,59 | 1,90-2,28 | 2,92 | 6,94 | 7,20 | 7,80 |
| 4 | e$^1$ | 4,97 | 3,50; 7,22-7,30 | 2,28-2,58 | 3,58 | 7,05 д | 7,41 т | 7,79 д |
| | c$^2$ | 4,91 | 3,47; 7,13-7,18 | 2,02-2,12 | 3,47 | 6,93 | 7,63 | 7,82 |

*Notes.* e – is the experimental spectrum; c-spectrum calculated according to the «MestReNova» program.

Table 2 – $^{13}$C NMR(δ, ppm) spectral data for compounds 1 – 4

| Comp. | A typespectrum | O–$\underline{C}H_2$ | $\underline{C}\equiv C$ | $C\equiv\underline{C}$ | $>C<$ | $CH_2$(cycle) | N–R ($CH_3$, $CH_2CH_2CH_3$, $CH_2Ph$) |
|---|---|---|---|---|---|---|---|
| 1 | e$^1$ | 56,53 | 78,47 | 93,01 | 67,20 | 24,84;<br>26,97;<br>41,86 | – |
|  | c$^2$ | 58,40 | 80,41 | 89,94 | 68,52 | 23,40;<br>25,40;<br>39,58 | – |
| 2 | e$^1$ | 56,73 | 78,47 | 92,32 | 65,09 | 40,50;<br>40,71 | 46,16 |
|  | c$^2$ | 58,40 | 80,41 | 90,13 | 66,99 | 35,48;<br>50,17 | 45,83 |
| 3 | e$^1$ | 56,78 | 79,12 | 92,20 | 65,64 | 39,51;<br>50,11 | 12,31; 20,14;<br>60,08; |
|  | c$^2$ | 58,40 | 80,41 | 90,13 | 66,85 | 37,63;<br>50,17; | 12,05; 20,25;<br>60,80 |
| 4 | e$^1$ | 56,49 | 78,83 | 79,60 | 61,34 | 41,21;<br>52,79 | 61,34;127,55;<br>128,74;<br>129,20 |
|  | c$^2$ | 58,40 | 80,41 | 90,13 | 66,99 | 37,45;<br>48,71 | 58,97;<br>129,44;<br>128,89;<br>131,48 |

| Comp. | Carbon atoms of the naphthalene ring |  |  |  |  |
|---|---|---|---|---|---|
|  | A typespectrum | $C^1C^5$ | $C^2C^6$ | $C^3C^7$ | $C^4C^8$ | $C^9C^{10}$ |
| 1 | e$^1$ | 153,15 | 107,29 | 125,97 | 114,83 | 126,58 |
|  | c$^2$ | 147,70 | 109,35 | 125,38 | 114,52 | 124,85 |
| 2 | e$^1$ | 153,23 | 107,57 | 125,91 | 114,75 | 126,67 |
|  | c$^2$ | 147,70 | 109,35 | 125,38 | 114,52 | 124,85 |
| 3 | e$^1$ | 153,18 | 107,46 | 125,82 | 114,72 | 126,65 |
|  | c$^2$ | 147,70 | 109,35 | 125,38 | 114,52 | 124,85 |
| 4 | e$^1$ | 153,18 | 107,14 | 125,92 | 114,90 | 126,60 |
|  | c$^2$ | 147,70 | 109,35 | 125,00 | 114,52 | 124,85 |

*Notes.* e – is the experimental spectrum; c-spectrum calculated according to the «MestReNova» program.

In the $^1$H NMR spectra of diacetylenic glycols 1-4 appear broadened singlets for the protons of the hydroxyl groups in the region 2.46–3.58 ppm, which indicates the occurrence of nucleophilic addition of 1,5-di (prop-2-ynyloxy)naphthalene at the carbonyl group of the cyclic ketones.

In the $^1$H NMR spectra of the glycol 4 (figure 2), in the strong field region of the spectrum, the chemical shifts for protons in the region 2.29 and 2.58 ppm were assigned to the cyclic protons forthe symmetrical methylene groups of two piperidine rings. The chemical shift in the region 4.96 ppm belongs to the protons of $OCH_2$ methylene groups. The protons of methylene substituents at the nitrogen atom are resonated as a broadened singlet in the region of 3.50 ppm. The signals for the protons of the naphthalene nucleus and of the benzene nucleus appear in the weak-field regions 7.05–7.79 ppm and 7.22–7.30 ppm, respectively.

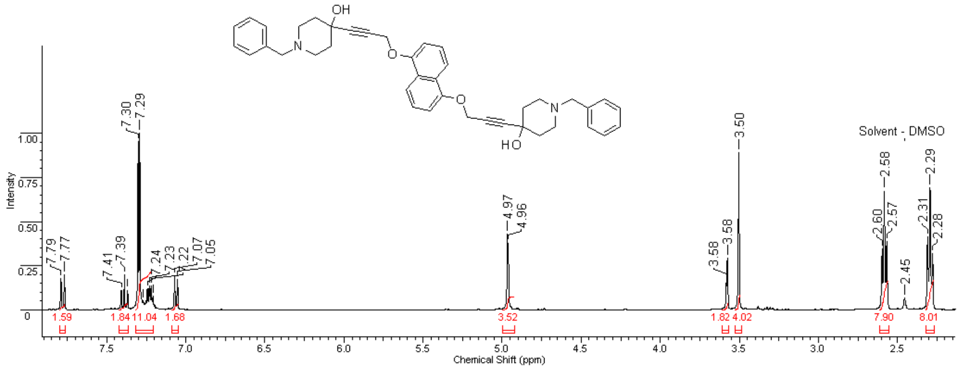

Figure 2 – $^{1}H$ NMR spectra
of 4,4'-3,3'-(naphthalene-1,5-diylbis(oxy))bis(prop-1-yn-3,1-diyl))bis(1-benzylpiperidin-4-ol)

In the $^{13}C$ spectra of diacetylenic glycols 1–4 (table 2) resonance signals appear in the corresponding region 61.34 –68.52 ppm characteristic for quaternary carbon atoms of saturated nitrogen cycles.

In the $^{13}C$ NMR spectra of glycol 4 (4,4'-(3,3'-(naphthalene-1,5-diylbis-(oxy))bis(prop-1-yn-3,1-diyl))bis(1-benzylpiperidin- 4-ol)) shown in figure 3, the most characteristic carbon atoms of the –C≡C– acetylenic bond resonate in the region 78.83 and 79.60 ppm.Chemical shifts for carbon atoms of the symmetric $CH_2$ groups of the piperidine rings are observedin the strong field region 41.21 and 52.79 ppm.Quaternary carbon atoms of the saturated nitrogen cycles resonate in the region δ 61.34 ppm.

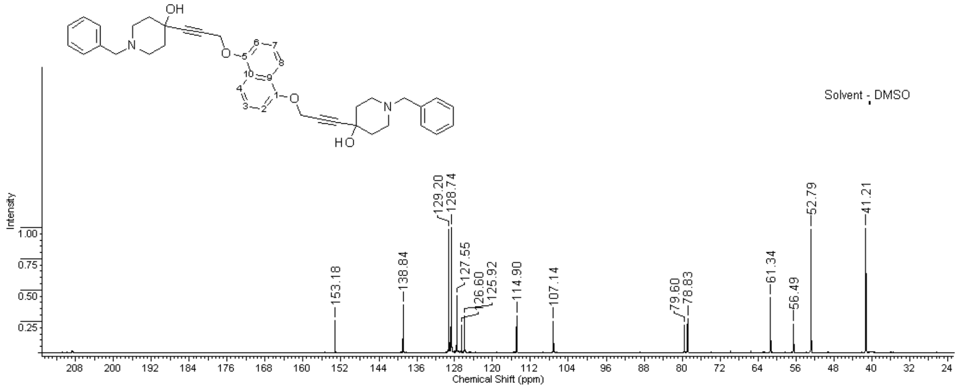

Figure 3 – $^{13}C$NMR spectra
of 4,4'-3,3'-(naphthalene-1,5-diylbis(oxy))bis(prop-1-yn-3,1-diyl))bis(1-benzylpiperidin-4-ol)

It should be noted that the chemical shifts for the methylene group of the benzyl substituent appear in the more weaker region (61.34 ppm) compared to the carbon atoms of the oxymethylene group (56.49 ppm), which is due to the influence of the nitrogen atom of the piperidine ring. In the weak field region 107.14 – 153.18 ppm and 127.55 –129.20 ppm the signals for the carbon atoms of the naphthalene and benzyl rings are observed.

The correct interpretation of the resonance signals is confirmed by the coincidence of the values of the chemical shifts observed in the experimentally obtained spectra with the corresponding values in the spectra calculated by the «MestReNova» program.

The results of the interpretation of the two dimensional spectrum in the HMQC ($^1$H –$^{13}$C) format make it possible to determine the correlation between chemical shifts of protons and carbon nuclei, spin –spin interaction between nuclei, which confirms the nature of heteronuclear interaction.

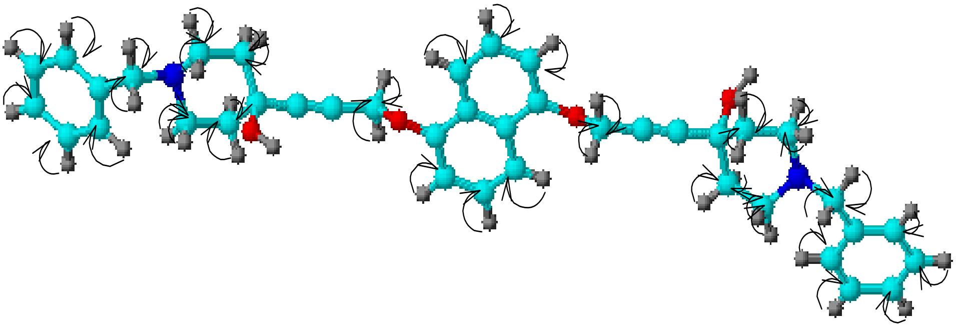

Figure 4 – Scheme of correlations of HMQC
($^1$H –$^{13}$C) 4,4'-3,3'-(naphthalene-1,5-diylbis(oxy))bis(prop-1-yn-3,1-diyl))bis(1-benzylpiperid-4-ol)

**Conclusion.** Summarizing the obtained data on the synthesis of new diacetylene glycols, it can be noted that 1,5-di (prop-2-ynyloxy) naphthalene readily reacts in Favorsky'sethynylation reaction and allows one to move relatively easily to an important class of tertiary acetylenic alcohols, which due to the presence in their structures acetylenic and tertiary alcohol groups can serve as initial synthons in the further synthesis of natural substancesanalogues.

Thus, as a result of studying the reactivity of 1,5-di(prop-2-ynyloxy)naphthalene in the Favorsky reaction with various cyclic ketones, formation of diacetylenic glycols in 50-87% yields was established. The structure of synthesized glycols was established based on the analysis of the $^1$H and $^{13}$C NMR spectral data.

## EXPERIMENTAL PART

The course of the reactions and the purity of the products were monitored by thin-layer chromatography on "Silufol UV–254" plates, the eluent was a mixture of benzene and ethanol (1:3) with the appearance of substances spots with iodine vapor. The IR spectra were recorded on a Nicolet 5700 spectrometer in KBr tablets. The $^1$H and $^{13}$C NMR spectra of the samples were recorded in DMSO-$D_6$ using a JNM-ECA 400 (Jeol) spectrometer with operating frequencies 400 ($^1$H), 100 MHz ($^{13}$C).

**1,1'-(3,3'-(naphthalene-1,5-diylbis(oxy))bis(prop-1-yne-3,1-diyl))dicyclohexanol 1.** A solution of0.5 g (0.0021 mol) of 1,5-di (prop-2-ynyloxy)naphthalene in 10 ml of etherwas added to a mixture of 0.47 g (0.0084 mol) of powdered technical KOH in 15 ml of ether. After 30 minutes 0.41 g (0.0042 mol) of cyclohexanone in 10 ml of ether was slowly added dropwise with stirring. After the end of the reaction, the mixture was decomposed with water(15 ml) under ice-cooling. The ether was separated, the aqueous layer was extracted with ether(5x20 ml), the ether extract was dried with potash. After distilling off the ether,diacetylene glycol 1 was obtainedin 0.45 g (50%) yield.

**4,4'-(3,3'-(naphthalene-1,5-diylbis(oxy))bis(prop-1-yne-3,1-diyl))bis(1-methyl-piperidin-4-ol) 2** was synthesized analogouslyfrom 0.5 g (0.0021 mole) of 1,5-di(prop-2-ynyloxy)naphthalene with 0.48 g (0.0042 mol) of 1-methylpiperidin-4-one in the presence of 0.47 g (0.0084 mol) of powdered technical KOH in ether at room temperature. The yield was 0.8 g (82%).

**4,4'-(3,3'-(naphthalene-1,5-diylbis(oxy))bis(prop-1-yne-3,1-diyl))bis(1-propylpiperidin-4-ol)3** was synthesized analogouslyfrom 1.0 g (0.0042 mole) of 1,5-di (prop-2-ynyloxy)naphthalene with 1.19 g (0.0084 mol) of 1-methylpiperidin-4-one in the presence of 0.94 g (0.016 mol) of powdered technical KOH in ether at room temperature. The yield was 1.66 g (75%).

**4,4'-3,3'-(naphthalene-1,5-diylbis(oxy))-bis(prop-1-yn-3,1-diyl))bis(1-benzylpiperidin-4-ol)4** was synthesized analogouslyfrom 0.5 g (0.0021 mole) of 1,5-di (prop-2-ynyloxy)naphthalene with 0.8 g (0.0042 mol) of 1-methylpiperidin-4-one in the presence of 0.47 g (0.0084 mol) of powdered technical KOH in ether at room temperature. The yield was 1.14 g (87%).

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## Резюме

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### СИНТЕЗ ДИАЦЕТИЛЕНОВЫХ ГЛИКОЛЕЙНА ОСНОВЕ 1,5-ДИ(ПРОП-2-ИНИЛОКСИ)НАФТАЛИНА

Разработаны условия синтеза новых потенциально биологически активных диацетиленовых гликолей. Изучена реакция нуклеофильного присоединения 1,5-ди-(проп-2-инилокси)нафталина по карбонильной группе циклических кетонов (циклогексанона и N-замещенных пиперидонов). Строение новых соединений установлено на основании анализа данных спектроскопии ЯМР $^1$Н и $^{13}$С.

**Ключевые слова:** 1,5-ди(проп-2-инилокси)нафталин, этинилирование, диацетиленовые гликоли, циклогексанон, N-замещенные пиперидоны.

## Резюме

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### 1,5-ДИ(ПРОП-2-ИНИЛОКСИ)НАФТАЛИН НЕГІЗІНДЕ ДИАЦЕТИЛЕНДІ ГЛИКОЛЕЙН СИНТЕЗІ

Жаңа тұрғыдағы биологиялық активті диацетиленді гликолдер синтезінің жүзге асыру жағдайлары қарастырылды. Тұйың сақиналы кетондардың (циклогексанон жəне N-орынбасқан пиперидондар) карбонил тобы бойынша 1,5-ди(проп-2-инилокси)нафталиннің нуклеофильді қосылу реакциясы зерттелінді. Жаңа қосылыстардың құрылымы ЯМР $^1$Н жəне $^{13}$С спектроскопиялық талдау негізінде ан-ықталынды.

**Түйін сөздер:** 1,5-ди(проп-2-инилокси)нафталин, этинилдеу, диацетиленді гликолдер, циклогексанон, N-орынбасқан пиперидондар.

УДК 677.027

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# SOL-GEL TECHNIQUE IN ECO-FRIENDLY COLORATION OF CELLULOSIC MATERIALS

**Abstract.** At this work, modified variant of sol-gel method is presented, which provides for carrying out of polycondensation not in the impregnation bath, but in the pores of cotton fibers. It is possible due to consistent impregnation in solution of precursor and colorant and catalyst of hydrolysis. The possibility of obtaining silica coating by this method has been proved by the results of scanning electron microscopy and energy dispersive analysis. An influence of treatment conditions on tensile properties and coloration intensity is studied. It was revealed that higher temperature of heat treatment leads to an increase of color fastness.

**Key words:** sol-gel, silica, sodium silicate, citric acid, cellulose, plant colorants, continuous dyeing, madder, chlorophyll

**Introduction.** The sol-gel technology is an effective method of introducing and fixing functional agents on the surface of substrates of various types. There are several advantages of using sol-gel technology in the functional finishing of textile materials, such as the possibility of high processing speed and the absence of damage to substrate materials. There are some papers about functional finishing of cellulose textile materials [1-16], which have proved the efficiency of fixing functional agents on the surface of cellulose fiber by using of a sol-gel method. The sol-gel technology implies obtaining functional coating on fiber, which consist metal (silica, aluminum, titan or zinc) oxide matrix and functional particles [17, 18]. Essential factors that limited using of sol-gel technology in mass production are the high cost of alkosilanes, which also requires the use of organic additives. At previous studies the existence of economically more advantageous ways of replacing alkosilanes by water-soluble silicates are explained. The most common water-soluble silicate is sodium or potassium liquid glass. There are several works about using of sol-gel method in dyeing of textile materials [19-21], where researchers applied an a colloidal sol-gel method with the use of aqueous solutions of sodium liquid glass (sodium silicate). Also, an eco-friendly method of dyeing involves the use of natural dyes. Application of plant colorants in textile materials dyeing is best known from antic period, however this type of dye implies the applying of a periodic dyeing method. So, in this research, extract of madder and chlorophyll copper complex choosen as colorants, these substances are commonly used in pharmaceutical and food industry. At this paper we suggest an environment-friendly 2 bath included continuous dyeing method of cotton fabrics, which is based on sol-gel process. General purpose of this research is development of safely and efficiently dyeing technology from economical point of view.

## EXPERIMENTAL PART

**Materials.** 100% bleached cotton fabric, article 1030, with size 200x200mm and surface density of 147 g/m$^2$ was purchased from Blakit (“BCPA” JSC, Belorussia). As precursors of sol-gel process an aqueous solution of sodium silicate (liquid glass of $Na_2SiO_3$ in the mass ratio of water: $Na_2SiO_3$ equal to 9: 1) with a density of 1.36 g/m$^3$, and as a catalyst of hydrolysis, citric acid (2-hydroxypropane-1,2,3-tricarboxylic acid) were chosen. At the research extract of madder (purchased from Vifitech, Russia) and chlorophyll copper complex (purchased from Ecoplant, Russia) were selected as colorants. $AlK(SO_4)_2$ was used as a mordant.

**Preparation of samples.** Samples of cotton fabric with size 200x200mm and were washed in distilled water at 40 °C, dried in a oven and kept in a desiccators for 24 hours to conditional mass achievement. After this a dyeing solution was prepared (bath module is 5:1), which consisted colorant (2% o.w.f.), diluted in NaOH 1% (1/5 of required volume of dyeing solution) and water glass (50-100 g/l). At next, tissue samples were impregnated in bath with a dye solution. Impregnation was carried out at a temperature of 65-70 °C for one minute, followed by padding. After this, the dyed samples were immersed in second bath, containing an aqueous solution of citric acid (20 - 50 g/l) at a temperature of 65-70 °C for one minute, followed by padding. After, cloths were dried at a temperature of 70-80 °C for 5 minutes and heat treated by heat at temperatures of 120-160 °C. Further, samples were washed with solution, which consist a surfactant (2 g/l) at 50 °C, and rinsed in distilled water.

**Research methods.** The color stability determination of dyed samples carried out, the PT-4 device and the gray standards scale were used in accordance standart «ГОСТ 9733.27-83» "Textile materials. Method of testing the color fastness to friction". The color intensity K/S of samples calculated according to equation from reflection coefficient R, which measured on a CarlZeiss spectrophotometer. The fact of the coating existence is one of the reasons of changing mechanical properties in comparison with the original fabric. Determination of the tensile strength of the fabric was carried out on a tensile machine RT-250M in accordance standart «ГОСТ 3813-72». "Textile materials. Fabrics and piece goods. Methods for determining tensile properties". For studying of sample’s surface morphology scanning electron microscopy used (SEM).

## RESULTS AND DISCUSSION

The result of color intensity determination is represented in table 1. The intensity measurement of samples, which were colored by madder extract, clearly show, that K/S value decreased versus high temperature of treatment, and reduced with higher citric acid concentration. This fact can be explained by the destruction of the colorant. K/S value of samples, which were colored by chlorophyll, has shown direct proportional dependability from temperature of heat treatment,

Table 1 – K/S value of colored and uncolored samples

| № | $C_{water\text{-}glass}$ ($C_{W.G.}$), g/L | $C_{acid}$, g/L | Temperature of treatment ($T_{T.H.}$), °C | K/S value | |
|---|---|---|---|---|---|
| | | | | Colored by madder | Colored by chlorophyll |
| 1 | 100 | 50 | 160 | 0.46152 | 0.24114 |
| 2 | 100 | 50 | 120 | 0.51376 | 0.23454 |
| 3 | 100 | 20 | 160 | 0.64314 | 0.19837 |
| 4 | 100 | 20 | 120 | 0.69955 | 0.18875 |
| 5 | 50 | 50 | 160 | 0.50088 | 0.20763 |
| 6 | 50 | 50 | 120 | 0.51779 | 0.19399 |
| 7 | 50 | 20 | 160 | 0.56889 | 0.18180 |
| 8 | 50 | 20 | 120 | 0.57339 | 0.17998 |
| 0 | Untreated, uncolored | | | 0.009713 | |

water-glass concentration and acid concentration. Therefore, next conclusions can be made: copper complex of chlorophyll has good thermal stability, in comparison with madder extract; increasing of intensity with the highest temperature and concentration of the liquid glass contributes to better fixation of the dye.

For identify patterns of color fixation from treatment parameters, PT-4 device and the gray standards scale were used. Result of color fastness test is shown in table 2.

Table 2 – Results of testing the color fastness to wet/dry friction

| № | $C_{W.G.}$, g/L | $C_{acid}$, g/L | $T_{T.H}$, °C | Colored by madder | | Colored by chlorophyll | |
|---|---|---|---|---|---|---|---|
| | | | | dry | wet | dry | wet |
| 1 | 100 | 50 | 160 | 5 | 4 | 5 | 4-5 |
| 2 | 100 | 50 | 120 | 5 | 3-4 | 5 | 4-5 |
| 3 | 100 | 20 | 160 | 5 | 3-4 | 5 | 4-5 |
| 4 | 100 | 20 | 120 | 5 | 3-4 | 5 | 4-5 |
| 5 | 50 | 50 | 160 | 5 | 4 | 5 | 4-5 |
| 6 | 50 | 50 | 120 | 5 | 4 | 5 | 4-5 |
| 7 | 50 | 20 | 160 | 5 | 4 | 5 | 4-5 |
| 8 | 50 | 20 | 120 | 5 | 4 | 5 | 4-5 |

It’s clearly shows, that increasing temperature of thermal fixation leads to best color fixation results. But high treatment temperature can injure cellulosic fibers. So, heating in temperature 120-160 °C of fabric is one of the reasons of changing mechanical properties in comparison with the original fabric, tensile strength had been measured consequently. Testing results are shown in table 3.

Table 3 – Tensile strength of the treated and untreated samples

| Number of regime | $C_{W.G.}$, g/L | $C_{acid}$, g/L | Tensile strength, N | |
|---|---|---|---|---|
| | | | $T_{T.H}$=160 °C | $T_{T.H}$=120 °C |
| Colored by madder extract | | | | |
| 1 | 100 | 50 | 388 | 462 |
| 2 | 100 | 50 | 458 | 497 |
| 3 | 100 | 20 | 365 | 488 |
| 4 | 100 | 20 | 411 | 452 |
| Coloured by chlorophyll copper complex | | | | |
| 1 | 100 | 50 | 281 | 284 |
| 2 | 100 | 50 | 311 | 333 |
| 3 | 100 | 20 | 260 | 306 |
| 4 | 100 | 20 | 358 | 428 |
| Untreated | 0 | 0 | 232 | 232 |
| Non-coloured, treated by $AlK(SO_4)_2$ | 0 | 0 | 0 | 409 |

It can be seen, that with decreasing of treatment temperature and acid concentration and increasing of water glass, the tensile strength has been enhanced.

Thus, optimal parameters of treatment can be chosen depend on color rubbing test results and K/S value. So, results of research are shown, that $C_{water\text{-}glass}$= =100 g/L, $C_{acid}$= 20 g/L and $T_{T.H}$ =120 °C are better parameters for sol-gel dyeing by madder extract. $C_{water\text{-}glass}$= 100 g/L, $C_{acid}$= 50 g/L and $T_{T.H}$ =160 °C are better parameters for sol-gel dyeing by chlorophyll copper complex.

For studying of surface morphology of treated and untreated samples SEM/EDX method was used. Images of fibers structure are shown on figure1. Surface images and EDX analysis is proving existence of silica oxide gel coating.

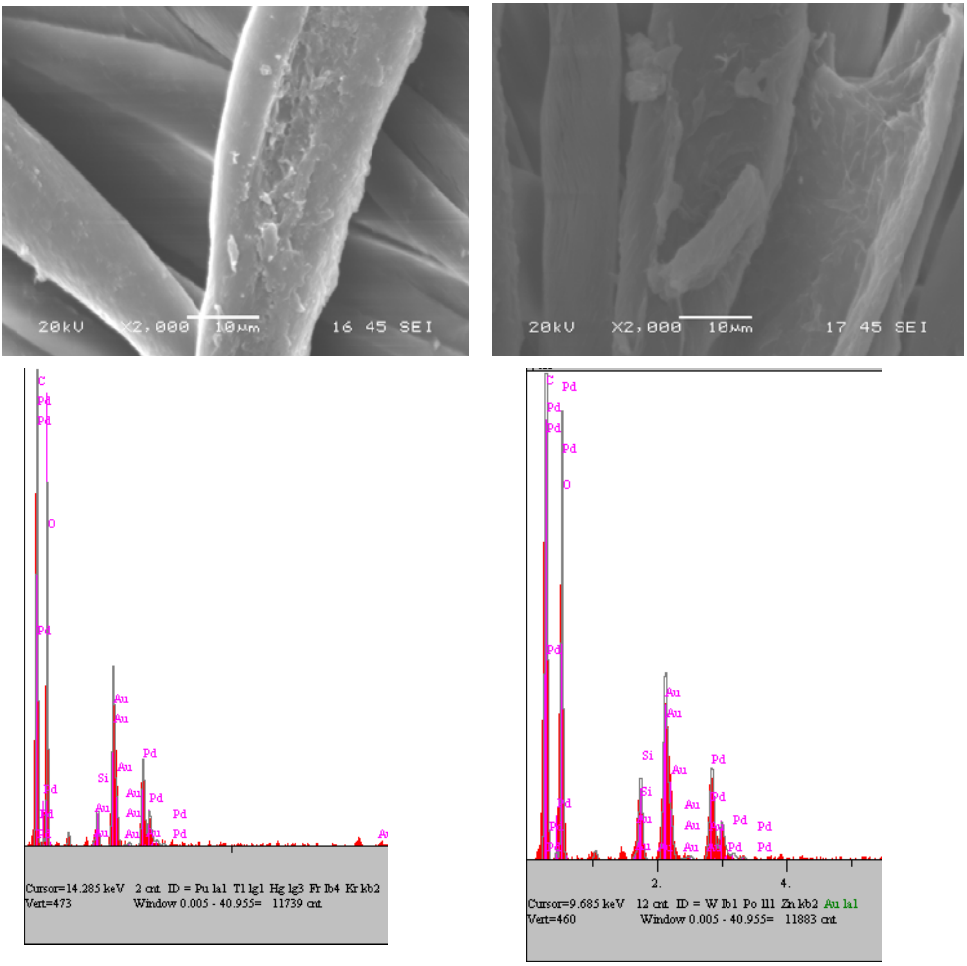
**Conclusion.**

1. The proposed coloring technology based on double-bath impregnation sol-gel method allows to obtain barrier silica coatings, where natural dye is included, it has been proved by images of SEM/EDX method.

2. The general advantages of this coloring method is that reaction of polycondensation doesn't proceeds in the bath, It occurs in the pores of cotton fiber, therefore present method makes it possible to increase the storage time of using solution up to several days without gelling and that the solution can be recycled and reapplicated again.

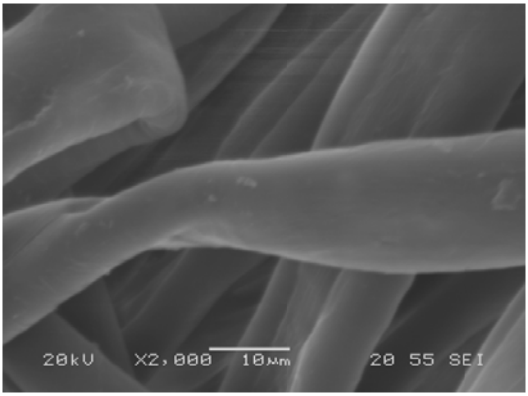
3. At work an eco-friendly natural colorants and environment safely fixation method of dyes through sol-gel process, applying of water-soluble precursor and non-mineral acid, was used.

4. It was found that $C_{W.G}$ = 100 g/l, $C_{acid}$= 20 g/l and $T_{T.H}$ =120 °C are better parameters for sol-gel dyeing by madder extract. Then $C_{W.G}$ = 100 g/l, $C_{acid}$= 50 g/l



a

b



c

Figure 1 –
SEM images of samples:
a – colored by chlorophyll,
b – colored by madder extract,
c – untreated cotton sample

and $T_{T.H}$ =160 °C are better parameters for sol-gel dyeing by chlorophyll copper complex.

Therefore, the process can be carried out on common industrial dyeing machines. General disadvantage is possibility of coloring hydrophilic fibers only. Results of this research can be used as basic for development of eco-friendly sol-gel dyeing technology.

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## Резюме

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### ЗОЛЬ-ГЕЛЬ ТЕХНИКА В ЭКОЛОГИЧНОМ КРАШЕНИИ ЦЕЛЛЮЛОЗНЫХ МАТЕРИАЛОВ

Описан двухванный золь-гель метод крашения целлюлозных текстильных материалов. Предложен экологически безопасный способ крашения целлюлозных текстильных материалов с применение натуральных красителей растительного происхождения (экстракт марены красильной и медного комплекса хлорофилла). Предложенный способ состоит в последовательной пропитке образцов хлопчатобумажной ткани сначала в прекурсоре золь-гель процесса, а затем в катализаторе гидролиза, с последующей сушкой и термической обработкой. Исследовано влияние концентрации прекурсора золь-гель перехода и катализатора гидролиза на колористические и прочностные свойства полученных образцов. Выявлено, что оптимальными параметрами для крашения являются: концентрация жидкого стекла $C_{W.G}$ = 100 г/л, концентрация лимонной кислоты $C_{acid}$ =50 г/л и температура термообработки $T_{T.H}$ = 160 °C для хлорофилла и $C_{W.G}$ = 100 г/л, $C_{acid}$ = 20 г/л and $T_{T.H}$ = =120 °C для марены красильной. Для исследования поверхности обработанных волокон применен метод электронной микроскопии, по результатам которого доказывается наличие кремнеземного покрытия. Результаты исследования могут быть применены в отделочном производстве текстильных целлюлозосодержащих материалов.

**Ключевые слова:** золь-гель, кремний, натрия силикат, лимонная кислота, растительные красители, непрерывное крашение, марена, хлорофилл.

## Резюме

*Ф. Р. Ташмухамедов, А. Ж. Кутжанова, Г. Е. Кричевский*

### ЦЕЛЛЮЛОЗДІ МАТЕРИАЛДАРЫН ЭКОЛОГИЯЛЫҚ БОЯУ КЕЗІНДЕГІ ЗОЛЬ-ГЕЛЬ ТЕХНИКАСЫ

Мақалада целлюлозалық тоқыма материалдарын бояуға арналған екі ванналық золь-гель әдісі сипатталған. Зерттеудің нәтижелері бойынша өсімдік табиғи бояғыштар (бояғыштың сығындысы және хлорофилдің мыс кешені) қолданылатын целлюлоздық тоқыма материалдарын бояудың экологиялық қауіпсіз әдісі ұсынылған. Ұсынылған әдіс алдымен золь-гель процесінің прекурсорларында мақта-мата үлгілерін сіңіріліп, содан кейін гидролиз катализаторында сіңіріліп, кейін кептіру және термиялық өңдеуден тұрады. Алынған үлгілердің түсі мен беріктігі қасиеттеріне золь-гельдік гидролиз катализаторының прекурсорлық концентрациясының әсері зерттелді. Өңдеу параметрлерінің текстиль материалының физико-механикалық қасиеттері, бояу интенсивтілігі мен беріктілігі зерделенген. Нәтижесінде, келесі оптимальді параметрлер анықталған: хлорофилл мыс комплексі үшін - натрий силикат концентрациясы $C_{W.G}$ = 100 г/л, лимон қышқылы концентрациясы $C_{acid}$ = 50 г/л және термоөндеу температурасы $T_{T.H}$ =160 °C; бояуринмен бояу процесі үшін - $C_{W.G}$ = 100 г/л, $C_{acid}$ = 20 г/л and $T_{T.H}$ = 120 °C. Сонымен қатар электронды микроскопия әдісін қолдана отырып функционалды жабын мен бояғыштың бекітілгені зерделенген. Зерттеу нәтижесі целлюлозалы текстиль материалдарын өңдеу өндірісінде пайдалауға болады.

**Түйін сөздер:** золь-гель, кремний, натрий силикаты, лимон қышқылы, өсімдік бояғыштар, үздіксіз бояу, бояурин, хлорофилл.

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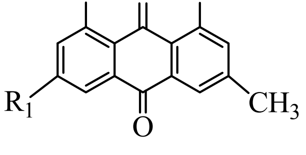
# CHARACTERISTIC OF MASS-SPECTROMETRIC FRAGMENTATION MOLECULAR IONS OF EMODINE AND ITS METHYL ETHERS

**Abstract.** The work is devoted to the mass-spectrometric study and comparative analysis of mass-spectrometric fragmentation of molecular ions of 1,6,8-trihydroxy-3-methyl-9,10-anthraquinone (emodin) and its mono- and dimethyl ether. The influence of the substituent on the stability of molecular ions to ionization by electrons is considered, and schemes for their mass-spectrometric decay proposed. It is shown that the fragmentation of the derivatives depends on the location of the substituent in the anthraquinone system.

**Key words:** mass-spectrum, molecular ion, fragmentation, electron ionization, elimination, derivatives of 9,10-anthraquinone

Anthraquinones represent the most numerous group of natural quinones with diverse biological activity [1, 2]. Among them, one of the most common derivatives of 9,10-anthraquinone is emodin (1), which is identified not only in the free state, but in glycosidated, dimeric and condensed forms, in plants of such families as Rhamnaceae (Rhamnus, Maesopsis, Ventilage), Fabaceae (Cassia), Senna, Polygonaceae (Rheum, Rumex, Polygonum), Liliaceae (Aloe, Bulbine), Hypericaceae [3-8]. Modern studies have made it possible to establish, in addition to the laxative, also its antibacterial, vasorelaxant, cardiotonic, hepatoprotective and antitumor effects [9-12], and the ability of derivatives of emodin to inhibit the enzymatic activity of ATP-citrate lyase (ACL), a key player in the metabolism of cancer cells [ 13].

Considering the importance of the emodin derivatives (1) as biologically active compounds and continuing research into the mass spectrometric fragmentation of 9,10-anthraquinone derivatives [14-17]. This article is devoted to the analysis of the mass spectra of 1,6,8-trihydroxy-3 -methyl-9,10-anthraquinone (emodin) (1) and its methyl esters (2,3). The structure of the derivatives is presented below:



1-3

1 $R_1$, $R_2$-OH
2 $R_1$- $OCH_3$, $R_2$-OH
3 $R_1$, $R_2$-$OCH_3$

Table 1 shows the total mass spectra of emodin (1) and its methyl esters (2,3), and table 2 shows the data on the stability of MI ($W_{mi}$) for ionization by electrons (IE), as well as the characteristic ions ($F_1$-$F_7$) from of the total ion current. From the data in table 1, it can be seen that for the anthraquinones studied the MI peak in the spectra is the maximum (I = 100%), and the MI stability to the IE ($W_{mi}$) is in the range 11.9 ÷ 40.6% (table 2).

Table 1 – Mass spectra of 9,10-anthraquinone derivatives (1-3)

| № | Compound | Mass spectrum: $M^{+\cdot}$, m/z ($I_{отс}$ в %)* |
|---|---|---|
| 1 | 1,6,8-Trihydroxy-3-Methyl-9,10-anthraquinone (emodin) | 271 (17), $M^{+\cdot}$ 270 (100), 269 (2), 255 (2), 254 (2), 253 (3), 243 (2), 242 (14), 241 (9), 227 (1), 226 (1), 225 (3), 224 (1), 215 (1), 214 (7), 213 (10), 200 (3), 199 (2), 197 (4), 196 (3), 195 (1), 186 (2), 185 (5), 172 (1), 171 (2), 169 (2), 168 (5), 167 (2), 158 (1), 157 (2), 155 (1), 145 (1), 141 (1), 140 (2), 139 (8), 137 (2), 136 (1), 135 (3), 129 (2), 128 (4), 127 (3), 126 (1), 121 (4), 116 (1), 115 (5), 114 (1), 108 (1), 107 (2), 106 (2), 105 (2), 102 (1), 101 (1), 92 (2), 91 (1), 90 (1), 84 (4), 79 (2), 78 (2), 77 (5), 76 (2), 75 (2), 74 (2), 70 (2), 69 (7), 65 (2), 64 (2), 63 (4), 62 (2), 53 (2), 52 (2), 51 (6), 50 (2), 39 (4). |
| 2 | 1,8-Dihydroxy-6-Methoxy-3-methyl-9,10-anthraquinone (physcion) (emethine methyl ester) | 286 (4), 285 (23), $M^{+\cdot}$ 284 (100), 283 (5), 269 (1), 267 (8), 257 (1), 256 (7), 255 (13), 254 (9), 253 (1), 242 (2), 241 (10), 239 (1), 237 (1), 228 (2), 227 (6), 226 (7), 225 (6), 214 (1), 213 (7), 212 (1), 211 (1), 210 (1), 199 (2), 198 (5), 197 (2), 195 (2), 185 (4), 184 (2), 167 (2), 139 (4), 129 (2), 128 (7), 127 (2), 115 (3), 106 (2), 105 (2), 79 (2), 78 (1), 77 (3), 76 (2), 75 (2), 63 (2), 51 (2), 28 (4). |
| 3 | 1-Hydroxy-6,8-dimethoxy-3-methyl-9,10-anthraquinone (emodin dimethyl ether) | 300 (4), 299 (21), $M^{+\cdot}$ 298 (100), 297 (8), 295 (2), 285 (2), 284 (5), 283 (5), 282 (5), 281 (22), 280 (49), 279 (3), 271 (2), 270 (7), 269 (26), 268 (10), 267 (5), 266 (3), 265 (15), 256 (3), 255 (9), 254 (6), 253 (19), 252 (70), 251 (6), 250 (3), 249 (2), 248 (2), 242 (1), 241 (4), 240 (5), 239 (10), 238 (11), 237 (27), 236 (2), 229 (3), 228 (8), 227 (6), 226 (10), 225 (7), 224 (7), 223 (7), 222 (3), 213 (3), 212 (7), 211 (10), 210 (12), 209 (13), 208 (3), 207 (3), 199 (4), 198 (5), 197 (13), 196 (6), 195 (5), 194 (4), 185 (3), 184 (10), 183 (7), 182 (11), 181 (15), 169 (12), 168 (8), 167 (4), 166 (4), 165 (6), 157 (4), 156 (8), 155 (8), 154 (5), 153 (11), 152 (10), 151 (7), 150 (5), 141 (12), 140 (9), 139 (20), 138 (4), 135 (24), 129 (5), 128 (17), 127 (13), 126 (7), 119 (7), 115 (17), 113 (7), 106 (7), 102 (7), 101 (6), 99 (6), 98 (6), 91 (9). |

**1,6,8-Trihydroxy-3-methyl-9,10-anthraquinone (1).** In the mass spectrum of 1,6,8-trihydroxy-3-methyl-9,10-anthraquinone (emodin) (2), the peak of MI has a maximum intensity (I = 100%), whose stability is $W_{mi}$ = 35.2% (table 2). The most intense peak of MI emodin (2) decays under the action of ionization by electrons (IE) along four directions and gives low-intensity ions (scheme 1).

Table 2 – Stability of molecular ions ($W_{mi}$) and characteristic ions ($F_1$-$F_7$) ($W_f$) from the total ion current of anthraquinone derivatives (1-3)

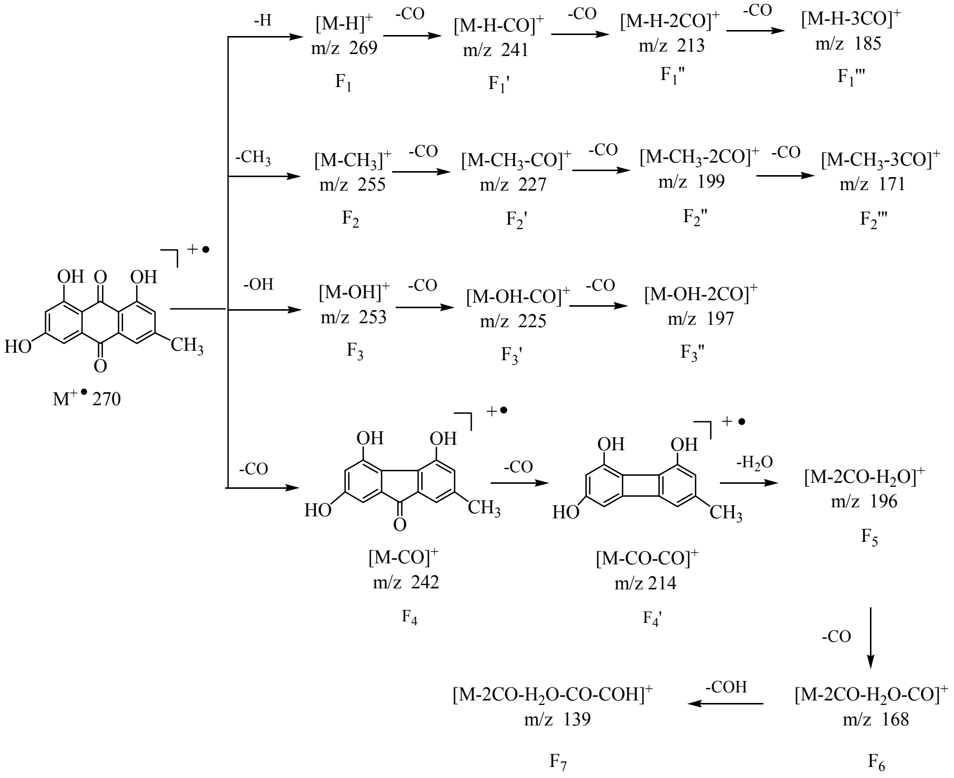
| № | $W_{mi}$, % | m/z ($W_f$, %) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | $F_1$ / $F_1'$- $F_1''''$ | $F_2$ / $F_2'$-$F_2''''$ | $F_3$ / $F_3'$-$F_3''''$ | $F_4$ / $F_4'$-$F_4'''$ | $F_5$ /$F_5'$ | $F_6$/ $F_6'$, $F_6''$ | $F_7$ |
| 1 | 35,2 | 269 (0,6)<br>241 (2,7)<br>213 (3,0)<br>185 (1,5) | 255 (0,6)<br>227 (0,3)<br>199 (0,6)<br>171 (0,6) | 253 (0,9)<br>225 (0,9)<br>197 (1,2)<br>169 (0,6) | 242 (4,1)<br>214 (2,0) | 196 (0,9) | 168 (1,5) | 139 (2,4) |
| 2 | 40,6 | 283 (1,6)<br>255 (4,2)<br>227 (1,9)<br>199 (0,65) | 269 (0,3)<br>241 (3,2)<br>213 (2,2)<br>185 (1,3) | 267 (0,65)<br>239 (0,3)<br>211 (0,3)<br>183 (0,3) | 256 (2,3) | 254 (3,0) | 226 (2,3) | 198 (1,6) |
| 3 | 11,9 | 297 (0,8)<br>269 (2,5) | 281 (2,1)<br>253 (1,8) | 280 (4,7)<br>252 (6,7) | 265 (1,4)<br>237 (2,6)<br>209 (1,2) | 268 (0,9)<br>238 (1,0) | 255 (0,9)<br>227 (0,6)<br>197 (1,2) | – |

When hydrogen is lost, a peak of the ion $F_1$ $[M\text{-}H]^+$ with m/z 269 (I = 2%) is formed, which successively loses three molecules of carbon monoxide, which leads to the appearance of the ions $F_1'$ $[M\text{-}H\text{-}CO]^+$ with m/z 241, $F_1''$ $[M\text{-}H\text{-}CO\text{-}CO]^+$ with m/z 213 and $F_1'''$ $[M\text{-}H\text{-}CO\text{-}CO\text{-}CO]^+$ with m/z 185. The most intense, from the formed peaks, with I = 10% is the peak of the ion $F_1''$ $[M\text{-}H\text{-}CO\text{-}CO]^+$ with m/z 213 and with I = 9% - the peak of the ion $F_1'$ $[M\text{-}H\text{-}CO]^+$ with m/z 241, and the intensity of the ion F1''' $[M\text{-}H\text{-}CO\text{-}CO\text{-}CO]^+$ is I = 5% (table 1).

The second direction of MI fragmentation occurs when a methyl radical is lost with the formation of the $F_2$ $[M\text{-}CH_3]^+$ ion with m/z 255. Further, the $F_2$ $[M\text{-}CH_3]^+$ ion sequentially eliminates three CO molecules to form $F_2'$ $[M\text{-}CH_3\text{-}CO]^+$ with m/z 227, $F_2''$ $[M\text{-}CH_3\text{-}CO\text{-}CO]^+$ with m/z 199 and $F_2'''$ $[M\text{-}CH_3\text{-}CO\text{-}CO\text{-}CO]^+$ with m/z 171, the intensity of the ions formed is I = 1-2%.

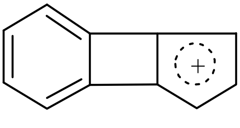
The third direction of fragmentation begins with the release of the OH group and the formation of the $F_3$ $[M\text{-}OH]^+$ ion with m/z 253, from which the CO molecules are eliminated, which leads to $F_3'$ $[M\text{-}OH\text{-}CO]^+$ fragment ions with m/z 225, $F_3''$ $[M\text{-}OH\text{-}CO\text{-}CO]^+$ with m/z 197 and $F_3''$ $[M\text{-}OH\text{-}CO\text{-}CO\text{-}CO]^+$ with m/z 169, with intensity I = 2-4% .

The fourth direction of MI disintegration proceeds analogously to the decay of MI 9,10-anthraquinone and is associated with the sequential elimination of the carbon monoxide molecule. The ions of 1,6,8-trihydroxy-3-methylfluorenone $F_4$ $[M\text{-}CO]^{+\bullet}$ with m/z 242 (I = 14%) and 1,6,8-trihydroxy-3-methylbiphenylene are formed $F_4'$ $[M\text{-}CO\text{-}CO]^{+\bullet}$ with m/z 214 (I = 7%). The formed ion $F_4'$, in turn, can consecutively lose the water molecule (the ion $F_5$ $[M\text{-}2CO\text{-}H_2O]^+$, m/z 196), CO (ion $F_6$ $[M\text{-}2CO\text{-}H_2O\text{-}CO]^+$, m/z 168) and CHO (ion $F_7$ $[M\text{-}2CO\text{-}H_2O\text{-}COOH]^+$, m/z 139) due to reorganization processes, that is scrambling of hydrogen atoms due to migration and scrambling of carbon atoms as a result of valence isome-



Scheme 1 – Fragmentation of a molecular ion 1,6,8-trihydroxy-3-methyl-9,10-anthraquinone (1)

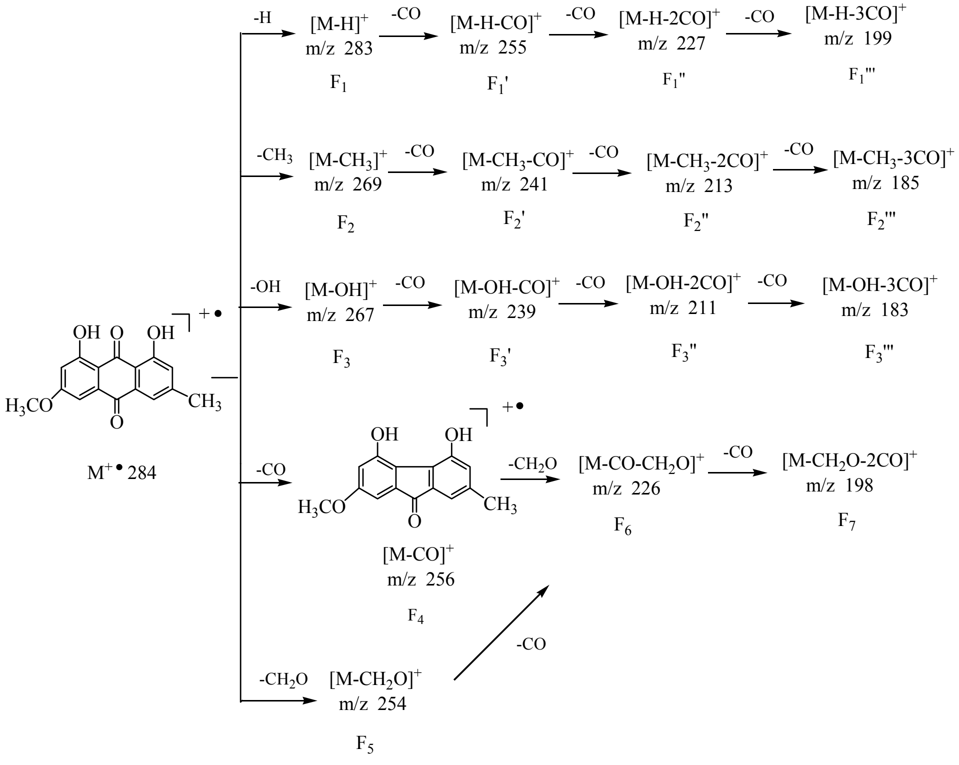
rism, as well as processes of randomization-displacement hydrogen atoms and carbon [18, 19]. Consequently, a significant peak with m/z 139 in the mass spectrum corresponds to the $F_7$ ion:



$F_7$ $[M\text{-}2CO\text{-}H_2O\text{-}COH]^+$, m/z 139

**1,8-Dihydroxy-6-methoxy-3-methyl-9,10-anthraquinone (2).** The substitution of the β-hydroxyl group for the methoxy group in the molecule of emodin (1) in the case of β-methoxyemodine (physcion) (2) practically does not affect the character of the initial MI decay in the mass spectrum, but increases the stability of MI ($W_{mi}$ = 40.6%) (table 2).

For the mass-spectrometric decomposition of 1,8-dihydroxy-6-methoxy-3-methyl-9,10-anthraquinone (2), the original fragmentation of MI, as in the case of the emodin molecule (1), occurs as a result of the splitting off of the hydrogen atom, OH and CO with the formation of primary fragment ions $F_1$ $[M\text{-}H]^+$ with m/z 283, $F_2$ $[M\text{-}CH_3]^+$ with m/z 269, $F_3$ $[M\text{-}OH]^+$ with m/z 267 and $F_4$ $[M–CO]^{+\bullet}$ with m/z 256 (scheme 2).



Scheme 2 – Fragmentation of a molecular ion
1,8-dihydroxy-6-methoxy-3-methyl-9,10-anthraquinone (2)

A distinctive feature of the mass-spectrometric decay of MI (2), in contrast to the emodin spectrum (1), is the elimination of the formyl radical $CH_2O$ and the formation of the fragment ion $F_5$ $[M\text{-}CH_2O]^{+\bullet}$ with m/z 254 (scheme 2). The intensity of the formed $F_1$-$F_5$ ions is I = 5-9% (table 1). The further decay of the fragment ions $F_1$ $[M\text{-}H]^+$ with m/z 283, $F_2$ $[M\text{-}CH_3]^+$ with m/z 269 and $F_3$ $[M\text{-}OH]^+$ occurs by successive elimination of carbon monoxide molecules, which leads to the formation of ions $F_1'$ $[M\text{-}H\text{-}CO]^+$ with m z 255, $F_1''$ $[M\text{-}H\text{-}CO\text{-}CO]^+$ with m/z 227, $F_2'$ $[M\text{-}CH_3\text{-}CO]^+$ with m/z 241, $F_3'$ $[M\text{-}OH\text{-}CO]^+$ with m/z 239, $F_3''$ $[M\text{-}OH\text{-}CO\text{-}CO]^+$ with m/z 211. The most intense of these are $F_1'$ (I = 13% ) and $F_2$ (I = 10%).

It is possible to eliminate the formyl radical $CH_2O$ from the $F_4$ $[M\text{-}CO]^{+\bullet}$ m/z 256 fragment with the formation of the $F_6$ $[M\text{-}CO\text{-}CH_2O]^+$ ion with m/z 226 (I = 7%). The $F_6$ ion can also arise from the $F_5$ ion, after the elimination of the carbon monoxide molecule. The emission of a CO molecule from the $F_6$

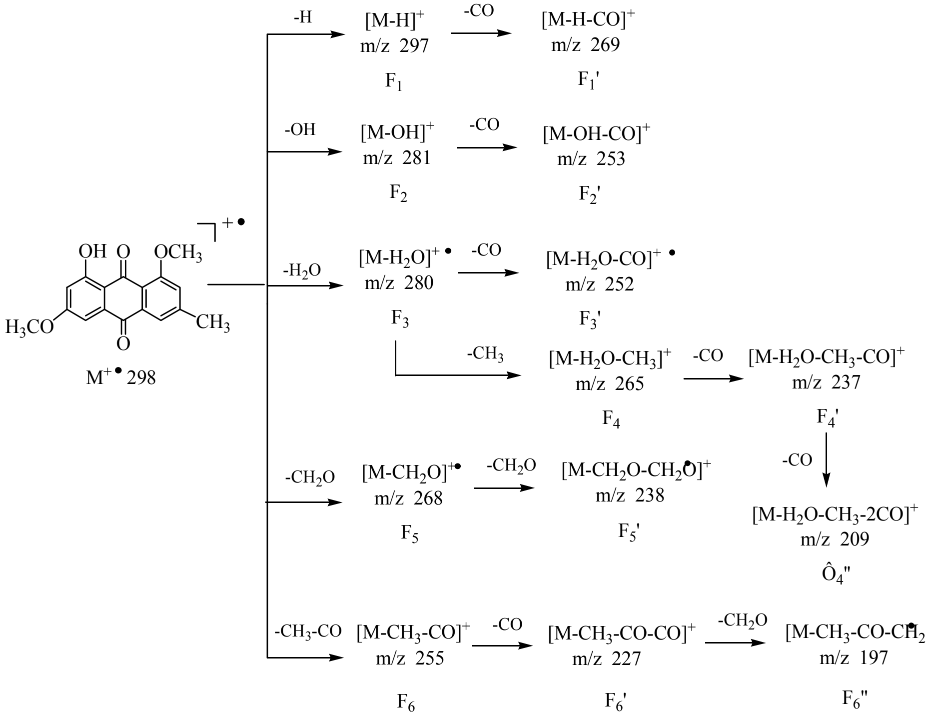
$[M\text{-}CO\text{-}CH_2O]^+$ ion with m/z 226 leads to the pairing of the $F_7$ $[M\text{-}CO\text{-}CH_2O\text{-}CO]^+$ ion with m/z 198 (I = 5%).

**1-Hydroxy-6,8-dimethoxy-3-methyl-9,10-anthraquinone (3).** The replacement of one α-hydroxyl group with an electron-donor methoxy group does not affect the intensity of MI of compound (3), which is I = 100% (table 1), but sharply decreases its stability - $W_{mi}$ = 11.9% (table 2). Due to the diversity of the MI decay channels, in the mass spectrum, multiple peaks of fragment ions are observed.

For 1-methoxyanthraquinone, the main direction of the mass-spectral decomposition of MI is the elimination of the carbon monoxide molecule to form the ion fragment $F_1$ (m/z 210), from which the methyl radical and CO, as well as the separation of H, HCO and $CH_2O$, $[M\text{-}H]^+$, $[M\text{-}HCO]^+$ and $[M\text{-}CH_2O]^{+\bullet}$ respectively [14]. The replacement of one α-hydroxyl group with a methoxy group in the case of the derivative (3) sharply changes the picture of the MI decay, in comparison with the mass spectrum of the physcion (2). In the case of mass-spectrometric fragmentation of 1-hydroxy-6,8-dimethoxy-3-methyl-9,10-anthraquinone (3), primary MI decays occur as a result of the splitting off of the hydrogen atom, OH, $H_2O$, $CH_2O$ and the group of $COCH_3$ atoms, of the primary fragment ions $F_1$ $[M\text{-}H]^+$ with m/z 297, $F_2$ $[M\text{-}OH]^+$ with m/z 281, $F_3$ $[M\text{-}H_2O]^{+\bullet}$ с m/z 280, $F_5$ $[M\text{-}CH_2O]^{+\bullet}$ with m/z 268, $F_6$ $[M\text{-}CO\text{-}CH_3]^+$ with m/z 255 (scheme 3). The most intense peaks in the spectrum are due to the release of the water molecule - $F_3$ $[M\text{-}H_2O]^{+\bullet}$ with m/z 280 (I = 49%) and OH- $F_2$ $[M\text{-}OH]^+$ with m/z 281 (I = 22 %) (table 1).

Further, the ions $F_1$-$F_3$ and $F_6$ eliminate the CO molecule, with the formation of the secondary fragment ions $F_1'$ $[M\text{-}H\text{-}CO]^+$ with m/z 269, $F_2'$ $[M\text{-}OH\text{-}CO]^+$ with m/z 253, $F_3'$ $[M\text{-}H_2O\text{-}CO]^{+\bullet}$ with m/z 252 and $F_6'$ $[M\text{-}CO\text{-}CH_3\text{-}CO]^+$ with m/z 227, and in the case of the $F_5$ ion $[M\text{-}CH_2O]^{+\bullet}$ с m/z 268, another formyl group of $CH_2O$ eliminates to form the radical cation $F_5'$ $[M\text{-}CH_2O\text{-}CH_2O]^{+\bullet}$ with m/z 238. The most intense peaks correspond to the ions $F_1'$ $[M\text{-}H\text{-}CO]^+$ with m/z = 269 (I = 26%), $F_2'$ $[M\text{-}OH\text{-}CO]^+$ with m/z 253 (I = 19%) and $F_3'$ $[M\text{-}H_2O\text{-}CO]^{+\bullet}$ с m/z 252 (I = 70%) (table 1). The fragment ion $F_3$ can also consecutively lose the methyl group and carbon monoxide molecules to form the $F_4$ ion $[M\text{-}H_2O\text{-}CH_3]^+$ with m/z 265 (I=15%), $F_4'$ $[M\text{-}H_2O\text{-}CH_3\text{-}CO]^{+\bullet}$ with m/z 237 (I = 27%) and $F_4''$ $[M\text{-}H_2O\text{-}CH_3\text{-}2CO]^{+\bullet}$ with m/z 209 (I = 13%). The secondary ion $F_6'$ $[M\text{-}CO\text{-}CH_3\text{-}CO]^+$ with m/z 227 due to the loss of the formyl group $CH_2O$ forms the fragment ion $F_6''$ $[M\text{-}CO\text{-}CH_3\text{-}CO\text{-}CH_2O]^+$ with m/z 197 (I = 13%).

Thus, an analysis of the mass-spectral decomposition of MI of the group of derivatives considered showed that if the decomposition of 1,8-dihydroxyanthraquinone (1) is associated with the successive elimination of two carbon monoxide molecules to form the cation of dihydroxyfluorenone with m/z 212 (I = 15%) and dihydroxybiphenylene $F_2$ $[M\text{-}CO\text{-}CO]^{+\bullet}$ with m/z 184 (I = 16%), the fragmentation of the derivatives (2,3) depends on the position of the substituent in the anthraquinone system. In the case of mass-spectrometric decomposition of emodin (1), in the region of high mass numbers, several low-intensity peaks of the



Scheme 3 – Fragmentation of a molecular ion
1-hydroxy-6,8-dimethoxy-3-methyl-9,10-anthraquinone (3)

characteristic ions associated with the initial decay of MI can be identified as a result of the splitting off of the hydrogen atom, $CH_3$, OH and CO with formation of primary fragment ions $F_1$ $[M\text{-}H]^+$, $F_2$ $[M\text{-}CH_3]^+$, $F_3$ $[M\text{-}OH]^+$ and $F_4$ $[M\text{-}CO]^{+\bullet}$. The main direction of the decomposition of stable MI of emodin (1) (I = 100%, $W_{mi}$ = 35.2%) is the consecutive elimination of CO molecules by the "anthraquinone" type with the formation of the radical cation 1,6,8-trihydroxy-3-methylfluorenone $F_4$ $[M\text{-}CO]^{+\bullet}$ with m/z 242 (I = 14%) and 1,6,8-trihydroxy-3-methylbiphenylene $F_4'$ $[M\text{-}CO\text{-}CO]^{+\bullet}$ with m/z 214 (I = 7%). MI physcion (2) decays with EI mainly by sequential ejection from MI of a hydrogen atom and two CO molecules, and for a dimethoxy derivative (3), the underlying direction of decomposition is the consecutive loss of $H_2O$ and CO molecules. The replacement of one or two hydroxyl groups by the methoxy group in compounds (2,3) causes the appearance of yet another direction of fragmentation associated with the elimination of the formyl radical $CH_2O$. As in the case of the previously considered methoxy derivatives of 9,10-anthraquinone [14, 17], substitution of the α-hydroxyl group by the methoxy group reduces the stability of MI to ionization by electrons. So, if the stability of the MI physcion (2) is $W_{mi}$ = 40.6%, then its α-methyl ester (3) - $W_{mi}$ = 11.9% (Table 2). The low stability of the MI compound (3) promotes the diversity of the MI decay channels, which is reflected in the mass spectrum of the derivative by the presence of a large number of peaks of fragment ions.

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## Резюме

*Т. В. Харламова, С. Ж. Жұмағалиев*

# ЭМОДИН ЖӘНЕ ОНЫҢ МЕТИЛ ЭФИРЛЕРІНІҢ МОЛЕКУЛАЛЫҚ ИОНДАРЫНЫҢ МАСС-СПЕКТРОМЕТРИЯЛЫҚ ФРАГМЕНТАЦИЯСЫНЫҢ СИПАТТАМАСЫ

Зерттеу жұмыс 1,6,8-үшгидрокси-3-метил-9,10-антрахинонның (эмодиннің) және оның кейбір метил эфирлерінің масс-спектрометрияы зерттеуіне және молекуларлық иондарының масс-спектрометралды фрагментациясының салыстырмалы талдауына арналған. Қарастырылған қосылыстар топтарына МИ қарқынды шыңы сипатты және оның тұрақтылығы $W_{ми}$=11,9÷40,6% құбылту мөлшерінде екені көрсетілген. Молекуларлық иондардың (МИ) ионизациялау электрондармен (ИЭ) мықтылығына орынбасардың әсері қаралған және олардың масс-спектрометралды ыдырау кестесі ұсынылған. Туындылардың фрагментациясы орынбасардың антрахинон ситемасында орналасқан орнына тәуелділігі көргелтілген. Эмодин молекуласының МИ бастапқы фрагментациясы сутегі атомы, $CH_3$, OH және CO бөліну нәтижесінде жүреді, ал оның метокситуындылары және формил радикалының $CH_2O$ элиминирленуі сипатты.

**Түйін сөздер:** масс-спектр, молекуларлық ион, фрагментациялау, электрондық ионизациялау, элиминирлеу, 9,10-антрахинон туындылары.

## Резюме

*Т. В. Харламова, С. Ж. Жумагалиев*

# ХАРАКТЕРИСТИКА МАСС-СПЕКТРОМЕТРИЧЕСКОЙ ФРАГМЕНТАЦИИ МОЛЕКУЛЯРНЫХ ИОНОВ ЭМОДИНА И ЕГО МЕТИЛОВЫХ ЭФИРОВ

Работа посвящена масс-спектральному исследованию и сравнительному анализу масс-спектральной фрагментации молекулярных ионов 1,6,8-дигидрокси-3-метил-9,10-антрахинона (эмодина) и его метиловых эфиров. Показано, что для рассматриваемой группы соединений характерен интенсивный пик МИ, а его стабильность варьируется в пределах 11,9÷40,6 %. Рассмотрено влияние заместителя на устойчивость молекулярных ионов к ионизации электронами и предложены схемы их масс-спектрального распада. Показано, что фрагментация производных зависит от расположения заместителя в антрахиноновой системе. Первоначальная фрагментация МИ молекулы эмодина происходит в результате отщепления атома водорода, $CH_3$, OH и CO, а для его метоксипроизводных характерно также элиминирование формильного радикала $CH_2O$.

**Ключевые слова:** масс-спектр, молекулярный ион, фрагментация, электронная ионизация, элиминирование, производные 9,10-антрахинона.

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# EFFECT OF THE POLYMER TEMPLATE MODIFICATION ON THE STUCTURE AND PROPERTIES OF THE COPPER NANOTUBES EMBEDDED IN COMPOSITE TRACK-ETCHED MEMBRANES

**Abstract.** This paper is devoted to the study of the preliminary oxidative modification effects as well as activation and sensitization conditions of PET track etched membranes (TeMs) on the structure of copper nanotubes (NTs) synthesized by the electroless deposition approach. The structure and composition of the synthesized composite membranes was studied by advanced methods such as: UV-Vis spectroscopy, energy dispersive analysis, scanning electron microscopy, X-ray diffraction and gas permeability.

The catalytic activity of Cu/PET TeM catalysts obtained under various deposition regimes has been studied using the benchmark reaction of the p-nitrophenol (p-NP) reduction in the presence of the sodium borohydride. It was shown that the highest value of the constant rate of the p-NP reduction reaction was determined for the composites prepared in the modified and double activated PET TeMs.

In the temperature range of 16-35 °C, the effect of temperature on the rate of the p-NP dehydrogenation reaction in the presence of composite catalysts based on copper NTs was studiedand the activation energy values were calculated. the lowest values of Ea were determined for samples synthesized in a matrix of unmodified and simple activated PET TeMs.

**Keywords:** copper nanotubes, electroless template synthesis, oxidation pretreatment, track-etched composite membranes, p-nitrophenol reduction

**Introduction.** Composite track-etched membranes (TeMs) with deposited nanotubes (NTs), nanowires (NWs) or nanoparticles (NP) form a new class of composite nanomaterials and are subject of investigation in various fields of membrane materials science. Literature data analysis shows that such composite membranes are a promising material for the development of lead-acid batteries, nanosized energy generators, high-sensitivity electrodes, elements of nano- and microelectronics, nanosensorics and photovoltaics, and magnetic devices [1–5]. Composite materials based on TeM s and NTs, NWs or NPs deposited by various methods have a large catalytically active specific surface, high mechanical strength, which allows them to be used for several consecutive reaction cycles without purification and activation. In most of the previously published works devoted to the study of the catalytic properties of the composite membranes a reduction reaction of p-nitrophenol (p-NF) is used [6,7]. The catalytic properties of monocomponent composites based on TeMs and gold NTs [8], AgNTs [9], Pt NTs [10], Au [11] and Pd [12], composites of mixed composition of Ni-Co Ni-Co [13], Ag/Au [14]. Moreover, in a number of works the authors managed to achieve an increase in the activity of composite materials by carrying out a preliminary modification of the polymeric template [11,15]. However, despite the diversity of the types of studied composite membranes, a limited amount of data on the reduction ability of copper NTs in composites has been found in the literature, although a number of review articles [16,17] indicate a significant potential for using nanosized copper and its compounds in organic synthesis as effective catalysts. In addition, nanostructures (NSs) based on copper and its oxide forms are objects of close study due to their surprising properties in the nanoscale state[18].

The purpose of this work is to study the effect of a preliminary oxidative modification of the activation conditions and sensitization of PET TM on the structure of copper NTs obtained by chemical deposition. It is of interest to consider the change in the catalytic properties of Cu/PET TeMs composite catalysts obtained under different deposition regimes.

## EXPERIMENTAL

**Chemicals.** Copper (II) sulfate pentahydrate, sodium potassium tartrate, sodium hydroxide, palladium chloride, p-nitrophenol (4-NP) and sodium borohydride (Sigma) and all the other chemicals were of the analytical or reagent grade and were used without further purification.

**Oxidation pretreatment of PET template.** PET TeM samples were oxidized in $H_2O_2$/UV system. Details of the method were described elsewhere [3]. Membranes were immersed in 300 mM $H_2O_2$ water solution at pH=3 (HCl) for 180 min under UV irradiation at 254 nm. After oxidation the samples were washed twice in deionized water, dried in air at room temperature for 5 h.

Determination of change in carboxyl groups on the surface of PET TeMs before and after oxidation was made according to the procedure were described elsewhere [4] using toluidine blue dye. The calculation is based on the assumption that 1 M of dye complexed with 1 M of carboxyl groups.

**Electroless template synthesis of copper NTs.** TeMs were prepared from 12.0 μm PET film by irradiation with$^{+15}$Kr$^{84}$ ions (energy = 1.75 MeV per nucleon, fluence = $4 \cdot 10^7$ ions/cm$^2$) at the DC-60 heavy ion accelerator in Astana, Kazakhstan. Subsequently, the irradiated film was etched 4.0 min in 2.2 M NaOH solution at 85 ± 1°C. The pore size did not exceed 395±5 nm.

Prior to electroless deposition (ELD) of copper, the PET template was exposed to activation and sensitization procedures [38]. On the first stage a sample of PET TeM was immersed in a solution containing 50 g/l of $SnCl_2$ and 60 ml/l of 37% HCl for 6 minutes, afterword it was thoroughly rinsed for 10 min under flowing warm water. At the next activation stage, the sensitized membrane was immersed for 6 min into solution of 0.1g/l of $PdCl_2$ and 10 ml/l of HCl to provide formation of the thin layer of Pd nuclei and finally dried on the air [32].

To study the effect of activation treatment on the copper NTs deposition process, sensitization and activation stages were repeated twice for a series of sample.

Deposition was carried out at the temperature of 10°C. The activated polymer matrix was immersed in a thermostated deposition solution ($KNaC_4H_4O_6 \cdot 4H_2O$ - 18 g/l, $CuSO_4 \cdot 5H_2O$ - 5 g/l, NaOH - 7 g/l) and carefully fixed to avoid its expulsion by bubbles of evolved hydrogen. The desired pH = 12.45 was adjusted by the addition of sulfuric acid. The copper deposition process started immediately after the addition of 0.13M formaldehyde, for all the regimes, the deposition time did not exceed 40 min. At the end of the ELD, the samples were washed in a 96% ethanol solution and in deionized water and dried in an inert atmosphere.

**Characterization.** The structure of the copper NTs deposited in PET TeMs was investigated using a scanning electron microscope (SEM) JEOL JFC-7500F. Hitachi TeM3030 SEM equipped with a BrukerXFlash MIN SVE microanalysis system was used to elucidate the chemical composition of the resulting NTs. X-ray diffraction (XRD) measurements of the “as-prepared” composite membrane samples were obtained on a D8 Advance (Bruker, Germany). X-ray was generated at 40 mA and 40 kV and the scanning position ranged from 15-90˚ 2(θ). The crystal grain sizes were calculated using Scherrer equation.

**Catalysis.** A sample of Cu NTs composite membrane of size 2×2 cm was immersed into the stirred reaction mixture of 10 ml of $7.82 \cdot 10^{-6}$ M 4-NP and the $7.82 \cdot 10^{-3}$ M $NaBH_4$ aqueous solution [5]. The reaction was monitored at a temperature of 25±0.1 °C every 5-7 minutes using UV-Vis spectrophotometer in the wavelength range 200-600 nm. All samples were tested 3 times. Pseudo-first order reaction rate constants were calculated by plotting $\ln(A_t/A_0)$ versus time ($A_t$ and $A_0$ is absorbance at $\lambda = 400$ at time t and in t=0). The slope of the line of best fit in the plot gives the pseudo-first order rate constant.

## RESULTS AND DISCUSSION

In this study, copper NTs deposition was carried out in etched (Etch-PET TM) as well as oxidized (OX-PET TeMs). Previously [21] was found that the treatment of PET TeMs in oxidation systems based on hydrogen peroxide allows to significant increase the concentration of terminal carboxyl groups. Within this study we have obtained modified PET templates with a concentration of terminal carboxyl groups on the surface and in channels of the membrane equal to $14.9 \pm 0.8$ nM/cm$^2$ (for only etched PET TM this value is $6.0 \pm 0.1$ nM/cm$^2$).

Determination of the synthesis optimal conditions is the quietly important issue due its impact not only on the structure of nanomaterials but also on properties. Thus, sensitization stage the adsorption of $Sn^{2+}$ ions occurs on the surface and in the pore channels of the PETTeMs (figure 1).

Further on the activation stage, $Sn^{2+}$ acts as the reductant of $Pd^{2+}$ ions afterward the formation of dense layer of nanosizedPdnanoparticles as a catalytic nuclei was observed.

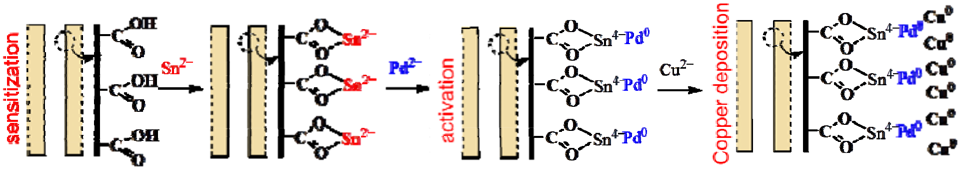

Figure 1 – General scheme of copper electroless deposition in the PET template

The formation of palladium nanoparticles at the activation stage (figure 2) was confirmed by X-ray diffraction (JCPDS 05-0681). And the dimension of nanoparticles (6.7±0.05) nm remains practically unchanged with several repeated procedures. Visual observation of the activated samples showed that multiple stages of sensitization and activation provide a denser layer of catalytic nucleation centers for palladium throughout the entire volume of the template.

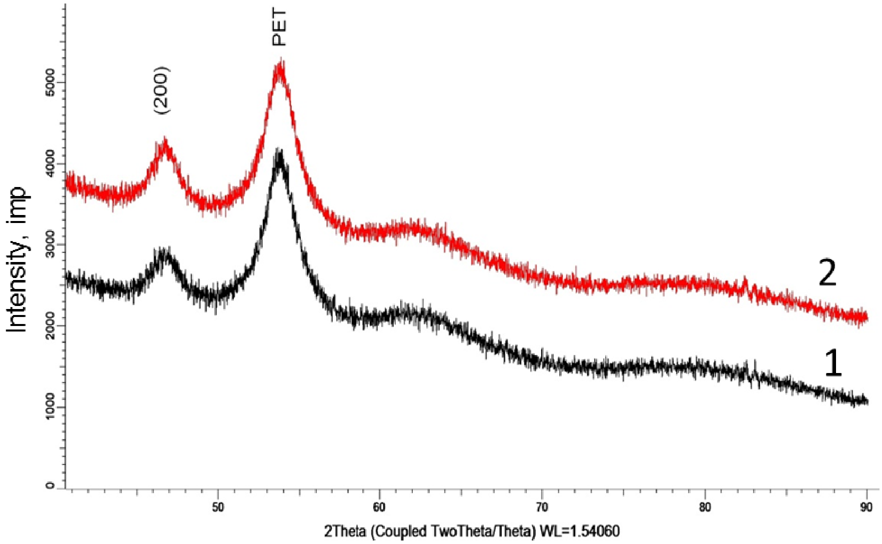

Figure 2 – XRD patterns of the PET TeM after single and double activation treatment

The energy-dispersive analysis was carried out to determine the chemical composition of copper NTs immediately after plating. It was found that the synthesized Cu NTs consist entirely of copper; the minor peak at 1.5 keV corresponds to SEM sample holder, peaks related to the carbon and oxygen are belong to the PET.

According to the XRD analysis data, all synthesized samples of the Cu NTs has afcclattice of copper and XRD pattern contained the(111), (200), (220) и (311), peaks related to the $Cu^0$. XRD data as well as copper deposition rate (R) and the structural parameters of final copper NTs are presented in the table 1. It’s should be noted that samples deposited in modified template possess a higher crystallinity.

Table 1 – Structural parameters of the copper NTs

| № | Template | Number of activation | L Nm | a, Å | Crystal-linity, % | R, mg/cm$^2$·h | Structural parameters of NTs | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | Wall thickness, nm | Inner diameter, nm |
| 1 | Etch-PET TeMs | 1 | 18,0±2,7 | 3,602 | 43,8 | 5,72 | 73,7 | 249 |
| 2 | Etch- PET TeMs | 2 | 19,9±2,9 | 3,594 | 52,5 | 5,632 | 88,15 | 203,3 |
| 3 | Ox- PET TeMs | 1 | 15,0±2,8 | 3,604 | 42,8 | 5,448 | 64,0 | 268,2 |
| 4 | Ox- PET TeMs | 2 | 21,4±3,2 | 3,597 | 53,1 | 5,748 | 79,5 | 237,3 |

SEMimages of the composites surface after copper deposition in the Etch-PET TeMa and Ox-PET TeMs samples after single and double activation treatment are presented on the figure 3. The sample code is given in accordance with table 2.

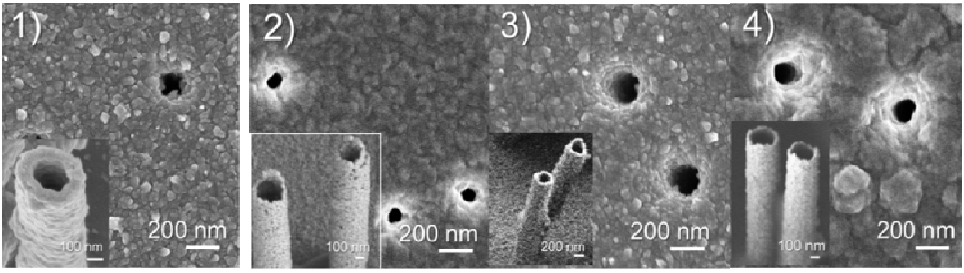

Figure 3 – SEM front side images of the Cu NTs composite membranes and magnified images of the released Cu NTs

As could be seen from SEM images of Cu-2 and Cu-4 a double repeated activation of the oxidized template surface provides the formation a copper layer consisting of more coarse-grained NPs, the wall thickness is almost 20% larger than in samples deposited in Etch-PET TeM templates.

Starting from Pradhan [28] reduction of 4-NP by sodium borohydride reaction has been used as a benchmark reaction for the evaluation of catalytic ability of nanosized catalysts [22].This reaction could be easily monitored by UV-vis spectroscopy: 4-NP shows a characteristic absorption peak at 400 nm in water solution from another hand the product, *p*-aminophenol (4-AP), exhibits a weak absorption peak at around 299 nm.The studied reaction has the pseudo-first order in the presence of excess of NaBH4, that allows to study the kinetics of the reaction to change the amount of the starting reagent 4-NP (figure 4).

As can be seen from the presented data, the preliminary oxidative modification of the PET template facilitates an increase in the catalytic activity of the composite membrane. In addition, for the OX-PET TeM sample (double activated) the of p-NPconstant rate increases by more than 40% compared to the sample prepared according to a standard procedure (Etch-PET TM, single activated).

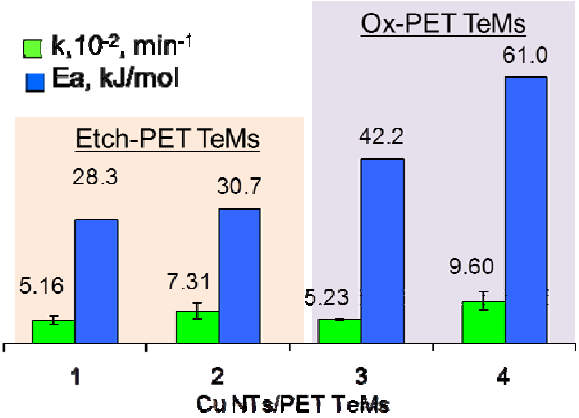

Figure 4 – The changes of constant rate and activation energy of the 4-NP reduction reaction in the presence of the composite membranes with embedded copper nanotubes

The impact of testing temperature on the catalyticability of the synthesized composite membranes were studied in the temperature range of 16-35 °C and the activation energy was calculated based on the Arrhenius plot (also presented in the figure 4).

The increased value of Ea for sample № 4 is caused by bigger size of copper crystallites than in other studied samples.

It is very difficult to carry out a comparative analysis of the Ea data obtained with the earlier studies of the temperature dependence of the catalytic activity of copper nanostructures, since the different shape of the copper tested NSs, their dimensionality, the type of substrate, the fixing method and test conditions may differ. Thus, for a hybrid microgel based on nanosized copper and a copolymer of N-isopropylacrylamide and acrylic acid, the Ea value in the reduction reaction of p-NP was claimed to be 0.8 kJ/mol [22], for an analogous reaction in the presence of nanosized copper stabilized with polyvinipyrrolidone, Ea equal to 45.76 and 82.96 kJ/mol for NPs with size of 9 and 11 nm respectively [23].

The main conclusions that can be drawn from thepresented above results are:

– A preliminary oxidative modification of the PET TeMs template allows a significant increase in the concentration of terminal carbonyl groups and, correspondingly, an increase in the amount of palladium NPs as active nuclei of the copper NTs growth.

– The highest value of the p-NP reduction reaction rate constant was determined for samples of composites synthesized in modified and double activated PET TeMs. However, the largest value of Ea was also calculated for this sample. We assume that main reason isa sharp increase of the reaction rate: with an increase in temperature from 16 to 35 ° C, the reaction rate increases by 9 times for sample №1, but for samples with a minimal Ea value this parameter increases only by 1.75 times in the same temperature range.

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## Резюме

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### ВЛИЯНИЕ МОДИФИКАЦИИ ПОЛИМЕРНОГО ТЕМПЛАТА НА СТРУКТУРУ И СВОЙСТВА НАНОТРУБОК МЕДИ В СОСТАВЕ КОМПОЗИТНЫХ ТРЕКОВЫХ МЕМБРАН

Работа посвящена изучению влияния предварительной окислительной модификации и условий активации и сенсибилизации ПЭТФ ТМ на структуру НТ меди, полученных методом химического осаждения. Структура и состав синтезированных композитных мембран была изучена методами: УФ-спектроскопия, энергодисперсионный анализ, растровая электронная микроскопия, рентгеновская дифрактометрия и метод газопроницаемости.

На примере классической реакции восстановления п-нитрофенола (п-НФ) в присутствии боргидрида натрия была изучена каталитическая активность катализаторов Cu/ПЭТФ ТМ, полученных при различных режимах осаждения. Показано, что наибольшее значение константы скорости реакции восстановления п-НФ было определено для образцов композитов, полученных в модифицированных и дважды активированных ПЭТФ ТМ.

В интервале температур 16-35 °С было исследовано влияние температуры на скорость реакции дегидрирования п-НФ в присутствии композитных катализаторов на основе НТ меди, на основании полученных данных были рассчитаны значения энергии активации. Наименьшее значение Ea было рассчитано для образцов, синтезированных в матрице не модифицированной ПЭТФ ТМ.

**Ключевые слова:** медные нанотрубки, синтез неорганических матриц, предварительная обработка окислением, композиционные мембраны с трек-травлением, снижение п-нитрофенола

## Резюме

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## КОМПОЗИТТІ ТРЕКТІ МЕМБРАНАЛАР ҚҰРАМЫНДАҒЫ МЫС НАНОТҮТІКШЕЛЕРІНІҢ ҚҰРАМЫ МЕН ҚҰРЫЛЫСЫНА ТҮРЛЕНГЕН ТЕМПЛАНТТЫ ПОЛИМЕРДІҢ ӘСЕРІ

Химиялық тұндыру әдісімен алынған мыснанотүтікшелерді (НТ) тотығу модификациясымен химиялық жауын шашын арқылы алынатын құрылымына ПЭТФ тректік мембраналарның (ПЭТФТМ) белсендірудің және сенсибилизацияның әсерін зерттеуге арналған. Синтезделген композиттік мембраналардың құрамымен құрамы: УК-спектроскопия, энергетикалық дисперсті талдау, сканерден өтетін электрондық микроскопия, рентгендік дифрактометрия және газ өткізгіштігі әдістерімен зерттелді.

Түрлі тұндыру режимдерінде алынған Cu/ТМ ПЭТФ катализаторларының каталитикалық белсенділігі натрий бор гидридінің қатысуымен п-нитрофенолды (п-НФ) азайту үшін классикалық реакцияны қолдану арқылы зерттелді. п-НФ төмендету реакциясының жылдамдық тұрақты константасының мәнінің ең жоғары мәні модификацияланған және екі есе актив тендірілген ТМПЭТФ алынған композит үлгілері үшін анықталған.

16-35°С температурада мыс НТ негізделген композициялық катализаторлардың қатысуымен п-НФ дегидрирленген реакциясының жылдамдығына температураның әсері зерттелді және алынған мәндер негізінде активтендіру энергия мәндері есептелген. Синтезделген үлгілер үшін ТМПЭТФ модифицирленген емес матрицасында ең төменгі Ea мәндері есептелген.

**Түйін сөздер:** бейорганикалық матрицаның синтезі, тотығудың алдын ала емдеуі, трек-өңделген композициялық мембраналар, р-нитрофенолды азайту.

УДК 541. 123.6

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# РАСТВОРИМОСТЬ СИСТЕМЫ $K_2SO_4$-$K_2CO_3$-$KHCO_3$-$H_2O$ ПРИ 0 °С

**Аннотация.** Рассмотрены результаты изучения растворимости в нонвариантных точках системы $K_2SO_4$-$K_2CO_3$-$KHCO_3$-$H_2O$ при 0 °С и диаграммы состояния при изотермических условиях.

**Ключевые слова:** растворимость, равновесие, жидкая фаза, химический анализ, кристаллооптический анализ, диаграмма, геометрические образы.

**Введение.** Четырехкомпонентная система $K_2SO_4$–$K_2CO_3$–$KHCO_3$-$H_2O$ является составной частью более сложной шестикомпонентной системы K,Ca//$SO_4$,$CO_3$,$HCO_3$,F-$H_2O$. Состояние фазовых равновесий и составляющих ее пяти- и четырёхкомпонентных системах определяют условия утилизации жидких отходов алюминиевого производства, которые содержат фториды, карбонаты, гидрокарбонаты и сульфаты натрия, калия и кальция [1, 2].

В настоящей работе рассмотрены результаты исследования системы $K_2SO_4$–$K_2CO_3$–$KHCO_3$-$H_2O$ при 0 °С методом растворимости с целю установления концентрационных параметров положения её геометрических образов и соотношения полей кристаллизации индивидуальных равновесных твёрдых фаз. Ранее [3] методом трансляции были установлены фазовые равновесия исследуемой системы и построена её фазовая диаграмма.

## ЭКСПЕРИМЕНТАЛЬНАЯ ЧАСТЬ

Равновесными твёрдыми фазами исследуемой системы при 25 °С являются: $K_2CO_3 \cdot 1{,}5H_2O$ – K·1,5; $K_2SO_4\cdot$ – Арканит (Ар); $KHCO_3 \cdot K_2CO_3 \cdot 1.5H_2O$ - S и $KHCO_3$ – калицинит (Кц).

Для опытов были использованы следующие реактивы: $K_2CO_3$ (ч); $K_2SO_4$ (х.ч); $KHCO_3$ (ч). Опыты проводили согласно методу донасыщения [4].

Исходя из данных [5, 6], нами предварительно были приготовлены смеси осадков с насыщенными растворами, соответствующими нонвариантным точкам, составляющих исследуемую четырехкомпонентную систему трехкомпонентных систем: $K_2CO_3$–$K_2SO_4$-$H_2O$; $K_2CO_3$-$KHCO_3$-$H_2O$ и $K_2SO_4$-$KHCO_3$–$H_2O$ при 0 °С. Затем, исходя из схемы трансляции нонвариантных точек уровня трехкомпонентного состава на уровень четырехкомпонентного состава [3], приготовленные насыщенные растворы, с соответствующими равновесными твёрдыми фазами, перемешивая термостатировали при 0 °С до достижения равновесия.

Термостатирование проводили в ультратермостате U–8. Перемешивание смеси осуществляли с помощью магнитной мешалки PD – 09 в течении 50–120 ч. Температура поддерживалась с точностью ± 0,1 °С с помощью контактного термометра. За кристаллизацией твёрдых фаз наблюдали с помощью микроскопа «ПОЛАМ-Р 311». После достижения равновесия в системе равновесные твёрдые фазы сфотографировали цифровым фотоаппаратом «SONY- DSC-S500». Достижение равновесия устанавливалось по неизменности фазового состава осадков. Отделение жидкой и твёрдой фазы осуществляли с помощью вакуумного насоса через обеззоленную (синяя лента) фильтровальную бумагу на воронке Бюхнера. Осадок, после фильтрации, промывали 96%-м этиловым спиртом и высушивали при 120 °С.

## РЕЗУЛЬТАТЫ И ИХ ОБСУЖДЕНИЕ

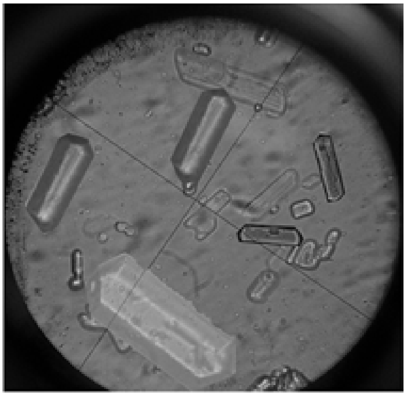
Химический анализ жидкой фазы проводили по известным методикам [7-9] (таблица 1).

Таблица 1 – Растворимость в узловых (нонвариантных) точках
системы $K_2SO_4$–$K_2CO_3$–$KHCO_3$-$H_2O$ при 0 °С

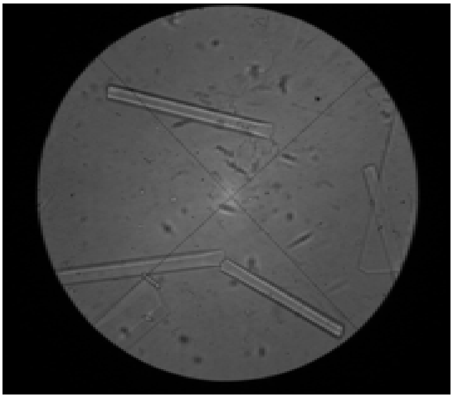
| Обозначения точек | Состав жидкой фазы, мас.% | | | | Фазовый состав осадков |
|---|---|---|---|---|---|
| | $K_2CO_3$ | $K_2SO_4$ | $KHCO_3$ | $H_2O$ | |
| $e_1$ | 51.70 | – | – | 48.30 | К·1.5 |
| $e_2$ | – | 6.78 | – | 93.22 | Ар |
| $e_3$ | – | – | 18.69 | 81.31 | Кс |
| $E_1^3$ | 51.30 | 0.15 | – | 48.55 | К·1.5+Ар |
| $E_2^3$ | 50.60 | – | 1.56 | 47.84 | К·1.5+S |
| $E_3^3$ | 49.10 | – | 2.19 | 48.71 | Кц+S |
| $E_4^3$ | – | 3.36 | 2.94 | 93.69 | Ар+Кц |
| $E_1^4$ | 20.70 | 3.42 | 13.90 | 61.98 | К·1.5+S+Ар |
| $E_2^4$ | 36.69 | 6.20 | 11.20 | 45.91 | Кс+S+Ар |

Результаты кристаллооптического анализа [10] равновесных твёрдых фаз (микрофотографии) представлены на рисунке 1.

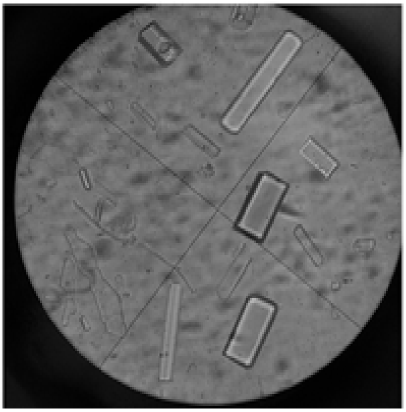
На основании полученных данных построена диаграмма растворимости системы $K_2SO_4$–$K_2CO_3$–$KHCO_3$-$H_2O$ при 0 °С, которая представлена на рисунке 2. Положения нонвариантных точек уровня трехкомпонентного ($E_n^3$) и четырехкомпонентного ($E_n^4$) составов, где n – номера точек, на диаграмме установлены по массцентрическому методу [11]. В связи с малой растворимостью солей Ар и Кц в приведенных условиях это сопровождается смещением положения фигуративных точек смесей к водному углу, концентрация воды 1:5.



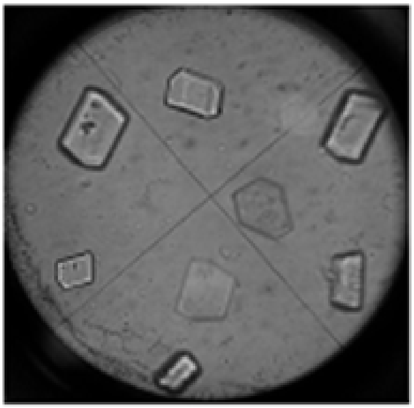
K·1.5



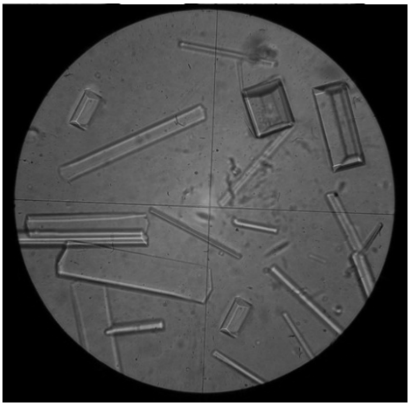
Ар



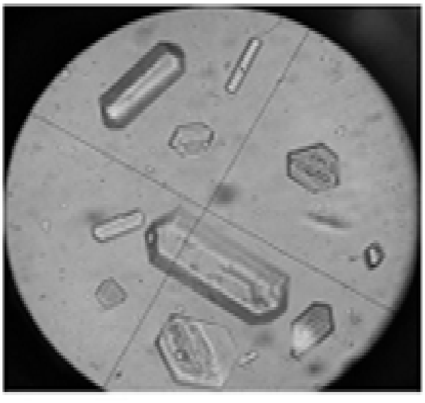
Кц



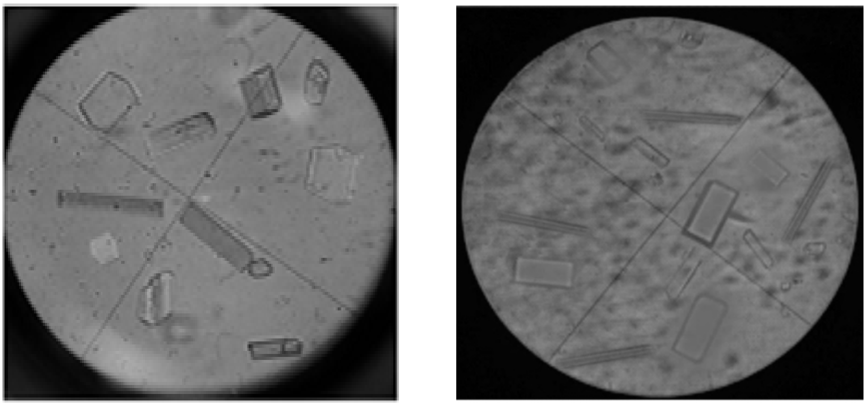
S



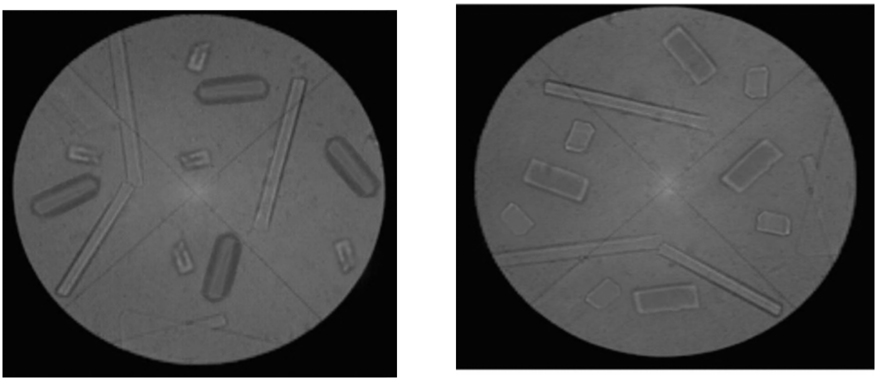
К·1.5+Ар



К·1.5+ S



S+Кц Кц+Ар



К·1,5+S+Ар Кс+S+Ар

Рисунок 1 – Микрофотографии равновесных твёрдых фаз системы $K_2SO_4$–$K_2CO_3$–$KHCO_3$-$H_2O$ при 0 °С (увеличение 260 раз)

На рисунке 2 приведена «общая» (а) и «солевая» (б) части диаграммы растворимости системы $K_2SO_4$–$K_2CO_3$–$KHCO_3$-$H_2O$ при 0 °С, где отражено взаимное расположение и относительных размеров полей кристаллизации соответствующих равновесных твёрдых фаз. Как следует из рисунка 2, при 0 °С в исследуемой четырёхкомпонентной системе поле кристаллизации арканита ($K_2SO_4$) занимает её значительную часть, что характеризует малую растворимость этой соли в приведённых условиях.

Описание содержания геометрических образов рисунка 2 (поля, кривые, точки) приведены в таблице 2.

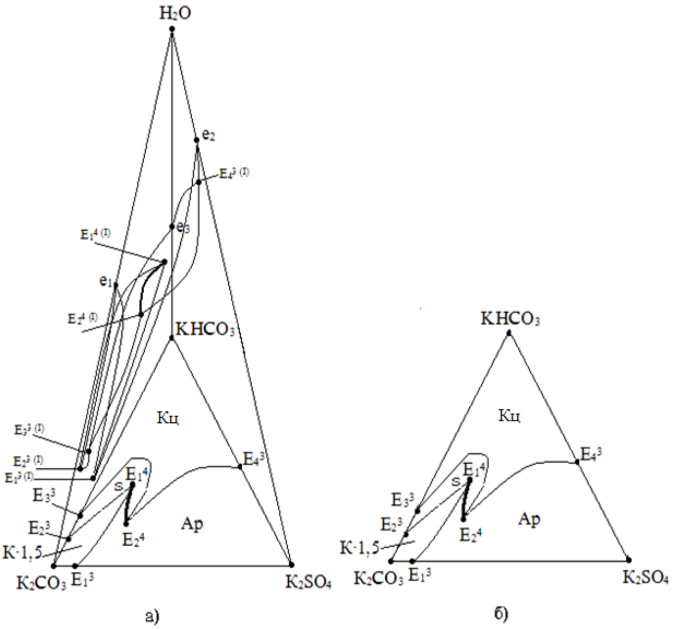


Рисунок 2 – Диаграмма растворимости системы $K_2SO_4$–$K_2CO_3$–$KHCO_3$-$H_2O$ при 0 °С:
а) общая; б) солевая часть

Таблица 2 – Описание содержания геометрических образов (поля, кривые, точки) на рисунке 2

| Обозначения геометрических образов | Расшифровка обозначений |
|---|---|
| 1 | 2 |
| $e_1$ | Растворимость карбоната калия в воде |
| $e_2$ | Растворимость сульфата калия в воде |
| $e_3$ | Растворимость гидрокарбоната калия в воде |
| $E_1^3$ | Точка совместной кристаллизации K·1.5+Ар в системе $K_2CO_3$-$K_2SO_4$-$H_2O$ |
| $E_2^3$ | Точка совместной кристаллизации K1.5+S в системе $K_2CO_3$-$KHCO_3$-$H_2O$ |
| $E_3^3$ | Точка совместной кристаллизации Кц+S в системе $K_2CO_3$-$KHCO_3$-$H_2O$ |
| $E_4^3$ | Точка совместной кристаллизации Кц + Ар в системе $K_2SO_4$-$KHCO_3$-$H_2O$ |
| $E_1^4$ | Точка совместной кристаллизации K1.5+S+Ар<br>в системе $K_2SO_4$-$K_2CO_3$-$KHCO_3$-$H_2O$ |
| $E_2^4$ | Точка совместной кристаллизации Кц+S+Ар<br>в системе $K_2SO_4$-$K_2CO_3$-$KHCO_3$-$H_2O$ |
| $e_1$-$E_1^3$ | Кривая кристаллизации K·1.5 в системе $K_2CO_3$-$K_2SO_4$-$H_2O$ |
| $e_1$-$E_2^3$ | Кривая кристаллизации K·1.5 в системе $K_2CO_3$-$KHCO_3$-$H_2O$ |
| $e_2$-$E_1^3$ | Кривая кристаллизации Ар в системе $K_2CO_3$-$K_2SO_4$-$H_2O$ |

*Окончание таблицы 2*

| 1 | 2 |
|---|---|
| $e_2$-$E_4^3$ | Кривая кристаллизации Ар в системе $K_2SO_4$-$KHCO_3$-$H_2O$ |
| $e_3$-$E_3^3$ | Кривая кристаллизации Кц в системе $KHCO_3$-$K_2CO_3$-$H_2O$ |
| $e_3$-$E_4^3$ | Кривая кристаллизации Кц в системе $KHCO_3$-$K_2SO_4$-$H_2O$ |
| $E_2^3$-$E_3^3$ | Кривая кристаллизации S в системе $K_2CO_3$-$KHCO_3$-$H_2O$ |
| $E_1^3$ - $E_1^4$ | Кривая совместной кристаллизации К·1.5+Ар в системе $K_2CO_3$-$K_2SO_4$-$H_2O$ |
| $E_2^3$ - $E_1^4$ | Кривая совместной кристаллизации К·1.5+S в системе $K_2CO_3$-$KHCO_3$-$H_2O$ |
| $E_3^3$ - $E_2^4$ | Кривая совместной кристаллизации Кц+S в системе $K_2CO_3$-$KHCO_3$-$H_2O$ |
| $E_4^3$ - $E_2^4$ | Кривая совместной кристаллизации Кц+Ар в системе $KHCO_3$-$K_2SO_4$-$H_2O$ |
| $E_1^4$ - $E_2^4$ | Кривая совместной кристаллизации S+Ар в системе $K_2CO_3$-$K_2SO_4$-$KHCO_3$-$H_2O$ |
| $e_1E_1^3E_1^4E_2^3e_1$ | Поле кристаллизации К·1.5 в системе $K_2SO_4$-$K_2CO_3$-$KHCO_3$-$H_2O$ |
| $e_2E_1^3E_1^4E_2^4E_4^3e_2$ | Поле кристаллизации Ар в системе $K_2SO_4$-$K_2CO_3$-$KHCO_3$-$H_2O$ |
| $e_3E_3^3E_2^4E_4^3e_3$ | Поле кристаллизации Кц в системе $K_2SO_4$-$K_2CO_3$-$KHCO_3$-$H_2O$ |
| $E_2^3E_3^3E_2^4E_1^4E_2^3$ | Поле кристаллизации S в системе $K_2SO_4$-$K_2CO_3$-$KHCO_3$-$H_2O$ |

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## Резюме

*Л. Солиев, Б. М. Ибрагимова, М. Т. Жұмаев*

### $K_2SO_4$-$K_2CO_3$-$KHCO_3$-$H_2O$ 0 °С ЖҮЙЕСІНДЕГІ ЕРІГІШТІК

$K_2SO_4$-$K_2CO_3$-$KHCO_3$-$H_2O$ жүйесінің 0 $^0$С ерігіштігі қарастырылды. Изотермиялық жағдайда ерігіштік диаграммасы келтірілді.

**Түйін сөздер:** ерігіштік, тепе-теңдік, сұйық фаза, қатты фаза, химиялық талдау, кристалды оптикалық талдау, диаграмма, геометриялық бейнелер.

## Summary

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### SOLUBILITY IN THE SYSTEM $K_2SO_4$-$K_2CO_3$-$KHCO_3$-$H_2O$
### AT 0 °C TEMPERATURE

In manuscript the investigation of solubility at invariant points in the system $K_2SO_4$-$K_2CO_3$-$KHCO_3$-$H_2O$ at $0^0$C is presented. The solubility diagram of the system is modeled according to the evidences obtained.

**Key words:** solubility, equilibruim, liquid phase, solid phase, chemical analysis, cristallooptical analysis, diagram, geometrical images.

УДК 546.267; 661.888; 546.73

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# ИССЛЕДОВАНИЕ ВЗАИМОДЕЙСТВИЯ В ГЕКСАЦИАНОФЕРРАТ (III)– ВАНАДИЛ–НИКЕЛЬ(II) СОДЕРЖАЩИХ СИСТЕМАХ

## Сообщение 1. Исследование систем $K_3[Fe(CN)_6]$ – $VOSO_4·3H_2O/NiSO_4·7H_2O$ – $H_2O$

**Аннотация.** С помощью метода pH метрического титрования исследован процесс эквимолекулярного взаимодействия в системе $K_3[Fe(CN)_6]$ – $VOSO_4·3H_2O/NiSO_4·7H_2O$ – $H_2O$. Установлено, что в гексацианоферрат (III) ион-ванадилсодержащей системе кривые титрования раствором гидрокисида натрия носят сложный характер и характеризуются наличием трех четко выраженных буферных зон ($0<pH<2.75$; $2.75<pH<6.75$; $6.75<pH<8$) и одной слабо выраженной буферной зоной в области pH от 8.9 до 10.6. В кислой среде протекает процесс комплексообразования, сопровождающийся понижением pH среды, которому соответствует первый скачок на кривой титрования в интервале pH 3.3-5.0. При дальнейшем повышении pH среды от 6.3 до 10 создаются условия протекания окислительно-восстановительных процессов с образованием ванадат (5+) и гексацианоферрат (II) ионов, а также гидроксида ванадия $V(OH)_2$. Кривая титрования в двойной системе $K_3[Fe(CN)_6]$ – $NiSO_4·7H_2O$ – $H_2O$ имеет одну буферную область в щелочной среде (pH 8). В кислой среде протекает процесс комплексообразования с образованием ферроцианида никеля. По мере накопления в системе $OH^-$ ионов с постоянным значением pH 8 раствор приобретает зеленоватый оттенок и мутнеет, что свидетедьствует об образовании в системе гидроксида никеля.

**Ключевые слова:** гексацианоферрат (III) калия, титрование, сульфат ванадила, сульфат никеля (II), комплексообразование, pH среды.

**Введение.** В связи с интенсивным развитием нефтедобывающей и нефтеперерабатывающих отраслей в процессе производства образуется значительное количество нефтеотходов. Среди них высокая доля приходится на нефтешламы, которые, в большинстве случаев, складируются либо подвергаются захоронению и оказывают негативное воздействие на биосферу [1]. В то же время, такие отходы содержат ценные компоненты, такие как ванадий и никель, которые востребованы в промышленности Казахстана.

Общеизвестно, что к нефтешламам относятся отходы, образующиеся при очистке нефти, замазученные грунты и донные отложения водоемов, образующиеся при разливе нефти, и т.д. При этом, они являются промышленными отходами 3-го класса опасности, так как содержат тяжелые металлы, такие как железо, кобальт, ванадий и никель, которые относятся к востребованным металлам в экономике.

Прямое извлечение из нефтешламов ванадия и никеля затруднительно и требует предварительной обработки. Например, прокаливание при 650-950$^o$C с последующим разложением полученного спека в минеральной кислоте либо выщелачивание растворами слабых кислот или аммиачно-карбонатным раствором и дальнейшим выделением из полученных растворов ванадия и никеля [2].

Существуют различные способы извлечения ванадия из ванадийсодержащих растворов. Выделение ванадия осуществляется гидролитическим осаждением путем смешивания слабощелочных и кислых растворов до pH 1,6-1,9 и их нагрева до температуры 90-95$^o$C. Выпавший осадок поливанадат натрия, марганца, железа, отфильтровывается и подвергается сушке и плавке, а маточный раствор направляется на химическую очистку от соединений ванадия и других элементов [3]. Недостатками рассмотренных способов является образование большого количества сульфатсодержащих сливных вод, с которыми теряется ванадий, а также образование маточного раствора.

Экстракционный метод с использованием органических реагентов (расплав смеси ПАН (1-(2-пиридилазо)-2-нафтола), пальматиновой кислотой) [4,5]. К недостаткам этих методов относится высокая температура, многостадийность процесса подготовки раствора к извлечению ванадия, повышенная температура (80-90$^o$C) и высокие энерго- и трудозатраты, обусловливающие низкую экономическую эффективность процесса.

В работе [5] показано, что повышение эффективности извлечения ванадия из нефти и нефтепродуктов достигается за счет использования отечественных высокомолекулярных соединений редокс–(со)полимеров с окислительно-восстановительными свойствами. Недостатком данного способа является повышенная температура процесс (60-68$^o$C), строгое соблюдение pH среды (2-3) и недостаточно высокое извлечение ванадия (93,7 %).

В настоящее время развивается сорбционный метод утилизации отработанных нефтепродуктов. Для извлечения ванадия из растворов предложены сильноосновные аниониты, хелатообразующие ионообменные смолы, активные угли и неорганические адсорбенты, а также волокнистые аниониты на основе целлюлозы и др. [6]. В работе [7] предлагаются инновационный способ извлечения попутно-добываемого ванадия из нефти и нефтепродуктов, основанный на сорбционных процессах с использованием полимеров, а также мембранной технологии.

Однако, авторы [8] считают, что среди множества применяемых сорбентов, неорганических и органических (природных и синтезируемых), наиболее перспективными для выделения ванадия являются те вещества, которые содержат элементы с близким к ванадию химическим строением.

В работе [9] показана применимость волокнистого катионита ФИБАН К-1 и аминокарбоксильного ионита ФИБАН АК-22, а также гранулированных сорбентов – макропористых слабоосновных анионитов CYBBER и наноструктурированных анионитов Россион для извлечения ванадия (V) из сернокислых хлоридных растворов. Однако все указанные сорбенты относятся к дорогостоящим и производимым в РФ. Кроме того, после отработки необходима утилизация сорбента.

Известно, что в технологических растворах сернокислотного выщелачивании термообработанных нефтешламов ванадий присутствует в виде катиона ванадила $V0^{2+}$, который характеризуется склонностью ко всевозможным реакциям комплексообразования [10].

Следует отметить, что сведения о сорбционном извлечении ванадия из высокоминерализованных растворов, влиянии типа ионитов и характера функциональных групп на сорбцию и десорбцию ионов ванадия, обоснования влияния pH, температуры и других параметров на селективность сорбционного процесса крайне ограничены и порой противоречивы. В связи с этим необходимо развивать новые методы обезвреживания и переработки нефтесодержащих отходов. На наш взгляд, перспективным методом является процесс комплексообразования.

Цель исследования – установить влияние pH среды методом титрования раствором гидроксида натрия на процесс взаимодействия в двойных «$K_3[Fe(CN)_6]$–$VOSO_4{\cdot}3H_2O$/ $NiSO_4{\cdot}7H_2O$–$H_2O$» системах.

## ЭКСПЕРИМЕНТАЛЬНАЯ ЧАСТЬ

Наиболее распространенными методами исследования процесса комплексообразования в растворе является спектрофотометрический и pH метрический методы, которые взаимно дополняют друг друга. Так применение спектрофотометрического метода позволяет установить, что в исследуемой системе протекает процесс комплексообразования, конкретизировать состав и строение образующихся в растворе комплексов. Метод pH метрии показывает устойчивость образующихся комплексов в зависимости от pH растворов.

Используемые для исследования растворы имеют нейтральную среду или кислую. Так, в воде гексацианоферрат (II) железа диссоциирует:

$$K_3[Fe(CN)_6] \longleftrightarrow 3K^{+} + [Fe(CN)_6]^{3-} \quad (1)$$

При этом раствор имеет нейтральную среду с pH 6.7.

Сульфат никеля $NiSO_4{\cdot}7H_2O$ гидролизуется по катиону, поэтому в растворе присутствуют катионы водорода $H^{+}$. Кроме того, по классификации Пирсона ион $Ni^{2+}$ принадлежит кислотам, занимающим промежуточное положение между жесткими и мягкими кислотами [15]. Соответственно в системе «$K_3[Fe(CN)_6]$–$NiSO_4{\cdot}7H_2O$–$H_2O$» образуется слабокислая среда (pH 5.03).

Поскольку вышеприведенные системы имеют кислую среду, то титрование эквимолекулярных смесей данных систем проводили раствором гидроксида натрия концентрацией 0,01, 0,1 и 0,2 моль/л.

Для приготовления растворов сульфата ванадила $VOSO_4{\cdot}3H_2O$, сульфата никеля $NiSO_4{\cdot}7H_2O$, гексацианоферрата (III) (ферроцианида) калия $K_3[Fe(CN)_6]$ использовали реактивы марки х.ч. Для исследования использовали эквимолекулярные смеси из растворов $K_3[Fe(CN)_6]$ и $SO_4{\cdot}3H_2O$ с концентрацией $2{\cdot}10^{-3}$ моль/л, а также $NiSO_4{\cdot}7H_2O$ с концентрацией $2{\cdot}10^{-3}$ моль/л.

Титрование аликвоты эквимолекулярных смесей проводили при комнатной температуре. Величину водородного показателя (pH) измеряли на универсальном pH-метре марки 150 МИ. В качестве индикаторного электрода использовали стеклянный электрод ЭЛС 6307. Электродом сравнения служил насыщенный хлорсеребряный электрод ЭВЛ-1М3.

## РЕЗУЛЬТАТЫ И ИХ ОБСУЖДЕНИЕ

В кислой среде ванадий присутствует в виде катионов $VO^{2+}$ и $VO^{3+}$, для которых характерен гидролиз с образованием аквакомплексов $[VO(H_2O)_5]^{2+}$, $[VO(H_2O)_4]^{2+}$ [11].

Известно, что соль ванадила взаимодействует с ферроцианидами (гексцианоферратами (II)) щелочных металлов с образованием комплексных соединений [12]. Наиболее изучен процесс комплексообразования в системах, содержащих соль ванадила и гексацианоферраты (II) натрия и калия «$VOSO_4$ – $Na_4[Fe(CN)_6]$/ $K_4[Fe(CN)_6]$». В системе «$VOSO_4$–$Na_4[Fe(CN)_6]$» при соотношении ФЦ/соль V (n), равном 0,5, образуется ферроцианид ванадила $(VO)_2[Fe(CN)_6{\cdot}xH_2O$:

$$2VOSO_4 + K_4[Fe(CN)_6] = (VO)_2[Fe(CN)_6 \cdot xH_2O + 2K_2SO_4 . \qquad (2)$$

При других соотношениях компонентов происходит образование фаз переменного состава. Причем в условиях избытка $Na_4[Fe(CN)_6]$ ($0{,}5<n<1{,}0$) образуются твердые фазы переменного состава $x(VO)_2[Fe(CN)_6] \cdot yNa_4[Fe(CN)_6]$, которые с повышением соотношения n пептизируются, а затем коагулируются и желтеют.

В системе «$VOSO_4$ – $K_4[Fe(CN)_6]$» выделено только смешанное комплексное соединение $K_2(VO)_3[Fe(CN)_6]_2 \cdot xH_2O$ (ферроцианид ванадила – калия):

$$VOSO_4 + K_4[Fe(CN)_6] = K_2(VO)_3[Fe(CN)_6]_2 + K_2SO_4 \qquad (3)$$

Интересно то, что ванадий в степенях окисления (V) и (IV) и железо в степени окисления (II) и (III) представляют собой весьма сложную окислительно-восстановительную систему. В кислой среде ионы Fe (II) восстанавливают V(V) до V(IV), а в щелочной, наоборот, ионы Fe (III) окисляют V(IV) до V(V) [13]. Причем получение осадков возможно при различных их соотношениях. Так, в работе [12] показано, что в кислой системе, содержащей V(V) и гексацианоферрат (II) анион $[Fe(CN)_6]^{4-}$, протекает окислительно-восстановительная реакция:

$$VO_3^- + [Fe(CN)_6]^{4-} + 8H^+ \rightarrow VO_2[Fe(CN)_6] + 2\,[Fe(CN)_6]^{3-} + 4H_2O, \qquad (4)$$

в которой V(+5) выступает в качестве окислителя и восстанавливается железом ($Fe^{+2}$) ферроцианидного аниона до более низкой валентности ($V^{+4}$). При этом Fe (II) окисляется до Fe (III) и происходит перестройка $[Fe(CN)_6]^{4-}$ аниона с образованием гексацианоферрат (III) аниона $[Fe(CN)_6]^{3-}$. Следует отметить, что гексацианоферрат (III) калия $K_3[Fe(CN)_6]$ очень сильный окислитель, особенно в щелочной среде.

Ионы двухвалентного никель Ni(II) относятся к группе комплексообразователей, имеющих не полностью заполненные d-орбитали. Такие катионы способны образовывать комплексы с кислород- и азотсодержащими лигандами и с лигандами, содержащими серу, фосфор и атомы других элементов [14]. В работе [12] показано, что соли никеля взаимодействуют с ферроцианидами щелочных металлов. В ранее изученной системе «$NiSO_4$–$K_4[Fe(CN)_6]$» выделен ферроцианид никеля $Ni_2[Fe(CN)_6]\cdot xH_2O$ в условиях значительного избытка $Ni^{2+}$. С ростом соотношения ФЦ/соль Ni образуется комплекс состава $K_2Ni_3[Fe(CN)_6]_2\cdot xH_2O$, что указывает на увеличение в осадке содержания $K_4[Fe(CN)_6]$. При соотношении ФЦ/соль Ni (n) равном 0,75 образуется соединение $K_4Ni_4[Fe(CN)_6]_3\cdot xH_2O$. После окончания процесса образования данной соли в жидкой фазе системы фиксируется избыточное содержание ионов $[Fe(CN)_6]^{4-}$, которые пептизируют выпавший осадок. Из полученных результатов следует, что ферроцианид никеля $Ni_2[Fe(CN)_6]\cdot xH_2O$ способен поглощать ферроцианид калия $K_4[Fe(CN)_6]$ с образованием смешанных солей. Кроме вышеприведенной смешанной соли могут образоваться $K_6Ni_5[Fe(CN)_6]_4\cdot xH_2O$ (n = 0,80), $K_{12}Ni_8[Fe(CN)_6]_7\cdot xH_2O$ (n = 0,87) и $K_2Ni[Fe(CN)_6]\cdot xH_2O$ (n = 1,0). Что же касается взаимодействия гексацианоферратов (III) калия $K_3Fe(CN)_6]$ с солями ванадила ($V^{4+}$) и никеля(II), то данные системы практически не исследованы. В то же время на основании вышепроведенного литературного анализа можно ожидать, что в двухкомпонентных системах «$K_3[Fe(CN)_6]$ – $VOSO_4\cdot 3H_2O/NiSO_4\cdot 7H_2O$ – $H_2O$», в которых участвуют катионы ванадила $VO^{2+}$, $Ni^{2+}$ и ионы железа (II, III), находящиеся во внешней и внутренней сферах ферроцианидного комплекса, процессы протекают с образованием разнообразных соединений.

Высокий заряд иона ванадия $V^{4+}$ и его малый радиус (0,61 Å) делает невозможным его присутствие в водных растворах, поэтому соединения ванадия (IV) в растворах представляют собой оксосоли. В кислых водных растворах солей ванадия (IV) присутствует единственный тип катионов – ионы оксованадия (IV), или ванадила $VO^{2+}$, как правило, в виде аквакомплексов $[VO(H_2O)_5]^{2+}$, $[VO(H_2O)_4]^{2+}$. Именно они придают этим растворам ярко-синий цвет, напоминающий окраску медного купороса. В ионе ванадила присутствует двойная связь V=O (0,155 – 0,168 нм), которая значительно короче одинарной (~0,23 нм). В кристаллогидратах солей ванадила, как правило, присутствуют изолированные ионы ванадила, имеющие форму октаэдра с одной укороченной связью V=O или квадратной пирамиды за счет координации воды или аниона. Такое строение характерно для трехводного сульфата ванадия $VOSO_4 \cdot 3H_2O$. Экспериментально установлено, что водный раствор $VOSO_4 \cdot 3H_2O$ имеет кислую реакцию – свидетельство протекающего гидролиза. По-видимому, именно этим объясняется кислая среда используемых в работе эквимолекулярных смесей растворов $K_3[Fe(CN)_6]$ с $VOSO_4 \cdot 3H_2O$ (pH 3.1).

На рисунке 1 приведены кривые титрования эквимолекулярных растворов в системе $K_3[Fe(CN)_6]$ – $VOSO_4 \cdot 3H_2O$–$H_2O$ с общей концентрацией $4 \cdot 10^{-3}$ моль/л. Откуда видно, что при титровании независимо от концентрации гидроксида натрия кривые титрования носят идентичный характер.

На кривой тирования наблюдаются два скачка. Первый в интервале pH 3.3-5.0, а второй при pH от 6.3 до 8.1. Первый участок на кривой характерен для титрования сильных кислот сильными основаниями и, по-видимому, он отвечает связыванию $OH^-$ ионами выделяющихся в процессе реакции ионов водорода. При этом, возможно, образуется комплексное соединение типа $(VO)K[Fe(CN)_6]$ или $(VO)_3 [Fe(CN)_6]$:

$$VOSO_4 + K_3[Fe(CN)_6] = (VO)K[Fe(CN)_6] + K_2SO_4 \quad (5)$$

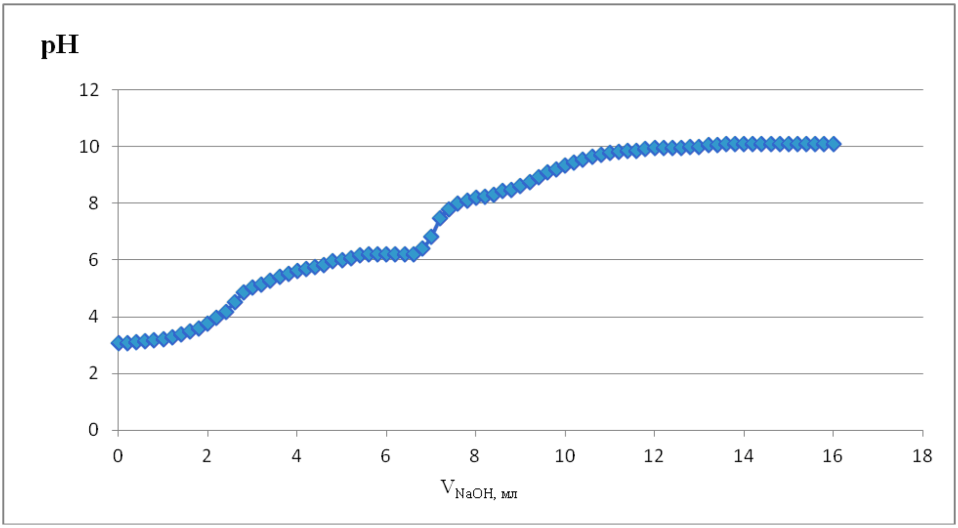
$$2VOSO_4 + 2K_3[Fe(CN)_6] = 2(VO)_3[Fe(CN)_6] + 3K_2SO_4 \quad (6)$$

При дальнейшем добавлении щелочи (pH>3.5) значения pH в системе понижается, т.е. щелочность среды возрастает. Это может быть следствием появления в образующихся продуктах $OH^-$ группы либо за счет ее внедрения в структуру, либо вследствие разрушения комплекса и образования нового соединения (комплекса), сопровождающееся выделением гидроксида ванадила или, как ее называют гипованадиевая кислота ($VO(OH)_2$, $H_2VO_3$) [14, 16]. Можно предположить, что образующееся комплексное соединение неустойчиво и в интервале pH 4.5-5.7 разлагается с выделением $OH^-$ в раствор, что сопровождается увеличением pH >7,8. Так как гидроксид ванадия (IV) обладает амфотерными свойствами, т. е. растворяется и в кислотах и в основаниях, то при увеличении расхода гидроксида натрия не исключено, что происходит его растворение в щелочи [14]. При этом образуется смесь комплексного соединения с ванадатами (IV) различного состава, например ванадатов с ионами $V_4O_9{}^{2-}$ или $V_3O_7{}^{2-}$:

$$4VO(OH)_2 + 2NaOH = Na_2[V_4O_9] + 5H_2O \quad (7)$$

$$3VO(OH)_2 + 2NaOH = Na_2V_3O_7 + 4H_2O \quad (8)$$

Наличие на кривой титрования мало выраженного скачка при pH 8,4 указывает на возможность протекания данного процесса с образованием соединений переменного состава.



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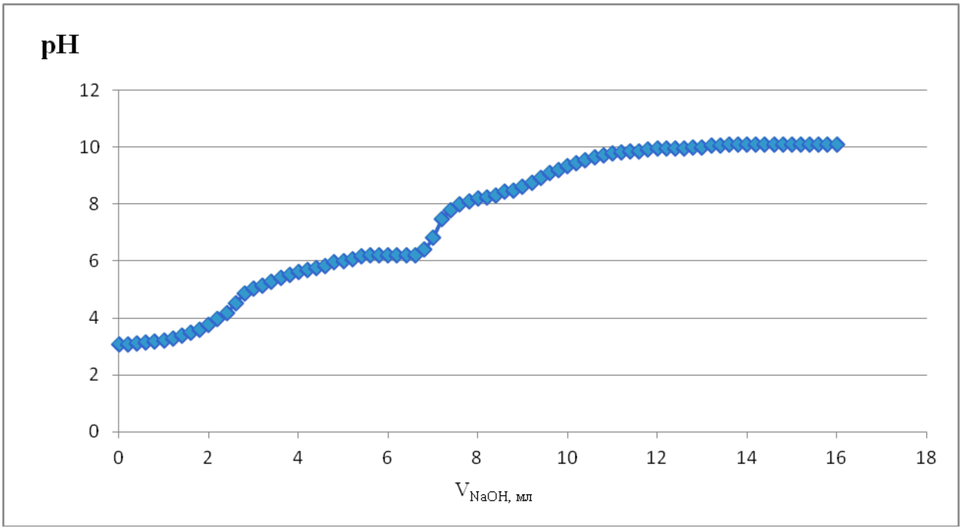


б

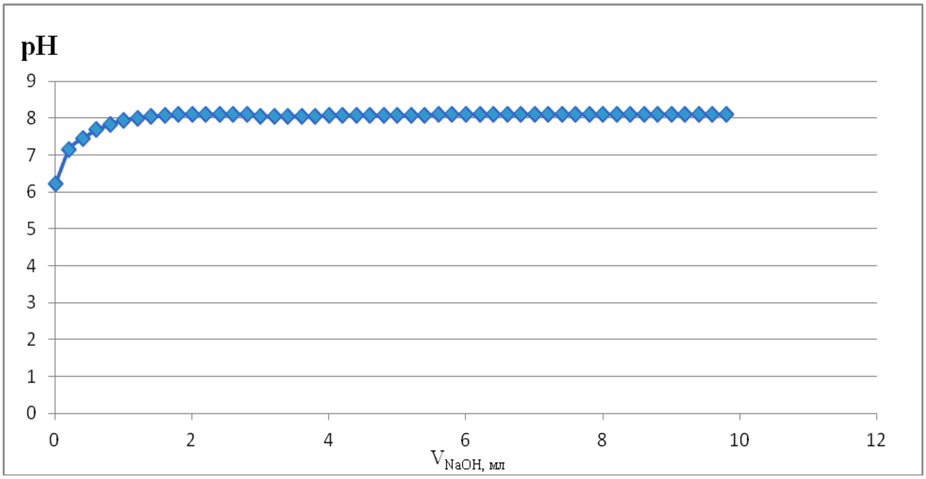
**С** $_{K3[Fe(CN)6]}$ = С $_{VOSO4·3H2O}$ = $2·10^{-3}$ моль/л

Концентрация NaOH: а – 0,01; б – 0,2 моль/л

Рисунок – 1 Кривые титрования эквимолекулярных растворов в системе $K_3[Fe(CN)_6]$ – $VOSO_4·3H_2O$ – $H_2O$

Следует отметить, что одновременное присутствие ванадия в степени окисления (IV) и (V) и железа в степени окисления (II) и (III) представляет собой весьма сложную окислительно-восстановительную систему. В связи с выше изложенным и согласно данным [17] возможно, что в щелочной среде, содержащей гексацианоферрат (III) и ванадил-ионы $VO^{2+}$, протекает процесс окисления ванадила ионами $[Fe(CN)_6]^{3-}$ до ванадата:

$$VO^{2+} + [Fe(CN)_6]^{3-} + 4OH^- = VO_3^- + [Fe(CN)_6]^{4-} + 2H_2O, \quad (9)$$



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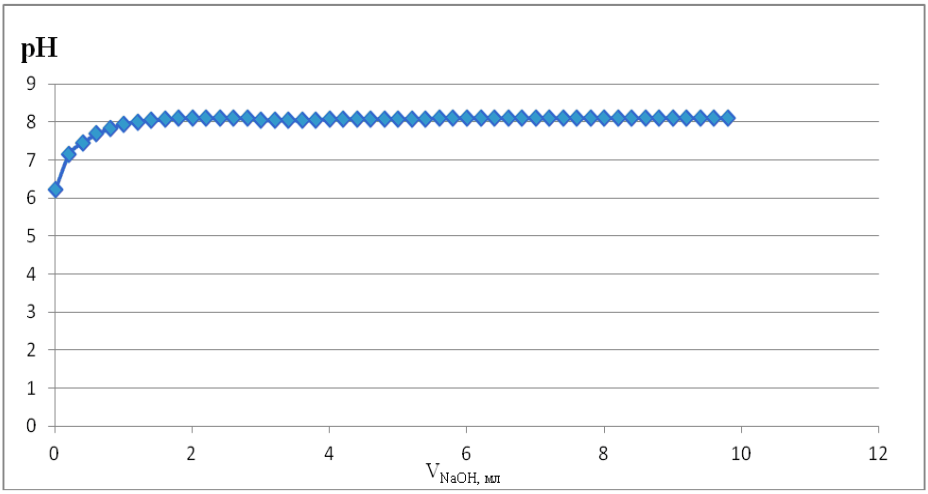

б

**C** $_{K3[Fe(CN)6]}$ = 2·10$^{-3}$ моль/л ; C $_{NiSO4·7H2O}$ = 2·10$^{-2}$ моль/л

Концентрация NaOH: а – 0,01, б – 0,2 моль/л

Рисунок 2 – Кривые титрования эквимолекулярных растворов в системе $K_3[Fe(CN)_6] – NiSO_4·7H_2O – H_2O$

Судя по характеру кривых титрования, в системе $K_3[Fe(CN)_6]$ – $VOSO_4{\cdot}3H_2O$ – $H_2O$ протекают сложные процессы с образованием продуктов, состав которых в значительной мере зависит от рН среды.

На рисунке 2 представлены кривые титрования эквимолекулярных растворов в системе $K_3[Fe(CN)_6]$ – $NiSO_4{\cdot}7H_2O$ – $H_2O$ с общей концентрацией $4{\cdot}10^{-5}$ моль/л. Из полученных результатов следует, что кривые титрования независимо от концентрации гидроксида натрия, имеют аналогичный характер. На кривой тирования проявляется одна буферная область в щелочной среде.

Судя по характеру кривых, в данной системе наряду с комплексообразованием протекает процесс образования гидроксида никеля (II). Об этом свидетельствует наличие горизонтального участка на кривой титрования при рН 8. Раствор при данном рН помутнел, а выделенный осадок имел зеленоватый цвет.

Исходя из литературных данных и полученных результатов следует, что в в кислой среде, эквимолекулярной системе $K_3[Fe(CN)_6]$ – $NiSO_4{\cdot}7H_2O$ - $H_2O$, образуется комплексное соединение, возможно гексацианоферрат (III) никеля:

$$2K_3[Fe(CN)_6]+3NiSO_4=Ni_3[Fe(CN)_6]_2+3K_2SO_4\,. \qquad (10)$$

В щелочной среде (рН 8) кривая носит горизонтальный характер, что подтверждает образование гидроксида никеля. Данный процесс отражается резким скачком на кривой титрования. Процесс протекает по реакции:

$$NiSO_4+ 2NaOH = Ni(OH)_2\downarrow + Na_2SO_4\,. \qquad (11)$$

Таким образом, методом рН-метрии установлено, что в двойных эквимолекулярных системах $K_3[Fe(CN)_6]$ – $VOSO_4{\cdot}3H_2O/NiSO_4{\cdot}7_2O$ – $H_2O$ протекает процесс взаимодействия. Показано влияние рН среды на возможность протекания в системе $K_3[Fe(CN)_6]$ – $VOSO_4{\cdot}3H_2O$– $H_2O$ окислительно-восстановительных процессов с образованием ванадатов (V) и гексациаоноферрат (II) – ионов. Выявлено, что в двойной системе $K_3[Fe(CN)_6]$ – $VOSO_4{\cdot}3H_2O$/ $NiSO_4{\cdot}7_2O$ – $H_2O$ в щелочной области образуется гидроксид никеля $Ni(OH)_2$.

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## Резюме

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# ГЕКСАЦИАНОФЕРРАТ (III), ВАНАДИЛ– ЖӘНЕ НИКЕЛЬ (II) ҚОСЫЛЫСТАРЫ БАР ЖҮЙЕЛЕРДІҢ ӨЗАРА ӘРЕКЕТТЕСУІ

## 1-хабарлама. $K_3[Fe(CN)_6]$ – $VOSO_4 \cdot 3H_2O/NiSO_4 \cdot 7H_2O$ – $H_2O$ жүйесін зерттеу

pH-метрикалық титрлеу әдісі арқылы іс – эквимолекулалық мөлшерде $K_3[Fe(CN)_6]–VOSO_4 \cdot 3H_2O/NiSO_4 \cdot 7H_2O–H_2O$ жүйесі зерттелді. Гексацианоферрат (III) ион-, ванадил жүйесінде қисық титрлеу ерітіндісімен натрий гидроксиді табиғатта күрделі сипатта болуымен сипатталады үш анық білінетін буферлік аймақтар (0<pH<2.75; 2.75<pH<6.75; 6.75<pH<8) және бір әлсіз айқын буферлік аймақ, облыс, pH 8.9 10.6. Қышқыл ортада өтетін процесс комплекс, төмендеуіне pH ортасын, оған сәйкес бірінші қадам " қисық титрлеу аралығында pH 3.3–5.0. Одан әрі жоғарылауы кезінде сілтілік орта аралығында 6.3–10-ға дейін pH) құрылады жүру шарттары тотығу-тотықсыздану бөлігі бар ванадат (5+) гексацианофер- рат (II) иондары, сондай-ақ ванадий гидроксиді $V(OH)_2$. Қисық титрлеу қос жүйесі $K_3[Fe(CN)_6]$ – $NiSO_4 \cdot 7H_2O$ – $H_2O$ бар бір буферлік облысы сілтілі ортада (pH-8). Қышқыл ортада өтетін процесс комплекс құрып ферроцианида никель. Қарай жинақтау жүйесінде ОЛ-иондарының бақыланған облысы тұрақты мәні pH 8 көрсетеді туралы білім жүйесінде никель гидроксиді ерітіндісі иеленеді жасылдау түске өзгереді.

## Summary

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## STUDY OF THE INTERACTION OF THE HEXACYANOFERRATE (III) ION, VANADIUM AND NICKEL(II)CONTAINING SYSTEMS

### Message 1. Study $K_3[Fe(CN)_6]$ – $VOSO_4 \cdot 3H_2O/NiSO_4 \cdot 7H_2O$ – $H_2O$ systems

The interaction process in the double equimolecular systems $K_3[Fe(CN)_6]$ – $VOSO_4 \cdot 3H_2O/NiSO_4 \cdot 7H_2O$ – $H_2O$ was studied using the pH metric titration method. It is established that in the hexacyanoferrate (III) ion, vanadijsoderzhashchih the system of curves of titration with a solution of sodium gidroksid are complex. There are three distinct buffer zones ($0<pH<2.75$; $2.75<pH<6.75$; $6.75<pH<8$) and one weakly defined buffer zone in the pH range from 8.9 to 10.6. In an acidic medium, the process of complex formation occurs, accompanied by a decrease in the pH of the medium, which corresponds to the first jump on the titration curve in the pH range 3.3-5.0. With a further increase in the alkalinity of the medium 6.3 to 10 pH, the conditions for the oxidation-reduction processes with the formation of vanadates (5+) and hexacyanoferrate (II) ions, as well as vanadium hydroxide $V(OH)_2$ are created. The titration curve in the double system $K_3[Fe (CN)_6]$ – $NiSO_4 \cdot 7H_2O$ – $H_2O$ has one buffer region in the alkaline medium (pH 8). In an acidic environment, the process of complex formation with the formation of Nickel ferrocyanide. As the ON - ions accumulate in the system, the observed region with a constant pH 8 indicates the formation of Nickel hydroxide in the system. The solution becomes greenish and becomes cloudy.

**Key words:** potassium hexacyanoferrate (III), titration, vanadyl sulfate, Nickel sulfate (II), complex formation, pH.

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# ANALYSIS OF COAL-TARRESIN FRACTION OF SHUBARKOL LOCATION

**Abstract.** In this article one of main type of raw material used for the production of sulfur-free petroleum and tetralin is considered. The physico-chemical characteristics of the coke-chemical resin produced by coal devolatilization of the Shubarkol raw and the tar fraction with boiling point up to 180, from180 up 230 and from 230 to 280°C have been examined. Three fractions of initial resin had been analyzed applying gas chromatography-mass spectrometry with boiling point up to 180, 180-230 and 230-280°C. It was pointed that the chemical composition of distillate fractions of resin consists of alkyl derivatives aromatic hydrocarbons with the number of aromatic rings of 1-4. Benzene and its methyl-, ethyl- and propyl- derivatives were identified with the boiling point up to 180°C.The composition of the fraction with boiling point up to180-230°C consists mainly of trimethyl- and ethyl derivatives of benzene, phenol and its methyl derivatives. The composition of distillates with boiling temperature up to 230-280° C includes individual aromatic compounds and their derivatives with a higher molecular weight.

**Key words**: coke-chemical resin, semi-coking, tetralin, resin fractions boiling point, naphthalene.

**Introduction.** Coke-chemical resin, consisting mainly of condensed aromatic hydrocarbons and other high-molecular compounds, also refers to hard-processed raw materials. In industry, the resin is subjected to dehydration and distillation into separate fractions, from which benzene, naphthalene, phenols, pyridine bases and other chemical products are obtained by the methods of alkaline and acid-type extraction, crystallization, hydro-treating. Each stage of chemical productsexudationcomes with use of redistillation, high heat and reagent consumption, loss of valuable products, for example, naphthalene [1-5]. Each stage of chemical products exudation comes with use of repeated distillations, a large consumption of heat and reagents, loss of valuable products, for example, naphthalene. A number of valuable chemical products, for example 2,6-dimethylnaphthalene, are currently not produced due to the low content and high cost of exudation. Currently, due to strengtheningof requirements for the quality of raw materials for organic synthesis, increased demand for benzene and naphthalene, experimental work to improve the processes of hydro-treatment of coke-chemical raw materialsare carried out [6-9].

## EXPERIMENTAL PART

The material composition of the resin fractions and the hydrogenates obtained from it were determined by gas chromatographymass spectrometry using a Chromatek-Cristal 5000 gas chromatograph with a mass-selective detector of model 5973 with ionization by electron impact (70 eV) under the following conditions: fused silica capillary column HP-5MS 25 mx 25 mm, the thickness of the phase film is 0.25 μm); injector temperature 280 °C, interface 290°C; the initial and final temperature of the thermostat is 35 and 280 °C respectively; column heating oven

at an initial temperature is1 min; the temperature of the column heating oven changed at a rate of 10°/min; carrier gas - helium; the volume of the introduced sample is 0.2 μl. Samples were introduced into a chromatograph in a 1:40 split ratio mode. The registration of the mass spectrum of the components of the raw materials and the products obtained was carried out in the regime of the total ion current. The resulting mass spectrum was compared with library mass spectrum (library NIST98, WILEY7n, PMW TOXR).

## RESULTS AND DISCUSSION

The article presents the results of a study of the chemical composition of distillate fractions with boiling point up to 180, 180-230 and 230-280°C, exudating from coal-tar resin obtained by the semi-coking of coal from the Shubarkol location. The objects of the study are the initial liquid resin of SaryArkaSpetskoks JSC, Karaganda, obtained by the semi-coking of coal from Shubarkol deposit; and distillate fractions of the resin with boiling point up to 180°C, 180-230°C and 230-280°C. The characteristics of the initial resin obtained by the semi-coking of coal from the Shubarkol location is represented in table 1.

Table 1 – Physicochemical index of coke-chemical resin

| Index | Index value |
|---|---|
| Density at 20 °C, kg/m$^3$ | 1,071 |
| Mass fraction of water, % | 3,40 |
| Mass fraction of insoluble matters in toluene, % | 1,30 |
| Mass fraction of insoluble matters in quinoline, % | 0,20 |
| Ash contents, % | 0,11 |
| Fraction composition, mass. %: | |
| Initial boiling point, °C, % | 130 |
| Boiling off up to 180 °C, % | 2,4 |
| 180-330 °C, % | 19,0 |
| upto330 °C+ losses | 78,6 |

As it shown in table 1, coal-tar resin boils off over a wide temperature range. The yield of fractions with a boiling point up to $180^0$C of the resin is 2.4 mass%, the yield of fractions with a boiling point of 180-330 °C is 19.0 mass% and above 330°C is 78.6 mass%. The composition of coal-tar resin includes: water 3.4% and the ash elements 0.11%. The elemental composition of the products is represented in table 2.

Table 2 – Elemental composition of the coke-chemical resin

| Elemental composition | mass. %: |
|---|---|
| C | 91,11 |
| H | 5,50 |
| S | 0,35 |
| N | 1,46 |
| O (by variety) | 1,58 |

The elemental composition of coal-tar resin is characterized by a higher carbon content of 91.11%, a low content of other elements: hydrogen of 5.50%; nitrogen 1.46%, sulfur 0.35%, oxygen 1.58% than is the case in petroleum products. Coal (coking) resin, consisting mainly of condensed aromatic hydrocarbons and other high-molecular compounds refers to hard-processed raw materials. The number of hydrocarbons of the coke-chemical resin is given in the table 3.

In table 3 represented basic hydrocarbons and 82 substances in the coke-chemical resin composition were detected by gas chromatography-mass spectrometry. From hydrocarbons, the resin contains nitrogen-containing compounds with spirrellic and pyridine rings, oxygen compounds (phenols, naphthols, furans), sulfur compounds (thiophenes, sulphides). In the course of the study, the chemical composition of the coke-chemical resin fractions was determined. The results of the study are given in table 4.

As can be seen from the table, indene, naphthalene and their alkyl derivatives as well as in a small amount of diphenyl, acenaphthene and dibenzfuranwere also identified in the fractions with a boiling point of 180-230 ° C. The composition of distillates with boiling pint 230-280 °C consists of individual aromatic compounds and their derivatives with a higher molecular weight. The nature of the distribution of S-, N-, O heteroatoms in the structure of aromatic structures is different. Nitrogen is found in both six-membered and five-membered rings (pyridine and pyrrole fragments), oxygen in the hydroxyl group and in the five-membered ring (furan freagment), and sulfur is only in the five-membered ring (thiophene fragment).In the fraction of the initial resin with boiling point at 280 ° -350 ° C contains: anthracene, phenanthrene, fluorene, fluoranthene, chrysene, pyrene and its isomers, benzfluoranthene, isomers of dibenzfluoranthene, high content of indeno- (1,2,3) -fluoranthene are registered.

Table 3 – Composition and concentration of coke-chemical resin

| Name of identified substances | Concentration, mass, % |
|---|---|
| Phenol | 2,373 |
| Methylphenol(cresol) | 7,69 |
| Ethylphenol | 2,673 |
| Azulene | 0,763 |
| Pyrocatechin | 6,41 |
| Methylnaphthalene | 2,091 |
| 2,3-dihydro-1H-indene-5-ol | 0,467 |
| 2,3-dihydroxytoluene | 0,257 |
| 4-ethyl-1,3-dihydroxybenzene | 6,92 |
| Tetradecane | 0,779 |
| 2-methylpentylbenzene | 0,217 |
| Pentadecane | 0,426 |
| Naphtol | 0,573 |
| Cetane | 0,482 |
| Methylnapthol | 1,205 |
| Tridecanes | 0,888 |
| 1-tetradecene | 0,300 |
| Octadecane | 0,21 |
| Hexadecane | 0,790 |
| Eicosane | 1,066 |
| Genekozan | 1,434 |
| Fluoranthene(standard) | 0,800 |
| Heptadecane | 0,896 |
| Cyclopentadecane | 0,888 |
| Saturatedhydrocarbons | 1,426 |

Table 4 – Chemical composition of distillate fractions of the initial coke-chemical resin

| Name of identified matters | Temperature, °C | Content in fractions with boiling temperature°C, mass.% | | |
|---|---|---|---|---|
| | | >180 °C | 180-250°C | 250-320°C |
| 1 | 2 | 3 | 4 | 5 |
| benzene | 80 | 9,63 | – | – |
| thiophen | 84 | 0,18 | – | – |
| toluene | 110 | 10,21 | – | – |
| m-Xylene | 139,138 | 6,24 | 0,58 | – |
| o-Xylene | 144 | 5,39 | 0,06 | – |
| propylbenzene | – | 0,41 | – | – |
| 1-ethyl-1-methylbenzene | 159 | 0,46 | 0,15 | – |

*Continuation of table 4*

| 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|
| quinoline | 236 | 0,13 | 0,54 | 2,51 |
| 3-methylpyridine | 144 | – | 1,44 | – |
| 2,4-dimethylpyridine | – | 0,60 | – | – |
| 7-methylindol | 231 | – | 0,61 | – |
| 2-methylquinoline | – | 0,13 | 0,17 | 0,17 |
| 3-methylquinoline | – | 0,11 | 0,03 | 0,25 |
| 2- methylnaphthalene | 241 | – | 4,25 | 9,71 |
| 1- methylnaphthalene | 245 | – | 1,82 | 5,77 |
| diphenyl | 255 | 0,82 | 0,92 | 4,22 |
| 2- ethylnaphthalene | 258 | 0,60 | 0,25 | 1,66 |
| 1-ethyl-3- methylbenzene | – | 1,4 | – | – |
| 1,2,3-trimethylbenzene | 176 | 0,16 | – | – |
| 1,2,4-trimethylbenzene | 169 | 2,12 | 1,40 | – |
| phenol | 182 | 4,67 | 3,35 | – |
| 1,3,5-trimethylbenzene | 165 | 2,86 | 0,27 | – |
| 1,2-diethylbenzene | – | 0,43 | – | – |
| indene | 183 | 4,5 | 9,69 | 0,76 |
| m-cresol | 202 | 1,79 | 4,31 | 1,0 |
| 2,4- dimethylphenol | – | 1,56 | 2,32 | 2,03 |
| 1-methyl-2-2propenylbenzene | – | 0,92 | 0,25 | – |
| naphthalene | 218 | – | 41,49 | – |
| 2(4)-ethylindyne | – | 0,19 | 0,28 | – |
| dimethylindyne | – | 0,13 | – | – |
| thymol | 233 | 0,03 | 0,08 | – |
| 2,3-dimethylpyridine | – | – | – | 0,29 |
| isochinoline | 243 | 0,46 | 0,81 | 3,29 |
| thiobenzene | 185 | – | 0,21 | – |
| o-cresol | 191 | 1,77 | – | – |
| 1-ethyl-2,4-dimethylbenzene | – | 1,14 | – | – |
| p-cresol | 202 | – | 1,02 | – |
| 1-methyl-inden | – | 1,53 | 1,45 | 0,30 |
| 4-methyl-inden | – | – | 0,9 | – |
| 3-ethyl-5methylphenol | – | – | 0,20 | 0,38 |
| 2,5-dimethyl phenol | – | 0,30 | 0,35 | – |
| o-ethylphenol | – | 0,44 | 0,73 | – |
| 1-ethylnaphthalene | 259 | 0,56 | 0,23 | 1,30 |
| 2,7-dimethyl-naphthalene | 262 | 0,29 | 0,27 | 2,25 |

**Conclusion.** Thus, the use of the method of group chemical analysis made it possible to separate a complex, multicomponent mixture of hydrocarbons and heteroatomic resin components into fractions of individual compounds with similar chemical properties. The obtained data on the composition of group fractions confirm the necessity of using coal tar coke as a raw material source for obtaining valuable aromatic hydrocarbons, their mixtures and commercial products based on them. At the same time, to improve their quality, as well as to increase the yield of the most valuable components, it is advisable to use, if possible, selective methods for pretreatment of the original resin, which not only allow to preserve the unique technological properties of the resin, but also to achieve a significant decrease in its toxic level and carcinogenicity.

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## Резюме

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## ШҰБАРКӨЛ КЕН ОРЫНЫНЫҢ ТАС КӨМІР ШАЙЫРЫ ФРАКЦИЯСЫНЫҢ ТОПТЫҚ ҚҰРАМЫН АНАЛИЗДЕУ

Күкіртсіздендірілген нафталин және тетралин алу өндірісінде қолданылатын негізгі шикізат түрі қарастырылды. Шұбаркөл кен орыны көмірін жартылай кокстеуден алынған коксохимиялық шайырдың және қайнау температурасы 180, 180-230, 230-280°С шайыр фракцияларының физика-химиялық сипаттамалары зерттелінді. Хроматомасс-спектроскопия әдісі арқылы қайнау температурасы 180, 180-230, 230-280°С бастапқы шайыр фракциялары анализделінді. Зерттеу нәтижесі бойынша шайырдың дистилляттық фракцияларының химиялық құрамы ароматтық сақина саны 1-4 тең ароматты көмірсутектердің алкилтуындыларынан тұратындығы көрсетілді. Химиялық құрамы жайлы алынған мәліметтер коксохимиялық таскөмір шайырынан құнды ароматтық көмірсутектер, олардың қоспаларын және осы көмірсутектер негізіндегі тауарлы өнімдер алуға болатындығы көрсетті. Қайнау температурасы 180°С дейінгі дистилляттық фракция құрамында бензол және оның метил-, этил- және пропил туындылары анықталды. Қайнау температурасы 180-230°С фракция құрамында да осы қосылыстардың іздері байқалды. Бұл фракцияның химиялық құрамы негізінен бензолдың үшметил- және этилтуындыларынан, фенол және оның метилтуындыларынан құралған.

**Түйін сөздер:** коксохимиялық шайыр, жартылай кокстеу, тетралин,қайнау температурасы, шайыр фракциялары, нафталин.

## Резюме

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## АНАЛИЗ ГРУППОВОГО СОСТАВА ФРАКЦИЙ КАМЕННОУГОЛЬНОЙ СМОЛЫ ШУБАРКОЛЬСКОГО МЕСТОРОЖДЕНИЯ

Рассмотрен основной вид сырья, применяемый для производства бессернистого нафталина и тетралина. Исследованы физико-химические характеристики коксохимической смолы, полученной путем полукоксования каменного угля Шубаркольского месторождения и фракции смолы с т. кип. до 180, 180-230 и 230-280°С. Методом хроматомасс-спектроскопии проанализированы три фракции исходной смолы с т.кип.: до 180, 180-230 и 230-280°С. Показано, что химический состав дистиллятных фракций смолы состоит из алкилпроизводных ароматических углеводородов с числом ароматических колец 1-4. Полученные данные о составе групповых фракций подтверждают необходимость использования каменноугольной коксохимической смолы в качестве сырьевого источника получения ценных ароматических углеводородов, их смесей и товарных продуктов на их основе. В составе дистиллятов с т.кип. до 180°С идентифицированы бензол и его метил-, этил- и пропилпроизводные. В составе фракции с т.кип.180-230°С обнаружены следы этих соединений. Эта фракция по своему химическому составу состоит в основном из триметил- и этилпроизводных бензола, фенола и его метилпроизводных.

**Ключевые слова:** коксохимическая смола, полукоксование, тетралин,фракции смолы с т. кип. до 180, 180-230 и 230-280°С, нафталин.

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# POTENTIAL OF PRODUCTION OF BIODEGRADABLE SURFACTANTS FROM SPIRULINA BIOMASS IN KAZAKHSTAN CONDITIONS

**Abstract.** The prospects of using Spirulina biomass in the process of creating a new class of natural non-ionic surfactants, such as alkyl amides (mono- or diethanolamides) of fatty acids, which are the most widespread and important class among nitrogen-containing nonionic surfactants are shown. The results of studies on quantitative growth and accumulation of biomass and its chemical composition are presented. The surface active properties of the isolated samples were studied. It was found that the biodegradable surfactants obtained from the Spirulina biomass could significantly reduce the surface tension of water.

**Key words:** biodegradable surfactant, microalgae, biomass, spirulina, properties.

**Introduction.** In the last decade, there has been a large surge in the interest given to production of biodegradable surfactants due to their advantages, mainly ecological ones. Moreover, their biological compatibility with living organisms and their non-toxicity makes them highly applicable in pharmaceutics, cosmetics and food industry as produce with high added value.

Synthetic surfactants from petrochemical materials is used in many industries, in most cases inflicting serious damage during their usage, both to the affected object and to the environment. This is way of developments, aimed the creation of non-toxic and biodegradable surfactants attract a lot of attention in the scientific circles. Particularly interesting are the biodegradable surfactants that consist of complex natural molecules of plant-based materials, that have high surface-active properties.

Although these natural compounds can not compete economically with their synthetic analogues due to their higher cost and deficiency of the original components, which provokes a disputable issue of their usability, the surfactants obtained from vegetable oils (rapeseed, olive and linseed) are nonetheless already available to consumers. It should be noted that the main problem here is the avaiability of competition with food products.

Thus, the search of new types of alternative resources for the production of biodegradable surfactants becomes very relevant. Great efforts have been put into perfecting the existing processes and the search for new means of fermentation of microorganisms (yeast fungi, bacteria, etc). However, the current progress in the creation of natural biodegradable surfactants (based on sugars, sterols and fatty acids) doesn't allow for their wide usage on a commercial scale. Main limiting factors are the high cost of production and the competitive struggle for the resources with the food industry. Usage of alternative, renewable resources that do not compete with food industry, such as microalgae, is, at this point, relevant and practically demanded. Among the available raw materials for the production of biodegradable surfactants, microalgae biomass have good potential due to the following reasons: higher growth rates, compared to the usual biomass sources; the ability to absorb gaseous $CO_2$ using solar energy during cultivation with various climates and on various territories; the ability to store solar energy in energy-rich compounds, such as lipids; lack of direct competition for land plots with food industry and the ability to use salt water sources.

The first such commercial production of betaine based on microalgae as an alternative to the plant-based amidopropyl betaine (figure 1) was created by the American branch of the BASF company (www.basf.us) under the commercial name Dehyton® AO45 based on the development of Solazyme (www.solazyme.com). Dehyton® AO45 is manufactured from microalgae made by Solazyme with the modern technology in a very short time.

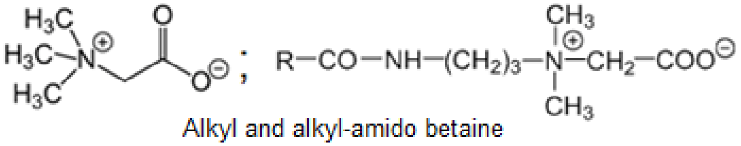


Figure 1 – Betaine molecule structure

The end goal of the current work is the evaluation of the possibility of creation of the material base for the biodegradable surfactants using Spirulina biomass as example in Kazakhstan-based conditions that do not compete with food industry, and synthesis of new derivatives of the biodegradable surfactants from the Spirulina biomass, and the evaluation of their surface-active properties, their potential.

As the object of research spirulina biomass has been chosen. The biomass was synthesized through autotrophic cultivation of a strain from the global culture collection located in the Norwegion Institute for Water Research. Spirulina is the most mass-produced among all of the industrially cultivated globally microalgae cultures.

## EXPERIMENTAL PART

*Cultivation of Spirulina microalgae.* Biomass Spirulina was obtained by cultivation in nutrient medium on the basis of mineral water of hydrocarbonate nature using two kinds of photobioreactor. The laboratory photobioreactor was used for growth and multiplication of the microalgae in the standard Zarrouk medium with the purpose of their usage as stock culture in the inoculation process in an industrial nutrient medium, while in the tubular experimental and the pilot photobioreactors of the reservoir pond type we cultivated the required amounts of the biomass in the main nutrient medium from subterranean mineral waters of bicarbonate nature, obtained at the depth of 1800 meters, at the temperature of 75 °C.

To obtain the inoculant solution a sterile Zarrouk medium used with the following composition: compounds containing macroelements (g/L) – $NaHCO_3$, 16,8; $K_2HPO_4$, 0.5; $NaNO_3$, 2.5; $K_2SO_4$, 1.0; NaCl, 1.0; $Na_2EDTA$, 0.08; $FeSO_4 \times 7H_2O$, 0.01; $CaCl_2$, 0.04; $MgSO_4 \times 7H_2O$, 0.02; + distilled water and compounds containing microelements (g/L) – $Na_2EDTA$, 0.5; $H_3BO_3$, 2.86; $MnCl_2 \times 4H_2O$, 1.81; $ZnSO_4 \times 7H_2O$, 0.222; $CuSO_4 \times 5H_2O$, 0.079; $MoO_3$, 0.015; $NH_4VO_3$, 0.02296; $Co(NO_3)_2 \times 6H_2O$, 0.04398; $K_2Cr_2(SO_4)_4 \times 24H_2O$, 0.0960; $NiSO_4 \times 7H_2O$, 0.04398; $Na_2WO_4 \times 2H_2O$, 0.01794; $Ti(SO_4)_3$, 0.040).

To obtain biomass, at first a mother liquor of microalgae was prepared in a pilot pool-type photobioreactor, which is a specially assembled test-storage unit of a tubular photobioreactor (figure 2) with a volume of 50 to 100 liters of the suspension in a sterile standard Zarrouk solution. The laboratory photobioreactor was fed with carbon dioxide and air mixture using an aquarium compressor with an average airspeed of 4.5 L/min. The time of cultivation was up to 17 days, under natural lighting corresponding to the solar intensity of 400 MJ/m$^3$ or more, in the summertime at the temperature range 20–30 °C. Cultivation of microalgae by this system allowed the cultivation of reliable and resistant laboratory-based mononucleic culture, that could be used as stock solution during inoculation.

Figure 2 – Laboratory setup of the tubular photobioreactor

Inoculation of the mixture to the industrial nutrient medium was performed through a sequence of growing additions of hydrocarbonate water refined with the required biogenic elements on a series of photobioreactors with volumes of 0,5;1,0; 3 $m^3$, and the collection of the required amount of biomass was performed from the bioreactor with the volume of 15 $m^3$. Biomass was separated through the filtration of the mixture, and then washed with fresh water, then dried and grinded. For cultivation in the industrial photobioreactor we developed a special nutrient medium based on hydrocarbonate water of the subterranean flowing well with the addition of the required biogenic elements for the effective growth of the biomass. To keep the temperature of the liquid nutrient medium constant and stable, thermal energy of the geothermal waters was used, which allowed to provide a stable production of biomass – 5kg of dry biomass per month. Cultivation was performed in the patented by the authors: nutrient medium [1] and photobioreactor [2]. Thanks to the fact that the temperature of the process (its nutrient medium) lies in the 25–35 °C range, biotechnological regime can be supported using the alternative energy source – the source of the low-temperature geothermal water well. The spirulina biomass obtained this way was used as an object of research to obtain biodegradable surfactants.

*Extraction of lipids from Spirulina biomass.* The researched dry Spirulina biomass was thoroughly rubbed with quartz sand. Then it was mixed with the extracting mixture, 1:1 by mass. The obtained extract, after filtration, was collected into the measuring cup. Then, the methanol mixture was removed by evaporation.

*Synthesis of methyl ethers of fatty acids.* 2.25 moles (91 ml) of methyl alcohol and 0.25 moles (218.75 g) of Spirulina extraction lipid were placed in a 500 ml round-bottomed flask. To the reaction mass, 5 weight percent (14.5 g) of the prepared solid phase catalyst (KOH / activated carbon) was added. The reaction mixture was heated to 73 ° C. The heating rate was 1.2-1.3 ° C per minute. The reaction mixture was kept at this temperature for 8 hours. The catalyst was filtered off and washed with two 200 ml portions of methanol and reused. The reaction mass was cooled to 30 ° C and a heavier lower glycerin layer was separated. Excess methanol was distilled and regenerated.

Synthesis of methyl esters is carried out according to the inter-esterification reaction (figure 3).

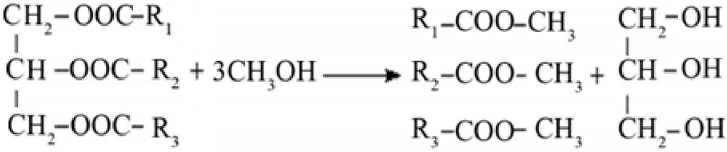


Figure 3 – Reaction of inter-esterification

*Synthesis of pyrolysis lipids from biomass.* Lipids from biomass were isolated by pyrolysis at temperatures up to 3000C and between 3000–4500C in a tubular quartz reactor in a current of inert gas of nitrogen. From the sample of

15.0 grams of biomass, the oil yield was 1.3 and 1.8 g. The obtained oil from the biomass was dissolved in hexane. The composition of the oil from the biomass was analyzed using gas-liquid chromotrophy (GLC) equipment equipped with a mass spectrometric detector.

*Determination of fatty acid composition by chromatography-mass spectrometry method.* Component compositions of the lipid obtained Spirulinae was identified by gas chromatography (GLC) AgilentTechnologies 5890N with a mass selective detector (mobile phase: chloroform: methanol = 1: 1, vol.%, HP-1 column type) by the procedure of [3] . The initial temperature of the column is 40 °C, the holding at the initial temperature is 1 min; programming temperature from 40 to 220 $^{o}$C, speed 15grad/min, from 220 to 320 $^{o}$C deg with the speed of 5 grad/min. Exposure at the last temperature of 15 minutes. The gas is helium osm. brand "5". The sample volume is 1 μl, the temperature of the evaporator is 280 °C.

Identification of the chromatograms was carried out manually by comparing the mass spectra of the test compounds with the library data of NIST05.

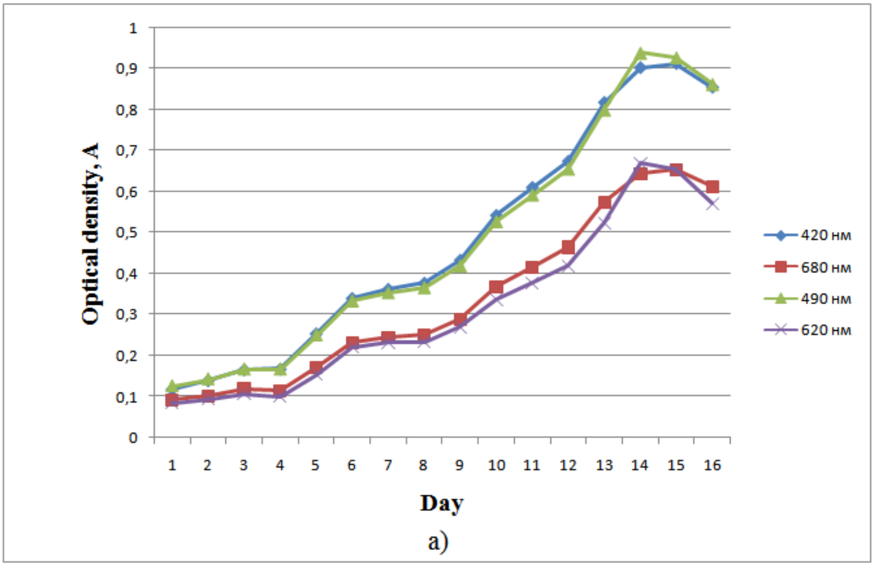
*Determination of surface-active properties.* The surface activity of the samples was evaluated on a KRUSS tensor K20 EasyDyne using the Wilhelm plate method. Surface and interfacial tension measurements were carried out at room temperature, or in the range of -10 to 100 °C using a thermostated jacket, the temperature of which is maintained by means of a circulating thermostat. At the same time, the surface tension of aqueous solutions was determined in the range of their concentration from 0.001 to 1 %.

## RESULTS AND DISCUSSION

Quantitative indicators of growth and biomass accumulation were assessed by measuring the optical density of culture media on a Perkin Elmer lambda-35 ultraviolet spectrometer in the wavelength range from 420 to 650 nm. In this case, a maximum intensity of 420-680 nm characterizes chlorophyll, 490 nm beta carotenoids, and 620 nm phycocyanin. The obtained experimental data on the accumulation of biomass are shown in figure 4.

A common characteristic pattern is the S-shaped form of the growth-time curve, although the specific shape for each nutrient medium is quite different, due to the difference in the biogenic constituents of the components. At the same time, the growth of the microalgae biomass eventually leads to an increase in the cell concentration to a certain maximum culture density. This limiting density turned out to be 0.4 g/L and is apparently related to some limitations, including: the exhaustion of mineral nutrient elements, the decrease in the penetration of the layer of light into the stratum or the accumulation of metabolites in the nutrient medium, as well as by other physicochemical conditions of the environment.

The growth dynamics of the studied culture in both media have a typical S-shaped curve, which can be conditionally divided into 6 sections. Note that, in general, the process of accumulation of Spirulina biomass in the studied nutrient media is similar to that of any other microalgae [4].



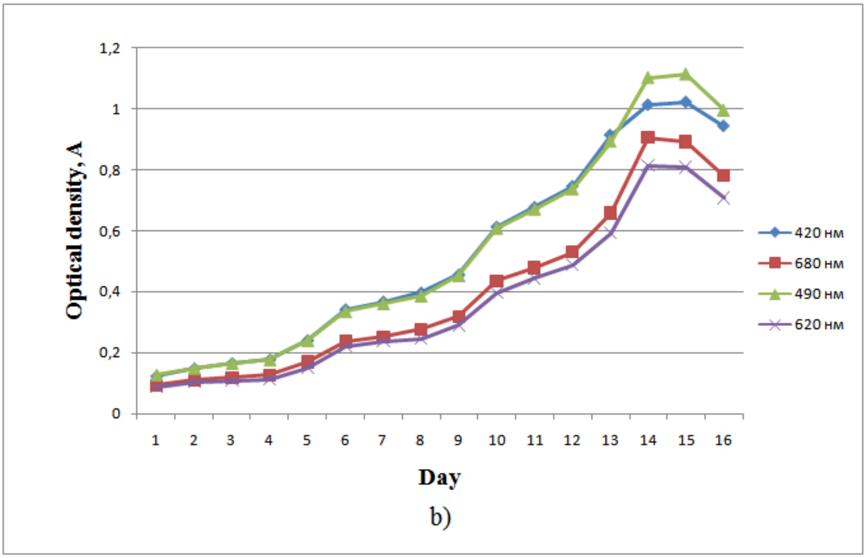


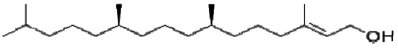
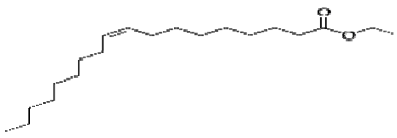
Figure 4 – Growth characteristics of biomass Spirulina in various nutrient media:
a) standard culture medium of Zarrouk;
b) commercial environment based on local bicarbonate mineral water

The composition of the nutrient media directly affects the component composition of the resulting biomass, which determines the final properties of the surfactant. This allows for directional biosynthesis. For example, the authors of [5] demonstrated the possibility of obtaining an extract of Spirulina biomass with specified surface-active properties.

The obtained results indicate that in the conditions of Kazakhstan it is possible to effectively cultivate Spirulina, suitable for the creation of biodegradable surfactants.

The chemical composition of the biomass oil obtained by extraction is determined, and results are given in table 1.

Table 1 – Chemical composition of the extraction oil of biomass from gas-liquid chromatography data

| Compounds | Structural formula | Content, % |
|---|---|---|
| Hexadecane |  | 1,17 |
| Heptadecane |  | 27,73 |
| 1, 19-Eicosadiene |  | 1,90 |
| n-Hexadecanoic acid |  | 3,53 |
| Hexadecanal |  | 2,29 |
| Hexadecanoic acid, ethyl ester |  | 16,15 |
| Phytol |  | 3,74 |
| 9,12,15-octadecatrienoic acid, ethyl ester (z, z, z) |  | 9,47 |
| 9,12-octadecadienoic acid, ethyl ester |  | 5,79 |
| Ethyl oleate |  | 1,23 |

The reaction of the esterification of triglycerides (lipid fraction) with methanol was carried out in the presence of a catalyst KOH. The component composition of the fatty acid methyl esters obtained was analyzed by GC on an Agilent Technologies 6890N (USA) instrument equipped with a mass selective detector. Identification of the compounds obtained was performed using a gas-liquid chromatography database. The obtained spectra are shown in figure 5.

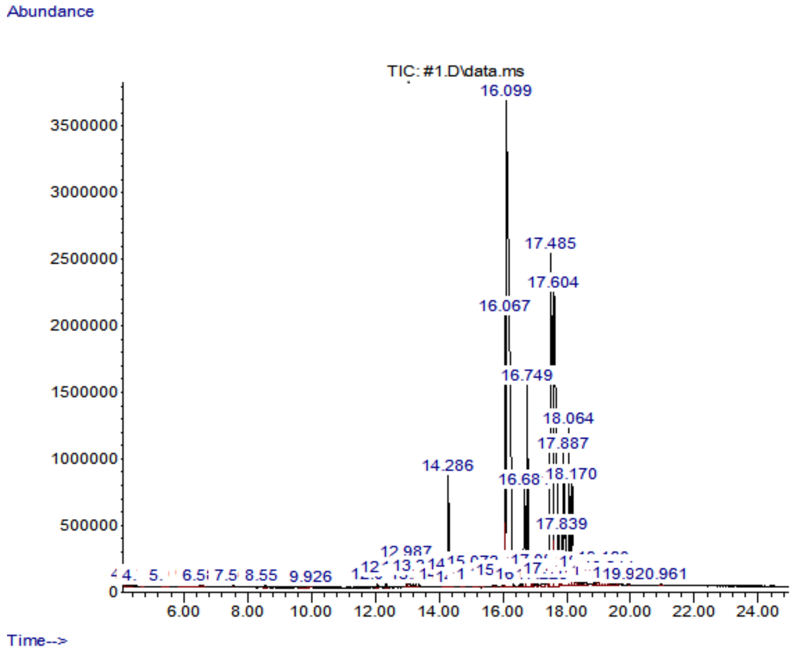


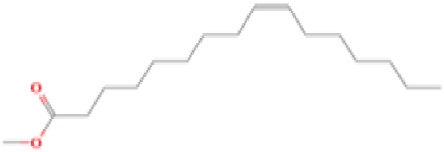
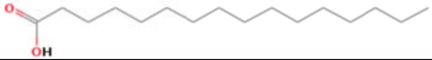
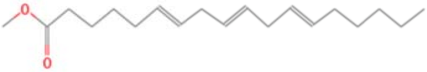
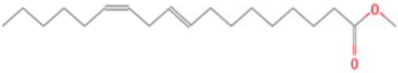
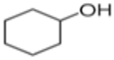
Figure 5 – Chromate-mass spectrometric data of biomass Spirulina

Based on the data of spectral studies, the chemical composition of the lipid constituents of the fatty acids of the Spirulina biomass is shown in table 2. It follows from the analysis of the table that the methyl lipid ester is mainly methyl fatty hexadecanoic acid.

Note that Spirulina biomass is very rich in amino acid compounds (65–70% protein compounds), the second leading component of its composition are carbohydrates (polysaccharides), and lipids occupy only 7–8%. Biomass microalgae also contains compounds such as glycolipids, phospholipids and neutral lipids [6, 7], in addition, sugars, sterols, terpenes and fatty acids, which serve as the main functional components of the composition of natural surfactants [8]. From each given group, in the future, the most suitable candidates for saccharides, peptides (amino acids) can be isolated as a starting material with significantly better hydrophilic properties for the production of biodegradable surfactants. As a hydrophobic compound from a lipid microalgae composition, one of the fatty alcohols can be selected. It is on this principle that a new 100% vegetable surfactant based on alkyl polyglucosides is created under the trade name EcoSense ™ from Dow Personal Care. This surfactant has the following superiority: excellent foaming, softness to the skin, does not contain preservatives, broad compatibility, easy biodegradation, low ecotoxicity.

Fatty acids are useful building blocks for the hydrophobic part of the surfactant molecule, since they contain a reactive carboxyl group. Simple alkenes are also of great interest, since it becomes possible to attach the units of the molecule

Table 2 – Products of the reaction of methylation of triglycerides

| Compounds | Structural formula | Content, % |
|---|---|---|
| Heptodecane |  | 2.915 |
| Methyl 9-hexadecenoic acid |  | 3.678 |
| Methyl ester of hexadecanoic acid |  | 33.979 |
| n-hexadecanoic acid |  | 2.569 |
| Ethyl ester of hexadecanoic acid |  | 6.227 |
| The methyl ester of 6,9,12-octadecatrienoic acid |  | 16.223 |
| Methyl 9,12-octadecadienoic acid |  | 13.428 |
| Cyclohexanol |  | 5.634 |
| 3-tridecene-1-yne |  | 3.707 |
| 9,17-octadecadienal |  | 2.497 |
| Other | | 9.143 |

at the site of the double bond, and thus can be converted to good hydrophobic compounds.

The compounds obtained by us in terms of molecular structure are close to those promoted by the American company in the field of biodegradable surfactants Elevance Renewable Sciences Inc. 9-decenoicacid (9-DA). The company offers 9-DA (  ) as a new special substance, which is a completely natural difunctional compound in the production of biodegradable surfactants. This comound allows us to create a technological platform for petrochemical products, acting as a building block, due to the presence of a difunctional group in the structure. This will significantly expand the market for innovation and the scope of their use.

Thus, the totality of the obtained data unambiguously testifies that Spirulina can be an effective renewable industrial raw material resource, which is an alternative to traditional types of plant raw materials, which give biopreparation lines, and not a separate, specific type of biodegradable products. And in our opinion, this is the main strength of Spirulina for the development of biodegradable surfactants.

Surface active properties of Spirulina samples were studied. The dependence of the surface tension on the surfactant concentration in the water solution is revealed. The results are represented in table 3.

Table 3 – Dependence of surface tension on concentration

| Concentration of surfactant, mass.% | Name | | | | | |
|---|---|---|---|---|---|---|
| | Spirulina biomass extract | Methyl ethers of Spirulina fatty acids | Methyl ethers of Spirulina fatty acids (extraction methanol: chloroform) | Pyrolysis oils, temperature under 300 °C | Pyrolysis oils, temperature 300–450 °C | New nonionic surfactant based on amide of fatty acids Spirulina |
| | Surface tension (mN/m) | | | | | |
| 0.001 | 56.1 | 63.6 | 64.2 | 69.3 | 44.1 | 59.2 |
| 0.01 | 49.8 | 61.5 | 43.8 | 65.8 | 43.5 | 41.4 |
| 0.1 | 45.5 | 54.1 | 37.2 | 61.7 | 35.4 | 31.0 |
| **1** | **34.8** | **310** | **23.3** | **45.3** | **32.2** | **29.7** |

As can be seen from this table, in the samples studied, the surface tension index decreases with increasing concentration. At the same time, the biomass extract obtained from methyl esters of fatty acids from spirulina triglycerides corresponds to lower values of the surface tension index (31.0 mN/m) compared to the pure extract (34.8 mN/m). This fact indicates that Spirulina is a suitable raw material for the production of a biodegradable surfactant, since according to [9] a good surfactant has the ability to reduce the surface tension of water from 72.0 to 35.0 mN•m$^{-1}$. By our amination of Spirulina fatty acids, a new nonionic surfactant with a surface tension of 29.7 mN/m (table 3) was obtained.

As is known, Spirulina produces such compounds as glycolipids, phospholipids and neutral lipids, which are classified as biological surfactants. Here the situation is similar to the case of controlled biosynthesis, in which complete elimination of phosphorus and an increased nitrogen content in the nutrient medium lead to a mixture of biomass extract having a low value of the surface tension index (31.2 mN·m$^{-1}$).

Thermochemically obtained pyrolysis lipids Spirulina also have acceptable surface-active properties. Moreover, the pyrolysis lipid fraction obtained at temperatures above 300 °C, has better surface-active properties, as can be seen from the data in table 3.

Thus, the conducted researches established that in the conditions of Kazakhstan it is possible to effectively produce biomass of Spirulina, which does not compete with crop production.

The prospects of using Spirulina biomass in the process of creating a new class of natural non-ionic surfactants, such as alkyl amides (mono- or diethanolamides) of fatty acids, which are the most widespread and important class among nitrogen-containing nonionic surfactants possessing detergent and cleaning action, wetting and emulsifying properties , regulating and stabilizing foaming, which affect the viscosity increase. All this ensures their use in cosmetics, liquid detergent formulations, pharmaceutical emulsions as an additive to soaps, hair dyes, as raw materials for the production of other surfactant classes, as well as in the textile industry, plastic processing, flotation, dry cleaning and processing of metals. It has been found that biodegradable surfactants from Spirulina's obtained biomass have the ability to reduce the surface tension of water significantly more (up to 23 $mN \cdot m^{-1}$) than many good surfactants, which lower this figure to 35,0 $mN \cdot m^{-1}$.

Although the production of a completely natural non-ionic surfactant requires advanced technologies, it is already becoming a commercial reality. As a source of natural non-ionic surfactant, the raw material resources of the biomass Spirulina can contribute to the further development of the microalga industry, the potential market in Kazakhstan in the feed, salmon and poultry industries, as well as nutraceuticals in the food industry.

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## Резюме

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## ҚАЗАҚСТАН ЖАҒДАЙЫНДА СПИРУЛИНА БИОМАССАСЫНАН БИОЫДЫРАМАЛЫ ББЗ ӨНДІРУ ӘЛЕУЕТІ

Азотты қосылысы бар бейионогенді ББЗ класының ішінде кең таралған және маңызды (моно- неимесе диэтаноламиді) алкилоламидті май қышқылдары болып табылатын жаңа табиғи бейионогенді ББЗ класын құру процесінде Спирулина биомассасының келешекте пайда-лануы көрсетілген.

Зерттеу нәтижелсінде биомассаның өсуі мен жинақталуының сандық көрсеткіштері мен оның химиялық құрамы анықталды. Бөлініп алынған үлгілердің беттік белсенді қасиеттері зерттелді.

**Түйін сөздер:** биоыдырамалы беттік-белсенді зат, микробалдыр, биомасса, спирулина, қасиеттері.

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## Резюме

*Ж. Н. Кайнарбаева, А. М. Картай, Р. Б. Сариева,*
*Б. К. Доненов, М. Б. Умерзакова*

## ПОТЕНЦИАЛ ПРОИЗВОДСТВА БИОРАЗЛАГАЕМЫХ ПАВ ИЗ БИОМАССЫ СПИРУЛИНЫ В УСЛОВИЯХ КАЗАХСТАНА

Показана перспективность использования биомассы Спирулины в процессе создания нового класса природных неионогенных ПАВ, таких как алкилоламиды (моно- или диэтаноламиды) жирных кислот, являющихся наиболее распространенным и важным классом среди азотсодержащих неионогенных поверхностно-активных веществ. Приведены результаты исследований по определению количественных показателей роста и накопления биомассы, ее химического состава. Изучены поверхностно активные свойства выделенных образцов.

**Ключевые слова:** биоразлагаемое поверхностно-активное вещество, микроводоросль, биомасса, спирулина, свойства.

UDC 547(1+435+6+822)+541.341

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# COMPLEXES OF 1-(2-ETHOXYETHYL)-4-(DIMETHOXYPHOSPHORYL)-4-HYDROXYPIPERIDINE WITH IONS OF BIOGENIC METALS: SYNTHESIS AND PROPERTIES

**Abstract.** The complexation of 1-(2-ethoxyethyl)-4-(dimethoxyphosphoryl)-4-hydroxypiperidine with ions of biogenic metals ($Co^{+2}$, $Ni^{+2}$, $Cu^{+2}$, $Mn^{+2}$) in the ligand : ion ratio of 2:1 had been studied. It had been turned out that cobalt and nickel ions generate stable complexes, whereas the product obtained with copper and manganese ions is basically a mixture of the ligand and the corresponding salt. By modeling with the semiempirical PM3 method, it had been shown that a complex in which the divalent metal ion forms coordination bonds with nitrogen atoms and oxygen with a double bond on phosphorus is energetically most advantageous, with the piperidine cycle being in the "boat" conformation. $CoL_2Cl_2$ (Kaz-10) and [$MnL_2SO_4$] (Kaz-11) at a concentration of 1.0.10-3% significantly stimulate the germination of barley and wheat seeds.

**Key words:** α-Hydroxyphosphonate, ions of biogenic metals ($Co^{+2}$, $Ni^{+2}$, $Cu^{+2}$, $Mn^{+2}$), complex, synthesis, structure, stimulator of germination of barley and wheat seeds.

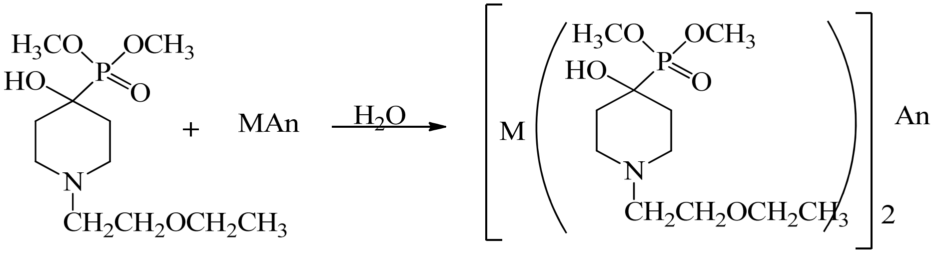
*Bioregulation* - an area that enables to regulate the direction and intensity of biochemical processes, which can be widely used in medicine, livestock and crop production. It is related to development of ways to restore the physiological function of the body both for the prevention and treatment of diseases and age pathologies. Complex compounds of organic ligands with ions of biogenic metals refer to promising biologically active compounds. The results of their biological effect tests showed that chemistry gives novel preparations to doctors, cattle breeders, agronomists and biologists, allowing them to actively influence the living cell, regulate the nutritional conditions, growth and development of living organisms [1-4].

Among the microelements, the content of which in the body amounts to thousands and even trillions of percent, are: iron, cobalt, manganese, copper, molybdenum, zinc, cadmium, fluorine, iodine, selenium, strontium, beryllium, lithium, etc. Despite the small quantitative content in organisms, microelements has a significant biological role in the processes of growth and development. It has been established that the excess of microelements, as well as their lack, adversely affects the plants.

α-Hydroxy- and α-aminophosphonates are of practical interest as substances with biological activity of widely spectrum and technological simplicity of their obtaining [5-9]. In addition, the ability of organophosphorus to complex formation with metal ions [10-14] contributes to the expansion and more intensive development of chemistry of this class of compounds. Complexes of aminophosphonates with lanthanides and actinides are used in medical NMR diagnostics. Using aminophosphonates, effective methods for separating gold ions, iron ions, copper ions, and also palladium extraction have been developed. Currently, there are a number of drugs based on nitrogen-containing bisphosphonates for patients with impaired calcium metabolism. Aminopolyphosphonates as complexing agents with high specificity for various cations are widely used in analytical chemistry and catalysis, in the paper and textile industries to remove trace amounts of metal ions in whitening baths, as well as in medicine to relieve metal overload in living organisms, particularly for the treatment of anemia overload of iron in the body.

The previously synthesized hydroxyphosphonate with the N-(2-ethoxyethyl)piperidine moiety [15, 16], at a concentration of $1.0\cdot10^{-3}$%, stimulates growth and increases resistance to drought of plants, and in an experiment on animals poisoned with salts of heavy metals, it treats their immune status.

To enhance the stimulating growth of plants there is set to study complexation of 1-(2-ethoxyethyl)-4-(dimethoxyphosphoryl)-4-hydroxypiperidine (ligand, L) with certain ions of biogenic metals - $Co^{+2}$, $Mn^{+2}$, $Cu^{+2}$ and $Ni^{+2}$. To prepare the complexes ligand and chlorides of cobalt, nickel, copper and manganese sulfate are taken with the ratio (metal ion : L) = 1: 2.



M =$Co^{2+}$, $Cu^{2+}$, $Ni^{2+}$, $Mn^{2+}$ ;
An = $2Cl^-$ or $SO_4^{2-}$

To obtain the complexes, the salt and ligand are separately dissolved in the solvent, then the solutions are drained and stirred at room temperature for 2 hours. The reaction mixture is then dried at 50 ° C until the solvent evaporates completely. Moreover, various solvents have been used to prepare the target complexes: ethanol, methylene chloride, acetonitrile, benzene, acetone and water. The best results were obtained using ethanol or methylene chloride.

The synthesized complexes are crystalline products, some have different colors ($Co^{+2}$ - dark blue, $Ni^{+2}$ - yellow-green, $Cu^{+2}$ - light blue), but only the complex of the ligand with $Mn^{+2}$ is white crystals.

In the IR spectrum of the ligand (figure 1), an intense absorption band is observed at 1037.5 $cm^{-1}$, which is characteristic of C-N stretching vibrations, the band at of 1226.2 $cm^{-1}$ is attributed to the absorption of P=O group, 3269.5 $cm^{-1}$ -

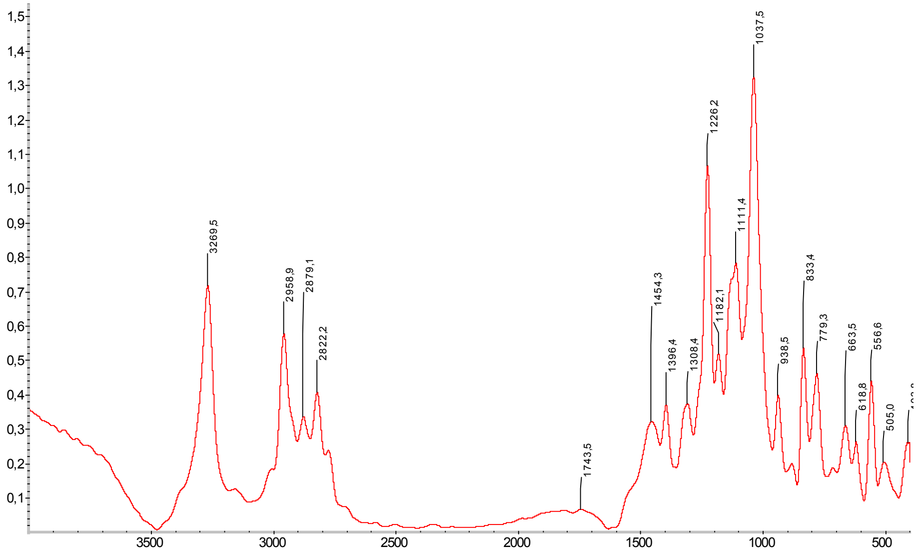


Figure 1 – IR spectrum of 1-(2-ethoxyethyl)-4-(dimethoxyphosphoryl)-4-hydroxypiperidine (L)

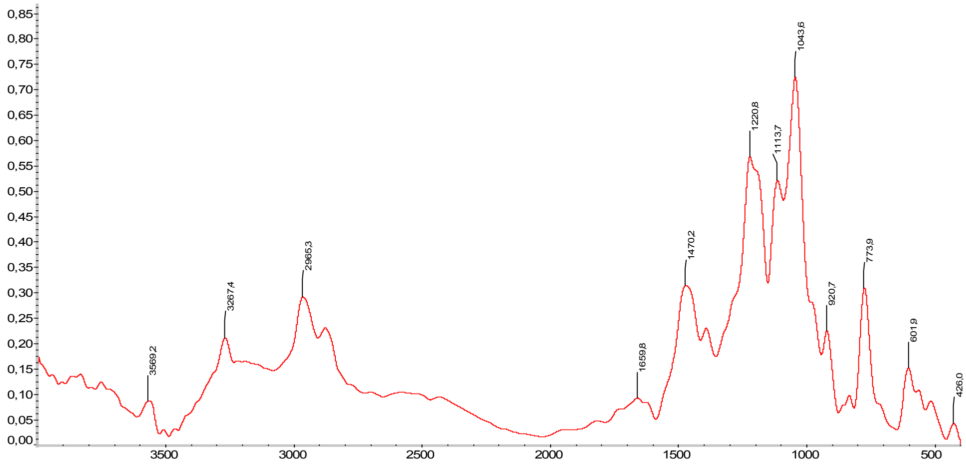


Figure 2 – IR spectrum of $CoL_2Cl_2$

to the uptake of O-H, 1182.1 $cm^{-1}$ – ($-CH_2-O-CH_2-$), 1454.3 $cm^{-1}$ - $P-OCH_3$, and also several absorption bands of $C_{sp2}-C_{sp2}$ (2822.2 $cm^{-1}$, 2879.1 $cm^{-1}$, 2958.9 $cm^{-1}$).

The IR spectrum of the cobalt complex (figure 2) suggests the formation of a complex. Thus, the shift of the absorption bands of the P=O group into the region 1220.6 $cm^{-1}$ and $P-OCH_3$ - at 1470.2 $cm^{-1}$ indicates the participation of the phosphonate fragment in the formation of the $Co^{+2}$ - ligand bond, and also the C-N bonds with 1037.5 $cm^{-1}$ to 1043.5 $cm^{-1}$. Absorption of the bonds of the hydroxyl group remains almost unchanged (C-O alcohol - 1037.5 $cm^{-1}$, 3267.4 $cm^{-1}$ - O-H). The IR spectrum of the nickel complex looks similar.

The average values of the absorption bands of the bonds of the P-$OCH_3$, P=O, C-N of ligand and its complexes are presented table 1.

Table 1 – IR spectra of the ligand and its complexes with ions $Co^{+2}$, $Ni^{+2}$, $Cu^{+2}$, $Mn^{+2}$

| Compound | IR spectrum, $cm^{-1}$ | | |
|---|---|---|---|
| | P-$OCH_3$ | P=O | C-N |
| Ligand (L) | 1454 | 1226 | 1037 |
| $CoL_2Cl_2$ | 1466 | 1200 | 1043 |
| $NiL_2Cl_2$ | 1456 | 1188 | 1049 |
| [$CuL_2Cl_2$] | 1454 | 1226 | 1038 |
| [$MnL_2SO_4$] | 1453 | 1226 | 1037 |

Infrared spectra of copper and manganese complexes are characterized by the presence of absorption bands of the above groups both in the ligand itself, which indicates that the resulting samples contain mainly the initial ligand. However, judging by some changes in the reaction solution (color, gradual dissolution of the precipitate of the salt), a complex is formed. Apparently, the technique used is not entirely suitable for the preparation of complexes with copper and manganese ions.

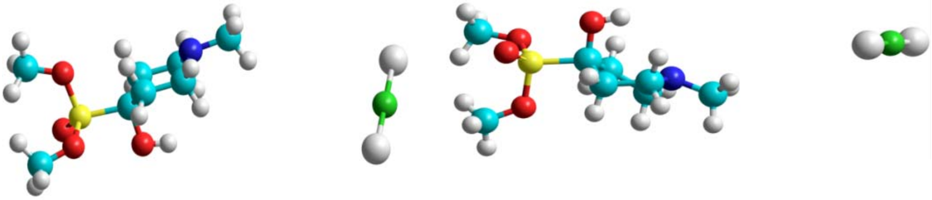
The NMR spectra of the obtained complexes due to the strong magnetic field of the metal ions turned out to be unsuitable for decoding and, accordingly, it is impossible to determine the structure of the complex. To solve this problem, the possibilities of computer chemistry are involved. The modeling was carried out using the semiempirical PM3 method. To accelerate the optimization of ligand structures and its complexes, its structure is simplified by replacing the substituent at the nitrogen of piperidine ring by the methyl group, while the extension of this substituent is assumed to have a slight effect on the heat of complex formation. As the complex-forming model compound, chloride of bivalent copper is taken. The accuracy of the optimization (gradient) is set to 0.01 kcal/mol.

To estimate the heat of formation of the copper ligand-chloride system, calculations were carried out for two conformational states of the heterocyclic ring ("*chair*" and "*boat*"), and the distance between the ligand and copper chloride was not less than 7A in order to avoid convergence and the formation of coordination bonds during optimization. Since the possibility of forming coordination bonds of three groups or fragments of the ligand was taken into account, four more probable structures (figure 3) of the complex were calculated.

After optimization of the most probable structures of the complex, the heat of formation was estimated. Calculations show that the formation of complex 4 (HF = -267.960 kcal/mol) is most profitable energetically. The main points for the generation of coordination bonds between the ligand molecule - 1-(2-ethoxyethyl)-4-(dimethoxyphosphoryl)-4-hydroxypiperidine, and the bivalent copper ion are nitrogen and oxygen with a double bond on phosphorus, which have the

Initial system (ligand "*chair*")

Initial system (ligand "*boat*")



Heat of formation HF = -200.893 kcal/mol

Heat of formation HF = -202.286 kcal/mol

***Complex 1***
(Cu$^{+2}$, N, «*chair*»)

***Complex 2***
(Cu$^{+2}$, N, OH, «*boat*»)

Heat of formation HF = -258.157 kcal/mol

Heat of formation HF = -261.256 kcal/mol

***Complex 3***
(Cu$^{+2}$, P=O, OH, «*chair*»)

***Complex 4***
(Cu$^{+2}$, N, P=O, «*boat*»)

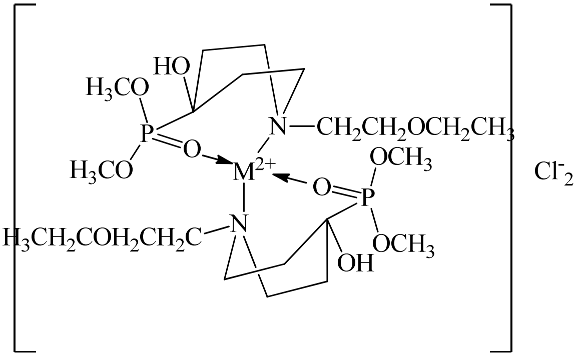
Heat of formation HF = -261.677 kcal/mol

Heat of formation HF = **-267.960** kcal/mol

Figure 3 – Probable conformation of the ligand and complexes and the values of Heat of formation

highest electron density. The second molecule of the ligand "joins" to metal ion in the same way. The nature of the substituent at the nitrogen atom of the piperidine ring and the metal does not significantly affect the heat of formation of the complex.

Thus, the most probable structure of 1-(2-ethoxyethyl)-4-(dimethoxyphosphoryl)-4-hydroxypiperidine complex with a divalent metal ion is:



The shift in the absorption bands of the P-$OCH_3$, P=O and C-N bonds in the IR spectra of $CoL_2Cl_2$ and $NiL_2Cl_2$ compared with analogous bands of ligand testifies the formation of this complex structure.

Test studies on the germination of seeds of two complexes of 1-(2-ethoxyethyl)-4-(dimethoxyphosphoryl)-4-hydroxypiperidine with cobalt ($CoL_2Cl_2$) and manganese ([$MnL_2SO_4$]) ions were carried out on the barley variety "Arna" (elite), wheat variety "Kazakhstan-10 "(elite) and maize variety "KazNIIZR-75". Table 2 presents the results of the first 3 days after the soaking of seeds in the corresponding solutions (concentration of Kaz-10 and Kaz-11 was $1{,}0 \cdot 10^{-3}$ %).

Table 2 – Test data Kaz-10, Kaz-11 and applied plant growth stimulants (Gumi-K+Vermicai) and Baikal EM-1 for germination of barley, wheat and maize seeds in model experiments on phytotron

| Preparation | The number of sprouted seeds for every 10 in the series, pcs. | | |
|---|---|---|---|
| | Barley variety "Arna" (elite) | Wheat variety "Kazakhstan-10" (elite) | Maize variety "KazNIIZR-75" |
| Control (Water) | 2,3/10 | 5,7/10 | no |
| Kaz-10 ($CoL_2Cl_2$) | 2,5/10 | 7,7/10 | no |
| Kaz-11 ([$MnL_2SO_4$]) | 3,0/10 | 6,7/10 | no |
| (Gumi-K+Vermicai) | 2,0/10 | 7,3/10 | no |
| Baikal EM-1 | 1,5/10 | 7,0/10 | no |

The stimulating effect of Kaz-10 and Kaz-11 and used stimulants (Gumi-K+Vermicai, Baikal EM-1) on seeds of cereal crops - barley and wheat is noted. On the seeds of maize varieties "KazNIIZR-75" during the first three days, the effect does not appear in all the solutions studied.

Thus, it had been shown that hydroxyphosphonate - 1-(2-ethoxyethyl)-4-(dimethoxyphosphoryl)-4-hydroxypiperidine, forms with the ions of biogenic metals ($Co^{+2}$, $Ni^{+2}$, $Cu^{+2}$, $Mn^{+2}$) complexes in the ratio of ligand: ion is 2 : 1. The cobalt and nickel ions generate stable complexes, whereas the product obtained with copper and manganese ions is basically a mixture of the ligand and the corresponding salt. It is energetically most advantageous a complex in which the metal ion $M^{+2}$ has coordination bonds with the nitrogen and oxygen of P=O group, and the piperidine cycle is in the "*boat*" conformation. $CoL_2Cl_2$ and $[MnL_2SO_4]$ under laboratory ciphers Kaz-10 and Kaz-11 significantly stimulate the germination of barley and wheat seeds at a concentration of $1.0 \cdot 10^{-3}$%.

## EXPERIMENTAL PART

Control over the reactions is carried out by thin layer chromatography on aluminum oxide of III degree of activity with the appearance of spots by iodine vapor. The IR spectra were recorded on a Nicolet 5700 FT-IR spectrometer in KBr tablets.

***Synthesis of di[1-(2-ethoxyethyl)-4-(dimethoxyphosphoryl)-4-hydroxypiperidine]cobalt (II) chloride.*** To a solution of 0.25 g ($9.0 \cdot 10^{-4}$ mole) of 1-(2-ethoxyethyl)-4-(dimethoxyphosphoryl)-4-hydroxypiperidine in 5-10 ml of ethanol (or methylene chloride) was added a solution of 0.1 g (4,5.10-4 mole) of cobalt (II) chloride hexahydrate in 5-10 ml of ethanol (or methylene chloride). Then a pink mixture is placed in an ultrasonic bath for 30 min. The reaction solution is then dried at 50°C, until the solvent has completely evaporated. The complex is obtained in the form of a crystalline powder of a dark blue color with a yield of 66.7% (0.21 g), m.p. 118-128 ° C (ethanol) and 60% (1.18 g), m.p.108-135° C (methylene chloride).

Calcd., %: C 38,16; H 6,988. $CoC_{22}H_{48}N_2O_{10}P_2Cl_2$.

Found., %: C 38,49; H 6,59.

IR, $cm^{-1}$: 1183 ($-CH_2-O-CH_2-$); 1466 ($-P-OCH_3$); 2965, 2966, 2969 ($C_{sp2}-C_{sp2}$); 1200 (P=O); 1044 (C-OH); 3267 ($C_{arom.}$-H).

***Synthesis of di[1- (2-ethoxyethyl)-4-(dimethoxyphosphoryl)-4-hydroxypiperidine]nickel (II) chloride.*** To a solution of 0.25 g ($9.0 \cdot 10^{-4}$ mole) of 1-(2-ethoxyethyl)-4- (dimethoxyphosphoryl)-4-hydroxypiperidine in 5-10 ml of ethanol (or methylene chloride) was added a solution of 0.1 g ($4{,}5 \cdot 10^{-4}$ mole) of nickel chloride hexahydrate (II) in 5-10 ml of ethanol (or methylene chloride). The mixture is then placed in an ultrasonic bath for 1 min. The reaction solution is then dried at 50°C, until the solvent has completely evaporated. The complex is obtained as a crystalline powder of a yellow-green color with a yield of 75.2% (0.23 g), m.p. 111-161°C (ethanol) and 57.2% (1.18 g), m.p. 141-151° C (methylene chloride).

Calcd., %: C 38,18; H 6,99. $NiC_{22}H_{48}N_2O_{10}P_2Cl_2$.

Found., %: C 38,71; H 6,81.

IR, $cm^{-1}$: 1115 ($-CH_2-O-CH_2-$); 1456 ($-P-OCH_3$); 2971, 2972, 2973 ($C_{sp2}-C_{sp2}$); 1188 (P=O); 1048 (C-OH); 3200 ($C_{arom.}$-H).

***Synthesis of di[1-(2-ethoxyethyl)-4-(dimethoxyphosphoryl)-4-hydroxypiperidine] copper (II) chloride.*** To a solution of 0.3 g ($7.8 \cdot 10^{-4}$ mole) of 1-(2-ethoxyethyl)-4- (dimethoxyphosphoryl)-4-hydroxypiperidine in 50 ml of ethanol (or methylene chloride) was added a solution of 0.005 g ($3.9 \cdot 10^{-4}$ mole) of copper (II) chloride in 5 ml of ethanol (or methylene chloride). The mixture is stirred for

1 h at room temperature and held for 20 min in an ultrasonic bath. The complex is obtained as a light blue crystalline powder in 75% yield (0.2 g), m.p. 107-112° C (ethanol) and m.p. 108-112 ° C (methylene chloride) (mixture of ligand, salt and complex).

Calcd., %: C 37,91; H 6,94. $CuC_{22}H_{48}N_2O_{10}P_2Cl_2$.

Found., %: C 42,54; H 7,64.

ИК спектр, $см^{-1}$: 1110 ($-CH_2-O-CH_2-$); 1454 ($-P-OCH_3$); 2821,7; 2880,6; 2959,3 ($C_{sp2}-C_{sp2}$); 1226,2 (P=O); 1037,5 (C-OH); 3269 ($C_{arom.}$-H).

***Synthesis of di[1-(2-ethoxyethyl)-4-(dimethoxyphosphoryl)-4-hydroxypiperidine] manganese (II) sulfate.*** To a solution of 0.9 g ($3.2 \cdot 10^{-3}$ mole) of 1-(2-ethoxyethyl)-4- (dimethoxyphosphoryl)-4-hydroxypiperidine in 50 ml of ethanol (or methylene chloride) was added a solution of 0.27 g ($1,6 \cdot 10^{-3}$ mole) manganese sulfate (II) monohydrate in 5 ml of ethanol (or methylene chloride). The mixture is stirred for 1 h at room temperature and held for 20 min in an ultrasonic bath. The complex is obtained as a white crystalline powder in 70% yield (0.18 g), m.p. 106-114°C (ethanol) and m.p. 109-113°C (methylene chloride) (mixture of ligand, salt and complex).

Calcd., %: C 33,95; H 6,78. $MnC_{22}H_{48}N_2O_{14}P_2S$.

Found., %: C 43,59; H 8,94.

IR, $cm^{-1}$: 1110 ($-CH_2-O-CH_2-$); 1452,7 ($-P-OCH_3$); 2957,5 ($C_{sp2}-C_{sp2}$); 1226,0 (P=O); 1038,3 (C-OH); 3267,9 ($C_{arom.}$-H).

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## Резюме

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## КОМПЛЕКСЫ 1-(2-ЭТОКСИЭТИЛ)-4-(ДИМЕТЕТОКСИФОСФОРИЛ)-4-ГИДРОКСИПИПЕРИДИНА С ИОНАМИ БИОГЕННЫХ МЕТАЛЛОВ: СИНТЕЗ И СВОЙСТВА

Показана возможность комплексообразования 1-(2-этоксиэтил)-4-(диметоксифосфорил)-4-гидроксипиперидина с ионами биогенных металлов ($Co^{+2}$, $Ni^{+2}$, $Cu^{+2}$, $Mn^{+2}$) в соотношении лиганд:ион = 2:1. Оказалось, что ионы кобальта и никеля образуют стабильные комплексы, тогда как полученный продукт с ионами меди и марганца представляет в основном механическую смесь лиганда и соответствующей соли. Моделированием полуэмпирическим методом РМ3 показано, что энергетически наиболее выгодно образование комплекса, в котором ион двухвалентного металла образует координационные связи с атомами азота и кислорода с двойной связью на фосфоре, при этом пиперидиновый цикл находится в конформации *ванна*. $CoL_2Cl_2$ и $[MnL_2SO_4]$ под лабораторными шифрами Каз-10 и Каз-11 в концентрации $1{,}0 \cdot 10^{-3}$ % заметно стимулируют прорастание семян ячменя и пшеницы.

**Ключевые слова:** гидроксифосфонат, ионы биогенных металлов, комплекс, синтез, структура, стимуляция прорастания семян ячменя и пшеницы.

## Резюме

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# 1-(2-ЭТОКСИЭТИЛ)-4-(ДИМЕТЕТОКСИФОСФОРИЛ)-4-ГИДРОКСИПИПЕРИДИННІҢ БИОГЕНДІ МЕТАЛДАР ИОНДАРЫМЕН КЕШЕНДЕРІ: СИНТЕЗІ МЕН ҚАСИЕТТЕРІ

Лиганд:ион = 2:1 қатынасында 1-(2-этоксиэтил)-4-(диметоксифосфорил)-4-гидроксипиперидиннің биогенді металдардың иондарымен ($Co^{+2}$, $Ni^{+2}$, $Cu^{+2}$, $Mn^{+2}$) кешен түзу мүмкіндігі көрсетілген. Мыс пен марганец иондарынан алынған өнімдер лиганд пен сәйкес тұздың механикалық қоспасы болып табылса, ал кобальта пен никеля иондары тұрақты кешен түзетіндігі анықталды. РМ3 жартылай эмпирикалық әдісімен модельдеу арқылы, екі валентті металдың ионы азот және фосфордағы қос байланысты оттегі атомдарымен координациялық байланыс түзгенде, пиперидин циклінің *ванна* конформацияда орналасуы кешен түзілуінің энергетикалық жағынан ең тиімді екендігі көрсетілген. Каз-10 және Каз-11 зертханалық шифрлармен берілген $CoL_2Cl_2$ және $[MnL_2SO_4]$ $1{,}0 \cdot 10^{-3}$ % концентрациясында арпа мен бидай тұқымдарының өсуін айтарлықтай ынталандырады.

**Түйін сөздер:** гидроксифосфонат, биогенді металдардың иондарымен, комплекс, синтез, структура, стимуляция прорастания семян ячменя и пшеницы.

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# INFLUENCE OF DISTANT ACTION EFFECT BETWEEN POLYMETHACRYLIC ACID AND POLY-4-VINYLPYRIDINE HYDROGELS ON THE SORPTION ABILITY OF ERBIUM IONS

**Abstract.** The phenomenon of sorption erbium ions by intergel system of polymethacrylic acid hydrogel (PMAA) and poly-4-vinylpyridine hydrogel(P4VP) was studied. It was established that the structure of the basic hydrogel has a significant influence on the self-organization of the PMAA hydrogels. The erbium ions extraction rateof individual hydrogels PMAA and P4VP was 42% and 16%, respectively. At ratios 5:1 (83% of gPMAA-17% gP4VP) and 4:2 (67% gMPAA-33% gP4VP), erbium ions were recovered up to 54% in both cases. The polymer PMAA and P4VP hydrogels have relatively low values of the polymer chain binding degree (0.54% and 0.20%, respectively).

The obtained results indicate the possibility of creating selective intergel systems for separation erbium ions.

**Key words:** intergel system, sorption, $Er^{3+}$ ions, hydrogels, polymethacrylic acid, poly-4-vinylpyridine.

**Introduction.** After optimization of the most probable structures of the complex, the heat of formation was estimated. Calculations show that the formation of complex 4 (HF = -267.960 kcal/mol) is most profitable energetically. The main points for the generation of coordination bonds between the ligand molecule - 1-(2-etho-xyethyl)-4-(dimethoxyphosphoryl)-4-hydroxypiperidine, and the bivalent copper ion are nitrogen and oxygen with a double bond on phosphorus, which have the

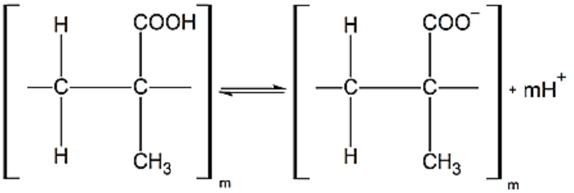
Rare-earth elements are used in various industries: radio electronics, instrument making, machine building, nuclear engineering, metallurgy, chemical industry, etc. Lanthanum, cerium, praseodymium, neodymiumare widely used in the glass industry in the form of oxides and other compounds [1]. These elements increase the translucence of the glass. Rare-earth elements are part of special-purpose glasses that transmit infrared rays and absorb ultraviolet rays, and heat-resistant glass [2].

Rare earth elements and their compounds are widely distributed in the chemical industry, for example, in the production of pigments, varnishes and paints, in the oil industry as catalysts. Rare-earth elements are used in the production of certain explosives, special steels and alloys, as degasifiers [3]. Single-crystal compounds of rare-earth elements (and also glasses) are used to create laser and other optically active and nonlinear elements in optoelectronics [4]. Based on erbium, neodymium, yttrium, samarium, europium with Fe-B mixture, alloys with recordable magnetic properties (high magnetizing and coercive forces) are produced to create permanent magnets of enormous power in comparison with simple ferroalloys [5]. Previous studies [6-9] have shown that mutual activation of polymer hydrogels leads to significant changes in their electrochemical and conformational properties. It should be noted that in previous studies, the starting polymers were applied in a dry state. Remote interaction is carried out by the following processes: rapid - hydration, ionization, dissociation, association and slow - change in the conformational state of inter-node links.It is obvious that the initial state of the rare-crosslinked hydrogels should influence the rate of interactions in the intergel system. Swollen polymers are better subjected to mutual activation due to the fact that the macromolecular ball unfolds during swelling, as a result, the activity of functional groups increases. In connection with this, the purpose of this work was to study the sorption ability of the intergel system gPMAA-gP4VP consisting of preliminary swollen hydrogels with respectto erbium ions.

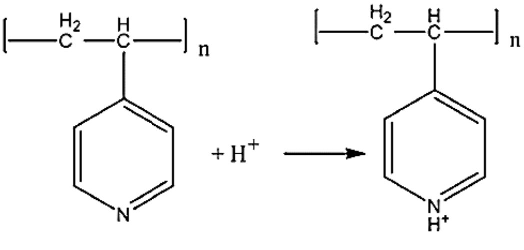
As a result of previous studies [1-6], it was established that the remote interaction of polymer hydrogels in intergel systems leads to significant changes in the conformational state as a result of their self-organization.In connection with this, the aim of this work was to study the effect of the second component (poly-base) on the self-organization of polymer hydrogels of polymethacrylic acid in the intergel system, as well as the study of the sorption properties of the gPMAA-gP4VP intergel systems with respect to erbium ions**.**

Two main reactions occur in intergel systems:

1. Acid hydrogel dissociation:



2. Binding of cleaved proton by nitrogen heteroatom:



## EXPERIMENTAL PART

**Equipment.** Optical density measurements for the subsequent calculation of the erbium nitrate concentration were made using a Jenway-6305 (SC) spectrophotometer.

**Materials.** The studies were carried out in an erbium(III) nitrate pentahydrate solution. The hydrogels of polymethacrylic acid were synthesized in the presence of the cross-linking agent N,N-methylene-bis-acrylamide and the oxidation-reduction system $K_2S_2O_8$-$Na_2S_2O_3$. The poly-4-vinylpyridine hydrogel (gP4VP) was synthesized by Sigma-Aldrich (2% cross-linking agent). The synthesized hydrogels in the aqueous medium constituted the intergel pair «polymethacrylic acid hydrogel – poly-4-vinylpyridine hydrogel» (gPMAA-gP4VP). The hydrogels swelling degrees were: α (gPMAA) = 20.65 g/g; α (gP4VP) = 2.65 g/g., respectively.

**Experiment.** The experiments were carried out at room temperature. Investigations of the intergel system were carried out as follows: the calculated amount of each hydrogel in dry form was placed in special polypropylene nets, the pores of which are permeable to low molecular ions and molecules, but impermeable to the dispersion of hydrogels. Then, an aliquot was taken for subsequent optical density measurements.

*Methodology of erbium ions determination.* The method for determining erbium ions in solution was based on the formation of a colored complex compound of the organic analytic reagent arsenazo III with erbium ions [7].

Extraction (sorption) degree was calculated by the following equation:

$$\eta = \frac{C_{\text{initial}} - C_{\text{residual}}}{C_{\text{initial}}} \times 100\% ,$$

where $C_{\text{initial}}$ is the initial concentration of erbium in solution, g/L; $C_{\text{residue}}$ is theresidual concentration of erbium in solution, g/L.

Polymer chain binding degree was determined by calculations in accordance withthe following equation:

$$\theta = \frac{\nu_{\text{sorbed}}}{\nu} \times 100\%$$

where $\nu_{sorbed}$ – the quantity of polymer links with sorbed erbium, mol; $\nu$ – thetotal quantity of polymer links (if there are two hydrogels in solution, it is calculatedas sum of each polymer hydrogel links), mol.

The effective dynamic sorption capacity was calculated by the following equation:

$$Q = \frac{\nu_{\text{sorbed}}}{m_{\text{sorbent(s)}}} ,$$

where $\nu_{\text{sorb}}$ is the amount of sorbed metal, mole; $m_{\text{absorbent}}$ – the mass of the sorbent (if there are two hydrogels in solution, it is calculated as the sum of the two hydrogels masses), g.

## RESULTS AND DISCUSSION

The erbium ions sorption by thegPMAA-gP4VP intergel system occurs by ionic and coordination mechanisms. The process of rare-earth elements sorption by the example of lanthanum is described in detail in our previous works [8-10].

*Erbium ions extraction by the gPMAA-gP4VPintergel system.* The dependence of erbium ions extraction degree by the gPMAA-gP4VP intergel system on the mole ratio of hydrogels in time is shown in figure 1. The maximum amount of erbium ions was extracted by the gPMAA-gP4VP intergel system at the ratio of hydrogels 5:1 (83%gMPAA-17%gP4VP) and 4:2 (67%gPMAA-33%gP4VP). The degree of erbium ions extraction after 48 hours at these ratios was 54%. The obtained results indicate that the degree of erbium ions extraction by individual hydrogels of polymethacrylic acid and poly-4-vinylpyridine is low, the extraction rates were 42% and 16%, respectively. The remaining ratios of the intergel pair in the gPMAA-gP4VP intergel system also have much higher erbium ion extraction rates compared to the erbium ions extraction of the PMAA and P4VP individual hydrogels.

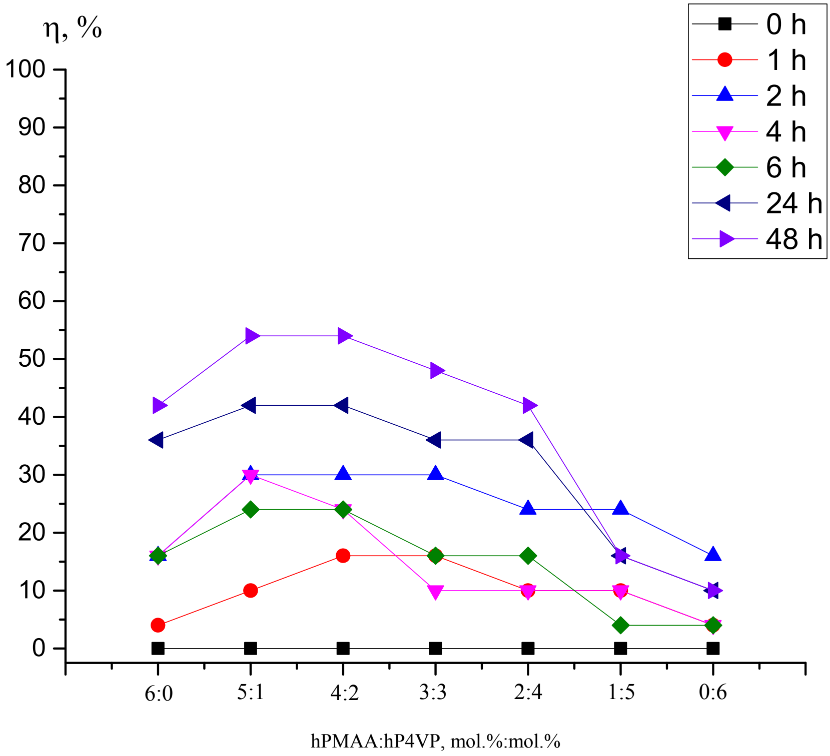


Figure 1 – The dependence on the erbium ions extraction degree by the gPMAA-gP4VP intergel system versus of the mole ratio of hydrogels at the various duration

Figure 2 shows the dependence on the polymer chain binding degree (with respect to erbium ions) of the gPMAA-gP4VP intergel system versus of duration of time. The maximum values of the polymer chain binding degree in the intergel system after 48 hours were 0.7% at ratios of gPMAA-gP4VP 5:1 and 4:2. The polymer chain binding degree values of polymethacrylic acid and poly-4-vinyl-pyridine individual hydrogels after 48 hours were 0.54% and 0.13%, respectively. At 2 hours of sorption, a certain increase in the polymer chain binding degree was achieved. At 24 and 48 hours, a significant increase in the polymer chain binding degreewas observed; this is particularly noticeable for 4:2 and 3:3 ratios.

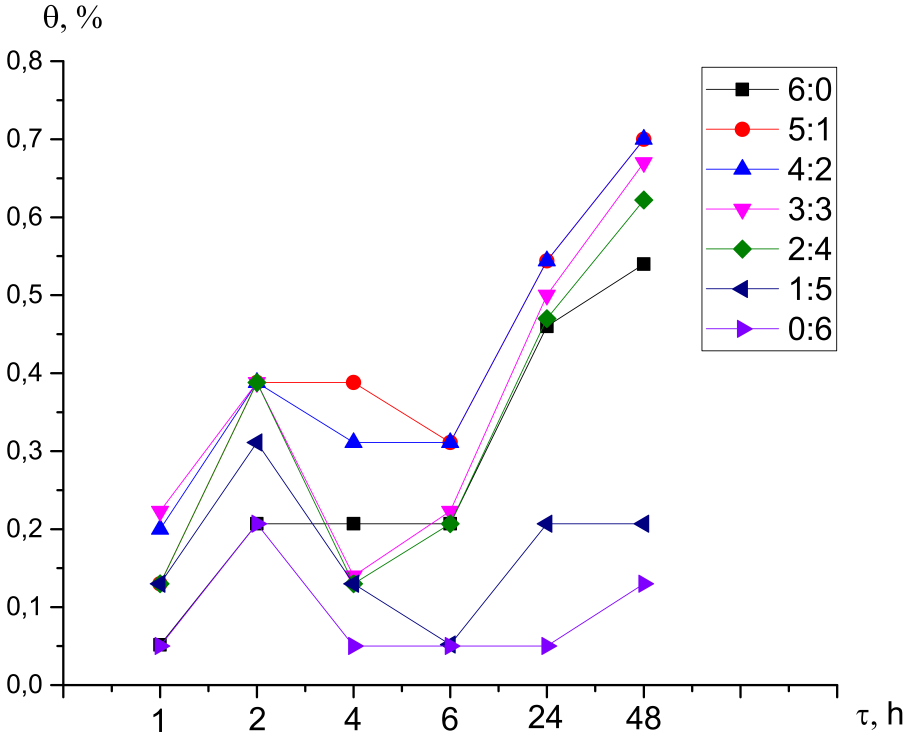


Figure 2 – The dependence on the polymer chain binding degreeof the gPMAA-gP4VP intergel system versus of duration of time in the erbium(III) nitrate pentahydrate medium

Figure 3 shows the dependence of the effective dynamic exchange capacity of the gPMAA-gP4VP intergel system on the molar ratio of hydrogels in time. The obtained data indicate that the mutual activation of polymer hydrogels in the intergel pair leads to a significant increase in the values of the exchange capacity in comparison with the individual hydrogels. The maximum value of the effective dynamic exchange capacity was achieved atgPMAA-gP4VPratio of 5:1 at 48 hours of remote interaction of the hydrogels. Further remote interaction of polymer hydrogels indicates that the gPMAA-gP4VP intergel system approaches

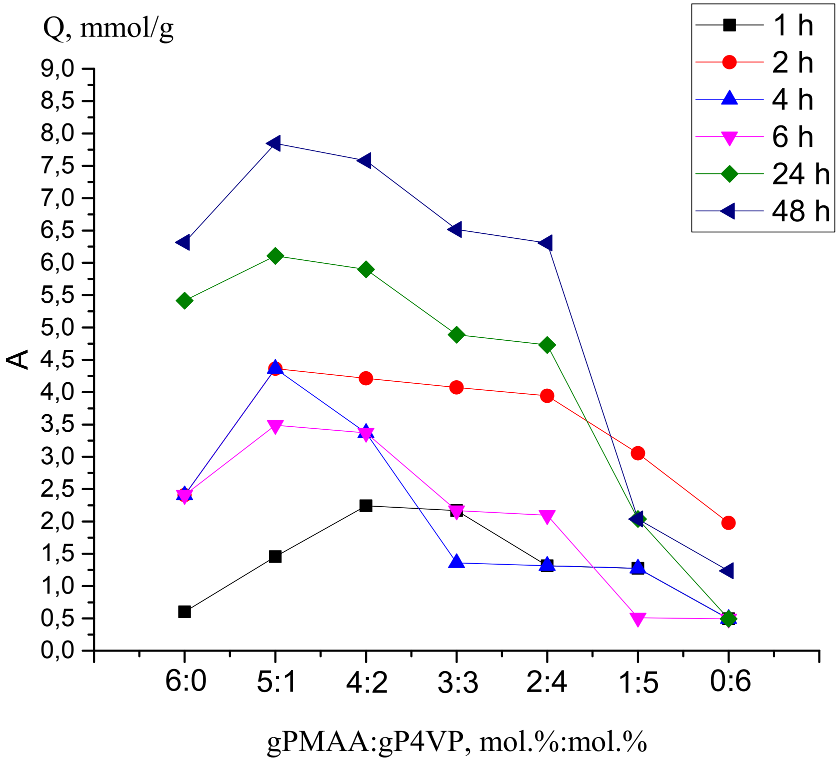


Figure 3 – The dependence on the effective dynamic exchange capacity of the gPMAA-gP4VP intergel system versus of mole ratio of hydrogels at the various duration

the equilibrium statewhich evidenced by slower growth of the effective dynamic exchange capacity as at the beginning of the remote interaction of the hydrogels.

The following ions are present in the solution: -COO$^-$, H$^+$, Er$^{3+}$ and NO$_3^-$. There is an occurrence of these chemical reactions in solution:

1. Dissociation of erbium nitrate along with carboxyl groups dissociation:

$$\text{-COOH} \leftrightarrow \text{-COO}^- + \text{H}^+$$

$$\text{Er(NO}_3)_3 \times 5\text{H}_2\text{O} \leftrightarrow \text{Er}^{3+} + 3\text{NO}_3^- + 5\text{H}_2\text{O}$$

2. Sorption oh erbium ions by polymer hydrogels:

$$3\ \text{-COO}^- + \text{Er}^{3+} \rightarrow \text{-COO}_3\text{Er}$$

$$3 \equiv \text{N} + \text{Er}^{3+} \rightarrow \equiv \text{N}^+{}_3\text{Er}$$

Electrochemical equilibrium in solution depends on these reactions and therecould be changes of electrical conductivity values in dependence of dominance ofany one of them.

**Conclusions.**

1. Individual hydrogels PMAA and P4VP do not possess sufficiently high sorption properties. The degree of erbium ions extraction is 42% and 16% for gPMAA and gP4VP, respectively.
2. The degree of erbium ions extraction in the intergel system reaches the maximum values of 54% at gPMAA-gP4VP ratios of 5:1 and 4:2 after 48 hours.
3. Individual polymer hydrogels PMAA and P4VP have relatively low values of the polymer chain binding degree (0.54% and 0.2%, respectively) with respect to erbium ions due to the absence of the mutual activation phenomenon.
4. The maximum values of the polymer chain binding degreein the intergel systems are 0.7% at gPMAA-gP4VP ratios of 5:1 and 4:2.
5. The obtained results show the possibility of creating erbium sorbents based on intergel systems when the conditions of activated hydrogels interaction with $Er^{3+}$ ions change.

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## Резюме

*Т. К. Джумадилов, Р. Г. Кондауров, Х. Химерсен, А. М. Иманғазы*

### ЭРБИЙ ИОНДАРЫН СОРБЦИЯЛАУ БАРЫСЫНДА ИНТЕРГЕЛЬДІ ПОЛИМЕТАКРИЛ ҚЫШҚЫЛЫ ЖӘНЕ ПОЛИ-4-ВИНИЛПИРИДИН ГИДРОГЕЛЬДЕРІНІҢ ӨЗАРА ӘСЕРЛЕРІ

Полиметакрил қышқылы гидрогелі (ПМАҚг) – поли-4-винилпиридин гидрогелі (П4ВПг) интергелді жүйесімен эрбий иондарын сорбциялау процесі зерттелді. Полиметакрил қышқылы гидрогелінің өзін – өзі ұйымдастыруына негізгі гидрогелдің құрылымы анағұрлым әсер ететіні анықталды. ПМАҚ және П4ВП жекелеген гидрогелдерінің эрбий иондарын шығару дәрежесі сәйкесінше 42% және 16% құрайды. 83%ПАҚг-17%П4ВПг және 67%ПАҚг-33%П4ВПг қатынастарында 54% эрбий шығарылады. ПАҚжәне П4ВП полимерлік гидрогелдері полимерлік тізбектердің байланысу дәрежесінің салыстырмалы төмен мәндеріне ие (сәйкесінше 0,54% және 0,20%).

**Түйін сөздер:** интергельді жүйе, сорбция, $Er^{3+}$ иондары, гидрогельдер, полиметакрил қышқылы, поли-4-винилпиридин.

## Резюме

*Т. К. Джумадилов, Р. Г. Кондауров, Х. Химерсен, А. М. Иманғазы*

### ВЛИЯНИЕ ЭФФЕКТА ДАЛЬНОДЕЙСТВИЯ МЕЖДУ ПОЛИМЕТАКРИЛОВОЙ КИСЛОТОЙ И ПОЛИ-4-ВИНИЛПИРИДИНОМ НА СОРБЦИОННУЮ СПОСОБНОСТЬ К ИОНАМ ЭРБИЯ

Изучен процесс сорбции ионов эрбия интергелевой системой гидрогель полиметакриловой кислоты(гПМАК) – гидрогель поли-4-винилпиридина (гП4ВП). Установлено, что значительное влияние на самоорганизацию гидрогелей ПМАК оказывает структура основного гидрогеля. Степень извлечения ионов эрбия индивидуальных гидрогелей ПМАК и П4ВП составляет 42 и 16%, соответственно. При соотношениях 5:1 (83%гПМАК-17%гП4ВП) и 4:2 (67%гПМАК-33%гП4ВП) извлекается до 54% эрбия в обоих случаях. Полимерные гидрогели ПМАК и П4ВП обладают относительно невысокими значениями степени связывания полимерной цепи (0,54 и 0,20%, соответственно).

**Ключевые слова:** интергелевая система, сорбция, ионы $Er^{3+}$, гидрогели, полиметакриловая кислота, поли-4-винилпиридин.

УДК 677.027.62

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# FIRE RETARDANT OF CELLULOSE TEXTILE MATERIALS BASED ON SOL-GEL COMPOSITION

**Abstract.** The article describes using the tetroetokisilane, thiourea and fire retardant to impart fireproof properties to cellulose textile materials. The influence of concentration of the initial components, temperature and duration of heat treatment on retardant properties was studied. The morphology of the surface of fibers of textile materials and elemental microanalysis of the fiber surface structure is studied.

**Key words:** cellulosic textile materials, fire resistance, sol-gel, tetro-ethoxysilane, thiourea, fire retardant.

**Introduction.** At present, a large number of easily combustible fabric materials, representing a significant fire hazard, are used in living quarters. Investigations of the causes of fires show that the interior elements of textiles (curtains, upholstery fabrics, carpeting) not only contribute to the rapid spread of fire, but also are a source of a number of asphyxiating gases in a fire. Reduction of fire danger is possible with the help of measures carried out by chemical methods of fire protection of soft and hard fabric materials. Preventing the development of fire, chemical means of fire protection facilitate firefighting, and in some cases exclude the possibility of a fire [1-3].

The actual problem of modern chemistry of polymers is the creation of materials of low combustibility, as well as the development of specific flame retardants, flame retardants, which in addition to high efficiency should show good compatibility with used polymers and meet environmental safety requirements [4-5].

**The purpose** of this study is to produce cellulose materials with flame retardant properties using sol gel technology.

**Experimental part.** The main component for the preparation of the sol is tetroethoxysilane, water and ethyl alcohol solvent, acetic acid hydrolysis catalyst, article 1030 cotton fabric with a surface density of 147g/m$^2$.

Tetroethoxysilane - is a volatile transparent colorless liquid with a characteristic spicy-sweetish, somewhat similar to an alcohol smell. It is well mixed with organic solvents, water, aqueous solutions of acids.

Ethyl alcohol - is a monohydric alcohol, under standard conditions a volatile, flammable, colorless transparent liquid.

Thiourea-$CS(NH_2)_2$ - thioglyclic acid diamide, white crystals of bitter taste, melting point 180-182 °C (with rapid heating, with slow decomposition); moderately soluble in water, methanol, pyridine, well in 50% aqueous pyridine.

Before carrying out the experimental work, the cotton bleached fabric of the coarse band art. 1030 was washed with a 2% non-ionic detergent at 40° C for 20 minutes and then washed with distilled water and dried. After drying, the desiccator was kept above dehydrated $CaCl_2$ for at least 24 hours to determine the exact sample weighed [6].

**Methods of research.** A sample of cotton fabric measuring 200 × 200 mm after determining the exact weight on an analytical balance was subjected to impregnation in a bath with tetroetoksisilan (at 1: 1: 8) for 1 minute, spin drying was 90%, followed by drying at 75 – 85 $^0$C for 8 - 10 min, then treated fabric was subjected to heat treatment at 110 $^0$C, 130 $^0$C, 150 $^0$C for 2 minutes, followed by rinsing in large amount of distilled water and then drying.

In the second stage after treatment with tetraethoxysilane, the samples were impregnated in aqueous solution of fire retardant and thiourea for 1 minute. After extraction 90%, drying at 75 $^0$C for 3 min in an oven, followed by washing in distilled water and dried at room temperature.

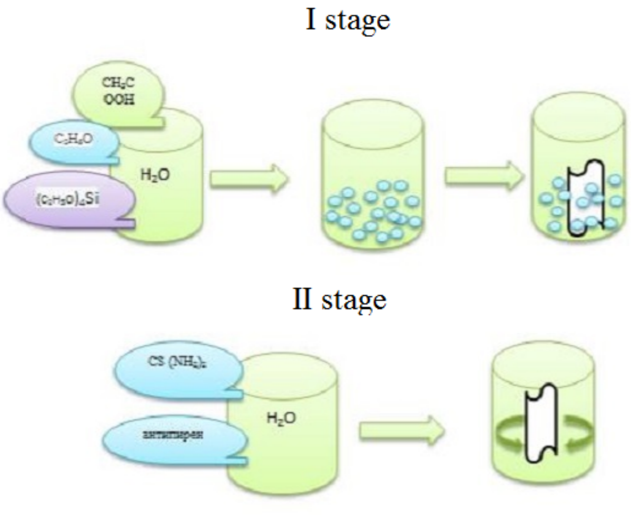

Figure 1 – Scheme for the production of fire-resistant composition

**Results and discussion.** The results of the test of flame retardant efficiency, tensile load and stability of impregnation after 5 washes are shown in table 1. As can be seen from the table, the sol-gel composition used provides a high degree of fire resistance and does not affect the physical and mechonical characteristics of cellulosic textile materials. This indicates the presence of $SiO_2$ coating and fixation of the fire retardant.

In order to fully elucidate the mechanism of interaction of the fire-resistant sol-gel composition with cellulose of cotton fiber, the IR spectra of samples of initial and processed tissues were studied in the work (figure 2). When analyzing the spectra shown in figure 2 and in table 2, it can be seen that the spectra of the cellulose treated with this composition compared to the original cellulose have

Table 1 – Results of the test of flame retardant efficiency and breaking load of treated cellulose materials

| № | Concentration of substances, g/L | | | Length of the char section, mm | | | Breaking load, N | | | Length of the charred area (after 5 washes), mm | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $(C_2H_5O)_4Si$ | CS $(NH_2)_2$ | flame etardant | Heat treatment temperature, ° C | | | | | | | | |
| | | | | 110 | 130 | 150 | 110 | 130 | 150 | 110 | 130 | 150 |
| 1 | Source sample | | | 220 | 220 | 220 | 202 | 202 | 202 | 220 | 220 | 220 |
| 2 | 100 | 60 | 200 | 110 | 123 | 124 | 203 | 199 | 198 | 135 | 182 | 166 |
| 3 | | | 300 | 102 | 109 | 113 | 201 | 202 | 199 | 121 | 139 | 165 |
| 4 | | | 400 | 95 | 105 | 112 | 205 | 200 | 196 | 112 | 139 | 124 |

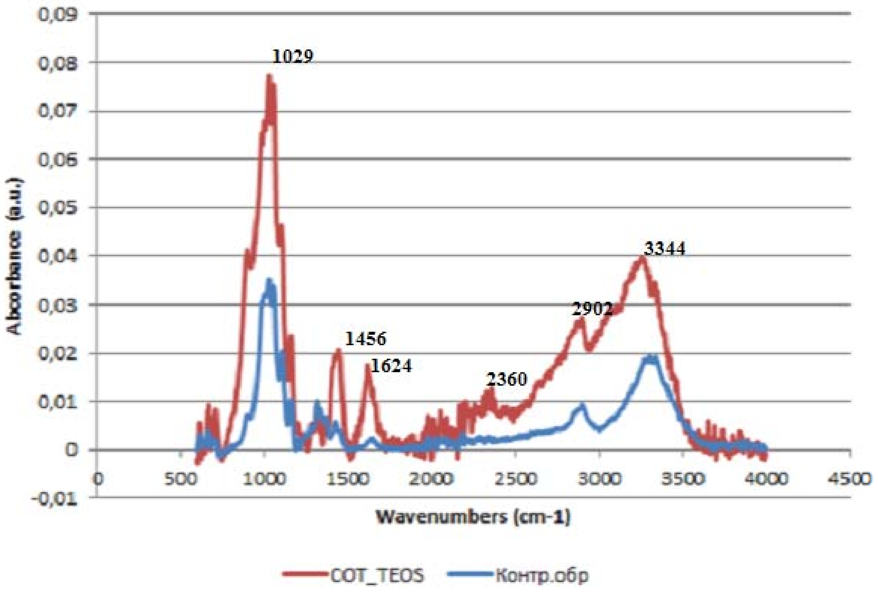

Figure 2 – IR spectra of a control sample and treated cellulose fibers with tetroethoxysilane

Table 2 – Basic vibration frequencies of processed cellulose textile materials

| The oscillation frequencies ($cm^{-1}$) | | Oscillatory modes |
|---|---|---|
| Counter. arr. | Arr. with TEOS | |
| 3336 | 3344 | $(NH_2)$ |
| 2904 | 2902 | (C-H) |
| | 2360 | (P-H) |
| | 1624 | (N-H) |
| | 1456-1392 | (C-N) |
| 1031 | 1029 | (Si-O- Si) |

undergone significant changes. In the IR spectrum of the processed sample, all absorption bands are retained, characteristic of untreated cotton fiber. The absorption bands of the processed sample indicate the presence of Si-O-Si bond bonds in the 1029 and 1031 cm$^{-1}$ regions, NH groups in the 1624 cm$^{-1}$ region, and also the P-H groups in the 2360 cm$^{-1}$ region, CN groups in the regions 1392-1456 cm$^{-1}$.

Based on the foregoing, it can be concluded that the interaction of the composition with the macromolecules of cellulose leads to a significant change in the absorption bands of the processed samples. Thus, taking into account the studies carried out, it can be concluded that when treating cellulose with this composition, chemical bonds are formed between the macromolecules of cellulose and sizing agents.

Investigation of the morphology of the surface of the fibers of textile materials and elemental microanalysis of the fiber surface structure used an auto-emission scanning electron microscope JSM-6490LA (Japan) with the X-ray spectral analyzer system JED-2300 Analysis Station. Based on the result of scanning electron microscopy, a polymeric layer is formed on the surface of the treated tissues in the form of an oxide-silicon matrix (figure 3). Figure 3 clearly shows that fire retardant particles are present on the treated fiber on the surface of the fiber, fire retardant plates of various shapes are noticeable.

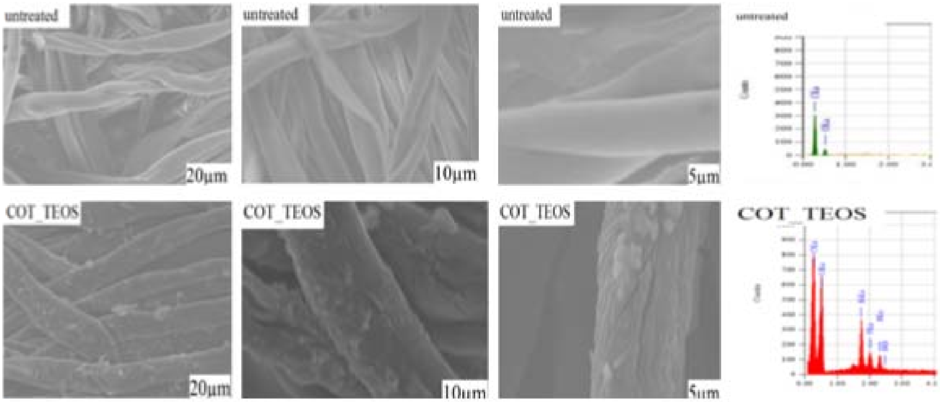

Figure 3 – Electron microscopic images of cotton fabric and treated with flame retardant composition with different resolution and energy dispersive microanalysis

According to the energy-dispersive microanalysis, the figure shows the presence of carbon and oxygen, which is natural for cellulosic materials. After processing, particles of Si, P, S are formed on the surface of the treated fabric and are distributed rather unevenly.

**Conclusion.** Analysis of the results of the study allows us to draw the following conclusions:

It is shown that this method of impregnating cellulosic textile materials in a precursor, followed by drying and heat treatment and flame retardant, makes it possible to obtain a silica coating with a fixed flame retardant of high degree.

The IR spectra data confirm the appearance of a chemical bond between the cellulose macromolecules and the flame-resistant sol-gel composition.

Using the method of electron-scanning microscopy, it has been established that the treatment of tissues with the developed compositions leads to a change in the morphology of the surface of the fibers.

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## Резюме

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### ОГНЕСТОЙКОСТЬ ЦЕЛЛЮЛОЗНЫХ ТЕКСТИЛЬНЫХ МАТЕРИАЛОВ НА ОСНОВЕ ЗОЛЬ-ГЕЛЬ КОМПОЗИЦИИ

В статье приведен новый способ разработки огнестойких целлюлозных текстильных материалов золь-гель методом с применением тетроэтоксисилана. Основным результатом проведенного исследования является разработанная экологически безопасная технология получения огнестойкой золь-гель композиции, которая протекает в две стадии. На первой стадии текстильный материал пропитывается в прекурсоре в течение минуты, а на второй – в ванне с антипиреном. Исследовано влияние параметров обработки на эффективность огнезащитности, на физико-механические свойства ткани и на стойкость огнестойкой золь-гель композиции после 5-ти стирок. Выявлено, что наилучшей эффективностью огнезащитности обладают образцы, обработанные при концентрации тетроэтоксисилана равной 100 г/л и прошедшие термическую обработку при 150 °С. Данные ИК-спектров подтверждают появление химической связи между макромолекулами целлюлозы и огнестойкой золь-гель композиции. Также применен метод электронной микроскопии, результаты которой доказывают наличие функционального покрытия и фиксации антипирена в его объеме. Результаты исследования могут быть применены в отделочном производстве текстильных целлюлозосодержащих материалов.

**Ключевые слова:** целлюлозные текстильные материалы, огнестойкость, золь-гель, тетроэтокисилан, тиомочевина, антипирен.

## Резюме

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## ЗОЛЬ-ГЕЛЬ КОМПОЗИЦИЯ НЕГІЗІНДЕГІ ЦЕЛЛЮЛОЗАЛЫ ТЕКСТИЛЬ МАТЕРИАЛДАРЫНЫҢ ОТҚА ТӨЗІМДІЛІГІ

Мақалада тетроэтоксисилан қолдана отырып золь-гель әдісімен отқа төзімді целлюлозалы текстиль материалын алу технологиясы сипатталған. Зерттеу жұмысының негізгі нәтижесі болып экологиялық қауіпсіз отқа төзімді золь-гель алу әдісі болып табылады. Бұл әдіс екі деңгейде жүзеге асады, біріншісі: текстиль материалының үлгісін золь прекурсорында сіңіріп, екінші деңгейде антипиренмен өңдейміз. Өңдеу параметрлерінің отқа төзімділік пен үзілу жүктемесіне, сонымен қатар өңдеу композициясының тұрақтылығына әсері зерделенді. Ең жақсы нәтижелерді тетроэтоксисиланның 100 г/л мөлшеріндегі 150 °C термоөңдеу өткен текстиль материалдары көрсетті. Сонымен қатар зерделенген ИК-спектр нәтижесі бойынша текстиль материалындағы целлюлоза мен отқа төзімді золь-гель композиция арасындағы химиялық байланыстың бар екенін көрсетті. Қолданылған электронды микроскоп әдісінің нәтижесі бойынша өңделген текстиль материалының бетінде функционалды жабын мен антипиреннің берік бекітілгенін көрсетті. Зерттеу нәтижелерін целлюлозалы текстиль материалдарын өңдеу өндірісінде қолдануға болады.

**Түйін сөздер:** целлюлозалы текстиль материалдары, отқа төзімділік, золь-гель, тетроэтоксисилан, тиомочевина, антипирен.

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# BASIC MAIN POLYPHENOLIC COMPOUNDS OF SOME PLANT SPECIES

**Abstract.** Data of some plant species containing polyphenolic compounds have been summarized. The dominant phenolic compounds of the investigated taxa were identified.The promising plant species for isolation of polyphenolic compounds as potential sources of original domestic pharmaceutical substances were determined.

**Key words:** polyphenolic compounds, flavonoids, glycosides, chalcones, *Asteraceae, Rosaceae, Salicaceae, Polygonáceae, Lamiáceae.*

Among the renewable sources of bioactive substances a special place belongs to plants traditionally used in folk and official medicine. There are some plant groups which are common or predominant in large areas and are interested for chemical and pharmacological studies.Plants of this kind are represented by the species of the following familiesin the territory of Kazakhstan:*Asteraceae* (*Compósitae*), *Salicaceae, Rosaceae, Polygonáceae, Lamiáceae* covering an extensive territory in the natural flora.

At present, researchers attention attracted to the phenolic compounds including flavonoids. Their interest in these substances is justified by their practical application in medicine.Flavonoids are referred tothe widespread plant metabolites. The elucidated structures of molecules have been described for over 8000 of flavonoids related to several dozens of structural types. A comprehensive study of flavonoids is done by scientists of major research centers of many countries in the world.The interest in these compounds is constantly growing due to the exclusively valuable properties of flavonoids such as antioxidant activity and related ability of many metabolites of this class toact as agents preventing or inhibiting tumors formation, strengthening blood vessels, protecting liver and a digestive tract, stimulating the brain and heart functions, making them biologically active additives (BAA) in medical and dietarynutrition [1-4].

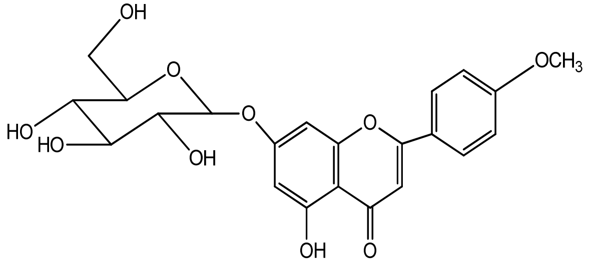
The following plants served as objects of our research of polyphenolic compounds such as *Tanacétum vulgáre*L., *Helichrysum arenarium* L., *Crataégus*, *Populus balsamifera* L., *Origanum vulgaris* L., *Polygonum aviculare* L., *Bídens tripartíta* L., *Ajania fruticulosa* (Ledeb.) Poljak), *Hypericum perforatum* L., *Serratula coronata L.,* and *Carduus*.

*Tanacetum vulgare* L. belongs to the widespreadherbs containing a wide range of biologically active substances: flavonoids, sesquiterpene lactones, essential oils. Flowers of *Tanacetum vulgare* L. are often used in various medicinal forms as the vermicidal and choleretic agents.Flavonoids from flowers of *Tanacetum vulgare* L. are mainly represented by apigenin (5, 7,4'-trihydroxyflavone), acacetin (5,7-dihydroxy-4'-metoxyflavone), luteolin (5,7,3',4'-tetrahydroxyflavone), cynaroside (7-O-b-D-glucopiranoside of 5,7,3',4'-tetrahydroxyflavone), eupatilin (5.7-dihydroxy-6,3',4'-trimetoxyflavone), jaceidin (5,7,4'-trihydroxy-3,6,3'-trimetoxyflavone), jaceosidine (5,7,4'-trihydroxy-3',6-dimetoxyflavone), besides the major compound is acacetine-7-*O-β-D*-glucopiranoside (tilianin **1**) about the yield 0,2% from the air dry raw materials weight [5, 6]. Based on the sum of flavonoids from *Tanacetum vulgare* L. isolated by extraction with ethyl alcohol, the drug Tanaceholwas developed with acholeretic action. The yield of flavonoids amount is 3,1% of the air-dry raw materials. The content of active ingredients (sum of flavonoids and phenolcarboxylicacids) in the product was determined by spectrophotometer and is at least 55% in terms of luteolin [7].

The flowers of *Helichrysum arenarium* (L.) Moench.contain the sum of flavonoids (at least 20 compounds), belonging to different groups: flavones (apigenin, luteolin), flavonols (kaempferol, quercetin, and their glycosides, 3,5-dihydroxy-6,7,8-trimetoxyflavonol glycosides), chalcones (isosalipurposide **2**), flavanonsnaringenin, salipurposide (**3**), and their glucosides. Besides, the major polyphenolic compounds include chalconeisosalipurposide (**2**) and flavanonsalipurposide (**3**), but there is no agreement which of these components is a predominant one [8].

The preparation Flamin was developed based on the amount of pharmacologically active flavonoids from flowers of *Helichrysum arenarium* L. The main phenolic ingredient in the product Flamin is a chalconeisosalipurposide (**2**). When examining the chemical composition of *Helichrysum arenarium* L., naringin and its water-soluble derivatives prunin, quercetin, apigenin, naringenin, as well as apigenin-5-*O*-glucoside and isosalipurposide (**2**) were determined. It was established by the molecular absorption spectroscopy that the analyzed extract contains 73.48 mg of flavonoids in terms of rutin, or 17.94 mg in terms of quercetinper 1g of dry extract which is 20.99 and 5.13%, respectively [9].

Flavonoid apigenin was detected in the raw flowers of *Helichrysum arenarium* L. using the HPLC method, which content varies within a range from 0.1453± 0.0068% to 0.1657 ± 0.0085% based on the dried raw material [10].



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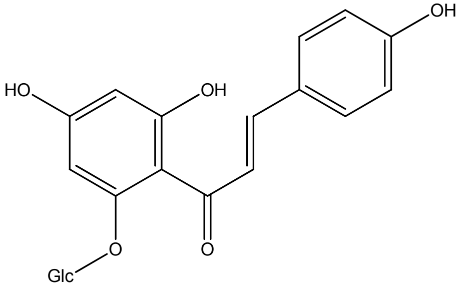

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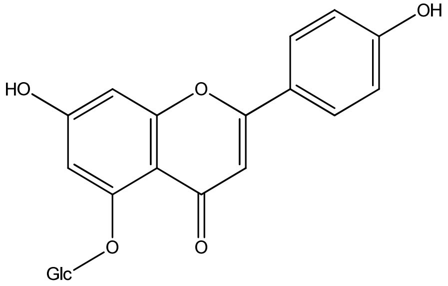

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In plants of the genus *Crataégus,* biologically active substances are flavonoids, anthocyanins, triterpenoids, which are used to prepare decoctions, extracts, tinctures, and tablets. Among flavonoids which are found in the leaves, flowers, and fruits of *Crataégus* there are santin, 5-hydroxyaurantine, apigenin, kaempferol, quercetin, apigenin-7-glucoside, kaempferol-3-galactoside, hyperoside (quercetin-3-galactoside), vitexin (apigenin C-glycoside), vitexin-4'-rhamnoside, vitexin-4'-rutinoside and also (-) and (+) epicatechins [11]. C-glycosides dominate in the leaves of *Crataégus*, while biosides, di-and leucoanthocyanidins ofoligoglycosides, and other flavane derivatives are synthesized in flowers [12].From leaves, flowers and fruits of *Crataegus stevenij* Pojark. 7 flavonoids were isolated and characterized;moreover, the lipophilic flavonoid scutellarian 4'7-dimethyl ester had beenisolated for the first time [13]. The main component of a flavonoid fraction in all organs of *Crataegus stevenij* Pojark. is hyperoside (**4**). The total flavonoid content in fruits of *Crataegus stevenij* Pojark. is within the range from 0,057 to 0,085% [14], the minimum content of flavonoids is observed in leaves and flowers 0,89%and1,39%, respectively. The hyperoside content in flowers ranges from 0,6 to 0,9%, in fruits - from 0,028 to 0,04%, in shoots - from 0,25 to 0,39% [15].

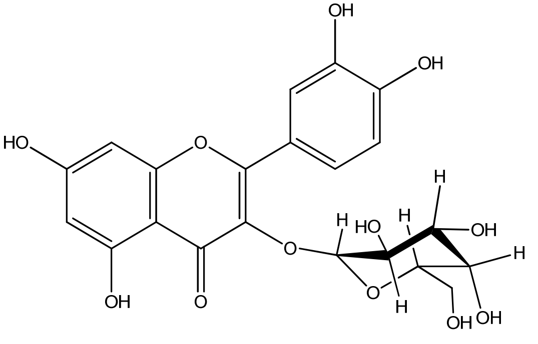
The phenolic composition of *Crataegus* leaves was studied;four new monoterpene glycosides and a new phenolic glycoside pinnatifidanoside E were isolated and identified in the process [16].

The fruits of two species *Crataegus monogyna*Jacq. And *Crataegus azarolus* L. were examined using the HPLC method. The phenolic composition of the investigated fruits showed some similarities and differences in the ratio of polyphenols between the two species. Twenty phenolic compounds were identified and distributed in four subclasses: four phenolic acids including three hydroxycinnamic acids and one hydroxybenzoic acid, eight flavonoids representing the most abundant subclass including six glucosylatedflavonols and two flavones; two anthocyaninswerepresent in the form of cyanidin glycosides with cyanidin-3-*O*-glucoside as the most common, and four flavanols. Epicatechinwas identified in all the fruit parts of both species [17].

*Populus* L. genus belongs to the family *Salicaceae* which is curious in its diversity, reserves, and distribution. *Populus* L. gemma are rich in the extractives with a broad spectrum of biological activity. It was previously determined that ethanol is the most effective solvent to extract substances from *Populus* L. gemma both from the technological and economic perspectives. The share of alcohol-soluble substances averages from 35 to 45% of the raw material weight depending on atree development stage [18].

Phenol glucosides, phenolcarboxylic acids (caffeic, ferulic, hydroxycinnamic), flavonoids, tannins were found in *Populus* L.bark and gemma [5]. It is well known that *Populus* L. gemma feature the presence of flavanones, flavones, and flavonols [19-20]. Thus, in the gemma of P. *nigra* L., P. *trichocarga* Toor. ex Gray, P. g*randidentata* Michx. growing in Germany the following phenolic compounds were identified: p-hydroxyacetophenone, dimethyl caffeic acid, cinnamoylcinnamate, vanillin, and a number of flavonoids: chrysin, chrysin-7-methyl ester, apigenin, galangin, 7-methylgalangin, 7-methylkaempferol, quercetin, 7-methylquercetin,3,7-dimethyl quercetin, pinocembrin, 7-methylpinocembrin, 2,5-dihydroxy-7-methoxyflavanone and 2',6'-dihydroxy-4'-methoxychalcone [21].

In *Populus balsamifera* L. gemma, the content of the following compounds was determined: pinostrobin (**5**), pinocembrin (**6**), chrysin, tectochrysin, apigenin, kaempferol, quercetin, myricetin, galangin, izalpinin, isorhamnetin, rhamnetin, 2,6-dihydroxy-4'-methoxychalcone, and 4',6'-dihydroxychalcone. In the extract from *Populus balsamifera* L. gemma, theprotocatechuic, gallic, trans-cinnamic, p-coumaric, ferulic, and caffeic acids were also found. The dominant flavonoids of the *Populus balsamifera* L. gemma are pinostrobin (**5**) and pinocembrin (**6**) [22-23].



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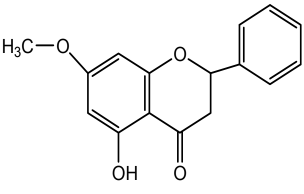

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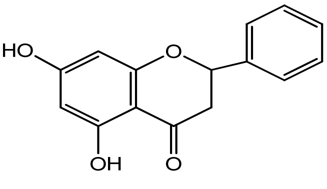

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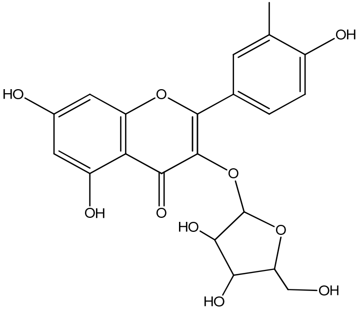
Plants of the genus *Origanum*are characterized by the presence of flavonoids (rutin, quercetin, luteolin, citrine, hesperidin, and their glycosides). The chemical composition of biologically active compounds (BAC) of *Origanum vulgaris* L. herb was studied which includes the essential oil components, triterpenoids, saponins, phenolcarboxylic acids, tannins, and flavonoids. Among the components of a polyphenol complex in *Origanum vulgaris* L. were noticed luteolin and its glycosides, cosmosyne (apigenin-7-glucoside), chrysin, and its glycosides, i.e. the flavonoid fraction of the plant is mainly represented by flavone derivatives. The total content of flavonoids in *Origanum vulgaris* L. samples varies in the range from 2,62 to 2,79% [24-27].

A promising source of polyphenolic compounds is *Polygonum aviculare* L. The aerial parts of *Polygonum aviculare* L. contain flavonoids (up to 9,4%), tannins, essential oils, carotene, vitamin C, vitamin $K_1$, saponins, coumarins (umbelliferone and scopoletin), anthraquinone glycosides. In the flowering plant about 30 glycosides of flavonoid nature were observed, which aglycons are rhamnetin, kaempferol, quercetin, and myricetin. The main flavonoid of *Polygonum aviculare* L. is considered avicularin (**7**) [28].

The chemical composition of *Polygonum aviculare* L. herb harvested during the flowering period was investigated. During the chemical composition analysis of flavonoids, 3 substances of a flavonoid character were identified and qualitatively determined: liquiritin (liquiritigenin4'-*O*-*β*-*D*-glucopyranoside), avicularin (quercetin 3-*α*-*L*-arabinofuranoside) (**7**), cinnaroside (luteolin-7-*O*-*β*-*D*-glucopyranoside). The latter ones, liquiritinand cynaroside, were isolated from *Polygonum aviculare* L. for the first time [29].

For *Bidens tripartita* L. antioxidant, antimicrobial, antifungal, hepatoprotective, immunostimulating, and hypotensive activities were established. These types of activity are associated with the presence of a series of phenolic compounds (flavones, chalcones, aurones), essential oils, and polyacetylenes in the herb [30, 31].

In research [32], the composition of the alcoholic extracts of *Bidens tripartita* L. is discussed where the main component of which is luteolin-*O*-7-glucopyranoside (cynaroside **8**). Luteolin and its glycosides were also defined in the



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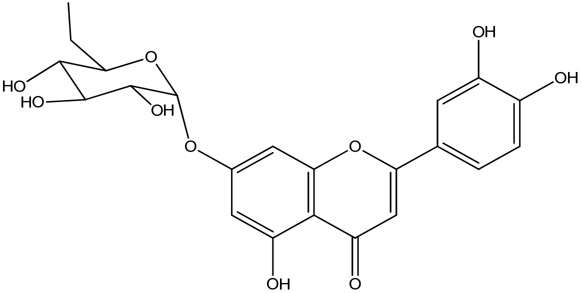

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extract. The total amount of the above-mentioned compounds in extracts is about 55% of all identified components. About 20% of all compounds contenting the extract belong to hydroxycinnamic acids – the derivatives of caffeic and quinicacids, and the same amount to chalcones with hydroxyl groups in the 3'- and 4'-positions.

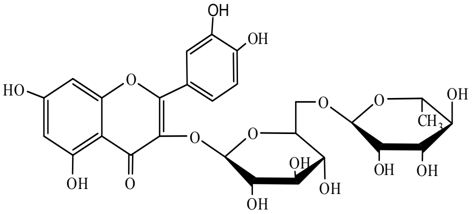
From the above-ground parts of *Bidens tripartita* L. fourteen phenolic compounds were isolated (butein, 3,2',4'-trihydroxy-4-methoxychalcone, 4'-*O*-*D*-glucopyranosyl-2'-3-dihydroxy-4-methoxychalcone, okanin, okanin4'-*O*-*D*-glucopyranoside, okanin4'-*O*-(6''-*O*-acetyl-*D*-glucopyranoside), bidenoside, luteolin, diosmetin, luteoside, achilarin, quercetagetin 3,6,3'-trimethyl ether, sulfuretin, 6,7,3',4'-tetrahydroxyauron), and two polyacetylenes [33].

As known, *Hypericum perforatum* L. herb has a complex chemical composition represented by flavonoids (rutin, hyperoside, bisapigenin, quercetin, luteolin, kaempferol, myricetin), anthracene derivatives (hypericin, pseudohypericin), and essential oils [34]. The following phenolic compounds were isolated from *Hypericum perforatum* L.: rutin, hyperoside, quercetin, 6,8'-diquertcetin, 3,8'-bisapigenin, phenylpropanoid, and a chlorogenic acid. Moreover, 3,8'-bisapigenin and 6,8'-diquertcetin have been isolated for the first time [35]. A comparative phytochemical study of samples of *Hypericum perforatum* L. and *Hypericum maculatum* Grantz was performed using the HPLC method. It has been established that the predominant flavonoid in *Hypericum maculatum* Grantz herb is hyperoside, and in *Hypericumperforatum* L. is rutin (**9**). Quercetin is observed in both species; however, the content of this component is low. The flavonoid bisapigeninis found only in *Hypericum perforatum* L. [36].

During the study of a phenolic composition of *Ajania fruticulosa* (Ledeb.) Poljak., oxyflavones 5,3',4'-trioxy-3,6,7-trimethoxy flavone, artemisetin (**10**), axillarin, phenolcarboxylic, chlorogenic and caffeic acids were identified [37, 38].

*Serratula coronata* L. is a promising source of ecdysteroids,its aerial parts also contain the phenolic compounds (apigenin, rutin, quercetin, luteolin), tannins, coumarins, essential oils, sesquiterpene lactones, and carotenoids. The majority of flavonoids in the above-ground part of *Serratula coronata* L. is concentrated in the leaves and ranges from 14,87 to 18,50%, much less in the inflorescences (4,18-5,88%), and a minimum amount in the stems (2,61-3,44%) in terms of rutin. The predominant flavonoid (aglycon) of the aerial part of the plant is 3-methylquercetin (**11**), which content in the inflorescences ranges from 10,4 to 11,9%, in leaves from 2,5 to 5,1%, and in stems – from 1,2 to 2,9% (in terms of the flavonoids total).

The quantitative content of phenolic compounds in *Serratula coronata* L. was studied. During the compositional analysis of flavonoids, 3 substances of a flavonoid nature were determined and identified, they were: apigenin (5,7,4'-trihydroxyflavone), 3-methylquercetin (5,7,3',4'-trihydroxy-3-methoxyflavone **11**), isokaempferide(5,7,4'-trihydroxy-3-methoxyflavone) [39].



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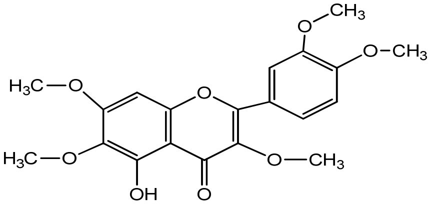

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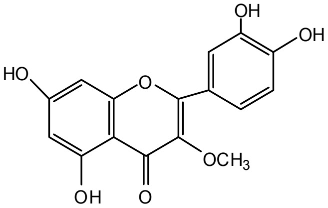

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In *Carduus* herb, saponins, coumarins, sesquiterpene lactones, and flavonoids (silymirin, sidichristin, and silidionin) were found [4].

The ethanol extracts of four *Carduus* species (*Carduus argyroa* Biv., *Carduus nutans* subsp. macrocephalus (Desf.) Nyman, *Carduus pycnocephalus* L., *Carduus cephalanthus* Viv.) were studied by HPLC; it was revealed that the phenolic compounds kaempferol-3-*O*-glucoside, kaempferol-3-*O*-rhamnoside, luteolin, apigenin, kaempferol, diosmetin, and tricin are present in all samples. The diosmetin derivatives were found only in *C.cephalanthus* and *C. pycnocephalus*, whereas luteolin*O*-arabinosylglucoside, apigenin*O*-rhamnosylglucoside and apigenin-7-*O*-glucoside were present only in *C. argyroa* and *C. nutans* subspecies [40].

The methanol extract of *Carduus* was studied using HPLC, and eight flavonoids and flavonoid glycosides were detected. It was revealed that among all identified flavonoids luteolin and apigeninhave the highest content [41].

From *Carduus pycnocephalus*L.the following flavonoid compounds were isolated and identified: apigenin, kaempferol, diosmetin, and their glycosides [42].

Thus, as a result of integrating data on the composition of polyphenolic compounds of some plant species of the families *Asteraceae* (*Compositae*), *Salicaceae*, *Rosaceae*, *Polygonáceae*, and *Lamiáceae* the promising flavonoid plants have been identified. The provided information helps evaluate the qualitative composition of polyphenolic compounds in plants and determine their major components.The promising sources for production of biologically active flavonoids (apigenin, tilianine, isosalipurposide, hyperoside, pinostrobin, pinocembrin, and avicularin) are *Helichrysum arenarium* L., *Polygonum aviculare* L., *Bídens tripartíta* L., *Populus balsamifera* L. gemma, *Tanacétum vulgáre* L., *Crataégussanguinea* Pall.

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## Резюме

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### ОСНОВНЫЕ ПОЛИФЕНОЛЬНЫЕ СОЕДИНЕНИЯ НЕКОТОРЫХ ВИДОВ РАСТЕНИЙ

Обобщены данные по полифенольным соединениям некоторых видов растений. При этом определены доминирующие фенольные соединения изучаемых таксонов. Выявлены перспективные виды растений для выделения полифенольных соединений – потенциальных источников оригинальных лекарственных веществ.

**Ключевые слова:** полифенольные соединения, флавоноиды, гликозиды, халконы, *Asteraceae, Salicaceae, Rosaceae, Polygonáceae, Lamiáceae.*

## Резюме

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### ӨСІМДІКТЕРДІҢ КЕЙБІР ТҮРЛЕРІНІҢ НЕГІЗГІ ПОЛИФЕНОЛДЫ ҚОСЫЛЫСТАРЫ

Өсімдіктердің кейбір түрлерінің полифенолды қосылыстары туралы мәліметтер жинақталды. Сонымен қоса зерттелген таксондардағы басым фенолды қосылыстар анықталды. Бірегей дәрілік заттардың ықтимал көздері болып табылатын полифенолды қосылыстарды бөліп алу үшін қолданылатын келешекті өсімдіктүрлері анықталды.

**Түйін сөздер:** полифенолды қосылыстар, флавоноидтар, гликозидтер, халкондар, *Asteraceae, Salicaceae, Rosaceae, Polygonáceae, Lamiáceae.*

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# FEATURES OF SORPTION CALCIUM IONS BY INTERGEL HYDROGELS OF POLYMETHACRYLIC ACID - POLY-4-VINYLPYRIDINE AND POLYACRYLIC ACID –POLY-2-METHYL-5-VINYLPYRIDINE

**Abstract.** Process of sorptioncalcium ions by intergelhydrogelsystems of polymethacrylic acid – poly-4-vinylpyridine and polyacrylic acid –poly-2-methyl-5-vinylpyridine were studied by methods of conductometry, pH-metry, ion-metry. Calcium sorption process with individual rare-crosslinked hydrogels of PAA, PMAA, P4VP, P2M5VP and intergel systems hPMAA-hP4VP, hPAA-hP2M5VP were accompanied by significant changes of initial electrochemical properties of calcium chloride solution (specific electric conductivity and pH decreases with time of sorption of the metal ions). Individual hydrogels of PAA, PMAA, P4VP, P2M5VP relatively fast reach electrochemical equilibrium in salt solution, consequent slight increase after 24 hours is evidence of this phenomenon, sorption degree after 2 days of sorption of the metal ions reaches 70%. Formation optimal conformation of the polymers occurs in the intergel systems at ratios hPMAA:hP4VP=4:2 and hPAA:hP2M5VP=2:4, however, ionization process of macromolecules are complicated due to the fact, that structures of hPMAA and hP2M5VP have bulk methyl substituent, which interfere undfolding of polymer globe in process of its ionization. Sorption degree of calcium ions by the intergel systems hPMAA:hP4VP=4:2 and hPAA:hP2M5VP=2:4 is 93% and 92% respectively.

**Key words:** intergelsystem, mutualactivation, sorption, $Ca^{2+}$ions, hydrogels, polyacrylic acid, polymethacrylic acid, poly-4-vinylpyridine, poly-2-methyl-5-vinylpyridine.

**Introduction.** Water treatment is the process of water coming from a natural water source to bring its quality in line with the requirements of technological consumers.It can be produced on water treatment facilities or installations for the needs of the municipal economy, practically in all industries (for example, heat-generating enterprises). To evaluate the quality of drinking water, various methods are used, suggesting the study of hydrochemical, microbiological and other indicators [1].Water treatment consists in the release of water from coarsely dispersed and colloidal impurities and salts contained in it, thereby preventing deposition of scale, removal of salts by steam, corrosion of metals, as well as contamination of processed materials when water is used in technological processes.

As you know, the high content of calcium and magnesium ions makes water hard and unsuitable for drinking. Boiling of hard water promotes the appearance of scale on the walls of the vessel [2]. The peeling of the accumulated scale causes malfunctions in the operation of household appliances. American scientists carried out a study, thanks to which it was possible to establish that a layer of scale with a thickness of one and a half millimeter reduces the heat transfer about

15%, the thickness of the scale in three millimeters - about 25%, etc. In addition, such harmful impurities in water, like calcium and magnesium compounds, require for heating the liquid up to 25% more electricity.

Over 90% of heating devices become faulty of constantly contacting with hard water [3-4]. Dissolved in water, calcium and magnesium compounds adversely affect the quality of the laundry washed in it, reducing its "life" from 15 to 30%, while increasing by 30% the amount of consumable washing powder. If you use special cosmetic products during washing, their useful properties become ineffective at the contact with hard water.

With prolonged washing with hard water, the human skin also suffers. This leads to clogging of the pores, weakening of protective properties of the fatty film on the surface of the skin, which causes flaking, irritation and the appearance of various rashes [5]. In addition to skin itself, the hair also suffers, which is accompanied by symptoms such as itching, dandruff. The very hair becomes dry and tough to the touch, stop "obeying", visually acquire a neglected appearance.

Such harmful impurities in water, like calcium and magnesium, are able to accumulate in the body, leading eventually to the deposition of stones in the kidneys and obstruction of the vessels [6]. Do not drink hard water if you do not want serious health problems.

On the other hand, in many industrial solutions, there are problems of separation of alkaline-earth metals ions from the ions of target metal. In leaching solutions, after extraction of main ion (for example, uranyl, gold, zinc ions, etc.), calcium ions and other alkaline and alkaline earth metals remain.

At present, industrial water treatment plants assume the use of ion exchange resins [7]. The purpose of this work is study the features of sorption calcium ions withintergel systems based on the rare-crosslinked polymer hydrogels of acid and basic nature.

## EXPERIMENTAL PART

*Equipment.* Specific electric conductivity was measured on conductometer MARK-603 (Russia), pH of the solutions was measured on pH-meter MetrohM 827 pH-Lab (Switzerland). Measurement of $Ca^{2+}$ ions were made on ion-meter I-160MI (Russia).

*Materials.*Investigations the solution of calcium chloride containing 50 mg/Lwere made. Hydrogels of polyacrylic (PAA) and polymethacrylic (PMAA) acids were synthetized in presence of crosslinking agent N,N-methylene-bis-acrylamide and redox system $K_2S_2O_8$–$Na_2S_2O_3$. Hydrogel of poly-4-vinylpyridine (P4VP) was synthetized (2% of crosslinking agent) by “Sigma Aldrich” company. Hydrogel of poly-2-methyl-5-vinylpyridine (P2M5VP) was synthetized in medium of dimethylformamide in presence of crosslinking agent epichlorohydrine. Intergel pairs hydrogel of polymethacrylic acid – hydrogel of poly-4-vinylpyridine and hydrogel of polyacrylic acid – hydrogel of poly-2-methyl-5-vinylpyridinewere made from the synthetized hydrogels. Swelling degrees of the hydrogels are: $\alpha_{(hPAA)}$=29.13 g/g, $\alpha_{(hPMAA)}$=23.76 g/g; $\alpha_{(hP4VP)}$=2.65 g/g, $\alpha_{(hP2M5VP)}$=1.98 g/g.

*Experiment.* Experiments were made at room temperature. Studies were conducted as follows: calculated amount of each hydrogel in dry state was put in special glass filters, pores of which is permeable for low-molecular ions and molecules, but impermeable for hydrogels dispersion. After that the parameters (specific electric conductivity, pH, $Ca^{2+}$ ions concentration) were measured during 48 hours. Measurements of above mentioned parameters were made in absence of the hydrogels in the solutions.

## RESULTS AND DISCUSSION

Sorption of low-molecular ions (calcium ions) from solution is usually accompanied by significant changes of electrochemical properties of the salt. It should be noted that conformation of the macromolecules is also changed during their self-organization during interaction with the metal solution. Sorption process of calcium ions by functional groups of the polymer hydrogels of acid and basic nature can be described by the following chemical reactions:

$$-COOH + Ca^{2+} \rightarrow (-COO)_2Ca + 2H^+ \quad (1)$$

$$N^+H + Ca^{2+} \rightarrow N^+{}_2Ca + 2H^+ \quad (2)$$

As seen from the reactions 1 and 2, sorption of calcium ions by the carboxyl group and heteroatom of pyridine ring occurs due to formation of coordination bonds.

*Sorption of calcium by intergel system hPMAA-hP4VP.* Figure 1 represents dependence on specific electric conductivity of calcium chloride from hPMAA:hP4VP molar ratios in time. Sorption of calcium provides decrease of the metal amount in the solution (in accordance with reaction 1), result of what is decrease of electric conductivity with time. It is seen from obtained data that maximum decrease of electric conductivity is observed at hPMAA:hP4VP=4:2 ratio, exact minimum is observed at 48 hours of remote interaction of the polymers. Also low values of electric conductivity are observed at hPMAA:hP4VP=3:3 ratio. In case with individual hydrogels of PMAA and P4VP electrochemical equilibrium is reached faster, after 24 hours electric conductivity decreases less intensive, what, in turn can be explained by absence of additional ionization of the macromolecules.

Sorption process of calcium ions by the intergel system hPMAA-hP4VP also impacts onconcentration of hydrogen ions in the solution (fig**ure** 2). Maximum release of protons is observed in presence of only acid hydrogel, what is due to absence of the polybasis which can associate protons in the process of ionization of the polymer hydrogels in intergel pairs. The lowest release of protons occur in presence of the basic hydrogel, what is due to low dissociation of water molecules. Decrease of pH with polyacid share in intergel pairs is due to predominance of carboxyl groups dissociation process over association process of hydrogen ions by nitrogen atom, also it should be noted that ionization of the polybasis at calcium sorption occurs also due to formation of coordination bonds between nitrogen atoms and the metal ion.

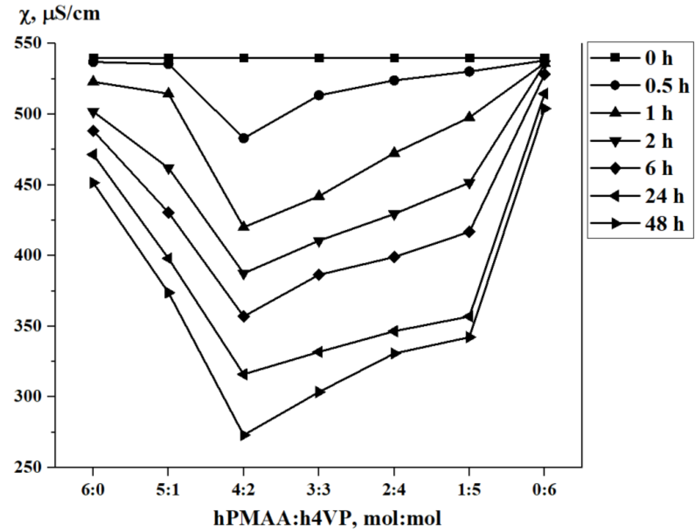

Figure1 – Dependence **on** specific electric conductivity
of calcium chloride versus of mole ratios of hPMAA:hP4VP

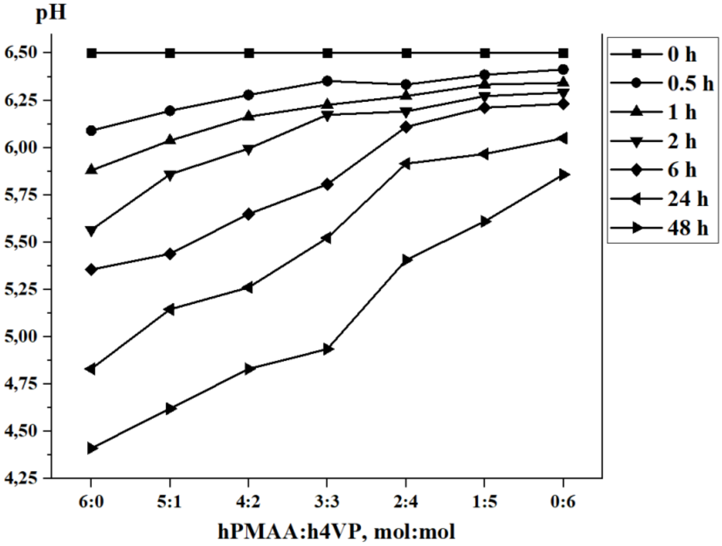

Figure 2 – Dependence on pH of calcium chloride versus of mole ratio hPMAA:hP4VP

Exact areas of maximum and minimum sorption of calcium ions by the intergel system are observed (figure 3). Calcium ions concentration decreases with time. High values of sorption degree of calcium ions are observed at ratios hPMAA:hP4VP=4:2 and 3:3, at that maximum amount of the metal is sorbed at ratio 4:2 (sorption degree is 93%), while individual hydrogels of PMAA and P4VP extract not more than 65% of calcium ions.

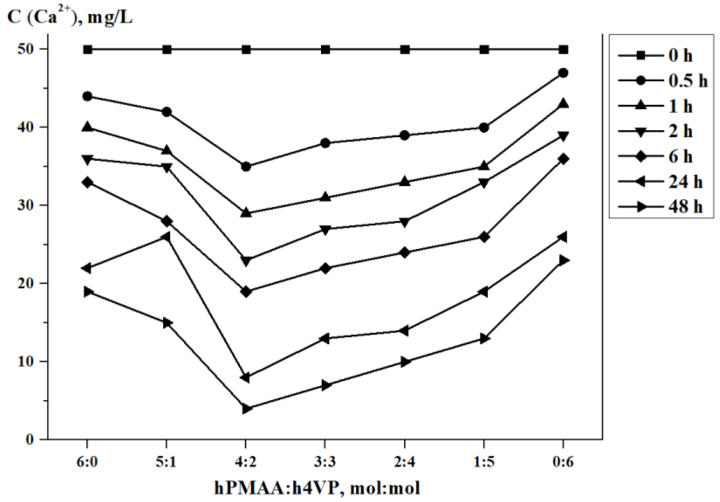

Figure3 – Dependence on $Ca^{2+}$ ions concentration versus of mole ratios of hydrogels

Obtained results show that in all intergel pairs sorption occurs intensively in comparison with individual polymer hydrogels. This is due to formation of optimal conformation of the macromolecules for calcium ions sorption at hPMAA:hP4VP=4:2 ratio due to unfolding of polymer globes due to repulsion of same-charged groups on internode links in result of the polymers remote interaction.

*Sorption of calcium by intergel system hPAA-hP2M5VP***.** Sorption of calcium by intergel system hPAA-hP2M5VP (figure 4) is accompanied with decrease of

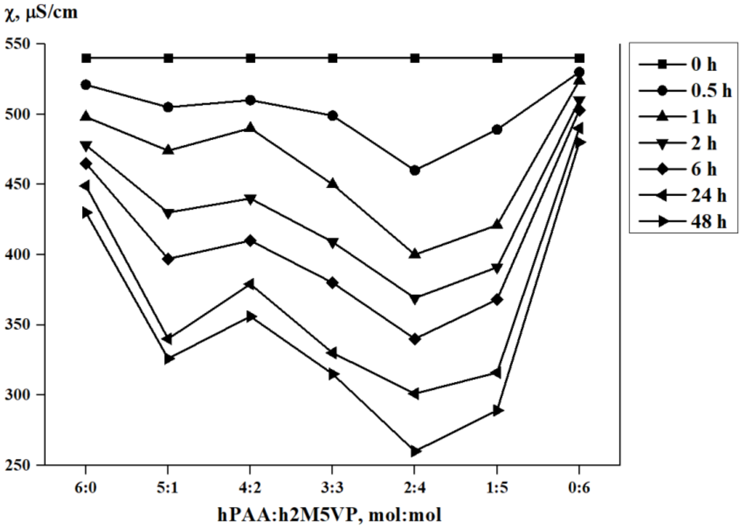

Figure 4 – Dependence on specific electric conductivity
of calcium chloride versus of mole ratios of hPAA:hP2M5VP

specific electric conductivity with time similarly to intergel system hPMAA-hP4VP (figure 1). However, in this case minimums of electric conductivity are observed at another ratios of the hydrogels in intergel pairs. Exact minimum of electric conductivity is observed at ratio hPAA:hP2M5VP=2:4 at 48 hours of hydrogels interaction with calcium chloride solution. Also low values of electric conductivity are observed at ratio hPAA:hP2M5VP=1:5. Similarly to hydrogels of PMAA and P4VP hydrogels of PAA and P2M5VP rather fast reach electrochemical equilibrium, what is evidenced by absence of significant decrease of specific electric conductivity after 24 hours.

Sorption of calcium also provides changes of pH of the salt solution (figure 5). As seen from figure, with polyacid share increase in the intergel pairs pH decreases. However, at ratio hPAA:hP2M5VP=5:1 pH values are higherthat at ratios hPAA:hP2M5VP=4:2 and 3:3, what indicates to prevalence of proton binding by nitrogen atom in pyridine ring process over dissociation process of carboxyl groups. Change of self-organization of the polymer macromolecules in process of calcium ions sorption provides protons release in solution, and, in the end, decrease of pH.

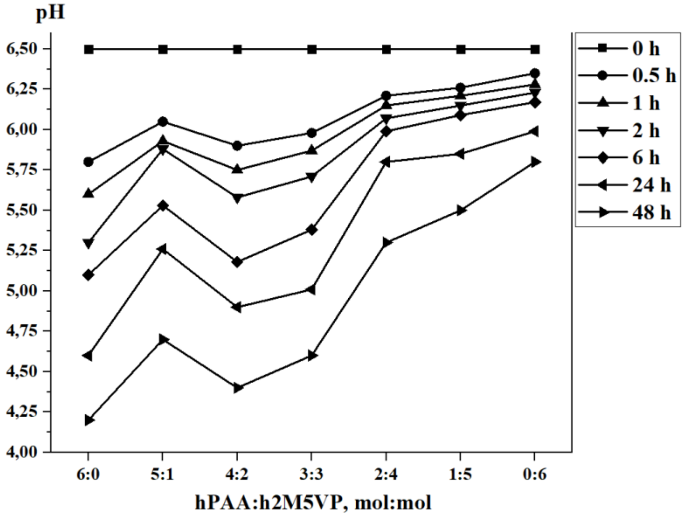

Figure 5 – Dependence of pH of calcium chloride from hPAA:hP2M5VP molar ratios in time

Dependence of calcium ions concentration from hydrogels molar ratios in presented on figure 6. Similarly to the case with PMAA and P4VP hydrogels (figure 6), hydrogels of PAA and P2M5VP do not have high values (not higher that 65%) of calcium ions sorption degree. High ionization of internode links of polymer chains of the polyacid and polybasis at hydrogels ratio hPAA:hP2M5VP=2:4 provides maximum sorption of calcium (92% of the metal is sorbed at 48 hours). More than 80% of calcium is extracted from the solution at ratios hPAA:hP2M5VP=3:3 and 1:5.

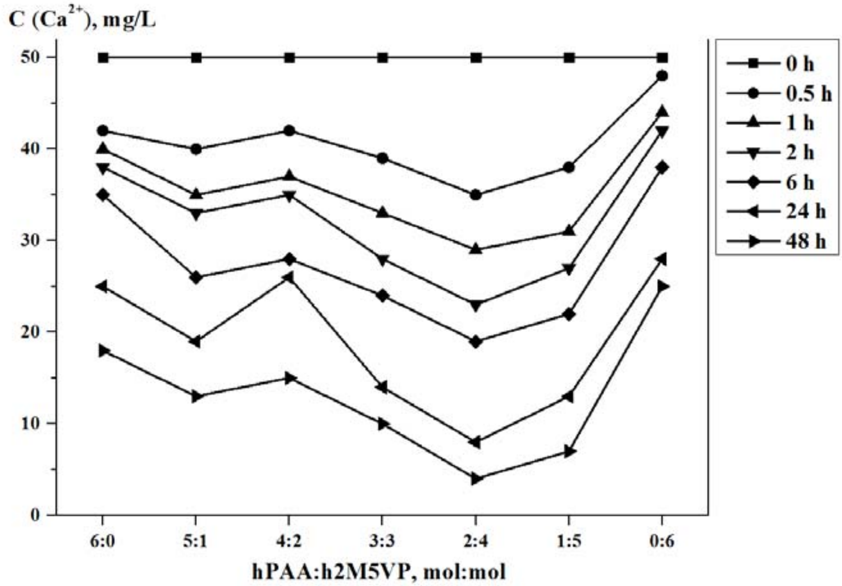

Figure 6 – Dependence of $Ca^{2+}$ ions concentration from hydrogels molar ratios in time

Analysis of obtained results on specific electric conductivity, pH provides conclusion that highly ionized state of hPAA, hPMAA, hP4VP and hP2M5VP is a consequence of the polymers mutual activation at their remote interaction. Also it should be noted that transition into highly ionized state can be complicated if there is a bulk substituent (ex. methyl) in structure of polymer, what, in turn, interfeersunloding of polymer globe during mutual activation. By this phenomenon different degree of sorption of calcium ions in the intergel systems hPMAA:hP4VP=4:2 and hPAA:hP2M5VP=2:4 can be explained. Obtained data on specific electric conductivity also indicates to high ionization of the polymers at these ratios.

**Conclusion.**

1. Sorption of calcium ions by intergel system hPMAA-hP4VP and hPAA-hP2M5VP is accompanied with specific electric conductivity and pH decrease due to change of initial electrochemical equilibrium in salt solution.
2. Absence of phenomenon of mutual activation and further transition into highly ionized state, provides fast reach of electrochemical equilibrium of individual hydrogels of PAA, PMAA, P4VP, P2M5VP, consequence of what is very slight increase of sorption degree after 24 hours of interaction. Sorption degree of calcium ions by above mentioned hydrogels does not exceed 70%.
3. Optimal conformation of polymer macromolecules in intergel systems hPMAA-hP4VP and hPAA-hP2M5VP for maximum sorption of calcium ions appears during their self-organization at ratios hPMAA:hP4VP=4:2 and hPAA:hP2M5VP=2:4, sorption degree is 93% and 92% respectively.

4. Significant difference (over 25%) of sorption degree of individual hydrogels and intergel systems is due to the fact that remote interaction in intergel systems provides formation of high density of charged functional groups without counter ions on internode links of polymer chains.

5. Intergel systems based on rare-crosslinked hydrogels of PAA, PMAA, P4VP, P2M5VP can be used for development of innovative technologies in water purification and hydrometallurgy.

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## Резюме

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### ПОЛИМЕТАКРИЛ ҚЫШҚЫЛЫ – ПОЛИ-4-ВИНИЛПИРИДИН ЖӘНЕ ПОЛИАКРИЛҚЫШҚЫЛЫ – ПОЛИ-2-МЕТИЛ-5-ВИНИЛПИРИДИН ГИДРОГЕЛЬДЕРІНЕН ҚҰРАЛҒАН ИНТЕРГЕЛЬДЕРІМЕН КАЛЬЦИЙ ИОНДАРЫН СОРБЦИЯЛАУДАҒЫ ЕРЕКШЕЛІКТЕР

Полиметакрил қышқылы (ПМАКг) – поли-4-винилпиридин (П4ВПг) және полиакрил қышқылы (ПАКг) –поли-2-метил-5-винилпиридин (П2М5ВПг) гидрогелдері арқылы құрылған интергелді жүйелерімен $Ca^{2+}$ ионын сорбциялау процессін кондуктометрия, pH-метрия, ионометрия әдістерімен зерттелді. Анықталғаны, кальций иондарының сорбциялау процесі жеке сирек торланған полимерлік ПАК, ПМАК, П4ВП, П2М5ВП гидрогелдерімен, сондай-ақ ПМАКг-П4ВПг, ПАКг-П2М5ВПг интергелді жүйелерімен кальций хлориді ерітіндісінің бастапқы электрохимиялық қасиеттері айтарлықтай өзгерістерін байқауға болады (уақыт өте келе металл ионын сорбциялауда меншікті электрөткізгіштігінің және pH мәндері төмендейді). ЖекеПАК, ПМАК, П4ВП, П2М5ВП гидрогелінде тұз ерітіндісінің электрохимиялық тепе-теңдік жылдам теңеседі, соның салдарынан бір тәулік өткеннен кейін аз ғана өсуі байқалады. Кальций иондарының соңғы сорбциялау дәрежесі 70% дейін жетеді. Интергелді жүйелерде полимерлердің оңтайлы конформациясы гПМАК:гП4ВП=4:2 және гПАК:гП2М5ВП=2:4 қатынастарында түзіледі. Алайда, макромолекулалардың ауысу процесі қиындық туғызады, өйткені ПМАК және П2М5ВП құрылымдарда метилді корынбасарлар көптігінен иондану процесінде полимерлік түйіндердің айналуына кедергі келтіреді. гПМАК:гП4ВП=4:2 және гПАК:гП2М5ВП=2:4 интергелді жүйелерімен сәйкесінше кальций иондарының сорбциялау дәрежесі 93% және 92% құрайды.

**Түйін сөздер:** интергелді жүйе, өзара белсендендіру, сорбция, $Ca^{2+}$ иондары жағдай, гидрогельдер, полиакрилқышқылы, полиметакрилқышқылы, поли-4-винилпиридин, поли-2-метил-5-винилпиридин.

## Резюме

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# ОСОБЕННОСТИ СОРБЦИИ ИОНОВ КАЛЬЦИЯ ИНТЕРГЕЛЕВЫМИ ГИДРОГЕЛЯМИ ПОЛИМЕТАКРИЛОВОЙ КИСЛОТЫ – ПОЛИ-4-ВИНИЛПИРИДИНА И ПОЛИАКРИЛОВОЙ КИСЛОТЫ – ПОЛИ-2-МЕТИЛ-5-ВИНИЛПИРИДИНА

Методами кондуктометрии, pH-Метрии, ионометрии исследован процесс сорбции ионов $Ca^{2+}$интергелевыми системами гидрогель полиметакриловой кислоты (гПМАК) – гидрогель поли-4-винилпиридина (гП4ВП) и гидрогель полиакриловой кислоты (гПАК) – гидрогель поли-2-метил-5-винилпиридина (гП2М5ВП). Установлено, что процесс сорбции ионов кальция как индивидуальными редкосшитыми полимерными гидрогелями ПАК, ПМАК, П4ВП, П2М5ВП, так и интергелевыми системами гПМАК-гП4ВП, гПАК-гП2М5ВП, сопровождается существенными изменениями исходных электрохимических свойств раствора хлорида кальция (со временем сорбции ионов металла происходит снижение значений удельной электропроводности и pH). Индивидуальными гидрогелями ПАК, ПМАК, П4ВП, П2М5ВП достаточно быстро достигается электрохимическое равновесие с раствором соли, вследствие чего происходит незначительный рост по истечению 1 сут, конечная степень сорбции ионов кальция достигает 70%. Образование оптимальной конформации полимеров в интергелевых системах происходит при соотношениях гПМАК:гП4ВП=4:2 и гПАК:гП2М5ВП=2:4, однако процесс перехода макромолекул затрудняется тем, что в структурах ПМАК и П2М5ВП присутствует объемный метильный заместитель, мешающий разворачиванию полимерного клубка в процессе его ионизации. Степень сорбции ионов кальция интергелевыми системами гПМАК:гП4ВП=4:2 и гПАК:гП2М5ВП=2:4 составляет 93 и 92% соответственно.

**Ключевые слова:** интергелевая система, взаимная активация, сорбция, ионы $Ca^{2+}$, гидрогели, полиакриловая кислота, полиметакриловая кислота, поли-4-винилпиридин, поли-2-метил-5-винилпиридин.

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# STRUCTURE AND BIOLOGICAL ACTIVITY OF THE MIXED-LIGAND COMPLEX OF COPPER WITH P-NITROBENZOIC ACID AND MONOETHANOLAMINE

**Abstract.** Analysis of the current state of theory and practice of various growth stimulants application allows to note their wide use in agriculture, where they play important role such as mineral fertilizers. In this connection, a lot of number growth stimulants are created, and compounds based on metal complexes take important place.

**Key words:** p-nitrobenzoic acid, monoethanolamine, Cu complex, molecular and crystal structure, SAR, TG-DSK, mass spectrum, growth stimulating activity.

**Introduction.** The possibility of an enhancement of biological action of the low-active organic substances by formation of monoligand metal complexes was studied in detail, and very promising results were obtained [1-3]. However, the literature analysis indicates that there are no works devoted to systematic study of bioactivity optimization in mixed-ligand complexes.

Very promising is the approach when cheap and commercially available substances demonstrating simultaneous antimicrobial and growth-stimulating actions will be used as the main ligand. The simplest mono-derivatives of benzoic acid, as nitro-, amino- and hydroxybenzoic acids are such compounds [4]. Ethanolamines, showing the same biological effect can be selected as an auxiliary ligand [5]. Based on this, we conducted the syntheses with participation of the p-nitrobenzoic acid (PNBA), monoethanolamine (MEA) and salt of copper (I) sulfate ($Cu_2SO_4$) salt.

Thus we have synthesized a new mixed-ligand metal complex of copper containing two molecules of PNBA and two molecules of MEA.

## EXPERIMENTAL PART

A hot solution of PNBA containing 0.167 g (1 mmol) in methanol was added to solution of water-methanol mixture (1: 0.25 by volume) containing 0.135 g (0.5 mmol) of $CuCl_2{\cdot}2H_2O$ in 4 ml. In to this mixture 62 μl of MEA was added dropwise with constant stirring. The reaction mixture was kept in an ultrasonic bath (30 kHz) for 10 minutes. The resulting solution was placed in a tub, not tightly closed (at 20° C). After 8 days prismatic crystals are formed. The yield was about 60%.

Experimental data for X-ray diffraction analysis were collected using the CrysAlisPro program [6] on an X-ray difractometer “Xcalibur R CCD” (Oxford diffraction, England) using CuK$_\alpha$ radiation with $\lambda$=1.5418Å (graphite monochromator, ω-scanning method). The correction for absorption was made by a multi-scan method of the same program. The structures were solved by a direct method and refined by the least square method [7] using the SHELXS-97 software packages [8]. Molecular and crystalline structures were plotted by the MERCURY software [9]. The crystallographic parameters and details of structure refinement are given in the table 1.

Table 1 – Crystallographic parameters and details of the structure refinement of the mononuclear mixed-ligand Cu complex.

| Characteristics | Amount of parameters value of quantity |
|---|---|
| Formula | $Cu[((PNBA)_2+(MEA)_2)]$ |
| Crystal system | Monoclinic |
| Etc. gr. | $P2_1/n$ |
| a, Å | 4.781(5) |
| b, Å | 21.252(5) |
| c,Å | 10.701(5) |
| α, deg | 90 |
| β, deg | 97.375(5) |
| γ, deg | 90 |
| V, Å$^3$ | 1078.3(13) |
| Z | 2 |
| ρ( calculated), g / cm$^3$ | 1.595 |
| μ, mm$^{-1}$ | 1.077 |
| Crystal dimensions, mm | 0.08 x 0.16 x 0.40 |
| Scanning interval θ, deg | 3.9, 50.2 |
| h, k, l range | -5:5; -25:24; -11:12 |
| Collected reflections | 7618 |
| $R_{int}$ | 0.034 |
| Reflections with $I > 2\sigma (I)$ | 1540 |
| GOOF (F2) | 1.08 |
| R1, wR2 ($I > 2\sigma (I)$) | 0.0601, 0.1956 |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$, e / Å$^3$ | -0.56, 0.48 |

The thermal analysis of compounds was carried out in an inert argon atmosphere under programmable non-isothermal heating conditions in mixture with $\alpha$-$Al_2O_3$ standard in ratio 1: 1 at heating rate of 10 deg / min in 25-400°C temperature interval on combined thermal analyzer STA 409 PC LUXX from Netzsch (Germany). Mass spectra were registered using an ion trap mass spectrometer and time-of-flight mass spectrometer Aglient 6400 TripleQuadrupole LC / MS (Germany) and Q-TOF Agilent 6520 va 6400 TripleQuadrupole LC / MS (Germany), respectively. The ionization was performed by electrospray, the mass spectra were recorded with the following experiment parameters: m / z range 50-400, dehydration gase flow rate (nitrogen) 3 ml / min at 300 ° C, gas pressure on nozzle needle 20 psi , the voltage of the fragmentator is 35 V, capillary voltage is 3500 V.

**Results and Discussion**. In the crystals~~,~~ the $Cu^{2+}$ ions located at inversion centers are coordinated chelatly by two MEA molecules through nitrogen and oxygen atoms (figure 1). Two more PNBA molecules are monodentately attached to metal ions, both by oxygen atoms of the carboxyl group, which is in carboxylate form in order to compensate positive charge of the copper ions. The carboxylate group is not coplanar with benzene ring - the corresponding dihedral angle is 25.28 °. The nitro group is inclined to aromatic nucleus at 11.51°.

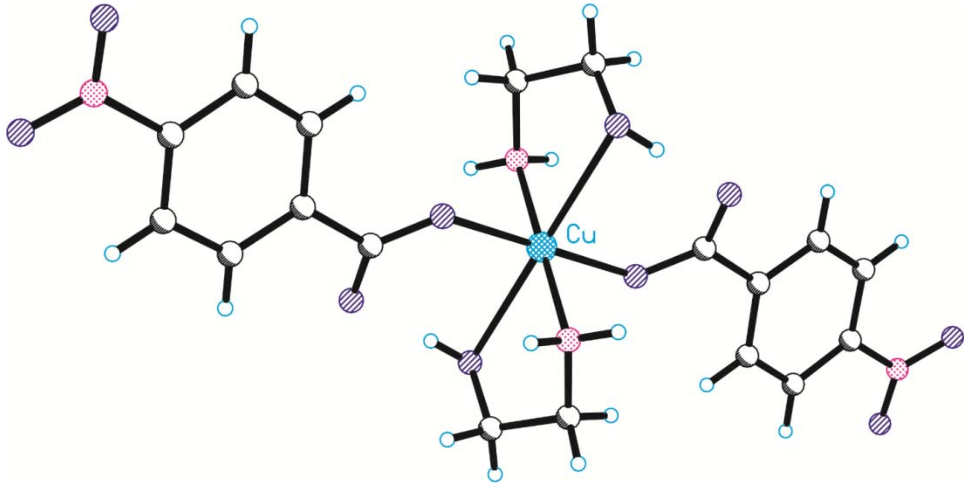

Figure 1 – The structure of the complex molecule in the Cu[((PNBA)$_2$+(MEA)$_2$)] compound

Polyhedron of the copper ions is octahedron which is strongly distorted by the Jahn-Teller effect [10-12].

The mixed ligand metal complex with composition of Cu [((PNBA)$_2$+ (MEA)$_2$)] is stable up to 167°C (figure 2) and loss of mass in the temperature range of 20-370 ° C occurs in one stage - 167-320° C, in this interval the thermal decomposition of the sample with loss of weight of 62.16% takes place. The DSC-curves show two peaks: endothermic - $T_{max}$ 155.2 and the immediately

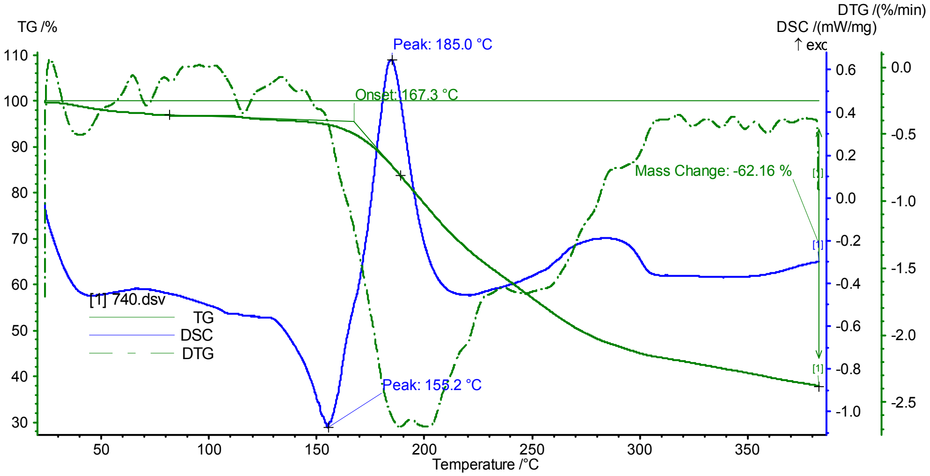

Figure 2 – Thermal analysis of the complex Cu[((PNBA)$_2$+ (MEA)$_2$)]

following exothermic peak at T$_{max}$ 185 ° C. The first peak corresponds to sample melting, and the subsequent thermal oxidative destruction is characterized by an exothermic peak. The total amount of energy corresponding to these processes is 157 J / g. The maximum degradation rate is 2.5% per minute.

To study the component composition, the complex compounds were analyzed by HPLC-mass spectrometry (figure 3). After the scan with positive ionization, a molecular fragments with the characteristics [M + H] = 518, [M = 517 + 1] were detected, and it can be assumed to formation of the complex, which is sufficiently resistant to external influences.

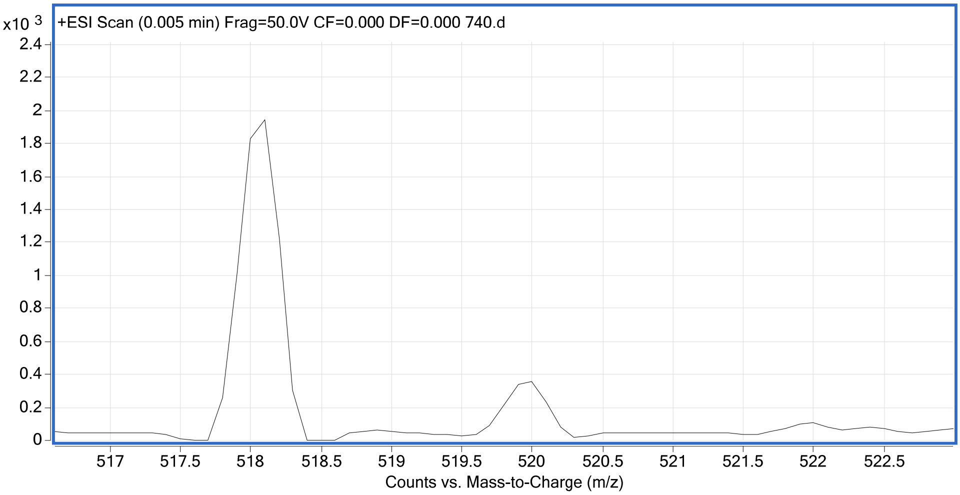

Figure 3 – Mass spectrometry of the complex Cu[((PNBA)$_2$+ (MEA)$_2$)]

Thus, the Cu[$((PNBA)_2$+$(MEA)_2)$] compound is a mixed-ligand mononuclear complex of Cu (II) with PNBA and MEA of 1: 2: 2 ratio.

**Growth stimulating activity.** PNBA shows growth stimulating activity, but significantly less than *p*-aminobenzoic acid [13]. The stimulating effect of MEA is much greater, and therefore preparations based on this substance are used as growth stimulants [14]. In this connection, synthesized compounds should exhibit enhanced growth-stimulating properties.

During the experiments, the testing compound - mononuclear complex of Cu with PNBA and MEA was designated as substance No.1.

In vegetative experiments, the effect of synthesized compound on the growth, development, and harvest of cotton-wool was studied. Before sowing, the seeds were soaked with water and tested stimulants with 0.001% concentration. In the growing phase of 3-4 true leaves, in the budding and flowering - fruit-formation phases of cotton growing, the plants were sprayed with the test preparation [15, 16].

When applying the plant growth stimulator, the general provisions are observance all rules of agricultural technology, support of good plant nutrition regime, and observing the rules for using the stimulant so as not to destroy the plant. The growth stimulator was stored in tightly closed glass container with plug glass stopper in dry and dark place or in opaque containers.

During the cotton growing period, careful maintenance of plants was carried out: watering, loosening of the soil, thinning, fertilizing, treatment of plants from diseases, phenological observations and biometric measurements were carried out. During the growing season, soil moisture was maintained at 60-65% of total moisture capacity.

The vegetation experience was carried out in 4-fold replication.

Soil under the experience: typical serozem (Calcisol, WRB, 2006) with the following characteristics: $C_{total}$ - 0.54%; $N_{total}$ - 0.09%; $P_{total}$ - 0.14%; pH 7.2.

The stimulator was studied on cotton crop (*Gossypium hirsutum*) of the "Akdarya-6" sort in vegetation experiments. The average vegetative period of plants varies from 117 to 128 days.

The land treatments were carried out according to generally accepted technique of Cotton Breeding, Seed Production and Agro-Technologies Research Institute (Tashkent, Uzbekistan).

In the experiments special attention was paid to acceleration of development rates of cotton- plants. In Fig. 4 the influence of studied stimulator on growth of main cotton-plants stem on different development stages is clearly traced. If in germination stage there was no significant difference in variants, then stimulating effect of studied complex on plant growth is found to phase of 3-5 true leaves (the length of the main stem is 61.3% longer than in control version). The highest plants are fixed in variant with stimulator, reaching a maximum of 18.0 cm, which exceeds the control variant by 6 cm (i.e. by 50%). In the flowering phase and in terminal stage of fruit formation (maturation), the intensification of plants growth was noted: in the stimulator variant the length of plant main stem were

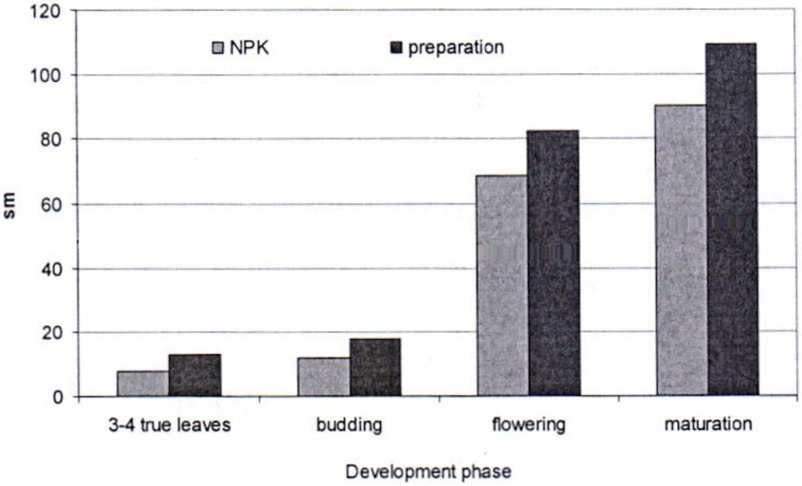

Figure 4 – Dynamics of cotton growth under the influence of the preparation

respectively 82.25 and 109.25 cm (which is 19.6 and 21.1% longer than in control).

The main criterion which make for effectiveness of studied preparation is the level of cotton-wool harvest. From the results presented in table. 2. it can be seen that the yield of in the test group of plants (with growth stimulator) was 28.3% higher than yield from the control plants (without stimulant). It is important that under influence of mixed-ligand complex, the opening and ripening of bolls is somewhat delayed. Thus, in the control variant 70% of cotton-wool was collect at first harvest, while in tested variant only 45.7%, for 2 harvest, respectively, 20.0 and 30.1%, for 3 harvest - 9.4 and 24.1% of the total harvest of cotton-wool.

It should be especially noted that in variant with mixed ligand complex, in addition to increasing bolls number from one plant (up to 33.75 pcs vs. 26.0 pcs in control, i.e. by 29.8% more), the complete ripening of formed bolls was fixed (the number of unripe fruit-elements in test variant was 41.5% less: 11.3 pieces versus 19.3 in the control). These phenomena together contributed to increase in yield of cotton-wool by 28.3%.

Table 2 – Cotton yield by applying mixed ligand complex as growth stimulants

| № | Variants | Weight of cotton-wool (seeds and lint), in g / per 1 plant | | | | Total harvest | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | harvest 1 28.08.16 | harvest 2 14.09.16 | harvest 3 30.09.16 | Total | Sum of bolls, units per 1 plant | Weight of boll, g | Imma-ture fruit , g | % |
| 1 | $N_{200}P_{140}K_{60}$-background | 80.25 | 22.97 | 10.8 | 114.6 | 26.00 | 4.4 | 19.30 | 100 |
| 2 | Prepration 1 | 67.25 | 44.25 | 35.5 | 147.0 | 33.75 | 4.35 | 11.3 | 129.8 |

So, on the basis of the carried out studies it was revealed that Cu [$((PNBA)_2$+ $(MEA)_2$)] compound, has stimulating activity on the growth and development of cotton. In this metal complex, growth of bioactivity to almost 30% is observed.

Multifunctional action on plants, apparently, is associated with the activation of phytohormones, which is expressed in acceleration of seeds germination, plants lenght, mass of aboveground part and roots, productive bushiness. The revealed positive qualities of the stimulant under investigation ultimately lead to yield increase and an improvement in the cotton fiber quality.

**Conclusion.** Thus, our complex of agrochemical vegetative studies, the qualitative characteristics of the studied compound, and its influence on the yield of the tested plants made it possible to conclude that effective stimulant of a new generation that positively influenced the growth and development of cotton was obtained.

The practical significance of synthesized compounds is growing if we take into account that it is the mononuclear copper complex that exhibits maximum antifuzario activity [10]. To apply this compound as a growth preparation, the cotton seeds are soaked in advance by inoculation. Since *Fusarium* fungi are constantly present in the soil, the preparation simultaneously exhibits both growth and antifungicidal actions. In this regard, we can argue that an effective dual-action complex has been obtained that is promising in terms of introduction into agriculture.

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## Резюме

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## п-НИТРОБЕНЗОЙ ҚЫШҚЫЛЫ МЕН МОНОЭТАНОЛАМИНМЕН МЫСТЫҢ АРАЛАС ЛИГАНД КЕШЕНІНІҢ ҚҰРЫЛЫМЫ ЖӘНЕ БИОЛОГИЯЛЫҚ БЕЛСЕНДІЛІГІ

Түрлі өсімдік өсімін ынталандырғыштар қолданудың теориясы мен практикасының ағымдағы жай-күйін сараптау олардың минералдық тыңайтқыштар сияқты маңызды рөл атқаратын ауыл шаруашылығында олардың кеңінен қолданылатындығын атап өтуге мүмкіндік береді. Осыған байланысты, көптеген өсімді ынталандырғыштар жасалып, металл кешендеріне негізделген қосылыстар маңызды орын алуда.

**Түйін сөздер:** п-нитробензой қышқылы, моноэтаноламин, Cu кешені, молекулалық және кристалды құрылым, SAR, TG-DSK, масс спектр, өсімді ынталандыратын белсенділік.

## Резюме

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# СТРУКТУРА И БИОЛОГИЧЕСКАЯ АКТИВНОСТЬ СМЕШАННО-ЛИГАНДНОГО КОМПЛЕКСА МЕДИ С п-НИТРОБЕНЗОЙНОЙ КИСЛОТОЙ И МОНОЭТАНОЛАМИНОМ

Анализ современного состояния теории и практики применения различных стимуляторов роста позволяет отметить их широкое использование в сельском хозяйстве, где они играют важную роль как минеральные удобрения. В связи с этим создается множество стимуляторов роста, и соединения, основанные на металлических комплексах, занимают важное место.

**Ключевые слова:** п-нитробензойная кислота, моноэтаноламин, комплекс Cu, молекулярная и кристаллическая структура, SAR, TG-DSK, масс-спектр, стимулирующая рост активность.

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# WATER SOLUBLE POLYMERIC DRUG FORM OF LOCAL ANESTHETIC BASED ON POLYVINYL ALCOHOL

**Abstract.** The new water soluble polymeric drug form of local anesthetic novocaine on the based synthetic polymer polyvinyl alcohol has been developed. By means equilibrium dialysis method the interaction of novocaine with polyvinyl alcohol was studied. The dynamic of drug release into physiological solution was investigated. It was concluded the possibility of the polymer application for prolongation action of novocaine.

**Key words:** polymeric form, local anesthetic, novocaine, polyvinyl alcohol, drug release.

**Introduction.** One of perspective directions in the field of drug delivery systems is development of complexes of drugs with various water-soluble polymers. Application of such complexes allows to lower of toxic action of drugs and also to receive long therapeutic effect. Rigid requirements of medicine (biocompatibility, solubility in water or physiological solution, ability to completely remove from organism, etc.) sharply narrow the circle of polymers used as drug carriers. For these purposes it is considered the most expedient application of polymers which have properties of blood substitutions [1, 2]. Among the high-molecular compounds having such properties, the wide spreading has found polyvinyl alcohol [3, 4].

One of the most important tasks in the field of chemistry of medico-biological polymers is the development of polymeric forms of anesthetic drugs. The existing arsenal of antipain drugs are small and many of them have a number of disadvantages, namely short duration of the anesthetic and toxic effects on the body associated with overdose of the drug. In many cases, especially in disaster medicine, to eliminate pain syndrome it is necessary to maintain the effective concentration of the analgesic drugs in the body for long time. A prolonged effect can be achieved by immobilizing anesthetic drugs to macromolecular carriers [5-8].

In the present study the polymeric water soluble forms of novocaine based on polyvinyl alcohol are described.

## EXPERIMENTAL PART

Polyvinyl alcohol (PVA) were purchased from Sigma Chemicals, St.louis, USA. Novocaine was used pharmaceutical grade.

For detailed understanding of character and nature of binding and the interaction between drug and macromolecules were studied by means equilibrium dialysis method. The release behaviour of novocaine from polymeric solutions was examined by dialysis method in a modelling biological medium at 37°C. The amount of drug released was determined spectrophotometrically by measuring the absorbance maximum UV spectra were recorded on a Jasco UV-VIS (Japan) spectrophotometer.

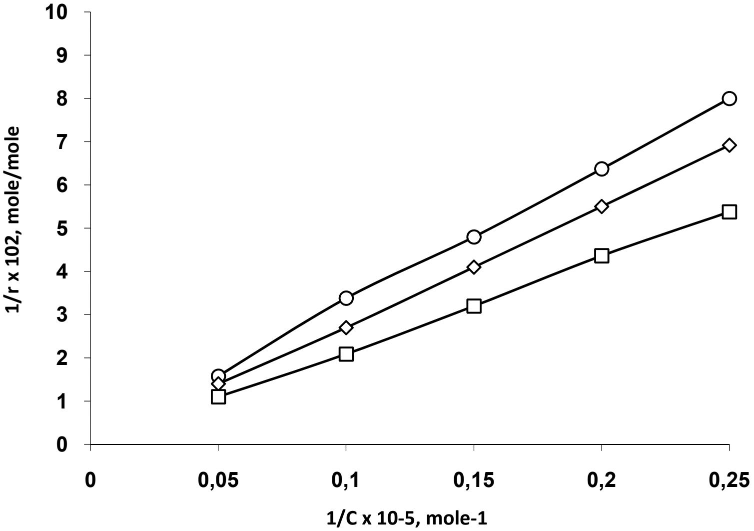
## RESULTS AND DISCUSSION

Polyvinyl alcohol has found wide application in medicine as blood substitute, bases for ointments, prolonger of action of many medicinal substances. The basic advantages of this polymer are solubility in water and other solvents, absence of toxic and allergenic action, high ability to complexation. To the purposes of prolongation, the polymer with molecular weight 15000-20000 was applied. That provides long stay of polymer and binding drug in living organism.

The determining role in binding of polyvinyl alcohol with various low-molecular substances is played hydrogen bonds and hydrophilic interactions. Presence in structure of drug the appropriate groups capable form weak complexes with PVA, gives the basis to use this polymer for prolongation of therapeutic action of drug. Interaction of drug with PVA was studied by means of various physical and chemical methods.

UV-spectroscopic researches are shown that at mixing water solutions of drug and polymer precise change in spectral characteristics novocaine at 202 nm as increase of the maximum of absorption. This process proceeded in time, increase of optical density occur within 6-8 hours. The given effect is caused complexation of molecules novocaine with OH-group of polymer due to formation of hydrogen bonds. Viscosimetric measurements also testified about complexation of drug and polymer. So, the intrinsic viscosity of 0,5 % solution of PVA at dilution water changes linearly, and at dilution the same solution of 0,5 % solution novocaine occurs sharp increase of the given viscosity in the field of small concentration of polymer, characteristic for polyelectrolites. The given effect testifies to increase of the linear sizes of macromolecules result of its association with novocaine. Measurement of viscosity of solutions at various mole ratio of components has shown, that at the ratio close to equimolar (0,8-0,9 mole novocaine on 1 part PVA), the sharp increase of viscosity testifying to formation of a complex of structure 1:1.

For more detailed investigation of interaction novocaine with PVA the method of equilibrium dialysis was used, allowing establish degree of binding between components in solution not only qualitative, but also quantitatively. Experiments carried out in water solution at various temperatures, using acetylcellulose dividing membrane. Drug, diffused from one cell through membrane, contacted with polymer which is taking place in other cell. Changing concentration of drug in various experiments with constant concentration of PVA, quantitative characteristics of process of interaction (coefficient of distribution, binding constant, thermodynamic parameters) were determined. The coefficient of distribution novocaine at equilibrium dialysis characterizes itself the relationship of drug amount in dialysed cell and outside solution. Constant of binding determined according to Klotz equation [9] by the diagram of dependence 1/a versus 1/C, where "a" is the parameter describing the share of macromolecules, formed complex, C - concentration or unbound drug (figure). This dependence represented a straight line which corner of inclination corresponded 1/Kc.



Dependence on novocaine versus interaction with PVA at the temperature:
□ – 25°C, ◊ – 37 °C, ○ – 50 °C.

Values of thermodynamic parameters of interaction at various temperatures are presented in table 1. The data indicate clearly that with increase of temperature parameters of drug the binding with PVA decrease.

Table 1 – Thermodynamic parameters of novocaine interaction with PVA

| Temperature, °C | $К_в \cdot 10^{-2}$, L/mole | Free Energy, kJ/mol | Enthalpy, kJ/mol | Entropy, E.u. |
|---|---|---|---|---|
| 25 | 41,4 | - 9,22 | -5,47 | 12,65 |
| 37 | 38,2 | - 9,39 | - 4,12 | 15,32 |
| 50 | 38,1 | - 9,48 | - 3,32 | 18,71 |

Process of complex formation has exothermic character, negative values of change testify to it enthalpy and free energy, and also positive change of entropy. Low absolute values thermodynamic parameters indicated the prevailing value of hydrogen bonds in process. Alongside with them existence of hydrophobic interactions between components in the complex is possible.

The release of drug from polymeric solution was investigated. Experiments carried out at various ratio polymer:drug - from 1:1 up to 4:1. For comparison the amount of drug, released through membrane in absence of polymer was determined. Results of investigation are presented in table 2.

Table 2 – Dynamic of novocaine release from PVA into physiological solution

| Ratio Drug:Polymer | Quantity released drug, % | | | | |
|---|---|---|---|---|---|
| | 1 h | 2 h | 3 h | 4 h | 6 h |
| 1:0 | 24 | 45 | 71 | 82 | 94 |
| 1:1 | 19 | 35 | 59 | 74 | 75 |
| 1:2 | 14 | 31 | 53 | 69 | 79 |
| 1:3 | 12 | 28 | 47 | 65 | 72 |
| 1:4 | 11 | 25 | 44 | 61 | 68 |

Received data indicate that at the presence of polymer the diffusion of novocaine through membrane is reduced. So, for 8 hours at molar ratio polymer:drug = = 1:1 preparation is diffused on 78 %, while from water solution novocaine is released on 96 %. On the basis of the received data the diagrams of logarithmic dependence of amount released novocaine in time were drawn and constants of rate of drug diffusion through the membrane are calculated (figure 2).

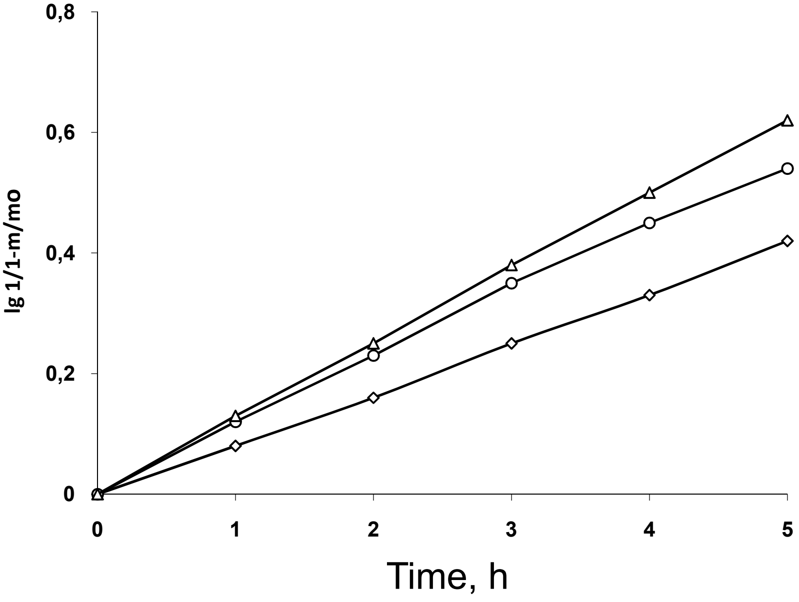


Figure 2 – Dynamic of novocaine release from PVA solution at different ratio polymer:drug. ◊ – 4:1, ○ – 2:1, Δ – 1:1.

It is shown that with increase molar ratio of reagents from 1:1 up to 1:4, the value of constant of diffusion decreases and makes 5,93; 5,61; 5,33 and 5,06·10-5 $s^{-1}$, accordingly. Kinetic curve of diffusions show, that the greatest prolonging effect achieved at a ratio PVA:drug equal 1:4.

**Conclusion.** Thus, the investigations have shown that local anesthetic novocaine in water solutions forms with synthetic polymer polyvinyl alcohol the complexes due to hydrogen bonds and hydrophobic interactions. Long therapeutic action of polymeric water-soluble complexes was established. The opportunity of creation on polyvinyl alcohol basis the injected medicinal forms prolonged the rapeutic actions were shown.

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## Резюме

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## ПОЛИВИНИЛ СПИРТІНЕ НЕГІЗДЕЛГЕН ЖЕРГІЛІКТІ АНЕСТЕТТИКТЕРДІҢ СУДА ЕРИТІН ДӘРІЛІК ТҮРЛЕРІ

Поливинил спиртінің синтетикалық полимеріне негізделген новокаинның жергілікті анестетиктерінің жаңа суда еритін полимерлі дәрілік формалары әзірленді.

Новокаиннің поливинил спиртімен өзара әрекеттесуі тепе-теңдік диализ әдісімен зерттелді. Физиологиялық тұзды дәрі-дәрмектерді босату динамикасы зерттелді. Новокаин әсерін ұзарту үшін полимерді қолдану мүмкіндігі туралы қорытынды жасалды.

**Түйін сөздер:** полимерлік түрлері, жергілікті анестетик, новокаин, поливинил спирті, дәрінің бөлінуі.

## Резюме

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## ВОДОРАСТВОРМЫЕ ЛЕКАРСТВЕННЫЕ ФОРМЫ МЕСТНОГО АНЕСТЕТИКА НА ОСНОВЕ ПОЛИВИНИЛОГО СПИРТА

Разработаны новые водорастворимые полимерные лекарственные формы местного анестетика новокаина на основе синтетического полимера поливинилового спирта. Методом равновесного диализа изучено взаимодействие новокаина с поливиниловым спиртом. Исследована динамика высвобождения препарата в физиологический раствор. Сделано заключение о возможности использования полимера для пролонгирования действия новокаина.

**Ключевые слова:** полимерные формы, местный анестетик, новокаин, поливиниловый спирт, высвобождение лекарства.

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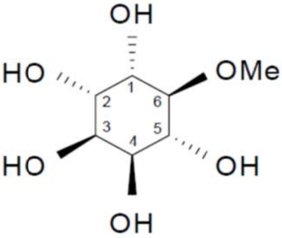
# SUPRAMOLECULAR SELF-ASSEMBLY OF D-PINITOL WITH CYCLODEXTRINES

**Abstract.** Water-soluble mixed complexes of D-pinitol with cyclodextrins in the ratio 1:1 composition were formedby the supramolecular interaction. The structure of supracomplexeswas studied by NMR spectroscopy methods.

**Keywords:** D-pinitol, cyclodextrins, supramolecular complexes, NMR spectroscopy.

One of the most promising and intensively developing areas of modern supramolecular chemistry is the preparation and investigation of complexes of biologically active compounds of plant origin with cyclodextrins (CDs) [1-5]. It is known, that inclusion supramolecular complexes of CDs with biologically active compounds make it possible to regulate the solubility of the latter in water, reduce their toxicity, permit the transfer of liquid substances to solid substances, and increase the stability of substances to oxidation and hydrolysis [6-8].

The choice of D-pinitol(**1**) as a substrate of supramolecular self-assembly is due to the fact that this compound of plant origin has antidiabetic and hypoglycemic properties and it is very promising for use in pharmaceutics [9].



**1**

CDs are relatively affordable compounds, manufactured from renewable raw materials such as starch. The α-, β- and γ-CDs containingglucopyranose units are the most common ones. The increased interest in CDs is primarily due to their cyclic structure and the ability to form supramolecular host-guest inclusion complexes with a variety of hydrophobic guests due to the internal cavity [10, 11]. The attractiveness of CDs as host molecules in the formation of inclusion complexes is also explained by their nontoxicity.

In supramolecular chemistry, the size and shape or geometric complementarity of the interacting components play a decisive role; therefore, α-, β- and γ-CDs of various sizes of the internal cavity as well as the more hydrophilized 2-HP-β-CD (2-hydroxy-β-CD) were used to obtain complexes with the substrate.

Supramolecular complexes of **1** with α-, β-, γ- and 2-HP-β-CDs were obtained by the interaction of equimolecular amounts of substrate with receptors in ethanol solutions of reacting substances at 50°C for 5 hours followed by isolation of supracomplexes drying.

Investigation of supramolecular complexes of **1** with CDs by NMR spectroscopyis based on the determination of the difference in the values of $^1$H chemical shifts of substrate**1** and receptors (CDs) in the free state and in the composition of complexes as a result of intermolecular interaction. One can judge the formation of internal or external complexes, respectively, according to the change of the value of chemical shifts of internal or external protons of CDs. The change in the chemical shifts of $^1$H NMR in the spectra of the substrate makes it possible to determine the direction of entry of the latter in the cavity of CDs [12, 13].

The substrate of supramolecular self-assembly **1** was obtained from SilenebranhuicaBoiss collected in the South Kazakhstan region in natural habitats and isolated by water-ethanol and isobutanol extraction [9]. Its structurewas established based on the results of $^1$H and $^{13}$C NMR spectroscopy obtained in DMSO-$d_6$ (table 1). The correctness of the assignment of one-dimensional $^1$H and $^{13}$C NMR spectra of **1** was confirmed by two-dimensional correlations of the NMR spectra such as $^1$H-$^1$HTOCSY, $^1$H-$^1$HROESY, $^1$H-$^{13}$CHMQCand$^1$H-$^{13}$CHMBCand coincided with the published results [9, 14, 15].

$^1$H NMR spectra data of α-, β-, γ- and 2-HP-β-CDs in the free state and supramolecular complexes on their basis with **1** obtained in $D_2O$ are represented in tables 2 and 1.

Table 1 – The values of the chemical shifts of $^1$Hand$^{13}$C NMR of **1**
in the free state ($\delta_0$, DMSO-$d_6$) and in the composition of the complexes (δ, $D_2O$), ppm

| C atom No. | $\delta_0$ ($^{13}$C) | $\delta_0$ ($^1$H) | δ ($^1$H) in the complex with | | | |
|---|---|---|---|---|---|---|
| | | | α-CD | β-CD | γ-CD | 2-HP-β-CD |
| 1 | 72.52 | 3.34 m, 4.41 d (OH) | Signals of CDs are overlapped by signals of **1** | | | |
| 2 | 73.12 | 3.60 m, 4.64 d (OH) | Signals of CDs are overlapped by signals of **1** | | | |
| 3 | 71.45 | 3.47 m, 4.38 d (OH) | Signals of CDs are overlapped by signals of **1** | | | |
| 4 | 72.92 | 3.60 m, 4.55 d (OH) | Signals of CDs are overlapped by signals of **1** | | | |
| 5 | 70.61 | 3.34 m, 4.25 d (OH) | Signals of CDs are overlapped by signals of **1** | | | |
| 6 | 84.33 | 2.97 t | 3.28t | 3.29t | 3.28t | 3.20 t |
| 6-$OCH_3$ | 60.15 | 3.41s | Signals of CDs are overlapped by signals of **1** | | | |

Table 2 – The $^1$HNMR chemical shiftsof α-, β-, γ- and 2-HP-CDs in the free state ($\delta_0$) and in the composition of the complexes ($\delta$), ppm

| H atom No. | α-CD | | | β-CD | | | γ-CD | | | 2-HP-CD | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\delta_0$ | $\delta$ | $\Delta\delta = \delta - \delta_0$ | $\delta_0$ | $\delta$ | $\Delta\delta = \delta - \delta_0$ | $\delta_0$ | $\delta$ | $\Delta\delta = \delta - \delta_0$ | $\delta_0$ | $\delta$ | $\Delta\delta = \delta - \delta_0$ |
| 1 | 4.91 | 5.00 | 0.09 | 4.87 | 5.02 | 0.15 | 4.96 | 5.05 | 0.09 | 4.92 | 4.95 | 0.03 |
| 2 | 3.49 | 3.58 | 0.09 | 3.45 | 3.60 | 0.15 | 3.51 | 3.60 | 0.09 | 3.46 | 3.48 | 0.02 |
| 3 | 3.84 | 3.93 | 0.09 | 3.77 | 3.91 | 0.14 | 3.78 | 3.88 | 0.10 | 3.87 | 3.86 | -0.01 |
| 4 | 3.44 | 3.53 | 0.09 | 3.39 | 3.54 | 0.15 | 3.44 | 3.53 | 0.09 | 3.46 | 3.48 | 0.02 |
| 5 | 3.71 | 3.82 | 0.09 | 3.68 | 3.83 | 0.14 | 3.72 | 3.81 | 0.09 | 3.72 | 3.74 | 0.02 |
| 6 | 3.71 | 3.82 | 0.11 | 3.68 | 3.83 | 0.14 | 3.72 | 3.81 | 0.09 | 3.72 | 3.74 | 0.02 |

A comparison of the integrated intensities of the $^1$H NMR signals of the molecule of **1** with α-, β-, γ-, and 2-HP-β-CDs in supramolecular complexes has shown that **1** forms complexes of 1:1 composition with all CDs.

Changes in the proton chemical shifts in cyclodextrin molecules Δδ occurred to an equal extent both for the internal hydrophobic protons H-3, H-5 and H-6, and for protons located in the outer hydrophilic surface H-1, H-2 and H-4at the formation of supramolecular complexes **1** with all CDs. Changes in the chemical shifts of the proton H-6in the molecule of **1** occurred to an equal extent in all the complexes formed by α-, β-, and γ-CDs. The chemical shifts of the proton H-6 in the complexes of **1** with 2-HP-β-CD were slightly different. Due to the similarity in the chemical structure of CDs with molecule **1**, almost all the proton signals of the substrate were not resolved because of the superimposition of cyclodextrin NMR responses on them. Integral intensities of the protons of CDs molecules were 6-8 times larger in magnitude than the corresponding signals of the molecule **1**. It can be assumed on the basis of the data obtained that the main interaction factors are hydrophilic interactions through hydroxyl-groups of interacting molecules with the formation of inclusion complexes, and complexes without inclusion in the supramolecular self-assembly of **1** with CDs molecules [16, 17]. The water-soluble aggregates formed thereby are able to solubilize the lipophilic molecules of substrate **1** through non-inclusive complexation [18]. This is confirmed by the good solubility of the obtained supramolecular aggregates of **1** with CDs in aqueous solutions.

In order to direct search of "candidate compounds" with the desired types of pharmacological activity, substrate **1**was tested using the PASSonline program (http://www.pharmaexpert.ru/passonline). The computer program PASSonline is based on the principle of "sliding control" of databases of chemical compounds, and allows selecting the most promising from the set of substances, i.e. with the desired pharmacological properties. The accuracy of the prediction of biological activity is 94% [19]. It is established that **1**potentially has a wide range of pharmacological properties as a result of PASS-prediction (table 3).

Table 3 – PASS prediction data of the compound **1**

| Type of biologicalactivity | Probability, % | Type of biologicalactivity | Probability, % |
|---|---|---|---|
| Anti-seborrheic | 86 | Antidiskinetic | 67 |
| Anti-eczemic | 82 | Fibrinolytic | 67 |
| Vasoprotective | **77** | Anthelmintic | 63 |
| Antineoplastic | **77** | Cytoprotective | 62 |
| Analeptic | 69 | Anti-infectious | 58 |
| Lipotropic | 67 | Anti-inflammatory | 58 |

As can be seen from table 3, antiseborrhoea and antiparasitic activities are predicted for the molecule **1** with a comparatively high probability of experimental confirmation, as well as other promising pharmacological properties.

Despite of the fact that the computer prediction data does not allow one to state absolutely exactly whether the substance under study will have predictable activity, nevertheless, the use of computer programs like PASSonline allows selecting the most promising substances for in-depth study in biological test systems *invitro* and *invivo* from the set of substances.

## EXPERIMENTAL PART

The α-, β-, γ- and 2-HP-β-CDs of “Fluka”company were used in the work with a purity of 99%; The $^1$H and $^{13}$C NMR spectra were recorded in DMSO-$d_6$ (**1**) and $D_2O$ (complexes) on a JNM-ECA Jeol400 spectrometer (399.78 and 100.53 MHz, respectively). Chemical shifts are measured relative to signals of residual protons or carbon atoms of deuterated dimethyl sulfoxide.

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## Резюме

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### D-ПИНИТОЛДЫҢ ЦИКЛОДЕКСТРИНДЕРМЕН СУПРАМОЛЕКУЛАЛЫ ӨЗІН-ӨЗІ ҚҰРАУЫ

D-пинитолдың циклодекстриндермен супрамолекулалық әрекеттесуі арқылы олардың 1:1 қатынас құрамдағы суда еритін аралас кешендер түзілді. Супракешендер құрылысы ЯМР спектроскопия әдістермен зерттелінді.

**Түйін сөздер:** D-пинитол, циклодекстриндер, супрамолекулалы кешендер, ЯМР спектроскопия.

## Резюме

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### СУПРАМОЛЕКУЛЯРНАЯ САМОСБОРКА D-ПИНИТОЛА С ЦИКЛОДЕКСТРИНАМИ

Путем супрамолекулярного взаимодействия D-пинитола с циклодекстринами образованы водорастворимые смешанные комплексы состава в соотношении 1:1. Строение супракомплексов изучено методами спектроскопии ЯМР.

**Ключевые слова:** D-пинитол,циклодекстрины, супрамолекулярные комплексы, спектроскопия ЯМР.

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# INFLUENCE OF VARIOUS FACTORS ON HYDROGENOLYSIS OF THE SHALE OF THE KENDYRLYK DEPOSIT

**Abstract.** The present work represents the results of studies on the hydrogenation of Kendyrlyk oil shale for the production of motor fuel components, assessment of the state and prospects of hydrogenation under low hydrogen pressure. According to the experimental data, the dependence of the yield of liquid products (YLP) on the temperature, pressure and duration of the experiment was determined by the method of nonlinear regression. It is shown that an increase in the temperature and duration of the experiment does not exert a noticeable effect on the shale hydrogenolysis indicators. And with increasing of hydrogen pressure in the range from 4.0 to 8.0 MPa, the degree of transformation of the organic mass of shale (OMS) increases by 20% and the amount of shale in the reaction of hydrogen is doubled, the yield of liquid products, gas and water is increasing.

**Key words:** hydrogenolysis of shale, the yield of liquid products, Kendyrlyk, bauxite, the organic mass of shale, the degree of conversion.

**Introduction.** Oil shale is one of the promising types of organic raw materials, which can largely compensate, and in the future replace oil products and gas. Unlike other types of solid fossil fuels (SFF), oil shales contain significant amounts of hydrogen in organic matter. The possibility of obtaining liquid and gaseous hydrocarbons from oil shales, similar in composition and properties to petroleum products and natural gas, makes it possible to consider them as important strategic resources [1].

World reserves of oil shale in the equivalent of shale resin are approximately 2.9 trillion barrels, but the industrial processing of oil shale is carried out only in a few countries. At the same time, research begun in the first half of the twentieth century in the field of the processing of oil shale in synthetic motor fuels and chemical products did not cease, and have again become relevant by now.

About 25 deposits and shows of oil shales dated to the Upper Devonian, Lower Carboniferous, Upper Paleozoic, Middle and Upper Jurassic and Paleogene deposits have been identified on the territory of Kazakhstan to date. They differ in the composition of the initial substance and the conditions of formation, which, largely, determined their qualitative and technological characteristics.

The shales of the Kendyrlyk Formation (the Kalynkar and Best layers) have been most thoroughly studied, the shales of the Saikansk Formation are the least studied. High-quality schists of the “Best” layer. The average content of resin exceeds 10%, reaching in some samples up to 27%. The distillation of the resin showed the possibility of using shale to produce artificial fuel. Earlier, we studied the thermodynamic analysis of gasification and the thermocatalytic processing of the Kenderlyk oil shale [2-5]. In the present work, the influence of various factors on the hydrogenolysis of the shale of the Kenderlyk field was studied.

**Experiment.** The work was carried out by researchers from the Research Institute of New Chemical Technologies and Materials and the Moscow State Mining University

As a raw material for hydrogenation, samples of oil shale of Kvarts JSC were applied, additionally enriched by flotation and centrifugal separation in heavy liquids. Shale concentrates had a particle size of less than 0,1-0,2 mm, contained (wt. %): $W^a$ – 1,2-1,3; $A^d$ – 18-22 (including carbon dioxide 2,4-2,5); $S^d$ – 1,7-1,8. The elemental composition of the samples was the following (% on daf): C – 74,2-74,7; H – 8,9-9,0; S – 1,2-1,4; N – 0,4-0,5; O – 14,5-15,0. Heat of combustion of oil shale $Q^{daf}$ was 31,5-33,4 kJ/kg.

Shale paste consisting of 40 wt.% shale and 60 wt.% liquid shale product with a boiling point above 300-320 °C, obtained in the process itself and during the pyrolysis of liquefaction residues was subject to hydrogenation. 0.5-3.0% catalysts were added to the paste, the corresponding polymetallic ores containing Fe, Ni, and Ti were used.

Hydrogenation was carried out at the Research Institute of New Chemical Technologies and Materials in an intensively shaken reactor with a volume of 0.2 liters and at Moscow State Mining University in a bench-type flow-through unit with a reactor volume of 0.8 liters, and the processing of slurry (the remainder of shale liquefaction) by pyrolysis in a flow unit with a moving downward layer of a solid coolant. The capacity of the unit was 3-10 kg of raw materials/h [9-14].

The results of the thermocatalytic hydrogenation of Kenderlyk shale in the intensively shaken reactor are shown in table 1.

Table 1 – Characterization of the process of thermocatalytic hydrogenation of Kendyrlyk shale.
Ratio shale : pasteurizer – 1 : 1,5; Pressure, MPa – 8,0; Duration, min. – 15;
Catalyst - Bauxite -094, wt.% – 2,0; $A^d$ – 15,0

| Process indicators | Temperature, ºC | | |
|---|---|---|---|
| | 410 | 420 | 440 |
| Degree of transformation of OMS, wt. % | 83,2 | 84,5 | 82,2 |
| Hydrogen in the reaction, wt. % | 0,8 | 1,2 | 1,5 |
| The yield of liquid products, wt. % | 50,3 | 49,7 | 46,2 |
| With boiling point higher 320 ºC | 27,2 | 28,4 | 29,5 |
| The remainder with boiling point higher 320 ºC | 23,1 | 21,3 | 16,7 |
| Gas, wt. % | 10,3 | 11,4 | 12,1 |
| Water, wt. % | 7,6 | 7,8 | 8,0 |
| Coke on the mineral part, wt. % | 2,5 | 2,9 | 3,6 |

According to table 1, the nonlinear regression method was used to determine the dependence of the yield of liquid products during the hydrogenation of shale on the temperature T and the degree of transformation of the OMS W:

$$YLP\ (T,W) = 0{,}18T + 0{,}49W - 0{,}0019 \cdot T \cdot W \qquad (1)$$

It was shown (figure 1) that the temperature dependence of YLP to the temperature is extreme, and the data in table 2 indicate that the function of YLP (T, W) satisfactorily reproduces the experimental data.

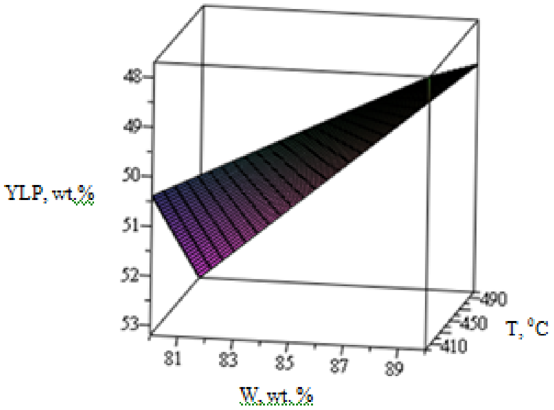

Figure 1 – Influence of temperature and the degree of transformation of OMS on the yield of liquid hydrogenation products

Table 2 – Comparison of experimental and calculated data on the yield of liquid products as a function of temperature and degree of transformation (shale: pasteurizer = 1: 1.5, τ = 15 min, P = 8.0 MPa, catalyst - bauxite No. 094)

| Temperature, °C | W, wt. % | The yield of total liquid products, % | | Δ = (exp.–calc.) | 100·Δ/exp., % |
|---|---|---|---|---|---|
| | | experiment | calculation | | |
| 410 | 83,2 | 50,3 | 55,0 | -5 | -10 |
| 420 | 84,5 | 49,7 | 54,0 | -4 | -8,0 |
| 440 | 82,2 | 46,2 | 52,0 | -6 | -13,0 |

The obtained results indicate that the temperature has a significant effect on the indices of the hydrogenolysis of oil shale. In the temperature range 410-440 ºC, the degree of transformation of the organic mass of shale reaches 82.2-84.5%, with increasing temperature, an increase in gas production and hydrogen consumption is observed from 0.8 to 1.5 wt. % as a result of the destruction of the fraction with a boiling point above 320 ºC, the content of which in hydrogenate decreases from 23.1 to 16.7 and the content of gasoline and diesel fuel increases. The content of coke on the mineral part is insignificant, but increases in the studied temperature range from 2.5 to 3.6 wt.%.

A similar effect on the process of hydrogenolysis of shale has an increase in the reaction time to 30-45 minutes. The data characterizing this fact are summarized in table 3.

Table 3 – Hydrogenolysis of Kendyrlyk shale. Ratio shale : pasteurizer 1 : 1,5; Pressure, MPa – 8,0; Temperature – 410 ºC; Catalyst - Bauxite -094, wt. %. – 2,0; $A^d$ – 15,0

| Process indicators | Duration of experience, min | | |
|---|---|---|---|
| | 15 | 30 | 45 |
| Degree of transformation of OMS, wt. % | 83,2 | 84,7 | 87,2 |
| Hydrogen in the reaction, wt. % | 0,8 | 1,35 | 1,7 |
| The yield of liquid products, wt. % | 50,3 | 49,8 | 49,4 |
| With boiling point higher 320 ºC | 27,2 | 29,6 | 30,1 |
| The remainder with boiling point higher 320 ºC | 23,1 | 20,2 | 19,3 |
| Gas, wt. % | 10,3 | 11,5 | 12,6 |
| Water, wt. % | 7,6 | 7,9 | 8,2 |
| Coke on the mineral part, wt. % | 2,5 | 2,8 | 3,9 |

The function describing the total YLP G (*t, W*) as a function of the duration of the experiment *t* and the degree of OMS conversion W, is as follows:

$$G(t, W) = -0{,}27t + 0{,}59W + 0{,}0030 \cdot t \cdot W \quad (2)$$

The reproducibility of the function is given in table 4, and its graph in the three-dimensional coordinate system is shown in figure 2.

We have studied the effect of pressure on the indices of hydrogenolysis in the interval 4-8 MPa. The results are shown in table 5.

With increasing hydrogen pressure in the range from 4.0 to 8.0 MPa, the degree of transformation of the organic mass of shale increases by almost 20%, and the amount of hydrogen involved in the reaction doubles, the yield of liquid products, gas, water increases, i.e. the process of hydrogenolysis of Kendyrlyk shale intensifies, the content of gasoline and diesel fuel increases. The hydrogen pressure above 8 MPa does not have a significant effect on the process indicators.

Table 4 – Comparison of the experimental and calculated data on the yield of liquid products as a function of the duration of the experiment and the degree of transformation (T = 410 ° C, P = 8.0 MPa, shale: pasteurizer = 1: 1.5, bauxite catalyst No. 094)

| Duration of experience, min | W, wt. % | The yield of total liquid products, % | | Δ = (exp.–calc.) | 100·Δ/exp., % |
|---|---|---|---|---|---|
| | | experiment | calculation | | |
| 15 | 83,2 | 50,3 | 49,0 | 1 | 2,0 |
| 30 | 84,7 | 49,8 | 50,0 | 0 | 0 |
| 45 | 87,2 | 49,4 | 51,0 | -2 | -4,1 |

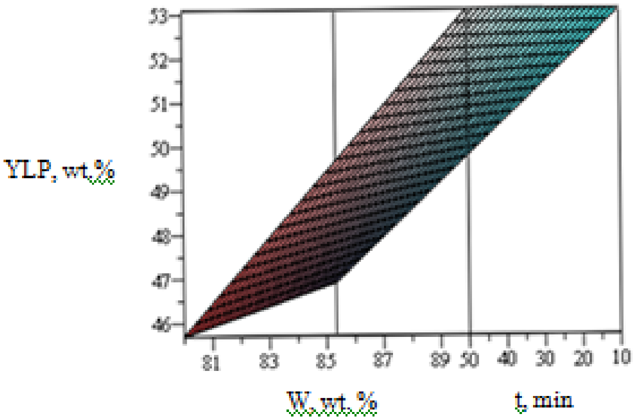

Figure 2 – The graph of the dependence of YLP on the duration of the experiment and the degree of transformation of OMS

Table 5 – Characteristics of hydrogenolysis of Kendyrlyk shale depending on the pressure of the process. Ratio shale : pasteurizer 1 : 1,5; Temperature – 420 ºC; Experiment duration – 15 min; Catalyst - Bauxite -094, wt. %. – 2,0; $A^d$ – 15,0

| Process indicators | The hydrogen pressure in the reactor volume, MPa | | | | |
|---|---|---|---|---|---|
| | 4,0 | 6,0 | 8,0 | 9,0 | 10,0 |
| Degree of transformation of OMS, wt. % | 64,1 | 76,3 | 83,2 | 84,1 | 83,1 |
| Hydrogen in the reaction, wt. % | 0,4 | 0,6 | 0,8 | 1,1 | 1,0 |
| The yield of liquid products, wt. % | 40,2 | 47,1 | 50,3 | 50,3 | 49,9 |
| With boiling point higher 320 ºC | 18,4 | 19,3 | 27,2 | 27,4 | 26,9 |
| The remainder with boiling point higher 320 ºC | 21,8 | 27,8 | 23,1 | 22,9 | 23,0 |
| Gas, wt. % | 6,8 | 8,9 | 10,3 | 11,0 | 10,5 |
| Water, wt. % | 5,7 | 6,8 | 7,6 | 7,8 | 7,8 |
| Coke on the mineral part, wt. % | 1,8 | 2,1 | 2,5 | 2,5 | 2,5 |

According to the data in table 5, hydrogen in the series of experiments varies insignificantly (from 0.4 to 1.1), so the total YLP can be represented as a function of *G (P, W)* from two variables: pressure (P) and degree of OMS transformation (W). Mathematical processing of the data of table 5 by the method of nonlinear regression showed the following relationship:

$$G(P, W) = 4{,}876 \cdot P + 0{,}5408W - 0{,}05184 \cdot P \cdot W \qquad (3)$$

Table 6 shows the data showing the reproducibility of the experimental data G (P, W), and figure 3 shows its graph, which clearly shows the dependence of the YLP in the hydrogenolysis of the Kenderlyk meteorite shale on the pressure and the degree of OMS transformation.

Table 6 – Comparison of the experimental and calculated data on the yield of liquid products as a function of the pressure of the process and the degree of conversion (T = 420°C; t = 15 min; shale : pasteurizer = 1:1,5; Catalyst - Bauxite № 094)

| Process pressure, MPa | W, wt. % | The yield of total liquid products, % | | Δ = (exp.–calc.) | 100·Δ/exp., % |
|---|---|---|---|---|---|
| | | experiment | calculation | | |
| 4,0 | 64,1 | 40,2 | 40,88 | -0,68 | -1,692 |
| 6,0 | 76,3 | 47,1 | 46,79 | 0,31 | 0,6582 |
| 8,0 | 83,2 | 50,3 | 49,50 | 0,80 | 1,5900 |
| 9,0 | 84,1 | 50,3 | 50,12 | 0,18 | 0,3579 |
| 10,0 | 83,1 | 49,9 | 50,62 | -0,72 | -1,443 |

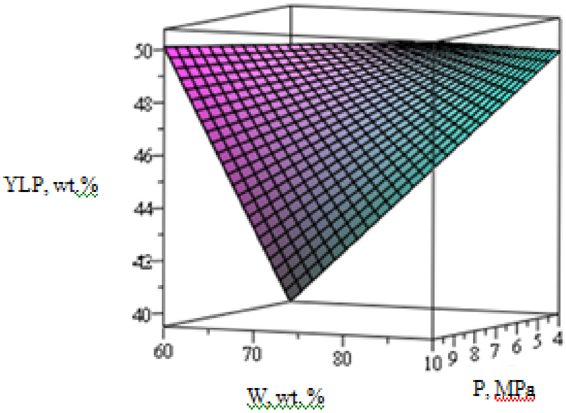

Figure 3 – Graph of the YLP function (P, W)

**Conclusion.** Thus, the analysis shows that during the hydrogenolysis of shale of Kenderlyk deposit, the temperature and duration of the experiment do not have a significant effect on the yield of liquid products, and increasing the hydrogen pressure in the interval from 4.0 to 8.0 MPa leads to an increase in YLP from 40.2 to 50.3 by weight %. The hydrogen pressure above 8 MPa does not have a significant effect on the process indicators.

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## Резюме

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## ВЛИЯНИЕ РАЗЛИЧНЫХ ФАКТОРОВ НА ГИДРОГЕНОЛИЗ СЛАНЦА МЕСТОРОЖДЕНИЯ «КЕНДЕРЛЫК»

В настоящей работе приведены результаты исследований по гидрогенизации Кендырлыкского горючего сланца для получения компонентов моторных топлив, оценка состояния и перспективы применения метода гидрогенизации под невысоким давлением водорода. По экспериментальным данным, методом нелинейной регрессии определены зависимости выхода жидких продуктов (ВЖП) от температуры, давления и продолжительности опыта. Показано, что увеличение температуры и продолжительности времени эксперимента не оказывают заметного влияние на показатели гидрогенолиза сланца, а с повышением давления водорода в интервале от 4,0 до 8,0 МПа на 20% увеличивается степень превращения органической массы сланца (ОМС) и количество вовлеченного в реакцию водорода увеличивается в два раза, нарастает выход жидких продуктов, газа и воды.

**Ключевые слова:** гидрогенолиз сланца, выход жидких продуктов, Кендерлык, боксит, органическая масса сланца, степень превращения.

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ЕМК Жаңа химиялық технологиялар және материалдарды ҒЗИ, Алматы, Қазақстан

## «КЕНДЕРЛІК» КЕН ОРНЫ ТАҚТАСЫН ГИДРОГЕНДЕУГЕ ӘРТҮРЛІ ФАКТОРЛАРДЫҢ ӘСЕРІ

Берілген жұмыста Кендерлік кен орнының жанғыш тақтатасын гидрогендеу арқылы мотор отындарының компоненттерін алу нәтижелері, күйді бағалау мен сутегінің төмен қысымында гидрогендеу әдістерін қолдану болашағы көрсетілген. Зерттеу нәтижелері бойынша сызықтық емес регрессия әдісі арқылы сұйық өнімдердің шығымының (СӨШ) температураға, қысымға және тәжірибенің ұзақтылығына тәуелділіктері анықталған. Нәтижесінде температура мен тәжірибенің ұзақтылығын жоғарылату тақтасты гидрогендеу көрсеткіштеріне айтарлықтай әсер етпейді, ал сутектің қысымы 4,0-тен 8,0 МПа аралығында жоғаралаған сайын тақтастың органикалық салмағының (ТОС) айналу дәрежесі 20 % жоғарылайды және судың, газдың, сұйық өнімдердің шығымы, реакцияға кіріскен сутектің мөлшері 2 есе жоғарылайды.

**Түйін сөздер:** тақтатасты гидрогендеу, сұйық өнімдердің шығымы, Кендерлік, боксит, тақтатастың органикалық салмағы, айналу дәрежесі.

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# SAFETY OF TEXTILE MATERIALS TREATED WITH ANTIMICROBIAL AGENTS

**Abstract.** The article is devoted about development of cellulose textile materials by sol-gel method, using safe antimicrobial agents. The influence of the sol-gel composition on the physical and mechanical properties and safety indices of textile materials were studied. Comparison obtained burst load data processed materials showed that a gelatin-based composition have reduced burst load parametersthan liquid glass . According to the results of the study, titanium dioxide has the lowest antimicrobial activity than zinc chloride. Optimal technological regimes for the production of antimicrobial cellulose textile materials have been developed.

**Key words:** sol-gel, ecological safety, antimicrobial activity, final finishing of textile materials, sodium metasilicate, gelatin, titanium dioxide, zinc chloride.

**Introduction.** The problem of clothing security is most relevant for the population. In addition, the trend of increasing use of materials from chemical fibers and threads, as well as their chemical finishes, along with economic advantages, also carries serious risks to human health.

A serious problem for the hygienic assessment of modern textiles is textile-auxiliary substances, the main component of which is formaldehyde, which belongs to the second class of danger, has a general toxic, irritant, allergenic, mutagenic, carcinogenic effect, causes damage to the central nervous system, lungs, liver , kidneys, organs of vision. The concentration of free formaldehyde in tissues exposed to additional final finishes with preparations based on precondensates of thermosetting resins is especially great. The allocation of chemical volatile substances in this case should not exceed the standards specified in TR TS 017/2011 "On the Safety of Light Industry Products".

The creation of materials with new preset properties is possible on the basis of chemical, colloidal processes. The technology of obtaining materials with certain chemical and physico-mechanical properties, including obtaining the sol and transferring it to the gel. Today's sol-gel technology is a way of obtaining multicomponent gels of high homogeneity and purity with the subsequent conversion into gel into: films, fibers, powders, monolithic, porous products [1].

Analysis of the literature showed that the sol-gel method in the final finishing of textile materials, as well as the safety study of these materials is still at the study stage.

In this regard, the development of a technology for the production of antimicrobial cellulosic textile materials and the study of the safety of these materials treated with antimicrobial preparations using sol-gel technology [2, 3], which simultaneously will not only reduce the resource costs, the availability of reagents and equipment, is topical.

Safety of light industry products is estimated by the following indicators:

– mechanical (breaking load, strength of fastening, flexibility, impact strength);

– chemical (the maximum permissible release of harmful chemicals into the air and (or) aquatic environment, the list of which is determined depending on the chemical composition of the material and (or) the purpose of the product);

– biological (hygroscopicity, air permeability, water resistance, electrostatic field strength, toxicity index or local irritant effect, color stability).

To obtain antibacterial textile materials, antimicrobials and conditions for the synthesis must be appropriately selected. Using appropriate synthesis conditions and careful selection of biocides, a large amount of biocide can be incorporated inside the silica matrix, so that the biocide becomes effective [4, 5].

## MATERIALS AND METHODS

**Materials.** The object of the study was 100% bleached cotton linen fabric with article 1030 and a surface density of 147 g / m$^2$.

**Preparation of samples.** For the sol-gel composition the following components were chosen: liquid glass concentration 5-10 g / l, gelatin 10-20 g / l, titanium dioxide, zinc chloride concentration 5-10 g / l, water solvent. After stirring the solution for 5-7 minutes, HNO3 3-5 ml / l or sodium carbonate 10-15 g / l (in portions) was added to the magnetic stirrer at room temperature, to a pH of 10-11.

Then, impregnation of tissue samples was carried out at room temperature for 2-4 minutes. After impregnation, the tissue was squeezed to a weight gain of 90-100%. Further, the samples were dried in a oven for 8-10 minutes at 70-90 °C. The heat treatment was carried out at temperatures of 100, 125, 150 ° C for two minutes.

**Research methods.** The tensile strength of the fabric was measured on a tensile machine RT-250M (Russia) in accordance with GOST 3813-72. "Textile materials. Fabrics and piece goods. Methods for determining tensile properties of tensile properties".

According to GOST 9.060-75 Unified system of protection against corrosion and aging. Fabrics. "The method of laboratory tests for resistance to microbiological destruction determined the biostability of tissues in laboratory conditions".

In accordance with GOST 12088-77 "Textile materials and products made of them". The method for determining air permeability was carried out on a machine MT-160 (Russia).

Determination of low-fissility of the fabric was carried out on a machine MT-022 (Russia) in accordance with GOST 19204-73 "Textile fabrics. Method for determination of non-rupture".

## RESULTS AND DISCUSSION

It is known that the finishing or coating of fibers can reduce the resistance of the tissue to rupture, so studies have been carried out to identify this fact, and the biostability of tissues in the laboratory has been determined, the results are shown in table 1.

Table 1 – Parameters of the absolute breaking load of the modified samples, kgf before and after biodegradation

| № | Concentration of components | | The catalyst | Heat treatment, °C | The absolute breaking load, kgf | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | ducks | | the substrate | |
| | | | | | F | L | F | L |
| 1 | $TiO_2/ZnC_2$ 5g/L | $Na_2SiO_3$ 5-10 g/L | $HNO_3$ 3-5 m/L, $NaHCO_3$ 10-15 g/L | 100 | 17.6 | 43.1 | 17.3 | 26.7 |
| | | | | | 17.2 | 38.2 | 16.4 | 28.1 |
| | | | | 125 | 16.3 | 25.1 | 18.7 | 30.1 |
| | | | | | 16.8 | 26.7 | 18.4 | 33.1 |
| | | | | 150 | 14.8 | 42.6 | 19.4 | 42.4 |
| | | | | | 14.1 | 39.2 | 18.3 | 29.9 |
| 2 | $TiO_2/ZnC_2$ 5 g/L | Желатин 20 g/L | | 100 | 17.8 | 38.6 | 18.4 | 48.4 |
| | | | | | 18.1 | 39.1 | 17.4 | 49.6 |
| | | | | 125 | 13.2 | 37.8 | 20.2 | 56.1 |
| | | | | | 12.8 | 36.2 | 18.2 | 49.1 |
| | | | | 150 | 13.1 | 41.7 | 17.8 | 37.9 |
| | | | | | 12.0 | 40.2 | 16.2 | 58.7 |
| 3 | Untreated sample | | | | 13.8 | 45 | 14.1 | 39.3 |

The obtained burst load data in comparison with liquid glass and gelatin showed that the processed materials with a gelatin-based composition have reduced burst load parameters, possibly due to an increase in the gelatin concentration to 20 g / L, a liquid glass concentration of 5-10 g / L, or a different the structure of precursors affecting textile material.

With increasing heat treatment temperature, the breaking load of the treated fabric is reduced. This is due to the fact that in the process of polymerization of the nanoscale solution and the formation of a polymer film on the fiber, the mutual mobility of macromolecules decreases.

Two antimicrobial agents were used, according to the results of the study, titanium dioxide has lower antimicrobial activity results than zinc chloride. This is evidenced by the results of the burst load after biodestruction, the strength indexes decreased by 3-5%.

Mildewedness was estimated from the total opening angle of fabric folds on the basis and weft in accordance GOST 19204-73 on the SMT instrument. The results are represented in table 2.

Table 2 – Effect the concentration of components of the composition on indices of low crumeness of cotton fabric

<table>
<tr><th rowspan="2">№</th><th colspan="2" rowspan="2">Concentration of components</th><th>Catalyst</th><th colspan="6">Heat treatment, °C</th></tr>
<tr><td rowspan="6">$HNO_3$ 3-5 ml/L, $NaHCO_3$ 10-15 g/L</td><th colspan="2">100</th><th colspan="2">125</th><th colspan="2">150</th></tr>
<tr><td rowspan="3">1</td><td rowspan="3">$TiO_2/ZnCl_2$ 5 g/L</td><td rowspan="3">$Na_2$ $SiO_3$ 5-10 g/L</td><td>ducks</td><td>the substrate</td><td>ducks</td><td>the substrate</td><td>ducks</td><td>the substrate</td></tr>
<tr><td>125</td><td>95</td><td>115</td><td>90</td><td>105</td><td>95</td></tr>
<tr><td colspan="2">220</td><td colspan="2">205</td><td colspan="2">200</td></tr>
<tr><td rowspan="2">2</td><td rowspan="2">$TiO_2/ZnCl_2$ 5 g/L</td><td rowspan="2">Желатин 20 g/L</td><td>120</td><td>115</td><td>115</td><td>105</td><td>105</td><td>95</td></tr>
<tr><td colspan="2">235</td><td colspan="2">220</td><td colspan="2">200</td></tr>
<tr><td rowspan="3">3</td><td colspan="3" rowspan="3">Untreated sample</td><td colspan="3">ducks</td><td colspan="3">the substrate</td></tr>
<tr><td colspan="3">105</td><td colspan="3">95</td></tr>
<tr><td colspan="6">200</td></tr>
</table>

The analysis of the results showed that in the samples treated with the proposed compositions, compared to non-impregnated tissue, the low-crease results are increased. With an increase in the concentration from gelatin to 20 g /Ll, the result of low crushing was 235 degrees, with a slightly higher temperature of heat treatment.

For many textiles, air permeability of the fabric is an important property, and studies have been carried out in connection with this. The results are shown in table 3. Based on the results obtained, it has been shown that the treatment of cellulosic materials using a sol-gel method based on liquid glass and gelatin does not lead to disruption of air and steam exchange, does not prevent the transport of moisture vapors from the surface of the human skin to the outer surface of materials, which ensures the maintenance of normal functions of thermoregulation of the human body.

Table 3 – Indices of air permeability of processed samples

<table>
<tr><th rowspan="3">№</th><th colspan="2" rowspan="3">The concentration of the components</th><th>The catalyst</th><th colspan="3">Air permeability, $dm^3/m^2 \cdot s$</th></tr>
<tr><td rowspan="4">$HNO_3$ 3-5 мл/л, $NaHCO_3$ 10-15 g/L</td><th colspan="3">Heat treatment, °C</th></tr>
<tr><th>100</th><th>125</th><th>150</th></tr>
<tr><td>1</td><td>$TiO_2/ZnCl_2$ 5 g/L</td><td>$Na_2$ $SiO_3$ 5-10 g/L</td><td>169,9</td><td>168,1</td><td>162,5</td></tr>
<tr><td>2</td><td>$TiO_2/ZnCl_2$ 5 g/L</td><td>Gelatin 20 g/L</td><td>168,5</td><td>167,3</td><td>166,8</td></tr>
<tr><td>3</td><td colspan="3">Untreated sample</td><td colspan="3">166</td></tr>
</table>

**Conclusion.**

1. Modified cellulose textile materials were taken using safe antimicrobial preparations with a sol-gel method;

2. When the temperature is raised to 150 ° C, a certain decrease in the strength parameters is observed. The results of the burst load after biodegradation showed a decrease in strength parameters by 3-5%;

3. Based on the results of the study, titanium dioxide has lower antimicrobial activity values than zinc chloride;

4. Studies of air permeability showed that with increasing temperature and concentration of liquid glass and gelatin, a slight decrease in air permeability occurs from 169.9 at 100 $^0$C to 162.5 at 150 $^0$C;

5. According to the results of the study of low-purity, it has been established that with an increase in the gelatin concentration to 20 g / L, the indices increase from 200 degrees to 235 degrees.

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## Резюме

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## АНТИМИКРОБТЫҚ ПРЕПАРАТТАРМЕН ӨҢДЕЛГЕН ТЕКСТИЛЬ МАТЕРИАЛДАРЫНЫҢ ҚАУІПСІЗДІГІ

Статияда золь-гель әдісін қолдану арқылы антимикробтық целлюлозалық модифицирленген текстиль материалдарын алу тәсілі жазылған. Қауіпсіз препараттар арқылы целлюлозалық модифицирленген текстиль материалдарын алу технологиясы жасалды. Ұсынылған тәсіл мақта мата үлгілерін золь-гель композициясына сіндіріп, содан кейін кептіру және термиялық өңдеуден өткізуден тұрады.

Модифицирленген үлгілердің беріктігіне және микробиологиялық тұрақтылығына шыны сұйықтығы мен желатин концентрациясының әсері зерттелді. Аппреттеу үшін оптимальды келесідей параметрлер ұсынылды: сұйық шыны концентрациясы 5-10 г/л, азот қышқылы концентрациясы 3-5 мл/л, цинк хлориді концентрациясы 5 г/л және термоөңдеу температурасы 125 °С. Жасалынған текстиль материалдарын өңдеу технологиясы текстиль материалдарының гигиеналық және эксплуатационды қасиеттерін сақтай отырып антимикробтық белсенділікті қамтасыз етеді.

**Түйін сөздер:** золь-гель, экологиялық қауіпсіздік, антимикробты өңдеу, текстильматериалдарын соңғы өңдеу, натрий метасиликаты, желатин, цинк хлориді.

## Резюме

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### БЕЗОПАСНОСТЬ ТЕКСТИЛЬНЫХ МАТЕРИАЛОВ, ОБРАБОТАННЫХ АНТИМИКРОБНЫМИ ПРЕПАРАТАМИ

Описан способ получения антимикробных целлюлозных текстильных материалов с применением золь-гель метода. Разработана технология модифицирования с применением безопасных препаратов. Предложенный способ состоит в последовательной пропитке образцов хлопчатобумажной ткани в золь-гель композиции с последующей сушкой и термической обработкой.

Исследовано влияние концентрации жидкого стекла и желатина на устойчивость к микробиологическому разрушению и прочностные свойства модифицированных образцов. Выявлено, что оптимальными параметрами для аппретирования являются: концентрация жидкого стекла 5-10 г/л, концентрация азотной кислоты 3-5 мл/л, концентрация хлорида цинка 5 г/л и температура термообработки 125 °С. Разработанная технология отделки текстильных материалов обеспечивает антимикробную активность текстильного материала с сохранением гигиенических и эксплуатационных свойств..

**Ключевые слова:** золь-гель, экологическая безопасность, антимикробная активность, заключительная отделка текстильных материалов, метасиликат натрия, желатин, диоксид титана, хлорид цинка

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# ПЯТЬ ГЛОБАЛЬНЫХ ВЫЗОВОВ XXI ВЕКА И ПРЕДЛОЖЕНИЯ ПО ИХ РЕШЕНИЮ

**Аннотация.** В обзорной статье рассматриваются пять глобальных вызовов XXI века, обозначенные Главой Государства, касательно обеспечения продуктами питания населения нашей планеты – угроза глобальной продовольственной безопасности, исчерпаемость ресурсов и деградация земель, проблемы кормовой базы и пастбищ для животноводства, острый дефицит воды, глобальная энергетическая безопасность, недостатки второй и третьей индустриальной революции. Представляются предложения по их решению.

На основании достоверных результатов исследований (2003-2016 гг.), проведенных в специализированных институтах, опытных, опытно-производственных работ, а также применения нового поколения фитобиопрепаратов – микробиоудобрения МЭРС в Республике Казахстан на площади более 3 млн. га (2003-2017 гг.), Государстве Туркменистан - 90 тыс. га (2015–2017 гг.), Республики Узбекистан в 9-ти областях (2013, 2014, 2017, 2018 гг.), в 6-ти субъектах Российской Федерации (2013–2014 гг.) микробиоудобрения МЭРС, установлено:

– получение на фоне минерального питания, дополнительного урожая яровой мягкой пшеницы на богарных землях - 3–3,5 ц/га, на поливе хлопка-сырца - 10-20 ц/га, картофеля и овощебахчевых культур – 150-300 ц/га, плодовых и виноградника – 100-150 ц/га, кормовых – 100-150 ц/га;

– повышение урожайности с/х культур при снижении нормы минеральных удобрений в 1,5-3 раза, дефиците поливной воды и почвенной влаги в 1,3 и 1,7 раза, засоленности земель, суховеев на 150-300%;

– покрытие, за счет реализации дополнительного урожая, полных затрат возделывания с/х культур на 30-100% и более;

– накопление в почве после уборки дополнительного урожая 38-40 кг/га усвояемых форм NPK питательных элементов и 5-20 т/га органики.

Полученные результаты являются основой решения пяти глобальных вызовов XXI века.

**Ключевые слова:** микробиоудобрение МЭРС, продовольственная безопасность, деградация земель, проблемы кормовой базы и дефицита воды, глобальная энергетическая безопасность, недостатки первой, второй и третьей индустриальной революций.

**Введение.** Обеспечение всевозрастающего населения нашей планеты полноценными продуктами питания в XXI-м веке является весьма актуальным, для которого инновационное развитие Агропромышленного комплекса, и, в частности, производство растениеводства, имеет большое значение [1].

Химизация производства растениеводства, в частности применение минеральных удобрений, привела к угрозе потери продовольственной безопасности Государств, основной причиной которой стали: деградации земель; снижение гумуса; ухудшение экологии почвы [3].

Президент Республики Казахстан в своем Обращении к народу Казахстана отмечает, что *вода - крайне ограниченный ресурс*, и борьба за обладание ее источниками уже становится важнейшим фактором геополитики и конфликтов на планете. Дефицит воды в недалеком будущем может создать большие проблемы в мегаполисах и в поливном земледелии.

Для решения вышеприведенных вызовов XXI века АО «Институт химических наук имени А.Б. Бектурова» совместно с ТОО Научно-производственное объединение «Ана Жер» разработало новое поколение фитобиопрепаратов – микробиоудобрение МЭРС, эффект действия которого основан на использовании неисчерпаемой бесплатной энергии почвенных микро- и макроорганизмов, что является новым направлением в обеспечении продуктов питания населения нашей планеты в XXI веке [2, 4].

Инвестирование МЭРС в растениеводство Республик Казахстан и Узбекистан, Государства Туркменистан может явиться основой выполнения направлений - развития и либерализации экономик, развития социальной сферы «Стратегии действий по дальнейшему развитию государств Центральной Азии на 2019-2023 годы.

## РЕЗУЛЬТАТЫ И ИХ ОБСУЖДЕНИЯ

### Анализ пяти глобальных вызовов XXI века и задач «Стратегии «Казахстан – 2050»

Президент Республики Казахстан Н.А. Назарбаев в обращении к народу Казахстана от 14 декабря 2012 года отметил 5 глобальных вызовов XXI века, связанных с обеспечением всевозрастающего населения нашей планеты продуктами питания.

В Послании народу Казахстана от 17 января 2014 года для обеспечения прогресса страны он выделил следующее: за счет внедрения наукоемкой модели экономики увеличить до 70% экспортный потенциал несырьевой продукции; в два раза снизить энергоемкость валового и внутреннего продукта; для создания новых технологических отраслей экономики обеспечить рост финансирования науки до уровня, не ниже 3,1% от ВВП.

### 1. Угроза глобальной продовольственной безопасности

Для выполнения поставленных задач Правительством РК было проведено Совещание с участием Президента Республики Казахстан (Протокол № 01-7.1 от 23.01.2013 г.), где в пункте 3.4 «Стратегия «Казахстан – 2050» предусмотрено «Внедрение передового опыта использования влаго- и ресурсосберегающих технологий, обеспечение сельского хозяйства семенами, удобрениями и средствами защиты растений».

*Наша справка.* В мире недобор урожая из-за засухи составляет более 30%, жаркого ветра (суховей) - 15% и из производимых 730 млн. т пшеницы доля слабой пшеницы (фуражное зерно) имеет значение 52-55%, (Узбекистане - 100%, Туркменистане - 70%, Российской Федерации - более 30%, Украине - более 27%).

Используемые в растениеводстве минеральные удобрения и средства защиты растений имеют ряд существенных недостатков. Коэффициент использования азота туков не превышает 35%, пентаоксида фосфора – 20%. Минеральные удобрения и средства защиты растений снижают качество сельскохозяйственных культур. Потенциал средств питания и защиты растений исчерпан и не в состоянии обеспечить продуктами питания (тем более качественными) население нашей планеты в XXI веке. Уже к 2040 году будет необходимо повысить урожайность продукции растениеводства на 70%.

Казахстан из-за несвоевременного выпадения осадков занимает последнее место в мире по сбору зерновых на единицу посевной площади.

Также следует отметить, что сельхозтоваропроизводителями используется не более 20% минеральных удобрений, выпускаемых в Республике Казахстан. При этом доля минерального питания в формировании растений составляет не более 10%, а оставшиеся 90% - приходятся на почвенные ресурсы.

*Наши предложения:* Необходимо создание и продвижение на рынок новых, абсолютно инновационных препаратов, которые могли бы обеспечить: более полное питание и защиту растений; повышение засухо- и жароустойчивости (суховей) растений; увеличение урожайности сельскохозяйственных культур на богарных землях на 20-50%, на поливе - 40-100%; получение качественной и экологически чистой продукции.

## 2. Исчерпаемость ресурсов земель

Наряду с природными богатствами мы должны бережно относиться к почвенному плодородию. Если мы *потеряем* почвенное *плодородие*, то нам *не нужны* будут *нефть*, *газ, электроэнергия.*

Почвенное плодородие является единственным источником для пропитания всего живого на Земле. Важным в сохранении баланса в экосистеме является почвенный покров. Наивности человечества нет предела, потеря почвенного плодородия и, соответственно, почвенного покрова остановит жизнь на нашей планете.

Сегодня из-за деятельности человека в мире теряется 26 млрд.т в год плодородного слоя почвы. При этом ежегодно наблюдается интенсивный процесс деградации почв, который в последние годы увеличился в 30 раз в сравнении с историческим периодом голоцена.

*Наша справка. Эффект Арала.* По данным ООН из-за высыхания Арала несколько сот миллионов тонн пыли, песка и соли витает в воздухе, и они уже достигли Индийского океана, нарушая экосистему 20–25% нашей планеты. Из года в год пахотные земли Республики Узбекистан сокращаются вследствие заноса их песком и солью.

Наши почвы дошли до критической точки. Дальнейшая деградация земель приведет к полной деструкции почв, и она превратится в пыль и выветрится. В результате: 1. Человечество ждет голод. 2. Пыль затмит солнце, что приведет к мировой катастрофе.

***2.1. Деградация земель и Парниковый эффект из-за применения минеральных удобрений.*** Для повышения урожайности с/х культур во всем мире используют минеральные удобрения. Однако минеральные удобрения, особенно азотные, резко увеличивают численность олиготрофных микроорганизмов в 5-9 раз, которые минерализуют гумус и органические вещества почвы. При внесении в почву 100 кг/га аммиачной селитры происходит разложение 250-500 кг/га органических веществ, при этом в газовую фазу выделяется 150-300 кг/га углекислого газа, 11,5-23 кг/га азота почв в виде диоксида и оксида, по эквиваленту превышающие азот вносимых удобрений.

По данным лауреатов Нобелевской премии за 2007 г. «вклад» минеральных удобрений в парниковый эффект составляет 20-22%. Их предложения: для снижения парникового эффекта из-за минерального питания и деградации земель уменьшить норму использования туков.

Сегодня 20–22% всего накопленного углекислого газа в атмосфере – это результат разрушения гумуса и органических соединений почвы вследствие применения минеральных удобрений.

В развитых государствах мира на поливных землях, где NPK-удобрения использовались согласно научно-обоснованным рекомендациям, потеряно до 60% гумуса. Если бы эти средства питания растений положительно влияли на гумус почвы, разве бы это случилось? Интенсивное применение минеральных удобрений в Китае привело к тому, что из 129 млн га посевных площадей 100 млн деградированы. Поэтому в Китае принято решение уменьшить нормы использования минеральных удобрений в 2 раза, обеспечивая их эффективность за счет микроорганизмов.

Человечество, удобряя почву, невольно удобряет и Мировой океан, вследствие чего повышается скорость поглощения углекислого газа, который приводит к интенсивному выделению в атмосферу закиси азота. При этом неумеренное потребление минеральных удобрений, и в первую очередь нитратов, снижает содержание кислорода в почве, а это способствует повышенному выделению в атмосферу закиси азота и метана.

Углекислый газ (диоксид углерода), пропуская длинноволновые лучи света к поверхности Земли, задерживает отражение коротковолнового излучения, что приводит к нагреванию поверхности планеты и изменению климата. Окислы азота оказывают отрицательное влияние на парниковый эффект, баланс различных экосистем и здоровье людей. Закись азота вредит нашей атмосфере в 300 раз интенсивнее, чем углекислый газ, и является главной причиной разрушения озонового слоя Земли. Метан – мощный парниковый газ, отрицательный эффект которого сильнее диоксида углерода в 21 раз.

***2.2. Проблемы кормовой базы и пастбищ для животноводства.***

1. Годовая потребность животноводства в кормах 30-32 млн т кормовых единиц.

2. Реальное потребление 18-20 млн т. Дефицит 38-40%.

3. Посевы многолетних трав сократились от 2,3 до 1,4 млн га, однолетних трав – от 2,2 млн га до 105 тыс. га.

4. Более половины используемых пастбищ – 70 млн га, деградированы.

5. Для полноценного обеспечения нынешнего поголовья скота пастбищным кормом, необходимо внести в оборот около 30 млн га пастбищ.

*Наши предложения:* Государство должно озадачить ученых созданием новых, абсолютно инновационных препаратов, которые могли бы обеспечить:

– снижение парникового эффекта;

– сохранение и повышение почвенного плодородия;

– получение высоких и качественных урожаев сельскохозяйственных культур;

– восстановление деградированных пастбищ и, в условиях дефицита почвенной влаги, продление периода вегетации растений;

– снижение себестоимости мясомолочной продукции за счет повышения рентабельности возделывания кормовых культур.

***2.3. Острый дефицит воды.*** Президент Республики Казахстан в своем обращении к народу Казахстана отмечает, что *вода - крайне ограниченный ресурс*, и борьба за обладание ее источниками уже становится важнейшим фактором геополитики и конфликтов на планете. Дефицит воды в недалеком будущем может создать большие проблемы в мегаполисах и в поливном земледелии.

*Наша справка:*

1. Как было отмечено, из-за дефицита почвенной влаги мы находимся на последнем месте в мире по сбору урожая пшеницы на единицу посевной площади.

2. В поливном земледелии 20-25 % выращиваемых овощебахчевых культур не востребовано населением.

3. В Алматинской области на посевной площади 470 тыс. га для полива расходуется более 2 млрд.куб.м. пресной воды, а годовая потребность в водообеспечении г.Алматы составляет не более 600 млн.куб.м. Снижение нормы поливной воды на 25 % может обеспечить водой еще один город с населением, большим, чем Алматы.

*Наше предложение*:

1. Необходимо разрабатывать инновационные препараты и технологии, обеспечивающие высокие урожаи с/х культур, кроме капельного орошения, при снижении нормы поливной воды в 1,3-1,7 раза.

2. С учетом потребительского спроса нужно наладить государствен-ное регулирование выращивания продукции растениеводства на поливе.

3. Очень интересная идея – использование подпочвенных вод за счет мощной корневой системы. Для этого нужно определить глубину залегания грунтовых вод по зонам и областям, определить препараты, усиливающие корневую систему растений.

4. Сбалансированная транспирация влаги из почвы в растение и снижение испарения влаги из растений может стать одной из основ повышения КПД использования почвенной влаги.

***2.4. Глобальная энергетическая безопасность.*** Глава Государства Н.А. Назарбаев отметил: «Наступает новая эра, в которой человеческая жизнедеятельность будет основываться не только и не столько на нефти и газе, сколько на возобновляемых источниках энергии».

*Наша справка*. Как было сказано ранее, для повышения урожайности с/х культур используют минеральные удобрения, а для ее сохранения - пестицидные препараты, производство которых очень энергоемко.

Для выпуска 1 т минерального питания необходимо 6 тыс. кВт электроэнергии. Следует отметить, что во времена СССР в конце 80-х годов в Казахстане применялось 1,3 млн т минеральных удобрений.

*Наше предложение*. Использовать в производстве растениеводства бесплатную энергию почвенных микроорга-низмов, численностью в одном грамме почвы 4-16 млрд.КОЕ, а также мощную корневую систему. Кроме того, необходимо создание новых иннова-ционных биопрепаратов, обеспечивающих высокую эффективность мине-ральных удобрений при снижении нормы их применения в 2-4 раза.

***2.5. Недостатки второй и третьей индустриальных революций.*** *Наша справка.* В XX в. численность населения нашей планеты увеличилась с 1,6 до 6 млрд. чел., в 2011 г. она достигла 7 млрд., а в 2014 г. – 7,3 млрд., поэтому все эти вызовы связаны с обеспечением всевозрастающего населения нашей планеты продуктами питания в XXI-м веке.

Научно-технический прогресс, вторая индустриальная революция и погоня за большими прибылями в XX-м веке привели к большим проблемам, связанным с нарушением экосистемы. В этом немалая доля принадлежит интенсивной химизации сельскохозяйственного производства с использованием минеральных удобрений и средств защиты растений, что привело к деградации земель и увеличению выбросов в атмосферу углекислого газа, метана и азота. Ученые экологи предупреждают, что если не сбавить обороты, то уже к 2050 г. человечество может столкнуться с экологической катастрофой. А это: изменение климата; необходимость многомиллиардных инвестиций на преобразование сельского хозяйства; рост цен на пищевые продукты; затопление больших территорий и голод; переселение людей, что неизбежно приведет к внутринациональным и межнациональным трениям и конфликтам.

Сегодня в мире более 1 млрд. чел. проживают за чертой бедности. Глобальное потепление или похолодание в итоге приведут к исчезновению жизни на земле. Деградация земель, дефицит поливной воды и почвенной влаги, заморозки, жаркие ветра повлекут за собой резкое снижение запасов продовольствия.

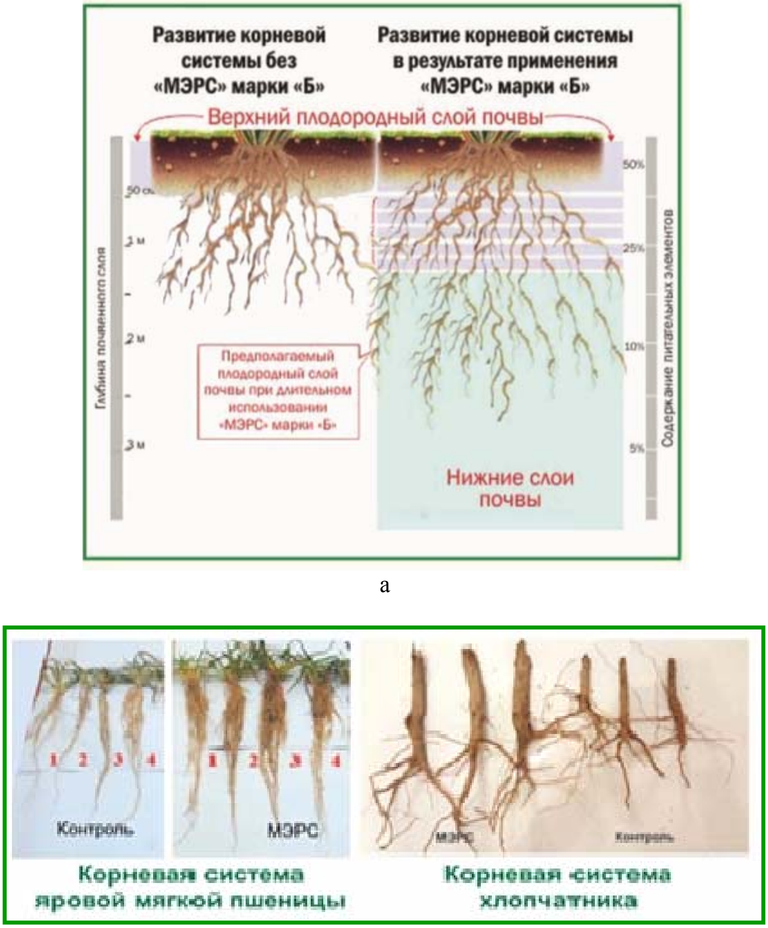
*Наше предложение:* Необходимы новые инновационные разработки в Четвертой индустриальной революции, скорее всего, «инновационной революции», устраняющие недостатки Второй и Третьей индустриальных революций, в частности, по: сохранению почвенного плодородия; снижению негативного влияния минеральных удобрений и пестицидов на парниковый эффект и деградацию земель; получению высоких стабильных урожаев с/х культур в экстремальных погодных условиях. Этим решением можно про-длить стабильность в мире на несколько столетий.

## 3. Новое поколение биопрепаратов – микробиоудобрение МЭРС в решении проблемных вопросов земледелия и растениеводства в XXI в. [4-6]

***3.1. Микробиоудобрение МЭРС - основа использования неисчерпаемой бесплатной энергии почвенных микроорганизмов и мощной корневой системы.*** Впервые в мировой практике предложен *уникальный механизм обеспечения* всевозрастающего населения нашей планеты продуктами питания, *сохранения* и воспроизводства почвенного плодородия, *получения* качественных и экологически чистых высоких урожаев продукции растениеводства *путем использования* неисчерпаемой бесплатной энергии почвенных микроорганизмов численностью в 1 г почвы от 4-16 млрд. КОЕ и *увеличения* массы корневой системы растений в 2-2,5 раза (рисунок 1), *за счет применения* отечественного биопрепарата – *микробиоудобрения МЭРС при снижении нормы* минеральных удобрений и поливной воды, *в условиях* дефицита почвенной влаги, высоких температур (45-50°С), суховеев, засоленности земель.

*Сочетанием* минеральных удобрений с отечественными биопрепаратами достигается *повышение* численности в 1,5-5 раз микроорганизмов, обеспечивающих накопление органических веществ и NPK питание растений и *снижение* в 1,7-9 раз численности бактерий, разлагающих гумус и нитратный азот почвы, *вследствие чего* каждый грамм *почвы* превращается в *мини завод* по производству питательных элементов и органических веществ.

В результате достигается: минерализация растительных остатков; фиксация атмосферного азота; перевод трудно- и нерастворимых соединений фосфора и других элементов в растворимые соли; снижение разложения гумуса и нитратного азота почв.



а

б

Рисунок 1 – Влияние микробиоудобрения МЭРС на корневую систему растений:
а – распространение корневой системы в глубь почвы; б – влияние МЭРС
на объем корневой системы яровой мягкой пшеницы и хлопчатника

Мощная корневая система является основой поступления дополнительных питательных элементов и влаги в растение из нижних незадействованных слоев почвы и является материалом для накопления в ней органических веществ.

В итоге, растения своевременно получают дополнительно влаги и питания на 20-25%, а почва – 5-20 т/га органоминеральных соединений.

Все это в комплексе позволяет не только *сохранить* почвенное плодородие, но и *дополнительно накопить* в почве 5-20 т/га органических веществ и 35–40 и более кг/га NPK- питательных элементов.

*Использование отечественных биопрепаратов* в течение 4–5 лет позволит довести плодородный слой почвы от 30–40 до 50–60 см.

***3.2. Производство и реализация биопрепарата МЭРС.*** По договоренности с ТОО «Ордабасы» на заводе по производству пестицидных препаратов в Шымкенте 2009-2016 гг. ТОО «Хазрат-Али-Акбар» выпускает микробиоудобрение МЭРС. Мощность производства позволяет полностью покрыть посевы Республики Казахстан, Российской Федерации, Узбекистана, Независимого Государства Туркменистан в биопрепаратах и биоудобрениях.

Микробиоудобрение МЭРС сертифицировано в Республиках Казахстан и Узбекистан, Государстве Туркменистан, Российской Федерации. Имеются все разрешительные документы на производство и применение.

В Республике Казахстан опытные, опытно-производственные и производственные работы проведены на 20 культурах, в Республике Узбекистан – 9 культурах, Российской Федерации – 7 культурах, Туркменистане – 10 культурах;

Производственное применение в Республике Узбекистан произведено в 8 областях, Государстве Туркменистан – 2 велаятах, Российской Федерации – 6 субъектах. За 2009–2017 гг. биопрепараты в Республике Казахстан реализованы по субсидии.

В 2014 г. в Республике Узбекистан МЭРС для применения на посевах с/х культур был подписан контракт на сумму 500 тыс. долл. США, однако из-за невозможности проведения валютных операций препарат был возвращен. После разрешения валютных операций в 2018 г. 150 сельхоз-товаропроизводителей Наманганской и Ферганской областей приобрели МЭРС в количестве 4 т и используют на посевной площади 2,5 га.

В 2016-2017 гг. Дайханским объединениям Государства Туркменистан поставлено 87 т МЭРС.

*Фактический доход СХТП Республики Казахстан от использования микробиоудобрения МЭРС в период 2003-2018 гг. на посевной площади 3 605 тыс. га составил более 80 млрд. тенге и фермеров Независимого Государства Туркменистан на площади 90 тыс. га – более 30 млн. долл. США.*

***3.3. Относительно качества продукции.*** В Краснодарском крае РФ 50% на посевах мягкой пшеницы, Республике Узбекистан – 95% и Независимом Туркменистане – 80% получают пшеницу меньше 3 класса, которые не пригодны в производстве хлебобулочных изделий без добавок из-за низкого содержания клейковины и плохого его качества (фуражная пшеница).

Проведенными фундаментальными и прикладными исследованиями в этих регионах установлено, что биопрепараты обеспечивают получение товарной пшеницы 3 класса с выходом качественной клейковины более 24%, обладающих хорошими качественными показателями муки, теста и выпеченного хлеба.

В таблице 1 представлены данные по влиянию МЭРС на урожай и качественные показатели озимой мягкой пшеницы (сорт Звезда, НИИ зерна и зернобобовых культур – Андижан, Республика Узбекистан, 2011 г.).

Таблица 1 - Влияние МЭРС на урожай и качественные показатели
озимой мягкой пшеницы (сорт Звезда)
(НИИ зерна и зернобобовых культур – Андижан, Республика Узбекистан, 2011 г.)

| Варианты | Прибавка урожая, ц/га | Натура, г/л | Клейковина | | |
|---|---|---|---|---|---|
| | | | кол-во, % | качество, ед. ИДК | группа |
| 1. Контроль | – | 870 | 28 | 115 | III |
| 2. Обработка семян с МЭРС, 200 мл/га, обработка растений с МЭРС в фазу кущения, 300 мл/га | 8,5 | 900 | 34 | 85 | II |
| 3. Обработка растений с МЭРС в фазу кущения, 200 мл/га и молочной спелости, 300 мл/га | 11,0 | 900 | 36 | 85 | II |
| 4. Обработка растений с МЭРС в фазу молочной спелости, 500 мл/га | 8,0 | 900 | 36 | 85 | II |

Из полученных данных следует, что МЭРС обеспечивает прибавку урожая 8–11 ц/га, дополнительное содержание клейковины 6–8 % и качество клейковины II группы (это соответствует мировому стандарту 3 класса мягкой пшеницы).

Результаты лабораторных испытаний в Кашкадарьинском НИИ селекции и семеноводства зерновых колосовых культур в сезон 2012 г. показали, что МЭРС обеспечил получение пшеницы с хорошими качественными показателями зерна, муки, теста и хлеба, в то время как на контроле показатели хлеба оказались ниже среднего.

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Контроль:

– мука – 150 г; масса хлеба - 0,480 кг; длина – 13,5 см; ширина – 7,5 см; высота – 7,4 см.

МЭРС - обработка семян, 0,1 л/га + обработка растений (кущение), 0,2 л/га + обработка растений (молочная спелость), 0,2 л/га:

– мука – 150 г; масса хлеба – 0,610 кг; длина – 13,5 см; ширина – 7,5 см; высота – 10 см.

Таблица 2 – Влияние биопрепарата “Риверм” (Украина) и микробиоудобрения МЭРС на качественные показатели теста

| Параметры | Варианты | | | | |
|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 |
| Удельная работа деформации теста (W), 10-4 Дж | 358 | 303 | 414 | 370 | 391 |
| Индекс разбухания теста (G), см$^3$ | 18,6 | 17,0 | 19,2 | 19,0 | 19,1 |
| Упругость теста (P), мм | 121,0 | 120,0 | 129,0 | 133,0 | 124,0 |
| Растяжимость теста (L), мм | 70 | 58 | 74 | 73 | 74 |
| Белок, % | 14,78 | 14,96 | 15,63 | 15,91 | 15,76 |
| Клейковина, % | 27,5 | 27,5 | 29,7 | 30,6 | 30,0 |
| Влажность, % | 10,68 | 10,64 | 10,80 | 10,66 | 10,59 |

Основным критерием приобретения странами Евросоюза пшеницы являются качественные показатели теста, особенно удельная работа деформации теста. В таблице 2 представлены результаты исследований, проведенные Казахстанским филиалом компании “SGS group” по влиянию биопрепарата “Риверм” (Украина) и микробиоудобрения МЭРС (Казахстан) на качественные показатели теста.

Компания “SGS group”, штаб-квартира которой находится в г. Женева, является мировым лидером на рынке контроля, экспертизы, испытаний и сертификации, в сети которой работает 56 000 сотрудников в более 1000 офисах и лабораториях по всему миру, признана мировым эталоном качества и деловой этики.

Из полученных данных следует, что все показатели микробиоудобрения МЭРС имеют лучшие значения в сравнении с контролем и эталонным препаратом.

Варианты:

1 – Контроль, протравитель семян “Скарлет”, 0,35 л/т + фунгицид “Титул-390”, 0,32 л/га;

2 – Эталон, биопрепарат “Риверм” (Украина), 0,4 л/т, “Скарлет”, 0,35 л/т + “Риверм”, 5,0 л/га, “Титул-390”, 0,32 л/га;

3 – Вариант-2, МЭРС, 0,15 л/т, “Скарлет”, 0,35 л/т + МЭРС, 0,03 л/га, “Титул-390”, 0,16 л/га;

4 – Вариант-3, МЭРС, 0,15 л/т, “Скарлет”, 0,175 л/т + МЭРС, 0,03 л/га, “Титул-390”, 0,32 л/га;

5 – Вариант-6, МЭРС, 0,15 л/т + МЭРС, 0,03 л/га, “Титул-390”, 0,16 л/га.

Исследования, проведенные в Краснодарском и Ставропольском краях Российской Федерации, Государства Туркменистан, также подтвердили повышение количества и качества клейковины озимой мягкой пшеницы.

*Если учесть, что в мире из выращиваемых 730 млн. т/год мягкой пшеницы более 50% является фуражной, то полученные результаты в целом имеют огромное значение для производства зерна в мире.*

Впервые в мировой практике МЭРС обеспечил получение экологически чистой пшеницы, соответствующей Европейским стандартам качества, которая в ТОО «Иволга-Холдинг» Республике Казахстан возделывалась с 2011 по 2013 гг. на общей посевной площади 36 тыс. га и поставлялась для Королевского двора Англии.

Дополнительный урожай экологически чистой пшеницы за период 2010-2012 гг. за счет применения МЭРС на посевной площади 12 000 га составил 10 800 т.

Установлено, что МЭРС повышает выход товарной продукции на 14-18%, сухого вещества на 12-22%, содержание витаминов, сахаров и полезных веществ на 8-10%; снижают нитраты на 32-37%; сокращают сроки созревания культур на 10-12 дней; продлевают фотосинтез на 5-12 дней в условиях засухи и накопление биомассы 20–40%; повышают кулинарные качества на 15-18%.

***3.4. Относительно энерго-, влаго- и ресурсосбережения.*** *Сочетанием биопрепаратов с минеральными удобрениями и пестицидами установлено:*

– *обеспечение* растений дополнительными 16 питательными элементами от потенциала почвы на 30-100%;

– *продление* жизнедеятельности овощебахчевых культур в 1,5-2 раза при своевременном созревании плодов за счет ресинтеза белка, что позволяет получить дополнительный урожай 100% и более;

– *сохранение* от использования МЭРС в баковой смеси с пестицидами минимально 0,8 т/га гумуса и 30 кг/га нитратного азота почвы, а это на площади 10 млн. га обеспечит сохранение гумуса – до 20 млн. т/г, нитратного азота почвы – до 1 млн.т/г;

– *накопление* дополнительных *усваиваемых* питательных элементов после уборки урожая в сравнении с применением традиционных удобрений, в пересчете на минеральные удобрения: аммиачной селитры – 50-200 кг/га, аммофоса – 40-200 кг/га, хлорида калия – 50-200 кг/га;

– *снижение* нормы использования минеральных удобрений в 2-3 раза, поливной воды – в 1,5-2 раза и степени риска возврата заемных средств за счет дополнительного урожая на 50-100%.

– *снижение* себестоимости продукции на 20-25% и химической нагрузки на почву на 30-35%;

*Если учесть, что почва является основным источником пропитания всего живого на земле, то приведенные полученные достоверные данные, даже в масштабах одной Республики, имеют колоссальное стратегическое значение.*

**3.5. Получение высоких качественных урожаев в экстремальных условиях дефицита поливной воды, почвенной влаги, холода, жарких ветров, засоленности земель.** В экстремальных условиях (суховей) при снижении нормы поливной воды в 1,3-2 раза МЭРС в ЮКО, Жамбылской и Алматинской областях обеспечивают увеличение выхода товарной продукции на 150-300% (рисунок 2, 3).

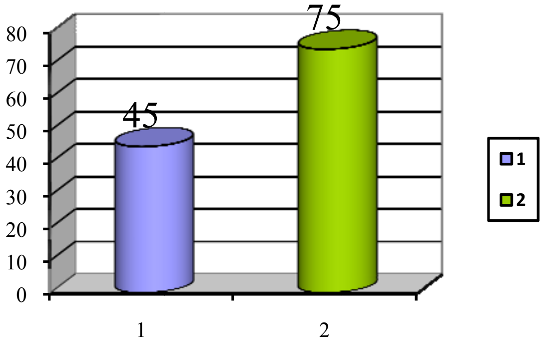

Рисунок 2 – Влияние МЭРС на урожай лука при снижении нормы поливной воды в 1,5 раза (ТОО “NAZDANA”): 1 – Эталон – аммиачная селитра (АС) – 800 кг/га; 2 – АС – 680 кг/га, МЭРС – 2 л/га

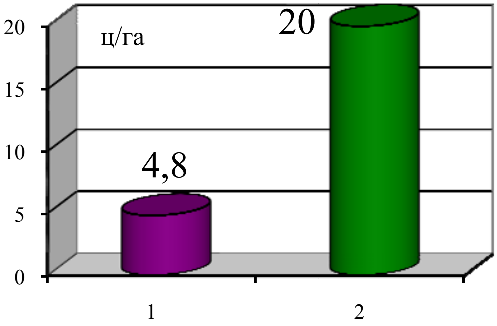

Рисунок 3 – Влияние МЭРС на урожай арбуза при снижении нормы поливной воды в 2 раза (КХ “Огай”): 1 – Эталон – АС – 200 кг/га; 2 – АС – 200 кг/га, МЭРС – 1,5 л/га

*Применение МЭРС в растениеводстве Алматинской области, при снижении нормы поливной воды на 25-30% позволит без ущерба для качества и количества с/х продукции обеспечить водой еще один мегаполис, такой, как Алматы.*

Отечественные биопрепараты за счет мощной корневой системы позволяют трансформировать влагу из нижних незадействованных слоев почвы и использовать грунтовые воды. Пример – получение в ЮКО (КХ «С-Қайрат» и КХ «Али Қожа» Мактааральский район, ТОО «Т-Куандык» Сарыагашский район, без единого полива, урожая хлопка-сырца 24-28 ц/га при контроле 4-8 ц/га (рисунок 4).

Микробиоудобрение МЭРС при снижении нормы поливной воды в 2 раза на посевах хлопчатника при использовании отечественных семян позволяет получить дополнительный урожай хлопка-сырца 10 ц/га, а при применении турецких семян без единого полива обеспечивает прибавку урожая 20 ц/га (рисунок 5). Реализация дополнительного урожая обеспечит покрытие затрат на одном гектаре на 100-200%.

В Республике Узбекистан МЭРС на посевах хлопчатника при искусственном снижении нормы поливной воды на 25-40% обеспечил полноценный урожай хлопка-сырца.

Без полива (2007 г., 2012 г.)

Урожай, ц/га

Рисунок 4 – Эффективность микробиоудобрения МЭРС на хлопчатнике (2007, 2012 гг.):
1 – АС – 200 кг/га;
2 – АС – 200 кг/га, МЭРС – 1,3 л/га

КХ «Сартай», с/о Жанааул
Отечественные семена
(полив 1 раз – 25 августа)

- Прибавка урожая: 10,0 ц/га
- Стоимость дополнительного урожая: 449 $/га
- Степень покрытия полных затрат за счет дополнительного урожая: 100 %

1. АС, 200 кг/га
2. АС, 200 кг/га + МЭРС, 1,0 л/га

СПКВ «Берекемакта» Колдашев Ж. с/о Казабек би
Турецкие семена (без полива)

- Прибавка урожая: 20 ц/га
- Стоимость дополнительного урожая: 898 $/га
- Степень покрытия полных затрат за счет дополнительного урожая: 200 %

1. АС, 200 кг/га
2. АС, 200 кг/га + МЭРС, 1,0 л/га

*а* *б*

Рисунок 5 – Эффективность микробиоудобрения МЭРС на хлопчатнике:
*а* – Отечественные семена; *б* – Турецкие семена

Полномасштабное применение МЭРС в Республике Узбекистан позволит сэкономить 2-3 млрд. м$^3$ дефицитной поливной воды при обеспечении количественных и качественных показателей продукции растениеводства.

Полученные результаты также имеют большое значение для мировой практики.

Биопрепараты способствуют в экстремальных условиях дефицита поливной воды, почвенной влаги, холода, жарких ветров, засоленности земель:

– *повышению* урожайности сельскохозяйственных культур на 30-100%;

– *повышению* сопротивляемости растений к негативному влиянию пестицидов;

– *повышению* урожайности сельскохозяйственных культур в отсутствие минерального питания в Северных регионах Республики Казахстан в условиях засухи на 20-80%, Южных - 25-50% и более.

– *снижению* нормы использования минеральных удобрений в 2–3 раза и получение дополнительного урожая в сравнении с полной нормой удобрения без МЭРС– 20-30%;

– *обеспечению* дохода в Северных регионах на зерновых на 1 тенге затрат в засушливых условиях – 4,7-6,8 тенге, при доходе от использования минеральных удобрений 0,1-0,5 тенге;

– *обеспечению* дохода в Южных регионах на поливе, на фоне минерального питания, на 1 тенге затрат на сое 5,75-10,25 тенге, рисе-шале, сахарной свекле и картофеле – 12,58-32,24 тенге, овощебахчевых культурах 130-200 тенге, при доходе от использования только минеральных удобрений 1,5-3 тенге;

– *сокращению* сроков созревания овощебахчевых культур на 8-10 дней, при сохранении их высоких вкусовых качеств.

*Решения проблем по обеспечению кормовой базы животноводства Республики Казахстан*

Применение микробиоудобрения МЭРС на посевах кормовых культур полностью покроет дефицит 38-40% и годовую потребность животноводства в кормах 30-32 млн.т, а также увеличит посевные площади и урожайность многолетних и однолетних трав в 2 раза путем повышения урожая люцерны.

Микробиоудобрение МЭРС в количестве 1,0-4,0 л/га обеспечивает получение дополнительного урожая к контролю 80-120%.

Таблица 6 – Зависимость качественных показателей сохранения почвенного плодородия, урожая и его качества от технологии обработки почвы, семенного материала, средств питания и защиты растений (Северный регион)

| Наименование фактора | Качественные показатели почвенного плодородия, % | | | | | | |
|---|---|---|---|---|---|---|---|
| | сохранение почвенной влаги | почвенное плодородие | повышение КПД удобрений | дополнительные питат. элементы | снижение негатива пестицидов | урожай | качество урожая |
| Нулевая технология | 25-30 | 45 | 0 | 0 | 0 | 30 | 0 |
| Семенной материал | 0 | 10 | 0 | 0 | 0 | 8 | 30 |
| Удобрения | Нет данных | <0 | 0 | 0 | 0 | 5 | 0 |
| Пестициды | Нет данных | <0 | 0 | 0 | 0 | 20 | 0 |
| МЭРС | 20-30 | 45 | 100 | 100 | 100 | 37 | 70 |

Таблица 7 – Зависимость качественных показателей сохранения почвенного плодородия, урожая и его качества от технологии обработки почвы, семенного материала, средств питания и защиты растений (Южный регион, полив)

| Наименование фактора | Факторы и их влияние, % | | | | | | |
|---|---|---|---|---|---|---|---|
| | сохранение почвенной влаги | почвенное плодородие | повышение КПД удобрений | дополнительные питатель элементы | снижение негатива пестицидов | урожай | качество урожая |
| Семенной материал | 0 | 10 | 0 | 0 | 0 | 10 | 30 |
| Удобрения | Нет данных | <0 | 0 | 0 | 0 | 20 | 0 |
| Пестициды | Нет данных | <0 | 0 | 0 | 0 | 20 | 0 |
| МЭРС | 100 | 90 | 100 | 100 | 100 | 50 | 70 |

Полномасштабное применение биопрепарата на посевах люцерны, кукурузы, ячменя обеспечит, наряду с повышением урожайности, и воспроизводство почвенного плодородия, а также внесет свою лепту в снижение многомиллиардных затрат по решению проблемы обеспечения кормовой базой животноводства Республики.

**Заключение.** На основании проведенного комплекса исследований нами установлены факторы, обеспечивающие решение некоторых вызовов XXI века и определяющие продовольственную безопасность Программы «Стратегия «Казахстан-2050». В таблицах 6 и 7 приведены зависимость качественных *показателей сохранения почвенного плодородия, урожая и ее качества от технологии обработки почвы, семенного материала, средств питания и защиты растений.*

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## Резюме

*С. Ұсманов*

### ХХІ ҒАСЫРДЫҢ БЕС ЖАҺАНДЫҚ МӘСЕЛЕЛЕРІ ЖӘНЕ ОЛАРДЫ ШЕШУ ТУРАЛЫ ҰСЫНЫСТАР

Мақалада Мемлекет басшысының белгілеуімен XXI ғасырдың бес жаһандық қауіп-қатерлері, соның ішінде біздің ғаламшарымыздағы халықты азық-түлікпен қамтамасыз ету үшін – азық-түлік қауіпсіздігі, ресурстардың сарқылуы және жердің тозуы, мал шаруашылығына қажетті жем-шөп базасы мен жайылымдық мәселелері, су тапшылығы, жаһандық энергетикалық қауіпсіздігі, екінші және үшінші өнеркәсіптік революция кемшіліктері қарастырылады. Оларды шешу бойынша ұсыныстар ұсынылады.

Фитобиопрепараттың жаңа буыны – МЭРС микробиотыңайтқышын 2003 – 2016 жж. аралығында мамандандырылған институттарда, тәжірибелі және тәжірибелік-өндірісте жүргізілген зерттеу нәтижелерінің, сондай-ақ Қазақстан Республикасында (2003-2017 жж.) 3 млн. га астам аймақта, Түрікменстан Мемлекетінде (2015-2017 жж.) – 90 мың га, Өзбекстан Республикасының 9 облысында (2013, 2014, 2017, 2018 жж.), Ресей Федерациясының 6 аумағында (2013-2014 жж.) қолдану нәтижелерінің негізінде анықталды:

– минералды қоректендіру негізінде тозған жерлердегі жаздық жұмсақ бидай – 3-3,5 ц/га, суармалы жердегі шитті-мақта – 10-20 ц/га, картоп және көкөніс-бақша дақылдары – 150-300 ц/га, жеміс-жидек және жүзім – 100-150 ц/га, жем-шөм – 100-150 ц/га қосымша өнім алу;

– минералды тыңайтқыштардың нормасын 1,5-3 есе азайту, суармалы су тапшылығы мен топырақ ылғалдылығы 1,3 және 1,7 есе, жердің тұздылығы, құрғақ желдің 150-300%-ға төмендеуі есебінен ауыл шаруашылық дақылдарының өнімділігін арттыру;

– қосымша өнімнің іске асырылуына байланысты ауыл шаруашылық дақылдарын өсірудегі жалпы шығындарын 30-100%-ға дейін жабу;

– өнім жиналғаннан кейін топырақта сіңімді түрдегі NPK қоректік элементтерді 38-40 кг/га және органикалық заттарды 5-20 т/га жинақтау.

Алынған нәтижелер XXI ғасырдың бес жаһандық қауіп-қатердің негізгі шешімі болып табылады.

**Түйін сөздер:** МЭРС микробиотыңайтқышы, азық-түлік қауіпсіздігі, жердің тозуы, жем-шөп базасы мен су тапшылығы мәселелері, жаһандық энергетикалық қауіпсіздігі, бірінші, екінші және үшінші индустриялық революция кемшіліктері.

## Summary

*S. Usmanov*

### FIVE GLOBAL CHALLENGES OF THE XXI CENTURY AND SUGGESTIONS FOR THEIR SOLUTION

The review article examines the five global challenges of the XXI century, identified by the head of state, concerning the provision of food to the population of our planet - the threat to global food security, resource depletion and land degradation, the problems of forage and pastures for livestock, acute water scarcity, global energy security, the shortcomings of the second and third industrial revolutions. Proposals for their solution are submitted.

Based on reliable research results (2003-2016) carried out in specialized institutes, experimental and pilot works, as well as the application of a new generation of phytobiopreparations – micro-biofertilization MERS in the Republic of Kazakhstan on an area of more than 3 mill.ha (2003-2017), the State of Turkmenistan - 90 thousand ha (2015-2017), the Republic of Uzbekistan in 9 oblasts (2013, 2014, 2017, 2018), in 6 regions of the Russian Federation (2013-2014) MERS microbiological fertilizer is established:

– obtaining, on the background of mineral nutrition, an additional harvest of spring soft wheat on rainfed lands – 3-3.5 c/ha, irrigation of raw cotton – 10-20 c/ha, potatoes and vegetables – 150-300 c/ha, fruit vineyard 100-150 c/ha, fodder-100-150 c/ha;

– increase the productivity of agricultural crops with a decrease in the norm of mineral fertilizers by a factor of 1.5-3 times, a deficit of irrigation water and soil moisture of 1.3 and 1.7 times, salinity of lands, dry winds by 150-300%;

– coverage, through the implementation of additional crops, the total cost of cultivation of agricultural crops by 30-100% or more;

– accumulation in the soil after harvesting of an additional crop of 38-40 kg/ha assimilated forms NPK nutrient elements and 5-20 t/ha organic.

The results are the basis for solving the five global challenges of the XXI century.

**Key words:** micro-biofertilizer of MERC, food security, land degradation, the problems of fodder and water scarcit, global energy security, disadvantages of the first, second and third industrial revolutions.

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# ПОЛУЧЕНИЕ И ПРИМЕНЕНИЕ НОВЫХ МОДИФИЦИРОВАННЫХ ГУМАТСОДЕРЖАЩИХ ПРЕПАРАТОВ

**Аннотация.** В статье представлены результаты исследования теоретических и технологических основ процессов получения модифицированных био- и микробиоудобрений и гуматсодержащих продуктов с высокой суммой питательных компонентов. Выявлены взаимосвязь состава и свойств новых видов продуктов, оптимизированы условия их получения.Проведены широкомасштабные агрохимические испытания био- и микробиоудобрений и гуматсодержащих препаратов на различных типах почв Казахстана и стран СНГна разных видах сельскохозяйственных культур. Установлено, что био- и микробиоудобрения и гуматсодержащие продукты обладают ростостимулирующими, мелиоративными, влагоудерживающими и фунгицидными свойствами. Показана перспективность применения гуматсодержащих препаратов для пескозадержания и предотвращения опустынивания в Мангистауской области путем выращивания адаптированных к местным условиям растений. Разработана практическая рекомендация по применению био- и микробиоудобрений и гуматсодержащих продуктов в агропромышленном комплексе.

**Ключевые слова:** био-и микробиоудобрение, гуматсодержащие продукты, технология, сельское хозяйство, агрохимические испытания.

В настоящее время в мировом масштабе актуальным является обеспечение население продовольствием, так как планета перенаселена, почвы перегружены, происходит процесс деградации земельных угодий. При этом наблюдается тенденция снижения содержания гумуса в почвах, за счет увеличения площади эродированных, засоленных, загрязненных и опустыненных земель, а также из-за постоянной эксплуатации почвы. Почва в среднем получает 10% минеральных веществ и 20% органических удобрений от необходимого объема. Кроме того, чрезмерное и нерациональное использование средств на минеральной основе, а также применение пестицидов способствуют загрязнению почвы тяжелыми металлами. Для решения этих проблем применяются био-, микробио- и гуматсодержащие продукты, сочетающие в себе действие органических и минеральных веществ, но при этом исключающих вредные для почвы добавки. Это позволяет использовать их абсолютно в любых условиях земледелия, при этом улучшается структура почвы и ее агрохимические, агрофизические и биологические характеристики, повышается содержание в ней гумуса, уменьшается детоксикация и уровень эрозии. Применение их способствуют получению высоких урожаев и качественной продукции. Немаловажным фактором является то, что сырьем для их получения используют природно-минеральное (фосфориты, бурые угли, растительные экстракты и пр.) и техногенное (фосфоритная мелочь, фосфогипс и др.) сырье Казахстана.

В Институте химических наук имени А.Б.Бектурова под руководством д.т.н., профессора С.У.Усманова лаборатория неорганического синтеза и материалов занимается разработкой фундаментальных и прикладных основ малотоотходной энергоресурсосберегающей технологии [1-4]. Работы направлены на создание производства, продвижение на рынок отечественных обогащенных био-, микробиоудобрений и пестицидных препаратов с регулируемым компонентным составом и заданными свойствами (рисунок 1).

Рисунок 1 – Испытание био- и микробиоудобрений на яровой пшенице

На основании проведенных фундаментальных и прикладных исследований в области химии, химической технологии, агрохимии, почвоведения, почвенной микробиологии, токсикологии и химической токсикологии впервые в Республике Казахстан разработаны действующие вещества и на их основе препаративные формы пестицидных препаратов – протравители семян хлопчатника, пшеницы, ячменя, системного, комбинированного, комплексного гербицидов, дефолиантов хлопчатника, химических мелиорантов, органоминеральных удобрений, биопрепаратов, стимуляторов роста и развития растений (2000-2005 гг.), биопестицидов, биофунгицидов, микробио-, микрофитобио- и биоудобрений (2004-2017 гг.).

На основании проведенных совместных исследований с Институтом общей неорганической химии АН, Институтами почвоведения, хлопководства и зерновых культур, МСВХ РУз С.У. Усмановым получены разрешительные документы на использование биопрепаратов и биоудобрений в Республиках Казахстан и Узбекистан, Туркменистане, Российской Федерации. В Республике Казахстан площадь использования препаратов, разработанных С.У.Усмановым в период 2001-2016 гг., составила 6,38 млн га. Препараты реализованы на сумму 2,7 млрд. тенге, из них по субсидии

800 млн тенге. В Туркменистане площадь применения микробиоудобрения МЭРС в 2016 г. составил 45 тыс. га. Биопрепарат в количестве 45 т реализован на сумму 810 тыс. долл. США.

В лаборатории химии удобрений и солей под руководством член-корреспондента НАН РК, У.Ж.Джусипбекова проводятся исследования в области получения новых модифицированных гуматсодержащих материалов и удобрений [5-7]. Созданы физико-химические основы процессов кислотной и щелочной модификации бурых углей, взаимодействия фосфор-содержащего сырья и гуминовых соединений. Предложен химизм протекающих при этом процессов и выявлены общие закономерности, установлена взаимосвязь состава и свойства гуматсодержащих продуктов от условий проведения процессов, разработаны инновационные способы получения модифицированных гуматсодержащих продуктов, позволяющие в одном технологическом цикле в зависимости от условий и параметров процесса получать разные продукты с заданными составом и прогнозируемыми характеристиками.

Проведены широкомасштабные производственные агрохимические испытания гуматсодержащих препаратов на полях РГП «Жасыл аймак» (г. Астана), НПЦ им. А.И. Бараева, РГКП «Кокшетауский лесной селекционный центр» (Акмолинская обл.) Института биологии и биотехнологии растений МОН РК, РГКП «Алматинский лесной селекционный центр», ТОО «Зеленстрой», ТОО «Жасыл алма», ТОО «Магнолия Дистард» (г. Алматы), ТОО «КазНИИ картофелеводства и овощеводства», СПК «Будан» (Алматинская обл.) [8-10]. К числу таких учреждений относится и Управление природных ресурсов и регулирования природопользования Мангистауской обл., ГКП «Коктем», ТОО «CaspiyOperating»,ТОО «Экспо-Трейдинг», ООО «Агророст» (г. Актау) и сш. №20 (г. Жанаозен), в хозяйствах Жанакорганского района (Кызылординская обл.) на зерновых, бобовых, технических, овощных, плодово-ягодных, цветочных, хвойных, лиственных, декоративных культурах на разных почвенно-климатических условиях (рисунок 2).

В ходе проведенных работ установлено, что их применение приводит к повышению всхожести семян и приживаемости рассады и саженцев (98-100%), увеличению урожайности испытуемых культур (15-45%) и улучшению качество готовой продукции, сокращению сроков вегетации, цветения и созревания (7-10 дней), к повышению устойчивости сельскохозяйственных культур к биотическим и абиотическим стрессам.

Препарат «Супергумат» внедрен в ТОО «Зеленстрой», ТОО «Жасыл алма» и ТОО «Магнолия Дистард» и используется для озеленения г.Алматы. Разработаны научно-обоснованные рекомендации по способам, нормам и срокам применения гуматсодержащих продуктов на различных сельскохозяйственных культурах и зеленых насаждениях.

С 2006 г.проводятся испытания гуматсодержащих препаратов в Мангистауском и Каракиянском районах Мангистауской обл. при рекульти-

Рисунок 2 – Испытание гуматсодержащих препаратов на различных культурах

вации загрязненных и деградированных почв области путем выращивания адаптированных к местным условиям растений (черного саксаула, жузгена, айланда, карагаша и др.). Установлено, что применение модифицированных гуминовых препаратов способствует формированию более разветвленной и мощной корневой системы, повышению коэффициента использования растениями почвенной влаги, приводит к восстановлению опустыненных почв и остановке подвижных барханов.

Таким образом, на основании проведенных систематических исследований созданы физико-химические и технологические основы процессов получения био-, микробио- и гуматсодержащих продуктов, модифицированных неорганическими и органическими макро- и микроэлементами из природного и техногенного сырья Казахстана, разработаны способы их применения для выращивания растений.

Проведены производственные агрохимические испытания био-, микробио- и гуматсодержащих продуктов в разных почвенно-климатических условиях Казахстана и стран СНГ на различных культурах.

*Соавторы выражают огромную благодарность и признательность доктору технических наук, профессору Султану Усмановичу за многолетнюю совместную плодотворную работу, конструктивные идеи и мудрые решения. От всего сердца поздравляем с юбилеем и желаем Вам дальнейших побед и достижений на профессиональном поприще.*

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## Резюме

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### ҚҰРАМЫНДА ГУМАТЫ БАР ЖАҢА ПРЕПАРАТТАРДЫ АЛУ ЖӘНЕ ҚОЛДАНУ

Қазақстанның табиғи және техногендік шикізаттарынан түрлендірілген био- және микробиотың айтқыштар мен құрамында гуматы бар өнімдерді алу үрдістерінің физика-химиялық және технологиялық заңдылықтары зерттелді. Жүргізілген агрохимиялық сынақтар алынған жаңа өнімдердің ауыл шаруашылық дақылдарын өсіруде тиімділігінің жоғары екендігін көрсетті. Бұл препараттардың әр түрлі топырақтық-климаттық жағдайларда қолдануға болатындығы анықталды.

**Түйін сөздер:** био- және микробиотыңайтқыштар, құрамында гуматы бар өнімдер, технология, ауыл шаруашылығы, агрохимиялық сынақтар.

## Summary

*S. U. Usmanov, U. Zh. Dzhusipbekov, G. O. Nurgalieva, G. T. Omarova*

### RECEIVING AND APPLICATION OF NEW MODIFIED HUMATE-CONTAINING PREPARATIONS

The physicochemical and technological regularities of the and technogenic raw materials of Kazakhstan are studied. Agrochemical tests of new types of products have shown their high efficiency in growing crops. The possibility of their use in different soil and climatic conditions is established.

**Key words:** bio- and microbiofluorification, humate-containing products, technology, agriculture, agrochemical tests.

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# ESTERS OF CYCLOPROPANECARBOXYLIC ACID DISPLAYING ANTI-INFECTIVE ACTIVITY

**Abstract.** A number of esters of cyclopropanecarboxylic acid of N-alkyl naphthyloxypropynylpiperidines antimicrobial activity have been studied in relation to the archival strains of microorganisms. The activities of the given preparations have been assessed *in vitro* in relation to *Bacillus subtilis* ATCC 6633*, Escherichia coli* ATCC 25922, *Salmonella enterica* ATCC 14028 and *Staphylococcus aureus* ATCC 6538-P, among which hydrochloride of 1-methyl-4-[3-(naphth-1-yloxy)prop-1-in-1-yl]-4-cyclopropanecarbonyloxypiperidine has displayed the greatest activity in relation to the archival strain of *Bacillus subtilis* ATCC 6633 in the concentration of 250 μg/ml.

Esters of cyclopropanecarboxylic acid of N-methyl phenoxypropynylpiperidine and phenyl ethinylpiperidine have displayed antimicrobial activity *in vitro* in relation to all seven strains of microorganisms, used in the experiment: *Escherichia coli* ATCC 25922, *Escherichia coli* ATCC-BAA-196, *Klebsiella pneumoniae* ATCC 10031, *Klebsiella pneumoniae* ATCC 700603, *Staphylococcus aureus* ATCC 6538-P, *Staphylococcus aureus* ATCC-BAA-39, *Candida albicans* ATCC 10231.

Hydrochloride of ester of N-benzylpiperidine-4-ketoxime of cyclopropanecarboxylic acid has a bactericidal activity in relation to the strains of the testing cultures of *Eshirichia Coli1257* and *Staphylococcus aureus 209-P*.

**Key words:** cyclopropanecarbonylchloride, piperidine, esters, antimicrobial activity.

Despite of a huge arsenal of available medicines, the problem of searching of new highly efficient medicinal preparations remains topical. This is stipulated by the lack or insufficient efficiency of medicinal preparations for treatment of certain diseases; side effects of certain medicinal remedies; their validity period limitations [1].

Based on the analysis of the scientific and patent literature the authors [2] point out, that the search of new synthetic medicinal preparations is mainly carried out in three directions:

1) modification or further development of the existing biologically active matrices;

2) molecular design of the structures, including the fragments of natural compounds;

3) molecular design of completely new classes of organic compounds, mainly of the heterocyclic series.

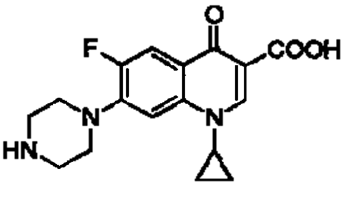
At present, the creation of innovative medicinal preparations include the obtaining of new chemical products and synthesis of pharmacologically active metabolites or their isomers. The development of modern medicinal forms with improved pharmacokinetic properties and new drug delivery means, creation of multicomponent biotechnological or bioengineered preparations and medicines.

The substances, containing in their structure as fragment of cyclopropane, are considerable interest for the both organic chemists and biochemists. A three-membered saturated carbocycle is a structural element with a huge synthetic potential, stipulated by a high voltage energy (~ 27,5 kcal/mol) of an unusual type of carbon-carbon bonds, called the "banana bonds". By their nature, they are intermediate between σ- and π-bonds, due to which cyclopropane derivatives enter into various reactions of cycle opening and extension, as well as the reactions of cycloaddition [3, 4].

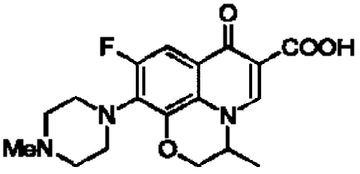
Many natural and synthetic compounds containing as cyclopropane fragment with a simple functionality, possess a wide spectrum of biological properties [5], ranging from enzyme inhibition to insecticidal, antifungal, herbicidal, antimicrobial, antibiotic, antibacterial, antitumoral [6] and antiviral, antiestrogenic, agonistic properties. The studies in the field of biosynthesis and metabolism of cyclopropane derivatives provide the information, which is required for the development of new medicinal preparations [7]. Heterocyclic compounds, possessing a cyclopropyl group as a substituent, are of special interest [8-10].

Being present in animals, plants and microorganisms or temporarily appearing upon primary and secondary metabolism, they provide convenient biological probes for mechanistic studies, and make it possible to develop new medicinal preparations.

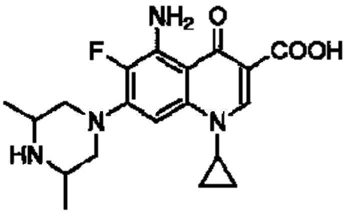
In terms of medical use, it is noteworthy, that eight of the two hundred best-selling pharmaceutical preparations are the compounds, containing a cyclopropane fragment [5]:



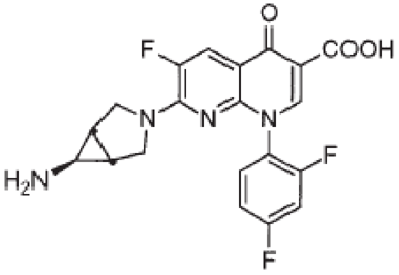
Ciprofloxacin



Ofloxacin



Sparfloxacin



Trovafloxacin

Thus, cyclopropane-containing antibacterial agents, such as ciprofloxacin CPFX, ofloxacin OFLX, sparfloxacin SPFX and trovafloxacin, are members of the principal class of broad-spectrum antibacterial medicinal preparations, and are widely used for the treatment of patients.

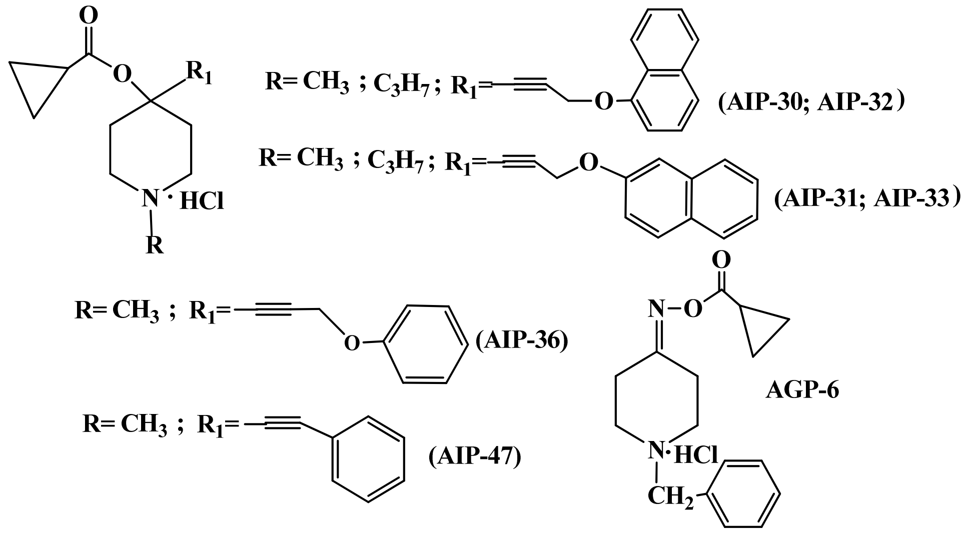
A piperidine ring is the ubiquitous structural feature of many alkaloid natural products and medicine candidates. Watson P.S. et al. [11] believe, that thousands of piperidine compounds have been mentioned in clinical and preclinical studies for the last decade. Nevertheless, the variety of functional and substituent structures, found in the piperidine targets, and the generally accepted concept, that the biological properties of piperidines strongly depend on the type and location of substituents on the heterocyclic ring.

The search for new compounds with antimicrobial and virucidal activities, including those capable to induce reversion of medicine susceptibility, is related to a priority direction in the field of development of new anti-infective medicinal preparations. The importance of the scientific research, despite the availability of a wide range of antibacterial medicinal remedies, is associated, first and foremost, with the high adaptability of pathogenic organisms to the medicinal preparations, including antibiotics [12-14].

This work is a continuation of the studies in the synthesis of new antibacterial medicinal preparations in a series of piperidine-containing derivatives of cyclopropanecarboxylic acid [15, 16].

The compounds with the codes AIP and AGP have been studied for an antimicrobial activity. The results of the biological tests are presented in tables 1-3. The research model includes the required minimum of tests with different degrees of sensitivity *in vitro* [17]. The research scheme has been implemented in accordance with the current methodical recommendations, approved by the State Pharmacological Committee of the Republic of Kazakhstan [18].

**Study of a biological activity.** The compounds with the codes AIP-30, AIP-31, AIP-32, AIP-33 have been studied for an antimicrobial activity in relation to the archival strains of microorganisms, the activities of these preparations have been assessed *in vitro* in relation to *Bacillus subtilis* ATCC 6633, *Escherichia coli* ATCC 25922, *Salmonella enterica* ATCC 14028 and *Staphylococcus aureus* ATCC 6538-P:



As it is seem from the results presented in table 1, the compounds AIP-30 and AIP-31 [19-20] possess an antimicrobial activity in relation to all strains of microorganisms, used in the experiment. The compounds AIP-30 and AIP-31 display antimicrobial effects to different extents, AIP-30 has displayed the greatest activity in relation to the archival strain of *Bacillus subtilis* ATCC 6633 in the concentration of 250 µg/ml. Streptomycin has been active in relation to the gram-negative strains of microorganisms (*Escherichia coli, Staphylococcus aureus, Salmonella enterica*), and its efficiency in relation to *Bacillus subtilis* makes up only 50-60%.

Table 1 – Antimicrobial activity of AIP-30 - AIP-33

| Strain / Code of the compound | MIC, µg/ml | | | |
|---|---|---|---|---|
| | *Bacillus subtilis* ATCC 6633 | *Escherichia coli* ATCC 25922 | *Staphylococcus aureus* ATCC 6538-P | *Salmonella enterica* ATCC 14028 |
| AIP-30 | 250 | 250 | 1000 | 500 |
| AIP-31 | 250 | 500 | 1000 | 1000 |
| AIP-32 | 1000 | – | – | – |
| AIP-33 | 500 | 2000 | – | – |

The compound AIP-32 [21] possesses an antimicrobial activity in relation to the archival strain of *Bacillus subtilis* ATCC 6633 in the concentration of 1000 µg/ml.

The compound AIP-33 [22] possesses an antimicrobial activity in relation to the archival strain of *Bacillus subtilis* ATCC 6633 in the concentration of

500 μg/ml, and it displays an activity in relation to *Escherichia coli* in the high concentration of 2000 μg/ ml.

Thus, it has been established, that AIP-32 displays a selective antimicrobial activity to the one type of the archival strains, and AIP-33 – to the two types of the archival strains, used in the experiment.

The compounds with the codes AIP-36, AIP-47 have been studied for an antimicrobial activity in relation to the archival strains of microorganisms, the activities of these preparations have been assessed *in vitro* for *Escherichia coli* ATCC 25922, *Escherichia coli* ATCC-BAA-196, *Klebsiella pneumoniae* ATCC 10031, *Klebsiella pneumoniae* ATCC 700603, *Staphylococcus aureus* ATCC 6538-P, *Staphylococcus aureus* ATCC-BAA-39, *Candida albicans* ATCC 10231:

Table 2 – Antimicrobial activity of AIP-36, AIP-47

| Strain / Code of the compound | MIC, μg/ml | | | | | | |
|---|---|---|---|---|---|---|---|
| | *Escherichia coli* ATCC 25922 | *Escherichia coli* ATCC-BAA-196 | *Klebsiella pneumonia* ATCC 10031 | *Klebsiella pneumonia* ATCC 700603 | *Staphylococcus aureus* ATCC 6538-P | *Staphylococcus aureus* ATCC-BAA-39 | *Candida albicans* ATCC 10231 |
| AIP-36 | 1000 | 2000 | 1000 | 2000 | 2000 | 2000 | 1000 |
| AIP-47 | 1000 | 2000 | 1000 | HA | 2000 | 2000 | 1000 |

As it is seen from table 2, the compound AIP-36 [23] possesses an antimicrobial activity in relation to all seven archival strains of microorganisms, used in the experiment: *Escherichia coli* ATCC 25922, *Klebsiella pneumoniae* ATCC 10031, *Candida albicans* ATCC 10231 in the concentration (MIC) of 1000 μg/ml, and in relation to *Escherichia coli* ATCC-BAA-196, Klebsiella *pneumoniae* ATCC 700603, *Staphylococcus aureus* ATCC 6538-P, *Staphylococcus aureus* ATCC-BAA-39 – in the concentration (MIC) of 2000 μg/ml.

AIP-47 [24] also displays an antimicrobial activity in relation to all seven archival strains of microorganisms, used in the experiment: *Escherichia coli* ATCC 25922, *Klebsiella pneumoniae* ATCC 10031 in the concentration (MIC) of 1000 μg/ml, and in relation to all other strains of microorganisms - in the concentration (MIC) of 2000 μg/ml.

Hydrochloride of ester of 1-benzyl-piperidine-4-ketoxime of cyclopropanecarboxylic acid with the laboratory code AGP-6 [25] has been studied for an anti-infective activity and acute toxicity. The data have been compared with the indices of streptomycin. The results of the study are presented in table 3.

The toxic dose of the preparation AGP-6 is 833.3 + 17.8 mg/kg, which is almost 4 times lower, than the toxicity of streptomycin, used as a reference. It has turned out, that the preparation AGP-6 possesses a bactericidal activity in relation to the testing cultures of *Eshirichia Coli1257* and *Staphylococcus aureus* 209-P both in the concentrations of 1% and 3%.

Table 3 – Results of the biological study of AGP-6 and streptomycin

| Prepa-ration | $LD_{50}$, mg/kg | Bactericidal activity in relation to | | | |
|---|---|---|---|---|---|
| | | 1 % concentration | | 3 % concentration | |
| | | *E. Coli 1257* | *St. aureus 209-P* | *E. Coli 1257* | *St. aureus 209-P* |
| AGP-6 | 833.3+ 17.8 | Growth inhibition of the microorganism the well | 15 mm | Growth inhibition of the microorganism the well | 25 mm |
| Strepto-mycin | 213.8+ 22.61 | Growth inhibition of the microorganism the well | Growth inhibition of the microorganism the well | Growth inhibition of the microorganism the well | Growth inhibition of the microorganism the well |

The total assessment score of a locally irritating effect of AGP-6 on skin and ocular mucosa (cornea and conjunctiva) is equal to 3. This value is related to the 4th class of chemical hazard by toxicological properties according to Methodology Guidelines 12.1105-02. Besides, slight erythema, scaling and irritation of skin have been observed for 10 days, all irritation signs disappearing completely on the 14th day.

Thus, according to the instruction for the experimental (preclinical) study of new pharmacological substances, the test compounds may be used in additional studies for revealing an antimicrobial activity on a wider range of microorganisms.

**Conclusion.** Hydrochloride of 1-methyl-4-[3-(naphth-1-yloxy)prop-1-in-1-yl]-4-cyclopropanecarbonyloxypiperidine (AIP-30) has displayed the greatest activity in relation to the archival strain of *Bacillus subtilis* ATCC 6633 in the concentration of 250 μg/ml.

Esters of cyclopropanecarboxylic acid of N-methyl phenoxypropynyl-piperidine and phenyl ethinylpiperidine, AIP-36 and AIP-47, have displayed an antimicrobial activity *in vitro* in relation to all seven strains of microorganisms, used in the experiment: *Escherichia coli* ATCC 25922, *Escherichia coli* ATCC-BAA-196, *Klebsiella pneumoniae* ATCC 10031, *Klebsiella pneumoniae* ATCC 700603, *Staphylococcus aureus* ATCC 6538-P, *Staphylococcus aureus* ATCC-BAA-39, *Candida albicans* ATCC 10231.

It has been also shown, that hydrochloride of ester of N-benzylpiperidine-4-ketoxime of cyclopropanecarboxylic acid (AGP-6) suppresses the growth of *E. Coli1257* and *St. aureus 209-P* with low toxicity.

Thus, it has been shown, that the directed introduction of a cyclopropanecarboxylic fragment into the structure of naphthyloxypropynylpiperidine, phenoxypropynylpiperidine, phenylethynylpiperidine and N-benzylpiperidine-4-ketoxime leads to the compounds of an anti-infective activity.

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## Резюме

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### ИНФЕКЦИЯҒА ҚАРСЫ ӘСЕРІ БАР ЦИКЛОПРОПАНКАРБОН ҚЫШҚЫЛЫНЫҢ КҮРДЕЛІ ЭФИРЛЕРІ

N-алкилнафтилокипсипропил пиперидиндердің циклопропанкарбон қышқылының күрделі эфирлерінің қатары микроорганизмдердің мұражайлы штаммдарына қатысты микробқа қарсы белсенділігі зерттелді. *Bacillus subtilis* ATCC 6633, *Escherichia coli* ATCC 25922, *Salmonella enterica* ATCC 14028 және *Staphylococcus aureus* ATCC 6538-P бойынша осы препараттардың әсері бағаланды, олардың арасында 1-метил-4-[3-(нафт-1-илокси)проп-1-ин-1-ил]-4-циклопропанкарбонилоксипиперидин гидрохлориді *Bacillus subtilis* ATCC 6633 мұражайлы штаммына қатысты 250 мкг/мл концентрацияда әлдеқайда жоғары белсенділік көрсетті.

N-метилфеноксипропинилпиперидин және фенилтинилпиперидиннің циклопропанцарбон қышқылының күрделі эфирлері тәжірибеге алынған барлық жеті микроорганизм штаммдарына: *Escherichia coli* ATCC 25922, *Escherichia coli* ATCC-BAA-196, *Klebsiella pneumoniae* ATCC 10031, *Klebsiella pneumoniae* ATCC 700603, *Staphylococcus aureus* ATCC 6538-P, *Staphylococcus aureus* ATCC-BAA-39, *Candida albicans* ATCC 10231 қатысты in vitro микробқа қарсы белсенділігін көрсетті.

Циклопропанкарбон қышқылы N-бензилпиперидин-4-кетоксим эфирінің 1% және 3% -ды гидрохлорид ерітінділері *Eshirichia Coli1257* және *Staphylococcus aureus 209-P* микроорганизмдерінің сынама-дақыл штамдарына қарсы бактерицидтік әсерге ие екендігі анықталды.

**Түйін сөздер:** циклопропанкарбонилхлорид, пиперидин, күрделі эфирлер, микробқа қарсы белсенділік.

## Резюме

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# СЛОЖНЫЕ ЭФИРЫ ЦИКЛОПРОПАНКАРБОНОВОЙ КИСЛОТЫ С ПРОТИВОИНФЕКЦИОННЫМ ДЕЙСТВИЕМ

Ряд сложных эфиров циклопропанкарбоновой кислоты N-алкил нафтилоксипропинилпиперидинов были изучены на антимикробную активность в отношении музейных штаммов микроорганизмов, оценены действия данных препаратов *in vitro* в отношении *Bacillus subtilis* АТСС 6633, *Escherichia coli* АТСС 25922, *Salmonella enterica* АТСС 14028 и *Staphylococcus aureus* АТСС 6538-Р, среди которых наибольшую активность проявил гидрохлорид 1-метил-4-[3-(нафт-1-илокси)проп-1-ин-1-ил]-4-циклопропанкарбонилоксипиперидина в отношении музейного штамма *Bacillus subtilis* АТСС 6633 в концентрации 250 мкг/мл.

Сложные эфиры циклопропанкарбоновой кислоты N-метил феноксипропинилпиперидина и фенилэтинилпиперидина проявили противомикробную активность *in vitro* в отношении всех семи штаммов микроорганизмов, взятых в эксперименте: *Escherichia coli* АТСС 25922, *Escherichia coli* АТСС-ВАА-196, *Klebsiella pneumoniae* АТСС 10031, *Klebsiella pneumoniae* АТСС 700603, *Staphylococcus aureus* АТСС 6538-Р, *Staphylococcus aureus* АТСС-ВАА-39, *Candida albicans* АТСС 10231.

Оказалось, что 1 и 3% растворы гидрохлорида эфира N-бензилпиперидин-4-кетоксима циклопропанкарбоновой кислоты обладает бактерицидным действием против штаммов тест-культур микроорганизмов *Eshirichia Coli1257* и *Staphylococcus aureus 209-P*.

**Ключевые слова:** циклопропанкарбонилхлорид, пиперидин, сложные эфиры, антимикробная активность.

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# *IN VITRO* ПРОТИВОТУБЕРКУЛЕЗНАЯ И ПРОТИВОДИАБЕТИЧЕСКАЯ АКТИВНОСТЬ О-ТОЗИЛАТОВ-β-АМИНОПРОПИОАМИДОКСИМОВ И ХЛОРИДОВ 2-(ГЕТЕРОАМИНО)-1,5-ДИАЗАСПИРО[4,5]ДЕКАН-1-ЕН-5-АММОНИУМОВ

**Аннотация.** Исходя из актуальности поиска более эффективных методов лечения туберкулеза и сахарного диабета II О-тозилаты-β-аминопропиоамидоксимов и хлориды 2-амино-4,5-дигидроспиропиразолиламмониумов, полученные с выходами 50–86%, были изучены на наличие in vitro противотуберкулезной и противодиабетической активности. В первом и втором ряду обнаружены соединения со средней активностью на ЛЧ штаммах M. tuberculosis H37Rv с МБК 50 мкг/мл. МВК рифампицина составляет 1,0 мкг/мл на ЛЧ штаммах M. tuberculosis. Противодиабетический скрининг выявил образцы с умеренной активностью (27–29%) в отношении фермента α-амилазы с эталонным препаратом акарбозой, проявляющей ингибирующую активность в отношении α-амилазы равную 51,6%.

**Ключевые слова:** О-тозилаты-β-аминопропиоамидоксимов, хлориды 2-амино-4,5-дигидроспиропиразолиламмониумов, *in vitro* противотуберкулезная и противодиабетическая активности.

Туберкулез является одной из основных проблем здравоохранения, ответственной за заболеваемость и смертность. Лечение лекарственно-чувствительного (ЛЧ) и многолекарственно-устойчивого (МЛУ) туберкулеза является длительным и дорогостоящим и имеет серьезные побочные эффекты, которые могут вызывать сопутствующую заболеваемость и даже смертность. Общая распространенность побочных эффектов при лечении ЛЧ туберкулеза препаратами первой линии оценивается в диапазоне от 8,0 до 85%. Возникновение побочных эффектов может зависеть от множества факторов и варьироваться от мягких желудочно-кишечных расстройств до серьезной гепатотоксичности, периферической нейропатии, кожных побочных эффектов и т.д. [1]. При лечении МЛУ туберкулеза отмечено более отягощенное проявление побочных эффектов. Один или несколько побочных эффектов наблюдались у 37,1% пациентов. Наиболее частыми были желудочно-кишечные (18,4%), психические расстройства (5,5%), артралгия (4,7%), гепатит (3,9%), периферическая невропатия (3,1%), гипотиреоз (2,3%), эпилептические припадки (2%), дерматологические эффекты (2%), ототоксичность (1,6%) и нефротоксичность (1,2%) [2].

В последнее время в мире наблюдается прогрессирование заболеваемости диабетом. По оценкам ВОЗ общая распространенность диабета, составляющая в 2013 г. 382 млн чел., к 2035 г. должна возрасти до 592 млн [3]. Широко распространена классификация диабета на диабет типа I и типа II. Обе формы диабета могут приводить к многосистемным осложнениям микрососудистых конечных точек, включая ретинопатию, нефропатию и невропатию, а также ишемическую болезнь сердца, инсульт и заболевания периферических сосудов. Преждевременная заболеваемость, смертность, снижение ожидаемой продолжительности жизни, финансовые и другие издержки лечения диабета делают его важной проблемой здравоохранения. Диабет типа 2 составляет около 85–90% всех случаев [4, 5].

Таким образом, существует острая потребность в инновационном подходе к поиску новых противотуберкулезных и противодиабетических средств, более эффективных, менее токсичных, более экономически доступных.

В ряду производных β-аминопропиоамидоксимов нами обнаружен препарат (TBD-12), обладающий бифункциональной активностью – противотуберкулезной и противодиабетической, имеющий более высокую по сравнению с рифампицином *in vivo* активность при лечении экспериментального ЛЧ и МЛУ туберкулеза. Эффективность лечения с его помощью ЛЧ и МЛУ туберкулеза, соответственно, в 1,5 и 2,3 раза выше, чем у рифампицина; токсичность TBD-12 в 5 раз ниже токсичности рифампицина [6]. Кроме того, у TBD-12 установлена *in vivo* противодиабетическая активность, которая в 1,2 раза выше, чем у базового противодиабетического средства метформина при более низкой (в 6,1 раз) острой подкожной токсичности [7].

Объект данной статьи – потенциальные биологически активные О-тозилаты-β-аминопропиоамидоксимов и продукты воздействия на последние хлористого водорода – хлориды 2-амино-4,5-дигидроспиропиразолиламмониумов [8, 9], биологические свойства которых не были изучены ранее.

Сульфогруппа является фармакофором, служащим основой сульфониламидных препаратов, широко использующихся в терапии с 30-х годов как антибактериальные средства (стрептоцид, норсульфазол, сульфазин, сульфадимезин, этазол, сульфадиметоксин, фталазол) [10]. Известны О-сульфонил–амидоксимы с антиоксидантной и липидной пероксидантной активностью [11].

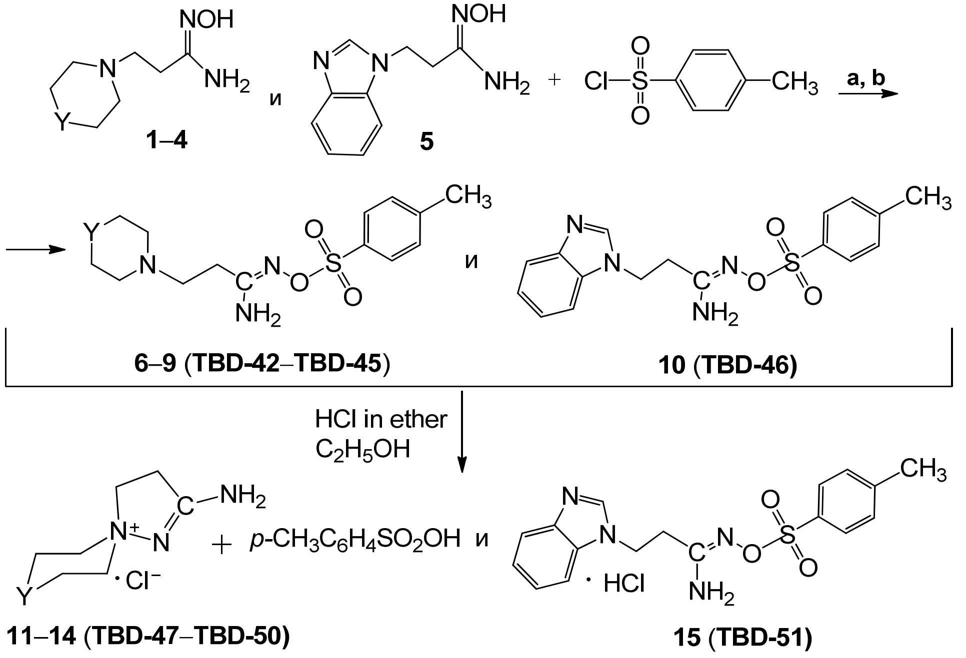
О-Тозилаты-β-аминопропиоамидоксимов (6–10, TBD-42–TBD-46) и продукты воздействия на них хлористого водорода – хлориды 2-(гетероамино)-1,5-диазаспиро[4,5]декан-1-ен-5-аммониумы (11–14, TBD-47–TBD-51) наработаны для проверки их *in vitro* противотуберкулезных и противодиабетических свойств.

О-Тозилаты 6–10 с выходами 50–82% получены при взаимодействии β-аминопропиоамидоксимов (β-аминогруппа: пиперидин-1-ил, морфолин-1-ил, тиоморфолин-1-ил, 4-фенилпиперазин-1-ил, бензимидазол-1-ил) с *p*-толуолсульфохлоридом в хлороформе или в смеси ацетона и хлороформа при комнатной температуре в течение 2–24 ч в присутствии триэтиламина (таблица 1, схема 1).

Солевые производные О-тозилатов β-аминопропиоамидоксимов 11–14 с лучшей, чем исходные соединения растворимостью в воде, выделены при воздействии на соединения 6–10 хлористого водорода до pH 2 и добавлении эквивалентного объема абсолютированного диэтилового эфира к этанольному раствору взаимодействующих веществ. Для β-пиперидинового, β-морфолинового, β-тиоморфолинового, β-фенилпиперазинового производных (6–10) получены продукты перегруппировки исходных О-тозилатов β-аминопропиоамидоксимов до хлоридов 2-амино-4,5-дигидроспиропиразолиламмониумов (11–14). *p*-Толуолсульфокислота выделяется при упаривании раствора, полученного от фильтрования спиропроизводных. Сохранение структуры и образование гидрохлорида 15 наблюдается для О-тозилата-β-(бензимидазол-1-ил)пропиоамидоксима (таблица 1, схема 1).

Физико-химические данные соединений 6–15 представлены в таблице 1.

**Схема 1**



**a:** chloroform (for **1**, **2**, **4**), $Et_3N$; **b:** ethanol:acetone (for **3**, **5**), $Et_3N$

Y = $CH_2$ (**1**, **6**, **11**), O (**2**, **7**, **12**), S (**3**, **8**, **13**), PhN (**4, 9**, **14**)

Таблица 1 – Физико-химические характеристики
О-тозилатов-β-аминопропиоамидоксимов (6–10) и
хлоридов 2-(гетероамино)-1,5-диазаспиро[4,5]декан-1-ен-5-аммониумов (11–15)

| № соед. | Выход, % | Время, ч | Т.пл., °С (р-тель при перекр) | $R_f$ | М.в. | Найдено, % Вычислено, % | | | Брутто-формула |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | C | H | N | |
| 6 | 59 | 2 | 180 (*i*-PrOH) | 0,46 | 325,43 | 55,36<br>54,86 | 7,12<br>6,63 | 12,91<br>12,41 | $C_{15}H_{25}N_3O_3S$ |
| 7 | 51 | 24 | 212 (*i*-PrOH) | 0,45 | 327,40 | 51,36<br>50,86 | 6,47<br>5,99 | 12,83<br>12,51 | $C_{14}H_{21}N_3O_4S$ |
| 8 | 60 | 24 | 264 (aceton: EtOH) | 0,12 | 343,46 | 48,96<br>48,23 | 6,16<br>5,71 | 12,23<br>11,69 | $C_{14}H_{21}N_3O_3S$ |
| 9 | 82 | 5 | 295 (*i*-PrOH) | 0,68 | 402,51 | 51,36<br>50,86 | 6,47<br>5,97 | 12,83<br>11,99 | $C_{20}H_{26}N_4O_3S$ |
| 10 | 50 | 24 | 210 (EtOH) | 0,80 | 358,42 | 56,97<br>55,99 | 5,06<br>4,56 | 15,63<br>15,11 | $C_{17}H_{18}N_4O_3SS$ |
| 11 | 60 | – | > 270 (*i*-PrOH) | 0,21 | 189,69 | 50,66<br>49,98 | 8,50<br>7,93 | 22,15<br>21,65 | $C_8H_{16}ClN_3$ |
| 12 | 57 | – | > 270 (*i*-PrOH) | 0,11 | 191,66 | 43,87<br>43,35 | 7,36<br>6,83 | 21,92<br>21,23 | $C_7H_{14}ClN_3O$ |
| 13 | 84 | – | > 270 (*i*-PrOH) | 0,08 | 207,72 | 40,48<br>39,89 | 6,79<br>6,15 | 20,23<br>19,73 | $C_7H_{14}ClN_3S$ |
| 14 | 67 | – | > 270 (*i*-PrOH) | 0,31 | 266,77 | 58,53<br>57,87 | 7,18<br>6,78 | 21,00<br>20,43 | $C_{13}H_{19}ClN_4$ |
| 15 | 86 | – | 130 (*i*-PrOH) | 0,86 | 394,87 | 51,71<br>51,21 | 4,85<br>4,35 | 14,19<br>13,69 | $C_{17}H_{19}ClN_4O_3S$ |

Образование гидрохлорида О-тозилата-β-(бензимидазол-1-ил)пропиоамидоксима (15), очевидно, связано с термодинамической невыгодностью существования спиропиразолиниевого соединения на основе О-тозилата β-(бензимидазол-1-ил)пропиоамидоксима.

Группа соединений 6–15 испытана на *in vitro* противотуберкулезную и противодиабетическую активности под шифрами, соответственно: TBD-42–TBD-51.

Исследования бактерицидной активности препаратов TBD-42–TBD-51 проведены на ЛЧ музейном штамме *M. tuberculosis* H37Rv, диком чувствительном штамме (I) и двух устойчивых диких штаммах *M. tuberculosis* [устойчивый к рифампицину (II) и МЛУ (III) – устойчивый к рифампицину и изониазиду] на жидкой среде Школьниковой. Результаты исследования представлены в таблице 2.

Из таблицы следует, что ряд соединений 6–14 (TBD-42–TBD-50) обладает бактерицидной активностью на ЛЧ штаммах *M. tuberculosis* H37Rv и I со значением МБК в 50,0 мкг/мл; данная группа соединений не активна по отношению к штамму, устойчивому к рифампицину (II) и МЛУ штамму *M. tuberculosis* (III). Препарат TBD-51 не имеет бактерицидной активности по

Таблица 2 – Значения МБК (мкг/мл) О-тозилатов-β-аминопропиоамидоксимов (TBD-42–TBD-46), хлоридов 2-(гетероамино)-1,5-диазаспиро[4,5]декан-1-ен-5-аммониумов (TBD-47–TBD-50) и гидрохлорида О-тозилата-β-(бензимидазол-1-ил)пропиоамидоксима (TBD-51) при *in vitro* анти-ТБ скрининге

| Шифр | | TBD-42 | TBD-43 | TBD-44 | TBD-45 | TBD-46 | Рифам-пицин |
|---|---|---|---|---|---|---|---|
| № соед. | | 6 | 7 | 8 | 9 | 10 | |
| *In vitro* анти-ТВ, мкг/мл | *M. tuberculosis* H37Rv | 50 | 50 | 50 | 50 | 50 | 1,0 |
| | I | 50 | 50 | 50 | 50 | 50 | 1,0 |
| | II | >100 | >100 | >100 | >100 | >100 | 2,0 |
| | III | >100 | >100 | >100 | >100 | >100 | 2,0 |

| Шифр | | TBD-47 | TBD-48 | TBD-49 | TBD-50 | TBD-51 | Рифам-пицин |
|---|---|---|---|---|---|---|---|
| № соед. | | 11 | 12 | 13 | 14 | 15 | |
| *In vitro* анти-ТВ, мкг/мл | *M. tuberculosis* H37Rv | 50 | 50 | 50 | 50 | >100 | 1,0 |
| | I | 50 | 50 | 50 | 50 | >100 | 1,0 |
| | II | >100 | >100 | >100 | >100 | >100 | 2,0 |
| | III | >100 | >100 | >100 | >100 | >100 | 2,0 |

отношению к ЛЧ штаммам *M. tuberculosis* H37Rv и к I, а также к устойчивому к рифампицину (II) и МЛУ штаммам *M. tuberculosis* (III). МБК рифампицина в этих условиях составляет 1,0 мкг/мл на ЛЧ штаммах *M. tuberculosis* и 2,0 мкг/мл на ЛУ и МЛУ штаммах *M. tuberculosis.*

*In vitro* противодиабетический скрининг в отношении фермента α-амилазы выполнен для группы соединений 6–15, испытанных под шифрами TBD-42–TBD-51 (таблица 3).

Таблица 3 – Оценка *in vitro* противодиабетического действия О-тозилатов-β-аминопропиоамидоксимов (TBD-42–TBD-46), хлоридов 2-(гетероамино)-1,5-диазаспиро[4,5]декан-1-ен-5-аммониумов (TBD-47–TBD-50) и гидрохлорида О-тозилата-β-(бензимидазол-1-ил)пропиоамидоксима (TBD-51) в отношении фермента α-амилазы (%)

| Шифр | | TBD-42 | TBD-43 | TBD-44 | TBD-45 | TBD-46 | Акарбоза |
|---|---|---|---|---|---|---|---|
| № соед. | | 6 | 7 | 8 | 9 | 10 | |
| *In vitro* анти-D, % | α-амилазная активность | 29,2±4,2 | 27,4±1,6 | 24,5±4,2 | 13,2±5,6 | 21,3±1,0 | 51,6±2,50 |

| Шифр | | TBD-47 | TBD-48 | TBD-49 | TBD-50 | TBD-51 | Акарбоза |
|---|---|---|---|---|---|---|---|
| № соед. | | 11 | 12 | 13 | 14 | 15 | |
| *In vitro* анти-D, % | α-амилазная активность | 28,3±2,6 | 22,2±1,2 | 14,4±4,0 | 23,6±1,0 | 22,0±1,4 | 51,6±2,50 |

Среди всех исследуемых образцов ингибиторную активность в отношении α-амилазы, превышающую 50%, ни один образец не проявил. Умеренной ингибиторной активностью (от 27 до 29%) обладают следующие соединения: TBD-42, TBD-43, TBD-47. Слабая ингибиторная активность (от 13 до 24%) обнаружена у следующих образцов: TBD-44– TBD-46, TBD-48–TBD-51. Препарат сравнения акарбоза проявил стандартную ингибиторную активность в отношении α-амилазы, составляющую 51,6%.

Можно заключить, что в изученных группах О-тозилатов-β-аминопропиоамидоксимов и хлоридов 2-(гетероамино)-1,5-диазаспиро[4,5]декан-1-ен-5-аммониумов обнаружены препараты с умеренной противотуберкулезной активностью на ЛЧ штаммах *M. tuberculosis* (МИК 50 мкг/мл), содержащие β-аминогруппы: пиперидин-1-ил, морфолин-1-ил, тиоморфолин-1-ил, 4-фенилпиперазин-1-ил, бензимидазол-1-ил (за исключением бензимидазольного производного в ряду спиропроизводных); и с умеренной противодиабетической активностью (от 27 до 29%) в первом ряду, содержащие β-аминогруппы: пиперидин-1-ил, морфолин-1-ил и во втором ряду – пиперидин-1-ил.

## ЭКСПЕРИМЕНТАЛЬНАЯ ЧАСТЬ

***Экспериментальная химическая часть.*** ИК-спектры сняты на приборе NICOLET 5700 FT-IR в таблетках KBr. Спектры ЯМР ($^1$H и $^{13}$C) зарегистрированы в ДМСО-$d_6$ на спектрометре Avance III 500 МГц (11,74 Tesla) с рабочей частотой для ядер $^1$H – 500 МГц и для ядер $^{13}$C – 126 МГц с внутренним стандартом гексаметилдисиланом (ГМДС; δ 0,05 м.д.); измерения были проведены при температуре 25°C.

Контроль за ходом реакции осуществлялся с помощью ТСХ на пластинках Sorbfil (ЗАО Сорбполимер) с нанесенным сорбентом – слоем силикагеля СТХ-1А, зернением 5–17 мкм, УФ индикатором УФ-254 с использованием в качестве элюента смеси растворителей этанола:бензол – 3:1 с добавкой концентрированного аммиака. Растворители, используемые при синтезе, перекристаллизации соединений и как элюенты для ТСХ (EtOH, *i*-PrOH, ацетон, хлороформ, диэтиловый эфир) приготовлены по стандартным методикам. Синтезы соединений 6–15 описаны в работах [8, 9].

*Взаимодействие β-(пиперидин-1-ил)пропиоамидоксима (1)* и *пара-толуолсульфохлорида.* К раствору 0,3 г (0,0017 моль) β-(пиперидин-1-ил)пропиоамидоксима (1), в 20 мл хлороформа, добавлено 0,17 г (0,0017 моль) триэтиламина. Реакционную смесь охлаждали до 0 °C и при перемешивании прикапывали 0,32 г (0,0017 моль) *пара*-толуолсульфохлорида в 2 мл хлороформа. Затем реакционной смеси позволяли дойти до комнатной температуры и перемешивали в течение 2 ч до окончания реакции. Контроль за ходом реакции проводили с помощью ТСХ. Обработку реакционной смеси выполнили после исчезновения пятен исходных соединений. Осадок О-тозилата-β-(пиперидин-1-ил)пропиоамидоксима (6) отфильтровали и перекристаллизовали из *i*-PrOH. Вес очищенного продукта 6 составляет 0,34 г (59%); т. пл. 180 °С, $R_f$0,46.

Синтез соединений 7–10 проводили аналогично; их физико-химические данные представлены в таблице 9.

*Взаимодействие О-тозилата-β-(пиперидин-1-ил)пропиоамидоксима (6) с эфирным раствором HCl.* В 2 мл абсолютированного этанола растворили 0,2 г (0,0006 ммоль) О-тозилата-β-(пиперидин-1-ил)пропиоамидоксима (6); затем до pH 2 добавили эфирный раствор HCl. Для выделения продукта к этанольному раствору взаимодействующих веществ добавили эквивалентный объем абсолютированного диэтилового эфира и потирали стеклянной палочкой о стенки колбы. Осадок хлорида 2-пиперидинспиропиразолиаммониума 11 отфильтровали и перекристаллизовали из *i*-PrOH. Вес очищенного продукта 11 составляет 0,07 г (60%); т. пл. > 270 °С, $R_f$0,21.

Получение остальных хлоридов 2-аминоспиропиразолиламмониумов (12−14) и гидрохлорида О-тозилата-β-(бензимиазол1-ил)пропиамидоксима (15) выполнено аналогично; физико-химические данные соединений 11–15 приведены в таблице 1.

***Экспериментальная биологическая часть.*** *Определение in vitro противотуберкулезного действия О-тозилатов-β-аминопропиоамидоксимов и хлоридов 2-(гетероамино)-1,5-диазаспиро[4,5]декан-1-ен-5-аммониумов (6–15).* В референс-лаборатории РГП на ПХВ «Национальный научный центр фтизиопульмонологии РК» МЗ РК проведены исследования бактерицидной активности препаратов TBD-42–TBD-51 на ЛЧ музейном штамме *M. tuberculosis* H37Rv, диком чувствительном штамме (I) и двух устойчивых диких штаммах *M. tuberculosis* [устойчивый к рифампицину (II) и МЛУ (III) – устойчивый к рифампицину и изониазиду] на жидкой среде Школьниковой. Бактерицидная активность рифампицина SV (МПК) на чувствительных штаммах *M. tuberculosis* и I равна 1 мкг/мл, а на устойчивых диких штаммах *M. tuberculosis* II и III – 2 мкг/мл.

*Общая методика определения in vitro бактерицидной противотуберкулезной активности на жидкой среде Школьниковой.* Культуру микобактерий, выращенную на плотной яичной среде в стерильных условиях (14–21 день), снимали с косяка одноразовой петлей и суспендировали в 0,9% растворе NaCl (физиологический раствор). Далее крупным частицам культуры дали осесть, выдерживая пробирку 20 мин при комнатной температуре. Взвесь бактерий отбирали пипеткой и переносили в другую пробирку, чтобы довести до необходимой оптической плотности. Необходимая оптическая плотность или мутность, соответствующая стандарту 5, достигалась добавлением в пробирку физиологического раствора. В 1 мл суспензии, соответствующей 5 стандарту оптической плотности, содержится 500 млн. микробных тел ($5x10^8$ микробных тел). Суспензию микобактерий туберкулеза засевали в жидкую среду из расчета 0,2 мл на 2 мл среды. Исходный раствор испытуемого соединения готовили с использованием диметилсульфоксида (ДМСО).

Навеску веществ растворяли в минимальном объеме растворителя и после этого разводили физиологическим раствором до нужной концентрации. Например, к навеске 10 мг вещества добавляли 1 мл ДМСО, встряхивали. После этого полученный раствор или гомогенную взвесь доводили физиологическим раствором до необходимой концентрации.

При применении высоких концентраций растворителей необходимо контролировать эффект воздействия этих веществ на рост микобактерий. При изучении бактерицидной активности испытуемых веществ исследовали широкий спектр концентраций. Расчет концентраций для изучения бактерицидной активности испытуемых веществ на жидкой среде Школьниковой: *I разведение:* 10 мг вещества + 10 мл жидкости (дистиллированная вода, этиловый спирт, физиологический раствор, ДМСО), что соответствует концентрации 1000 мкг/мл; *II разведение:* 1 мл от разведения I + 9 мл среды Школьниковой, что составляет общий объем в 10 мл с концентрацией 100 мкг/мл. Исследование противотуберкулезной бактерицидной активности препаратов проводили для концентраций от 100 до 0,01 мкг/мл.

В каждую опытную и контрольную пробирки (питательная среда без препарата) вносили по 0,1 мл взвеси микобактерий туберкулеза в 0,2 мл физиологического раствора. Пробирки инкубировались при 37 °С в течение 10 суток. Через 10 дней инкубации на жидкой среде осадки отмывались физиологическим раствором и засевались на плотную среду Левенштейна-Йенсена. Учет роста культур проводился дважды – через 1 и через 2,5 мес. Опыт проводился дважды.

Результаты определения *in vitro* противотуберкулезной активности соединений 6–15, испытанных под шифрами TBD-42–TBD-51, представлены в таблице 2.

*Определение in vitro противодиабетического действия.* В лаборатории токсикологии и фармакологии РГП на ПХВ «Национальный центр биотехнологии КН МОН РК» выполнен *in vitro* противодиабетический скрининг группы соединений 6–15, испытанных под шифрами TBD-42–TBD-51. Исследование степени ингибирования α-амилазной активности выполняли по стандартному методу [12]. В каждую лунку 96-луночного планшета добавляли реакционную смесь, содержащую 50 мкл фосфатного буфера (100 мМ, pH=6,8, Sigma-Aldrich), 10 мкл α-амилазы (2 ЕД/мл, Sigma-Aldrich) и 20 мкл соединений в концентрации 1,0 мг/мл, которую затем инкубировали при 37 °С в течение 30 мин. После этого добавляли 100 мкл DNS (Dinitrosalicylic acid solution) окрашивающего реагента и кипятили в течение 10 мин. Оптическую плотность полученной смеси измеряли при 540 нм на планшетом спектрофотометре. В качестве препарата сравнения использовали акарбозу в концентрации 1,0 мг/мл (позитивный контроль). Параллельно ставили негативный контроль (фосфатный буфер) без добавления испытуемых соединений. Все пробы исследовали в триплетах. Ингибиторную активность выражали в процентах (%) по степени ингибирования α-амилазы в сравнении с негативным контролем.

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## Резюме

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### О-ТОЗИЛАТ-β-АМИНОПРОПИОАМИДОКСИМ ЖӘНЕ 2-(ГЕТЕРОАМИН)-1,5-ДИАЗАСПИРО[4,5]ДЕКАН-1-ЕН-5-АММОНИУМ ХЛОРИДТЕРІНІҢ *IN VITRO* ТУБЕРКУЛЕЗГЕ ҚАРСЫ ЖӘНЕ ДИАБЕТКЕ ҚАРСЫ БЕЛСЕНДІЛІГІ

О-Тозилат-β-аминопропиоамидоксим және 2-амино-4,5-дигидроспиропиразолиламмони хлоридтері *in vitro* туберкулезге қарсы және диабетке қарсы белсенділікті зерттеуге арналған. Туберкулезге қарсы орташа белсенділігі бар ДТ штамды *M. tuberculosis* (МБК 50 мкг/мл) препараттары қосылыстардың екі тобында анықталды, құрамында β-амин топтары бар: пиперидин-1, морфолин-1, тиоморфолин-1, 4-фенилпиперазин-1, бензимидазол-1 (спиро туындыларының сериясындағы бензимидазол туындысын қоспағанда) және бірінші қатарда қалыпты диабетке қарсы α-амилаза белсенділігі бар (27%-дан 29%-ға дейін), құрамында β-амин топтары бар: пиперидин-1, морфолин-1 және екінші қатарда – пиперидин-1.

**Түйін создер:** О-тозилат-β-аминопропиоамидоксимдер, 2-амино-4,5-дигидроспиропиразолиламмониум хлоридтері, *in vitro* туберкулезге қарсы және диабетке қарсы белсенділік.

## Summary

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## *IN VITRO* ANTI-TUBERCULOSIS AND ANTI-DIABETIC ACTIVITY OF O-TOSYLATES-β-AMINOPROPIOAMIDOXIMES AND CHLORIDES OF 2-(HETEROAMINO)-1,5-DIAZOSPIRO[4,5]DECANE-1-EN-5-AMMONIUMS

O-Tosylates-β-aminopropioamidoximes and chlorides of 2-amino-4,5-dihydrospyropyrazolylammoniums have been studied *in vitro* for anti-tuberculosis and anti-diabetic activity. In two groups of compounds containing β-amino groups: piperidin-1-yl, morpholin-1-yl, thiomorpholin-1-yl, 4-phenylpiperazine-1-yl, benzimidazol-1-yl (with the exception of the benzimidazole derivative in the spiro derivative series), drugs with an average anti-tuberculosis activity were detected on the DS strains of *M. tuberculosis* (MBC 50 µg/ml) and with moderate anti-diabetic α-amylase activity (27% to 29%) in the first row, containing β-amino groups: piperidin-1-yl, morpholin-1-yl and in the second row – piperidin-1-yl.

**Key words:** O-tosylates-β-aminopropioamidoximes, chlorides of 2-amino-4,5-dihydrospyropyrazolylammoniums, *in vitro* anti-tuberculosis and anti-diabetic activity.

UDC 678-13+539.374·665.637,7

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# MODIFIED ETHYLENE-VINYL ACETATE COPOLYMER AS A DEPRESSANT OF POUR POINT WAX OIL

**Abstract.** The ethylene–vinyl acetate copolymer (EVA) was modified by hydrolysis of acetate groups. The separately hydrolysed copolymer was characterized by Fourier transform infrared spectroscopy(FTIR). Research was carried out to determination the influence of modified EVA polar groups on decrease the pour point temperature of oil.The results showed that EVA greatly decrease the Pour Point Temperature (PPT) of paraffin oil. In addition, EVA with strong polarity could provide greater electrostatic repulsion force to wax crystals, which made the wax crystals have more difficulty to connect together and form a much looser network structure.

**Key words:** Pour Point Depressant (PPD), ethylene–vinyl acetate copolymer (EVA), modified copolymer, wax.

**Introduction.** Nowadays oil and gas industry undergoes significant financial expenses and technical and technological difficulties due to the current trend of increasing content of heavy and viscous oil. Those abnormal rheological properties that are mainly introduced as high viscosity and high temperature of solidification correspond to oil from Kazakhstan's oil fields (deposits of Mangyshlak Peninsula, Akshabulak and other regions). Almost all types of oil in Kazakhstan can be classified as waxy, solidifying at positive temperatures, and high viscous oil. In particular, viscosity of high viscous oil even under normal conditions fluctuates in the range of several hundred, and sometimes thousands of centipoises [1-3].

Wax deposition are both a down hole and topside problem blocking the flow of hydrocarbons fluids as they are cooled [4].

Wax deposition is one of the major flow assurance risks and it should be considered during the transportation of heavy, waxy and high viscous crude oil. Flow assurance risks including wax deposition and wax gelation become a bigger concern for oil transportation sector [5].

Therefore, an important issue is to synthesize or modify polymeric depressants that will provide the improvement of rheological characteristics of waxy and high viscous oil that present in Kazakhstan's oil fields. The key role played by this additive is co-crystallizing with the paraffin existent in oil, promoting the highest possible disarrangement of wax crystallization process [6].

In this study, ethylene–vinyl acetate copolymer (EVA) was modified by alkali-catalyzed alcoholysis and investigated the properties of the resulted copolymer into pour point depressant of crude oil.

# EXPERIMENTAL PART

## Materials and methods

**Characteristic of initial reagents.** Poly (ethylene-co-vinyl acetate) with the content of vinyl acetate monomeric unit of 25 wt.% and exhibiting melt flow indices of 19 g/min produced by "Sigma-Aldrich Chemicals GmbH" was used without further purification.

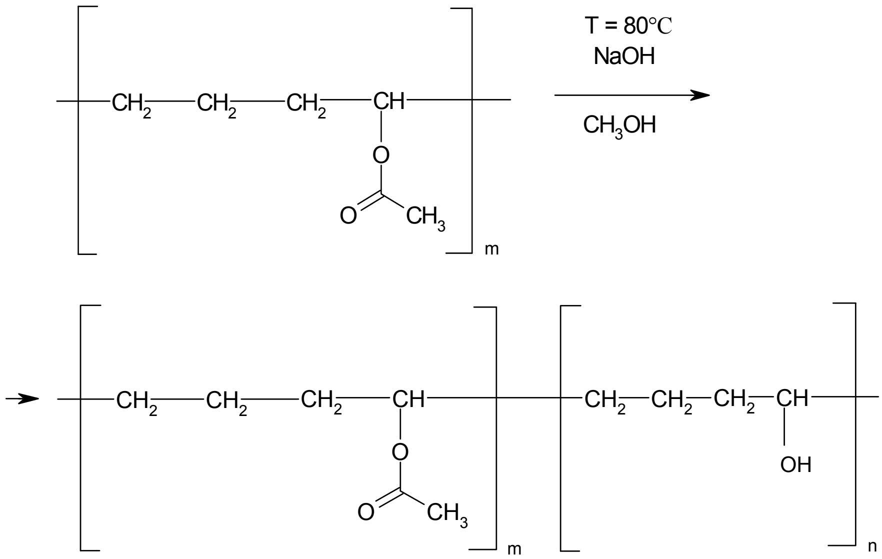
Methanol produced from "Sigma-Aldrich Chemicals GmbH" was used without further purification.

Sodium hydroxide from "Sigma-Aldrich Chemicals GmbH" was used without further purification.

Toluene was used as an organic solvent for the reaction of hydrolysis. The purification of toluene was performed according to standard procedures. The density is 0.865 g/mL at 25°C and boiling point is 110-111°C. The vapor point is equal to 26 mm Hg (25°C).

Depressant additive DMN-2005 of company "DEPRAN" (Russia) was used without further purification.

**Procedure of modification of ethylene-co-vinyl acetate polymers with base.** In a three-necked round bottom flask fitted with a reflux condenser (Dean-Stark apparatus), a thermometer, a magnetic stirrer, 2.0 g of EVA copolymer (containing vinyl acetate groups 25% wt.) was dissolved in 30 ml of toluene. After that, 1 mL of 2% solution of sodium hydroxide in methanol was added to the solution of the copolymer. Partial hydrolysis reaction proceeds according to the following scheme [6]:



The reaction was refluxed at 80°C during predetermined period equal to 30 minutes. Sodium hydroxide solution was neutralized with alcoholic solution of hydrochloric acid. Then, inorganic layer was eliminated, the polymer (organic) layer was reprecipitated into methanol, filtered and dried in vacuum at 50°C until constant weight. Under these conditions the modified EVA copolymer obtained hydrolysis degree of 5 mol. % (related to acetate moietites).

**Determination of thePour Point of wax oil.** The methodology used for the assessment of the oil pour points was based on an adaptation of the ASTM Method 5853. The cooling bath was equipped with two thermostats: LAUDA RE-415 that maintains the temperature of 0°C, LAUDA RE-210 that maintains the temperature of -17°C.

## RESULTS AND DISCUSSION

**Modification of ethylene-co-vinyl acetate copolymers with bases.** Modification of ethylene-co-vinyl acetate copolymers with sodium hydroxide solution was carried out in the conformity with standard procedures of partial hydrolysis. The results of the reaction can be detected through the application of different methods of examination. The degree of hydrolysis and the yield of the modification reaction were investigated by means of FTIR-spectroscopy of obtained products. Below the spectrums of initial agents and products are described.

Figure 1 shows the FTIR spectrum of EVA copolymer. Characteristic absorption bands of the copolymer EVA are in:

– 1735 $cm^{-1}$, corresponding to the absorption of the stretching vibrations of C = O carbonyl group in esters;

– 2915 and 2847 $cm^{-1}$, relating to the absorption of the stretching vibrations of $CH_3$ groups and -$CH_3$-$CH_2$-ester groups.

Figure 2 represents the FTIR spectrum of partially hydrolyzed ethylene-vinyl acetate copolymer (degree of hydrolysis - 5%). There are a reduction of band intensity in the range of 1735-1738 $cm^{-1}$ - stretching vibrations of the carbonyl group -C=O in esters and an appearance in the spectrum of the hydrolyzed EVA of a wide absorption band of 3236 $cm^{-1}$, corresponded to the stretching vibrations of the -OH group.

Moreover, a reduction of the intensity of the absorption bands in the 2915 and 2847 $cm^{-1}$, related to the absorption of the stretching vibrations of $CH_3$- groups and -CH3-CH2-ester groups, and a strong reduction in the intensity of the absorption band of 1236 $cm^{-1}$ in the spectrum of the initial EVA, corresponded to absorption band of fluctuations with regard C-O group in acetate are observed.

Above-mentioned absorption band is absent in the spectrum of the completely hydrolyzed EVA that is presented on Figure 3.3 and it indicates a complete hydrolysis of ethylene-co-vinyl acetate. On the evidence of this: there is the almost a complete reduction in the intensity of the absorption bands observed in 2915 and 2847 $cm^{-1}$ relating to the absorption of the stretching vibrations of -$CH_3$ groups and -CH3-CH2-ether groups. In addition, there is an almost a complete

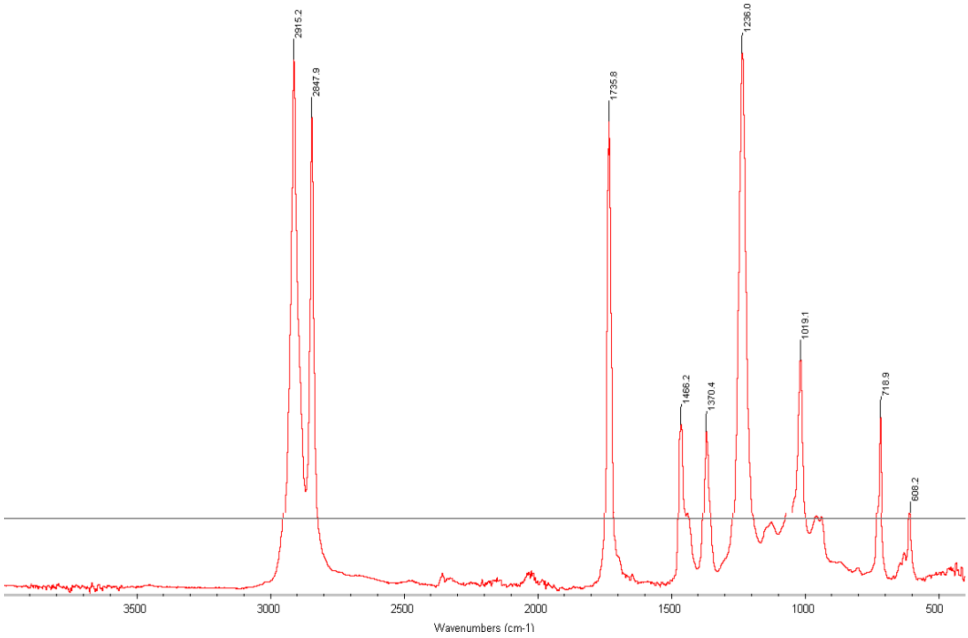


Figure 1 – FTIR spectrum of EVA copolymer

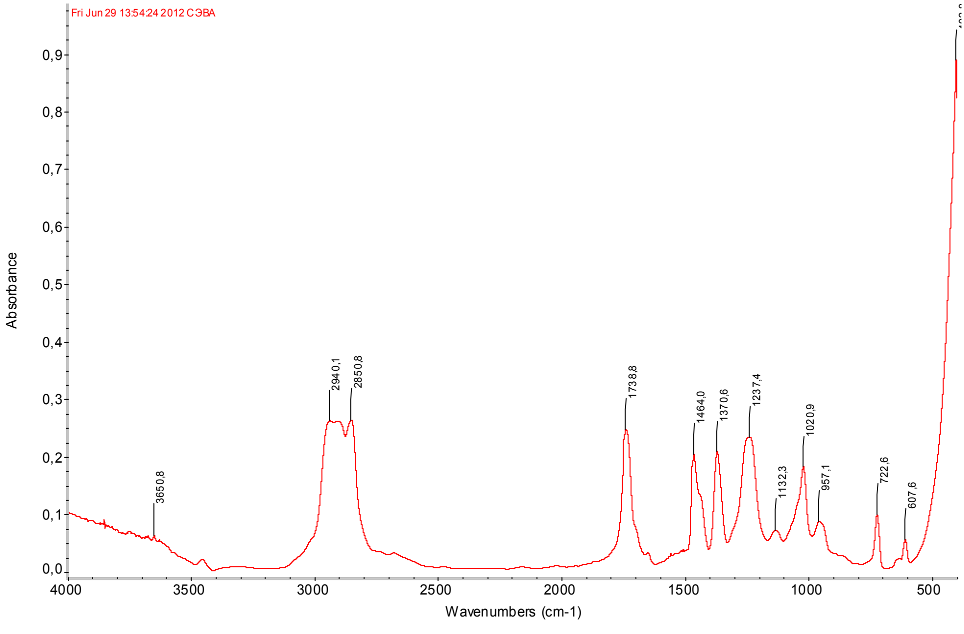


Figure 2 – FTIR spectrum of partially hydrolyzed EVA copolymer (hydrolysis degree – 5%)

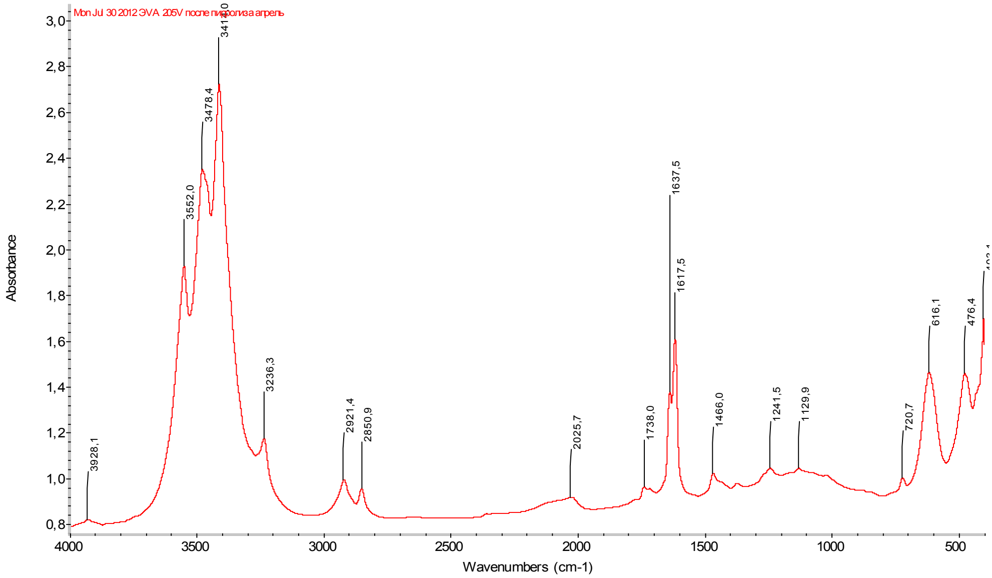


Figure 3 – FTIR spectrum of completely hydrolyzed EVA

absence of bands in the 1735-1738 $cm^{-1}$ - stretching vibrations of the carbonyl group C = O in esters, the presence of a broad absorption band of 3236 $cm^{-1}$ corresponding to the stretching vibrations of -OH groups [7].

Table 1 – General physical, chemical and rheological characteristics of oils of oil fields in the South Turgay basin [8]

| № | Crudeoil | $d_4^{20}$, $kg/m^3$ | WAT °C | Wax, % | Asphalt., % | Resins, % | Fraction, % | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | 200 °C | 300 °C | 350 °C |
| 1 | Kumkol' | 810,4 | 12 | 14,4 | 0,1 | 7,6 | 29 | 49 | 59 |
| 2 | Akshabulak | 829,7 | 21 | 14,3 | 0,6 | 8,6 | 29 | 48 | 58 |
| 3 | Konys | 874,4 | 24 | 16,5 | 2,0 | 7,1 | 15 | 33 | 47 |
| 4 | Bektas | 825,7 | 21 | 19,4 | 1,2 | 9,6 | 29 | 48 | 58 |
| 5 | Aschysay | 878,2 | 21 | 20,1 | 1,3 | 9,2 | 20 | 39 | 51 |

**Effect on wax appearance temperature of waxy crude oils.** The pour point depressant that was injected into oil disperse system modifies formed crystals of paraffin and regulates the structure of oil dispersion by means of increasing its aggregative stability. Therefore, a certain pour point corresponds to determined oil type with certain injected depressant additive. According to the results of experimental tests on determination of wax appearance temperature, conclusions on the influence of modified pour point additives have been done.

The key point is the impact of additives on the pour point depression and cloud point depression for different types of oil and oil mixtures. Compared to the original ethylene-vinyl acetate copolymer, the chemical structure of modified EVA displays more polarity due to the presence of hydroxyl groups, which promote better disarrangement during wax crystallization process. The lack of paraffinic chains in the structure of partially hydrolyzed EVA is one of the reasons of better results achieved by modified EVA copolymers [7].

Table 2 shows wax appearance temperature change of crude oils and oil mixtures when heat-treated and treated with additives. As it can be seen from the table, modified additive has high performance and this magnitude is stable for different types of oil.

Table 2 – Wax appearance temperature of waxy crude oils
in the South Turgay basin after heat and additive treatments

| Waxy crude oil | Treatment | Pour Point, °C |
|---|---|---|
| Akshabulak | Heat treatment | +18 |
| | Industrial additive | +6 |
| | Modified EVA | 0 |
| Achysay | Heat treatment | +21 |
| | Industrial additive | +15 |
| | Modified EVA | +9 |
| Konys-Bektas | Heat treatment | +24 |
| | Industria ladditive | +12 |
| | Modified EVA | +6 |
| Kumkol | Heat treatment | +12 |
| | Industrial additive | 0 |
| | Modified EVA | -3 |

**Conclusion.** Modified a new ethylene–vinyl acetate copolymer (EVA) with alcohol in presence of sodium hydroxide.The alcoholized copolymer was characterized by Fourier transform infrared (FTIR) spectroscopy. The obtained copolymer was tested into pour point depressant(PPD) of crude oil of different crude oils from different oil basin. The results showed that EVA greatly decreases the Pour Point of crude oil compared to industrial additives and heat treatment.

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## Резюме

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### ЭТИЛЕН-ВИНИЛАЦЕТАТТЫҢ ТҮРЛЕНДІРІЛГЕН СОПОЛИМЕРІН ПАРАФИНДІ МҰНАЙДЫҢ ҚАТУ ТЕМПЕРАТУРАСЫН ТӨМЕНДЕТУДЕ ҚОЛДАНУ

Этилен және винилацетаттың сополимері (ЭВА) ацетаттық топтың гидролизі арқылы түрлендірілді. Ішінара гидролизденген сополимер инфрақызыл Фурье спектроскопиясы (FTIR) арқылы сипатталды. ЭВА түрледірілген полярлы тобының, мұнайдың аққыштығын жоғалту температурасының төмендетуіне әсері зерттелді. Нәтиежесінде ЭВА парафинді мұнайдың аққыштығын жоғалту температурасын едәуір төмендететіні анықталды. ЭВА сополимері түрдендіруден кейін парафин кристалдарын үлкен электростатикалық тебіліс күшімен қамтамасыз етеді және де әлсіз байланысқан парафин кристал торларының қалыптасуына жағдай жасайды.

**Түйін сөздер:** аққыштық температурасын төмендету қоспасы, этилен және винилацетаттың түрлендірілген сополимері (ЭВА), парафин.

## Резюме

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### МОДИФИЦИРОВАННЫЙ СОПОЛИМЕР ЭТИЛЕН-ВИНИЛАЦЕТАТ КАК ДЕПРЕССАНТ ТЕМПЕРАТУРЫ ПОТЕРИ ТЕКУЧЕСТИ ПАРАФИНИСТОЙ НЕФТИ

Модифицирован сополимер этилена и винилацетата (ЭВА) путем гидролиза ацетатной группы.Частично гидролизованный сополимер изучали инфракрасной Фурье спектроскопией (FTIR). Исследовано влияние модифицированных полярных групп ЭВА на снижение температуры потери текучести нефти. Результаты показали, что ЭВА значительно снижает температуру потери текучести (ТПП) парафинистой нефти. Сополимер ЭВА после модификации может обеспечить большую электростатическую силу отталкивания кристаллов парафина, и создает условия для формирования гораздо более слабосвязанной кристаллической сетки парафинов.

**Ключевые слова:** депрессант температуры потери текучести (PPD), модифицированный сополимер этилена и винилацетата (ЭВА), парафин.

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# SYNTHESIS OF NEW DERIVATIVES OF PHENYLOXYPROPARGYL PIPERIDINES

**Abstract.** 4-(3-phenoxyprop-1-yn-1-yl)piperidine-4-ol has been obtained by condensation of 1-methyl-piperidine-4-one with phenoxypropargyl in the Favorsky reaction conditions in absolute benzene, in the presence of a fivefold excess of powdered technical KOH at the ratio of piperidone-4:phenoxypropargyl = 1:1.5. Upon acylation of tertiary phenoxypropynyl piperidol by cyclobutane-, cyclopentane-, cyclohexanecarbonyl chlorides in dioxane at the room temperature or upon heating, the corresponding hydrochlorides of esters have been formed. The structure of the synthesized compounds has been confirmed by the NMR and X-ray spectroscopy data.

**Key words:** phenoxypropargylpiperidine-4-ol, cyclobutane-, cyclopentane-, cyclohexanecarbonyl chlorides, esters.

The search of new compounds for antimicrobial and virucidal activities, including those capable of inducing a reversion of medicine susceptibility, is related to the priority direction for the development of new anti-infective medicinal preparations. The topicality of the research, despite of a large range of antibacterial remedies available, is connected, first and foremost, with a high adaptability of pathogenic organisms to medicinal preparations, including antibiotics [1-3].

The directed construction of new molecules from pharmacophore structural fragments, among which the saturated nitrogenous heterocycles play the leading role, being synthetic analogues of natural alkaloids, is deemed to be an efficient way of searching for effective biologically active compounds (BAS). Alkyloxy-, aryloxy- and heteroaryloxypropinylcarbinols, various by their structure [4-7], have proved to be convenient reactive “building blocks” in the organic synthesis, including those for BAS.

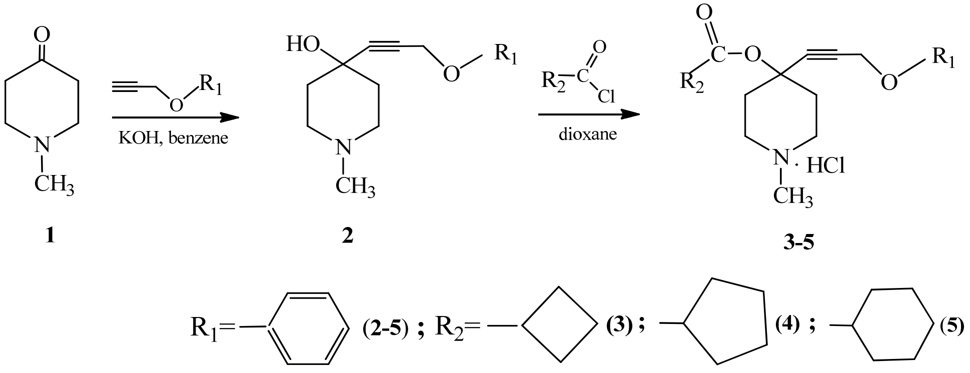
The current situation in organic chemistry reflects the lack of new leader structures, which may be optimized to therapeutically useful preparations. The scientific research, aimed at creating new materials for practical medicine and agriculture, is of top priority in the entire world.

The basis for the present studies has been a high biological activity of the previously synthesized esters of 1-(2-ethoxyethyl)-4-hydroxy-4-[3-(aryloxy)propyn-1-yl]piperidines [8] and piperidine-containing esters of cyclopropanecarboxylic acid [9-12].

A directed introduction of a cyclopropanecarbonyl fragment into the phenoxypropylpiperidine structure has lead to the compounds of an anti-infective activity. It has been shown, that hydrochloride of 1-methyl-4-(3-phenoxypropyn-1-yl)-4-cyclopropanecarbonyloxypiperidine with the code AIP-36, displays an antimicrobial activity in relation to all seven archival strains of microorganisms, used in the experiment: *Escherichia coli* ATCC 25922, *Klebsiella pneumoniae* ATCC 10031, *Candida albicans* ATCC 10231 in the concentration (MIC) of 1000 µg/ml, and in relation to *Escherichia coli* ATCC-BAA-196, *Klebsiella pneumoniae* ATCC 700603, *Staphylococcus aureus* ATCC 6538-P, *Staphylococcus aureus* ATCC-BAA-39 in the concentration (MIC) of 2000 µg/ml. Hydrochloride of 1-propyl-4-(3-phenoxyprop-1-yn-1-yl)-4-cyclopropanecarbonyloxypiperidine/ with the code AIP-37, suppresses the growth of 6 strains of microorganisms [9-14].

The present work aims the directed synthesis of new phenoxypropargylpiperidines with a potential antibacterial activity by varying the nature of an acyloxy group and introducing additional pharmacophors, the fragments of small cycles – cyclobutane-, cyclopentane-, cyclohexanecarbonyls, into the molecules.

Condensation of 1-methyl-4-oxopiperidine (1) with phenoxypropargyl in the Favorsky reaction conditions [13, 14] leads to a tertiary phenoxypropargyl alcohol (2).



Phenyloxypropynylpiperidol has been obtained with good yield (table 1) with the following optimum paraneters of the reaction: a ratio of piperidone:phenyloxypropine = 1:5, absolute benzene, a fivefold excess of technical caustic potassium.

Acylation of phenoxypropynyl piperidol (2) by cyclobutane-, cyclopentane-, cyclohexanecarbonyl chlorides, taken in excess, is carried out at the room temperature or upon heating in dioxane. The esters of cyclobutane-, cyclopentane-, cyclohexanecarboxylic acids (3-5) are crystalline powders of white, cream color, easily soluble in water, ethanol, and acetone.

The composition and structure of the synthesized compounds (2-5) have been confirmed by elemental analysis, IR spectroscopy, $^{13}$C NMR-spectroscopy, individuality has been confirmed by TLC (table 1).

Table 1 – The yields and physical and chemical characteristics of the compounds 2-5

| Compound | Yield, % | $R_f$ | t m.p., °C | IR spectrum, $cm^{-1}$ | | Empirical formula |
|---|---|---|---|---|---|---|
| | | | | OH | C=O of ester | |
| 2 | 74.6 | 0.27 | 84-86 | 3414 | – | $C_{15}H_{19}NO_2$ |
| 3 | 68.31 | 0.82 | 140-143 | – | 1735 | $C_{20}H_{26}NO_3Cl$ |
| 4 | 72.1 | 0.91 | 163-165 | – | 1736 | $C_{21}H_{28}NO_3Cl$ |
| 5 | 24.6 | 0.83 | 181-183 | – | 1737 | $C_{22}H_{30}NO_3Cl$ |

In the IR spectrum of piperidol (2), absorption bands of stretch vibrations of a hydroxyl group are observed in the region of 3414 см$^{-1}$, and that of the aromatic ring – in the region of 617-774 см$^{-1}$. Intensive absorption bands in the region of 1735-1737 см$^{-1}$, caused by C = O vibrations of an ester group, testify to the formation of the target esters of 4-phenoxypropynyl piperidols-4 of cyclobutane-, cyclopentane-, cyclohexanecarboxylic acids (3-5).

Table 2 shows the values of chemical shifts of carbons, which fully confirm the carbon composition of esters of 4-phenoxypropynyl piperidols-4 of cyclobutane-, cyclopentane-, cyclohexanecarboxylic acids (3-5).

Table 2 – The values of chemical shifts of carbon atoms in $^{13}C$ NMR- spectra of esters of 4-phenoxypropynyl piperidine-4-ols of cyclobutane-, cyclopentane-, cyclohexanecarboxylic acids (3-5)

| Compound | Chemical shift ($CDCl_3$), δ, ppm. | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $C_{3,5}$ | $C_{2,6}$ | $C_4$ | CH | $CH_2$ | C=O | ≡C-$CH_2$ | $C_4$-C≡ | O-$CH_2$ | OPh | N-$CH_3$ |
| **3** | 33.83 | 48.69 | 72.35 | 42.35; cyclobutane | 18.22;<br>25.03 cyclobutane | 173.22 | 81.88 | 86.07 | 56.01 | 115.58;<br>121.86;<br>129.98;<br>157.67 | 37.96 |
| **4** | 36.37;<br>36.54 | 56.03;<br>56.16 | 78.38 | 50.83 cyclopentane | 25.85;<br>29.83 cyclopentane | 174.36 | 81.72 | 91.16 | 61.02 | 115.47;<br>121.72;<br>130.01;<br>157.89 | 48.85 |
| **5** | 33.15;<br>33.80 | 50.17;<br>50.84 | 80.04 | 42.76 cyclohexane | 25.31;<br>25.77;<br>28.85 cyclohexane | 174.36 | 70.84 | 81.74 | 56.03 | 115.48;<br>121.79;<br>129.92;<br>157.59 | 48.85 |

In the $^{13}C$ NMR spectra (table 2) of cyclobutane-, cyclopentane-, cyclohexane- carbonyloxy derivatives (3-5), singlet signals of carbon atoms of the ester carbonyl region are observed in the region of 173.22-174.36 ppm, a singlet signal of $C_4$ resonates in the region of 72.35 -80.04 ppm, a carbon atom of a methylene group of the propylene fragment is observed in the region of 56.01-61.02 ppm. The weak-field region (115-157 ppm.) of the spectra is “populated” by the signals of aromatic carbons. The signals in the region of 18.22-29.83 ppm. and 42.35-50.83 ppm. are assigned to carbons of the cyclobutane, cyclopentane, cyclohexane rings. Besides, there is a doublet set of $C_{3.5}$ and $C_{2.6}$ signals, respectively, in the region of 33.80-36.54 ppm. and 48.69-56.16 ppm. of the piperidine cycle, associated with a slow inversion of the latter due to the bulky substituents at $C_4$.

## EXPERIMENTAL CHEMICAL PART

The course of the reaction and individuality of the compounds were controlled by TLC on aluminum oxide of the III degree of activity, with the development of spots by iodine vapors. The IR spectra were recorded on a Nicolet 5700 spectrometer in a thin layer between the KBr plates. $^1H$ and $^{13}C$ NMR spectra were recorded on a JNM-ECA400 spectrometer of the company JEOL (400 and 100,8 MHz, respectively) in $CDCl_3$, HMDS was used as an internal standard.

*1-methyl-4-(3-phenoxypropyn-1-yl)-4-hydroxypiperidine (2).* 14.85 g (0.2652 mol.) of powdered potassium hydroxide in 40 ml. of absolute benzene was introduced into a flat bottom flask, after 10 min. 34.03 ml. (0.2652 mol.) of 3-phenoxypropine-1 in 40 ml. of absolute benzene was slowly added dropwise upon stirring. Herewith, a slight heating and change of color of the solution were observed. After 30 min. a solution of 10 g (0.0884 mol.) of 1-methyl-piperidine-4-one in 30 ml. of absolute benzene was added dropwise. The reaction mixture was stirred for 5-6 hours at the room temperature. The reaction course was controlled by TLC. 150 ml. of distilled water was added to the reaction mixture, the layers were separated. The aqueous layer was extracted with benzene. The combined organic layers were washed with a 10% solution of hydrochloric acid, and the aqueous-acidic layer was extracted with benzene for the complete removal of the neutral products. Then it was alkalinized with a saturated solution of sodium hydroxide NaOH, extracted with benzene, and dried over magnesium sulfate. The drying agent was filtered, the solvent was vaporized, and the residue was re-crystallized from hexane. 17.51 g (74.6% of the theoretic value) of alcohol (2) was obtained in the form of white crystals, m.p. 84-86 °C, $R_f$ 0.27 (eluent - benzene:dioxane-4:1).

*Hydrochloride of 1-methyl-4-(3-phenoxypropyn-1-yl)-4-cyclobutanecarbonyloxypiperidine (3).* A solution of 1.05 ml. (0.0092 mol.) of cyclobutanecarbonyl chloride in absolute dioxane was slowly added upon stirring to a solution of 1.5 g (0.0061 mol.) of 1-methyl-4- (3-phenoxypropyn-1-yl)-4-hydroxypiperidine (2) in absolute dioxane. Herewith, a heating of the reaction mixture was observed. The mixture was kept at the room temperature for 24 hours. The reaction course was controlled by TLC. The solvent was removed. The residue was washed with diethyl ether, re-crystallized from isopropanol. 1.52 g (68.31% of the theoretical value) of hydrochloride of 1-methyl-4-(3-phenoxypropyn-1-yl)-4-cyclobutanecarbonyloxypiperidine (3) was obtained in the form of crystals, m.p. 140-143 $^0$C, $R_f$ 0.82 ($Al_2O_3$, eluent - benzene:dioxane - 3:2).

*Hydrochloride of 1-methyl-4-(3-phenoxypropyn-1-yl)-4-cyclopentanecarbonyloxypiperidine (4).* A solution of 1.11 ml. (0.00915 mol.) of cyclopentanecarbonyl chloride in absolute dioxane was slowly added upon stirring to a solution of 1.5 g (0.0061 mol.) of 1-methyl-4-(3-phenoxypropyn-1-yl)-4-hydroxypiperidine (2) in absolute dioxane. Herewith, a heating of the reaction mixture was observed. The mixture was kept at the room temperature for 24 hours. The reaction course was controlled by TLC. The solvent was removed, and the residue was washed with diethyl ether, re-crystallized from isopropanol. 1.66 g (72.1% of the theoretic value) of hydrochloride of 1-methyl-4-(3-phenoxypropyn-1-yl)-4-cyclopentanecarbonyloxypiperidine (4) was obtained in the form of crystals, m.p. 163-165 $^0$C, $R_f$ 0.91 ($Al_2O_3$, eluent - benzene:dioxane - 4:1).

*Hydrochloride of 1-methyl-4-(3-phenoxypropyn-1-yl)-4-cyclohexanecarbonyloxypiperidine (5).* 1.5 g (0.007 mol.) of 1-methyl-4-(3-phenoxypropyn-1-yl)-4-hydroxypiperidine (2) was dissolved in a small amount of absolute dioxane, then a solution of 1.26 ml. (0.014 mol.) of cyclohexanecarbonyl chloride in absolute dioxane was added. Herewith, a heating of the reaction mixture and change of color of the solution from light yellow to light brown were observed. The mixture was held overnight at the room temperature. The solvent was removed, and the residue was re-crystallized from isopropanol. 1.5 g (24.6% of the theoretical value) of hydrochloride of 1-methyl-4-(3-phenoxypropyn-1-yl)-4-cyclohexanecarbonyloxypiperidine (5) was obtained, mp. 181-183 $^0$C, $R_f$ 0.83 ($Al_2O_3$, eluent - diethyl ether).

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## Резюме

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### ФЕНИЛОКСИПРОПАРГИЛПИПЕРИДИНДЕР ҚАТАРЫНЫҢ ЖАҢА ТУЫНДЫЛАРЫН СИНТЕЗДЕУ

Фаворский реакциясы жағдайында 1-метил-пиперидин-4-он- ды абсолютты бензолда бес есе артық мөлшерде алынған техникалық КОН ұнтөғы қатысында, пиперидон-4:феноксипрорпаргил = 1:1,5 қатынасында феноксипропаргилмен конденсациялау арқылы сәйкесінше 4-(3-феноксипроп-1-ин-1-ил)пиперидин-4-ол алынды. Үшіншілік феноксипропинилді пиперидолды циклобутан-, циклопентан-, циклогексанкарбонилхлоридтермен диоксанда ацилирлеу кезінде бөлме температурасында немесе қыздырғанда сәйкесінше күрделі эфирлердің гидрохлоридтері түзіледі. Синтезделген қосылыстардың құрылымы ЯМР және ИҚ спектроскопия арқылы дәлелденді.

**Түйін сөздер:** феноксипропаргилпиперидин-4-ол, циклобутан-, циклопентан-, циклогексанарбонилхлоридтер, күрделі эфирлер.

## Резюме

*Г. С. Ахметова, У. Б. Исаева, К. Д. Пралиев, Н. В. Коротецкая, О. Т. Сейлханов*

### СИНТЕЗ НОВЫХ ПРОИЗВОДНЫХ РЯДА ФЕНИЛОКСИПРОПАРГИЛПИПЕРИДИНОВ

Конденсацией 1-метил-пиперидин-4-она с феноксипропаргилом в условиях реакции Фаворского в абсолютном бензоле в присутствии пятикратного избытка порошкообразного технического КОН при соотношении пиперидон-4:феноксипрорпаргил = 1:1,5 получен соответствующий 4-(3-феноксипроп-1-ин-1-ил)пиперидин-4-ол. При ацилировании третичного феноксипропинилового пиперидола циклобутан-, циклопентан-, циклогексанкарбонилхлоридами в диоксане при комнатной температуре или нагревании образуются соответствующие гидрохлориды сложных эфиров. Строение синтезированных соединений подтверждены данными спектроскопии ЯМР и ИКС.

**Ключевые слова:** феноксипропаргилпиперидин-4-ол, циклобутан-, циклопентан-, циклогексанарбонилхлориды, сложные эфиры.

# ЮБИЛЕЙНЫЕ ДАТЫ

Коллектив ордена Трудового Красного Знамени Института химических наук имени А.Б. Бектурова сердечно поздравляет главного научного сотрудника лаборатории неорганического синтеза и материалов доктора технических наук, профессора **Султана Усманова** с 70-летним юбилеем!

Султан Усманов после окончания Ташкентского политехнического института имени А.Р. Беруни с 1969 по 1992 г. работал младшим, старшим научным сотрудником и заведующим лабораторией Всесоюзного института хлопководства Министерства сельского хозяйства и Института химии Академии наук Республики Узбекистан.

В апреле 1992 г. был избран директором вновь организованного Института удобрений Академии наук Республики Узбекистан, который возглавлял до сентября 1997 г.

После реорганизации в системе Академии наук Республики Узбекистан вернулся на историческую родину в Республику Казахстан и был назначен на должность председателя правления ТОО «АПК «Сункар», а в октябре 2003 г. стал президентом ТОО «Научно-производственное объединение «Ана Жер», с 2006 г. является председателем правления ТОО «Хазрат-Али-Акбар». Сочетая руководящую работу с научной деятельностью, с 2006 г. по настоящее время, трудится главным научным сотрудником в АО «Институт химических наук имени А.Б. Бектурова».

С. Усманов в 1974 г. успешно защитил кандидатскую, а в 1986 г. – докторскую диссертацию по специальности «Технология неорганических веществ», в декабре 1988 г. ему присвоено ученое звание «профессор».

С 1992 г. по 1996 г. являлся председателем Регионального Специализированного Совета по защите докторских диссертаций по специальности «Технология неорганических веществ» для республик Средней Азии и Казахстана.

***Научным направлением С. Усманова*** является разработка фундаментальных и прикладных основ малоотходной энерго-ресурсосберегающей технологии; *создание* производства, *продвижение* на рынок отечественных минеральных, био-, микробио-, органоминеральных удобрений, пролонгированного действия и пестицидных препаратов с регулируемым компонентным составом и заданными свойствами.

Научные результаты и разработанные технологии изложены в 2 монографиях, 12 – книгах, 6 – брошюрах, 460 – статьях, 54 – авторских свидетельствах СССР, 36 – патентах Республики Казахстан и Республики Узбекистан, 1 – патенте на изобретение Евразийского патентного ведомства. Им подготовлено 2 доктора, 18 кандидатов наук и 2 магистра.

С. Усмановым на основании проведенных фундаментальных исследований в многокомпонентных водно-солевых системах, включающих индивидуальные мочевино-формальдегидные соединения, хелатные формы фитосоединений (Cu, Zn, Co, Mo, Mn, B, Fe), фосфаты, нитраты, хлориды и сульфаты некоторых цветных и черных металлов, установлены области кристаллизации 30 новых двойных соединений.

Исследование состава и свойств полученных новых фаз явились научной основой:

– создания нового класса медленно действующих азотных, комплексных пролонгированных и органоминеральных удобрений, химических мелиорантов, кондиционирующих агентов, действующих веществ, технических продуктов и препаративной формы препаратов полифункционального действия, протравителей семян, гербицидов, фитобиоудобрений с высокой биологической, агрохимической и экономической эффективностью на засоленных землях, положительно влияющих на почвенное плодородие и качество продукции;

– определения оптимальных технологических параметров их получения, выбора аппаратуры по отдельным стадиям технологии, обоснования условий их хранения и внесения в почву;

– установления закономерности влияния препаратов на ***повышение*** численности микроорганизмов почвы, фиксирующих атмосферный азот и мобилизующих нерастворимые фосфорные соединения почвы, ***снижения*** численности олиготрофов, минерализирующих гумус и разлагающих нитратный азот почвы.

Полученные результаты исследований впервые были успешно применены в СССР на Чирчикском производственном объединении «Электрохимпром» (ныне – АО «MAXAM-CHIRCHIQ») для экспортной поставки карбамида. Карбамид с добавкой карбамидо-формальдегидными соединениями по настоящее время поставляется в Венгрию. На Самаркандском химическом заводе было организовано производство протравителя семян хлопчатника П-4, который по сей день используется сельхозтоваропроизводителями, возделывающими хлопчатник Республик Узбекистан и Таджикистан, Государства Туркменистан.

Получены разрешительные сертификаты на выпуск и использование:

– пестицидов - протравители семян зерновых и хлопчатника, системные гербициды, фунгициды, дефолианты, биопрепараты, стимуляторы роста и развития растений (1999-2011 гг.) в Республике Казахстан на 13 препаратов, в Кыргызской Республике – 7, в Государстве Туркменистан – 4, в Республике Узбекистан – 3 препарата;

– фито-, фитобиопрепаратов и удобрений в Республике Казахстан, свидетельство о регистрации химической продукции, сертификат соответствия, паспорт безопасности химической продукции, сертификат происхождения, стандарт организации (до 2023 г.);

– фитобиопрепарата МЭРС и биоудобрения Биобарс-М в Российской Федерации, Республике Узбекистан, Государстве Туркменистан (до 2023 г.).

Создано производство протравителей семян, гербицидов, биопрепаратов и стимуляторов роста и развития растений.

Разработанные препараты С. Усманова широко используются в растениеводстве Казахстана и в странах Средней Азии.

С. Усмановым подготовлены и представлены проекты в Правительства Республик Казахстан – 13 и Узбекистан – 4, Государства Туркменистан – 3, Кыргызской Республики – 1, Российской Федерации – 1, Малайзии – 1 по сохранению почвенного плодородия, получения высоких качественных урожаев сельскохозяйственных культур в условиях засоленности земель и суховеев при дефиците почвенной влаги и поливной воды.

*Коллектив Института химических наук имени А.Б. Бектурова сердечно поздравляет доктора технических наук, профессора Султана Усманова с юбилеем и желает ему крепкого здоровья, счастья, благополучия и новых творческих успехов на благо экономического и социального процветания Республики Казахстан.*

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## Требования для оформления статей в журнале «ХИМИЧЕСКИЙ ЖУРНАЛ КАЗАХСТАНА»

Научный журнал открытого доступа «Химический журнал Казахстана» издается ордена Трудового Красного Знамени Институтом химических наук имени А.Б. Бектурова с периодичностью 4 номера в год.

Цель Журнала – освещение новых научных результатов и идей, проблемных вопросов науки и техники, последних разработок и исследований по актуальным проблемам фундаментальных и прикладных исследований в области неорганической и органической химии, химии и технологии мономеров и высокомолекулярных соединений, ионного обмена, нефтехимии и нефтехимического синтеза, химии лекарственных веществ и физиологически активных соединений, химической экологии, химии удобрений и солей, физической химии для широкого круга специалистов. В Журнале публикуются научные статьи и обзоры ученых, докторантов, магистрантов, производственников, имеющие теоретическое и практическое значение.

Статьи, представленные в редакцию Журнала, должны удовлетворять следующим требованиям:

**Общие требования.** Редакционная коллегия принимает статьи, набранные в текстовом редакторе MS Word в электронном виде, а также на бумажном носителе, причем, последняя страница подписывается всеми авторами с проставлением даты.

Рисунки представляются с разрешением минимум 300 dpi, в формате *.bmp, .tiff. Схемы, графики выполняются во встроенной программе MS Word или в MS Excel.

**Язык статьи**. Статьи принимаются на казахском, русском или английском языках, однако, в целях популяризации Журнала, редакционной коллегией приветствуется прием статей на английском языке.

**Параметры страницы.** Формат страницы: А4 (210х297 мм).

Поля: верхнее – 2 см, нижнее – 2 см, левое – 3 см, правое – 1,5 см. Расстановка переносов не допускается. Фбзацный отступ – 1,0 см.

**УДК.** В начале статьи, в верхнем левом углу указывается номер по Универсальной десятичной классификации (УДК), соответствующий заявленной теме. Далее, после отступа строки, указываются инициалы и фамилии автора(-ов), еще через строку следуют названия организации(-й), в которой(-ых) работают авторы, название города и страны. Еще ниже, через строку указывается название статьи прописными буквами. Шрифт - полужирный.

**Аннотация.** Предоставляется на языке статьи (объем не менее 150 слов).

**Ключевые слова.** Слова и словосочетания (6-8), обеспечивающие наиболее полное раскрытие содержания статьи, представляются на языке статьи.

**Гарнитура.** Текст статьи набирается в гарнитуре Times New Roman, размер кегля 14 пт, межстрочный интервал - одинарный, форматирование - по ширине.

**Структура и объём статьи.** Структурирование статьи производится в соответствии с общепринятыми стандартами: **"Введение"** (должно включать в себя пояснение, в связи с чем проведено данное исследование, обзор актуальной литературы, обоснование выбора методологии исследований), **"Экспериментальная часть"** (описание проводимых исследований), "**Результаты и их обсуждение"** (полученные в ходе исследования результаты), "**Выводы"** (касательно полученных результатов, в том числе соответствуют ли они ожиданиям или нет). Объем статьи, включая аннотацию и список литературы: от 6 до 10 страниц. Обзорные статьи могут быть до 20 страниц.

**Ссылки на использованные источники.** Ссылки на использованные источники приводятся после цитаты в квадратных скобках, с указанием порядкового номера источника цитирования, в соответствии с ГОСТ 7.1–2003 «Библиографическая запись. Библиографическое описание. Общие требования и правила составления».

**Список литературы.** Располагается после текста статьи. Нумерация начинается с первого номера, предваряется словом «ЛИТЕРАТУРА» и оформляется в порядке упоминания или цитирования в тексте статьи. Рекомендуемое количество ссылок – не менее 20, в том числе не менее 50% – ссылки на международные источники (журналы, входящие в международные базы данных Clarivate Analytics, Scopus, Springer Nature). Далее в том же порядке приводится транслитерация списка. Под одним номером указывается только один источник. Список литературы должен быть представлен наиболее свежими и актуальными источниками.

**Резюме.** После списка литературы должны быть представлены резюме. К примеру, если статья написана на казахском языке, то на русском и английском языках даются резюме, состоящие из ФИО автора (-ов), названия, текста ( не менее 150 слов), ключевых слов, организации, где выполнялась работа.

**Сопроводительные документы, прилагаемые к статье.** К статье прилагаются сопроводительные документы (на казахском или русском языке):

1. Письмо-направление в редакционную коллегию Журнала от организации, в которой данное исследование выполнено.

2. Акт экспертизы.
3. Сведения об авторах: Фамилия, имя и отчество каждого автора с указанием ученой степени и ученого звания, служебные и домашние номера телефонов, домашние адреса с указанием почтового индекса, адрес электронной почты (в 2-х экземплярах).
4. Рецензия.
5. Научные учреждения, высшие учебные заведения, промышленные предприятия и каждый автор научной статьи, имеющий ученую степень доктора или кандидата наук, представляют ксерокопию или скан-версию квитанции **о годовой подписке** на «Химический журнал Казахстана». (Подписной индекс в каталоге АО «КазПочта» или в дополнении к нему – 75 241). Без этого документа статьи не принимаются.

Материалы, не соответствующие указанным требованиям, возвращаются на доработку.

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