



XXII MENDELEEV CONGRESS
ON GENERAL AND APPLIED CHEMISTRY

BOOK OF ABSTRACTS

IN 7 VOLUMES

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**XXII MENDELEEV CONGRESS
ON GENERAL AND APPLIED CHEMISTRY**

*Dedicated to the 190th anniversary
of D.I. Mendeleev and the 300th anniversary
of the Russian Academy of Sciences*

BOOK OF ABSTRACTS

Volume 5

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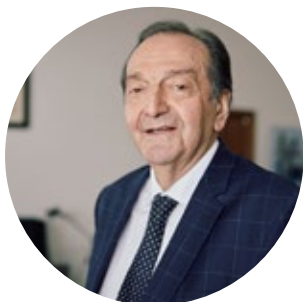
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F-BLOCK ELEMENTS: RECENT ADVANCES AND CHALLENGES

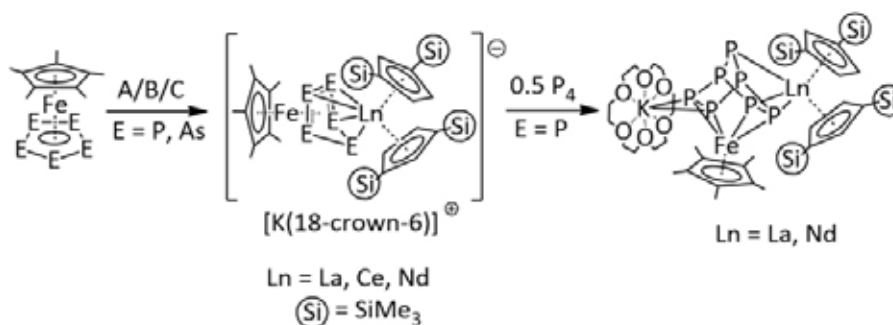
d/f-POLYPNICTIDES DERIVED BY NON-CLASSICAL LN(II) COMPOUNDS

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Chemistry of molecular f-element polypnictide complexes starts from two compounds described by W.J. Evans.^{1,2} 20 years later it was continued by the first Ln polyphosphide $[(Cp^*Sm)_4P_8]$,³ and later by its heavier congeners $[(Cp^*Sm)_4E_8]$ (E = As, Sb) and a series of Sm/d-metal polypnictides.⁴⁻⁶ All the compounds were obtained using a reductive approach: reactions of appropriate pnictogen compounds with Sm(II) complexes as reducing agents. The structure diversity of the Sm/d-metal polypnictides obtained is fantastic, but step by step the chemistry of the only of 4f-elements became a bit boring.

An availability of molecular Ln(II) compounds of almost all lanthanides makes this chemistry very interesting again. Herewith we report new d/f-polypnictides – $[K(18\text{-crown-6})][Cp^*_2Ln(E)_3FeCp^*]$ (Ln = La, Ce, Nd; E = P, As) – prepared using non-classical Ln(II) complexes $[(Cp^*_2Ln)_2(\mu-\eta^6:\eta^6-C_6H_6)]^{n-}$ (Ln = La (**A**, n = 1), Ce and Nd (**B**, **C**, n = 2)) as reducing agents towards $[Cp^*Fe(\eta^5-E_3)]$. It was found also that the new d/f-polyphosphides react with P₄ resulting in a selective expansion of $\{P_5\}^{3-}$ unit to P_7^{3-} : $[K(18\text{-crown-6})][Cp^*_2Ln(P_7)FeCp^*]$ (Ln = La, Nd).⁷



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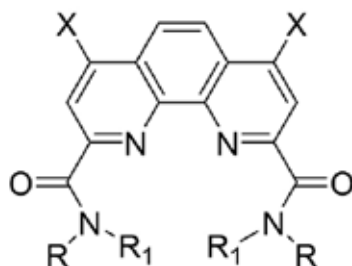


DESIGN AND SYNTHESIS OF PHENANTHROLINEDIAMIDES FOR SEPARATION OF F-BLOCK ELEMENTS

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The development of highly selective ligands for the separation of f-block elements is a very important task. Such ligands are needed in the production of high-purity rare earth elements (REE), without which the existence and development of innovative technologies in energy, electronics, transport, communication systems and many other important areas of modern technology is impossible. The use of such ligands underlies extraction technologies for the reprocessing of spent nuclear fuel (SNF) in nuclear power. Diamides of 1,10-phenanthroline-2,9-dicarboxylic acid represent one of the most promising classes of ligands for solving such problems.



PHOSPHORS – REE³⁺ ACTIVATED STRONTIUM PHOSPHATES: CRITERIA FOR PROPERTY FORMATION

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Phosphors based on oxosalts of strontium are used in various areas of photonics, including lighting. They possess high luminous quality, long service life, and energy conversion efficiency. In particular, phosphors with a SALON (or SIALON) structure, such as $\text{Sr}[\text{Li}_2\text{Al}_2\text{O}_2\text{N}_2]\text{:Eu}^{2+}$, are used as a component of red luminance in commercial LED devices. The stimulus for continuing the development of new phosphors is the complexity of synthesis and high cost of SALON phosphors.

Phosphors based on strontium phosphates have a number of advantages: high thermal and chemical stability, isomorphic capacity, volumetric coordination polyhedra of strontium atoms, which contributes to substitution for REE ions without causing concentration quenching effects. From the point of view of implementing luminescent properties of REE, mainly palmerite structures $\text{Sr}_3(\text{PO}_4)_2$, eulytite $\text{Sr}_3\text{R}(\text{PO}_4)_3$ ($\text{R} = \text{REE}$)³, strontiowhitlockite $\text{Sr}_9\text{Mg}(\text{PO}_4)_6(\text{HPO}_4)_4$ are represented in the literature.

The work compares phosphors of the structural families of palmerite, eulytite, and strontiowhitlockite and considers crystal chemical criteria for the formation of luminescent properties of REE ions in them. The boundaries of existence of substitution solid solutions and the main regularities of phase formation have been determined. It was shown that among the mentioned families of phosphors, the structure of strontium whitlockite allows for obtaining phosphors with the greatest intensity of photoluminescence regardless of the type of REE ion. The conditions of synthesis and chemical composition for obtaining phase-pure phosphors based on strontium phosphates with a whitlockite (or strontium whitlockite) structure are discussed.

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THE QUESTIONS OF DEVELOPMENT OF COMPUTATIONAL CHEMISTRY METHODS FOR F-ELEMENTS

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The f-elements chemistry, especially the actinide one, is characterized both by the least amount of experimental data available and the greatest difficulties arising when using computational chemistry methods. Thus, the reliable ab initio approaches of quantum chemistry, face problems of taking into account relativistic effects and the multiconfigurational nature of the wave function in addition to high computational resources demand. Less resource-intensive semiempirical methods (starting with density functional theory functionals) face problems with the scope of their parameterization, which usually does not include data on the properties of f-elements. The development of new semi-empirical methods, in turn, is limited by the lack of data for their parameterization.

The report examines the development of new methods suitable for modeling different levels of organization of f-element compounds: from modeling their electronic structure to empirically assessing the stability of compounds containing actinides and lanthanides. The process of developing the first low-parameter DFT functional is shown, which made it possible to simulate the geometry and enthalpy of formation of target compounds with an accuracy close to experimental one. Interatomic potentials were also proposed to describe Me-O type bonds and model at the atomistic level solid solutions of non-boundary compounds, including f-elements, as well as supramolecular effects in the formation of metal-organic framework compounds. Finally, a neural network architecture capable of “predicting” the stability constants of complexes of trivalent f-elements with an error of <1 [lgK] was proposed.

In all cases, both the details of creating new numerical methods and limitations of their use are discussed.

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LIQUID-LIQUID EXTRACTION TECHNOLOGIES FOR SEPARATION TRIVALENT F-ELEMENTS IN THE NUCLEAR FUEL CYCLE

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Nuclear energy is the safest and most concentrated source of energy. This year marks a significant milestone: 70 years since the first in the world grid-connected nuclear power plant was commissioned in Obninsk (Russia) in 1954. Nuclear reactors and the nuclear industry have made great strides since that time. However, it is evident that the potential of nuclear fuel is yet to be fully realized. The closing of the nuclear fuel cycle, that is, the extraction and reuse of valuable components from the spent nuclear fuel, could potentially lead to an increase in the performance factor of natural uranium and thorium. In contrast to the initial composition of nuclear fuel, which is primarily composed of uranium, oxygen, and plutonium, spent nuclear fuel contains over 50 chemical elements. Consequently, the extraction and separation of these elements necessitates the development of efficient and selective industrial chemical processes.

One of the most challenging chemical tasks of the closed nuclear fuel cycle is the separation of americium(III) from other trivalent f-elements, namely curium(III) and lanthanides(III), due to their close chemical properties, electronic structures, and ionic radii. Liquid-liquid extraction is an optimal method for this task, as the structure of the extractants can be modified to achieve the highest degree of selectivity towards a target cation. Nevertheless, selectivity is not the sole criterion for the extraction system (extraction system = extractant + diluent). In addition, the system should be radiolytically stable, exhibit good kinetic properties (i.e., rapid extraction), be non-flammable, etc.

The presentation will include a discussion of the recent results on the development of extraction systems for the separation of Am/Ln and Am/Cm pairs and their use in pilot-scale experiments.

UNIVERSAL TOOLS FOR RARE EARTH COMPLEX DESIGN: N-HETEROCYCLIC TRIDENTATE LIGANDS

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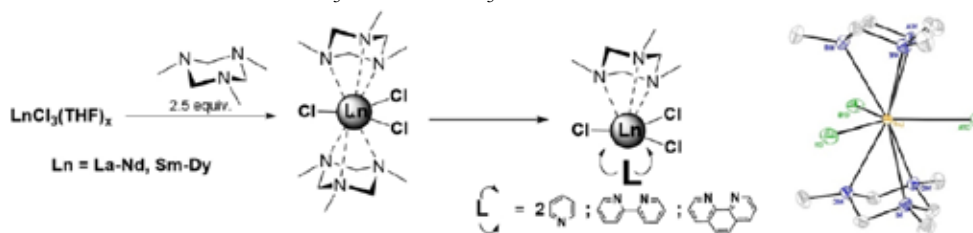
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Of particular interest in modern 4f-element chemistry is the design of complexes with a given structure that provide a desired set of physicochemical properties. Tridentate N-heterocyclic ligands 1,3,5-trimethyltriazacyclohexane (Me₃tach) and 1,4,7-trimethyltriazacyclononane (Me₃TACN) can be used as auxiliary ligands in the synthesis of a wide range of organometallic ([Cp'LnCl₂L] (Cp'=Ph₂C₅H₃, Ph₃C₅H₂, Ph₄C₅H; L=Me₃tach, Me₃TACN)¹ and coordination ([LnCl₃L₂], [LnCl₂L(thf)(μ-Cl)]₂, [LnCl₂L₂]⁺[LnCl₄L]⁻, L=Me₃tach; [LnCl₃L(thf)], L= Me₃TACN) REE compounds.²

Introduction of Me₃tach and Me₃TACN into the coordination sphere of the REE ion stabilises different structural types of complexes.

Lanthanides at the beginning of the series form complexes ([LnCl₃L₂], or [LnCl₂L(thf)(μ-Cl)]₂, depending on the reaction stoichiometry; heavier lanthanides form complexes such as [LnCl₂L₂]⁺[LnCl₄L]⁻, L=Me₃tach. The complexes [LnCl₃L₂] are extremely soluble in organic solvents, including hydrocarbons, and are characterised by an unusual planar-trigonal structure of the {LnCl₃} fragment. The complexes of Pr, Sm, Eu, Tb and Dy are luminescent in the visible region. The talk will discuss the synthesis, structure, photophysical and magnetochemical properties of different types of lanthanide coordination compounds with Me₃tach and Me₃TACN ligands.



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HALOGENATION OF LIGANDS AS A WAY TO CONTROL THE LUMINESCENCE EFFICIENCY OF EUROPIUM(III) 1,3-DIKETONATES

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The rational design of efficient luminophores based on lanthanide complex compounds is an urgent task of modern coordination chemistry and chemical materials science. One such approach is based on the optimization of energy transfer pathways between the organic ligand and the central emitter ion.

We have shown that the introduction of halogen atoms into various fragments of 1,3-diketonate ligands has a significant effect on several factors that determine the efficiency of electron excitation energy transfer. In particular, by such modification of the structure it is possible to flexibly tune the energies of the corresponding singlet and triplet levels of the ligand, to suppress undesirable processes of excitation-free relaxation of excited states, and in some cases, to completely "switch" the pathways of excitation energy transfer between the ligand and the ion.

In the report will be discussed in detail different types of structural modification of 1,3-diketonate ligands and their influence on the photophysical properties of the resulting neutral coordination compounds of the Eu³⁺ ion.

Acknowledgements: The synthetic part of the project was supported by the Ministry of Science and Higher Education (project #FFZZ-2022-0012).

LUMINESCENT THERMOMETER: FROM FUNDAMENTALS TO THE PROTOTYPE

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About 30% of all the measurements refer to thermometry. However, the use of the convenient thermometers, which require electricity, is hampered when strict demand of the intrinsic safety and fire safety exists, i.e. at the oil and gas production. Luminescent thermometry can serve a perfect solution to this: required electricity can be significantly remote from the measurement region, if the information transfer is provided by the optical fiber. It is also one of the most accurate methods of temperature measurement, which allows for continuous real-time measurements and even mapping.

One of the most important applications of luminescent thermometry is the measurement of high temperatures, where inorganic lanthanide-based materials are usually used due to their high stability, combined with the narrowband emission at the constant wavelengths. However, very low luminescence intensity hampers their practical application, while the thermal stability of brightly luminescent coordination compounds is usually insufficient.

We proposed using heterometallic lanthanide metal-organic frameworks (MOFs), which are stable up to of 400-600 °C and exhibit very intense luminescence. Fundamental studies of these systems, including mathematical description, has allowed us to obtain composite materials capable of operating up to 400 oC in both the visible and NIR ranges. As a result, the first prototype of a luminescent thermometer was obtained [1].



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STUDY OF THE COMPOSITION AND STRUCTURE OF OXIDE MATERIALS USING LOCAL CATHODOLUMINESCENCE METHOD

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Cathodoluminescence is radiation in the optical range that occurs as a result of irradiation of samples with an electron beam. Most often, this research method is implemented on electron microscopes, which use electron beams with energies of 1-50 keV. The local cathodoluminescence method is a very promising method for studying oxide materials activated by transition ions, including ions of rare earth elements. Compared to photoluminescent research methods, cathodoluminescence has a number of features:

- the ability to obtain cathodoluminescent images and study the distribution of inhomogeneities associated with the uneven distribution of impurities, intrinsic defects, and detect inclusions of other phases.
- determine impurities of rare earth elements with high sensitivity and study the nature of their distribution over the sample.
- to study the local symmetry of rare earth ions, including in inclusions, by the nature of the splitting of Stark components in the emission spectra.
- determine the efficiency of excitation capture by the luminescence center based on measuring the dependence of the cathodoluminescence growth rate on the electron beam current density.
- study trap states and their influence on luminescent properties.

Research was carried out on oxide materials $\text{Y}_3\text{Al}_5\text{O}_{12}$, ZrSiO_4 , $(\text{Zr,Hf,Y})\text{O}_2$, $\text{Gd}(\text{Nb,Ta})\text{O}_4$, etc.



STRUCTURAL AND DYNAMICAL PROPERTIES OF THE $\text{ThF}_4\text{-LiF-KF}$ MELT ALTERED BY Mg CATIONS

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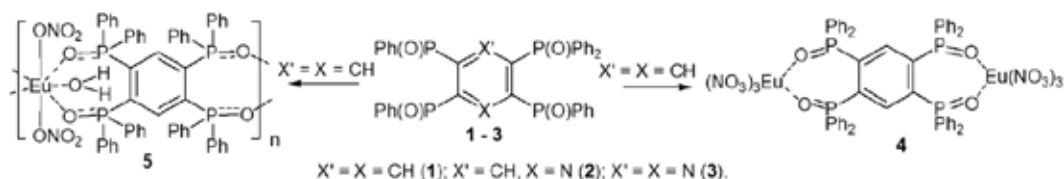
Electrorefining is a promising way to reprocess spent nuclear fuels and separate lanthanides and actinides. Recent electrochemical studies showed that addition of alkaline earth cations to alkali halide melts containing cations of the f-block elements can substantially change the electron transfer activation energies of the latter. However, the understanding of such behavior on atomistic level is lacking. Here we employ a combination of molecular dynamics simulations and quantum chemistry calculations to unravel the effect of Mg cations on the $\text{ThF}_4\text{-LiF-KF}$ melt, which is an important system in the context of Molten Salt Nuclear Reactors. The particular emphasis is made on changes in structural (Th coordination numbers, composition of the second coordination sphere) and dynamical (diffusion coefficients, viscosity, and electrical conductivity) properties of the melt. Analyzing the frontier molecular orbitals by means of quantum chemical calculations allows us to characterize how Mg cations alter the electronic structure of Th complexes in the melt and predict the most probable pathways for the electrochemical electron transfer in the $\text{ThF}_4\text{-LiF-KF}$ melt.

PHOSPHORUS- AND PHOSPHORUS-NITROGEN LIGANDS AS EFFECTIVE COMPLEXING AGENTS FOR THE CREATION OF LIGHT-EMITTING MATERIALS

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Effective methods for obtaining new phosphorus- and phosphorus-nitrogen ligands **1-3** have been developed and their complexes with *d*- and *f*-elements have been studied. In the study of complexation reactions, it was shown that, depending on the conditions of the reaction, can be formation of both individual complexes¹ Eu⁺³ and Tb⁺³ **4** and their coordination polymers² **5**. Complexes with these lanthanides were isolated and characterized by modern methods, including X-ray diffraction analysis. During their study, it was found that the Eu⁺³ and Tb⁺³ complexes are thermally stable and have luminescent properties, with sufficiently high photophysical characteristics.



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INTENSIFICATION OF REE EXTRACTION BY LOCAL VIBRATION IN THE DYNAMIC INTERFACIAL LAYER

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Liquid-liquid extraction is widely used for the recovery and separation of rare earth elements (REE). It is usually carried out in emulsion mode, dispersing one of the liquids into another. This leads to increased energy consumption, since the entire volume of one of the liquids is dispersed. In addition, the resulting emulsion is often stable and requires additional energy for separation. It is of interest to improve pre-emulsion technology based on local energy supply to the dynamic interfacial layer.

This report presents data on the intensification of the process of extraction of rare earth elements under local vibration in a dynamic interfacial layer.

To assess the effect of vibration on the process of REE extraction, we used the extraction acceleration coefficient (E), determined by the ratio of REE concentrations in the organic phase to a given time with vibration and in its absence.

If tributylphosphate is used as an extractant, then the value of E for a flow system is 1,2–1,5 and static system is 2,3–2,8. The value of the intensification effect is determined by the nature of the solvent, the frequency and amplitude of vibration of the vibrating element, the speed of fluid movement and weakly depends on the nature of the rare earth elements.

If di-(2-ethylhexyl)phosphoric acid is used as an extractant, then the E value for a flow system is 2,3–2,8 and for a static system – 4.2–4,5. The value of E is influenced by the nature of REE.

The observed effect of extraction intensification is caused by a change in the intensity of convection flows in the dynamic interfacial layer. The wedge-shaped shape of the vibrating element allows you to create transverse and longitudinal displacement of liquid particles, increasing convective transfer. The presented method for increasing the extraction intensity can be useful in the development of energy-saving technologies that include liquid-liquid extraction stages.

The work was carried out with the financial support of a grant from the Government of the Tula Region in the field of science and technology DS/104 dated September 27, 2023.

DEEP-LEARNING ENHANCED DESIGN OF COMPLEXING AGENTS FOR REPROCESSING OF SPENT NUCLEAR FUEL

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One of the main methods of working with spent nuclear fuel is solvent extraction. Significant attention is paid to the search for new promising complexing agents - small organic molecules that are used to separate highly active waste into various fractions. When designing a new ligand, it is necessary to take into account several parameters at once. The main property of a complexing agent is its selectivity, but in addition to this, it is also important to consider the radiation resistance of the molecule, solubility in the target solvent, synthetic accessibility, and the possibility of subsequent re-extraction.

The use of machine learning methods for the design of new chemical compounds is a popular and rapidly developing area. One of the most promising directions in this field is de novo design - the application of artificial intelligence methods for the automatic generation of chemical objects with specified properties.

In this work, we have developed a generative system that combines a predictive graph machine learning model adapted for working with small data¹⁻² with an evolutionary algorithm that suggests structures of promising complexing agents. With the developed approach, we can both predict the stability constants of ligand complexes with metals from the lanthanide series and part of the actinide series, and suggest new small organic molecules as complexing agents.

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LUMINESCENT HETEROMETALLIC Eu(III)-BASED TEREPHTHALATE MOFS

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In this work, the structure and photophysical properties of the three series of luminescent heterometallic europium-containing terephthalate metal–organic frameworks ($\text{Eu}_{1-x}\text{M}_x)_2\text{bdc}_3 \cdot 4\text{H}_2\text{O}$ ($\text{M} = \text{Y}, \text{La}, \text{Gd}$; $x = 0-1$) were studied in details in a wide concentration range of Eu^{3+} ion (0.1 -100 at %). All synthesized materials are isostructural to $\text{Eu}_2\text{bdc}_3 \cdot 4\text{H}_2\text{O}$.¹ The unit cell parameters were refined for the compounds corresponding to $\text{Ln}_2\text{bdc}_3 \cdot 4\text{H}_2\text{O}$ crystalline phase. We observed that the substitution of Eu^{3+} for larger La^{3+} ions increases the unit cell volumes, whereas doping by the smaller Y^{3+} ion results in a decrease in the unit cell volume. The ionic radius of the Gd^{3+} ion is close to that of Eu^{3+} . Therefore, the unit cell parameters do not change significantly as a result of substitution of Eu^{3+} by Gd^{3+} . All the synthesized samples demonstrate an “antenna” effect²: a bright-red emission corresponding to the $^5\text{D}_0$ - $^7\text{F}_j$ transitions of Eu^{3+} ions is observed upon 300-nm excitation into the singlet electronic excited state of terephthalate ions. The Eu^{3+} concentration dependence on excited state lifetime, radiative, nonradiative, total decay rates, quantum efficiencies, quantum yield of formation of the $^5\text{D}_0$ level of Eu^{3+} ; photoluminescence quantum yield, and asymmetric ratio was carefully studied.

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LANTANIDE PYRENATES: FEATURES OF REACHING A HIGH QUANTUM YIELD IN POWDER AND OBTAINING SENSORY MATERIALS

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NIR-emitting phosphorous based on lanthanide coordination compounds (CCs) are promising materials for sensors, since their radiation enters the windows of biological and telecommunication transparency, and the narrowness of emission bands and long-term lifetime provides the possibility of detecting a high-accuracy signal. To achieve low resolution, high intensity of the sensory signal is also necessary. However, for NIR-emitters, even when using an effective absorbing ligand, the intensity is insufficient for practical applications.

An increase in the efficiency of NIR-luminescence becomes possible to minimize many processes of extinguishing: oscillatory, concentration extinguishing and extinguishing on defects. Speaking about CCs with organic ligands, the last type is rarely considered, and it is believed that morphology almost does not affect luminescence. In our works, however, we noticed that this is not so, and **the purpose of this study** was to identify the influence of morphology on the fluorescent properties of the ytterbium CCs.

As a ligand, a pyrenate-ion, was chosen. It has a low energy of a triplet state ($T_1 = 14\,600\text{ cm}^{-1}$), so we expected that it would ensure the effective sensitization of Yb^{3+} ion, high absorption and minimal vibrational quenching. Despite this, $\text{Yb}(\text{pyr})_3$ complex, obtained at room temperature, had extremely weak luminescence. The variation of the synthesis time and gadolinium fraction in the complex, made it possible to obtain samples with high crystalline and record for coordination compounds of ytterbium in powder a quantum yield value of 6%.

Thanks to the obtained data on the dependence of the morphology of the powder and, as a result, the intensity of the luminescence, on the conditions of the synthesis and composition of the sample, it was also possible to get compounds with the luminescence of two ions: ytterbium and neodymium. Their high thermal stability made it possible to obtain fluorescent thermometers with a working range of **35-250 °C** for 10 measurement cycles and a sensitivity up to **3%K⁻¹**.

The work was supported by RSF (№ 20-73-10053).

U(VI) COORDINATION BY POLYDENTATE N,O-DONOR LIGANDS

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Phenanthroline- and pyridine-based ligands (Figure 1) are promising for group separation of actinides. Previously it has been shown that such N,O-donor ligands efficiently extract U(VI) and Th(IV) at concentrations $10^{-7} - 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ of metal in ligand excess to form 1:1 complexes $\{[\text{UO}_2\text{L}(\text{NO}_3)]^+(\text{NO}_3)_2\}$. However, the composition and structure of complexes during extraction from highly concentrated industrial solutions ($>0.1 \text{ mol} \cdot \text{L}^{-1}$) in metal excess over ligand have not been determined. In an effort to fill this gap, we investigated the extraction of macroquantities of uranium by tri- and tetra-dentate ligands in F3 solvent

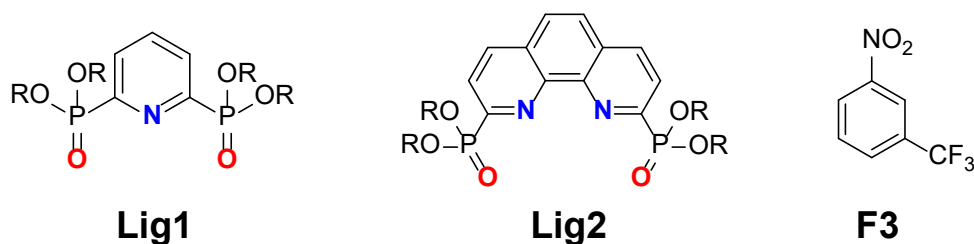


Figure 1. Structures of pyridine-(**Lig1**), phenanthroline- (**Lig2**) diphosphonates and F-3 diluent.

First of all an isotherm for the extraction of uranyl nitrates were constructed. Phenanthroline- based ligands demonstrated a high U(VI) capacity providing an U:‘**Lig2**’ concentration ratio in the organic phase up to 2:1. Whereas, U:‘**Lig1**’ ratio is slightly above 1:1.5, making room for discussions of possible complexes formed in the organic phase.

Using combination of spectroscopic techniques (UV-vis and EXAFS) and theoretical methods we showed that UO_2^{2+} forms complexes with the structure of tight ion pairs $([\text{UO}_2\text{LNO}_3]^+[\text{UO}_2(\text{NO}_3)_3]^-)$ with tetradentate phenanthroline-based ligands. While, with tridentate pyridine-based ligands U(VI) forms a mixture of complexes with different stoichiometry $([\text{LUO}_2(\text{NO}_3)_2], [2\text{LUO}_2](\text{NO}_3)_2, [2\text{LUO}_2][\text{UO}_2(\text{NO}_3)_3])$. Moreover, both ligands show high loading capacity, being promising for industrial use as U(VI) extractants.

This work was supported by the Russian Science Foundation, grant 23-73-30006.

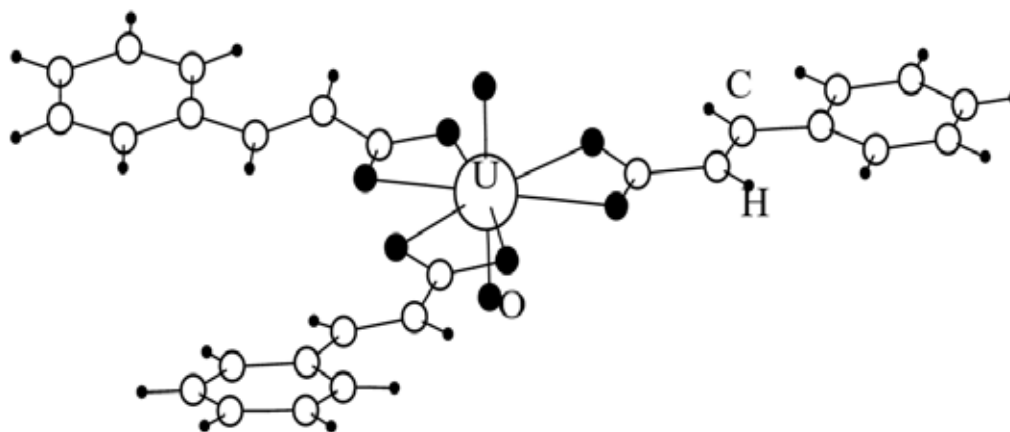
NEW CINNAMATE-CONTAINING URANIL COMPLEXES

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As part of our study of cinnamate-containing uranyl coordination compounds, new tricinnomatouranilate complexes were obtained and studied by X-ray diffraction analysis: $M[UO_2Cyn_3]$ ($M = NH_4, NEt_4, K, Rb, Cs$, hydroxylammonium, guanidinium, aminoguanidinium and 4-(dimethylamino)anilinium), $Na[UO_2Cyn_3] \cdot 1.5H_2O$, $Ba_2[UO_2Cyn_3]_4 \cdot 5.5H_2O$, $Mn[UO_2Cyn_3]_2 \cdot 2H_2O$, $UO_2Cyn_2 \cdot 2EtOH$ и $Cu[UO_2Cyn_3]_2 \cdot 6H_2O$, where Cyn is the cinnamate anion (trans-phenylacrylate anion). The uranium-containing structural units in all obtained complexes are mononuclear $[UO_2Cyn_3]^-$ groups shown in Fig. 1, and belonging to the crystal chemical group AB^{01}_3 ($A = UO_2^{2+}$, $B^{01} = Cyn^-$). Designations of ligand coordination types and crystal chemical formulas are given in accordance with Serezhkin's taxonomy¹.



Uranium atoms in the synthesized structures exhibit coordination numbers equal to 8, forming coordination polyhedra in the form of a hexagonal bipyramid, in the equatorial plane of which the oxygen atoms of three bidentate cyclic cinnamate anions are located, and the axial positions are occupied by the oxygen atoms of the uranyl group. The crystal chemical role of outer-sphere cations is obtained by means of the intersecting spheres method². The synthesized compounds were characterized by IR spectroscopy and thermogravimetric analysis.

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COMPLEXES OF RARE-EARTH ELEMENTS WITH IMINOPHOSPHONAMIDE LIGANDS: SYNTHESIS, PROPERTIES, REACTIVITY

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Iminophosphonamides ($R_2P(NR')-$, NPN) are the closest analogues of the chelating N-donor ligands amidinates and guanidines, but with phosphorus as the central atom. Its presence allows the use of ^{31}P NMR spectroscopy to study reaction routes. Many complexes with NPN ligands for *s*- and *d*-elements are known. With rare earth metals (Ln), their amount is smaller and in most researches with them the catalytic properties of the resulting compounds are studied.

This work is aimed at the synthesis, study of reactivity and photophysical properties of Ln complexes with NPN ligands with chromophore Pbt substituents (Pbt = 2-(benzothiazol-2-yl)phenyl). Two ligands $[Ph_2P(-NR)(=NR')]^-$ were used: symmetrical (L^1), where R, R' = Pbt and asymmetrical (L^2), where R = Pbt, R' = Mes (Mes = 2,4,6-trimethylphenyl). By ion exchange reactions of deprotonated L^- proligands with anhydrous Ln chlorides, a number of homoligand complexes $[Ln(L^1)_2](L^1)$ (Ln = Y, Gd, Dy, Sm; **1–4**, respectively) and heteroligand complexes $[Ln(L^2)Cl_2(thf)]$ (Ln = Y, Gd, Tb; **5–7**, resp.; thf = tetrahydrofuran) were obtained. For symmetric NPN, the heteroligand complex $[Yb(L^1)_2]$ (**8**) is formed only in the case of transmetallation reactions between the freshly prepared $[Cu(L^1)]_2$ and $[YbI_2(thf)_2]$. In complex **4**, in contrast to **2** and **3**, a number of well-resolved narrow bands corresponding to the emission of the Sm^{3+} cation were detected against the broad band of the outer sphere ligand's emission. Complexes **5–7** are able to enter into exchange reactions with KSPb to form $[(L^2)Ln(\mu_2-SPh)_2(\mu_3-SPh)K(thf)]_2$ (**9–11**).

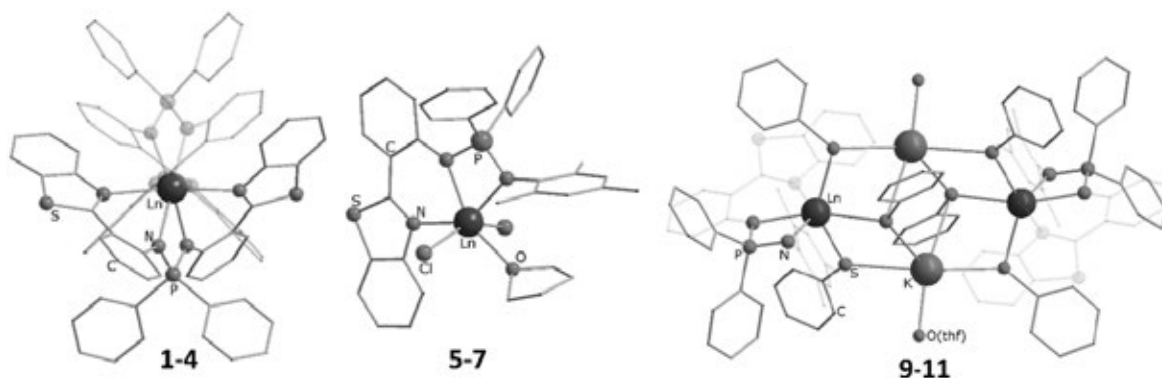


Figure 1. Structure of the complexes (for **1–4** the cationic part is shown).

STRUCTURAL FEATURES OF PHOTOLUMINESCENT RARE EARTH METALS COMPLEXES BASED ON β -ENAMINDIONE AND ISOTHIAZOLE DERIVATIVES

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Rare earth elements (REE, Ln) coordination chemistry is an actively developing field - a numerous of organic compounds that can be used as ligands leads to a variety of obtained structures. This work is devoted to the synthesis, characterization and the photoluminescent properties investigation of REE(III) compounds based on derivatives of 2-[(phenylamino)-methylene]-5,5-dimethyl-cyclohexane-1,3-dione (β -enaminedione, L^1) and dichloroisothiazolecarboxylic acids (L^2). According to the single-crystal X-ray diffraction analysis, β -enaminedione derivatives are coordinated by the oxygen atoms of the cyclohexanedione moiety and exhibit a monodentate or bidentate-bridging coordination mode resulting in the formation of complexes with the general formulas $[Ln(L^1)_2(H_2O)(NO_3)_3]$, $[Ln(L^1)_3(NO_3)_3]$ or $[Ln(L^1)_2(NO_3)_3]_n$. In the case of isothiazole derivatives, chelate or bidentate-bridging coordination is observed, involving the nitrogen atom of the isothiazole ring, as well as the oxygen atoms of the carboxyl group. As a result, polynuclear coordination compounds $[Ln_6(L^2)_{18}(H_2O)_{10}]$, $[Ln(L^2)_2(OAc)(H_2O)]_n$ or $[Ln(L^2)_2(OAc)]_n$ are formed. The photoluminescent properties of organic ligands and the obtained REE complexes as polycrystalline samples at room temperature have been investigated. The highest quantum yield among the series of compounds based on β -enaminedione derivatives is achieved for europium(III) complexes, whereas with isothiazole derivatives - for terbium(III) compounds. The excited states lifetimes of REE coordination compounds are in the millisecond range.

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Tb-Eu BENZOATES FOR LUMINESCENT THERMOMETRY

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Temperature is the most frequently measured parameter in all natural and engineering systems. At the same time, most known temperature sensors are not applicable for measuring moving objects, or with limited access to the surface and micro level. Non-contact luminescent thermometry is the solution to such problems due to its fast response, high thermal and spatial resolution, high temperature sensitivity and the possibility of applying a layer of temperature-sensitive material to any surface. Among luminescent materials, coordination compounds of lanthanides are promising due to their narrow luminescence bands with a constant position, Stokes shift, long lifetimes and bright luminescence. The Tb-Eu pair makes it possible to use the ratio of the luminescence bands of the ions of the two metals as a response, eliminating the need for additional calibration of the sensor. Nevertheless, luminescent materials based on complexes of lanthanides, whose sensory response is based only on the efficiency of temperature-dependent energy transfers, have low values of temperature sensitivity¹. A way to increase sensitivity may be the introduction of an additional temperature-dependent process that occurs with different efficiencies for Tb³⁺ and Eu³⁺².

We assumed that since the water molecules in the complexes quench the luminescence of Tb³⁺ and Eu³⁺ with different efficiencies, dehydration during heating will significantly affect the luminescence spectrum. Hydrated heterometallic benzoates were used to test this hypothesis Tb_{1-x}Eu_x(bz)₃(H₂O)_n (x = 0.005, 0.01, 0.03).

The maximum Sr of Tb_{0.97}Eu_{0.03}(bz)₃(H₂O)_n water suspension is due to the processes of cleavage and attachment of water molecules, which occur in different temperature ranges during the heating and cooling of the suspension. In this case, Sr reaches 55 %/C at 65 °C, which is the maximum value for luminescent thermometers. The powders of the coordination compounds showed temperature sensitivity in the range of 25-400 °C. At the same time, the maximum temperature sensitivity is observed precisely with structural changes in the complexes - with dehydration (50-100 °C).

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PROBING THE STRENGTH OF MAGNETIC EXCHANGE COUPLING IN LANTHANIDE – RADICAL SYSTEM

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Direct contact of paramagnetic centers in metal–radical complexes is known to give large magnetic exchange coupling values.¹ Unlike traditional *3d* transition metal single-molecule magnets (SMMs), strong intramolecular magnetic exchange interactions are rare in multimetallic *4f*-complexes because the contracted *f*-type orbitals render the superexchange way inefficient. Strong exchange interactions between lanthanide (Ln) ions can be realized by bridging radical ligands due to direct overlap of magnetic orbitals,² and leading to a well-isolated bound ground state onto which the magnetic anisotropy of Ln ions is projected. Some examples of such systems with high *J* and *S_G* values are known in literature.³ In addition, the presence of strong exchange coupling in a heterospin system effectively reduces magnetization tunneling.⁴

However, in order to clarify mechanism and nature of the exchange interactions, as well as to clarify the relationship between the coordination symmetry the central ion in polynuclear 0D or 1D Ln – radical systems,⁵⁻⁷ preliminary studies are required for more simpler mononuclear complexes with one or two radical ligands.

We have obtained a series of complexes of Ln³⁺ with a stable tridentate tripodal nitroxide radical with, in which a record magnetic coupling for mononuclear systems (more than 20 cm⁻¹) was recorded.^{8,9} In addition, the compound terbium, [TbRad(NO₃)₃], was found to be SMM without bias, while its congeners of Eu and Lu exhibit field-induced magnetic relaxation. For Eu-Rad complex, the strong antiferromagnetic coupling (*j*~20 cm⁻¹) was experimentally (magnetically and by EPR), and theoretically proven.

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EXTRACTION OF ACTINIDES AND RARE EARTH ELEMENTS IN CARBONATE MEDIA WITH METHYLTRIOCTYLAMMONIUM CARBONATE IN 3-NITROBENZOTRIFLUORIDE

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In recent years, a new method for reprocessing spent nuclear fuel (SNF) in carbonate media has been developed - the CARBEX-process, in which the use of quaternary ammonium compounds (QAC) is considered as an extractant.

In this work, a systematic study of the chemistry of extraction of actinides and rare earth elements from carbonate media was carried out using methyl-trioctylammonium carbonate (MTOA) as solvent in 3-nitrobenzotrifluoride. The distribution coefficients of U(VI), Pu(VI), Am(III), Cm(III), Sc(III), Y(III), Ln(III) were determined depending on the concentration of the components of the aqueous and organic phases.

It was found that the degree of uranium extraction into the extract for the extraction systems under consideration is significantly higher than for all other elements considered. Based on the data obtained, the separation coefficients of U(VI) and Pu(VI), Am(III), Cm(III), Eu(III) were calculated. Over the entire range of sodium carbonate concentrations, the separation coefficients are greater than 10, which makes it possible to organize a highly efficient uranium extraction process. Under the conditions considered, no group separation of REEs is observed; the separation coefficients of neighboring REEs throughout the entire range of sodium carbonate concentrations do not exceed 1.5.

Using the dilution method for the studied extraction systems, the stoichiometric ratios of Metal:[(R₄N)₂CO₃] and Metal:[CO₃]²⁻ in the extracted complex compounds for U(VI), Pu(VI), Am(III), Cm(III), Sc(III), Y(III) and Ln(III) were established. It was shown that for several elements extraction of partially hydrolyzed compounds is possible; for all the cases the composition of the extracted complexes was proposed.



BIOLOGICAL POTENTIAL OF $\text{NaGd}_{0.7}\text{Eu}_{0.3}\text{F}_4$ AND $\text{KGd}_{0.8}\text{Eu}_{0.2}\text{F}_4$ NANOPARTICLES COATED BY APTMS

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Inorganic nanomaterials containing various lanthanide ions are interesting for bioimaging due to combination of optical, magnetic, radioactive, and other properties. These properties enable the development of multimodal materials for molecular imaging and non-invasive optical diagnosis of tissues in living organisms using magnetic resonance imaging (MRI).¹ However, the use of inorganic nanoparticles in luminescent systems requires specific characteristics such as small size, colloidal stability, and the ability for further functionalization.² In this paper, we consider the properties of $\text{NaGd}_{0.7}\text{Eu}_{0.3}\text{F}_4$ and $\text{KGd}_{0.8}\text{Eu}_{0.2}\text{F}_4$ nanoparticles coated with (3 aminopropyl)trimethoxysilane (APTMS).

It was previously revealed that the optimal concentrations of Eu^{3+} in $\text{NaGd}_{0.7}\text{Eu}_{0.3}\text{F}_4$ and $\text{KGd}_{0.8}\text{Eu}_{0.2}\text{F}_4$ compounds are 30 at.% and 20 at.% Eu respectively.³ Gd^{3+} doping allows us to reduce the size of the synthesized nanoparticles⁴. These nanoparticles were synthesized using the hydrothermal method, and they had a size of approximately 50 nm and 35 nm for particles with sodium and potassium, respectively. However, the colloidal solutions were unstable (with a z-potential of 10 and 14 mV, respectively), so the nanoparticles were stabilized with CTAB and then coated with APTMS to create a shell that would allow functionalization. The size of these coated nanoparticles was measured using dynamic light scattering, and it was found to be 142 nm for Na-coated particles and 229 nm for K-coated particles. The thickness of the nanoparticle shell was approximately 10 nm and was determined using scanning electron microscopy (SEM).

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EFFECT OF YTTERBIUM CONCENTRATION ON LUTETIUM EXTRACTION BY 2-ETHYLHEXYL-PHOSPHONIC ACID MONO(2-ETHYLHEXYL) ESTER

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2-ethylhexylphosphonic acid mono (2-ethylhexyl) ester (HEH[EHP]) provides a high value of the separation factor as well as high capacity in the solvent extraction (SX) of heavy REE, in particular Yb and Lu. Traditionally, regularities of SX are considered at comparable concentrations of separated lanthanides and at low extractant loading. However, the task of isolating n.c.a. ^{177}Lu from neutron-irradiated Yb involves separating micro-quantities of lutetium from macro-quantities of ytterbium at a mass ratio of 1:100 in a multi-stage mode, like extraction chromatography (EXC). An increase in the amount of ytterbium in the organic phase negatively affects the efficiency of the EXC separation of lutetium on a sorbent with HEH[EHP], which was demonstrated in work1.

The lanthanide distribution ratio (in our case, D_{Lu}) depends on the concentration of the extractant, which practically does not change in the case of extraction of trace amounts of metal. However, in the case of isolation of weight amounts of lanthanides, a decrease in the concentration of the free extractant, S , should be taken into account, due to the formation of extractable complexes with a macro component (Yb):

$$D_{Lu} = K_1 \frac{(S/2 - 2.5[Yb^{3+}]_{org})^{2.5}}{[H^+]_{(w)}^3}$$

where K_1 is the lutetium extraction constant, S – initial concentration of extractant.

The results of experiments on the extraction of tracer-level concentration of Lu and macro-concentration of Yb (in the joint presence) with HEH[EHP] solutions in hexane, performed at $[\text{HNO}_3]=0.5-2$ mol/l and $[\text{HEH[EHP]}]=0.5-2$ mol/l, are presented in the report. They confirmed Lu distribution ratio decrease while ytterbium concentration, $[\text{Yb}]$, increases from 0.1 to 5 g/l in the entire studied range of extractant and nitric acid concentrations. A significant change in the chromatographic behavior of both ytterbium and lutetium due to the effect of the macro component is demonstrated.

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DIRECTED DESIGN OF BRIGHTLY LUMINESCENT MIXED-CARBOXYLATE BENZOATE-PENTAFLUOROBENZOATE LANTHANIDE COMPLEXES

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Coordination compounds of lanthanides may be applied as sensors, diodes, and lasers or in catalysis and biomedical imaging. The introduction of the d-block which consists of d¹⁰ metal ions and organic ligands may affect the photoluminescent properties of lanthanide complexes positively due to the antenna effect. Using two types of anions of aromatic acids of different nature leads, on the one hand, to the stabilization of the crystal structure due to the occurrence of strong non-covalent interactions¹ and, on the other hand, to an improvement in their photoluminescent characteristics². In this work mixed-carboxylate {Zn₂Ln₂} complexes [Zn₂Ln₂(bz)_x(pfb)_{10-x}(phen)₂] (Ln = Eu(**1Eu**), Tb(**1Tb**), Gd(**1Gd**); bz – benzoate anion; pfb – pentafluorobenzoate anion; phen – 1,10-phenantroline; x=5,4; 1,2) and their benzoate and pentafluorobenzoate analogues [Zn₂Ln₂(bz)₁₀(phen)₂] (**2**) (Ln = Eu, Tb) and [Zn₂Ln₂(pfb)₁₀(phen)₂] (**3**) (Ln = Eu, Tb) were obtained. The obtained compounds were characterized by XRD, CHN analysis and IR spectroscopy. In the structure of compounds **1** the occupancy of four anions is non-integer and bz- and pfb-anions occupy the same position. It has been shown that simultaneous coordination of bz- и pfb-anions to the REE ion with 1,10-phenantroline leads to the emergence of non-covalent interactions which stabilize the crystal packaging of the complexes. In the case of compounds **1**, an increase in luminescence efficiency is observed to 50% and 54% for **1Eu** and **1Tb**, respectively, which is about 1,3 times more than for their benzoate and pentafluorobenzoate analogues **2** and **3**.

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COMPOUNDS OF SUBSTITUTED TRIAZACYCLOHEXANE COMPLEXES OF LANTHANIDES WITH ANTENNA LIGANDS

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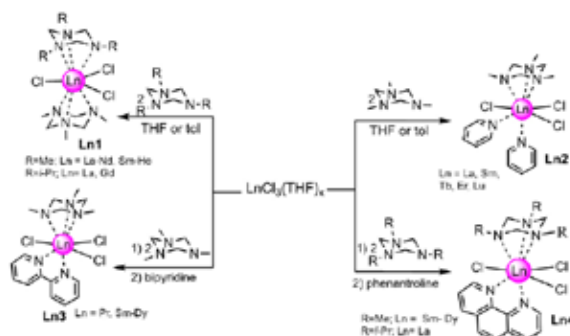
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Lanthanide complexes are widespread in modern chemistry. Their application in optical materials seems to be the most interesting, since most lanthanides with partially filled 4f-shells luminesce in the whole spectral range. The luminescence intensity of lanthanide ions is rather low due to the poor absorption capacity of Ln^{3+} . To increase the luminescence intensity, "antenna ligands" containing π system, which can provide indirect energy transfer to the lanthanide ion, are often used. However, when introducing such ligands, there is a problem of polynuclear complexes formation, which leads to luminescence quenching due to additional interactions. This problem was solved by the introduction of chelating nitrogen-containing ligands, such as 1,3,5-trimethyl-1,3,5-triazacyclohexane (Me_3tach) and 1,3,5-triisopropyl-1,3,5-triazacyclohexane ($i\text{-Pr}_3\text{tach}$), which are able to block several sites of the coordination sphere of the lanthanide ion.¹

We previously prepared complexes $\text{LnCl}_3(\text{Me}_3\text{tach})_2$ and $\text{LnCl}_3(i\text{-Pr}_3\text{tach})_2$ (**Ln1**) from the reaction of lanthanide chlorides with chelating ligands. We then investigated the reactivity of **Ln1** with various nitrogen-containing antenna ligands such as pyridine, bipyridine and phenanthroline. The reactions yielded **Ln2**, **Ln3** and **Ln4** complexes. All **Ln2** complexes are isostructural among themselves, as well as **Ln3** and **Ln4**. All the obtained complexes show bright luminescence.



Scheme 1. Synthesis of various complexes with nitrogen-containing ligands

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SOLVENT EXTRACTION OF URANIUM(VI) WITH TETRAALKYLDIPHOSPHONIUM SALTS

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Quaternary ammonium and phosphonium salts are being actively explored for the recovery of various metals from solutions. However, the efficiency of extraction of uranium(VI) from a nitric acid medium with these substances is quite low.^{1,2} Since uranium(VI) is present in nitric acid solutions in the form of anionic nitrate complexes, extraction in this case proceeds through the anion exchange mechanism, and its efficiency may depend on the charge of the cation. In this work we synthesized a series of tetraalkyldiphosphonium salts, which consist of two phosphonium fragments connected by a carbon chain of different lengths (Figure 1). The extraction of uranium(VI) and thorium(IV) as a model tetravalent actinide with synthesized compounds was studied.

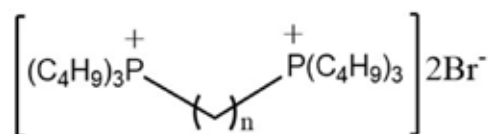


Figure 1. The general structural formula of the studied tetraalkyldiphosphonium salts L1-L3, n=2-4 respectively.

The dependence of the extraction efficiency of uranium(VI) and thorium(IV) on the concentration of ligands in m-Nitrobenzotrifluoride was studied, as a result of which it was found that the distribution ratios for a ligand with an average length of the carbon chain (L2) are significantly higher than for other compounds. Next, extraction at saturation of the organic phase was studied. The results obtained indicate that the metal:ligand ratio with a large excess of uranium(VI) is 3:2.

In order to assess the structural features of the complexes formed during extraction in the organic phase, a number of spectroscopic studies were carried out. Raman spectroscopy showed the presence of a peak responsible for the anionic nitrate complex of the uranyl cation only in the case of L2. Thus, it can be assumed that the different lengths of the carbon chain between positively charged phosphorus atoms affects the mechanism of extraction.

In order to eliminate the influence of the bromide anion on the extraction, ligands were converted to the nitrate form. It was found that converted ligands extracts both uranium(VI) and thorium(IV) much less efficiently.

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HYDROPHOBIC ANIONS AS MODIFIERS OF EXTRACTION SYSTEMS FOR SEPARATION OF An(III) AND Ln(III) BASED ON N,O-DONOR LIGANDS

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Management of high-level waste from spent nuclear fuel reprocessing is a challenge. The solution of this task involves separating Am(III), Cm(III), and lanthanides(III). However, this process is difficult due to the similar physicochemical properties of these elements.

Solvent extraction, a method widely used in chemical technology, is considered the most suitable for addressing this challenge. The current research in this field is primarily focused on the development of highly selective ligands. Promising are extraction systems based on N,O-donor ligands in combination with polar fluorinated organic solvents. For example, meta-nitrobenzotrifluoride (**F-3**), which has a high dissolving ability for polar compounds and is resistant to chemical and radiation effects.

Another area of interest is the enhancement of the extraction parameters of the system by introducing anionic synergistic additives. It is hypothesized that the addition of hydrophobic anions to the extraction system could increase the selectivity of extractants for actinides in the presence of lanthanides.

In this study, we explored the possibilities of modifying extraction systems for the separation of *f*-elements based on diamides of 1,10-phenanthroline-2,9-dicarboxylic acid and diamides of 2,2'-dipyridyl-6,6'-dicarboxylic acid by introducing hydrophobic anions into the organic phase: chlorinated cobalt dicarbollide (**CCD**[−]) or bis(trifluoromethanesulfonyl)imide (**NTf₂**[−]), with the ionic liquid C₄mimNTf₂ serving as the anion source.

Special attention was devoted to establishing the mechanism of complexation and the forms of minor actinides and lanthanides in the studied systems. Various methods including UV-visible titration, Raman spectroscopy, XRD-study, radiometric methods, and DFT-calculations, were used for this.

The work was carried out with the financial support of the Russian Science Foundation, project 23-73-30006.

CATIONIC BIS(ALKOXIDE) DYSPROSIUM (III) COMPLEXES: SYNTHESIS AND STRUCTURES

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Cationic Dy(III) bis(alkoxide) complexes are promising candidates for innovative information storage solutions and the development of quantum computers. An important challenge in this field is to understand the influence of the coordination environment of a metal ion on slow relaxation of magnetization.

In this work, we developed an efficient synthetic approach to cationic bis(alkoxide) Dy(III) complexes based on the protonolysis of thermally stable cationic bis(*N,N*-dimethylbenzyl) precursors by various fluorinated alcohols under mild conditions. All the obtained complexes are isostructural and represent a separated ion pair consisting of the cation $[\text{Dy}(\text{OR})_2(\text{THF})_4]^+$ and the anion $[\text{BPh}_4]^-$. The obtained complexes are of octahedral geometry, with four coordinated THF molecules, and two alkoxide ligands arranged in *cis*-configuration, irrespective of the steric hindrances of the ligands. Although such geometry is undesirable for achieving a high anisotropic barrier and blocking temperature, the method is a viable source of cationic alkoxide precursors, the THF molecules of which can be further replaced with various Lewis bases.

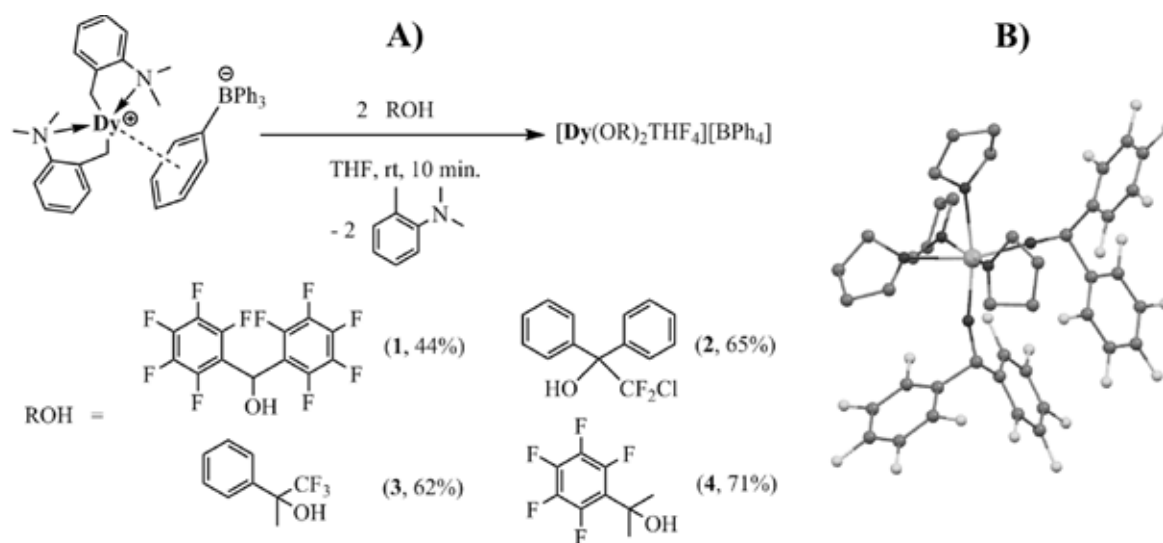


Figure 1. A) Synthesis of complexes 1-4, B) Molecular structure of 1, hydrogen atoms and BPh_4^- anion are omitted for clarity.

This work was supported by the Russian Science Foundation (project № 24-13-00275).

NEW MIXED-METAL EUROPIUM AND TERBIUM COMPLEXES WITH A TRIFLUORINE(β -DIKETONATE) LIGAND

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A series of lanthanide organic complexes, namely, $[\text{LnL}_2(\text{NO}_3)(\text{TPPO})_2]$ and $[\text{LnL}_3(\text{TPPO})_2]$, $\text{Ln} = \text{Tb}, \text{Eu}, \text{Tb}_{0.5}\text{Eu}_{0.5}$ (Fig. 1) were obtained, where 4,4,4-trifluoro-1-(furan-2-yl) butane-1,3-dione was selected as the ligand L, since the energy of its triplet level (20500 cm^{-1}) is close to the energy of the resonance level of Tb^{3+} cations (20400 cm^{-1}). The luminescent properties of the obtained compounds were studied and it was shown that the color of luminescence and the contribution to the emission of terbium and europium transitions significantly depend on temperature, which makes the obtained objects promising as luminescent thermometers.



Fig. 1. Crystal structure of the $[\text{TbL}_2(\text{NO}_3)(\text{TPPO})_2]$ complex

This work was carried out with the financial support of the Russian National Fund within the framework of project 23-23-00393.

EXTRACTION OF F-ELEMENTS BY TETRA-(2-ETHYLHEXYL) DIAMIDE OF DIGLYCOLIC ACID IN FLUORINATED DILUENTS

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Development of new methods for the extraction of minor actinides from nitric acid media and their separation from lanthanides is one of the important tasks for the development of the closed nuclear fuel cycle. It is known that solutions of tetraoctyldiamide diglycolic acid (TODGA) in ethyl hydrocarbons efficiently extract f-elements (minor actinides and lanthanides), but are prone to the formation of a third phase at saturation. It was shown earlier that solutions of TODGA in meta-nitrobenzotrifluoride (F-3) do not form a third phase during extraction¹, while for aliphatic fluorinated diluents complete saturation cannot be achieved.

In the present work, the extraction of f-elements N, N, N', N', N'- tetra-(2-ethylhexyl)diamide diglycolic acid² (T2EHDA) in F-3 as well as in aliphatic fluorinated diluents (2,2,3,3,3-tetrafluoropropan-1-ole carbonate (BK-1); 2,2,2,3,3,3,4,4,4,5,5,5,6,6,6,7,7-dodecafluoroheptyl methyl ether (DDFHME)) was studied (Fig. 1). During the experiments, the formation of the third phase was not observed until complete saturation of the organic phase.

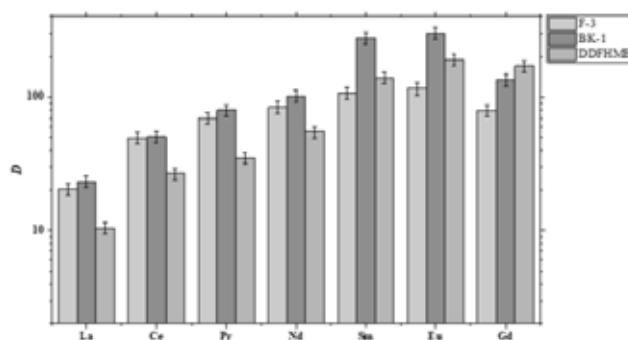


Figure 1. Extraction of light lanthanides ($\Sigma C_{\text{REE}} = 1.7 \text{ g/l}$) from a model raffinate solution of 0.1 M T2EHDA in polar fluorinated diluents from 3 M HNO_3

It is shown that T2EHDA in aliphatic fluorinated diluents provides high extraction capacity to f-elements.

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SEPARATION OF AMERICIUM FROM CURIUM AND LANTHANIDES USING POTASSIUM HEXACYANOFERRATE (III)

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Separation of trivalent actinides (Am, Cm) from lanthanides is one of the most difficult tasks in the process of fractionating high-level waste (HLW). Three groups of methods are mainly used for it: extraction, precipitation, and chromatography. Hexacyanoferrates can be used to separate Am, Cm and lanthanides by precipitation methods. In addition to being stable in acidic, carbonate and alkaline solutions, the $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$ system can form insoluble precipitates with various metals including lanthanides. Also, the $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$ system can be involved in redox processes to form various forms of actinides.¹

The possibility of separating Am and Cm from lanthanides using $\text{K}_3[\text{Fe}(\text{CN})_6]$ in HNO_3 medium was investigated. It was shown that Am and Cm form insoluble complexes with the $[\text{Fe}(\text{CN})_6]^{3-}$ ion in HNO_3 solutions, and about 50% of the initial amount of Am and Cm can be separated from Pr by this method. Based on absorption spectrum of the precipitate dissolved in 1 mol/L H_2SO_4 medium it was concluded that Pr is absent in the precipitate and Am is in the form of Am(III).

The possibility of oxidation Am(III) to Am(V) by exposure to $\text{K}_3[\text{Fe}(\text{CN})_6]$ in NaOH medium was demonstrated. It was established that only half of initial amount of Am(III) is oxidized to Am(V) under the selected conditions. It was noted that varying of oxidation parameters, such as $\text{K}_3[\text{Fe}(\text{CN})_6]$ and NaOH concentration, time and temperature of oxidation, do not effect on the completeness of oxidation of Am(III).²

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The work was carried out according to the state assignment of the GEOKHI RAS.

KINETICS OF SOLVENT EXTRACTION OF Am(III)/Eu(III) PAIR BY N,O-DONOR PHENANTHROLINE LIGANDS

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One of the most studied and effective methods of separation of multicomponent systems such as high-level waste is solvent extraction. To date, two main types of extractors are used in industry: centrifugal extractors and sump mixers. Small contact time of phases in centrifugal extractors allows to reduce radiolysis of components of extraction systems, however, it increases the requirements to the extraction rate.

It is necessary to develop laboratory methods to compare and quantify extraction rates and mass transfer rates. This approach will help to select the extractants that provide rapid extraction of the target component and the establishment of structure-property relationships for ligands. Microfluidic technique has been used to quantitatively describe the kinetics of solvent extraction.

One of the most promising extractants for the separation of f-elements is N,O-donor ligands. The bipyridine diamide ligand was chosen as an extractant. Structural modifications of the ligands included replacement of the bipyridyl fragment with a phenanthroline fragment, which can affect the mobility of the backbone and increase the number of conformations. The substituent at the amide group (PhenEt/Phen) was also varied.

In this work, we quantitatively investigated the kinetics of extraction of Am(III)/Eu(III) pair for a selected series of extractants and determined the rate constants of the process. The structure-kinetic properties relationship (interfacial transfer rate constant for Am(III) and Eu(III)) for this series was established and the influence of structural modifications on the extraction rate was shown. Also, we measured interfacial tension to characterize the interface in the studied systems.

Also we have shown how protonation affects the kinetics of extraction and ligand pre-organization. We determined Am(III)/Eu(III) mass transfer constants in different media in a system with bipyridine diamide using a microfluidic setup. To explain the differences in the extraction kinetics and the relation of kinetic parameters to the pre-organization of the ligand, we obtained single crystals of protonated and de-protonated forms of the ligand, used NMR spectroscopy to describe conformational transformations.

The work was supported by Russian Science Foundation (Grant 20-73-10076)

SORBENTS WITH SYNERGISTIC INTERACTION OF MATRIX WITH LIGANDS FOR SEPARATION OF f-ELEMENTS

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Extraction chromatography, as one of the methods of separating and concentrating radionuclides, is used in various fields of radiochemistry: nuclear medicine, radioecology and the nuclear fuel cycle. This method combines the advantages of liquid extraction (selection of an extractant with target properties) and chromatography (simplicity of conducting a dynamic experiment)¹.

We proposed the idea of studying the synergistic interaction of a polymer matrix and a ligand on its surface to separate *f*-elements. Polymer matrices were obtained on the basis of methacrylic acid with phosphonate derivatives cross-linked with triethylene glycol dimethacrylate or divinylbenzene. For matrices were synthesized allyl diethyl phosphonate and allyl dibutyl phosphonate (Fig. 1).

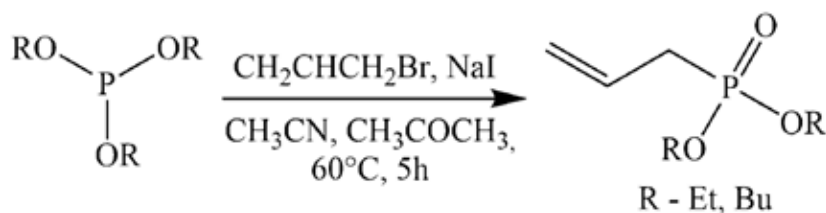


Figure 1. Schemes synthesis of phosphonates

To study the synergistic interaction, we selected well-studied ligands, which parts are used to separate *f*-elements – tributyl phosphate, trioctylphosphine oxide, tetra-*n*-octyl diglycolic acid. We used the impregnation and the in situ methods to insert ligands into the matrix. The study was carried out on the sorption of the Am(III)/Eu(III) pair and a number of lanthanides from La to Lu (without Pm) for the obtained sorbents. In the result, high distribution coefficients from 100 to 1000 were determined, confirming the synergistic interaction of the polymer matrix and the ligand.

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The work was supported by contract 50EP/2024.

A NOVEL APPROACH FOR SYNTHESIZING NITRIDES OF LANTHANIDES AND ACTINIDES AT LOW TEMPERATURES

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Nitrides of f-elements are of great importance from the fundamental point of view, as well as in different applications. Nowadays, lanthanide nitrides are actively applied in the production of materials for permanent magnets, which is associated with high uniaxial anisotropy and high Curie temperatures. Actinide nitrides are used in the nuclear power applications. However, the common techniques to synthesize nitrides (such as carbothermic reduction or ammonolysis) require long-term heating up to 1400-1600 °C. However, novel synthetic strategies via solid-state reactions, applying solid nitrogen sources such as sodium amide¹ or lithium nitride² were demonstrated for synthesis of d-elements nitrides. The similar approach can be effectively implemented to obtain f-element nitrides.

In this work, nitrides of f-elements, both lanthanides and actinides, have been synthesized by the low-temperature combustion reaction between corresponding metal anhydrous chlorides and sodium amide in the inert glovebox. The reaction products were analyzed by powder X-ray diffraction analysis (PXRD), the temperatures of the reaction were determined with differential scanning calorimetry (DSC). Samples for all analyses were placed in the special holders under inert conditions. These holders allow avoiding any contact with oxygen and/or water before and during the measurements. The impact of metal chloride/sodium amide ratio on phase composition have been investigated.

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NOVEL GLASS MATERIALS IN THE $\text{ZnNbOF}_5\text{-BaF}_2\text{-ErF}_3$ SYSTEM

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Oxyfluoroniobate glasses share the best properties of both crystalline fluorides and oxide glasses similar to majority of oxyfluoride glasses. They are characterized by low phonon energy, low linear refractive index, high transmittance in IR and UV and high Rare Earth Elements solubility (REE). The latter makes them a convenient base for doping with RE-ions and creating new laser materials based on them. The introduction of REE into the glass not only provides luminescent properties, but can modify the characteristics of glasses.

In this work, new glasses in the $\text{ZnNbOF}_5\text{-BaF}_2\text{-ErF}_3$ system with varying ErF_3 concentrations from 0.1 to 5 mol.% are considered. The work was undertaken to study the effect of rare earth elements on glass formation, the possibility of obtaining glass ceramics, and analysis of luminescent properties in systems with different dopant contents. During an investigation of the $\text{ZnNbOF}_5\text{-BaF}_2\text{-ErF}_3$ system the following was revealed:

- Depending on the concentration of ErF_3 in the glass crystallization occurs via a single, two or three stage route. BaNbOF_5 crystal phase was shown to be present in all products of heat treatment of glasses discussed;
- changing the amount of erbium trifluoride, you can control the process of obtaining glass ceramics in the glass of the system under discussion;
- varying concentration of ErF_3 from 0,1 to 5 mol % doesn't radical or regular changes in the molecular network structure of glasses, as a whole;
- Er^{3+} photoluminescence contribution corresponding to emission levels of 544 nm and 550 nm upon scattering excitation by a laser at 532 nm was detected during analysis the spectra of inelastic light scattering of the studied glasses;
- luminescence spectra of glasses under study feature intense lines in the region of 500-575nm. corresponding to transitions: $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ (543 nm), $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ (522 nm), $^4\text{F}_{9/2} - ^4\text{I}_{15/2}$ (660 nm);
- luminescence intensity increases as ErF_3 concentration increases from 0,1 to 1 mol %. Further increase in the concentration of ErF_3 in the glass leads to smooth decrease in luminescence intensity; luminescence intensity falls sharply upon glass ceramic formation as well as complete crystallization of the glass.

This work is supported by the RSF grant № 24-13-00133.

NEW NANOCRYSTALLINE PHOSPHORS

$\text{MYF}_4: \text{Eu}^{3+}$, $M = \text{K}, \text{Rb}, \text{Cs}$

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New luminescent nanomaterials $\text{MYF}_4: \text{Eu}^{3+}$ ($\chi(\text{Eu}) = 0-100$ at. %) were synthesized by hydrothermal method at 180 °C. It was shown that the phase composition varies depending on the alkali metal and europium concentration. The crystalline phase of $\text{KYF}_4: \text{Eu}^{3+}$ samples corresponds to cubic- KY_3F_{10} regardless of the europium concentration. The crystalline phase of $\text{RbYF}_4: \text{Eu}^{3+}$ samples corresponds to orthorhombic- RbSm_2F_7 at europium concentration 0 - 10% and cubic- $\text{RbY}_3\text{F}_{10}$ at europium concentration 20 - 100%. The crystalline phase of $\text{CsYF}_4: \text{Eu}^{3+}$ samples corresponds to orthorhombic- CsY_2F_7 at europium concentration 0-80%. 100-% Eu Cs-based sample is formed in hexagonal- EuF_3 crystalline phase. Also for Cs-based samples at 80% of europium content, an admixture of EuF_3 phase was observed.

Analysis of the luminescence spectrum showed that under excitation at 395 nm all samples exhibit luminescence corresponding to f-f transitions of Eu^{3+} ion. For each series, the quantum yield maximum corresponds to the content of europium ions of 20-30 at. %. The luminescence spectra of each series of samples indicate a unique fine structure of luminescence bands depending on the phase.

For each crystalline phase, a monotonic increase in the average particle size is observed with increasing europium concentration. The smallest particles are observed for K-based samples: 20-60 nm in diameter. The particles of Rb-based samples have a diameter of 20-220 nm. Particles of Cs-based samples have a diameter of 60-2000 nm.

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The measurements were performed at the Research Park of Saint-Petersburg State University ("Magnetic Resonance Research Centre", "SPbU Computing Centre", "Cryogenic Department", "Interdisciplinary Resource Centre for Nanotechnology", "Centre for X-ray Diffraction Studies", "Chemical Analysis and Materials Research Centre", and "Centre for Optical and Laser Materials Research").

EFFECTS OF NATURE OF SUBSTITUENT ON STRUCTURE AND LUMINESCENT PROPERTIES OF LANTHANIDE ACYLPYRAZOLONATES

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Nowadays the rational design of efficient phosphors based on lanthanide complexes is still an urgent task. Ligands 4-acylpyrazolones (Fig. 1) are used to solve this problem. These compounds have been known for a long time, but the number of systematic studies in which the structure of such ligands is related to the luminescent properties of the lanthanide complexes is relatively small.

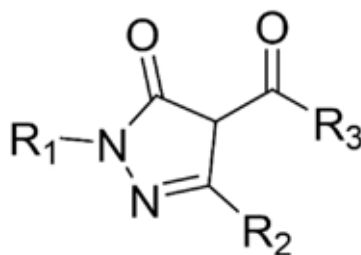


Fig. 1. Structural formula of the ligand.

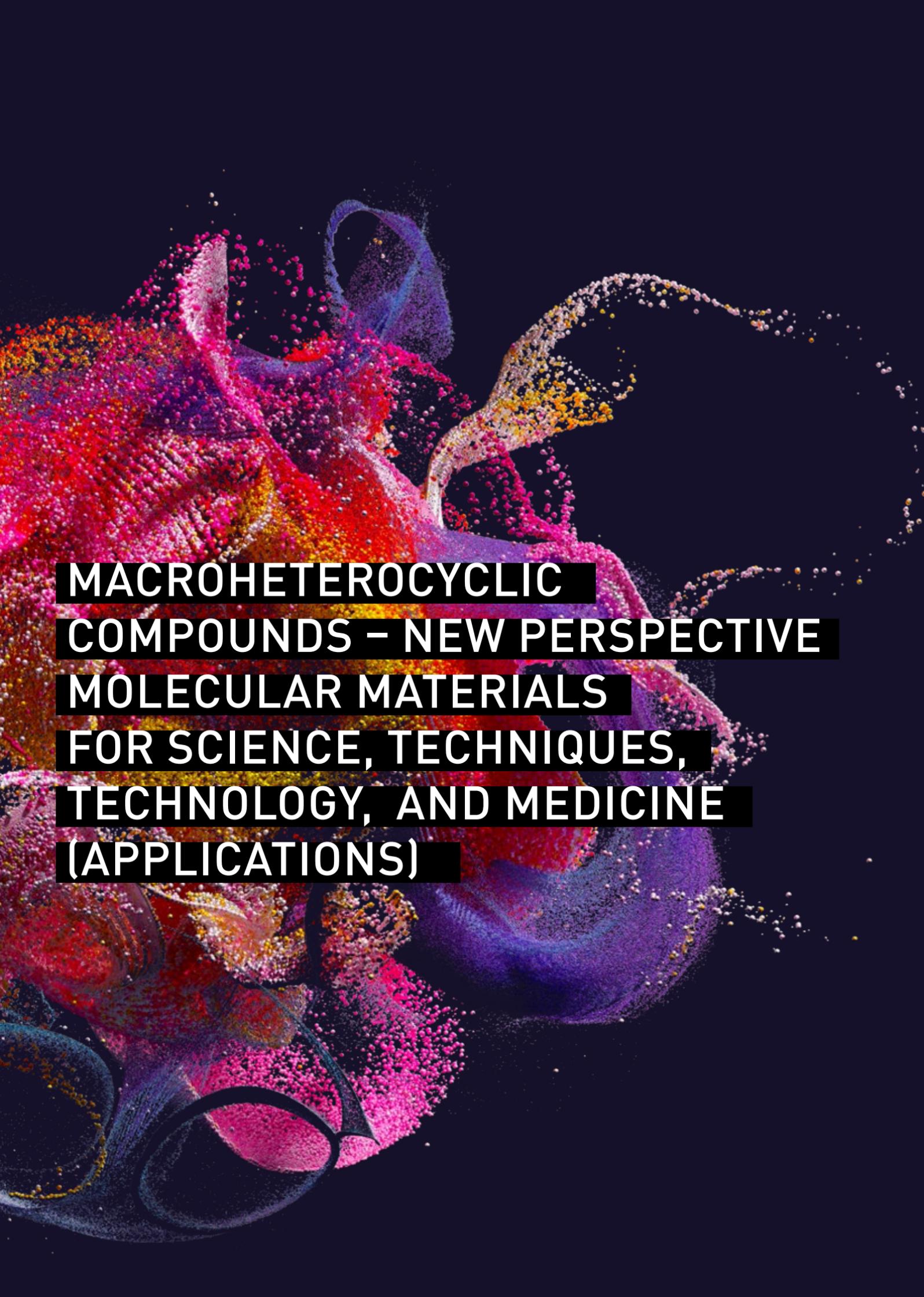
This work is devoted to the synthesis, study of structural features and luminescent properties of lanthanide complexes based on ten 4-acylpyrazolones with the general formula $[LnQ_3L_n]$, where Q is the anion of the corresponding acid HQ^{R_1,R_2,R_3} with $R_1 = 1-Nh, Ph, t-Bu, C_6F_5$, $R_2 = 1-Nh, Ph, Me, CF_3$ and $R_3 = Ph, Me, Cp, Tp, Ln$ – lanthanide Gd, Sm, Eu, Tb, Dy or Yb, and L – additional ligand $H_2O, DMF, TPPO$ or 2,2'-bipy. In some cases, tetraphenylphosphonium salts of *tetrakis*-acids have been synthesized.

Improved methods for the synthesis of *tris*- and *tetrakis*-complexes of trivalent lanthanide ions are proposed.

The greatest influence on the energy of the first singlet level S_1 is found to exerted by an increase in the length of the aromatic system of the substituent at the nitrogen atom N(1) – the energy of this level decreases, while the energy of the triplet level T_1 weakly depends on such substituents.

It is shown that the greatest influence on the energy of the first triplet level is exerted by an increase in the donor effect of the substituent at the carbonyl group of the C(4) atom. At the same time, there is an increase in both T_1 and S_1 levels.

The work was carried out with the financial support of the Russian Science Foundation, project No. 23-23-00393.

An abstract, colorful visualization of a complex molecular structure, possibly a macroheterocyclic compound. The structure is composed of numerous small, colored spheres (pink, red, orange, yellow, and purple) arranged in a dense, interconnected network. The background is dark blue, and the overall shape is irregular and flowing, suggesting a dynamic or flexible molecular framework. The text is overlaid on the central part of the image.

**MACROHETEROCYCLIC
COMPOUNDS – NEW PERSPECTIVE
MOLECULAR MATERIALS
FOR SCIENCE, TECHNIQUES,
TECHNOLOGY, AND MEDICINE
(APPLICATIONS)**

PORPHYRINOIDS BASED CHEMICAL SENSORS

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Porphyrins and related macrocycles have attracted the researcher's attention because of the richness of their properties, which are functional to several application fields, ranging from material to medical science.¹ The synthetic pathways elaborated for the preparation and functionalization of these macrocycles allow a fine tuning of their properties, optimized for the particular purpose. Among the different porphyrin analogs, our group has been particularly focused on the corrole, a contracted tetrapyrrole that shares the molecular skeleton with corrin and an 18 e⁻ π -aromatic system of porphyrin.² We have exploited both porphyrins and corroles to develop chemical sensors, using them as receptors in different application fields (Figure 1).³ The preparation of these macrocycles and some examples of their sensor applications will be presented and discussed.

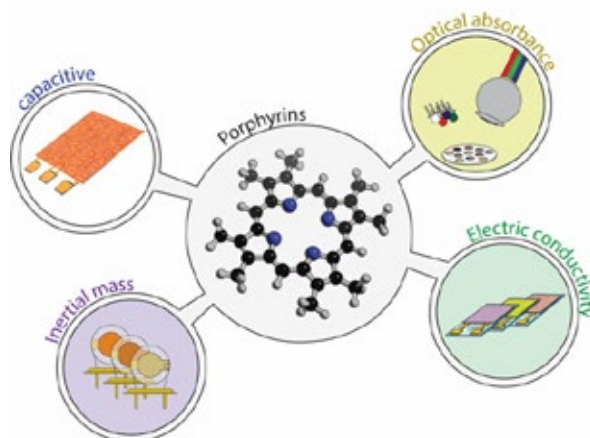


Figure 1

References

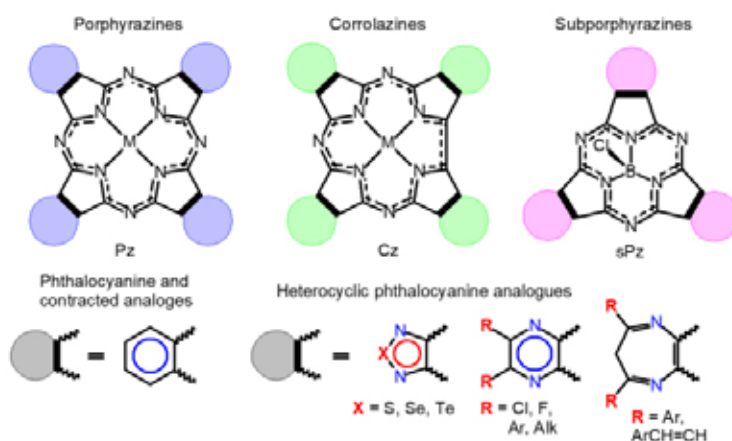
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NOVEL PERSPECTIVE MACROHETEROCYCLES - PHTHALOCYANINE ANALOGUES WITH FUSED HETEROCYCLES

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Phthalocyanines (tetrabenzoporphyrines) and their analogues containing contracted macrocycle – tetrabenzocorrolazines and subphthalocyanines are actively studied already for several decades as perspective materials for various application fields (dyes, organic electronics, catalysis, medicine, etc.) For many applications, e.g. in organic electronics, the phthalocyanine-type macrocycles should have high electron affinity which is usually achieved by halogenation of benzene rings.



Another way to enhance and tune the electron affinity of the macrocycle developed in our works is annulation of the electron deficient aromatic heterocycles.¹⁻³ Porphyrazines, (Pz), corrolazines (Cz), and subporphyrazines (sPz) bearing fused 1,2,5-chalcogenadiazole, pyrazine, or 1,4-diazepine fragments instead or in combination with benzene rings have demonstrated perspective properties for use in photovoltaic, biomedical and sensor applications⁴⁻⁸ and in design of organic frameworks.

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Funding from Russian Science Foundation grant № 23-43-00146 is gratefully acknowledged.

GOLD COMPLEXES BASED ON N-HETEROCYCLIC LIGANDS: SYNTHESSES, NON-COVALENT INTERACTIONS AND APPLICATIONS

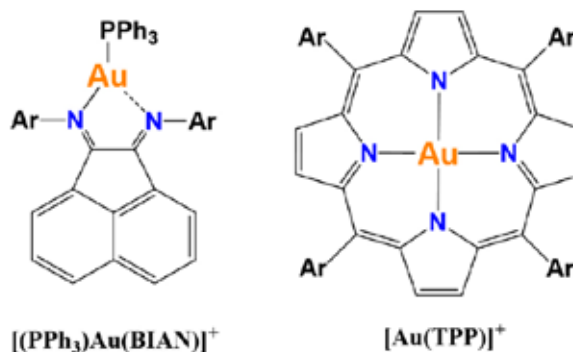
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Coordination chemistry of gold is an actively developing area of modern chemical science. Gold complexes with N-donor ligands are widely used for the development of luminescent materials, catalysts and anticancer drugs, as well as for the preparation of thin metal films and nanoparticles.

In this study, we report the synthesis and characterization of a series of gold complexes based on N-heterocyclic ligands. These are Au(I) complexes with aromatic acceptor diimines, such as phenanthrolines, 2,2'-bipyridines, bis(arylimino)acenaphthenes (BIAN), as well as complexes Au(III) complexes with macrocyclic tetraarylporphyrins (TPP) (see Chart).



The work presents information about synthetic procedures, structural features, aurophilic and other non-covalent interactions, as well as photoluminescent, redox properties and antitumor activity.¹⁻⁴

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COMBINATORIAL 2D-3D SELF-ASSEMBLY OF FUNCTIONAL HYBRID MATERIALS

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Functional hybrid materials combining organic and inorganic components and achieving synergy of their properties are the basis of future technologies that will reduce the anthropogenic pressure on the environment while ensuring the desired efficiency of devices and processes.¹ The development of these materials is one of the most urgent interdisciplinary tasks of modern science at the intersection of biology, nanoscience, colloidal, supramolecular and physical chemistry. The combinatorial approach to the design of functional materials is based on various combinations of low-dimensional nanoparticles and functionalized organic molecules, such as macro- and polycyclic chromophores with useful optical, catalytic, photochemical and receptor properties, for their integration into hybrid structures. The versatile set of non-covalent chemical interactions, which is provided by different binders (metal ions, metal clusters and UV-curable polymers), provides the opportunity of control the functional synergy of hybrid materials by manipulating the sequence of chemical bond formation between components and their spatial distribution. The combinatorial strategy can be applied both for the preparation of ultrathin 2D film hybrids for organic electronics and photonics² and for the self-assembly of dispersed 3D hybrids with unique catalytic and photocatalytic properties³.

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The project is supported by RSF (grant no. № 23-73-00095).

SUPRAMOLECULAR TAILORING OF THE MAGNETIC PROPERTIES OF LANTHANIDE TRISPHTHALOCYANINATES

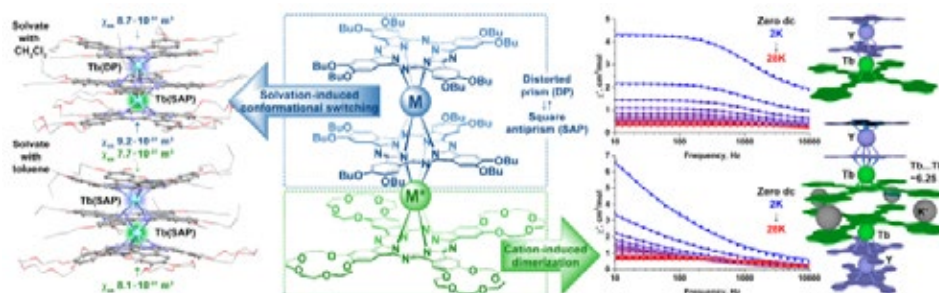
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Sandwich lanthanide phthalocyaninates are distinguished from other coordination compounds with tetrapyrrole ligands by their molecular magnetism. In addition to modification of the coordinating ligands, tuning the magnetic properties of these complexes can take advantages of supramolecular interactions.¹ Here we discuss the influence of such interactions on the magnetic properties of novel homo- and heteronuclear heteroleptic trisphtalocyaninates $[B_4]M[B_4]M^*[C_4]$ containing octa- β -butoxy- and tetra-15-crown-5-substituted phthalocyanine ligands - $[B_4]$ and $[C_4]$, respectively, where M and M* are Tb, Dy and/or Y.^{2,3}

The conformational state of these complexes can be switched by changing the solvation environment – in aromatic solvents all ligands adopt staggered pairwise conformations, while in halogenated alkanes the fragment " $[B_4]M[B_4]$ " switches to the gauche state, however retaining the staggered conformation of the " $[B_4]M[C_4]$ " fragment. The nature of the noncovalent interactions leading to this switching was identified by the quantum theory of atoms in molecules, and the analysis of lanthanide-induced shifts in NMR spectra demonstrated the growth of the axial anisotropy of lanthanide ions, χ_{ax} with the decrease of the symmetry of Ln^{3+} coordination surrounding.

In addition, the presence of crown-ether units allowed the application of cation-induced supramolecular assembly to form six-deck dimers with collinear metal centers, which exhibit efficient through-space f - f interactions causing a spectacular decrease in the magnetization relaxation rate.



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This work was supported by Russian Science Foundation, project 18-73-10174-P.

APPROACHES FOR RATIONAL DESIGN OF THE CRYSTALLINE MATERIALS USING COORDINATION COMPOUNDS OF (THIA)CALIX[4]ARENES

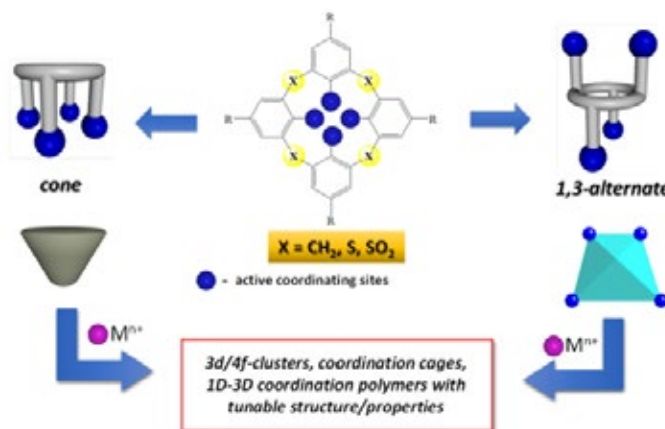
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(Thia)calix[4]arenes (Scheme 1), adopted in the *cone* or *1,3-alternate* conformation are versatile molecular building blocks that are widely used in coordination supramolecular chemistry to create functional crystalline materials.¹ This work reports on the basic approaches, aimed to control the crystalline self-organization of (thia)calix[4]arene based 3d-/4f- coordination compounds, in order to construct supramolecular coordination compounds able to display tunable magnetic, luminescence properties or intrinsic porosity.²⁻⁴ The principal factors, influencing on the spontaneous self-assembly of 1D-3D coordination polymers, discrete 3d/4f clusters or coordination cages based on the use of (thia)calix[4]arenes as well as the structure–property relation will be discussed.



Scheme 1

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SYNTHETIC AND NATURAL ETIOPORPHYRINS AS THIN-FILM MATERIALS FOR OPTOELECTRONIC APPLICATIONS

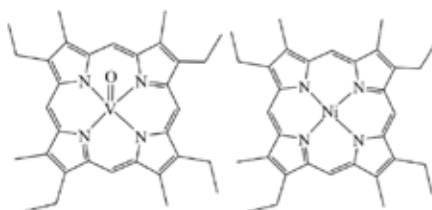
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Etio-type porphyrin complexes with vanadyl and nickel ions can be either synthesized in laboratory or (certain isomers) isolated from fossil fuels as mixtures with other petroporphyrins^{1,2}. Like many other macroheterocycles, they are intensively colored, chemically and thermally stable and tend to self-assemble into large-sized aggregates upon concentration or solidification. It is therefore very tempting to explore the potential of using such petroleum byproducts (see, Figure below) for optical, catalytic or medical applications.



Most optoelectronic devices, including those based on small molecules or polymers, have essentially a multilayer thin-film architecture. Thus, this work studies the formation of thin layers by petroporphyrin molecules during various deposition processes (thermal vacuum evaporation, spin-coating, drop-casting), optical and charge transport properties of these layers, and stability of their morphology and chemical composition under illumination.

Our results indicate that with appropriate optimization of growth conditions, it is possible to obtain petroporphyrin films with structural quality that allows the fabrication of multilayer photovoltaic converters where these molecules serve as light-absorbing (donor) components.

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This work was supported by RSF grant no. 20-13-00285.

FLUORESCENT MATERIALS BASED ON QUINOXALINE DERIVATIVES

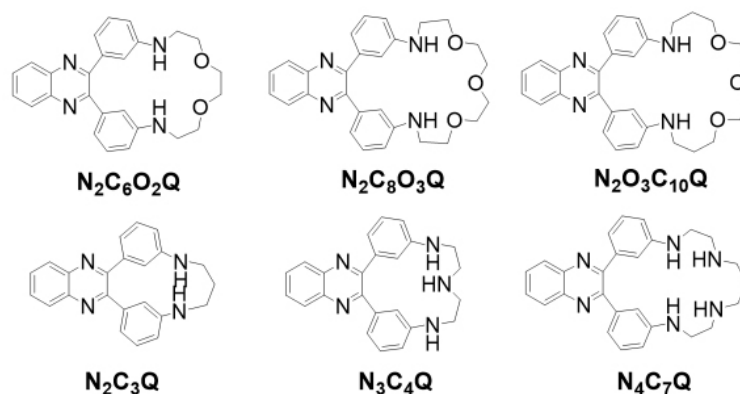
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Luminescent materials attract living interest in both fundamental and applied science holding great promise for the conversion of academic research into technological innovations. Among light-emitting compounds, quinoxalines have attracted significant attention. 2,3-diphenylquinoxaline derivatives exhibit a distinctive propeller-shaped structure. Such compounds possess aggregation-induced emission (AIE), when molecules that are non-emissive in solution exhibit substantial light emission in solid phases or within supramolecular systems.



In this work, we explore the preparation of 2D sensing films using AIE-exhibiting 2,3-diphenylquinoxaline-based diazapolyoxy- and polyazamacrocycles via the Langmuir-Blodgett (LB) technique. It was shown that macrocyclic compounds bearing 2,3-diarylquinoxaline residues, which exhibit very low emission in chloroform solutions, can form stable monolayers at the air/water interface. Upon transfer onto solid supports, these monolayers give rise to emissive films containing AIE-exhibiting aggregates. Through careful optimization of molecular precursor, we were able to prepare multilayered AIE-exhibiting and pH-sensitive LB film suitable for visual measurements of acidity in gaseous phase.

This work was supported by Russian Science Foundation, Grant № 23-73-01159

MAGNETIC COUPLING IN HETEROMETALLIC COORDINATION COMPLEXES OF METAL MACROHETEROCYCLES

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Metal macroheterocycles (porphyrins, phthalocyanines and their analogues) are widely as a base for the preparation of functional materials. Construction of distinctive magnetic materials is possible upon the coordination of different metal complexes to metal macroheterocycles with the formation of paramagnetic heterometallic assemblies.

We developed methods for the synthesis of coordination complexes based on different metal macroheterocycles with various transition metal compounds.¹ The complexes were formed by direct metal-metal bonding. A series of such heterometallic complexes were obtained in the form of crystals and fully characterized. Their structures, optical and magnetic properties were studied.

It was shown that in such complexes red-ox active macroheterocyclic ligand can have different charge states: diamagnetic dianionic and tetraanionic as well as paramagnetic trianion-radical one. Complexes with several paramagnetic centers were obtained upon coordination of paramagnetic metals as well as introduction of Cp^*Cr^+ ($S = 3/2$) cations in structures. Complexes with a dense packing of macrocycles show strong magnetic coupling (the exchange interaction J reaches -180 K).

Thus, we showed that metal macroheterocycles are suitable paramagnetic ligands for transition metals allowing the preparation of heterometallic complexes with rich and distinctive magnetic behavior. The compounds are highly soluble, which is unusual for macroheterocycles, have intense absorption over a wide range, and can have strong magnetic exchange between paramagnetic centers. The developed methods can be used for the synthesis of materials with desired and tunable properties.

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The work was supported by the Russian Science Foundation (grant № 24-13-00060).

PHOTOACTIVATED PT(IV) PRODRUGS: ONE-POT CHEMOTHERAPY, PHOTOTHERMAL AND PHOTODYNAMIC THERAPY

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Vaneev A.N.,^{a,b} Erofeev A.S.,^{a,b} Gorelkin P.V.,^{a,b} Skvortsov D.A.,^a Ipatova D.A.,^a
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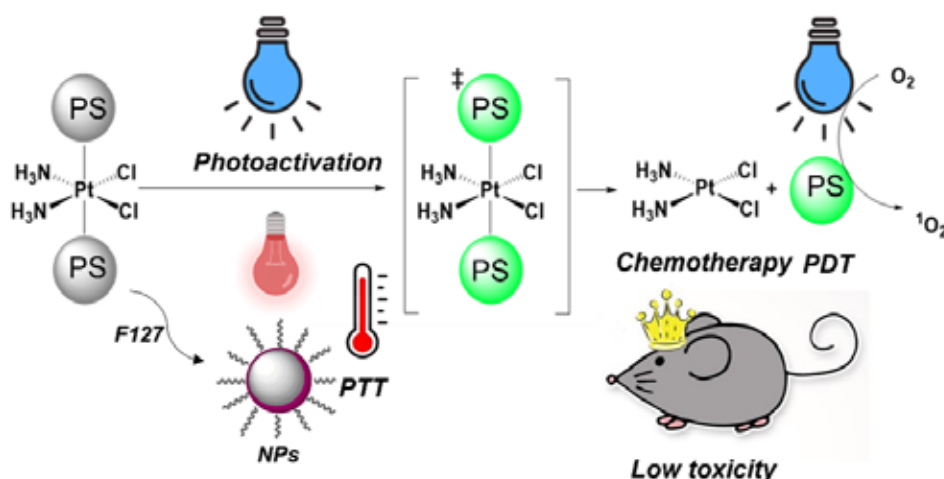
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The design and synthesis of low-toxic Pt(IV) prodrugs is a novel approach to overcome a low selectivity and high toxicity of Pt(II)-based chemotherapy. To design photoactivated dual-action Pt(IV) prodrug, a photosensitizer (PS) is introduced into the axial position of Pt(IV). Photoactivable Pt(IV) prodrug acts as a dual PDT/PTT agent, via light-controlled drug release along with ROS generation.



We have developed Pt(IV) prodrugs with PS based on riboflavin and BODIPY, which act as agents of photoactivatable chemotherapy, PDT and PTT. Prodrugs developed are capable of controlled photorelease of cisplatin and ROS generation of *in vitro* and *in vivo*; nanoparticles based on amphiphilic NIR-absorbing Pt(IV)-BODIPY prodrugs also exhibit high PTT efficiency. *In vivo* studies confirm high antitumor efficacy of prodrugs, along with low toxicity.

The work was carried out with the financial support of the Russian Science Foundation, project 22-15-00182.

COORDINATION OF DYSPROSIUM TO HEMIHEXAPHYRAZINE

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Extended porphyrinoids (for example, hemihexaphyrazine) are analogues of porphyrins with larger cores. These derivatives are known for exhibiting a rich coordination chemistry, whereby multiple metals can be accommodated in their inner cavities. Expanded porphyrinoids can efficiently satisfy the tendency of earth-rare metals to present high-coordination numbers. However, despite their envisioned potential, the coordination of magnetically active metals with expanded Ps focused on developing SMMs remains elusive. That is due to very little is still known about the coordination chemistry of these compounds and lanthanides.

We have demonstrated that H₃Hhp is a promising ligand for fabricating magnetically active Dy³⁺ complexes. In this regard, we found that performing complexation under reductive conditions is a powerful strategy to control the selectivity without altering the oxidation state of the expanded porphyrin. The resulting mononuclear complex **1**, was found to exhibit an offcentered, out-of-plane coordination, as well as a directional supramolecular organization directed by π - π interactions with Cp^{*}₂Co molecules.¹

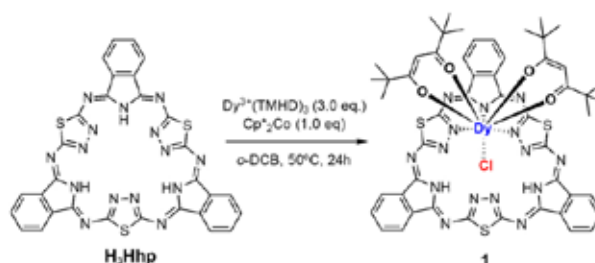


Figure 1. Synthesis of H₃Hhp-Dy complex **1**.

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The work was supported by the Russian Science Foundation (the grant № 24-13-00060).

SELF-ASSEMBLY OF PILLAR[5]ARENES CONTAINING AMINO ACIDS RESIDUES WITH NUMBER OF HERBICIDES

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Clean water is an irreplaceable and essential natural resource, playing a vital role in the medical, food and energy industries. Water pollution is mainly caused by insufficient treatment of industrial and agricultural effluents, which can make the water in rivers and lakes unsuitable for living organisms. Contaminants of greatest concern include heavy metals, herbicides, dyes, and pharmaceuticals, which can accumulate in the food chain and adversely affect everyone involved. Herbicides quickly enter water and soil, causing serious environmental damage. Supramolecular chemistry can solve problems associated with herbicide contamination and its harmful effects on humans and the environment. Pillar[n]arene derivatives are of considerable interest among the variety of host molecules due to their ability to incorporate a wide range of substrates into the macrocyclic cavity.

This work proposes the use of water-soluble, low-toxicity pillar[5]arene derivatives containing amino acid residues to bind a number of herbicides (glyphosate, paraquat, pyridate, glufosinate, and 3-(methylphosphinico)propionic acid). The charge influence in the pillar[5]arene substituents and their self-assembly on the toxicity of the synthesized macrocycles towards the A549 and LEK cell lines was demonstrated. The selectivity of pillar[5]arene betaine derivatives towards pyridate, glyphosate, and paraquat has been demonstrated. An approach using pillar[5]arene betaine derivatives to protect nucleic acids (DNA) from glyphosate damage by competitive binding to the macrocycle has been proposed and implemented for the first time.

This work was financially supported by the Russian Science Foundation (Grant No. 23-73-01087, <https://rscf.ru/project/23-73-01087/>).

FLUOROUS PORPHYRINOIDS FOR ENHANCED PHOTODYNAMIC THERAPY

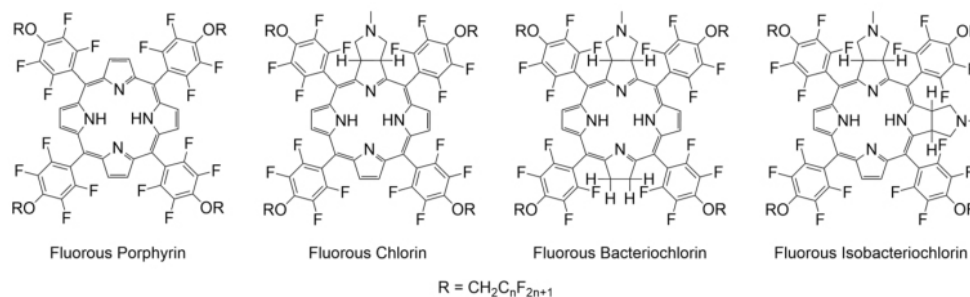
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Perfluorocarbons have been effectively used as an oxygen carrier for various biomedical applications.¹ Amongst them photodynamic therapy seems to benefit greatly from perfluorocarbons due to its oxygen-dependent mechanism of action.² Therefore, the use of fluoruous photosensitizers, which are soluble in perfluorocarbons and are in close proximity to dissolved oxygen, is promising.³



Our group has synthesized fluoruous porphyrin derivatives and designed perfluorocarbon nanoemulsions with them for photodynamic therapy *in vitro*. These formulations have shown to be efficient in killing cancer cells in both normoxic and hypoxic conditions following light irradiation with minimal dark cytotoxicity, making them promising tools for treating hypoxic tumours.

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The study was carried out using the equipment of the Core Facility “New Materials and Technologies” at the Emanuel Institute of Biochemical Physics, Russian Academy of Sciences.



THERAPEUTIC NUCLEIC ACID DELIVERY SYSTEMS BASED ON DENDRONIZED THIALICALIXARENES

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In recent decades, targeted controlled delivery systems for therapeutic nucleic acids have become widespread due to their great potential in solving a variety of problems specific to existing dosage forms. Complexes of nucleic acids with liposomes, cationic linear polymers and dendrimers are the most widely used for this purpose. Dendrimers are attractive carriers for therapeutic nucleic acids because of their unique properties (monodispersity, stability, ability to vary terminal groups, etc.). At the same time, the main problem for their widespread use is the low yield of high-generation dendrimers, and, as a consequence, a significant increase in their cost. In addition, such dendrimers show high *in vitro* and *in vivo* toxicity. Therefore, the development of low-toxic dendrimers capable of binding and delivery of therapeutic nucleic acids already at low generations is an urgent task. Among the platforms for controlled drug delivery, macrocyclic compounds are attracting increasing interest due to significant developments in the field of nanomedicine. Combining the properties of dendrimers and macrocyclic compounds can lead to synergistic effects and a new generation of targeted delivery systems.

In this work, methods for the synthesis of dendronized thiacalixarenes in *cone*, *partial cone*, and *1,3-alternate* stereoisomeric forms were proposed and developed. The hemo- and cytotoxicity of the obtained compounds was established, and it was also shown that the obtained dendronized thiacalixarenes are able to bind therapeutic nucleic acids (siRNAs) with subsequent release into tumor cells.

This work was financially supported by RSF, project No. 24-43-10005 (<https://rscf.ru/en/project/24-43-10005/>) and BRFB, project No. B23RNFM-041

CONDUCTING POLYMERS BASED ON PORPHYRINS WITH DIFFERENT MOLECULE STRUCTURES

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Electrically conductive polymers are a new class of polymers that have appeared relatively recently. In recent years, this direction in polymer chemistry has been developing rapidly. One type of such materials is polyporphyrin coatings (films, layers), which have attracted much attention due to their potential for various practical applications such as polymer-based light-emitting diodes, solar cells, and others.

The main objective of the study is to expand the range of precursors and establish the influence of the structural features of monomer molecules and the nature of solvents on the physicochemical and electrophysical (in particular, semiconductor) properties of electroactive polyporphyrin coatings. The structural units in the production of polyporphyrin blocks (films) are tetraphenylporphin derivatives with different arrangements of substituents in the phenolic rings, which makes it possible to obtain not only bulk cross-linked but also linear polymers, which in a certain way affects the final properties of the resulting polyporphyrin materials.

The processes of electrochemical (methods of cyclic voltammetry, stationary electrolysis, rotating disk electrode, electrochemical quartz microbalance) production of thin polyporphyrin conductive films based on porphyrin molecules of different nature and structure using solvents of various classes: dimethyl sulfoxide and ethyl alcohol have been studied. Polyporphyrin films are deposited on electrodes of various natures: glassy carbon, platinum, transparent oxide (ITO) and fluorine oxide (FTO) electrodes. Their physicochemical properties were studied and the mechanisms of film polymerization were established (electronic and IR spectroscopy, quartz microbalance method, spectroelectrochemistry, electrode impedance spectroscopy). The photo-EMF and Mott-Schottky methods were used to determine the types of conductivity of the resulting materials.

The use of low-volatile and low-toxic solvents in the electrochemical formation of films makes the technology for producing polyporphyrin films environmentally safe.

The work was supported by the Russian Science Foundation, grant No. 24-13-00010.

PHOSPHORUS (V) TETRAPYRROLIC COMPLEXES: FROM SYNTHESIS TO BIOMEDICAL APPLICATIONS

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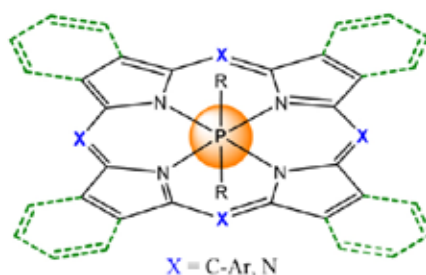
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The development of efficient photosensitizers for biophotonics is an important task for contemporary science at the interface of chemistry, biology and medicine. Tetrapyrrolic macrocycles are known photosensitizers, including drugs that have already been used in clinical practice (e.g., Photosens). The introduction of a P(V) atom leads to a significant bathochromic shift of absorbance maximum as well as an increase of solubility in water due to the appearance of a positive charge and axial ligands^{1,2}.



We have demonstrated that P(V) porphyrins and phthalocyanines are highly effective at generating singlet oxygen under light irradiation. P(V) porphyrins were found to exhibit high light-induced cytotoxicity ($IC_{50}=0.010$) which is promising for photodynamic therapy (PDT).

In contrast, P(V) phthalocyanines demonstrate relatively low dark and light cytotoxicity rendering the complexes unsuitable for PDT. Nevertheless, recently we have shown that they can be employed as photoinitiators for photocuring of bio-compatible polymers and subsequently for tissue engineering.

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This work was supported by the Russian Science Foundation (grant № 24-73-10192).

POLY(AMIDOAMINE) DENDRIMERS ON THE THIALCALIX[4]ARENE PLATFORM: SYNTHESIS AND INTERACTION WITH BIOSUBSTRATES

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Poly(amidoamine) (PAMAM) dendrimers have significant potential for the binding and delivery of biologically important substrates. However, a number of significant drawbacks of these branched macromolecules (such as cytotoxicity, multi-step synthesis and difficulty in purification of the most used high generation) prevent most dendrimers from reaching the stage of clinical trials.

We propose using a macrocyclic thiacalix[4]arene platform as the core of PAMAM dendrimers. The thiacalixarene platform is non-toxic, and different spatial configurations of thiacalix[4]arene (*cone*, *partial cone* and *1,3-alternate*) will result in dendrimers with varying shapes, from classical true symmetric (*1,3-alternate*) to amphiphilic (*cone*). Additionally, the macrocyclic core will increase the internal space of the dendrimers. This approach will make it possible to obtain low-toxic dendrimers with increased internal pseudo-cavity, capable of efficient multipoint interaction with substrates, even in low (1-3) generations.

In this work, we have proposed the design and implemented approaches for the synthesis of first, second and third generation poly(amidoamine) dendrimers on the thiacalix[4]arene platform in different configurations (*cone*, *partial cone* and *1,3-alternate*). It was found that the obtained dendrimers are able to efficiently bind a number of biologically substrates (including DNA, lysozyme protein, and a number of catecholamines), which have wide applications in medicine. The constants and mechanism of interaction, the size and shape of the formed particles were determined and the unique properties of the obtained supramolecular systems were revealed.

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DEPENDENCE OF LUMINESCENCE OF HYBRID CRYSTALS OF THE TYPE $[\text{NH}_3-(\text{CH}_2)_n-\text{CH}_3]\text{PbX}_4$ ON THE STRUCTURE OF THE ORGANIC CATION AND THE TYPE OF ANION

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In the presented work, the regularities of low-temperature luminescence of hybrid crystals based on alkandiamines and lead halides of the type $[\text{NH}_3-(\text{CH}_2)_n-\text{NH}_3]\text{PbX}_4$ ($n=4-8$, $\text{X}=\text{Cl}, \text{Br}, \text{I}$) are considered depending on the length (n) and parity of the organic cation, as well as on the type of anion (X). Figure 1 shows typical low-temperature photoluminescence spectra, luminescence excitation spectra, and corresponding diffuse reflection spectra for the analyzed samples.

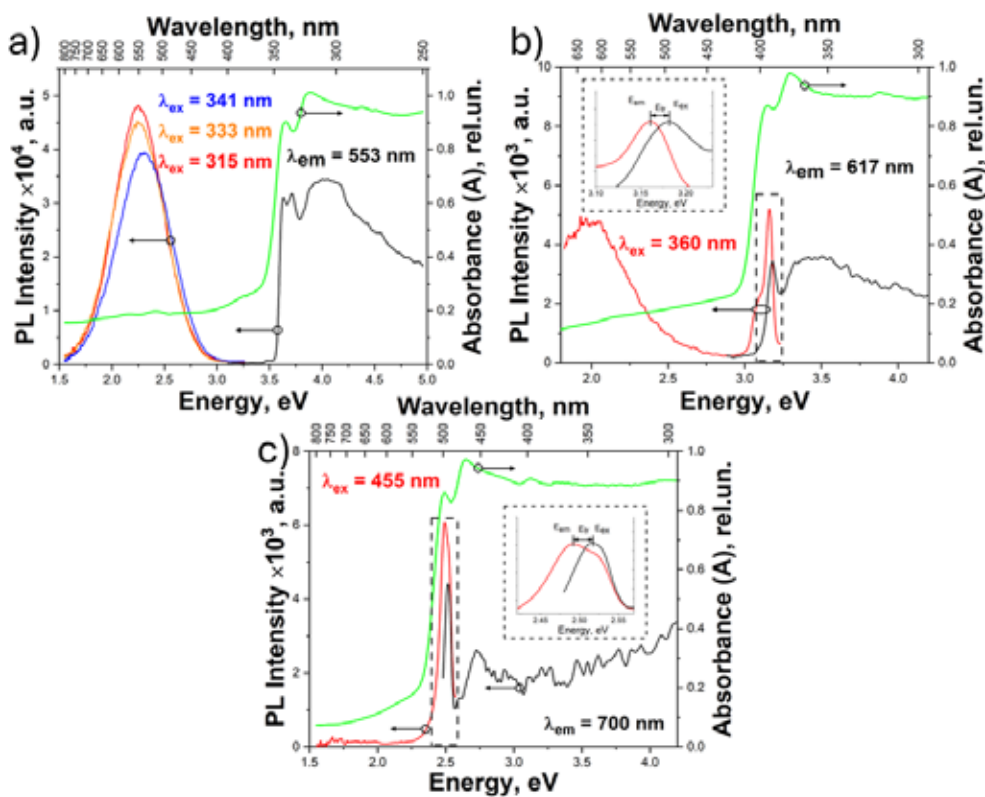


Figure 1. Typical luminescence of hybrid crystals based on:
(a) lead chlorine ($n=4$), (b) lead bromine ($n=8$) and (c) lead iodine ($n=6$)

Chlorine crystals are characterized only by broadband luminescence of autolocalized excitons (STE). Bromine and iodine crystals are characterized by the presence of two types of luminescence: STE and narrow-band luminescence of free excitons (FE). Moreover, for bromine crystals the STE/FE ratio depends on the length of the organic cation and decreases with its growth. For iodine crystals it is found that only crystals with an even number of carbon atoms in its structure (n) have luminescent properties.

PHOTOCONDUCTIVITY, ELECTROLUMINESCENCE AND ELECTRON MOBILITY IN COMPOSITES WITH SEMISYNTHETIC MACROCYCLIC COMPOUNDS

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Semisynthetic macrocyclic compounds (MCCs), such as porphyrins, pheophorbides, chlorins, etc., are of great interest as photo- and electroactive components of composite materials for the research and development of photovoltaic and electroluminescent devices.

It was shown for the first time that the Cu-MCC component (Figure 1) in a mixture with a polymer (poly(N,N'-bis-4-butylphenyl-N,N'-bisphenyl)benzidine, poly-N-vinylcarbazole) can (1) expand the photoconductivity of the composite in the blue and red spectral bands, (2) serve as an electron acceptor in relation to the polymer in the same way as fullerene, (3) provide transport both electrons and holes, (4) serve as light emitting dopant demonstrating electroluminescence in the near-IR range.^{1,2}

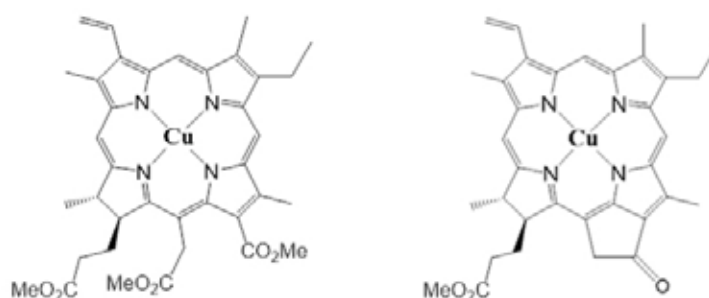


Figure 1. The structure of the studied MCCs:
Cu (II) pyropheophorbide (left) and chlorin Cu-C-e6 (right).

The corresponding mechanisms of hopping transport of charge carriers, photoconductivity and electroluminescence in the studied composites, as well as the operating parameters of the developed devices are discussed.

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EXPLORING REACTIONS OF AMBIPHILIC SELENYL REAGENTS WITH UNSATURATED SUBSTRATES: SYNTHESIS, STRUCTURES, AND IMPLICATIONS TO SUPRAMOLECULAR CHEMISTRY

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Small molecules, such as N_2O , N_2 , CO_2 , CH_4 , simple nitriles, alkenes, isocyanides, and others, have the potential to become alternative cheap and readily available raw materials for the synthesis of more complex compounds (1). Throughout the past century, the activation of the aforementioned small molecules has almost exclusively been associated with the use of transition metals. Catalytic transformations involving transition metals, developed over recent decades, have, without exaggeration, transformed both the chemical industry and human activity as a whole. Despite the appeal of transition metals, their use comes with several drawbacks, such as the high cost and toxicity of some derivatives. In 2006, Stephan made a groundbreaking discovery: he demonstrated that an effective system exists that does not contain transition metals and is capable of reversibly activating a small molecule like hydrogen (2). This discovery served as a starting point, after which the theme of using the concept of frustrated Lewis pairs for the activation of small molecules has been developed by many leading chemical centers worldwide.

In this report, our progress towards the application of another system—ambiphilic selenyl platforms—for the activation of unsaturated substrates will be highlighted. It will be shown that they are capable of forming covalent adducts with a number of unsaturated substrates, such as nitriles, isocyanates, isothiocyanates, isoselenocyanates, ketones and others. It will be demonstrated that these reactions are reversible. Furthermore, it will be shown that the aforementioned new reactions allow the synthesis of selenium-containing compounds that are inaccessible through other known methods. Many new electron-deficient selenium heterocycles are donors of the so-called chalcogen bond. The types of supramolecular organization of the new selenazoles in the solid phase, as well as their potential for directed construction of supramolecular assemblies, will be discussed in the report (3).

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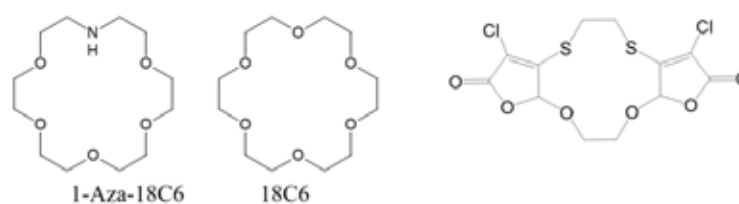
THERMODYNAMICS OF COMPLEXFORMATION OF Ni(II) AND Ag(I) WITH HETERO-CROWN ETHERS IN AQUEOUS-ORGANIC SOLVENTS

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The development of new chemical technologies based on crown ether complexes with *d*-metal ions is promising. Thermodynamic parameters of the complexation of metal ions with crown esters are necessary to identify the role of coordination compounds in the formation of catalytically active structures in the hydrogenation of hydrocarbons.

The study of the complexation of Ni²⁺ and Ag⁺ with crown esters 1-Aza-18-crown-6 (1-Aza-18C6), 18-crown-6 (18C6) and thia-crown ether (M1), in aqueous ethanol and dimethyl sulfoxide was carried out in this work by isothermal calorimetry titration methods, UV spectrophotometry, potentiometric titration at *T*=298.15.



With an increase in ethanol concentration, there is a tendency to decrease the stability of the [Ni 18C6]²⁺ complex. In contrast, the stability of the [Ag18C6]⁺ complex in water-ethanol solvents increases.

Under the experimental concentration conditions used, limited by the low solubility of M1 in ethanol, the formation of an M1 complex with nickel (II) and silver (I) cations ($\lg K [\text{Ni M1}]^{2+} = 3.44 \pm 0.35$ and $\lg K [\text{Ag M1}]^+ = 3.73 \pm 0.24$) was established.

The formation of the [Ag 1-Aza-18C6]⁺ complex in DMSO was established and the thermodynamic parameters of complex formation were determined: $\lg K = 3.1$, $\Delta H = -14.9 \pm 1.2$ kJ/mol, $\Delta S = 10.14$ J/mol K, $\Delta G = -17.88$ kJ/mol.

The analysis of the influence of the composition and nature of solvents on the stability of complexes was carried out from the standpoint of the solvation approach.

The study was supported by the Russian Science Foundation, project 23-23-00526.

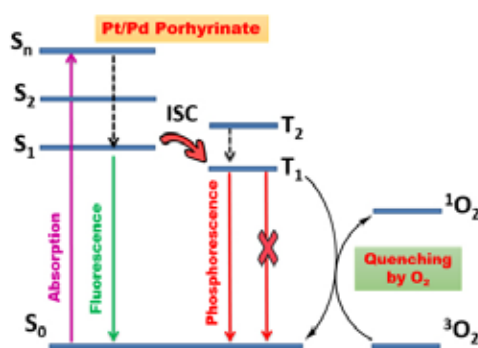
OPTICAL NANOSENSORS BASED ON PALLADIUM(II) AND PLATINUM(II) PORPHYRINATES FOR THE DETERMINATION OF DISSOLVED OXYGEN IN LIVING SYSTEMS

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Real-time measurement of dissolved oxygen (DO) concentration in living systems is an urgent problem for modern science and many areas of physiology and medicine. Among the known classical approaches (iodometric titration, electrochemical, colorimetric) optical methods based on luminescence lifetime detection allow one to work within a wide range of the O₂ concentrations, provide the possibility of more accurate determination without destroying the analyte. Among the oxygen-sensitive phosphors, metal complexes of Pt(II) and Pd(II) with porphyrins are among the most popular.^{1,2} Such tetrapyrrole molecules have intense absorption in the UV (370-420 nm) and visible (500-570 nm) regions, as well as bright, well-resolved emission in the near-infrared range (650-750 nm) with lifetimes in the range of 10-1000 μ s, which persists at room temperature and in aqueous solutions. The optical and chemical properties of the optodes based on tetrapyrrole complexes can be fine-tuned by the modifying of porphyrin structure as well as changing of their microenvironment, including hybrid structure formation.



The present report will provide an overview of the Pt(II) and Pd(II) porphyrinates employed in the optical oxygen sensors. It will outline the most crucial requirements for the modern optodes allowing DO determination in the living systems. The current methodologies for the modification of organic phosphors, including the preparation of hybrid nanostructures, which afford the transition from *in vitro* to *in vivo* O₂ detection, will be discussed.

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SUPRAMOLECULAR ASSEMBLY OF ULTRATHIN HYBRIDS BASED ON GRAPHENE OXIDE AND ZINC PORPHYRINATE FOR ORGANIC ELECTRONICS

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Hybrids based on graphene oxide (GO) and macrocyclic chromophores are promising materials for use as absorbing layers in organic photovoltaic devices. Graphene oxide can act as both electron acceptor and electron donor, initiating charge transfer in the system. The large number of oxygen-containing groups on the surface of the sheets gives graphene oxide the properties of a surfactant and allows controlled grafting of a wide range of organic compounds to them using both covalent and non-covalent bonds. This enables the GO sheets to act as a structuring template for the assembly of ultrathin hybrids compatible with common photovoltaic device architectures. Among the chromophores, porphyrins and phthalocyanines have the greatest potential due to their ability to absorb light in a wide wavelength range; however, due to their high aggregation tendency, the structure variation of hybrids based on them is very limited. Meanwhile the electrophysical properties of hybrids largely depend on their structure, since it determines the efficiency of energy/charge transfer between the components. The aim of this work is to study the dependence of the photophysical properties of hybrids based on GO, zinc tetracarboxyphenyl-porphyrinate and diacetylene surfactant on the porphyrin packing in the layer. A hybrid, in which porphyrin is uniformly distributed in the GO layer but does not form an ordered structure, was obtained by a one-step self-assembly method at the air/water interface. In the hybrid obtained by layer-by-layer liquid epitaxy, the porphyrin is organized into an ordered monolayer on the surface of the GO layer. Comparison analysis of the volt-ampere characteristics of electric cells based on the obtained hybrids showed that the efficiency of cells of the second type is higher, which may be due to the directional charge transfer between the components. The obtained results indicate the possibility of controlling the properties of organic photovoltaic cells by changing the structure of the absorbing layer.

The work is supported by Russian Science Foundation (№ 23-73-00095).



PHOTOCATALYTIC REAGENTLESS SENSOR SURFACE BASED ON PHTHALOCYANINES AND PLASMONIC STRUCTURES

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One of the promising directions of modern bioanalytical chemistry is the development of reagentless optical sensor elements (no reagents need to be added externally except for analytes) based on enzymes or their mimetics for the determination of a wide range of biologically active substances.

Sensor systems and methods to increase the rapidity of analysis, its accuracy, sensitivity, while ensuring its simplicity are being actively sought.

Surface-enhanced Raman spectroscopy is one of the promising methods for solving these problems. This method allows to identify analytes in complex matrices with high sensitivity (at the level of single molecules) without preliminary sample preparation.

In this case, to expand the possibilities of SERS, the capability to detect compounds whose bond vibrations don't appear or have a low intensity in the Raman spectrum is of particular interest at present. Examples of such compounds are classical indicator molecules in biocatalytic sensor systems based on oxidoreductases such as o-phenylenediamine (o-PDA) and 3,3',5,5'-tetramethylbenzidine (TMB).

In the present work, we have developed an ultrathin reagentless photocatalytic SERS-sensor system based on the sodium salt of zinc octa (3',5'-dicarboxyphenoxy) phthalocyaninate, which was immobilized on a graphene oxide modified surface, and silver nanoparticles. The photocatalytic activity of zinc phthalocyaninate in reactions of oxidation of o-PDA and TMB under visible light and the possibility of detection of oxidized forms of these biocatalytic indicators by SERS method were demonstrated.

This work was financially supported by The Russian Science Foundation, Agreement 23-73-00095.

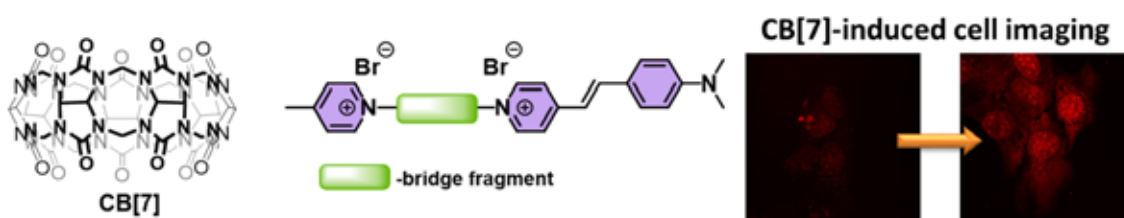
CUCURBITURIL-BASED FLUORESCENCE SUPRAMOLECULAR ASSEMBLIES OF STYRYL DYES IN SOLUTION AND LIVING CELLS

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Cucurbit[n]urils (CB[n]) as macroheterocyclic host molecules are promising compounds for application in biological chemistry and medicine owing to their good water solubility, high binding constants with guest molecules, negligible cellular toxicity at high doses, ability to cross cell membranes and absence of crossing the blood-brain barrier.¹ DNA–CB[n] supramolecular systems make a successful impact in numerous bio-related fields, such as drug and gene delivery, governing of the DNA-binding mode of small molecules, DNA photocleavage, fluorescent and electrochemical sensing, fluorescent cell-imaging, and other.²



In our investigation, dicationic styrylpyridinium dyes distinguishing by a bridge fragment connecting pyridinium rings and possessing different binding modes with CB[7] and DNA were used. The formation of a ternary system or a system with the relocation of the dye between host molecules are observed depending on the dye bridge fragment. A series of experiments such as UV/vis and fluorescence titrations, competitive displacement assays, CD spectral analysis and NMR techniques were performed to confirm the supramolecular interactions. Fluorescence signal of supramolecular systems was tested in solution and living systems using cancer cell line of mouse. The work significantly contributes to the combination of chromophoric molecules and supramolecular macroheterocycles for bioimaging.³

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FIRST EXAMPLE OF USING BINAPHTHYL-SUBSTITUTED RUTHENIUM PHTHALOCYANINATES AS CATALYSTS FOR ENANTIOSELECTIVE CYCLOPROPANATION

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Phthalocyanine complexes are widely used as catalysts for various types of reactions,¹ but despite the wide range of known chiral phthalocyanines,² their application in enantioselective catalysis is limited to single examples³. Herein di-R-binaphthoxy-substituted ruthenium phthalocyaninate (BNP)₂PcRuCO was synthesized for the first time and its catalytic activity was explored in carbene transfer reactions from diazoacetates N₂CHCO₂R (R = Et, tBu, Bn) to the C=C bond of styrene. Despite the remoteness of the chiral groups from the catalytic center, significant diastereo- and enantioselectivity was observed, that allowed to obtain substituted cyclopropanes with trans/cis ratio up to 98:2 and *ee*_{trans} up to 69%.



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TUNING CYTOTOXIC PROPERTIES OF PHOSPHORUS(V) PORPHYRINS

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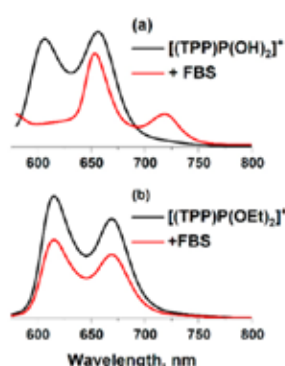


Fig. 1. Emission spectra of PorPs in PBS before and after addition of FBS (48h, 37°C).

Meso-substituted phosphorus (V) porphyrins are promising photosensitizers.¹ Recently, the dephosphorylation of P(V) *meso*-mono-pyridyl- porphyrin with axial OH-groups [(MPyP)P(OH)₂]⁺ in the presence of proteins in cells was demonstrated.² Therefore this fact can be used for the delivery of free-base porphyrins inside cells.

This study demonstrated that tetra-*meso*-substituted P(V) porphyrins (with the number of -Py n=0-2) with axial -OH groups undergo dephosphorylation at pH = 7.4 in the presence of FBS, as evidenced by the change in fluorescence (Fig. 1a). In contrast, similar complexes with axial -OEt and -OPrOH groups remained in the initial state (Fig. 1b).

Using dephosphorylation of hydroxyl-complexes in cells, the cytotoxicity of free-base porphyrins and their complexes can be compared. P(V) complexes exhibit greater light-induced cytotoxicity than corresponding free-base porphyrins. Among them, [(TPP)P(OEt)₂]⁺ and [(MPyP)P(OEt)₂]⁺ are the most promising for PDT, with nanomolar IC₅₀ values.

Compound	IC ₅₀ dark, μM	IC ₅₀ light, μM	IF	Compound	IC ₅₀ dark, μM	IC ₅₀ light, μM	IF
[(TPP)P(OH) ₂] ⁺	1.60	0.40	4.0	[(TPP)P(OEt) ₂] ⁺	0.22	0.010	22.6
[(MPyP)P(OH) ₂] ⁺	5.82	0.60	9.7	[(MPyP)P(OEt) ₂] ⁺	0.21	0.011	19.1
[(DPyP)P(OH) ₂] ⁺	16.3	4.34	3.8	[(DPyP)P(OEt) ₂] ⁺	0.10	0.092	1.1
				[(MPyP)P(OPrOH) ₂] ⁺	3.25	0.31	10.5

Table 1. IC₅₀ value and phototoxicity index for IC₅₀ complexes on A-549 cells, 72 h of incubation, MTT assay.

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ANIONIC COMPLEXES OF FLUORINATED COPPER (II) PHTHALOCYANINES: CRYSTAL STRUCTURES, OPTICAL AND MAGNETIC PROPERTIES

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Phthalocyanines (Pcs) are a family of macrocyclic compounds used as industrial dyes, currently investigated as materials for optical, electronic, and photoelectronic devices, catalysts, etc. Their properties can be effectively tuned by variations of the central atoms, axial ligands, and macrocycle substituents yielding macrocycles with potentially wide applications. Another strategy to tune the properties of Pcs is their oxidation or reduction forming species with an unpaired electron delocalized over the macrocycle. Acceptance of additional electrons by the macrocycles under reduction provides new properties since unpaired spin can participate in the magnetic coupling of spins or high conductivity. Metallomacrocycles with paramagnetic central metal atoms are of special interest since spin localized on metals can interact with electrons delocalized over the macrocycles.

We studied gradual one- and two-electron reductions of $\text{Cu}^{\text{II}}(\text{F}_x\text{Pc})$ ($x=8, 16, 64$) (Figure 1) to form mono- and dianion species, respectively. A series of complexes based on paramagnetic $[\text{Cu}^{\text{II}}(\text{F}_x\text{Pc}^{\cdot 3-})]^-$ and $[\text{Cu}^{\text{II}}(\text{F}_x\text{Pc}^{4-})]^{2-}$ anions was obtained as crystals.¹

We studied and compared the effect of reduction on molecular structure, optical and magnetic properties of the fluorinated copper(II) phthalocyanines including the partial or full fluorine substitution and the introduction of bulky extremely electron-withdrawing perfluoroisopropyl (C_3F_7) groups. Reduction is mainly centered on the macrocycles yielding $[\text{Cu}^{\text{II}}(\text{F}_x\text{Pc}^{\cdot 3-})]^-$ and $[\text{Cu}^{\text{II}}(\text{F}_x\text{Pc}^{4-})]^{2-}$ species with two (Cu^{II} and $\text{F}_x\text{Pc}^{\cdot 3-}$) and one (Cu^{II}) paramagnetic centers, respectively. The structural, optical, and magnetic properties of the new materials reveal trends imparted by electrons addition and degree of fluorination in phthalocyanines.

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STRUCTURAL FEATURES OF PHOSPHOROUS (V) PHTHALOCYANINE WITH DIFFERENT COUNTERIONS

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Phosphorus (V) phthalocyanines (PcPs) are promising photosensitizers for biomedical applications due to their absorption in visible and near-IR range of spectrum, intensive fluorescence and efficient reactive oxygen species generation.¹⁻⁴ However, they remain exotic and rarely studied compounds.

Phosphorus introduction into the macrocycle causes specific structural features, in particular distortion of the molecule. There are several reasons for macrocycle distortion: small ionic radius of phosphorus, nature and position of porphyrinoid substituents, nature of axial ligands on P(V), however no attention was earlier paid to the counterions nature.

In this work for the first time we systematically studied a series of cationic P(V) phthalocyanines [PcP(OMe)₂]⁺ with different anions: I⁻, CF₃COO⁻, TsO⁻, BPh₄⁻, CF₃SO₃⁻, HCOO⁻. All compounds were characterized by set of methods and we succeeded to grow single crystals for each complex. Single crystal XRD (SCXRD) allowed us to determine macrocycle distortion and analyze structural features for the same phosphorus(V) complex with different anions. The degree of Pc core ruffling depends on the anion and increases in the following row: I⁻ < CF₃COO⁻ < HCOO⁻ ≈ CF₃SO₃⁻ < TsO⁻ << BPh₄⁻.

The bond lengths of Pc core were analyzed by the harmonic oscillator model of aromaticity (HOMA). HOMA indices are close for all structures and none of them loses its aromaticity during distortion.

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DEVELOPMENT OF METHODS FOR OBTAINING HYBRID SYSTEMS BASED ON GRAPHENE OXIDE AND ZINC PHTHALOCYANINATE

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This work presents a novel approach to non-covalent self-assembly of hybrid systems, which can be utilized as photocatalysts, based on graphene oxide (GO) and 2,3,9,10,16,17,23,24-octa[(3,5-sodium biscarboxylate) phenoxy] zinc (II) phthalocyaninate (ZnPc₁₆). Previously, the possibility of generation of singlet oxygen by ZnPc₁₆ has been investigated [1]. It has been demonstrated that this method allows the synthesis of hybrid materials comprising porphyrin metal-organic framework structures and GO, while simultaneously conferring the requisite stability and high photocatalytic activity to the materials [2].

Using a set of physicochemical analysis methods (SEM, fluorescence microscopy, PRD, etc.), the morphology and structure of the obtained hybrid materials were studied and the successful integration of ZnPc₁₆ with GO nanosheets was confirmed. According to UV-visible spectrophotometry data, it was found that the hybrid material obtained by the formation of coordination bonds between the components using the coordinating metal cluster Zn(OAc)₂ is able to exhibit photocatalytic activity in oxidative photodegradation reactions of organic substrates (rhodamine 6G, 1,5-dihydroxynaphthalene, 1,4-nitrophenol). At the same time, the material obtained by aromatic stacking of the system components did not exhibit photocatalytic activity at all.

The results obtained showed that the method of non-covalent assembly of hybrid material using metal cluster as a binding component allows to obtain more stable and efficient photocatalysts.

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This work was supported by the Russian Science Foundation (project No 23-73-00095).

MAGNETIC ANISOTROPY OF HOMO- AND HETERONUCLEAR Tb(III) AND Dy(III) TRISPHTHALOCYANINATES DERIVED FROM PARAMAGNETIC ¹H-NMR INVESTIGATION

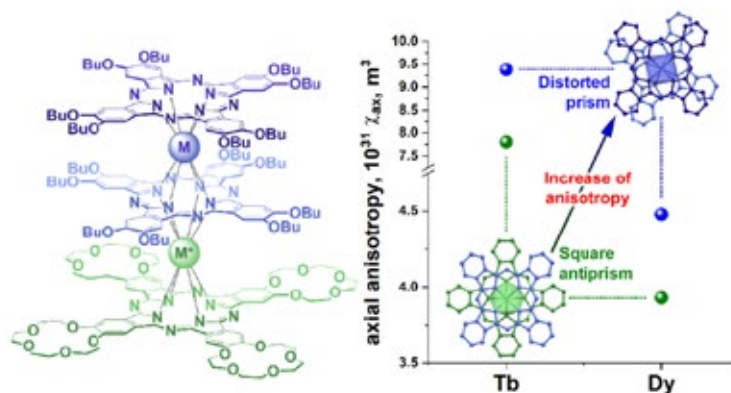
**Kormshchikov I.D.,^a Polovkova M.A.,^a Kirakosyan G.A.,^{a,b} Martynov A.G.,^a
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¹H-NMR spectroscopy of lanthanide complexes is a powerful tool for deriving spectral–structural correlations, providing a clear link between the symmetry of the coordination environment of paramagnetic metal centers and their magnetic properties. In the present work we provide an algorithmic approach for the analysis of the ¹H-NMR spectra of a series of homo- (M = M* = Dy) and heteronuclear (M ≠ M* = Dy/Y and Dy/Tb) triple-decker complexes [B₄]M[B₄]M*[C₄] containing octa-β-butoxy- and tetra-15-crown-5-substituted phthalocyanine ligands - [B₄] and [C₄], respectively.

The synthesized complexes exhibited pronounced solvatochromic properties associated with the switching of the “[B₄]M[B₄]” fragment from the staggered state in toluene to the gauche state in halogenated aliphatic solvents. Application of ¹H-NMR allowed to extract the axial component of the magnetic susceptibility tensor, χ_{ax} and show how this term is related to the nature of the lanthanide ion and distortion of its coordination polyhedron, providing an experimental basis for further theoretical interpretation of the revealed correlations.



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SILICON PHTHALOCYANINES AND TETRABENZOTRIAZACORROLES

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Tetrapyrrole complexes are among the most promising compounds in terms of their application in solar cells and generation of reactive oxygen species in living cells^{1,2}. A distinctive feature of silicon phthalocyanines and tetrabenzotriazacorroles is the presence of axial positions of Si(IV). The characteristics of macrocycles can be altered, opening new possibilities for the development of hybrid materials based on them, by inserting different types of substituents into these positions (Fig. 1)³.

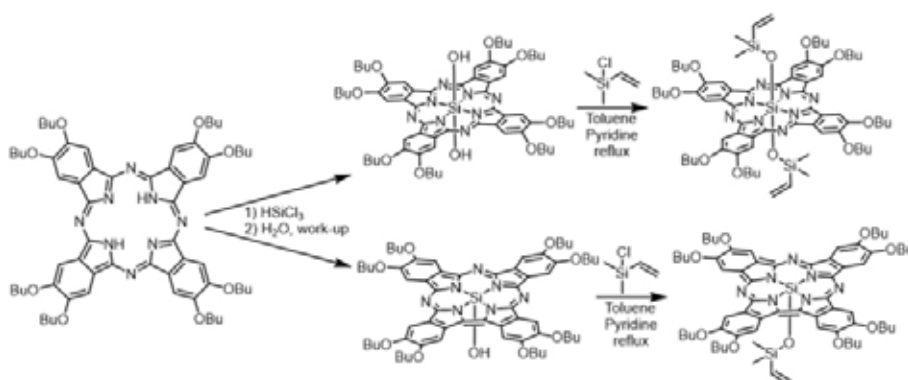


Fig. 1. Synthesis of silicon phthalocyanines and tetrabenzotriazacorroles

In this work, new silicon complexes based on phthalocyanines and tetrabenzotriazacorroles containing substituents of different nature in peripheral, non-peripheral, and axial positions have been synthesized. The structure - photophysical properties relationship has been established for a number of synthesized compounds. The obtained complexes were characterized by MALDI-TOF mass spectrometry, UV, ¹H, ¹³C NMR spectroscopy.

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DESIGN OF NEW PYRAZINOPORPHYRAZINES AND QUINOXALINOPORPHYRAZINES

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This report presents the development of approaches for the preparation of new octa-carboxyphenyl-substituted pyrazinoporphyrazines (MPyzPzR₈) and quinoxaline-porphyrazines (MQPzR₈), their ester derivatives, sodium salts, acids and metal complexes.¹⁻²



Patterns of change in the aggregation behavior of synthesized macroheterocycles in solutions as a function of the nature of the substituents and the solvent have been found, allowing control of the photophysical properties of the complexes. It was shown that quinoxalinoporphyrazines can act as photosensitizers for singlet oxygen generation. In combination with the absorption in the near-infrared therapeutic window and the higher stability compared to naphthalocyanines, this determines the prospects of the obtained quinoxalinoporphyrazines as photosensitizers for PDT.

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SYNTHESIS AND PHOTODYNAMIC ACTIVITY OF NEW
TETRACATIONIC ZINC PHTHALOCYANINATES

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Phthalocyanines are promising photosensitizers for photodynamic therapy (PDT). In our work, new non-aggregating water-soluble tetracationic zinc phthalocyaninates were obtained using reductive amination (Fig. 1)¹.

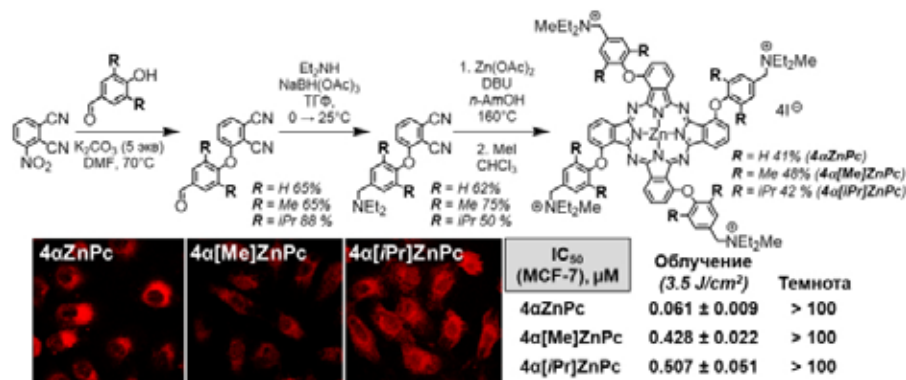


Figure 1. Synthesis, intracellular accumulation and PDT activity of of new tetracationic zinc phthalocyaninates.

The obtained complexes **4aZnPc**, **4a[Me]ZnPc** and **4a[iPr]ZnPc** exhibit high photodynamic activity against MCF-7 cells. Thus, they can be considered prototypes of effective photosensitizers for PDT.

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THE EFFICIENCY OF AMBIVALENT PHOTOCATALYSTS BASED ON PORPHYRINIC SURMOF AND GO

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Heterogeneous photocatalysis holds great promise for solving the energy crisis and reducing the anthropogenic burden on the environment by using sunlight as an unlimited source of energy to produce new chemical products, reduce CO₂ emissions and treat wastewater. However, its low efficiency remains a major limitation for its large-scale application.

In this work, a hybrid material consisting of graphene oxide (GO) and a surface-attached metal-organic framework (SURMOF) based on meso-tetra(pyridyl)zinc(II) porphyrinate (ZnTPyP) assembled by non-covalent assembly in Pickering emulsion is proposed as an efficient photocatalyst.

According to the data obtained by X-ray diffraction analysis, UV-Vis spectroscopy and MALDI-TOF mass spectrometry, the SURMOF/GO hybrid can utilize two different mechanisms to produce different products for the photocatalytic degradation of 1,5-dihydroxynaphthalene (DHN). Porphyrin centers provide oxidation through photoinduced formation of ¹O₂ in the presence of oxygen. Under anaerobic conditions, SURMOF/GO promotes reduction through direct electron transfer to substrates in the pores of SURMOF.

The potential to enhance photocatalysts efficiency by applying a non-contact external electric field (EEF) is of significant interest. Research has shown that applying an EEF with an intensity of up to 4 kV can double the rate of photodegradation of DHN, regardless of environmental conditions.

The results obtained are the basis for the development of substrate-selective hybrid photocatalysts with synergetic photocatalytic activity.

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NEW *O*-XYLENEDIAMINE BASED SALEN-TYPE LIGAND FOR 3d METAL COMPLEXES FORMATION OF VARIOUS NUCLEARITY

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Salen-type ligands are widely used in coordination chemistry, due to two *endo*-oriented salicylideneamine moieties capable to accommodate different number of metal cations. These complexes are of particular interest and still attract much attention, owing to various functions that they can exhibit. In this respect, one can notice the complexes involving on 3d metals displaying single-molecule magnet behavior, spin-crossover or catalytic activity [1-4].

In contrast to conventional salen type ligands based on *o*-phenylenediamine derivatives, the use of *o*-xylenediamine molecular platform, displaying more flexible conformational behavior, can results in a variety of motifs of coordination compounds upon binding with 3d-metals.

In this work the synthesis of new salen like ligand based on *o*-xylenediamine functionalized by salicylideneamine coordinating sites is presented. The obtained compound was found to be prone to form complexes of various nuclearity (mono-, di-, and tri-) when binding with 3d metal ions, such as Cu(II), Ni(II), Fe(III), Mn(III). The crystal structures of obtained coordination compounds will be discussed.



Figure №1. New *o*-xylenediamine based ligand, demonstrating salen like coordination pocket and its complexes of various nuclearity with 3d metals.

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CONDUCTING POLYPORPHYRIN FILMS BASED ON AMINO-SUBSTITUTED TETRAPHENYLPORPHYRINS WITH VARIABLE AMOUNTS OF AMINO-PHENYL SUBSTITUTENTS

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Recent research into the development of new materials is increasingly aimed at the use of macroheterocyclic compounds and their metal complexes as monomers for the production of conducting polymers [1, 2]. Among a number of macrocyclic ligands, special attention has been focused on porphyrins with certain substituents [3]. This is due to the fact that, after polymerization, porphyrins form a conductive polymer film, which has a number of practically useful properties.

The purpose of this work is to examine the effect of substituents in the porphyrin macrocycle on the process of electrochemical formation and electrical conductivity of polyporphyrin films using the example of amino-substituted tetraphenylporphyrins. The process of electrodeposition of polyporphyrins was studied using cyclic voltammetry from solutions in ethanol. The physicochemical properties of the films were determined by spectroscopic methods, and the surface morphology was studied using scanning electron microscopy.

The semiconductor properties of the films were assessed by the value of the optical band gap calculated on the basis of the electronic absorption spectra of the films. The optical band gap was determined based on the dependence of the absorption of films near the wavelength of the absorption edge in Tauck coordinates.

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WATER SOLUBLE NEAR-IR PHOTOINITIATOR BASED ON P(V) PHTHALOCYANINE WITH GALACTOSE FRAGMENTS

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The search for a new water soluble photoinitiators with absorption in the therapeutic window for biophotonics is a crucial task of modern chemistry. Previously, it was demonstrated that the P(V) 15-crown-5-phthalocyanine bearing diethylene glycol monoethyl ether as axial ligand, which exhibits low cytotoxicity and high yield of ROS generation, can be used as a non-toxic photoinitiator.¹

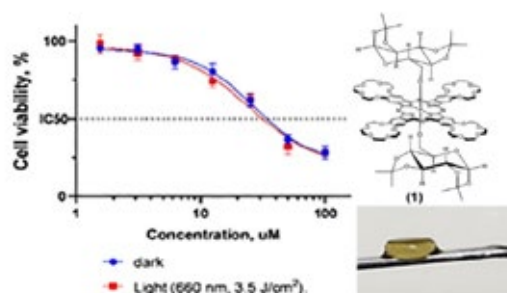


Fig. 1. Dark and light cytotoxicity curves in MCF-7 tumor cell culture, MTT test, 72 h incubation.

In this work we developed an approach for the synthesis of a new phosphorus (V) tetra-15-crown-5-phthalocyanine bearing two galactose fragments as axial ligands (**1**). The resulting compound **1** demonstrated good solubility in water and organic solvents, absorption and fluorescence in the near-IR region of the spectrum ($\lambda_A = 716$ nm, $\lambda_F = 735$ nm, $\Phi_F = 0.09$, DMSO), and the ability to generate singlet oxygen ($\Phi_A = 0.20$, DMSO). Studies on human carcinoma cells showed low both dark ($IC_{50} = 26.59 \pm 7.01 \mu M$) and light toxicity ($IC_{50} = 24.62 \pm 5.21 \mu M$) (Fig. 1). In conjunction with the successful crosslinking of PEG-DA ($M_n = 575$) we concluded that **1** is a promising photoinitiator for photocuring biocompatible materials for tissue engineering.

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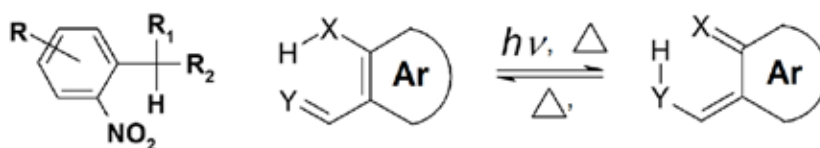
The research was supported by RSF (grant № 24-73-10192).

PROTON PHOTOTRANSFER IN BIS(HETERYL)ALKANES

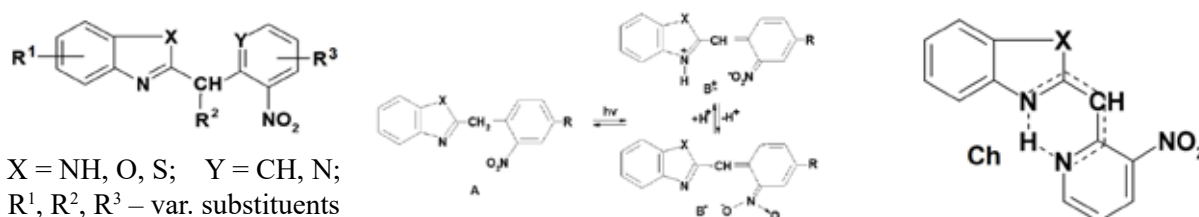
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The photochemical reaction of prototropic isomerization underlies the photochromic transformations of ortho-nitroarylmethyl compounds.



Using the method of pulsed photolysis, the spectral and kinetic characteristics of photoinduced forms of mono-, dinitrobenzyl derivatives of benzazoles and compounds containing a nitro group in a heterocyclic fragment - 2-(3'-nitro-2'-pyridylmethyl)-benzazoles - were studied.



For nitropyridyl-substituted benzazoles, three photoinduced forms have been registered, and not two as in the case of mono- and dinitrobenzylbenzazoles: at pH>10 – anion (B⁻), pH~4 – azamerocyanine (B[±]), pH~1 – monomethine cyanine (BH⁺). When irradiated with light in solutions with pH~4 derivatives of low-basic heterocycles of benzoxazole and benzothiazole form neutral chelates (Ch), in which a hydrogen atom is bonded simultaneously to two nitrogen atoms: pyridine and azole. The introduction of a basic center into the nitrobenzyl chromophore moiety results in an additional photoinduced form and a longer lifetime of the detected photoinduced form.

This work was supported by the Ministry of Science and Higher Education of the Russian Federation (state assignment FSEN-2023-0002).

MIXED PORPHYRIN FILMS DEPOSITED FROM SOLUTION: OPTICAL AND CHARGE-TRANSPORTING PROPERTIES

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Etioporphyrins are large macrocyclic tetrapyrroles, the closest analogues of natural chlorophyll and heme. Availability, thermal stability and photophysical properties are driving research into the use of these fascinating molecules and their closest analogues in optoelectronic devices, particularly in photovoltaic cells of various type.¹

In this work, we studied the absorption spectra and photoconductivity of two-component thin films obtained by spin-coating the toluene solution of a mixture of indium(III) chloride etioporphyrin-I InCl-EtioP-I as a donor (Fig. 1), with several small acceptor molecules, such as Cl₆SubPc, TPATDI, Green 36 or MnCl-EtioP-I. Molar concentrations, component ratios and deposition conditions for each D/A blend were carefully adjusted to achieve optimal structural quality and specific conductivity of molecular layers.

It was found that InCl-EtioP-I:Cl₆SubPc and InCl-EtioP-I:TPATDI mixtures with a ratio of 4:1 form continuous layers with high photoconductivity, and for the InCl-EtioP-I:Green 36 mixture this ratio is equal to 8:1. In the latter case, the photo-to-dark current signal is the highest ($\sim 1.6 \times 10^2$ under 1sun illumination), despite the weak optical absorption in the porphyrin “green gap” region – Fig. 1.

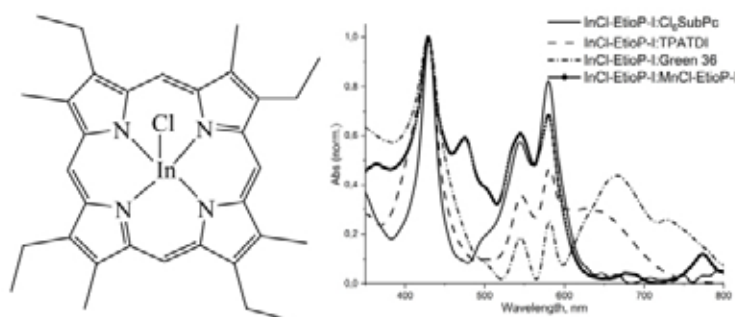


Figure 1. Molecular structure of the InCl-EtioP-I and absorption spectra of mixed layers deposited by spin-coating on sapphire substrates

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SYNTHESIS OF PORPHYRIN SENSITIZERS FOR SOLAR CELLS

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The development of various porphyrin derivatives for use in photovoltaic devices, such as dye-sensitized solar cells (DSSCs) or Gretzel cells, has been a topic of great interest for scientists for several decades¹.

Porphyrin photosensitizers suitable for DSSCs must have an "anchor" substituent, generally a carboxyl group, which is necessary to bind the photosensitizer to the semiconductor surface. In addition, a coupling between the π -system of the macrocycle and the "anchor" group is necessary to increase the absorption range and the efficiency of electron transfer, leading to an increase in the efficiency of solar cells².

The aim of this work was to develop photosensitizers based on the zinc complex of 5,10,15,20-tetraphenylporphyrin containing residues of α,β -unsaturated carboxylic acids conjugated to the macrocycle. The chemical modification of the pre-synthesized formyl derivative of tetraphenylporphyrin was carried out using the Wittig and the Knevanagel reactions to obtain the final products.

Thus, the interaction between the formyl derivative and carbomethoxy-methylenetriphenylphosphorane led to the formation of the product with the acrylic acid methyl ester residue predominantly in the *E* configuration. The reaction with diethyl malonate gave rise to the derivative containing the bis(ethoxycarbonyl)vinyl group. Isomerization of the minor *Z*-isomer was carried out using iodine. Demetallization of the copper complex, saponification of the ester groups and the introduction of zinc into the porphyrin macrocycle allowed to obtain target tetraphenylporphyrin derivatives, which were later used as photosensitizers in the dye-sensitized solar cells we designed.

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DESIGN OF NEW 3d METAL DISCRETE COMPLEXES AND COORDINATION POLYMERS BASED ON *BIS*- AND *TRIS*-1,2,3-TRIAZOLYLETHYLAMINE DERIVATIVES

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Polytriazolyl derivatives are convenient ligands for the preparation of crystalline coordination compounds capable of exhibiting various physical properties, such as magnetic (molecular magnetism, spin crossover) or catalysis [1,2].

This work focussed on the target synthesis of new discrete complexes and coordination polymers using combination of a series of *bis*- and *tris*-[2-(1,2,3-triazol-1-yl)ethyl]amine derivatives, demonstrating *endo* and *exo* orientation of triazolyl binding sites, respectively, with different 3d metal ions (Cu^{II} , Co^{II} , $\text{Fe}^{\text{II/III}}$) (Fig. 1). As a result, new supramolecular architectures, presenting the formation of *bis*-chelate discrete complex, 1D chain or 2D honeycomb-like coordination polymers were generated in the crystalline phase and studied using single-crystal X-ray diffraction. It was established that conformational behaviour of the studied triazolyl containing ligands influences on the crystal structures of the obtained complexes.



Figure №1. Design of crystalline 0D-2D coordination compounds.

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This work was supported by Russian Science Foundation (grant № 22-73-10139).

NEW SUPRAMOLECULAR NANOCONTAINERS BASED ON SULFONYLCALIX[4]ARENE 3d METAL CLUSTERS AND CHIRAL 5-HYDROXYISOFTALIC ACID DERIVATIVES FOR MOLECULAR RECOGNITION

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Molecular coordination cages (or containers) based on sulfonylcalix[4]arene supported 3d metals clusters present attractive metallo-supramolecular materials, which binding properties towards different guest molecules can be tuned up by varying the geometry and nature of organic polytopic carboxylic linkers[1]. The functional derivatives of 5-hydroxyisophthalic acid are suitable linkers for the formation of coordination cages with controlled molecular recognition ability. [2-3].

This work focusses on the synthesis and structural study in solution and crystalline phase of new enantiomerically pure supramolecular nanocontainers resulting from the combination of chiral derivatives of 5-hydroxyisophthalic acid with *in situ* generated sulfonylcalix[4]arene supported [M^{II}₃] and [M^{II}₄] 3d metal clusters (M=Co, Ni, Zn). The preliminary adsorption properties of obtained porous coordination species towards different guest molecules such as organic dyes and chiral amines and aminoacids will be presented and discussed.

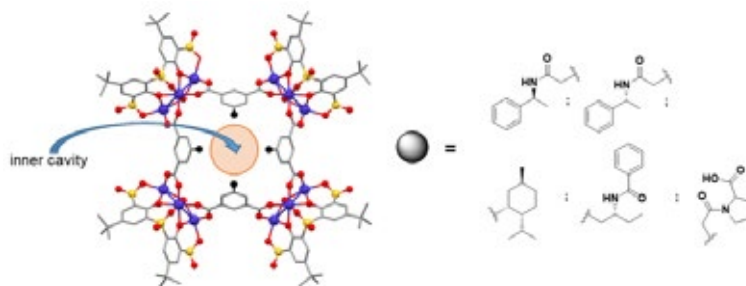


Figure 1. New supramolecular nanocontainers based on combination of sulfonylcalix[4]arene supported 3d metals clusters and enantiomerically pure 5-hydroxyisophthalic acid for tunable molecular recognition.

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NON-COVALENT SELF-ASSEMBLY OF HYBRID MULTIMODAL CATALYSTS BASED ON ORGANIC CHROMOPHORES AND LOW-DIMENSIONAL INORGANIC NANOPARTICLES

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Porphyrin-based metal-organic frameworks (MOFs) are functional coordination polymers with a unique combination of high porosity with catalytic and optical activity, which makes MOFs a potential basis for the creation of new materials for heterogeneous catalysis and photocatalysis. Such hybrid catalysts can be obtained by self-assembly of MOF on the surface of two-dimensional inorganic nanoparticles in the form of thin films (SURMOFs) through multiple noncovalent interactions, yielding mechanically and chemically stable materials with synergistic properties. In this work, the non-covalent self-assembly method was used to synthesize hybrid materials based on 5,10,15,20-tetrakis(4-carboxyphenyl)zinc porphyrinate (ZnTCPP) and two-dimensional nanosheets of molybdenum disulfide MoS₂ and layered europium hydroxochloride (LEuH). ZnTCPP-based SURMOF is integrated with the surface of nanosheets via intermolecular interactions between the material components and the anchoring adsorption layer of zinc acetate metal clusters. The obtained hybrid material SURMOF/LEuH demonstrates the properties of an artificial enzyme, an analog of phosphodiesterase, in the model reaction of bis(4-nitrophenyl)-phosphate hydrolysis. At the same time, the hybrid material SURMOF/MoS₂ performs in a model reaction of photodegradation of 1,5-dihydroxynaphthalene as a multimodal photocatalyst, controllably switching between 3 modes of catalysis¹. In summary, we believe that the noncovalent self-assembly method opens up a wide range of opportunities for the development of new multicomponent hybrid materials on planar solid supports.

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SYNTHESIS OF A NEW WATER-SOLUBLE PHTHALOCYANINE WITH 32 CARBOXYLATE GROUPS

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Phthalocyanines are promising photosensitizers for photodynamic therapy due to their favorable photophysical properties and the possibility of relatively simple modification. However, the low solubility in aqueous media and the tendency to aggregate in aqueous media of compounds of this class impair their photodynamic activity. The introduction of bulk charged substituents allows to increase the solubility of phthalocyanines in water and to prevent their aggregation¹.

In the present work, the sodium salt of zinc phthalocyaninate containing sixteen 3,5-dicarboxyphenoxy groups was prepared (Fig. 1a). The complex obtained remains monomeric in aqueous solutions up to 500 μM (Fig. 1b).

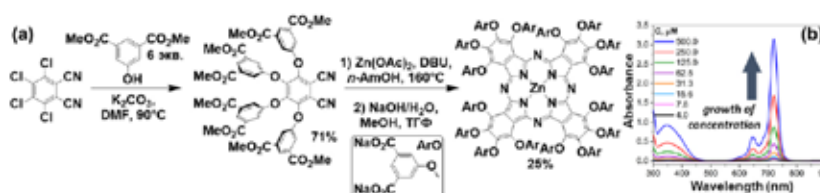


Figure 1. Synthesis of a new phthalocyanine with 32 carboxylate groups.

Our work exemplifies a strategy to prevent aggregation of phthalocyanine photosensitisers in aqueous media by introducing bulk substituents, in order to preserve their photophysical properties.

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This work was financially supported by Russian Science Foundation (№ 24-13-00479).

STRUCTURAL DIVERSITY AND RELATED SPIN PROPERTIES STUDY FOR NEW SULFONYLCALIX[4] ARENE SUPPORTED DI-AND TETRANUCLEAR Fe(III) COMPLEXES

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Sulfonylcalix[4]arene is attractive macrocyclic compound for design of various metallosupramolecular architectures, due to its conformational flexibility and high coordinating ability, providing four OH- and SO₂ coordinating sites [1,2]. Despite a lot of examples of complexes based on tetrasulfonylcalix[4]arene and 3d metal ions (Co^{II/III}, Zn^{II}, Ni^{II}) are widely encountered in the literature, there are only few complexes, involving Fe(III) cations, which is of particular interest for the magnetic properties studies.

In this work, we report on the synthesis and crystal structures of new polynuclear Fe(III) complexes based on tetrasulfonylcalix[4]arene, which motif can be tuned up by the switching the macrocycle conformation (*cone* or *1,2-alternate*) and involvement of different *N,N*-donor coligands (Fig.1). The spin properties of obtained polynuclear Fe(III) complexes was studied by ⁵⁷Fe Mössbauer spectroscopy.

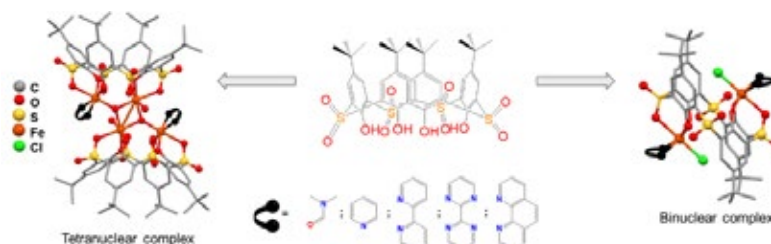


Figure 1. The formation of new Fe(III) complexes based on sulfonylcalix[4]arene and various *N,N*-donor coligands.

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FIRST EVIDENCING OF SIMULTANEOUS SOLVENT AND TEMPERATURE INDUCED SPIN TRANSITIONS IN A SERIES OF NEW Fe(III) COMPLEXES BASED ON DIIMINE DERIVATIVES OF (THIA)CALIX[4]ARENES WITH CONTROLLED STRUCTURE

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Control over spin states of the crystalline metallocusters, especially those based on 3d cations, can contribute to revolution in development of the quantum computing [1] or external stimuli responsive switchable devices[2].

In this report, the control over the motif and metal coordination sphere of Fe(III) complexes based on (thia)calix-arene Schiff base ligands was performed due to alkyl spacer length variation and insertion of EDG or EWG into iminophenolic coordinating sites. As a result, the irreversible solvent-induced Low Spin (LS) to High Spin (HS) transition both with reversible thermal spincrossover was firstly evidenced for Fe(III) complexes based on calix[4]arene, which was attested by ⁵⁷Fe Mössbauer spectroscopy.

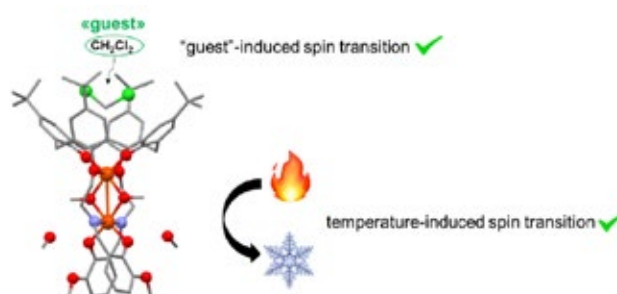


Figure 1. Fe(III) complex, based on diamine derivative of calix[4]arene, shows spin transition.

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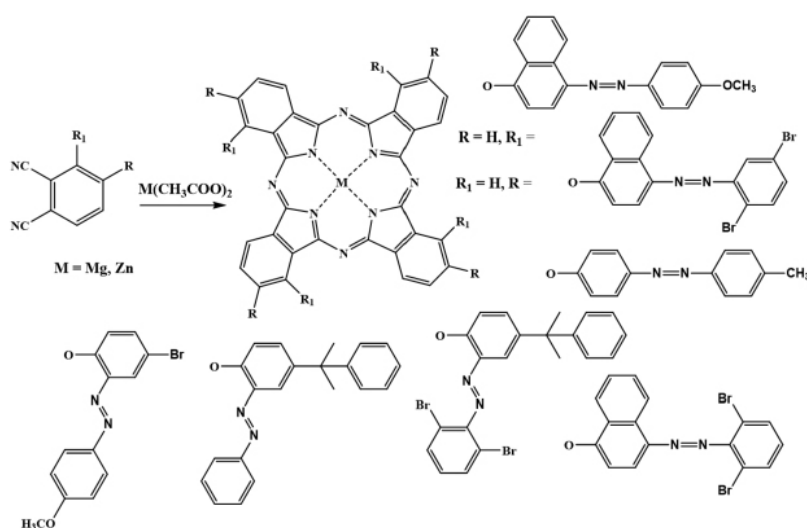
SYNTHESIS AND PROPERTIES OF AZO DYES AND PHTHALOCYANINES CONJUGATES

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The synthesis and design of new phthalocyanines (Pc) containing various peripheral and non-peripheral substituents is an important strategy for the development of science and technology. An interesting direction is the production of conjugates containing two chromophores simultaneously (phthalocyanine and azo- one). The expansion of the light absorption range due to the introduction of an azochromophore into the molecule makes it possible to use phthalocyanines as sensors, materials for solar cells and photosensitizers for PDT.



Metal complexes were synthesized by template condensation of substituted phthalonitrile azo dyes with magnesium or zinc acetates.

Spectral-luminescent properties of synthesized metal complexes in organic solvents have been studied. The influence of the substituent, the metal-complexing agent and the nature of the solvent on the nature of the spectrum, the quantum yield of luminescence and the generation of singlet oxygen is shown.

The work was carried out with financial support of Russian Science foundation, project 22-73-10158.

ENTHALPY CHARACTERISTICS OF SOLVATION OF 1-AZA-18-CROWN-6 IN AQUEOUS-ETHANOL SOLVENT

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In this work, the effect of the composition of a water-ethanol solvent on the solvation of 1-Aza-18-crown-6 (1-Aza-18C6) was studied. The enthalpy characteristics of solvation of 1-Aza-18C6 and 18-crown-6 (18C6) were compared. To determine the heat of dissolution of 1-Aza-18C6, a variable temperature calorimeter with an isothermal shell was used¹. Experimental results are presented in the table 1.

X_{EtOH}	0	0.1	0.2	0.4	0.8
ΔH_{sol} (kJ/mol)	-65.11±0.26	-4.47±0.28	25.55±0.28	36.19±0.26	90.47±0.43

Table 1. Enthalpies of dissolution of 1-Aza-18C6 in a water-ethanol solvent, $T = 298.15$ K

In water and with initial additions of EtOH up to 0.1 mol.fr., the dissolution of 1-Aza-18C6 is accompanied by an exothermic effect, and a further increase in the concentration of EtOH is characterized by endo-effects of 1-Aza-18C6 dissolution and is accompanied by an increase in positive values of $\Delta H_{tr, sol}$ (1-Aza-18C6). In proton donor media, the main contribution to the enthalpy of solvation of crown ethers comes from the hydrogen bond between the oxygen atoms of the macrocycle and the hydrogen atoms of the solvents². The weakening of the solvation of crown ethers in aqueous solutions of ethanol is associated with a decrease in the proton donor properties of the solvent. Enthalpy of transfer of 1-Aza-18C6 from water to a water-ethanol solvent of composition 0.8 mol.fr. EtOH is 155.6 kJ/mol, which is almost three times more than in the case of 18C6³ due to the solvation contribution of the nitrogen atom in the structure of 1-Aza-18C6. The results obtained are necessary for assessing the reactivity of 1-Aza-18C6 in complex formation reactions with d -metals.

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The study was supported by the Russian Science Foundation, project 23-23-00526.

COVALENT IMMOBILIZATION OF CHLORIN e_6 ON CHITOSAN

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Photodynamic therapy is a modern treatment method, the effectiveness of which depends on the amount of photosensitizer (PS) at the site of action. The use of polymeric carriers, such as chitosan, can enhance the effectiveness of PS by improving delivery, bioavailability, as well as their biocompatibility and other beneficial properties¹.

In this study, we conducted covalent immobilization of chlorin e_6 on chitosan. To enhance water solubility and introduce a functional group for covalent binding, N-carboxymethylation of chitosan was performed to obtain the sodium salt of N-carboxymethyl chitosan (N-CMC). Three approaches were used for immobilizing chlorin e_6 derivatives on N-CMC (see Figure 1): by attachment through spacer groups such as epichlorohydrin (i) and 5-bromovaleric acid (ii), and by activating the hydroxyl group in chlorin e_6 derivatives with mesyl chloride (iii).

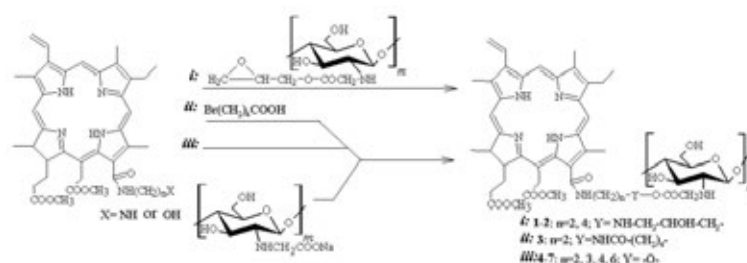


Figure 1. Scheme of covalent immobilization of chlorin e_6 on chitosan

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An abstract visualization of particle interactions or molecular dynamics. It features a dense, swirling mass of small, multi-colored spheres (pink, red, orange, yellow, and purple) against a dark blue background. The spheres are arranged in complex, flowing patterns that suggest a dynamic, energetic process. The overall effect is one of intense, colorful activity.

SYMPOSIUM ON NUCLEAR CHEMISTRY (BRICS+)



PROGRESS OF RADIOCHEMICAL SEPARATION AND ANALYSIS IN CHINA

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Abstract: Separation and analysis of radionuclides is the most basic aspects in many aspects of nuclear industry as well as fields of nuclear technique application. This work summarize the status and progress in China of materials and techniques developed for the separation of radionuclides, including nuclear extractants, extraction chromatographic resins, adsorption materials for radionuclides. The development on instruments and methods for measurement radionuclides are also summarized, including the methods for measure ultra low-level radionuclides and rapid, automated, and on-line measurement techniques. Meanwhile, a comparison on the radiometric technique and mass spectrometric techniques for measurement of long-lived radionuclides are compared. The new challenge on the separation and determination of radionuclides, and the corresponding strategies are also discussion.

IAEA'S PERSPECTIVE ON THE CHEMICAL CHALLENGES OF RADIOACTIVE WASTE ARISING FROM SMALL MODULAR REACTORS

Meyer Willem, Carl Hunter

The International Atomic Energy Agency (IAEA) promotes the safe and peaceful uses of nuclear energy including the management of radioactive waste according to nationally and internationally agreed principles and standards with safe disposal as endpoint for all waste types.

The need to increase access to affordable electricity resulted an increasing interest in small modular reactors that produce electricity of up to 300 MW(e) per module, resulting in more than 80 concepts under development. SMR concepts vary from evolutionary variants of Light Water Reactors (LWR-SMRs, either land or marine based), that benefit from many decades of operating experience of the current fleet of LWRs; High Temperature Gas Cooled Reactors (HTGR-SMRs); Liquid Metal Fast Reactors (LMFR-SMRs) and molten salt reactors (MSR-SMRs). SMR designs use a variety of coolants (e.g., water, liquid metal, molten salts) and fuel forms (e.g., oxide/ceramic, metal, TRISO, liquid fuel salts).

Small modular reactor (SMR) concepts are designed to ensure minimal waste arisings during operation and the establishment of waste management processes to ensure that radioactive waste could be managed safely and cost effectively. However, remarkably few studies have analysed the management and disposal of their radioactive waste streams

The majority of operational low- and intermediate-level (LILW) streams from SMRs will be similar to Nuclear Power plants (NPPs) and will require treatment/conditioning to meet the Waste Acceptance Criteria (WAC) for storage and / or disposal facilities. Many technologies, thermal and non-thermal, are operational world-wide are available to produce stable waste forms suitable for storage and disposal.

As some SMR wastes will be chemical and physical different from waste from NNPs there remain some waste streams from SMRs for which either a suitable technology does not exist or pose additional chemical processing challenges. These includes the chemical radioactive coolants (e.g., metallic sodium, metallic uranium, and uranium tetrafluoride), activated neutron reflectors (beryllium) or shielding materials (graphite), neutron activated and corroded metals. Some of these waste streams t are susceptible to react exothermically when in contact with the disposal conditions (environment) and needs to be treated, conditioned, and appropriately packaged prior to geological disposal. Unfortunately experience regarding the processing and disposal of these chemically unstable waste streams are limited.

The IAEA recognizes the increasing interest in small modular reactors that could produce electricity of up to 300 MW(e) per module to facilitate the increase access to affordable electricity and a such the IAEA has initiated platforms to share waste management information.

The paper conveys the IAEA perspective on processing options for radioactive waste arising from SMRs, including chemical challenges for certain radioactive waste streams that needs to be treated, conditioned, and appropriately packaged prior to geological disposal.

OUTPUTTING OF GENERAL AND MEDICAL RADIOISOTOPE PRODUCTS IN UZBEKISTAN

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Outputting of radioisotope products for general and medical purposes has historically been one of the activities of the Institute of Nuclear Physics of the Academy of Sciences of the Republic of Uzbekistan, which consolidates the following areas: outputting of radioisotope products, production of radiopharmaceuticals based on these radioisotopes, sale of isotope products for nuclear medicine, industry and scientific research.

Currently, the Institute of Nuclear Physics of the Academy of Sciences of Uzbekistan produces phosphorus-32, phosphorus-33, sulfur-35, mercury-203 and iron-55, etc., used in industry and scientific research, as well as iodine-125, iodine-131, samarium-153, Lutetium-177 and a technetium generator-99m, including more than 10 types of radiopharmaceuticals and 13 types of cold kits for the technetium-99m generator, which are used in medical practice in the diagnosis and treatment of various diseases. The production line for the production of radiopharmaceuticals and cold kits is certified in accordance with GMP (Good manufacturing Practice) standards, which fully meets the needs of domestic consumers and ensures their accessibility to other countries interested in cooperation.

Currently, the market for the development of new technologies for the production of radioisotope products is assessed by business experts as comparable to the radioisotope market and, in turn, designates the following concept: the production of new types of high-purity radioisotopes, the production of radiopharmaceuticals based on these radioisotopes and successful application in medical practice for diagnosis and therapy, an environmental safety system and protection personnel in production, product sales, etc. Today, the Institute meets the republic's demand for these products, and also exports it to more than 10 countries around the world.

Based on the above, the development of new technologies for producing radioisotope products today is one of the strategic goals of the Institute of Nuclear Physics of the Academy of Sciences of the Republic of Uzbekistan.



FIRST NUCLEAR CHEMISTRY EXPERIMENTS AT THE SUPERHEAVY ELEMENT FACTORY

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Relatively high stability of new superheavy elements (SHE) with atomic numbers 112–118 (from Cn to Og), recently discovered at FLNR, present unique possibilities to study their chemical properties. The main research focus is on their chemical identification and to reveal the influence of relativistic effects on the law of periodicity predicted in the field of SHE which completes 7th period of the D.I. Mendeleev Periodic System.

The new JINR basic facility dedicated to study properties of SHE – accelerator complex SuperHeavy Element Factory (SHE Factory) started operating at FLNR in 2019. Nuclear chemistry research is one of the key areas of its fundamental research program. The increased beam intensities at the new DC-280 heavy ion accelerator open up unique possibilities for study of chemical properties of SHE which synthesized in fusion reactions with extremely low cross sections at a new statistical level¹. In this sense, the most important research topic in SHE chemistry is currently considered to be the experimental study of the volatility and adsorption behavior of Cn, Nh and Fl². Having started in 2007 at the U-400 accelerator at FLNR^{3,4}, we continue to study the chemical properties of these elements and its lighter homologues in Periodic Table using gas adsorption thermochromatography in a new round of experiments at the SHE Factory.

For this purpose, we have created an experimental complex, including an improved chemical setup for separation and detection of short-lived isotopes of Cn and Fl in the gas phase behind the new gas-filled separator GRAND. The review also combines first results on Fl properties obtained at the SHE Factory as well as the ongoing preparation for the upcoming full-scale experiment, theoretical research, studies of stopping ranges and gas flow dynamics of recoils, and adsorption experiments with short-lived radioisotopes of At, Tl and Hg in on-line model thermochromatography studies.

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AZACROWN COMPOUNDS AND THEIR CONJUGATES WITH NANOPARTICLES, ANTIBODIES AND PEPTIDES AS A PLATFORM FOR RADIOPHARMACEUTICALS

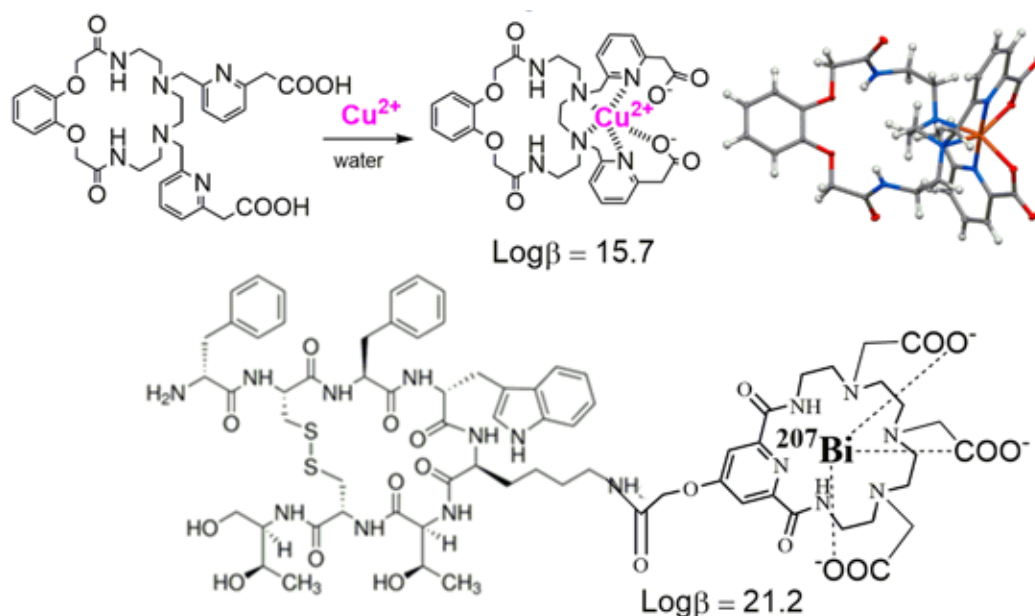
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Bifunctional chelating agents have been used widely to derivatize tumor-specific monoclonal antibodies with radiometal ions for cancer imaging and therap. Since most radionuclides are metals, the conjugation of antibodies to radiometal complexes represents one of the most versatile strategies for selective delivery of diagnostic or therapeutic radiation to primary tumors or metastatic disease.

In the present report the synthesis and complex formation analysis of the bifunctional derivatives of the azamacrocyclic chelating agents are presented.



Novel generation of produced bifunctional radiometal chelates has improvements with greater thermodynamic, kinetic, and physiological stability, as well as more versatile chemistry for attachment to biomolecules. s.

We thank the Russian Scientific Foundation № 23-13-00424.

CRYSTAL CHEMISTRY STUDIES OF SECONDARY MINERALS AND TECHNOGENIC MINERAL PHASES OF URANIUM TO ENSURE THE NUCLEAR FUEL CYCLE ENVIRONMENTAL SAFETY

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It is very difficult to overestimate the importance of uranium for modern civilization, and if consider the entire nuclear fuel cycle, then its initial and final stages (i.e. exploration of uranium deposits, mining and processing of uranium ores, storage and processing of radioactive wastes) are inextricably linked with mineralogical research: which rocks and their constituent minerals are best used for uranium mining, what happens to uranium compounds in contact with the environment, how do secondary uranium minerals differ in their physical and chemical properties? In this regard, it is very important to conduct crystal chemical studies involving both natural and synthetic objects. Stable and sparingly soluble uranium compounds can prevent the migration of radionuclides from the zones of uranium ores oxidation or from the repository of radioactive wastes, so, the study of the features of water-soluble uranium compounds is necessary to understand the processes of transfer of radionuclides in geological conditions.

Nowadays, there are more than 300 U-bearing minerals known that contain uranium in various forms. And this amount exceeds 5% of the total number of known minerals! The discovery of a large number of new U⁶⁺ minerals in recent years demonstrates the unique evolution of the natural material within the uranium deposits. At the same time, the processes of direct alteration of mineral species remain largely unexplored and not fully understood.

With this regard investigation of synthetic analogs of minerals and structurally related compounds shed the light on the formation mechanisms of such phases in nature, which in turn should help to implement a more balanced policy in the field of environmental safety.

This work was supported by the Russian Science Foundation (grant No. 23-17-00080).

ON THE POTENCY OF MULTISCALE SIMULATION METHODS IN ANALYZING THE PERFORMANCE OF NUCLEAR FUEL UNDER IRRADIATION: A REVIEW

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Nuclear fuels possess distinct characteristics that necessitate a comprehensive understanding of the underlying phenomena at various scales. The behaviors and performance of these key components play a crucial role in determining the overall performance of the nuclear reactor system. Consequently, the analysis of nuclear fuel performance holds significant importance in both the design and safety evaluation of the nuclear reactor system. Unfortunately, using experimental methods such as irradiation tests to achieve performance analysis is time and resource consuming. A possible route to overcome this obstacle is to simulate nuclear fuel from the perspective of multiscale phenomena. In this regard, the multiscale approach, as a subfield of computational material science, plays a crucial role. The essence of multiscale simulation lies in accurately defining the objectives to be achieved and determining the appropriate methods to be utilized. Presently, there exists a requirement for a more systematic methodology in the advancement of multiscale simulation for nuclear fuel materials. In light of this, the current review commences by presenting an overview of the fundamental principles and applicability of commonly utilized simulation methods in nuclear fuel research. Emphasis is placed on the selection of the most appropriate simulation method to address specific issues. Finally, a prospective analysis and comprehension of potential approaches for integrating multiscale simulation, along with the associated challenges, are provided.

RADIONUCLIDE BEHAVIOR AND HYDROGEOCHEMISTRY IN TWO DIFFERENT URANIUM MINES IN BRAZIL

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This study compares the environmental behavior of radionuclides and uranium hydrogeochemistry at two different sites. The Caetité Uranium Production Unit (URA), the only plant operating in Brazil, is in a semi-arid region dominated by fissured aquifers with plagioclases, where groundwater is the potentially most sensitive environmental medium¹. The other one is the decommissioning site of Poços de Caldas (UDC), located in a region characterized by the occurrence of radioactive anomalies and bauxite associated with fluorite, manganese oxide and pyrite, which is related to sources of Acid Mine Drainage (AMD)².

The aqueous speciation of uranium was evaluated, as well as the interaction mechanisms between water, rock, and soils, using tracers (environmental isotopes), statistical and geochemical models.

At the URA site, such tools made it possible to identify the main recharge area, formed by fractured rocks recovered by a thin layer of weathering mantle or sediments. Uranium forms aqueous complexes with carbonates that are predominant (> 80%). Furthermore, there were uranium complexes with fluorides and hydroxides in pH ranges below 7. The residence time assessed by the tracers was between several months and a few years. The low storage of aquifers combined with rapid recharge in the rainy season, promoted full replenishment at this time.

Regarding UDC, the higher rainfall rates (1800mm.y⁻¹) associated with the occurrence of pyrite in the host rocks, give rise to AMD and make continuous discharges of treated effluents on a major environmental issue. Radionuclides show variation related to rainfall throughout the year, with statistically significant variation between the rainy and dry seasons. The long-term component of contaminant release into the environment, for instance, precludes the adoption of active controls for decommissioning, e.g., collection and treatment. Instead, passive controls must be put in place, e.g. layer of impermeable material.

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COLLOIDS MEDIATED TRANSPORT OF URANIUM POSE CHALLENGE FOR THE IMMOBLIZATION REMEDIATION OF URANIUM CONTAMINATED SITES

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The occurrence forms and migration behaviors of uranium in the environment are crucial for nuclear environmental safety assessment. Based on the geochemical process of uranium in the environment, strategies including phosphate, bacteria, and redox reagents treatment, have been proposed to immobilize uranium in the contaminated sites, solutes migration models have been constructed as well to describe and predict uranium migration laws and then evaluate the effectiveness of immobilization remediation. However, the migration distance of on-site monitoring is often greater than the predicted migration results, studies have found that colloids play an important role in radionuclide migration. Uranium is prone to form intrinsic colloids under groundwater environment conditions due to the nucleation and crystallization process, and also easily associates with the widely existed environmental colloids to form pseudo colloids. The existence of colloids significantly affects the occurrence mode and migration law of uranium. In this work, aiming at the migration behavior and interface mechanism of typical uranium colloids, the column experiment method was used to reveal the transport law of uranium intrinsic and pseudo colloids, the colloidal interface reaction process and microscopic mechanism were clarified with the aid of advanced spectroscopic technologies, and the migration law of uranium colloids under different environmental conditions was revealed, and a transport model considering colloidal radionuclides was constructed. The retention, distribution, migration, and fate of key uranium colloids in different types of environmental media were elucidated, and the governing strategies for reducing colloids mobility was proposed. Relevant achievements provide theoretical basis and technical support for the migration mechanism of uranium in geological media and the remediation of contaminated site, and provide important reference for nuclear environmental safety assessment.

TWO-COMPONENT NUCLEAR POWER: CHALLENGES OF RADIOCHEMICAL TECHNOLOGY DEVELOPMENT

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The nuclear power development strategy of the Russian Federation envisages a transition to a two-component structure of nuclear power based on thermal and fast neutron reactors (TR and FR). This marks a transition to the use of U-Pu fuel and large-scale industrial reprocessing of TR and FR spent nuclear fuel (SNF). The development of new technologies for TR SNF reprocessing is being carried out within the framework of the formation of a pilot demonstration centre (ODC) at FSUE MCC, and for FR SNF – in the "Proryv" project area of the processing module (PM) creation for the pilot demonstration power complex (ODEC) with the BREST-300-OD reactor at the site of JSC SCC. Consequently, the first task of radiochemical technology development is to design a new TR SNF technology for a large-scale plant, taking into account the most efficient technological operations developed for RT-1, ODEC and in the "Proryv" project area.

Involvement of Pu in the nuclear fuel cycle (NFC) leads to an increase in the production of minor actinides (MA) and requires their afterburning in FRs or molten salt reactors (MSR). To date, it has not been determined which MA (Np, Am, Cm, or all of them together) will be afterburnt. Therefore, the second task of the radiochemical technology development is the recovery and separation of MA, for which both hydrometallurgical and pyroelectrochemical or plasma technologies can be used.

Another critical task is to reduce the volume of radioactive waste (RAW) to be buried in depth. Recovery and afterburning of MA reduces the volume of long-living RAW. It is also possible to extract short-living nuclides (cesium and strontium) into a separate fraction. Such a fraction does not necessarily require a deep geological depositary. Effective technologies development for extraction and solidification of this fraction as well as its safe disposal is the third task of radiochemical technologies development.

The analysis of possible options for solving these tasks should be carried out taking into account the fact that by 2030 it is necessary to modernize the RT-1 plant, to bring the ODC (FSUE MCC) to its design capacity, to launch the ODEC PM (JSC SCC) and to design a large-scale SNF processing facility.

U-RICH ZIRCON IN CHERNOBYL LAVA – FORMATION AND PROPERTIES

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Interaction of molten fuel, cladding and construction materials during accident at Chernobyl Nuclear Power Plant (ChNPP) led to formation of large amount of “Chernobyl lava” – glassy material with high content of uranium^{1,2}. Zircon (ZrSiO_4) with unusually high uranium content (up to 15 mass% of U) is one of the most remarkable crystalline phase in the lava^{1,3}. Investigation of solid phases in lava gives unique opportunity to constrain conditions in the fuel-cladding melt in real nuclear accidents. Formation of the U-rich zircon remains poorly constrained. Here we report new spectroscopic and structural data on unique collection of the U-rich zircon crystals extracted from lava.

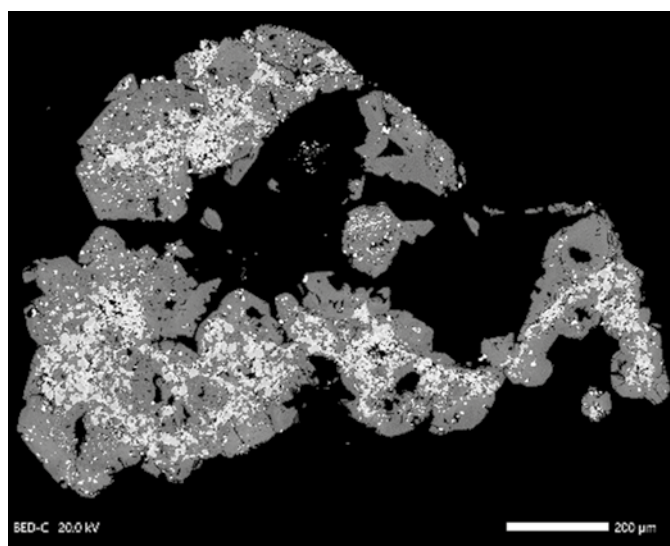


Figure 1. SEM image of a U-rich zircon

SEM image of one the studied zircon crystals is shown in figure 1. Complex internal structure of the specimen reveals domains with widely different concentration of uranium and presence of numerous inclusions represented by $(\text{Zr,U})\text{O}_2$, UO_2 , steel and lava droplets (silicate glass). Detailed examination of textural relationships between the phases unambiguously proves that U-rich zircon was formed during interaction of $(\text{Zr,U})\text{O}_2$ with the silicate melt. Polymorphic modification of relic zirconia (monoclinic, tetragonal or even cubic) depends on U content. Concentration of U in zircon depends on concentration of this element in the precursor zirconia.

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THE DEVELOPMENT OF DIAGNOSTIC AND THERAPEUTIC ANTITUMOR RADIOPHARMACEUTICALS

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Cancer remains one of the leading causes of mortality both in Russia and worldwide. Significant progress in the diagnosis and therapy of malignant neoplasms has been achieved due to the introduction of radiopharmaceuticals (RP) into clinical practice.

To date, radiopharmaceuticals for diagnosis and therapy of prostate cancer, neuroendocrine tumors, inoperable liver cancer has been developed in A. Tsyb Medical Radiological Research Centre – branch of the National Medical Research Radiological Centre of the Ministry of Health of the Russian Federation.

Radiopharmaceuticals, which are designed for diagnosis and therapy of prostate cancer, are low-molecular-weight inhibitors of prostate-specific membrane antigen (PSMA), urea derivatives, labeled with radionuclides ^{99m}Tc, ¹⁷⁷Lu, ²²⁵Ac.

Radiopharmaceuticals based on synthetic analogs of somatostatin with radionuclide ¹⁷⁷Lu was proposed for the treatment of neuroendocrine tumors. Radiopharmaceuticals with ^{99m}Tc and ²²⁵Ac are in developmental stage.

A unique innovative radiopharmaceutical based on albumin microspheres and generator-based ¹⁸⁸Re radionuclide for radioembolization of inoperable primary and metastatic liver cancer was developed.

The work was financially supported by the Ministry of Health of the Russian Federation, № R&D 121051700162-0, 121051700200-9, 124030500022-1.

COLLOIDS POSE AN ENHANCED TRANSPORT RISK OF ACTINIDE IN SATURATED POROUS MEDIA

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The occurrence forms and migration behaviors of actinide in the environment are crucial for nuclear environmental safety assessment. Based on the geochemical process of actinide in the environment, solute migration models have been constructed to describe and predict the migration behaviors and laws of radionuclides. However, the migration distance of on-site monitoring is often greater than the predicted migration results, a large number of studies have found that colloids play an important role in radionuclide migration. The actinide elements are prone to form intrinsic colloids under groundwater environment conditions due to the nucleation processes, and also easily associate with the widely existed environmental colloids to form pseudo colloids. The existence of colloidal phase will significantly affect the occurrence mode and migration law of actinide.

In this work, aiming at the migration behavior and interface mechanism of typical colloids of actinide, including Uranium, Americium/Europium. The column experiment was used to reveal the transport law of intrinsic and pseudo radioactive colloids, the colloidal interface reaction process and microscopic mechanism were clarified with the aid of advanced spectroscopic technologies, and the migration law of radioactive colloids under different environmental conditions was revealed, and the transport model considering cotransport of colloids and radionuclides was constructed. Basing on the retention, distribution, and migration law, the fate of key actinides in different types of environmental media were elucidated, and the governing strategies for reducing colloids mobility was proposed. Relevant achievements provide theoretical basis and technical support for the migration mechanism of actinide in geological media, and provide important reference for nuclear environmental safety assessment.



MITIGATION OF THE INHERENT RISK POSED BY THE RELEASE OF A DAUGHTER RADIOISOTOPE IN THE CASE OF AUGER EMITTING RADIONUCLIDES

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Targeted Auger electron therapy is potentially more powerful and more precise than targeted alpha therapy. The release of daughters from Ac-225's targeting vector during its *in vivo* alpha decay chain is well known. We investigated the same potential risks for daughter radioisotopes in Auger emitters.

The release of the daughter could be from the classical Szilard-Chalmers effect in the form of recoil as is the case for radionuclides undergoing alpha decay or high energy beta decay. Our calculations based on the Standard Model¹ proved that for the Auger emitters the recoiling daughter nuclide does not have enough kinetic energy to be ejected from the classical chemical bond which has an energy in the range of 3 eV. Experiments were carried out to monitor the release of radionuclides from a series of mother/daughter combinations. The mother radionuclide was labelled and trapped on a STRATA-X SPE column where after the daughter release was monitored with washes over multiple time points.

We found a good relation between the ratio of the Auger electrons in the decay and that of the ratio of the released daughter radioisotope. This was proven experimentally with a number of the pairs of radioisotopes investigated.

Therefore, it is necessary to also consider the fate of the ejected daughter radioisotope for Auger emitters and if possible prevent its release in the first place. Potential parameters to be considered are decay type of the daughter, the half-life, microbiological aspects, active or/and passive transport of the "chemically free" radioisotope and the biological danger of the decaying daughter isotope.

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DEVELOPMENT OF NEW METHODS FOR PRODUCING RADIOACTIVE ISOTOPES AS RESULT OF FUNDAMENTAL CHEMICAL RESEARCH

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Systematic fundamental study of elements of D.I. Mendeleev Periodic Table results in the development of new effective chemical technologies.

As long ago as in 1976, at G.N. Flerov LNR of JINR (Dubna), we carried out the first work on studying high-temperature chemistry of mendelevium (^{256}Md), which included its isolation from molten metals and thermochromatographic separation in the elemental state. Later, other heavy actinides, as well as lanthanides and trans-actinides (^{260}Rf) has been studied using this approach, and the volatility of the elements was shown to correspond to quantum chemical calculations of promotion energy. In the search for superheavy elements with Z-108-116 in natural materials and in the products of nuclear reactions at heavy ion accelerators, as well as in the study of nuclear reactions with medium-energy protons (70–500 MeV), the process of isolation of many elements from various materials was studied, and the possibility of separating sublimated elements through chemical interaction with the stationary phase at high temperature.

These studies have found practical application in the development of methods for producing radionuclides for medical diagnostics and therapy, as well as for physical research and industry. Thus, new effective methods have been developed for preparing thin sources of actinides and lanthanides, producing radionuclides ^{22}Na and ^{109}Cd that are important in technology and industry, and isolating medical radionuclides – ^{72}Se , ^{223}Ra , ^{68}Ge from irradiated targets. The $^{225}\text{Ac}/^{213}\text{Bi}$ medical gas chemical generator is being developed on this principle.

But the most effective was the isolation of ^{82}Sr by direct sorption from molten metallic rubidium irradiated with accelerated protons (^{82}Sr is used in medicine in ^{82}Rb generators for PET diagnostics). This technology is now used in high-scale production at a French company ARRONAX. Hundreds of thousands of patients have already passed diagnostics using ^{82}Sr obtained by this method. A license for this invention was also granted to the State Scientific Center IPPE (Obninsk) and American companies.



NANOCOMPOSITE-BASED STRATEGIES FOR ENHANCING RADIATION THERAPY IN HUMAN COLORECTAL CANCER CELLS

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Radiation therapy is a crucial treatment modality for colorectal cancer¹. However, there is a growing interest in improving its efficacy and reducing side effects. This study explores the potential of nanocomposites as a means to enhance radiation therapy for human colorectal cancer cells². Specifically, the focus is on the development and application of nanocomposites comprising silver (Ag) and manganese (Mn) nanoparticles^{3,4}. The investigation considers the impact of nanoparticle composition, size, and irradiation on the cytotoxicity and therapeutic outcomes. Preliminary findings indicate that nanocomposites can significantly enhance the cytotoxic effects of radiation on colorectal cancer cells⁵. The study sheds light on the promising role of nanocomposites in optimizing radiation therapy and provides insights into the design considerations for effective nanocomposite-based strategies in colorectal cancer treatment.

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DILUENTS IN RADIOCHEMISTRY. HISTORY AND CURRENT STATUS

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The most popular method of radionuclide extraction from PUREX-process raffinates is solvent extraction. Numerous extractants of various structures have been proposed for extraction of radionuclides both in Russia and in other countries. Most of these extractants are polar compounds and their solubility in aliphatic hydrocarbons, the classical diluents of the PUREX process, is severely limited. In some cases, the problem can be solved by using aliphatic hydrocarbons modified by the addition of a polar additive (tributyl phosphate or aliphatic alcohol) as diluents. The problem becomes even more difficult for compounds such as polynitrogen-containing heterocyclic compounds (bis-triazinylpyridines and their analogs), amides of heterocyclic dicarboxylic acids (pyridine dicarboxylic acid, phenanthroline dicarboxylic acid) and cobalt dicarbollide. The use of highly polar diluents is necessary for the use of such extractants. Various alcohols, ketones, esters and their mixtures with aliphatic hydrocarbons were tested as polar “light” diluents. For example, solutions of polynitrogen-containing ligands in substituted cyclohexanones have demonstrated high extraction capacity and selectivity for the separation of MA/REE, however, these diluents have insufficiently high flash points, which limits their use¹. Alkyl alcohols (C8 and higher) can be used as diluents for diglycolic acid diamides² or crown ethers³, however, there is a danger of their oxidation in contact with nitric acid when heated.

“Heavy” fluorinated diluents have been studied for various extractants⁴. Meta-nitrobenzotrifluoride (F-3) or trifluoromethylphenylsulfone (FS-13) have been used as diluents for compounds as diverse as chlorinated cobalt dicarbollide, polynitrogen-containing heterocyclic compounds, and calix-crown ethers. However, the density of these diluents is insufficient for use as a diluent for TBP. Polyfluoro-substituted non-aromatic diluents such as, for example, fluorinated alcohol carbonates can be used as a diluent not only for diglycolic acid diamides but also for TBPs⁵. It has been shown that TODGA in formals or ethers of fluorinated alcohols forms a third phase upon metal loading; however, this can be avoided by using diglycolic acid diamides with branched or shorter alkyl radicals. Ionic liquids advertised as “green” diluents have no advantage over molecular diluents because of their high viscosity and marked solubility in water.

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EVALUATION OF THE STATUS OF THE ETHIOPIAN NUCLEAR INFRASTRUCTURE DEVELOPMENT

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Access to modern energy service is a development imperative. Ethiopia is rich in energy resources, but it has not sufficiently exploited them for its economic growth and as a result its socioeconomic development is not satisfactory. Its citizens are energy poor and don't have sufficient access to modern energy services. As part of its multi-layered activities in the Ten-Year Perspective Plan (TYPP 2021–2030), the current Ethiopian government, in addition to its renewable energy development plans has considered a nuclear power program (NPP) in its energy mix and desires to apply nuclear science and technology in its sustainable development strategies. The country is planning and preparing on infrastructure requirements for effective implementation of the national NPP. This review paper focuses on the role of nuclear science and technology in energy production and sustainable development, and evaluates the status of nuclear infrastructure development in the Ethiopian national nuclear program. The review discusses the main issues in a national nuclear program, nuclear energy management and nuclear knowledge management demands and strategies for its effective application. Knowledge-driven commitment to the nuclear science and technology program in developing countries like Ethiopia can boost economic growth.

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CHEMICAL ALTERATION OF HIGHLY RADIOACTIVE URANIUM-BEARING MATERIALS FORMED AS A RESULT OF SEVERE NUCLEAR ACCIDENTS AT CHERNOBYL AND FUKUSHIMA-1 NPP'S

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Severe accidents at nuclear power plants (NPP) such as: TMI-2 (USA, 1979), Chernobyl (1986, USSR) and Fukushima-1 (Japan, 2011) were accompanied with formation of corium (Zr-U-O) and spreading of highly radioactive “lava”-like silicate melt (product of fuel-corium interaction with molten silicate materials at ChNPP and F-1 NPP). Long-term aging of corium and “lava” is a subject of precise experimental research in order to understand the environmental behavior of these extremely dangerous materials containing long-lived radionuclides (Pu, Am, etc.). The following Chernobyl highly radioactive samples of two types have been applied for long alteration experiments in distilled water for 1 year at 150 °C: 1) brown “lava” (with bulk U-content 7–8 wt.%); and 2) corium-steel interaction material (with bulk U-content less than 1 wt.%). Also, secondary uranium minerals formed on the surface of black “lava” (with bulk U-content 3–4 wt.%) directly inside “Shelter” have been studied too without alteration test. Some new-formed artificial minerals: $\text{UO}_4 \cdot 4\text{H}_2\text{O}$ (studtite); $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ (epiianthinite); $(\text{UO}_2)\text{CO}_3$ (rutherfordine); $\text{Na}_4(\text{UO}_2)(\text{CO}_3)_3$ (unnamed); $(\text{Ca}[(\text{UO}_2)_6\text{O}_4(\text{OH})_6] \cdot 8\text{H}_2\text{O})$ (becquerelite) and $(\text{Ca}_2[(\text{UO}_2)_3\text{O}_2(\text{PO}_4)_2] \cdot 7\text{H}_2\text{O})$ (phurcalite) have been identified. Basic properties of these minerals are discussed.

Formation of such secondary uranium-bearing phases affects significantly the radionuclide redistribution and migration. It must be taken into consideration for modeling of long-term environmental behavior of damaged spent nuclear fuel and final geological disposal.

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BENZO- AND PYRIDINE- AZACROWN ETHERS AS PERSPECTIVE TOOL FOR TARGETED RADIOPHARMACEUTICALS

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For effective diagnostics and treatment by targeted radiopharmaceuticals it is important to prepare them with variable personalized set of radiation and biomolecule. Due to development of production routes and a diversity of properties provided by radiometals their application for nuclear medicine has significantly grown. The traditional way of binding of an appropriate radiometal with the biomolecule is using a bifunctional chelator. In our work we consider series of benzo- and pyridine-containing 15- and 18-membered azacrown-ethers with varied pendant arms as chelators for such radiopharmaceuticals. Their bifunctionalization can be achieved via aryl-moiety. With respect to the wide range of complexation properties enabled by variation of ligand structure medically relevant cations Cu^{2+} , Y^{3+} , Pb^{2+} , Bi^{3+} , Ac^{3+} , Th^{4+} , etc. of different size, charge and hardness are studied with these ligands. Starting with physical chemical features of complexes such as $\log\beta$ and structure we perform labeling of the most effective chelates with corresponding radionuclides and continue with *in vitro* and *in vivo* stability.

Picolinate derivatives have been shown to be suitable for softer and borderline cations such as Cu^{2+} , Pb^{2+} and Bi^{3+} . Due to the presence of many donor atoms they form not only mono-, but also dinuclear complexes. Tetrapicolinate quickly forms *in vitro* inert complex with Cu^{2+} even though the coordination of cation is out of macrocycle. However, biodistribution of the complex shows that it is not 100% inert *in vivo* and part of radionuclide is released in the organism. Surprisingly smaller tripicolinate derivative strongly binds both Pb^{2+} and Bi^{3+} enabling its application with ^{212}Pb .

Among the most effective complexes found in our series are Ac^{3+} , Bi^{3+} and Pb^{2+} with benzoazacrown tetraacetate. They are featured by high values of $\log\beta$ and demonstrate not only long-term inertness *in vitro* and *in vivo*, but also high rate of labeling without additional heating.

Thus, 15(18)-azacrown-5(6)-ethers due to not highly restricted macrocycle combine properties of acyclic polyamines (fast binding of cations) and macrocyclic ligands (inertness of formed complexes in challenging medium). They can form in- and out-cage complexes with cations of various ionic radius enabling binding of a wide range of medically relevant radiometals.

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RECOVERY OF ^{225}Ac FROM PROTON-IRRADIATED THORIUM AND DEVELOPMENT OF $^{225}\text{Ac}/^{213}\text{Bi}$ GENERATOR

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Due to particular chemical and nuclear properties ^{225}Ac ($T_{1/2}=9.9$ d) is very prospective for targeted alpha therapy of various forms of cancer. It can be used either directly or as a generator of daughter ^{213}Bi (46 min). Clinical trials of ^{225}Ac - and ^{213}Bi -labeled compounds are carried out in many oncological centers. However, their wide application in routine medical practice is restricted mainly by the limited production capabilities of ^{225}Ac .

A prospective method for producing ^{225}Ac via irradiation of metallic thorium with medium-energy (>100 MeV) protons has been developed at the Institute for Nuclear Research of Russian Academy of Sciences (INR) in collaboration with Lomonosov Moscow State University, Karpov Institute of Physical Chemistry, and LUCH Scientific Production Association. Efficient thorium targets were designed and tested to withstand thermal and radiation impacts caused by intense irradiation. A procedure of ^{225}Ac recovery from the irradiated target and purification from numerous products of nuclear reactions of spallation and fission was developed¹ and pure ^{225}Ac samples with activity of 300–400 MBq were obtained². Furthermore, it was demonstrated that in one irradiation and processing cycle the production yield may achieve 70 GBq of ^{225}Ac . This is comparable to the current level of annual world production. Since the final ^{225}Ac -product contains an impurity of 0.2% ^{227}Ac (21.8 years) it seems more prospective to use it in a $^{225}\text{Ac}/^{213}\text{Bi}$ generator.

Original circulating generator systems were elaborated to accumulate ^{213}Bi separately from the parent ^{225}Ac via continuous elution and decay of intermediate ^{221}Fr (4.9 min)³. For this purpose, weakly acidic or neutral physiological solutions were used. In that solutions Bi(III) ions tend to hydrolyze and can be retained by different sorbents. Flexible structure of the proposed generator scheme provided a good purification of ^{213}Bi from long-lived radionuclide impurities, as well as significant reducing the total time of preparation of labeled bioconjugate.

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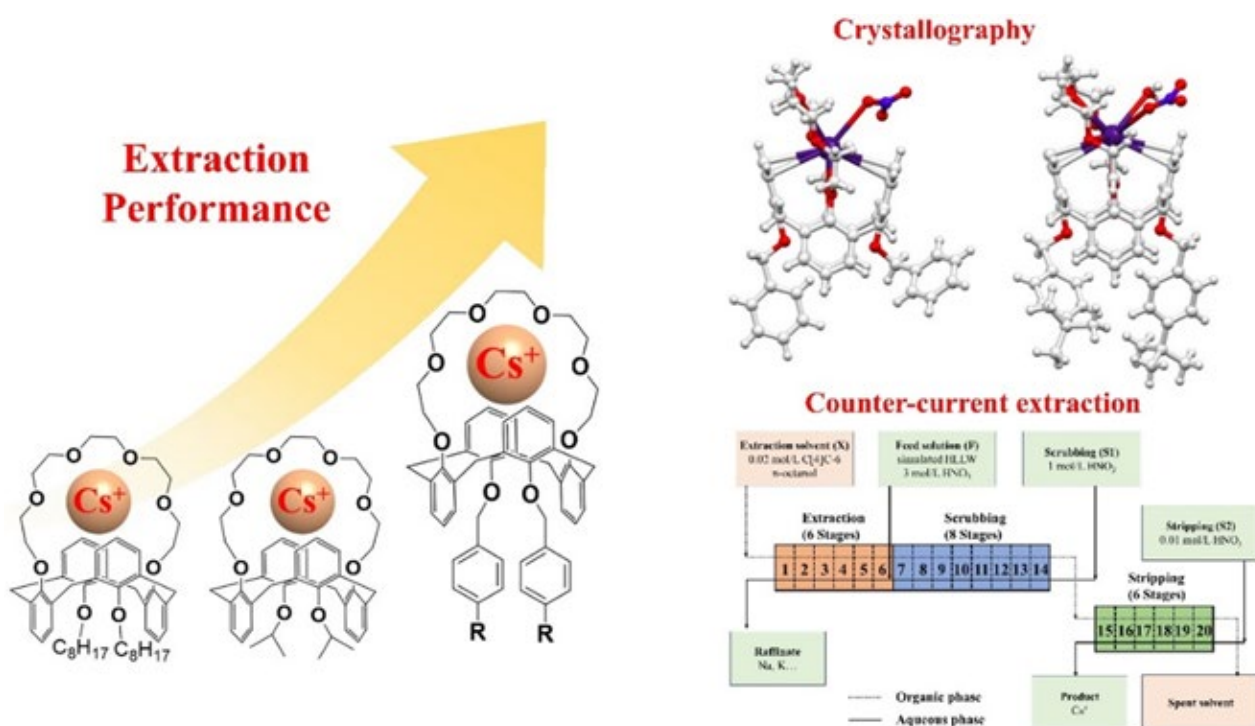
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BENZYL SUBSTITUTED 1,3-ALTERNATE CALIX[4] ARENE-CROWN-6 ETHERS FOR CESIUM SEPARATION FROM HIGH-LEVEL LIQUID WASTE

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1,3-alternate Calix[4]arene-crown-6 ethers show good selectivity for Cs^+ .¹⁻² In this study, new benzyl substituted 1,3-alternate Calix[4]arene-crown-6 ligands (i.e., Bn-C[4]C-6 and tBu-Bn-C[4]C-6) were synthesized and studied as Cs^+ extractants for liquid-liquid extraction from PUREX raffinate. The complexation of the ligands with Cs^+ was confirmed by ^1H NMR titration and X-ray crystallography. The stability constants were investigated by spectrophotometric titrations. Multistage counter-current extraction process was developed with the new ligands.



Both Bn-C[4]C-6 and tBu-Bn-C[4]C-6 exhibited better extraction performance and higher selectivity to Cs^+ than the analogues C8-C[4]C-6 and iPr-C[4]C-6 under the same conditions. The new ligands had satisfactory acid tolerance and irradiation stability.

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DEVELOPMENT OF A COMPREHENSIVE DECOMMISSIONING PLAN FOR NUCLEAR FACILITIES

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Argentina currently operates three Nuclear Power Plants (NPPs) and is constructing a Small Modular Reactor prototype (CAREM25). The country also hosts five research reactors, with a sixth one under construction, along with three hundred nuclear medicine centers, and several nuclear fuel cycle and technology facilities. The estimated decommissioning dates for the first NPPs are projected around 2046.

Under Law 24804 on Nuclear Activity, National Atomic Energy Commission (CNEA) is mandated to determine the decommissioning procedures for nuclear facilities in Argentina and has the responsibility of dismantling and decommissioning Argentine NPPs. Unfortunately, despite a prior Nuclear Facilities Decommissioning Sub-Program (2000–2013), this initiative was discontinued, leading to retirement or reassignment of many involved personnel. Now, National Radioactive Waste Management Program (PNGRR) within CNEA is developing a Comprehensive Decommissioning Plan for Argentina's nuclear facilities. This plan is crucial to address current and future generations' interests and legal responsibilities of CNEA.

The plan starts with decontamination and dismantling tasks for selected nuclear facilities as case studies. Firstly, an alloy melting workshop with an induction melting furnace underwent cleaning and decontamination processes. It was used to fabricate U-Si alloy for the research reactor RA-6 and for the Open Pool Australian Light Water Reactor (OPAL), U-Mo alloys for research and development, among others. The estimated activity based on safeguards values are 10g of U-20%, 6.4 MBq, and 50g of depleted uranium, 1.2 MBq.

Secondly, a mass spectrometry laboratory belonging to the Nuclear Fuel Cycle, operational for 25 years, started the decommissioning process. Analyses of samples with varying isotopic abundances were conducted in it, with access to a wide range of certified isotopic reference standards for measurement. The approximate activity measured in the laboratory was 0.1 GBq.

The Comprehensive Decommissioning Plan progresses through three stages with incremental goals: surveying the current situation, defining strategies, and implementing them. Each phase involves coordinating research and development efforts, planning strategies based on knowledge management, and transferring information between past and present professional and technical personnel. Additionally, specific techniques and technologies will be applied in precise case studies, competencies will be mapped to design tailored training and human resources development programs, and international cooperation agreements will be fostered to exchange knowledge on the subject.

INNOVATIVE ^{177}Lu -BASED RADIOPHARMACEUTICALS FOR NUCLEAR MEDICINE

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Currently targeted radionuclide therapy is experiencing a rapid development. Use of radiopharmaceuticals with α - and β -emitting radionuclides, mainly with the β -emitter lutetium-177 (^{177}Lu), is now widely distributed to routine clinical practice. Kurchatov Institute has developed three domestic ^{177}Lu -based radiopharmaceutical prototypes.

These studies appeared feasible by the implementation of a unique technique for isolating of no-carrier-added ^{177}Lu based on multi-stage cementation with a final coefficient 10^5 .

An innovative prototype based on the targeted affibody molecule to HER2/neu antigen on tumor cells demonstrated satisfactory distribution in vivo with planted breast tumor. Therapeutic effect and toxicological safety were also demonstrated.

Radiopharmaceutical based on methotrexate molecule has also been developed for the treatment of autoimmune arthritis. Selective accumulation in the affected tissues was demonstrated, as well as significant clinical improvement was observed since 48 hours after administration (reducing the swelling of affected joint, almost complete restoration of integumentary tissues color).

PSMA-based molecule with ^{177}Lu as therapeutic agent for the treatment of metastatic castration-resistant prostate cancer is now also under preclinical research.

This work was carried out in accordance with the Kurchatov Institute comprehensive Research and Development program “Applied Research and Development for the Use of Nuclear Technologies in Medicine”, as well as under Agreements No. 774/164-D / 651/CCFHT and No. 598/CCFHT/313/1746-E between JSC “Science and Innovations” (General Customer) and NRC “Kurchatov Institute”.

ABSCOPAL AND BYSTANDER EFFECTS OF RADIOPHARMACEUTICALS

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Systemic targeted radiotherapy (STR) has entered a new era. The specific administration of radioactive compounds for delivering lethal radiation doses to the tumor while preserving normal is a successful goal for cancer treatment. However, evidence show that cells not accumulating the labelled molecule can be killed as a result of being hit by radiation emitted from neighboring cells: phenomena named by radiation-induced bystander effect, abscopal effects and cross-fire effect. Abscopal effects implicate the immune system. Bystander effect implicates the killing of cells not directly exposed to radiation via an increase in nitrosative and oxidative stress, cytokine release, stimulation of DNA repair and gap junctional intracellular communication. Bystander effects can be both detrimental and beneficial in dependence on dose, dose-rate, cell type, genetic status and experimental condition. The present study provides a review on radiopharmaceuticals induced bystander, abscopal and crossfire effects exhibited by radionuclides emitting beta- and alpha-particles and Auger electrons used in tumor radiotherapy and diagnostics.

THERMAL STABILITY OF SOLID-PHASE EXTRACTANTS BASED ON TRIBUTYL PHOSPHATE, N,N,N,N-TETRAOCTYLDIAMIDE OF DIGLYCOLIC ACID, DIBENZO-21-CROWN-7 IN NITRIC ACID SOLUTIONS, IN RELATION TO SNF REPROCESSING

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The use of solid-phase extractants (levextrel resins) is potentially being considered at SNF processing plants. In this work, the levextrel resins based on tributyl phosphate (TBP), N,N,N,N-tetraoctyldiamide of diglycolic acid (TODGA), dibenzo-21-crown-7 (DB21C7) on the organic matrix were studied. These resins can be used to extract radionuclides from nitric acid solutions during the processing of spent nuclear fuel: uranium and plutonium – by TBP; americium and curium – by TODGA; cesium and strontium – by DB21C7. At the same time, it is necessary to study the thermal stability of the above-listed levextrel resins in contact with nitric acid, since the ongoing oxidative processes can be accompanied by active heat and gas release.

Levextrel resins studies have been conducted in relation to the conditions of normal operation, as well as emergency modes. It is shown that:

- heating of the levextrel resins saturated with HNO_3 (4–7 mol/l) at atmospheric pressure is accompanied by the oxidative processes associated with the interaction of the extractant with nitric acid and leading to heat release at temperatures of 150–350 °C. The values of the exothermal effect for the levextrel TODGA and levextrel DB21C7 are about 200–300 J/g, and for the levextrel TBP it is noticeably lower, about 50 J/g;
- heating under isochoric conditions leads to a significant increase in heat generation due to the accumulation of oxidizer in the system. The values of the exothermal effect for the levextrel TBP saturated with 7 mol/l HNO_3 and the levextrel TODGA saturated with 4 mol/l HNO_3 are about 1000 J/g;
- the presence of metal nitrates leads to a decrease in the temperature of the beginning of heat release and an increase in its intensity;
- at the temperatures above 350–400 °C, thermal decomposition of the polystyrene-divinylbenzene matrix of the levextrel resins occurs, resulting in the release of benzene derivatives, including styrene, toluene, ethylbenzene and others.

IMPROVEMENT OF METHODOLOGICAL APPROACHES TO ANALYZING RADIOCHEMICAL PURITY OF RADIOPHARMACEUTICALS

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One of the main quality criteria for radiopharmaceuticals (RPs) used in clinical practice is radiochemical purity (RCP). The choice and routine use of one or another method of RCP analysis in quality control of RPs manufactured locally for use directly in a medical organization is entirely left to that organization. When analyzing the literature data of different research groups on the synthesis and studies of the same RP, it is possible to pay attention to significant differences in the presented results of determining the value of RCP. Often, the analysis performed by a single, even pharmacopoeial method, may indicate a high RCP, while the analysis by a more precise and detailed method (taking into account current data on possible impurities) will allow to establish that the real RCP of the preparation is below the permissible limits. In the case of receptor-specific preparations based on metal radionuclides, the combination of different methods (radio-TLC and radio-HPLC) is necessary due to the peculiarities and nature of possible radiochemical impurities. At the same time, significant difficulties in the analysis of RPs and determination of possible impurities in their composition are associated with their specificity (for example, nonspecific sorption of the ionic impurity of the n.c.a. radionuclide on the reversed phase in the analysis by radio-HPLC method, distorting the result of the determination of RCP).

The aim of this study was to compare the methods for analyzing the RCP of different RPs published so far by different scientific groups and to find and develop optimal analytical approaches in this context. On the example of vector preparations with different diagnostic and therapeutic radionuclides (^{44}Sc , ^{90}Y , ^{153}Sm , ^{177}Lu) the influence of the method and analysis parameters on the efficiency of detection of various radiochemical impurities (unbound forms of radionuclides, colloids, products of thermolysis and radiolysis of the vector molecule) and determination of the RCP in general was demonstrated.

The work was carried out within the framework of the state assignment of FMBA of Russia 122031100121-4.

NEW APPROACHES TO THE CONDITIONING OF SPENT ION-EXCHANGE RESINS (SIER)

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Here we address the problem of decontamination of spent ion-exchange resins (SIERs) generated yearly in large volumes at nuclear power plants (NPPs). At present, there are no technical solutions for removal of not-exchangeable radionuclides, which are entrapped by poorly soluble inorganic deposits on SIERs. We have suggested a novel approach to solve the problem of conditioning of SIERs, which consists in application of chemical deactivation with subsequent electrochemical extra-decontamination. Chemical deactivation stage is comprised of magnetic separation, chemical deactivation in alkaline solution in the presence of a magnetic resorcinol-formaldehyde resin, and deactivation using acidic solution containing Zn(II)-EDTA. Subsequent reprocessing of the formed liquid radioactive waste (LRW) can be performed using hydrothermal oxidation and selective sorption, which enable one to remove radionuclides of cobalt and cesium, respectively.

Application of the proposed scheme on the sample of the intermediate-level activity SIER resulted in the decontamination coefficients above 10^3 for cesium and 10^2 for cobalt and niobium radionuclides. Electrochemical decontamination using the direct current allowed mechanical removal of the insoluble crud particles, which contained a major part of activity after the stage of chemical deactivation. At the stage of electrochemical processing, a small amount of the Cs-137 radionuclides ($< 5\%$) was transferred into the electrolyte. Electrochemical extra-decontamination using titanium electrodes coated with iridium provided 100-fold extra reduction of the activities related to Cs-137 and Co-60 for SIER generated at Kurskaya and Kalinskaya NPPs and 100-1000-fold reduction related to Nb-94, Am-241, and Eu-152/Eu-154 radionuclides for intermediate-level activity SIER from Kurskaya and Novovoronezhskaya NPPs.

Thus, a new approach to the reduction of the radioactive wastes volume to be disposed after SIER deep decontamination has been demonstrated.

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R&D TO SUPPORT DECOMMISSIONING ACTIVITIES

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In 2021–2022, the JSC VNIINM carried out works in order to identify ways to minimizing formation of radioactive waste at the final stage of the life cycle of Rosatom nuclear facilities.

Analysis of the most perspective pathways on decommissioning of nuclear sites and waste treatment was carried out; the most promising technologies in management of solid and liquid radioactive waste, as well as decontamination were selected. All these technologies were consolidated into a single list for the key Rosatom facilities, to select the most required in the short term from the point of view of the Rosatom in general and the subsidiary TVEL JSC. On the basis of repeated facilities survey the analysis of needs, necessary optimizations of existing technologies, estimated development time and criteria for technical solutions to be developed were carried out. Based on this analysis, a target scheme for the introduction and use of new technologies in the subsidiary TVEL JSC and a consolidated model for the strategic development of R&D for the decommissioning of nuclear facilities have been developed.

Based on the developed approach to planning, the following R&D were already implemented and planned in near-future:

- “Development of a polymer decontamination composition based on a hydrogel with the properties of a dilatant liquid”;
- “Study of the effectiveness of combined decontamination technologies”;
- “Development of current and research for new directions of laser decontamination of various surfaces at operating facilities and during decommissioning works”;
- “Development of technologies and laboratory testing of methods for management of contaminated equipment of the oil and gas complex”;
- “Development of integrated technology and system of foam decontamination and protection of contaminated objects using the system of application, collection and utilization of decontamination compositions”;
- “R&D to support the establishment of a facility to process metal radioactive waste contaminated with transuranic radionuclides”;

The conducted analysis and collaboration with the concerned facilities made it possible to effectively outline the range of necessary developments and optimize the timeframe of works. The key results of the conducted R&D will be presented in the paper.

The work was performed with financial support by TVEL JSC.

RADIATION-CHEMICAL INSIGHT INTO FUNCTIONAL STABILITY OF STRONTIUM-SELECTIVE MACROCYCLIC EXTRACTANTS

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Radiation-resistant strontium-selective extractants are one of the key components of modern and promising technologies for spent nuclear fuel reprocessing. They aim to remove the radionuclide ^{90}Sr characterized by high heat generation and specific activity, and to minimize the volume of radioactive waste being disposed.¹ 18-membered dicyclohexano-substituted crown ethers (CE) are known to be promising candidates for this role. The currently dominant approach to assessing the radiation resistance of the macrocyclic extractants is based on an analysis of a decrease in the strontium distribution coefficient with an increase in the absorbed dose. This approach is not sufficient for a correct prediction of their behavior under the action of ionizing radiation and should be supplemented by radiation-chemical studies that take into account the possibility of the following processes: the transfer of absorbed energy between the components of the solution at the early stages of radiolysis; the interactions of the intermediates generated from the solvent with dissolved CE in secondary radical reactions; interactions of final acidic products of the solvent radiolysis with the macrocycle to form a protonated form; the transfer of absorbed energy between components of a macrocyclic complex with strontium salt; etc.

The experimental data illustrating the contribution of the above factors to the general mechanism of radiolysis of the macrocyclic extractants are analyzed in the present study.²⁻³

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228-RADIUM MASS BALANCE APPROACH TO INVESTIGATE SUBMARINE GROUNDWATER DISCHARGE INTO THE CILICIAN BASIN, NORTHEASTERN MEDITERRANEAN SEA

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The coastal nutrient budget has been substantially impacted by submarine groundwater discharges, which can cause eutrophication and harm marine ecosystems. We investigate submarine groundwater discharges into the Cilician basin by using 228-Radium mass balance method. Here, we show early findings from our pilot sampling session of groundwater, river, and seawater.

We have conducted one pilot sampling campaign, two seasonal cruises, and two catchment expeditions for ²²⁸Ra sampling. We used MnO₂-impregnated acrylic fibers to pre-concentrate the Ra. ¹ Ra activities were measured by High Purity Germanium detectors at Louisiana State University and the Turkish Acceleration and Radiation Laboratory.

Here, we present the ²²⁸Ra activities of the pilot campaign samples (4 seawater, 2 groundwater, 1 river). The groundwater from the deeper well had the maximum activity (61.64 dpm.m⁻³, depth=50 m), while the lowest activity was found in the deep seawater (7.47 dpm.m⁻³, depth=580 m). Coastal surface seawater activity was the highest among the seawater samples (25.75 dpm.m⁻³, depth=3 m). Given that the deep water layer in the Mediterranean Sea has the lowest activity levels, this pattern was anticipated. ²

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This study is funded by The Scientific and Technological Research Council of Turkey (TÜBİTAK, 120Y082) and The Marine Ecosystem and Climate Research Center.

PLUTONIUM AND NEPTUNIUM INORGANIC COMPOUNDS – WE STILL HAVE A LOT TO EXPLORE

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Due to the unique electronic configuration of f-electrons and distinct chemical properties, the field of inorganic chemistry involving actinides is multifaceted, dynamic, and scientifically challenging. At the same time, understanding actinide behaviour in aqueous media is essential for preventing and predicting the spread of radionuclides in the environment. Modelling the behaviour of actinides in the environment is associated with understanding the actinide species under certain conditions and the thermodynamic description of the processes related to its formation (precipitation, sorption, etc.).

Most of the ecotoxicological risk caused by spent nuclear fuel stems from only a few chemical elements, among which the actinides plutonium (Pu) and neptunium (Np) prevail after about 10^5 years. Here, we investigate the formation patterns of Np and Pu-containing particles in aqueous media, focusing on their interactions with vital inorganic ligands such as hydroxide, carbonates, and phosphate. Given Pu and Np complex redox chemistry and high radiotoxicity, our study also includes their less radioactive monovalent thorium (Th) analogue and non-radioactive cerium (Ce) for comparison. We aim to establish the relationship between actinide particle formation conditions, size, structure, and thermodynamic properties. Current knowledge gaps exist in the structural information of Pu and Np carbonates and phosphates due to the challenges posed, particularly by handling radioactive compounds for investigation. To address these challenges, we utilize synchrotron radiation, allowing us to study small quantities of substances and samples with low crystallinity. Our methodology involves X-ray Absorption Spectroscopy (EXAFS/XANES), Powder X-ray Diffraction with subsequent Pair Distribution Function Analysis.

The structures of double carbonates of Np(V) and Pu(V), as well as double phosphate of Pu(IV), Th(IV), and Ce(IV), have been decoded for the first time. The solubility constants for $\text{Ca}_{0.5}\text{NpO}_2\text{CO}_3$ and $\text{Mg}_{0.5}\text{NpO}_2\text{CO}_3$ were calculated through dissolution experiments. Additionally, the Pourbaix diagrams for Pu and Np in the presence of Na^+ and K^+ cations were reconsidered based on experimental data on solids formation.

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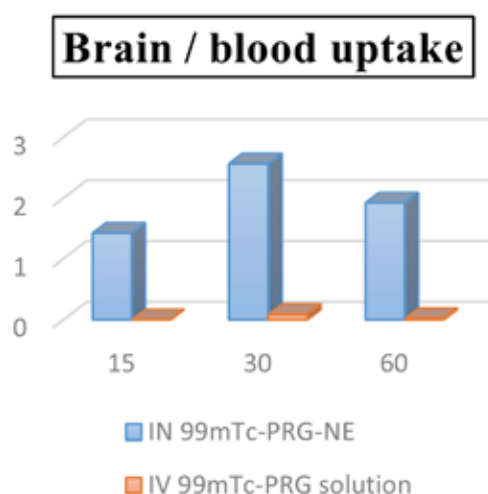
INTRANASAL NANOEMULSION OF PREGABALIN: FORMULATION & RADIOKINETIC EVALUATION WITH ^{99m}Tc

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Pregabalin (PRG) is used for management of neuropathic pain, seizures, and anxiety disorders¹. A required frequent high dosing of oral PRG due to variations in absorption lead to dose-limiting side effects as dizziness, sleepiness, dry mouth, blurred vision, difficulty with concentration². To improve brain uptake with minimal side effects, nano-emulsion (NE) formula of PRG (for intranasal injection) was prepared using isopropyl myristate (10% v/v), Tween 80 (27.5% v/v), and PEG 400 (27.5% v/v). For in-vivo biological evaluation of PRG-NE, radiolabeling of PRG using ^{99m}Tc was performed by direct chelation method³. Maximum RCY of 92.6% was achieved using 150 μg of PRG and 15 mg of sodium dithionite at pH 6 for 45 minutes. Radiokinetic evaluation was studied in albino mice by comparing biodistribution of IN ^{99m}Tc -PRG-NE and IV ^{99m}Tc -PRG solution at different times (15, 30 and 60 minutes). Results should higher brain/blood ratio of radioactivity for IN ^{99m}Tc -PRG-NE compared to IV ^{99m}Tc -PRG solution at all times. Such findings suggest I.N. PRG-NE as a hopeful strategy for enhancing PRG brain delivery.



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STATUS AND PROSPECTS FOR THE USE OF TECHNOLOGIES FOR HANDLING TRITIATED GAS AND WATER STREAMS

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In connection with the development of nuclear energy and various enterprises in the nuclear industry, the genetically significant radioactive isotope of hydrogen – tritium – is currently attracting increasing attention from environmental services and the population. During the operation of these facilities, large quantities of gaseous and aqueous waste are generated, the concentration of tritium in which exceeds the standards established by law. Public opinion does not allow these wastes to be managed using the methods previously used, for example by diluting them to ensure the required tritium content. Therefore, in the technical literature and at conferences, various options for using of physico-chemical methods of isotope separation to purify waste streams while simultaneously obtaining minimal volumes of tritium concentrate for the purpose of its further disposal or processing up to tritium as a product are actively discussed.

The report reviews various hydrogen isotope separation methods for solving detritiation problems. One such task, tritium removal from heavy water, has been used on various scales for over 50 years using a combination of different methods, yielding tritium as a product. When detritiation of gas flows, combined technologies are also used, in the first stage of which the catalytic oxidation of all tritium-containing compounds to water is used, followed by the removal of water vapor from the gas using various methods. The problem of detritiation of light water is associated with the fact that the flow rates are usually large, and the tritium concentration is low and does not allow one to count on obtaining a significant amount of pure tritium. In this regard, the cleaning process is very expensive. A method that involves the transit use of molecular hydrogen, significant quantities of which are expected to be produced as part of the hydrogen energy development program, is being considered as a promising purification option.

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APPLICATION OF GRAPHENE QUANTUM DOTS IN THE DECONTAMINATION OF RADIONUCLIDE- POLLUTED SURFACES

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Nuclear terrorism involves the use or threat of nuclear weapons or radioactive materials by non-state groups, primarily for ideological or political motives^{1,2}. This includes activities such as detonating nuclear devices, dispersing radioactive materials (known as “dirty bombs”), sabotaging nuclear facilities, and smuggling nuclear materials. The proliferation of nuclear knowledge and materials has increased the theoretical possibility of terrorist groups constructing nuclear devices, although technical and resource barriers remain significant. As an alternative, terrorist groups have opted to use “dirty bombs,” which are easier to construct yet can still cause panic and significant damage³.

These bombs combine conventional explosives with radioactive materials to contaminate a wide area⁴. The resulting radiological and environmental impact can have long-term consequences for public health and the environment. Therefore, there is interest in exploring the potential of materials such as graphene quantum dots (GQDs) for the rapid and effective decontamination of areas exposed to radioactive materials⁵.

Strategies involving functionalization are employed to augment the attraction of GQDs towards specific isotopes, thereby enhancing the decontamination process. The results indicate that GQDs could assume a pivotal role in mitigating the repercussions of dirty bomb detonations, presenting a swift and efficient approach to diminish the radiological ramifications in affected regions⁶.

The study enhances comprehension of nanomaterial applications in responding to radiological emergencies, positioning GQDs as a feasible solution to tackle one of the contemporary challenges in public health and security. The ramifications of this research extend beyond immediate decontamination efforts, suggesting broader utilities of GQDs in environmental safety measures and nuclear security protocols.

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ULTRAFAST AND SELECTIVE CAPTURE OF $^{99}\text{TcO}_4^-/\text{ReO}_4^-$ FROM WASTEWATER BY HYPER-BRANCHED QUATERNARY AMMONIUM GROUP-FUNCTIONALIZED RESIN

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^{99}Tc primarily exists high mobility in the natural aqueous environment due to its extremely high solubility and non-complexing features, which can easily cause radioactive pollution. We herein report a general strategy for constructing a novel resin (SiPAN-PEI) with multiple positive charges nitrogen, exhibiting ultrafast adsorption kinetics (<3 min), superior adsorption capacities (463.96 mg g⁻¹), and excellent selectivity in the presence of excess competitive anions, which exceed those of most commercial resins. Moreover, based on impressive structure stability in extreme conditions, SiPAN-PEI can still maintain superior adsorption abilities after suffering irradiation, calcination, and immersion in strong acid. In addition, the separation performance kept excellently after five loading-washing-eluting cycles and the total adsorption ratio can still reach 97%. Outstandingly, SiPAN-PEI can remove most of ReO_4^- from simulated nuclear wastewater through a sequential injection automatic separation system and can reduce the concentration of ReO_4^- to the maximum concentration standard set by the World Health Organization (WHO) in a short time. Leveraging density functional theory calculations and other characteristics clearly elucidated adsorption mechanism of anion-exchange between Cl^- and $\text{TcO}_4^-/\text{ReO}_4^-$. In terms of superior adsorption property, SiPAN-PEI is demonstrated to be a pretty candidate for ^{99}Tc elimination from wastewater.

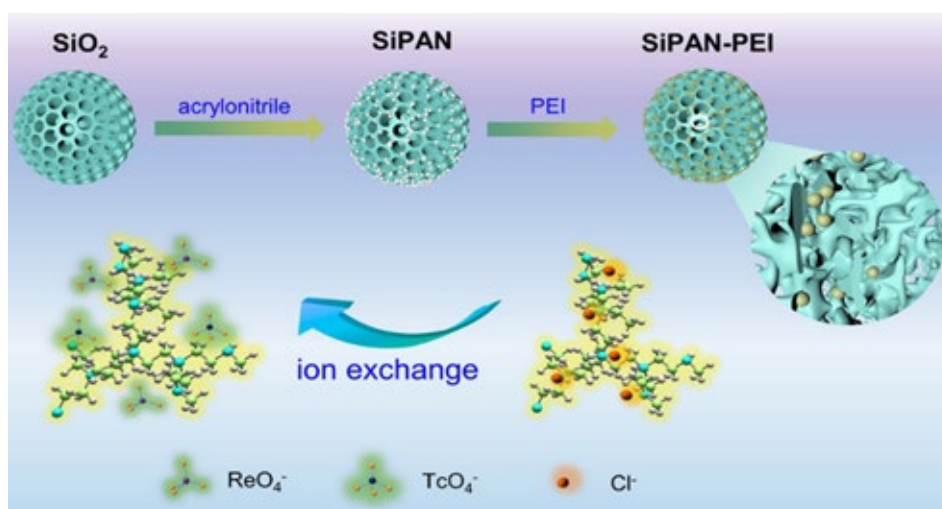


Figure 1. Schematic illustration of facile synthesis to SiPAN-PEI

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MODELING OF RADIOLYTIC STABILITY OF COMPLEXING AGENTS FOR SPENT NUCLEAR FUEL REPROCESSING AND RADIOPHARMACEUTICALS

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Radiolytic stability is one of the main requirements for new complexing agents in spent nuclear fuel reprocessing and radiopharmaceuticals. Due to the high activity of the solutions, organic molecules are transformed and change their chemical and physical properties. The traditional method of radiolysis investigation involves organic synthesis, research of extraction properties, and radiolysis investigation in experimental studies. Each step is expensive and time-consuming, but it is necessary to ensure the stability of the new system.

Here we would like to present the model, that estimates the radiolytic stability of molecules based on their 2D structure. The suggested approach is based on the quantum chemical calculation and swarm intelligence method. The main advantage of the model is a possibility to use it at the pre-synthetic stage. The model was tested using experimental and literature data from radiation experiments.

The model consists of two main components. The first involves generating molecular conformations to account for the strong dependence of electronic properties on molecular conformation. We use an Artificial Bee Colony algorithm for global and local conformational search. The next step is quantum chemical calculation of atomic site reactivity using the D3-B3LYP/def2-TZVP level of theory, considering the steric accessibility of active centers. By incorporating artificial intelligence conformation generation, condensed dual descriptor, and surface accessible surface area calculation, we develop a new reactivity descriptor (CRD – conformational reactivity descriptor). We achieve a high correlation ($R^2=0.97$) between experimental radiolytic constants and CDR values.

The investigations were supported by financing Interdisciplinary Scientific and Educational Schools of Moscow M.V. Lomonosov State University (No. 23-III03-04). The research was carried out using the equipment of the shared research facilities of HPC computing resources at Lomonosov Moscow State University.

NEW ^{99m}Tc RADIOPHARMACEUTICALS FOR MYOCARDIAL METABOLIC PROCESSES

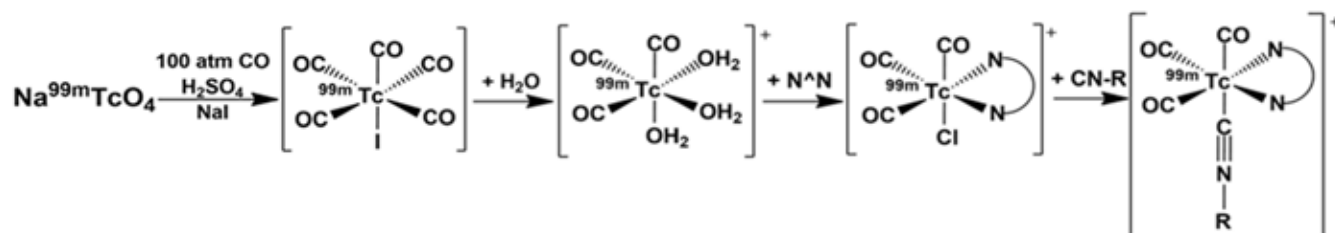
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Previously we showed that the heart uptake of “2+1” tricarbonyl complexes of technetium with 1,10-phenanthroline and 2,2'-bipyridine is comparable to that of MIBI¹. We also found that isocyanides form strong complexes with technetium(I)². These data suggest that “2+1” tricarbonyl complexes of technetium with 1,10-phenanthroline and 2,2'-bipyridine show promise for introduction of technetium *via* the isocyanide group into fatty acids³ with the aim to develop a new technetium radiopharmaceutical for heart metabolic process. In this work we developed a procedure for preparing “2+1” tricarbonyl complexes of technetium-99 and rhenium with a combination of the bidentate ligands and fatty acid isocyanides (CN(CH₂)₄CH(COOMe)SC₁₀H₂₁, CN(CH₂)₁₀COOMe). The complexed were isolated and characterized by IR and NMR spectroscopy. The IR spectrum of the complexes contains three bands typical for the tricarbonyl fragment. The coordination of the isocyanide group is confirmed by the ¹H NMR. Based on the results obtained we developed the procedure for preparing “2+1” tricarbonyl complexes of technetium-99m:



These complexes were obtained and characterized by HPLC using technetium-99 analogs as the reference. The lipophilicity of the technetium-99m complexes was measured.

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STATUS MA SEPARATION PROCESSES AT “PRORYV” PROJECT

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In Russia, active work is underway to isolate americium and curium as the framework for the PRORYV project. This project involves a two-step process. It includes the extraction and separation of Americium, Curium, and Rare Earth Elements from a PUREX raffinate, followed by sorption separation and obtaining a pure Americium fraction. After a cycle of laboratory studies, comparative dynamic tests of extraction systems based on TBP, CMPO, TODGA, ATP-CCD, Dyp-7 were carried out. According to the results of these tests, the TODGA system was selected for further testing on a real HLW. “Hot” dynamic testing of the process for extracting actinides from PUREX refineries was carried out at Mayak Production Association and the JSC Radium Institute using the TODGA extraction system. Deep extraction of Americium and Curium (99.9% initial content) has been demonstrated. Resource testing was conducted, organic phase entrainment with water flows was determined. In addition, the TODGA – F3 system showed high hydrodynamic and radiation resistance.

A number of techniques have been tested for separating americium and curium. During the deposition of complex carbonate, a high-purity product is obtained. However, losses of TPE with the washing solution was from 15% to 20%. Experiments on the production of americium in higher oxidation states, followed by its separation from REEs, have yielded non-reproducible and ambiguous results. Reference literature data could not be reproduced. Sorption chromatographic separation of americium and curium under pressure was selected as the basic option. Successful experiments on chromatographic separation of americium, curium, and REE have been carried out at sites of the Mayak Production Association and JSC “VNIINM” using concentrate Am, Cm, and REEs isolated from SNF products from WWER-1000 reactors.

As a result, americium fractions with a purity of 99.9% were produced, which are suitable for inclusion in a nuclear fuel compositions.



ENVIRONMENTAL BEHAVIOR OF URANIUM ACCUMULATED AT NUCLEAR LEGACY SITES

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Uranium mobility in the environment depends both on its original form, including oxidation state, and on the geochemical conditions of the environment (pH-Eh; presence of carbonates, organic matter, biota etc.). At nuclear legacy sites, artificial uranium entered the environment mainly during technological discharges of liquid radioactive waste into surface reservoirs and underground storages, as well as in the form of aerosol accidental fallout and during nuclear weapons testing¹. Each site requires a separate scientifically based approach to safe decommissioning and further management of a historically contaminated facility, taking into account the current forms of radionuclides and their possible transformations in the future.

In this work, our comprehensive approach, combining the methods of classical wet chemistry, advanced spectrometry and electron microscopy methods, as well as modeling, was applied to the analysis of uranium forms of radioactively contaminated objects of different origin and age.

Understanding the migration behavior of long-lived radionuclides under geochemical environmental conditions is the basis for predicting the spread of radionuclides and justifying measures to reduce this spread, which is necessary for the formation of favorable public opinion.

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This work was supported by Russian Science Foundation (grant #19-73-20051).

LONG-TERM TRENDS OF ARTIFICIAL RADIONUCLIDES IN BIOTA OF THE YENISEI RIVER (SIBERIA, RUSSIA)

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The Yenisei River receives controlled radioactive discharges from the Krasnoyarsk Mining-and-Chemical Combine (MCC). In the last two decades, the composition and activity of radionuclides entering the Yenisei River with radioactive discharges has changed significantly as a result of the modernization of the production activities of the MCC. Aquatic biota species-specifically accumulates radionuclides in its biomass and participates in their transfer in the ecosystem. Therefore, hydrobionts are informative indicators of radioactive contamination of aquatic ecosystems, allowing studying the forms and mechanisms of radionuclide transfer. In this work, we studied the time-dependent trends of technogenic radionuclides in the biomass of key species of aquatic biota of the Yenisei, representing different ecological groups: submerged macrophytes, benthic invertebrates and commercial fish, in the period from 2003 to 2023. The study showed multidirectional trends of plutonium (^{238}Pu , $^{239,240}\text{Pu}$) and gamma-emitting radionuclides (^{60}Co , ^{137}Cs , ^{152}Eu , etc.) in aquatic organisms, reflecting the dynamics of controlled radioactive discharges. The plutonium content in aquatic organisms increased in response to increased plutonium discharges; the content of isotopes with induced activity (^{60}Co , etc.) in aquatic organisms decreased following a decrease in discharges of these isotopes; no trends in the ^{137}Cs content in aquatic organisms were identified, which is consistent with the absence of stable trends in the discharges of this isotope. Aquatic biota showed higher sensitivity to increased radioactive releases to the river than bottom sediments. The species-specific sensitivity of aquatic organisms to changes in the releases of radionuclides into the river is shown, the rates of the decrease in the content of radionuclides in biota and the efficiency of the trophic transfer of radionuclides are assessed.

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DETERMINATION OF ^{249}Bk CONTENT IN THE IRRADIATED MATERIAL SOLUTIONS

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The industrial-scale production of ^{252}Cf is a long-term (7-8 years), multistage process including irradiation of gram mass of plutonium and curium. During ^{252}Cf production, ^{249}Bk ($T_{1/2}=330$ full days) is accumulated in targets and as a result of its irradiation within 1-2 months additional amount of ^{252}Cf can be produced.

It is quite challenging to determine the burnup of initial Bk during irradiation when producing Cf from Bk targets. ^{249}Bk isotope is a soft β – emitter with maximum energy of 124keV ($E_{\text{ave}}=36$ keV), and alpha-particles yield with energy of 5.4MeV during decay is only 0.0014%. It is impossible to determine the Bk activity in the solution on the background of Cm, Es, Cf isotopes and fission fragments.

The target containing ^{249}Bk and ^{249}Cf in the amount of 1.2mg and 0.27mg, respectively, was irradiated during 20.1 effective full days in the SM-3 reactor neutron trap. The copper powder was used as a diluter.

^{249}Bk was extracted in two stages. At the first stage, ^{144}Ce was sorbed on BioRad AG1x8 anion exchange resin; the sorption was performed from mixture of 8 M HNO_3 and 0.1 M HBrO_3 to retain Bk in the oxidation state +4. After Bk elution with 0.5 M HNO_3 , it was purified from Cf and fission fragments with Ln-resin sorbent. The sorption was performed from 6 M HNO_3 and 0.1 M HBrO_3 , and Bk was eluted with the mixture of 4 mol/l HNO_3 and 0.1 mol/l N_2H_4 , converting it to the oxidation state +3.

The ^{249}Bk activity was determined in the purified solution by measuring the accumulation rate of the daughter ^{249}Cf , which decays with the emission of gamma rays with the energy of 388keV. The ^{249}Bk burnup was experimentally measured during irradiation and made up 98.4 %.

EVALUATION OF DISTRIBUTION COEFFICIENTS FROM DATA OF SORPTION AND DIFFUSION EXPERIMENTS

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The standard method for determining the numerical values of distribution coefficients (K_d) of elements is static sorption experiments. If the sorbate concentration in the solution decreases significantly during the experiment, the use of the final concentration value for calculating K_d (SE method) will be incorrect. In this case, equilibrium is not established between the concentrations of the element in the solid and liquid phases, since the element accumulates on the sorbent throughout the experiment, both at initially high and at finitely low concentrations in the solution. To solve this problem, a method for taking into account changes in concentration when processing the results of static experiments based on kinetic curves (SE+K) is proposed.

Another method for determining K_d is the experiments on diffusion of elements in a pore solution (DE). Both types of experiments were carried out with clay materials KhB and M by using radiochemical tracers: ^{90}Sr , ^{137}Cs , ^{233}U , ^{237}Np , ^{238}Pu , ^{241}Am in the leachates of model borosilicate glasses: BS-1 and BS-2. The results of calculating K_d (cm^3/g) based on through diffusion and static sorption data are given in the table. The comparison shows good agreement between the results of DE and SE+K methods for well-sorbed strontium and cesium, which confirms the correctness of the proposed SE+K method. Small differences are associated with different densities (sorption surface) of materials in different types of experiments.

Solution/material	Method	Element					
		Sr	Cs	U	Np	Pu	Am
BS-1/KhB	SE	910	640	20	–	6990	–
	SE+K	78	71	13	–	130	–
	DE	–	62	14	–	–	–
BS-2/KhB	SE	740	10600	38	–	5990	–
	SE+K	78	131	21	–	140	–
	DE	–	94	6.6	–	–	–
BS-2/M	SE	580	1300	3.4	37	230	450
	SE+K	71	92	3.4	23	55	78
	DE	20	7	2.8	–	–	–



CARBOHYDRAZIDE BEHAVIOR PATTERNS IN ELECTROCHEMICAL PROCESSES OF SNF REPROCESSING TECHNOLOGY

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Carbohydrazide (CHZ) is a new reductant, that will be used in U/Pu re-extraction processes at spent nuclear fuel (SNF) reprocessing facilities that are under construction in Russia. SNF reprocessing technology includes electrochemical processes for Pu(IV) stabilization and decomposition of excess amount of reductant.

The main goal of this work was studying of CHZ behavior in electrochemical processes in "CHZ – HNO₃", "UO₂(NO₃)₂ – CHZ – HNO₃" and "Pu – CHZ – HNO₃" systems.

A linear decrease of CHZ concentration under electric current was observed. The main mechanisms of CHZ decomposition are oxidation of CHZ at anode and chemical reaction between CHZ and HNO₂ forming at cathode. Presence of UO₂(NO₃)₂ and/or Pu(III) reduces the rate of CHZ oxidation.

CHZ behavior patterns were characterized by cyclic voltammetry. Variants of chemical reactions for definition of electrolysis processes are suggested. CHZ influence on Pu(III, IV, VI) behavior at "Pu – CHZ – HNO₃" electrolysis was described.

DEVELOPMENT AND EVALUATION OF ALTERNATIVE SCHEMES OF GENERATOR OPERATING BASED ON ION EXCHANGE IN CARBOXYLIC ACID MEDIA

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In the present work, the operating of the reverse-tandem scheme of the radionuclide generator is considered, as exemplified by the radionuclides pair ^{172}Hf ($T_{1/2} = 1.87 \text{ y}$) / ^{172}Lu ($T_{1/2} = 6.7 \text{ d}$), ^{140}Ba ($T_{1/2} = 12.751 \text{ d}$) / ^{140}La ($T_{1/2} = 1.67858 \text{ d}$), ^{90}Sr ($T_{1/2} = 28.91 \text{ y}$) / ^{90}Y ($T_{1/2} = 64.05 \text{ h}$), and ^{44}Ti ($T_{1/2} = 59.1 \text{ y}$) / ^{44}Sc ($T_{1/2} = 4.042 \text{ h}$). The main parameters of the generators are discussed as well. General scheme of the generator is shown on the Figure 1. All of the generators were developed based on the study of the ion-exchange behavior of radionuclides, which was carried out by the authors.^{1,2,3}

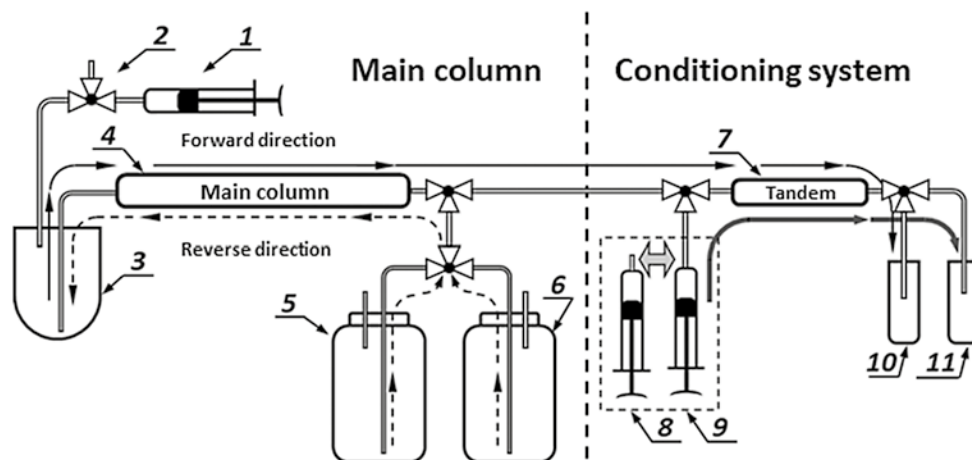


Figure 1. Reverse-tandem scheme of the generator. (1) – syringe for maintaining pressure / underpressure, (2) – valve, (3) – reverse storage vessel, (4) – main column, (5, 6) – solutions for washing column in reverse direction, (7) – tandem column, (8, 9) – solutions for conditioning and eluting of daughter radionuclide, (10) – waste vial, (11) – vial with the radiopreparation of daughter radionuclide

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CERAMIC MATRICES BASED ON BENTONITE CLAY FOR IMMOBILIZATION OF RADIOACTIVE WASTE FROM REPROCESSING OF SPENT NUCLEAR FUEL OF MOLTEN SALT REACTORS

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Molten salt reactors have been developing for the purpose of “transmutation” of minor actinides. The working body in such reactors is assumed to be a molten salt: a eutectic mixture of fluoride salts, either FLiNaK (lithium, sodium, potassium fluorides) or FLiBe (lithium and beryllium fluorides). At present, there are no simple and reliable technologies for immobilization of complex radioactive waste represented by a mixture of fission product fluorides.

In this work, matrix samples of a eutectic mixture of FLiNaK with imitators of high-level waste (up to 30 wt.%) and natural raw bentonite were synthesized. The samples in the form of tablets were annealed at different temperatures (700–1000 °C), their phase composition has been determined. The high chemical resistance at 25 °C (caesium leaching rate $< 10^{-5}$ g/(cm²·day)) and high mechanical durability (> 9 MPa) at all selected annealing temperatures (650–900 °C) has been observed. It has been determined by X-ray diffraction analysis with in-situ heating and thermogravimetry with differential scanning calorimetry that the most significant changes in the structure of matrix samples occur at a temperature of ~700 °C. It has been found that fluorine binds to clay components at temperatures below 800 °C. The optimal temperature range for synthesis is found to be between 650–800 °C. It is shown that the addition of calcium compounds has a positive effect on the binding of fluoride ion, which leads to an increase in the temperature of the onset of HF release and the durability of the samples and reduces cesium leaching. The spark plasma sintering method allows to produce matrix samples with similar characteristics. In addition, this method allows for faster synthesis and is potentially suitable for obtaining massive samples.

In conclusion, the results demonstrate the principal possibility of using materials based on bentonite clay for immobilization of fluoride radioactive waste.

USE OF T-3K SORBENT TO CONCENTRATE Sr-90 IN RADIOACTIVE WASTE MANAGEMENT

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The main tasks in the final phase of radioactive waste management are the treatment and disposal of radioactive waste (RAW). It is necessary to control the release of radionuclides into the environment at the disposal of RAW. The concentration of radionuclides for RAW treatment and radiochemical analysis may be carried out using the same sorption materials. The sorbent T-3K, manufactured by JSC “Inorganic sorbents” can be used for concentrating Sr-90 when solving problems of handling RAW. The regularities of the concentration of Sr-90 sorbent T-3K from a model alkaline high-activity waste (HAW) corresponding to the composition of HAW accumulated at FSUE PA “Mayak” were investigated. Conditions are provided for their treatment.

Developed a method to determine Sr-90 in the water of observation wells of the storage and burial facilities of radioactive wastes with a detection limit of 0.02 Bq/l. The method was tested during radio-ecological monitoring of water of 18 surface sources in the territories of Sverdlovsk and Chelyabinsk oblasts, as well as 12 sources of groundwater and sewage, selected on the territory of the storage and burial facilities of radioactive wastes FSUE “Federal environmental operator” and FSUE “National operator for radioactive waste management”.

It is shown that the Sr-90 content in the waters of the observation wells of the storage and burial facilities of radioactive wastes does not exceed the permissible, and in the waters of the examined natural water bodies, rivers and lakes in the territories of Sverdlovsk and Chelyabinsk regions does not exceed the level of intervention for drinking water, except for the Techa River.

The study was supported in part by the RFBR and the Government of the Sverdlovsk Region within the framework of project № 20-43-660055, the Ministry of Science and Higher Education of the Russian Federation (the basic part of the state assignment, project № FEUZ-2023-0013).

INFLUENCE OF REGENERATION METHOD ON THE LOWER TEMPERATURE LIMIT OF FLAME PROPAGATION OF IRRADIATED EXTRACTION MIXTURE

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Under the influence of ionizing radiation on the extraction mixture, the initial substances decompose, and due to the presence of an active oxidizing agent – nitric acid, oxidation and nitration products are formed. This reduces the efficiency of radionuclide separation and worsens the hydrodynamic characteristics of the mixture. In addition, highly volatile radiolysis products are formed, which reduce the lower temperature limit of flame propagation (T_f) and the flash point (T_{fl}) of the irradiated extraction mixture, which makes the SNF reprocessing process fire and explosion hazardous.

To restore the performance characteristics of the extraction mixture, it is washed with a solution of soda or alkali. This study is devoted to determining the influence of regeneration of an extraction mixture of 30% TBP in Isopar-M irradiated to 2 MGy, saturated with 3.4 mol/l HNO_3 by different methods on the value of T_f .

All studied regeneration methods are effective for increasing T_f (Table 1). However, regeneration with carbonate solutions is the simplest and most economical method in terms of technical performance in radiochemical production.

Table 1. The value of T_f after regeneration of mixtures using various methods

Regeneration method	T, °C	Reagent options	T_f , °C
washing with carbonate solutions	25	0.5 mol/l NaHCO_3 , 1 mol/l $\text{C}_3\text{H}_{12}\text{N}_6\text{O}_3$, 1 mol/l $\text{C}_2\text{H}_7\text{NO}_3$	68–69
steam distillation	105	without reagents	73
installation of counter flows	40	air	79
fractional vacuum distillation	82.5	without reagents	80
column-type separator with upper separation chamber ¹	40	– 1 mol/l Na_2CO_3 , 0.1 mol/l NaOH , 1 mol/l $(\text{NH}_4)_2\text{CO}_3$; – air; – without reagents	72

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QUALITY INDICATORS OF MAGNESIUM POTASSIUM PHOSPHATE COMPOUND FOR SOLIDIFICATION OF NPP NITRATE EVAPORATOR BOTTOMS

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Evaporator bottoms (EBs) are radioactive waste (RW) generated during evaporation of liquid RW (LRW) at nuclear power plants (NPP). These are high-salt solutions with concentration up to 500–600 g/L contaminated with fission, activation, and corrosion products. EBs are classified as intermediate level waste (ILW) according to the activity level and must be solidified¹. Cementation is a common method of solidification of LRW due to the simplicity of the process². However, this technology has a number of significant disadvantages, primarily the low salt background of the waste and the degree of salt incorporation in the cement compound, as well as its low water resistance and frost resistance. The efficiency of low-temperature mineral-like magnesium potassium phosphate (MPP) matrix of composition $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ as an alternative to cement compound for solidification of RW of different chemical, radionuclide, and aggregate states was shown earlier in GEOKHI RAS². The purpose of this study was to test the MPP matrix for solidification of high-salt nitrate EBs simulator and to determine the quality indicators of the resulting compound.

MPP compound samples containing up to 22.3 wt.% NaNO_3 (NaNO_3 content in solution was 620 g/L) and up to 20 wt.% CaSiO_3 as a reinforcing additive were obtained. It was found that the crystalline phase $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ is the main phase of the obtained samples. It was noted that KNO_3 phase is formed in the samples, which indicates the substitution of potassium for sodium from the composition of the EBs simulant. Compressive strength of the samples meets the regulatory requirements of NP-019-15 for solidified ILW (not less than 4.9 MPa), including after studying their resistance to thermal cycles of freezing/thawing and water resistance. The leaching rate of ^{137}Cs from the MPP compound is low: no more than 10^{-3} g/(cm²·day). Thus, the possibility of using the MPP compound for solidifying high-salt nitrate EBs of NPP has been demonstrated.

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VALIDATION OF A CHROMATOGRAPHIC MODEL FOR THE SEPARATION OF ACTINIDES FROM PRODUCTS OF NUCLEAR REACTIONS INDUCED BY HEAVY IONS

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The only way to produce transfermium elements for their study is the accelerator production method in particular multinucleon transfer nuclear reactions with heavy ions¹. Neutron-rich isotopes of these elements can be synthesized as a mix of reaction products with predicted half-lives from 1 min to 1 day. Such nuclear physical properties and very similar chemical properties of heavy actinides limit a number of separation methods. A method that meets all the requirements is cation exchange chromatography in α -hydroxyisobutyrate ammonia (α -HIB)².

We developed the semi-empirical model of predicting the chromatographic parameters, elution and position of actinides peaks on the chromatogram. The validation of the model was performed in application of high-pressure liquid chromatography to separation of Cf and Fm from irradiated uranium target. In this work we irradiated thin ^{238}U target with 1150 MeV Xe ions with an average intensity of 20 nA for 48–72 hours at the U-400 accelerator (FLNR). After cooling for 1 hour, we dissolved U target to make a separation. Radiochemical separation procedure was performed in two steps. Separation of target material, neptunium and plutonium using UTEVA resin followed by cation exchange separation of Cf and Fm fractions with α -HIB. The later followed by preparation of spectrometric sources by LaF_3 co-precipitation method. The optimal amount of carrier and the thickness of the spectrometric sources were calculated with the SRIM program taking into account energy losses. Using this approach an energy resolution of 70 keV was achieved. Final samples were analyzed with gamma- and alpha-spectrometry to search isotopes of Cf and Fm, estimate the yield and the cross section.

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COMPARISON OF SORPTION BEHAVIOR OF URANIUM AND AMERICIUM ON POLYMINERAL AND BENTONITE CLAYS

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Most concepts for safe disposal of radioactive waste involves application of clay materials in a construction of protective barriers.¹ The bentonite clay is usually applied at a final isolation of high-level waste and spent nuclear fuel.² In case of near surface disposal facilities for intermediate level and low-level waste the kaolinite-montmorillonite clay mix is used.³ The montmorillonite(30–35%)-kaolinite(20–25%)-illite(10–15%) polymineral clay of the Biklyanskoe deposit is the analogue of widely used clay mixes. In the present work the sorption behavior of U-233 and Am-241 on this polymineral clay was studied and compared with the bentonite clay of the Dinozavrovoe deposit, containing about 80% of montmorillonite.

It was found that distribution coefficients (K_d) for ^{233}U in the pH range 4–9 on the clay of the Biklyanskoe deposit was several times higher than K_d values obtained on the bentonite. The highest extent of sorption ($\leq 98\%$) was observed in the pH range 5–7 in case of both studied clays.

The distribution coefficient value for ^{233}U at pH 8 on the polymineral clay was an order of magnitude more than the one obtained on the bentonite when the both clay samples were pre-rinsed with a modeling water.

Americium sorption on the studied clay of the Biklyanskoe deposit was marginally lower than on bentonite clay of the Dinozavrovoe deposit. However, the both clays provide high americium uptake from liquid phase ($\leq 98\%$) at pH values greater than 3. The values of sorption for ^{241}Am at pH 8 were the same for clay mix and bentonite clay when the clay samples were pre-rinsed with a modeling water.

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SECONDARY RADIOACTIVE CONTAMINATION OF A FRESH WATER ECOSYSTEM: MODEL EXPERIMENTS

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An important issue is to be considered in the investigations of the propagation of radioactive contamination: any freshwater ecosystem is a natural barrier for the migration of radioactive substances. Though there is a huge amount of information concerning primary radioactive contamination, secondary radioactive contamination raises a number of questions and hypotheses.

The present study is aimed at revealing the mechanism of secondary contamination of a freshwater ecosystem using model experiments (on the example of the river Yenisei).

Taking into account the predominantly sand-and-shingle bottom sediments of the river Yenisei, in the model experiments use was made of flood plain soils sampled in the area located in the direct proximity of the buffer zone of the Mining and Chemical Combine¹. The results of the spectrometry investigations showed the presence of Pu isotopes, ¹³⁷Cs, ⁶⁰Co, ²⁴¹Am, as well as Eu and U isotopes and a considerable amount of metals. The samples were exposed to: 1) the river water, only, 2) the water with an introduced dissolved organic substance, 3) the model system additionally contained growing aquatic plants which are most widely spread in the ecosystem of the river Yenisei. Taking into account the long duration of the experiments, the radioactivity and content of metals were controlled with a periodicity of 30 days. After 365 days from the beginning of the experiment, the content of radionuclides and metals in the flood plain soils under study was found to be <MDA-15% from the initial content. The lowest content was observed in the system with the growing plants. After the experiment, the plants were also studied. The largest amount of the accumulated radionuclides and metals was observed to be assimilated in the above-ground part of the plants. A conclusion was made about a significant impact of the organic substances on the radionuclide migration and a preliminary model of this mechanism was created.

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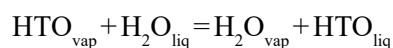
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PHASE ISOTOPIC EXCHANGE AS A METHOD FOR TRITIUM REMOVAL AND CONTROL

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Tritium is a radioactive isotope of hydrogen with soft beta radiation ($E_{\beta}=0-18.6$ keV). Usual, its external irradiation doesn't hazard, but being inside organisms in the form of tritiated water (HTO) can induce mutations in DNA¹. Japan government decision to discharge tritium-containing water into the Pacific Ocean attracted the public attention and increased efforts to assess tritium impact on flora and fauna². Methods for extracting tritium from gas streams typically involve catalytic conversion of all tritium-containing compounds into vapor of tritiated water, followed by extraction of HTO through sorption or gas scrubbing methods. Due to high specific activity of tritium ($A_{sp}=356.3$ TBq/g), a high degree of purification is required. Currently, Russia is rapidly developing and implementing technology based on phase isotopic exchange (PhIE)³:



Tritiated water vapor with carrier-gas are introduced into counter-current packing columns. By the PhIE reaction, tritium is transferred from the gas phase to the liquid phase, this allows to achieve almost any degree of gas purification from tritium. The process is technically scalable for various tasks, from small-scale operations of a few liters per hour to thousands of cubic meters per hour. This feature enables to use the PhIE not only for tritium removal from gas streams but also for its sampling for radiation control purposes⁴. This work outlines the fundamental physicochemical and kinetic principles of the implementation of the PhIE process.

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TRITIUM PROBE AND SUPERCOMPUTER SIMULATION OF STRUCTURE OF COMPLEXES AND INTERACTIONS BETWEEN CARBON NANOTUBES, CHITOSAN AND ALBUMIN

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Single-walled carbon nanotubes (SWCNT) demonstrate outstanding durability and elasticity, very special electrophysical properties; their internal cavity may serve as a nanocontainer for drugs, that is the reason for SWCNT being considered as a component of new materials contacting with biological media. Biocompatibility of SWCNT may be enhanced by their surface modification with biopolymers such as chitosan but the structure of SWCNT-chitosan is not sufficiently studied. It is of great importance to study SWCNT interactions with biological media when considering them as components of biocompatible materials – most particularly – with blood serum containing albumin as a major component.

Composition of SWCNT-biopolymer complexes has been estimated by us recently with tritium probe method. [³H] bovine serum albumin and [³H]chitosan were obtained with tritium thermal activation technique but interactions in system SWCNT-biopolymer can be hardly detailed with tritium probe only. Calculations were performed with GROMACS software with bovine serum albumin (PDB: 4F5S) as a model protein, polysaccharide chitosan ($M_w = 8.8$ kDa) in protonated form, fluorinated SWCNT (F content 6_{at.%}). Simulation time for each system was 100 ns, preliminary and primary calculations were performed with various thermostat algorithms.

Tritium probe method allowed determination of biopolymers quantity on SWCNT surface. The simulations allowed confirmation of mostly hydrophobic interactions and formation of hydrogen bonds during non-covalent interaction between biopolymers and SWCNT. The conformation of biopolymers on SWCNT surface was established.

The research is carried out using the equipment of the shared research facilities of HPC computing resources at Lomonosov Moscow State University.

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IMMOBILIZATION OF SPENT SULFONIC CATION EXCHANGE RESIN IN MAGNESIUM POTASSIUM PHOSPHATE COMPOUND

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Combined pyrochemical and hydrometallurgical technology of spent nitride fuel reprocessing is planned to be implemented within the framework of the PRORYV project at the pilot demonstration energy complex.¹ The final stage of this technology is the separation of Am and Cm by displacement complexation chromatography using sulfonic cation exchange resin.² Spent sulfonic cation exchange resin is classified as radioactive waste (RW), which must be converted to a stable compound to be radioecologically safe for the environment. Currently, magnesium potassium phosphate (MPP) compound is considered as a promising compound for immobilization of this type of RW.

MPP compound samples containing up to 20 wt.% of pre-saturated with water sulfonic cation exchange resin SPS SAC (8%)-50 grade (Technosorbent LLC, Russia), as well as wollastonite FW-200 grade (Nordkalk, Finland) with particle size of 0.07–0.16 mm in an amount of 10 wt.% as a reinforcing additive³ were obtained in this work. Phase composition, mechanical strength, resistance to thermal cycles of freezing/thawing (in the temperature range –40...+40 °C), water resistance after 90 days immersion in water, and hydrolytic stability in accordance with GOST R 52126-2003 of the obtained samples were studied.

It was found that the main crystalline phase of the studied MPP compound samples is $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$, which is an analogue of the natural mineral K-struvite. Samples containing 10 wt.% of wollastonite have a compressive strength of about 10 MPa, which corresponds to the regulatory requirements of NP-019-15 for cement compound (no less than 4.9 MPa). These samples have the necessary water resistance and resistance to leaching of both americium and curium radionuclides and matrix-forming components.

Thus, the possibility of immobilization up to 20 wt.% of pre-saturated with water sulfonic cation exchange resin in MPP compound has been shown. The quality indicators of the obtained MPP compound meet the requirements of NP-019-15 for solidified RW.

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The work was carried out according to the state assignment of the GEOKHI RAS.

CONDITIONING OF NPP BORON-CONTAINING EVAPORATOR BOTTOMS IN MAGNESIUM POTASSIUM PHOSPHATE COMPOUND

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Boron-containing evaporator bottoms (BEBs) are formed at nuclear power plants (NPPs) with VVER type reactors. Deep evaporation of BEBs to salt melt is an economical method of its reprocessing.¹ The resulting salt melt after additional evaporation contains nitrates and borates of sodium and potassium, and its specific activity is 10^6 – 10^8 Bq/dm³, which is mainly due to ^{134,137}Cs radionuclides.² Currently, several tens of thousands of metal containers with salt melt have already been accumulated at the Balakovo and Novovoronezh NPPs.¹ Various methods have been considered for its processing, one of which is the inclusion in low-temperature mineral-like magnesium potassium phosphate (MPP) matrix.^{1,2} Thus, the purpose of this study was to evaluate the possibility of conditioning BEBs simulator in MPP compound.

MPP compound samples containing up to 25 wt.% of BEBs simulator salts, which were partially dissolved in bidistilled water before solidification (the content of NaNO₃, KNO₃ and H₃BO₃ in the simulator was 412.0, 172.4 and 415.5 g, respectively, per 1 L of H₂O), were synthesized in this work. The synthesis was carried out at the mass ratio of components MgO:H₂O:KH₂PO₄ = 1:2:3, including the effect of CaSiO₃ wollastonite (FW-200) in an amount of up to 20 wt.% on the properties of matrix was investigated. Samples containing ¹³⁷Cs (without a carrier) with a specific activity $(7.1 \pm 0.3) \cdot 10^3$ Bq/g, which was previously bound in potassium-cesium-nickel ferrocyanide, were obtained to study hydrolytic stability. The phase composition, structure, compressive strength, resistance to thermal cycles of freezing/thawing (30 cycles in the temperature range –40...+40 °C), water resistance (after 90 days immersion in water) of the obtained samples, as well as resistance to leaching of ¹³⁷Cs and matrix-forming components from the samples were determined.

The possibility of conditioning up to 14 wt.% of BEBs simulator in MPP compound containing 15–20 wt.% of wollastonite has been demonstrated. The quality indicators of the obtained MPP compound meet the regulatory requirements for the cement compound for LRW conditioning.

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MEASURING ISOTOPIC COMPOSITION OF URANIUM AND PLUTONIUM IN SPENT NUCLEAR FUEL USING THERMAL IONIZATION MASS SPECTROMETRY

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U and Pu are among the target components of spent nuclear fuel (SNF) reprocessing. Isotopic composition of U and Pu is very important due to their further application in the nuclear fuel cycle.

High radioactivity level and complex composition of SNF limit the use of “direct” measurement methods of mass spectrometry. The analysis of U and Pu isotopic composition in SNF involves preliminary recovery of U and Pu by sorbent extraction chromatography impregnated with diisooctyl methylammonium nitrate and methyl trioctyl ammonium nitrate, respectively.

To carry out automatic sample preparation, a special system (consisting of highly efficient chromatographic pumps, a distribution column and a sample introduction system) has been developed and adapted for use in a hot cell. Sorption and desorption are performed automatically, which significantly reduces occupational radiation exposure.

The purified solution is analyzed using thermal ionization mass spectrometry (TIMS). A purpose-designed system automatically applies a sample onto the filaments. This operation is performed remotely from the operator’s console using video monitoring. The equipment arrangement prevents the operator’s contact with the sample, which is critically important when working with highly active samples.

MEASUREMENT OF COMPOSITION OF SHORT-LIVED FRACTION RETURNED TO THE FOREIGN CUSTOMER IN THE FRAMEWORK OF BALANCED NUCLEAR FUEL CYCLE

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The concept of balanced nuclear fuel cycle implies return of vitrified short-lived fraction containing mainly ^{137}Cs and ^{90}Sr to the customer. In order to ensure radiation safety during subsequent long-term storage of the short-lived fraction, it is essential to determine its radionuclide composition.

This study has developed analytical approaches that make it possible to perform measurements for radionuclides found in trace amounts in the short-lived fraction but still presenting a radioecological hazard. These radionuclides include ^{14}C , ^{99}Tc , ^{126}Sn , ^{129}I , ^{135}Cs , $^{234,235,236,238}\text{U}$, ^{237}Np , $^{238-242}\text{Pu}$, $^{241,243}\text{Am}$ and $^{245,246}\text{Cm}$. Determination of these radionuclides is complicated by significant disturbing effect of macroactive components, such as ^{137}Cs и ^{90}Sr , the activity of which is 10^6-10^{12} times higher than that of the target radionuclides.

Table 1. Some methods for preparing samples and measuring short-lived fraction composition

Radionuclide	Sample preparation	Method
^{14}C	Neutralization, precipitation as BaCO_3 . Precipitate dissolution in HNO_3 with stripping of CO_2 . Repeated precipitation of BaCO_3 and stripping. The counting sample was prepared with the use of OptiPhase HiSafe 3 scintillator	Liquid scintillation spectrometry (LSS)
^{99}Tc	Extraction chromatographic (EC) separation from 0.1 M HNO_3 on the sorbent impregnated with methyltriethylammonium nitrate (MTOAN). 8 M HNO_3 desorption (two cycles)	ICP-MS
^{129}I	NaNO_2 oxidation to I_2 . CCl_4 extraction. Na_2SO_3 reextraction (5 cycles). Ultima Gold AB scintillator	LSS
U isotopes	EC separation from 4 M HNO_3 on the sorbent impregnated with diisooctyl methylphosphonate. 0.01 M HNO_3 desorption	ICP-MS
^{238}Pu	EC separation from 4 M HNO_3 on the sorbent impregnated with MTOAN. $(\text{NH}_4)_2\text{C}_2\text{O}_4$ desorption	α -spectrometry
$^{239-242}\text{Pu}$, ^{237}Np		ICP-MS
$^{241,243}\text{Am}$, $^{245,246}\text{Cm}$	EC separation from 4 M HNO_3 on the sorbent impregnated with tetraoctyldiglycolamid. Desorption with diethylenetriaminepentaacetic acid	ICP-MS

STUDY OF ^{137}Cs , ^{85}Sr , ^{60}Co RADIONUCLIDES ADSORPTION AND IMMOBILIZATION BY (Ca, Mg)-Zr PHOSPHATES

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^{137}Cs , ^{90}Sr , ^{60}Co radionuclides made the main contribution to the dose load of liquid radioactive waste (LRW), which forms during the operation of nuclear power plants. Adsorption on inorganic adsorbents is one of the most effective methods for the removal of these radionuclides. Of particular relevance is the development of adsorbents that self-immobilize into solid-state matrices for safe disposal. The work aimed to substantiate the possibility of using adsorbents based on (Ca, Mg)-Zr phosphate for the removal and immobilization of ^{137}Cs , ^{90}Sr , ^{60}Co radionuclides.

Adsorbents based on (Ca, Mg)-Zr phosphate were obtained by heterogeneous interaction of phosphatized dolomite and an aqueous solution of zirconyl nitrate with a molar ratio of $\text{Zr}/(\text{Ca}+\text{Mg})$ from 0.10 to 0.62. The batch adsorption of ^{137}Cs , ^{85}Sr , ^{60}Co radionuclides was studied in their joint presence in solution with an initial activity of 100 kBq/L, V/m of 500 mL/g, contact time of 24 h and pH range of 4.0–10.0. A heat treatment of saturated adsorbents was performed at 1000 °C. The leaching test of adsorbents before and after calcination was carried out in distilled and sea water (salinity of 35.0 g/L) at the V/m of 500 mg/L and contact time of 1 h to 28 days.

The distribution coefficient (K_d) of ^{137}Cs , ^{85}Sr , ^{60}Co radionuclides was $(0.37\text{--}1.6)\times 10^4$, $(2.5\text{--}6.2)\times 10^3$, $(0.18\text{--}1.1)\times 10^4$ mL/g, respectively. The K_d of ^{137}Cs and ^{85}Sr were similar in all pH range, while the K_d of ^{60}Co decreased by 1.9–2.2 times in acidic and alkaline solutions. ^{137}Cs , ^{85}Sr , ^{60}Co leaching was 1.3–15.1% in distilled water and increased to 28.0–90.4% in sea water. The heat treatment of adsorbents led to decrease of ^{137}Cs leaching to less than 4% in sea water, while ^{85}Sr and ^{60}Co were not detected (activity <20 Bq/L) in solutions after 28 days of contact. This was due to the formation of double phosphates $\text{CsZr}_2(\text{PO}_4)_3$, $\text{SrZr}_4(\text{PO}_4)_6$, $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Zr}_4(\text{PO}_4)_6$, $\text{CoZr}_4(\text{PO}_4)_6$ with NZP type structural, which is a known matrix for radionuclide immobilization.

Thus, adsorbents based on (Ca, Mg)-Zr phosphates are promising materials for the LRW treatment of ^{137}Cs , ^{90}Sr , ^{60}Co radionuclides with subsequent immobilization into solid-state matrices for safe disposal.

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PLUTONIUM BEHAVIOR UNDER CONDITIONS OF DEEP STRATUM OF LIQUID RADIOACTIVE WASTE DISPOSAL SITE

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For the first time, liquid radioactive waste was injected into a deep geological horizon (aquifer) in 1963 at Seversk site, Tomsk. This was determined by immediate necessity of disposal of great amounts of waste emerged due to arising development of nuclear industry. Since then, above 43 million cubic meters LRW were injected into the stratum at 270–390 m deep.¹ The long-term safety of the injected waste was to be guaranteed by isolating impenetrable argillaceous beds underlying and overlying the aquifer (stratum-collector). One of the most hazardous components of LRW is plutonium due to long half-lives of its isotopes and complex chemical behavior. In this work, Pu binding with stratum rocks was studied under conditions² simulating the injection modes of LRW into the stratum-collector (high temperature, high acidity, high salinity).

In the studied conditions Pu binds preferentially with newly formed Fe- and Cr- containing phases formed from corrosion products contained in LRW during hydrothermal conditioning, although innate bedrock minerals retain Pu as well. Plutonium sorption strongly depends on final pH values. Due to the elevated temperature conditioning, Pu is sorbed on the solid surface in tetravalent form rather than precipitating as PuO₂. Solid-bound species were studied by XAFS and HRTEM. Elevated temperature at the injection zone enhances the sorption and stability of solid-bound Pu species.

The stability of solid-bound Pu species on LRW precipitates and deep bedrock was studied during seven years by acidic leaching (pH around 1) imitating the injection of pushing solutions into the stratum-collector of the disposal site. The Pu fraction slowly leached from the LRW precipitates reached 25% after 7 years. In the presence of bedrock and after repeated hydrothermal conditioning, the leaching did not exceed 4% through 7 years. The solvent extraction method showed that Pu is remobilized in pentavalent form. The acidic leachate of Pu from the bedrock put in contact with fresh bedrock sample demonstrated sorption around 60% at pH=2 which is rather high for this acidity. Subsequent migration of plutonium in the geosphere is expected to be retarded *via* the sorption on stratal minerals in remote zones with circumneutral pH values.

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SORPTION OF ACTINIDES AND NUCLEAR FISSION PRODUCTS BY NANOSIZED NEEDLE COKE

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Carbon nanomaterials are known to retain many metals, which, in particular, allows to consider them as sorbents for radionuclides^{1,2}.

Needle coke, one of the products of petroleum industry, is used in the production of graphite electrodes. Activated needle coke with the size of its particles not exceeding 10 nm has high specific surface area, which allows to consider this nanosized needle coke as a promising sorbent for actinides and nuclear fission products for the purpose of their separation from liquid radioactive waste.

In this work, the sorption of actinides and nuclear fission products by the samples of nanosized needle coke were studied in solutions of nitric acid with different pH. Dependency of sorption on pH, kinetics, and sorption capacity for elements mentioned above were also determined for every sample of needle coke.

The conditions for quantitative sorption of actinides and nuclear fission products by nanosized needle coke were determined.

Obtained results have shown that nanosized needle coke is a promising sorbent for actinides and nuclear fission products.

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ESTABLISHMENT OF THE DEPENDENCE OF THE SORPTION OF URANIUM AND THORIUM FROM LIQUID MEDIA ON THE CHARACTERISTICS OF THE SYNTHESIS OF COMPOSITE MATERIALS BASED ON 4-AMINOFURAZANE-3 CARBOXYAMIDOXIME

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As a result of the mining and processing of uranium-thorium ores, the discharge of polluted mine waters, abundant pollution of water resources occurs, which in turn serve as accumulators and migration routes for radionuclides. Therefore, an important task is the extraction and concentration of uranium and thorium radionuclides from liquid media, in order to prevent pollution of water resources, as well as to return valuable components of raw materials.

Among all known methods, sorption ones have the greatest advantages. Previously, we showed that adsorbents containing amidoxime functional groups in the form of 4-aminofurazane-3-carboxamidoxime have a number of advantages in comparison with existing analogues (increased selectivity, chemical resistance, etc.). However, these materials have limitations when used under dynamic sorption conditions.

In view of this, a one-step method was developed for the production of composite materials based on 4-aminofurazane-3-carboxamidoxime and chitosan (43AF/hit), used as a durable polybase with increased ionic permeability. Additionally, to increase the degree of thorium binding by complexation, the Se-derivative 4-aminofurazane-3-carboxamidoxime (Se-am/hit) was used as a sorption-active component, with its different ratio to the biomatrix. As a result of the study of physico-chemical properties, it was found that the introduction of a chelating selenium atom contributes to a change in the acid-base properties of the adsorbent, and allows the extraction of radionuclides in a wide pH range. In particular, when using Se-am/hit to extract uranium (VI) from solutions with a pH of 5–9, the value of SEC is 600–800 mg/g, when using 43AF/hit to extract thorium from solutions of pH 3–5, respectively SEC = 600–900 mg/g.

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ADSORPTION OF STRONTIUM AND CESIUM IONS FROM AQUEOUS SOLUTIONS USING ZEOLITE SAMPLES

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Radioactive dust created by nuclear or radioactive fallout is directly sent to the atmosphere, which is highly dangerous, particularly in terms of the fission products such as radioactive cesium (^{137}Cs) and strontium (^{90}Sr). Adsorption is one of the widely used treatment process for the remediation of the environment due to its application easiness and cost. In this process, the selection of adsorbents and the adsorption conditions is critical for the removal efficiency of the radionuclides. In this study, the effects of experimental conditions on the adsorption of Sr^{2+} and Cs^{+} ions from the aqueous solutions were investigated by using different zeolites, namely clinoptilolite (natural zeolite mineral, CL), zeolite 4A (synthesized zeolite, Z4A) and surface modified clinoptilolite via iron incorporation (MCL). The effects of temperature, pH, adsorbent dosage, ion concentration, and time on the Sr and Cs adsorption capacity and the removal percentages of zeolite adsorbents were investigated in the batch adsorption experiments. As a result of the adsorption experiments, and a careful inspection of the adsorption capacities of the zeolite samples together with the removal percentages of Sr and Cs, the optimum adsorption conditions were determined. The adsorption capacities of CL, MCL, Z4A at optimum conditions, were found as 25.2mg/g, 28.3mg/g, 33.8mg/g for Sr and 36.0mg/g, 18.7mg/g, 37.2mg/g for Cs, respectively. The results also showed that the adsorption occurred both with cation exchange and electrostatic interactions. To conclude, all the adsorbents used in this study were suitable to be used for the remediation of Sr and Cs from aqueous solutions, Z4A having the highest adsorption capacity.

IMMOBILIZATION OF ORGANIC RADIOACTIVE WASTE IN MAGNESIUM POTASSIUM PHOSPHATE COMPOUND

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Currently, a significant amount of organic liquid radioactive waste (OLRW) is accumulated at nuclear fuel cycle facilities. Such waste include spent tributyl phosphate (TBP) with hydrocarbon diluent used in spent nuclear fuel reprocessing technology and vacuum oils from primary coolant pumps and turbines of nuclear power plants.¹⁻² Different management methods of OLRW, such as degradation of organic compounds, their purification and recycling, immobilization into different types of matrices (cement or polymer) are considered. Immobilization of OLRW appears to be the most promising and simple method.² Earlier we have shown the prospectivity of magnesium potassium phosphate (MPP) matrix for solving the tasks of the management of “problematic” RW. Therefore, the aim of our research was to test an immobilization method of simulants of spent TBP in dodecane and VM-4 vacuum oil using the MPP matrix.

In the work samples of MPP compound containing up to 37 vol.% of 30% TBP solution (CAS:126-73-8) in dodecane (TU 6-09-3730-74) and up to 33 vol.% of VM-4 vacuum oil (TU 38.401-58-3-90) were synthesized. OLRW simulants were previously sorbed on aerosil (SiO_2) with a specific surface area of 380 m^2/g . The absorption capacity of 1.0 g of aerosil was 7.1 g of TBP in dodecane and 7.3 g of vacuum oil. In addition, the effect of CaSiO_3 wollastonite (FW-200) on the strength of the samples was investigated. Compressive strength of the obtained samples, their water resistance (after 90-day immersion in water), resistance to thermal cycles of freezing/thawing (30 cycles in the temperature range of $-40 \dots +40$ °C), as well as hydrolytic stability in accordance with the standard test of GOST R 52126-2003 were determined.

The possibility of immobilization of OLRW simulants, previously sorbed on aerosil, into MPP compound containing 15–20 wt.% wollastonite has been demonstrated. The quality indicators of samples containing at least up to 33 vol.% TBP in dodecane and up to 25 vol.% vacuum oil meet the current regulatory requirements for conditioned LRW.

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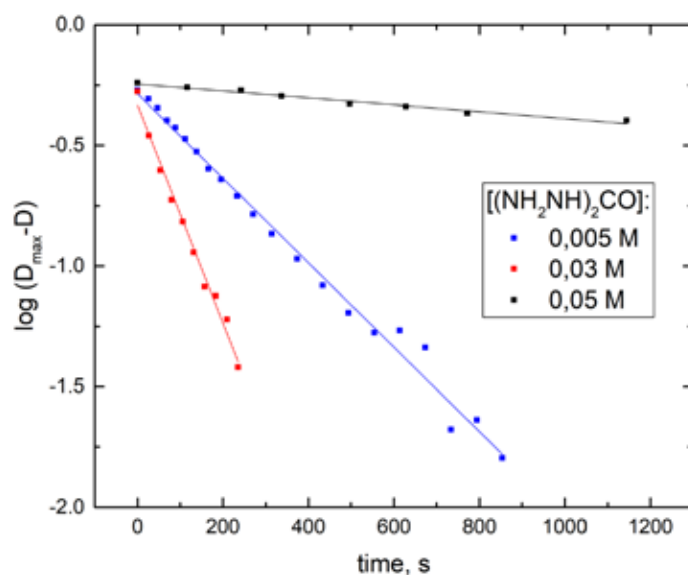
KINETICS OF PLUTONIUM REDUCTION BY CARBOHYDRAZIDE AND DIFORMYLHYDRAZINE IN THE PERCHLORIC ACID

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One of the benefits of the closed nuclear fuel cycle is minimization of the final high-level waste by separating and isolating the most long-lived components. For instance, plutonium and neptunium are regenerated via the application of extraction technologies. Carbohydrazide $((\text{NH}_2\text{NH})_2\text{CO})$ and diformylhydrazine $\text{N}_2\text{H}_2(\text{CHO})_2$ are prospective reagents for the recovery of actinides, yielding minimal quantities of inorganic by-products. Existing literature delineates the processes of neptunium Np(VI) reduction by carbohydrazide in solutions of nitric¹ and perchloric acids.² Notably, the reduction of Np(VI) to Np(V) occurs at an elevated rate at ambient temperature. Both the stoichiometry and kinetics of this reaction have been extensively investigated.

The present study introduces the outcomes of plutonium reduction processes using carbohydrazide and diformylhydrazine in a perchloric acid medium. The reactions were investigated considering Pu(VI) and Pu(IV) as initial solutions. In each instance, the reaction rate was ascertained by monitoring the decrease in the concentration of plutonium in its initial oxidation state within the solution. The concentration of plutonium in the solution was quantified via spectrophotometry in visible region. Dependencies of the reaction rate on the concentrations of reductant, plutonium, and perchloric acid were established, and the reaction orders for all components were determined. Additionally, the stoichiometry and temperature dependence of the ongoing redox reaction were examined.



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NEW MOLYBDATE COMPLEXES OF Np(VI) AND Pu(VI)

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New molybdate complexes of Np(VI) and Pu(VI) have been synthesized. The structure of the compounds has been established by X-ray diffraction analysis (Table 1). The compounds were characterized thermogravimetrically, electronic and IR spectra of crystalline compounds were measured. The complex formation of AnO_2^{2+} and molybdate ions in solutions was studied. The structure features of new compounds were analyzed in comparison with known compounds of pentavalent actinides with alkali metal cations with different ratio of NpO_2 : MoO_4^{2-} .¹⁻³ It was found that in the structure of the synthesized compound $\text{CsNa}[\text{NpO}_2(\text{MoO}_4)_2] \cdot 4\text{H}_2\text{O}$ the coordination polyhedron of the central neptunium atom is a pentagonal bipyramid, the equatorial plane of which is formed by oxygen atoms of five MoO_4^{2-} anions. There is no cation-cation interaction between the neptunyl groupings of NpO_2^{2+} . The neptunoyl-molybdate anion chains form the basis of the complex; hydrated Na^+ and Cs^+ cations are located in the interlayer space. In the case of $\text{Na}_2[\text{NpO}_2(\text{MoO}_4)_2] \cdot 5\text{H}_2\text{O}$ and $\text{Na}_2[\text{PuO}_2(\text{MoO}_4)_2] \cdot 5\text{H}_2\text{O}$, the anionic layer has a similar composition. The coordination polyhedron of the central neptunium atom is a pentagonal bipyramid, the equatorial plane is formed by the oxygen atoms of five monodentate coordinated MoO_4^{2-} .

Table 1. Crystal cell parameters of new molybdates Np(VI) and Pu(VI)

Compound	Spatial group	Crystal cell parameters			
		a, Å	b, Å	c, Å	β, град
$\text{CsNa}[\text{NpO}_2(\text{MoO}_4)_2] \cdot 4\text{H}_2\text{O}$	$P 2_1/c$	9.816	11.262	13.923	101.214
$\text{Na}_2[\text{PuO}_2(\text{MoO}_4)_2] \cdot 5\text{H}_2\text{O}$	$P 2_1/c$	11.137	6.834	18.799	99.426
$\text{Na}_2[\text{NpO}_2(\text{MoO}_4)_2] \cdot 5\text{H}_2\text{O}$	$P 2_1/c$	11.162	6.845	18.826	99.537

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NEW CHROMATE COMPLEXES OF Np(VI) AND Pu(VI)

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A number of new compounds Np(VI) and Pu(VI) have been synthesized and structurally characterized in the course of a systematic study of complex formation of hexavalent actinides with tetraoxoanions of elements of group VI of the periodic system (Table 1). The electronic and IR spectra of crystalline compounds have been measured. The peculiarities of changes in the spectra in solutions and crystals at complex formation with chromate ions have been noted. Peculiarities of structure of new compounds in comparison with similar known compounds of pentavalent actinides have been analyzed¹⁻³.

Table 1. Crystal cell parameters of new double chromates Np(VI) and Pu(VI).

Compound	Spatial group	Crystal cell parameters			
		a, Å	b, Å	c, Å	β, град
Na[NpO ₂ (CrO ₄)(OH)]·2.5H ₂ O	P 2 ₁ /c	8.5550(2)	11.0889(4)	9.3647(3)	91.793(2)
NH ₄ [NpO ₂ (CrO ₄)(OH)]·2H ₂ O	P 2 ₁ /c	8.3604(5)	11.1706(6)	9.4035(6)	91.960(3)
K[PuO ₂ (CrO ₄)(OH)]·1.5H ₂ O	P 2 ₁ /c	8.3903(5)	10.8695(7)	9.3582(5)	93.7830(10)
(NH ₄) ₂ [(PuO ₂) ₂ (CrO ₄)(OH) ₂]·3H ₂ O	P 2 ₁ /n	8.7654(5)	13.7681(7)	13.5193(6)	102.374(4)
Rb ₂ [(PuO ₂) ₂ (CrO ₄) ₂ (OH) ₂]·3H ₂ O	P 2 ₁ /n	8.7754(4)	13.7871(6)	13.4921(5)	102.592(2)

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ORGANIC FORMS OF NATURAL RADIONUCLIDES AND RARE EARTH ELEMENTS IN PEAT OF THE UPPER PEAT TYPE

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A topical issue for science is the determination of the forms of radionuclides and other hazardous elements associated with natural organic matter. Correct interpretation of mechanisms of radionuclides connection with organic matter will increase the reliability of numerical modeling of elements migration in the environment. The paper summarizes the results on the study of stability of REE and natural radionuclides complexes with humic substances (HS).

In the presented work we studied samples of peat from the Petropavlovskiy Ryam deposit, which is located on the trace of the accident at the Siberian Chemical Combine (SCC) in the Tomsk region in 1993. The content of HW in peat is about 55%, in terms of dry matter it reaches 73% of the organic matter of peat. The optical and fluorimetric characteristics of alkaline extracts of peat from different depths at gradient acid fractionation in the pH range from 12 to 0,5 were studied. Changes in element concentrations were detected mass spectrometrically.

The growth of humification of peat organic matter with depth according to the group composition data was noted. Differences in the shape of the normalized REE spectrum in different peat layers confirm the manifestation of the trace from the accident at SCC. It is found that the proportion of organically bound REE forms varies slightly with depth, but the strength of the bond decreases in more mature peat layers. The destruction of REE complexes and natural radionuclides occurs in the region of pH 2–2,5, which coincides with the precipitation of humic acids. The more transformed deep layers are characterized by a higher release of REE and Th into solution. In the upper peat layers, thorium complexes with humic acids remained stable in the whole pH range, while in more humified layers they are unstable at pH below 1. The curves of changes in the optical descriptors E_2/E_3 and E_4/E_6 are inversely proportional to changes in organic carbon concentrations and also confirm the precipitation of humic acids at pH below 4. The descriptor E_4/E_6 is more sensitive to structural changes of natural organic matter and as well as E_2/E_3 is inversely proportional to the molecular weight of HS, as well as closely related to the carbon content.

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STABILITY OF CLAY COLLOIDAL SUSPENSIONS OF DIFFERENT DIPOSITS IN THE ENVIROMENT OF UNDERGROUND RAW DISPOSAL

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The stability of clay materials is a particular challenge because the interaction of radionuclides with colloids is of great importance to the safety of a nuclear waste repository. Colloids are ubiquitous in groundwater and can be formed by erosion of engineered barriers at the disposal site. The presence and formation of colloids significantly changes the transport behavior of radionuclides, and the study of this system will improve the quality of predictive geomigration modeling. The paper summarizes the results of two-year static experiments on the behavior of colloidal particles of clay materials of Taganskoe, Kantatskoe and 10-Khutor deposits in deionized water and simulated groundwater of “Yeniseisky” site with monitoring of colloidal particle sizes, ζ -potential and concentration of colloids in solution by methods of dynamic light scattering and electrophoretic mobility using Malvern Zetasizer Nano ZS device.

Evaluation of the change in mean hydrodynamic diameter in deionized water showed that particles start to aggregate slightly only after 30 days. And in the case of groundwater simulant, a significant enlargement of particles of 10-Khutor deposit is noticeable, and insignificant aggregation of particles in Tagansky and Kantatsky deposits, which is confirmed by literature results. The difference in the behavior of clay colloids from Tagansky/Kantatsky and 10-Khutor deposits is due to the increased content of Ca-clay in the latter, which produces colloids with a large size¹. The analysis of ζ -potential values indicates good stability of the system in deionized water. In the case of groundwater bentonite colloids ζ -potential values decrease during the experiment from -17 to -1.5 mV, which indicates the instability of the considered systems. It is also observed that the stability of the systems under consideration increases with increasing concentration of colloids in solution. The change of water composition is analyzed and it is shown that there is a change of ionic composition and pH value of solutions.

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BINDING OF LEAD CATIONS BY POLYAMINES CONTAINING AMIDE SUBSTITUENTS

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The ²¹²Pb/²¹²Bi radionuclide pair is used for the treatment of cancer, since the alpha particles emitted by ²¹²Bi have a low range in body tissues and can effectively destroy malignant cells. In this case, it is necessary to deliver the emitter of these particles inside the affected, rather than healthy, cell. It is known that chelators with amide substituents are more effective for strong binding of Pb²⁺ to the vector molecule. In this connection, pyridine-aza-crown ethers with different macrocycle sizes and different numbers of amide substituents (from two to five) were chosen as objects of study. Also in this work, an acyclic ligand was studied, which has a similar structure to the studied aza-crown ethers, but has a high mobility of the polyamine chain.

In this work, the protonation constants of the studied ligands were determined by potentiometric titration. Using the liquid extraction method using 2-ethylhexyl diphenyl phosphate in toluene as an extractant and/or potentiometric titration, the stability constants of complexes with Pb²⁺ cations were determined.

²¹⁰Pb-labeled complexes with the studied pyridine-aza-crown ethers were obtained. To determine the efficiency of labeling, the optimal concentration of the ligand, and also to analyze the stability of these complexes in the environment of biologically relevant cations, the TLC method was used. To assess the stability of the complex *in vitro*, the stability of the labeled complexes in the competitive environment of the fetal bovine serum was studied.

Pyridine-aza-crown ethers with four and five amide substituents turned out to be the most effective for binding Pb²⁺ cations. The complexes have the highest stability constants and are also stable *in vitro* after 24 hours: more than 85% of the metal cations were complexed with the pentaamide ligand.

The work was carried out with the financial support of the Russian Science Foundation, grant № 23-13-00424

RADIATION AND THERMAL STABILITY OF ANION EXCHANGE RESINS

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Synthetic anion exchange resins are widely used in the process of radiochemical reprocessing of spent nuclear fuel for the isolation and separation of radionuclides, in particular for the extraction of Pu-238. Moreover, the conditions for using anion exchangers are associated with exposure to ionizing radiation, oxidizing agents (nitric acid solutions with a concentration of up to 8 mol/l) and elevated temperatures (up to 70 °C). Under such conditions, the sorption characteristics of the anion exchanger and its thermal stability may change, which may negatively affect the fire and explosion characteristics of the system.

In this work, the thermal stability of anion exchangers of the AV-17×8, VP-1AP, VP-3AP, VPA brands, saturated with nitrate anions and thorium hexanitrate, was studied. The kinetic characteristics of the thermolysis of anion exchangers were obtained and the change in these characteristics after exposure to ionizing radiation was established.

Using differential scanning calorimetry, it was established that when irradiated to a dose of 2 MGy, the starting temperatures of exothermic reactions decrease by values from 30 to 80 °C.

When moving from the nitrate form of the anion exchanger to the hexanitrate form (thorium hexanitrate complex), an increase in starting temperatures is observed for non-irradiated samples. For irradiated samples, the opposite trend was established: for sorbents in the hexanitrate form, the starting temperatures decrease more significantly than for the nitrate form.

When sorbents are irradiated, the spectrum of gaseous thermolysis products increases, while the products characteristic of the oxidation of the functional group remain the same, and the spectrum increases due to the appearance of new products of interaction of the oxidizer with the sorbent matrix. Thus, irradiation has a significant impact on the structure and thermal stability of anion exchangers.



ACCUMULATION OF RADIONUCLIDES IN BOTTOM SEDIMENTS OF TUUL RIVER IN MONGOLIA

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Aquatic ecosystems play an important role in the migration of both natural and man-made radionuclides, as well as their redistribution. Bottom sediments are the most informative component, they accumulate pollutants in a highest level coming from the catchment area over a long period of time¹. The Tuul River basin is a part of an international transboundary territory, including the Selenga River and Lake Baikal, a UNESCO World Heritage Site. The most anthropogenically transformed part of the basin is located within the city limits of the capital of Mongolia, Ulaanbaatar. The specifics of the location of all industries and traffic flow in Ulaanbaatar have formed a multicomponent concentrated linear type of pollution of the coastal zone and surface water of the Tuul River². A study of natural (U- and Th-series, ⁴⁰K) and man-made (¹³⁷Cs) radionuclides was conducted in the bottom sediments of the Tuul River. The activity concentration of radionuclides was determined by gamma-spectrometric method. The content and distribution of radionuclides in bottom sediments along the Tuul River and the possibility of their intake from the catchment area have been studied. We observed imbalance of ²³⁸U/²²⁶Ra ratio and complex dynamics of several mixed sources in bottom sediments. The estimation of the radioecological risks for humans and biota associated with these activity concentration of radionuclides was carried out. The data obtained in this study can be used for further monitoring of the activity concentration of natural and man-made radionuclides, in particular ¹³⁷Cs.

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YTTRIUM-STRONTIUM SEPARATION IN CARBONATE MEDIA WITH A MIXTURE “HYDROXIAROMATIC COMPOUND – MTOAC”

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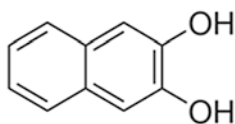
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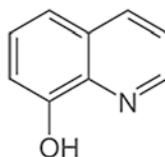
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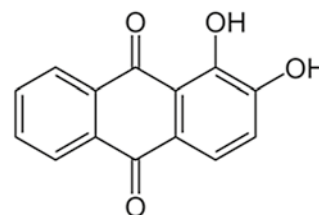
A systematic study of yttrium and strontium extraction in carbonate media with extraction mixtures based on such hydroxyaromatic compounds as 8-hydroxyquinoline (8HQ), alizarin and 2,3-dihydroxynaphthalene (2,3DHN) in various organic solvents (butyl acetate, toluene, 2-nitrotoluene) was carried out.



2,3-dihydroxynaphthalene
(2,3DHN)



8-hydroxyquinoline
(8HQ)



alizarine

Methyltrioctylammonium carbonate (MTOAC) was used as a synergistic additive to chelating ligands. Extraction systems of the following composition are of the most interest for yttrium and strontium separation in carbonate media with pH > 12:

1. 8HQ (10^{-3} M) + MTOAC ($1.5 \cdot 10^{-3}$ M) in butyl acetate ($\lg SF_{Y/Sr} = 1.7$) or in toluene ($\lg SF_{Y/Sr} \sim 3$);
2. 2,3DHN (10^{-3} M) + MTOAC ($1.5 \cdot 10^{-3}$ M) in butyl acetate or in toluene ($\lg SF_{Y/Sr} > 5.5$).

The study was supported by a grant from the Russian Science Foundation No. 24-63-00006, <https://rscf.ru/project/24-63-00006/>



HOW DOES GREEN CHEMISTRY PLAY A ROLE IN THE FIELD OF NUCLEAR FUEL CYCLE? A REVIEW

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Green chemistry is a cutting-edge discipline that focuses on developing strategies and techniques to minimize the use of hazardous substances in the design of products and processes. While nuclear power plants are known for their lack of air pollution and carbon dioxide emissions during operation, the nuclear fuel cycle itself can have adverse environmental effects. The extraction and processing of uranium ore, for instance, contribute to environmental degradation and pollution due to the high energy requirement involved. Furthermore, the management of nuclear waste is a significant environmental concern. In the realm of the nuclear fuel cycle, green chemistry aims to reduce the environmental impact and enhance the safety of nuclear fuel production, reprocessing, and waste management. To achieve these goals, green chemistry offers various solutions, such as the utilization of ionic liquids, biomass materials, and supercritical carbon dioxide. Ionic liquids are employed as solvents in the reprocessing of spent nuclear fuel, effectively removing the contamination of metal waste. Another approach involves using biomass materials to extract uranium from seawater through adsorption, which minimally affects the equilibrium concentration of uranium in the oceans. Finally, the design of processes that require less energy, such as the utilization of supercritical carbon dioxide in manufacturing, can significantly reduce the overall energy consumption. In conclusion, the integration of green chemistry principles into the nuclear fuel cycle represents a promising direction towards enhancing the sustainability of nuclear energy.

RADIOLABELLED SURFACE MODIFIED CeO₂ NANOPARTICLES FOR EVENTUAL APPLICATION IN NUCLEAR MEDICINE

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The main goal of developing radiopharmaceuticals is to select the right components – a vector, a bifunctional chelator, and a radionuclide. Nanoparticles are used as vectors to deliver the radionuclides to the tumour tissue, which is a promising field in nuclear medicine. In addition, nanoparticles can act as a platform for various radionuclides due to their ability to modify their surfaces.

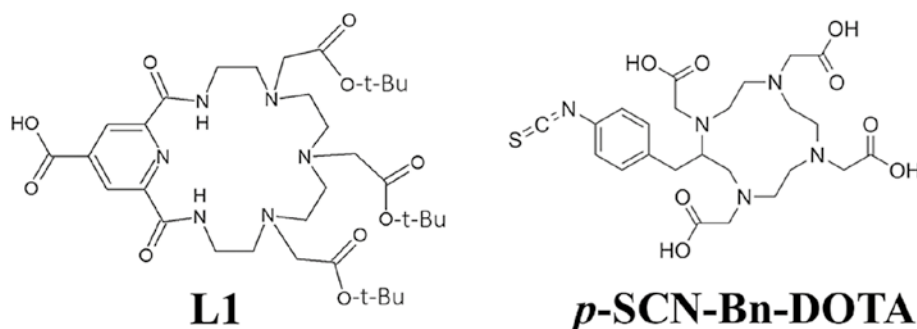


Figure 1. Azacrown ligands L1 and p-SCN-Bn-DOTA

In this work, conjugates of CeO₂ nanoparticles (d=3 nm) and azacrown ligands (Fig. 1) were synthesized using various linkers. Optimal conditions were selected for labelling with radionuclides: ⁶⁵Zn (β⁺, T_{1/2}=243.93 days), ⁴⁴Sc (β⁺, T_{1/2}=3.9 h) and ²⁰⁷Bi (α, T_{1/2}=46 min). The kinetic stability of these complexes in biologically relevant media was evaluated, and the results obtained allowed us to select the most promising complex for biomedical applications and further *in vitro* and *in vivo* experiments.

It has been shown that CeO₂ nanoparticles and its derivative are not cytotoxic to human endothelial cells EA.hy926 at various concentrations. The biodistribution of the complex with ⁴⁴Sc has been studied and its stability in a living organism has been evaluated.

In this study, it was demonstrated that functionalized cerium oxide nanoparticles form stable systems with radionuclides that can be used for targeted drug delivery, diagnosis, and treatment of oncological diseases.

Conducting experiments using animals has been approved by the Commission on Bioethics of Lomonosov Moscow State University (№ 153-d held on 22.06.2023).

IN VITRO AND IN VIVO EXAMINATION OF CeO_2 NANOPARTICLES IN LUNG FLUIDS: A NON-RADIOACTIVE MODEL FOR PuO_2

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Studying actinide-containing nanoparticles (NPs) in the media of biological significands is vital for predicting radionuclide bioavailability. Identifying the primary interaction mechanisms of PuO_2 NPs with components of living systems at a molecular level will also enhance existing concepts for monitoring the radionuclides spread through food chains and improve the dosimetry standards in the nuclear industry. Plutonium's complex chemical properties, explored through simpler non-radioactive analogues – CeO_2 , drive research progress. This study aimed to investigate the cerium species following contact 2 nm CeO_2 NPs in vitro with media of biological significands (lung fluid, culture medium and bovine serum) and in vivo within the lungs of laboratory mice after particle inhalation. The interaction of CeO_2 with biological media was studied using X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS) and transmission electron microscopy (HRTEM) methods.

It was observed during *in vitro* experiments that the concentration of dissolved cerium in simulated lung fluid after one year of NP storage is approximately 10^{-6} M. Over time, CeO_2 converts into $\text{Ce}(\text{III})\text{PO}_4 \cdot \text{H}_2\text{O}$ with a rhabdophane structure. The conversion of $\text{Ce}(\text{IV})$ oxide into $\text{Ce}(\text{III})$ phosphate occurs more rapidly in environments with high concentrations of reducers such as cell culture medium and bovine serum.

In vivo, biodistribution was analysed by intratracheal instillation of labelled $^{139}\text{[Ce]CeO}_2$ nanoparticles and control (PBS) to CD-1 mice. Mice were anaesthetised and intubated with a 22-gauge catheter, after which the obtained particles were instilled. One day after injection, there was a relatively high concentration of NPs in the lungs and gastrointestinal tract, as identified by gamma spectrometry. Within 14 days nearly 100% of the nanoceria had been excreted in the faeces from the gastrointestinal tract. Sequential analysis of lungs over 14 days showed slow lung clearance of $^{139}\text{[Ce]CeO}_2$. At the same time, less than 1% of instilled ^{139}Ce was measured in selected extrapulmonary organs in the 1-day and 14-day groups. The slow clearance and lack of accumulation of ^{139}Ce in other organs may be due to the transformation of CeO_2 NPs in the lungs into low-solubility $\text{Ce}(\text{III})$ phosphate.

Conducting experiments using animals has been approved by the Commission on Bioethics of Lomonosov Moscow State University (№ 171-a-a held on 21.03.2024). This work was supported by the Russian Science Foundation (grant No. 23-73-30006)

CARBONYL-DIKETONATE COMPLEXES OF TECHNETIUM (I)

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Recently, the diketonate-phosphine system has been actively studied for the introduction of a technetium into an organic molecule in the form of $\text{Tc}(\text{CO})_3$ fragment. For this purpose the water ligands in $[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ precursor are substitute by three dentate- of combination of mono and bidentate ligands (2+1 approach). One of the promising systems for the latter approach are acac-PPh_3 , $\text{acac-PPh}_2\text{Cy}$, acac-PCy_2 , hfa-PPh_3 . Our preliminary studies have shown that complexation with these systems can be complicated by formation of side dicarbonyl complexes.

The aim of the work is to find out to what extent the formation of dicarbonyl complexes depends on the donor properties of the diketonate ligand. In this connection, the following systems were studied: acac-PPh_3 , acac-Py , acac-Imd , hfa-PPh_3 , hfa-Py , hfa-Imd . Acetylacetone (acac) acts as a strong-donor diketonate ligand, and hexafluoroacetylacetone (hfa) acts as a weak-donor ligand.

We found that the formation of a mixture of dicarbonyl and the target $[2+1]$ tricarbonyl complexes is observed even at the equimolar ratio of acac-PPh_3 . Only when hexafluoroacetylacetone is used instead of acetylacetone the pure $[2+1]$ complex is formed.

If the monodentate ligand exhibits weak π -acceptor properties or pure δ -donor properties (Py , Imd), no dicarbonyl technetium complexes are also formed.

Thus, the use of diketonate ligands in the framework of the $[2+1]$ approach for introduction of $\text{Tc}(\text{CO})_3$ fragment into biomolecules requires combination of weakly donating diketonate ligands and monodentate ligands with weak π -acceptor properties or pure δ -donor properties.

The study was financially supported by the Russian Science Foundation (project no. 22-13-00057).



INFLUENCE OF Na-AL PHOSPHATE GLASS LEACHATES ON CLAYS SORPTION BEHAVIOR TOWARD RADIONUCLIDES

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The presence of leaching products in the liquid phase of an alumophosphate matrix for radioactive waste immobilization significantly affects the behavior of radionuclides, both fission products – strontium and cesium, and actinides. Cesium sorption on clays slightly decreases in the presence of leaching products, presumably due to an increase in ionic strength, the main contribution to which is made by sodium and phosphate ions. Strontium sorption on bentonites depends more on the properties of the clay than on the composition of the liquid phase, but as the concentration of phosphates increases, the proportion of firmly fixed forms increases.

Uranium and neptunium in oxidation states U(VI) and Np(V) are considered as mobile radionuclides in environmental conditions due to their low distribution coefficients from groundwater, which are several orders of magnitude smaller than the corresponding values for plutonium or americium. The presence of leaching products of alumophosphate glass in the liquid phase significantly increases their sorption on bentonites and the proportion of strongly bound forms of radionuclides, which undoubtedly has a positive effect on the efficiency of the anti-migration clay engineering barrier.

Plutonium and americium have high distribution coefficients on clays in the conditions of a high-level radioactive waste repository. The presence of leaching products of alumophosphate glass slightly increases sorption, while the proportion of strongly bound forms increases with the concentration of phosphate ions.

The presence of leaching products of phosphate glass in the liquid phase does not negatively impact the ability of engineering barriers based on bentonite clays to prevent radionuclide migration from the radioactive waste repository. In some cases, it significantly enhances the barrier properties of the studied materials in the conditions of a high-level radioactive waste repository towards such mobile radionuclides uranium and neptunium.

CONDITIONS FOR THE SAFE USE OF CROWN ETHERS FOR EXTRACTION SHORT-LIFE FRACTION OF CESIUM AND STRONTIUM DURING SNF PROCESSING

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Currently, a proven method for managing liquid radioactive waste generated during spent nuclear fuel reprocessing is liquid-liquid extraction, which makes it possible to separate the raffinate fission products into fractions, including the extraction of short-lived cesium-strontium. For these tasks, crown ethers are considered as the main extractants, selective for cesium – dibenzo-21-crown-7 (DB21K7) and 4,4'(5')di-tert-butyl-dibenzo-18-crown-6 (DTBDB18K6), for strontium – dicyclohexyl-18-crown-6 (DCG18K6), a mixture of isomers. For the practical use of extraction mixtures based on crown ethers in organic diluents, it is necessary to determine the conditions for their safe use in technological equipment. Since the possibility of interaction of oxidizing agents with the extractant, accompanied by heat and gas release, including the initiation of cesium and strontium by heating, cannot be excluded.

To establish such conditions, the method of simultaneous thermal analysis combined with gas chromatography was used in the work. For the studies, were chosen individual DB21K7, DTBDB18K6 and DCH18K6, as well as organic solutions containing 0.1 mol/L crown ether in diluents 1,2-dichloroethane (DCE), 1,1,7-trihydrododecafluoroheptanol (FH). The aqueous phase consisted of solutions of cesium and strontium nitrates, as well as a multicomponent solution, the composition of which was close to real HLW. In this case, the concentration of nitric acid varied from 1 mol/L to 7 mol/L.

As a result of the research, it was found that:

- individual DB21K7, DTBDB18K6 and DCH18K6 are thermally stable in both inert and oxidizing atmospheres up to temperatures of 170 °C;
- thermal destruction of organic solutions is accompanied by the formation of gaseous products;
- the concentration of nitric acid and the presence of metal nitrates have a significant effect on heat generation.

EXAFS ANALYSIS SHEDS LIGHT ON THE RELATIONSHIP BETWEEN PRECIPITATION CONDITIONS AND STRUCTURAL PROPERTIES OF DOUBLE ACTINIDE CARBONATES AND PHOSPHATES

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Building a complete picture of actinide compounds' behaviour in the natural environment requires structural characterization of morphologically complex samples. Extended X-ray absorption fine structure (EXAFS) spectroscopy is a powerful synchrotron-based element-specific technique capable of elucidating the spatial arrangement of atoms in the vicinity of the absorber element.¹

We have applied EXAFS analysis towards solving the local structure in a range of relevant, novel actinide compounds, including hydrothermally prepared a) sodium/thorium and b) sodium/plutonium double phosphates, as well as c) double carbonates of neptunium precipitated in presence of a range of alkali and alkaline earth metals. Modeling the EXAFS data with reference crystalline standards reveals the relationship between synthesis conditions (such as the pH and composition of the medium) and the resultant structural parameters. Striking similarities were observed in the crystalline phases obtained for the thorium (IV) and plutonium (IV) phosphates under a common set of growth conditions. The identity of the heteroatom in the mixed neptunium (V) samples was found to determine the resultant crystalline phase, consistent with prior work.² We go beyond fitting to theoretical standards and apply a range of modern analytical techniques, such as the wavelet transform, the cumulant expansion, multiple-scattering analysis and principal component analysis to rationalize our findings. Combined with approaches such as atomic pair distribution function (PDF) and small angle X-ray scattering (SAXS), EXAFS analysis furthers our knowledge about the structural detail of morphologically complex actinide compounds.

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ISOTOPE REMOVAL FROM SOIL AND RHIZOSPHERE DURING FLOODS IN THE KRASNOYARSK MCC NEAR IMPACT ZONE

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Methods of modelling isotope transport in river systems that have experienced significant impact from the NFC (including incidents) are based, in particular, on quantitative assessment of mobile forms of isotopes in floodplain soils and bottom sediments¹⁻³.

The first data on the ratio of gamma-emitting isotopes (¹³⁷Cs, ¹⁵²Eu, ¹⁵⁴Eu, ⁶⁰Co) speciation in the floodplain soil and rhizosphere of floodplain plants of the Balchugovskaya channel (Yenisei River, the Krasnoyarsk MCC near impact zone) has been obtained.

The formation of temporary streams during high floods affects the spatial distribution of isotopes and their speciation in soil and rhizosphere. The total specific activities of isotopes in soil and rhizosphere vary in a very wide range and reach 800 Bq kg⁻¹. Migration properties of isotopes are mainly determined by their behaviour in exchangeable and organic fractions of soil and rhizosphere.

The isotopes amount secondary entering river waters from soil and rhizosphere as a result of flood is 10⁸–10⁹ Bq per season in the low annual flood scenario on the studied area of the Yenisei River floodplain in the Krasnoyarsk MCC near impact zone. These amounts are comparable to the annual input of these isotopes into the Yenisei floodplain from the Krasnoyarsk MCC⁴.

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The study was carried out by a grant from the Russian Science Foundation (project No 23-27-00364). The work was carried out at the Analytical Center for multi-elemental and isotope research SB RAS.



U(VI) SORPTION ON NATURAL SOIL

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Climate change and related global ecological trends commit the society to search and develop cleaner energy supplies. From this point of view, nuclear industry actively develops as a powerful source of “green” energy. Nuclear fuel cycle includes numerous stages from mining and milling of Uranium ore to radioactive waste isolation. Uranium as an environmental contaminant is highly toxic and radioactive material, which requires special attention since it is the main component of the current industrially implemented nuclear fuel cycle variations. Generally, fate of Uranium in the environment is mainly controlled by external factors: oxic/anoxic conditions, presence/absence of natural organic matter, carbonates, phosphates, clay minerals, Fe/Mn oxides, etc¹. Uranium is highly mobile in natural aquifers in the form of uranyl-cation $U^{VI}O_2^{2+}$, its carbonato-complexes, or in the form of colloids with mineral phases. Reduced species of U^{IV} or adsorbed/precipitated $U^{VI}O_2^{2+}$ are usually immobilized. In natural systems, the behaviour of U contaminant is influenced by many multidirectional factors. Aim of the present work was to study Uranium sorption by natural soil as a function of soil composition. pH dependencies of U(VI) sorption under various experimental conditions and different soil horizons² (organic-rich and non-silicate-Fe-rich) were experimentally obtained and modeled. To support thermodynamic modelling, additional experiments with simplified binary/ternary systems were carried out. It was shown that in organic-rich horizons, U(VI) sorption is controlled by the amount of soil organic matter present at low pH and mineral phases (most likely clay minerals) at higher pH. In lower horizons (non-silicate-Fe-rich), U(VI) is quantitatively adsorbed in a wide range of pH by mineral phases. The obtained data on the regularities of U(VI) adsorption on natural soil samples are relevant for anticipating U behaviour in natural systems.

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STRUCTURAL FEATURES OF U(VI) SORBED ON CLAY MINERALS

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Control of the uranium fate in the environment is one of primary tasks at the final stages of the nuclear fuel cycle, since it is the main component of spent nuclear fuel by mass and highly toxic heavy metal. Radioactive waste storage facilities are generally multibarrier systems that include bentonite barrier as well to ensure long-term isolation, low hydraulic permeability and conductivity, etc. Regularities of uranium sorption on bentonite materials are thoroughly studied in wet chemistry experiments over a wide range of conditions¹. However, none of these studies provide a justified nanoscale structural model of actual adsorbed uranium species due to: (i) difficulties with experimental investigation of radionuclide complexes on clay minerals at trace concentrations; (ii) complex structure and composition of adsorbed species, the absence of long-range order; (iii) irregularity and uncertainty in clay structure, especially at edge sites. Recent advances in computational chemistry make it possible to approach the modeling of complex systems such as clay minerals² and partly overcome some of the difficulties outlined above. Aim of the present study is to find the relationship between the accumulated experimental data on the local structure of uranium complexes on clay minerals and atomistic modeling, resulting in rationalized structural models of adsorbed uranium species at nanoscale. For this, EXAFS spectra of U(VI) sorbed on smectites in wide range of pH and [UO₂²⁺] were recorded. Several atomistic models with different composition (magnitude and localization of substitutions) and a number of U adsorption modes (interlayer, adsorption on basal surface and complexation with edge sites) were used to simulate the EXAFS spectra at U L₃ edge and compare them with experimental data.

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PENTAVALENT PLUTONIUM CARBONATE SOLID PHASE: FORMATION AND STRUCTURE

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Plutonium aqueous solution chemistry is fascinating and highly complex. This element has the potential for simultaneous existence in solution in four oxidation states under certain conditions and the chemical behaviour of each of them is different. Previously, Kvashnina et al.¹ showed that the formation of PuO₂ nanoparticles from Pu(VI) solutions by adding ammonia, occurs through the formation and subsequent dissolution of the NH₄PuO₂CO₃ phase. Nitsche et al.² observed the formation of NaPuO₂CO₃ phases from Pu(V) and Pu(VI) solutions in a brine simulant reveal to the Waste Isolation Pilot Plan. These studies demonstrate the potential stability of Pu(V) carbonate solid phases, however, the available information is currently insufficient.

This work discusses the process of KPuO₂CO₃ solid phase formation from a Pu(VI) solution. It was observed that potassium plutonyl carbonate precipitates over approximately 30 days in a Pu(VI) solution containing Na⁺, K⁺ and carbonates from the air, within a pH range of 8 to 10. Various parameters were monitored during plutonium precipitation, including Eh values. The findings suggest a correlation between plutonium oxidation state and redox potential, indicating that changes in oxidation state may influence redox potential shifts.

The formula and structure of the solid phase were determined using a range of methods such as XRD, HRTEM, SEM-EDX, XANES, and EXAFS. Microscopic analysis revealed the solid phase forming hexagonal plates of approximately 1 μm in size. Microscopy data confirmed the presence of K within the structure. KPuO₂CO₃ crystallizes in a hexagonal unit cell (space group *P6₃/mmc*), sharing structural similarities with KNpO₂CO₃. The distance from the Pu atom to the axial oxygens (O_{ax}) was determined to be 1.81 Å based on EXAFS data, notably different from previous findings by Ellinger³.

For the first time, this work presents the Pourbaix diagram showcasing the stability region of KPuO₂CO₃, calculated using Np(V) thermodynamic constants.

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RADIONUCLIDES IN THE ABIOTIC ENVIRONMENTAL OBJECTS IN THE FAR EASTERN REGION

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Using samples of marine and freshwater ecosystems as an example, the complex of radionuclides, their sources, physicochemical forms and possible migration paths were determined. The work was carried out jointly with Chinese colleagues from the University of Lanzhou, the methods of isolation and determination of actinides (Pu, Np, Am) and fission products (Tc, I) were improved, their contents in bottom sediments and water of Lake Khanka and the Sea of Japan were quantified. The use of analytical capabilities of Chinese colleagues, namely modern equipment (tris quadrupole ICP and accelerator mass spectrometers) made it possible to determine radionuclides in ultra-low concentrations (up to 0.01 mBq/l). The concentrations of ^{239,240}Pu and ²⁴¹Am in all bottom sediment samples ranged from 0.01 Bq/kg to 2.02 Bq/kg and from 0.01 Bq/kg to 1.11 Bq/kg, respectively, which is comparable to the average values in the northern hemisphere.

The migration mobility of actinides was determined using distribution coefficients (suspended matter-water). They were 0.11–0.3; 0.02–0.07 for ²³⁷Np, ^{239,240}Pu, respectively. Thus, in this work we quantified the distribution of actinides in suspended matter of 1–5 μm size in Peter the Great Bay. The amount of neptunium and plutonium migrating with 1–5 μm suspended matter is estimated to be 0.04% for plutonium and 0.1% for neptunium. Transition coefficients of actinides in Peter the Great Bay have been determined: dissolved, including colloids – suspended matter (1–5 μm) – bottom sediment for the marine environment. Transition coefficients (l/kg) for suspended matter (1–5 μm) are 0.11–0.30 for ²³⁷Np and 0.02–0.07 for ^{239,240}Pu.

Atomic ratios clearly indicate the source of radionuclide intake – global fallout (²⁴¹Pu/^{239,240}Pu – 0.17–0.21). It was determined that the accident at the Fukushima-1 plant and in Chazhma Bay had no effect on the actinide content in the region. The ²⁴⁰Pu/²³⁹Pu atomic ratios (0.20±0.02 and 0.21±0.01) and ²⁴¹Am/²³⁹⁺²⁴⁰Pu activity ratios (3.32±2.76 and 0.45±0.17) in sea and lake cores showed that the sources of Pu and Am in the area are global fallout and Pacific nuclear weapons test sites belonging to the USA.

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PRODUCTION OF ^{230}Pa AS A SOURCE OF RADIONUCLIDES ^{230}U AND ^{226}Th FOR TARGETED ALPHA THERAPY

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Alpha-emitting radionuclides are successfully used in the therapy of various oncological diseases. Alpha particles are more effective in destroying tumor cells than beta particles due to the high linear energy transfer in a biological tissue. ^{230}Pa ($T_{1/2} = 17.4$ days) is of interest together with widespread ^{223}Ra and ^{225}Ac . This radionuclide decays to ^{230}U (20.8 days), generating a cascade of five alpha particles with a total energy of 33.5 MeV, which enhances the therapeutic effect. In addition, ^{230}U is prospective as a parent radionuclide for a generator of short-lived ^{226}Th (31 min).

The above-mentioned radionuclides are generated under irradiation of natural thorium with protons. Large amount of $^{230}\text{Pa}/^{230}\text{U}$ can be produced by commercial cyclotrons accelerating protons to energies of 70 MeV, whereas higher proton energies are required for effective production of ^{225}Ac and ^{223}Ra .

In this work, the isolation of $^{230}\text{Pa}/^{230}\text{U}$ from proton-irradiated thorium was studied by liquid-liquid extraction and extraction chromatography methods. The best results in the separation of Pa(V) and U(VI) from macro quantities of Th(IV) and thorium irradiation products were obtained using alcohols (octanol-1) and quaternary ammonium salts (tricaprylmethyl ammonium chloride, aliquate 336) as extractants¹. The separation procedure was developed as a part of simultaneous isolation of ^{225}Ac , ^{223}Ra and $^{230}\text{Pa}/^{230}\text{U}$ from thorium irradiated with high-energy protons, as well as it can be used in the case of irradiation with low-energy protons, when ^{230}U is the main product. Possible generator schemes of ^{226}Th production and its subsequent binding to the antibody Nimotuzumab for the treatment of epithelial tumors² are also considered.

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SORPTION RECOVERY OF PLUTONIUM FROM PROCESS SOLUTIONS WITH THE USE OF NEW DOMESTICALLY PRODUCED ANION-EXCHANGE MATERIALS

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The production activity of many operating nuclear facilities leads to generation of large amounts of process solutions having low actinide content and complex salt composition and awaiting further processing with a view to recovering valuable components. Conventionally used but no longer manufactured domestically produced ion-exchange materials capable of selectively sorbing radionuclides from such media have been replaced by the materials produced abroad, the use of which in a multi-cycle mode under industrial conditions demonstrated several disadvantages of these materials. The potential for synthesis of alternative materials by Russian manufacturers and an import substitution trend have brought up an issue of substituting available modern domestically produced ion-exchange materials for foreign ion exchangers used in the production process.

The study has evaluated physical-chemical properties, sorption capacity with respect to thorium and plutonium, thermal and radiation resistance of sorption materials of AXIONIT VPA grade manufactured by JSC *Axion – Rare and Noble Metals*. The obtained laboratory and pilot-scale testing data have made it possible to recommend the use of anion-exchange material AXIONIT VPA-2 for recovery of plutonium from industrial nitric acid solutions. At present, this material is successfully used at the sorption unit of the chemical-metallurgical plant of the Mayak PA.

Not long ago, Russian company LLC GP *Smoly* proposed to use new grades of anion-exchange materials at the facilities of the nuclear power-engineering complex. Physical-chemical properties, sorption capacity with respect to thorium and plutonium and radiation resistance of AM-4VP, AMP-p and AM-p anion-exchange materials have been evaluated. The laboratory testing data have confirmed that these anion-exchange materials are promising for plutonium recovery from industrial nitric acid solutions. The AM-4VP anion-exchange material has been recommended for use at the radiochemical plant of the Mayak PA.

Therefore, modern sorption materials manufactured in Russia successfully find an industrial application at domestic radiochemical facilities.

PHOTONUCLEAR AND REACTOR POSSIBILITIES TO PRODUCE THERANOSTIC RADIONUCLIDE ^{195m}Pt

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Platinum based complexes are widely used in chemotherapy to treat various cancers. The use of an appropriate platinum radionuclide as a part of a suitable radiopharmaceutical during its targeted delivery to malignant cells allows to achieve a bigger therapeutic effect with less toxic impact. There are some effective with this respect isotopes such as ^{191}Pt , ^{195m}Pt , and ^{197}Pt . One of the most perspective platinum radioisotopes is ^{195m}Pt , and high yield of Auger electrons of ^{195m}Pt (33 electrons per decay) in combination with mild γ -radiation (98.9 keV, 11.4%) makes it expedient for theranostics.

The main methods to produce ^{195m}Pt up to now are enriched ^{194}Pt irradiation at a nuclear reactor and enriched ^{192}Os irradiation by α -particles. The reaction $^{194}\text{Pt}(n,\gamma)^{195m}\text{Pt}$ cross section equals to 0.09 b and this method results in low specific activity of the aimed radionuclide. The reaction $^{192}\text{Os}(\alpha,n)^{195m}\text{Pt}$ provides with the specific activity higher by two orders of magnitude than that for the neutron reaction, but the yield and cross section 3.7 b are much lower. Thus, conventional methods are unable to ensure enough specific activity so it is of a great importance to continue investigating ^{195m}Pt production routes.

In the current work two perspective approaches are considered: enriched ^{193}Ir neutron bombardment and a photonuclear method. The first approach concerns an irradiation by the reaction $^{193}\text{Ir}(n,\gamma)^{194}\text{Ir}(n,\gamma)^{195m}\text{Ir}\beta^- \rightarrow ^{195m}\text{Pt}$. The aim of our research was to determine previously unknown parameters of the reaction $^{194}\text{Ir}(n,\gamma)^{195m}\text{Ir}$. Two enriched iridium targets one of them Cd covered were irradiated for 17 days at the reactor IBR-2 (JINR, Dubna). Measurement of the separated aliquots of the radionuclide of interest helped us for the first time deduce the reaction $^{194}\text{Ir}(n,\gamma)^{195m}\text{Ir}$ resonance neutrons cross section which is 2900 b.¹⁻²

The second approach includes irradiation of a mixture of cisplatin and cryptomelane at the microtron MT-25 in JINR, FLNR. Cryptomelane serves as a collector of recoil nuclei, higher specific activity is achieved by Szilard-Chalmers effect.

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IMMOBILIZATION OF ANIONIC FORMS OF LONG-LIVED RADIONUCLIDES IN RADIOACTIVE WASTE REPOSITORY

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In modern nuclear energy, the problem of radioactive waste management (RW) is acute. In accordance with the strategy of the Rosatom State Corporation, it is planned to create an underground repository for final disposal¹. During construction, it is planned to use bentonite clays as an engineering barrier material, which have high sorption characteristics with respect to the cationic forms of the main radionuclides that make up the radioactive waste. However, this material is not able to confine the anionic forms of long-lived radionuclides, such as ⁷⁹Se and ⁹⁹Tc. It is proposed to use sulfide minerals as a sorbent for the immobilization of selenium² and technetium³ by reducing them to low soluble forms

The purpose of this work was to study the sorption characteristics of various sulfide minerals toward selenite ions and pertechnetate ions in aqueous solutions.

The following sulfide minerals were selected as the studied materials: chalcopyrite, sphalerite, stibnite, pyrite, bornite, cinnabar, pyrrhotite, galena, marcasite, orpiment, molybdenum and pentlandite. It was found that stibnite, bornite, pyrrhotite, marcasite and pentlandite have the best sorption characteristics toward selenite ion, and stibnite, marcasite, auripigment and pentlandite toward pertenechate ion. When these minerals were added to bentonite clays and subsequent sorption of selenium and technetium from solutions of model waters, kinetic dependences of sorption processes under oxygen and oxygen-free conditions were established. It has been shown that stibnite is best suited for the immobilization of both ions, namely the selenite ion and the pertechnetate ion in the conditions of a radioactive waste storage.

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REMOVAL OF ^{137}Cs AND ^{90}Sr FROM LIQUID RADIOACTIVE WASTE WITH HIGH SALINITY BY PHARMACOSIDERITE TYPE TITANOSILICATES

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Pharmacosiderite type titanositicates are successfully used for the purification of liquid radioactive waste from cesium and strontium. In this research, samples of dual-cation (sodium-potassium) incorporated pharmacosiderite type titanositicate were synthesized by directed hydrothermal synthesis with varying conditions of synthesis duration from 24 hours to 7 days at 180 °C, as well as in atmospheric synthesis at 25 °C for 4 days.

The sorption characteristics of the samples for ^{137}Cs and ^{90}Sr were studied in batch sorption mode.

Table 1. The distribution coefficient (K_d) values ^{90}Sr at sorption from 0.01 mol/dm³ calcium chloride solution

Sorbent name	K_d ^{90}Sr , cm ³ /g
GTS-1	46300
GTS-2	36100±8600
GTS-3	7920±800
GTS-4	9750±600

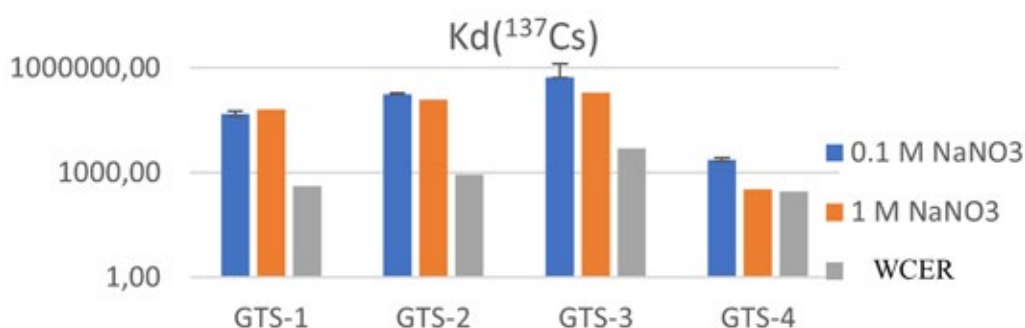


Figure 1. The distribution coefficient (K_d) values for ^{137}Cs under conditions of adsorption of microquantities from model solutions of LRW

The study was performed within the framework of the government assignment of the Ministry of Science and Higher Education of the Russian Federation no. FZNS-2023–0003, theme: Fundamental Principles of Chemical Designing of Novel Functional Materials Adaptive to Nuclear and Radiation Technologies.

DIFFUSION OF RADIOACTIVE WASTE ELEMENTS IN PORE SOLUTIONS OF CLAY MATERIALS

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The self-diffusion of water (HTO) as well as the diffusion of radioactive waste (RW) elements in a pore solution of compacted clay materials of various mineral composition were studied at room temperature using the through-diffusion method with radiochemical ($^3\text{H/T}$, ^{99}Tc , ^{137}Cs , ^{233}U) and stable (P, Se, Br, Mo, Cs, U) tracers. The simulated media were artificial groundwater and the leachate of model phosphate glass (PG) for RW with a total salt content of 0.4–0.7 g/l and a pH range 8.1–8.6. The effective diffusion coefficients (D_e , cm^2/s) for water and RW elements in clay materials and the distribution coefficients for sorbing elements were calculated based on experimental data.

The dependencies of the diffusion transfer of elements on diffusion partial factors were revealed for porosity of the material (ϵ , dimensionless), the proportion of the swelling mineral phase (C_{sm} , dimensionless) and the concentration of elements in the pore solution (C_{pore} , mg/l). The partial factors of diffusion for each of the elements were united into a general factor of diffusion (F_D , dimensionless), which determines the value of D_e of the element. The equations for calculating the numerical values of F_D and D_e of water and RW elements in the pore solutions of clay materials for two studied simulated media are given in the table. Of the studied elements, uranium and selenium were shown to be sensitive to the composition of chemical environment.

Element	Artificial groundwater	Simulated leachate of PG
HTO	$F_D^{\text{HTO}} = \epsilon (1 - 0.4C_{sm})$ $D_e^{\text{HTO}} = 5.11 \cdot 10^{-7} (F_D^{\text{HTO}})^{0.32} (R^2 = 0.80)$	
Cs	$F_D^{\text{Cs}} = \epsilon (1 - 0.1C_{sm}) + 0.5C_{pore}^{\text{Cs}}$ $D_e^{\text{Cs}} = 7.60 \cdot 10^{-7} (F_D^{\text{Cs}})^{2.09} (R^2 = 0.83)$	
U(VI)	$F_D^{\text{U}} = 2\epsilon (1 - 0.7C_{sm}) - 0.33C_{pore}^{\text{U}}$ $D_e^{\text{U}} = 6.53 \cdot 10^{-8} (F_D^{\text{U}})^{0.48} (R^2 = 0.41)$	$F_D^{\text{U}} = \epsilon (1 - 0.5C_{sm}) + 3C_{pore}^{\text{U}}$ $D_e^{\text{U}} = 3.00 \cdot 10^{-6} (F_D^{\text{U}})^{6.80} (R^2 = 0.80)$
Se(IV)	$F_D^{\text{Se}} = \epsilon (1 - 0.7C_{sm}) + 0.5C_{pore}^{\text{Se}}$ $D_e^{\text{Se}} = 2.29 \cdot 10^{-7} (F_D^{\text{Se}})^{1.36} (R^2 = 0.51)$	$F_D^{\text{Se}} = \epsilon (1 - 0.2C_{sm}) + 0.5C_{pore}^{\text{Se}}$ $D_e^{\text{Se}} = 1.71 \cdot 10^{-7} (F_D^{\text{Se}})^{1.53} (R^2 = 0.40)$
Mo	$F_D^{\text{Mo}} = \epsilon (1 - 0.7C_{sm}) + 0.33C_{pore}^{\text{Mo}}$ $D_e^{\text{Mo}} = 1.23 \cdot 10^{-7} (F_D^{\text{Mo}})^{0.52} (R^2 = 0.29)$	
Br	$F_D^{\text{Br}} = \epsilon (1 - 0.5C_{sm}) - 0.5C_{pore}^{\text{Br}}$ $D_e^{\text{Br}} = 5.89 \cdot 10^{-7} (F_D^{\text{Br}})^{1.46} (R^2 = 0.63)$	
P	—	$F_D^{\text{P}} = \epsilon (1 - 0.2C_{sm}) + 0.005C_{pore}^{\text{P}}$ $D_e^{\text{P}} = 6.11 \cdot 10^{-8} (F_D^{\text{P}})^{0.61} (R^2 = 0.73)$

CASCADE FRACTIONATION OF ANTHROPOGENIC URANIUM FORMS IN THE NATURAL-TECHNOGENIC SYSTEM OF THE TAILING DUMP OF PJSC NOVOSIBIRSK CHEMICAL CONCENTRATES PLANT

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The method of cascade fractionation of surface and ground waters as applied to the natural-technogenic system of the tailing dump of PJSC NZHK makes it possible to conduct a detailed study of the forms of uranium and its compounds, identify mechanisms and forecast the spread of contamination from the source.¹

To study the forms of uranium migration and deposition, groundwater and surface water samples were taken at different distances from the tailing dump bowl. By the method of cascade filtration of solutions the forms of uranium location were established: in surface waters uranium migrates in the true dissolved form, in ground waters – with colloids. Experimental data were confirmed by physicochemical modeling in the program “HCh”.²

All studies were carried out at the Analytical Center for multi-elemental and isotope research SB RAS.

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SYNTHESIS OF NEW SORBENTS BASED ON AMIDOXIME FUNCTIONAL GROUPS FOR THE EXTRACTION OF TECHNETIUM FROM LIQUID MINERALIZED ENVIRONMENT

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Technetium is a fission product of uranium–plutonium fuel. Technetium enters to the environment as an emissions product of nuclear power facilities. Currently, the problem of its extraction from liquid mineralized environment is relevant due to the peculiarities of the chemical behavior of Tc and the lack of effective methods of its extraction.

Sorption purification methods are the most technologically available compared to other methods. Extraction of technetium from liquid environment by currently known materials is complicated by the presence of the element in a wide range of oxidation states (from +7 to –1), as well as significant variability of ionic forms depending on the composition and pH of the solution.

Of particular interest are materials with grafted amidoxime groups, both in pure form and as part of organic radicals. These materials are characterized by increased sorption-selective properties to actinoids and lanthanides due to the redistribution of electron density, which was established in this work.

During a one-stage polycondensation reaction, by grafting the Se-derivative 4-aminofurazane-3-carboxamidoxime to a matrix of ionites of the KU-2-8 / AB-17-8 spherical granulated composite materials with increased mechanical and chemical resistance were obtained and characterized. Under static conditions of Tc sorption, it was found that in a wide pH range of 3–6, the values of the distribution coefficients exceed 104. The possibility of radionuclide elution has been demonstrated. The elution efficiency exceeds 90%. The research results indicate the prospects of the developed materials, further research of which will allow us to offer new solutions to urgent environmental and technological problems.

The work was carried out with the financial support of the Russian Science Foundation, project 24-23-00160.

PRODUCTION OF CRYSTAL MATRICES FOR THE INCORPORATION OF HIGHLY ACTIVE WASTE

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An important and urgent scientific and technical task is the management of highly radioactive waste from the defense industry and peaceful nuclear energy. It is proposed to include such highly radioactive waste in special matrices for further placement in the geological store^{1,2}.

In addition to the glasses already used for the immobilization of highly radioactive waste, various crystal matrices are promising, the main task is to move from their laboratory synthesis with simulators to a real production technology. The main difficulties include: preparation of radioactive charge, compact hardware design with high performance, remote maintenance and repair using various manipulators.

A new method of immobilization of highly radioactive waste is considered, which combines the production of a granular precursor and its melting at an IPT installation with the formation of a final matrix. This approach will reduce entrainment and dust formation, reduce the corrosive effect on the granulator due to the formation of a garnishing layer, and increase the energy efficiency of induction melting with a cold crucible due to a decrease in the water content in the precursor to 20 wt. % H₂O.

At the pilot plant, blocks of various matrices were obtained in a mode close to the conditions of the real process, which corresponds to the readiness level of this technology equal to TRL 6. The characteristics of the obtained matrices comply with the regulatory requirements (GOST R 50926-96, NP-093-14) for highly radioactive waste matrices. The results of the study confirmed the possibility of a two-stage synthesis, including the production of a precursor granulate and its subsequent by the induction melting with a cold crucible method into a compact product³.

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LAYER-BY-LAYER METHOD IN DETERMINING PARAMETERS OF DYNAMIC RADON ADSORPTION

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The problem of radon is global since the longest-lived isotope ^{222}Rn makes the main contribution to the collective radiation dose of the population. The design of air purifying systems requires information on both equilibrium and kinetic parameters of radon dynamic adsorption. This work proposes a simple method for calculating the parameters of dynamic radon adsorption based on the results of a gamma-spectrometric measurement of the sorbent when radon is supplied to the column with a short pulse. An analytical expression was obtained that relates the Henry's constant (K_H) and the thickness of the equilibrium adsorption layer (L_e) of radon with the experimental conditions and the measured distribution of activity along the sorbent bed:

$$A(n) = \left[\frac{\Gamma\left(\frac{n \cdot h}{L_e}, b \cdot t\right)}{\Gamma\left(\frac{n \cdot h}{L_e}\right)} - \frac{\Gamma\left(\frac{(n-1) \cdot h}{L_e}, b \cdot t\right)}{\Gamma\left(\frac{(n-1) \cdot h}{L_e}\right)} \right] \cdot \frac{\Gamma\left(\frac{L}{L_e}\right)}{\Gamma\left(\frac{L}{L_e}, b \cdot t\right)}$$

$$b = \frac{u}{L_e \cdot (\varepsilon + (1 - \varepsilon) \cdot K_H)}$$

Here $A(n)$ – relative radon activity in n -th section of the column (related to total activity of all sections), h – sorbent bed thickness in section, u – superficial (referred to the total section of the layer) linear flow velocity, t – time of exposition, L – column length, ε – external porosity of the column bed, $\Gamma(z)$ – Euler's gamma-function, $\Gamma(z, x)$ – upper incomplete gamma-function.

Good agreement was shown between the measured and calculated distribution of radon during dynamic adsorption on various brands of activated carbon in a wide range of experimental conditions.

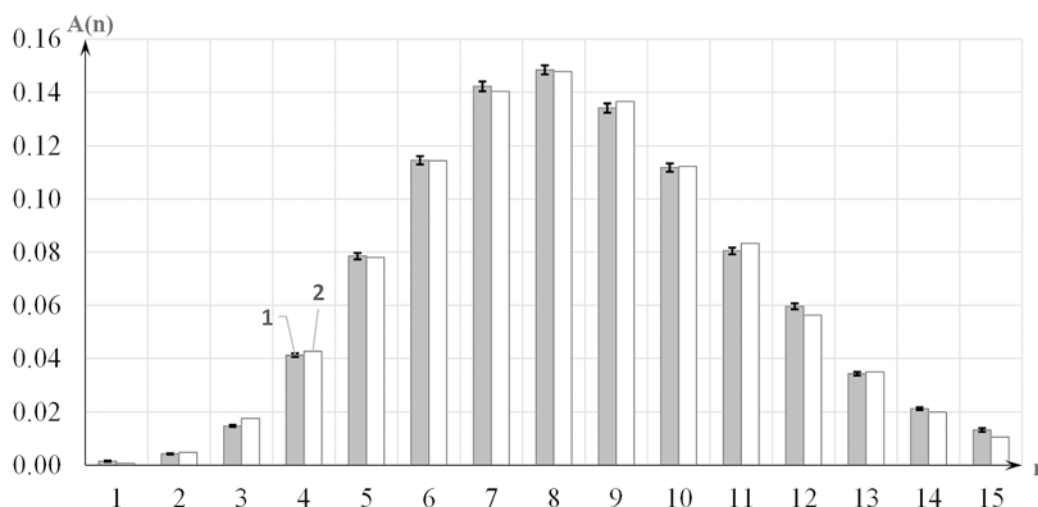


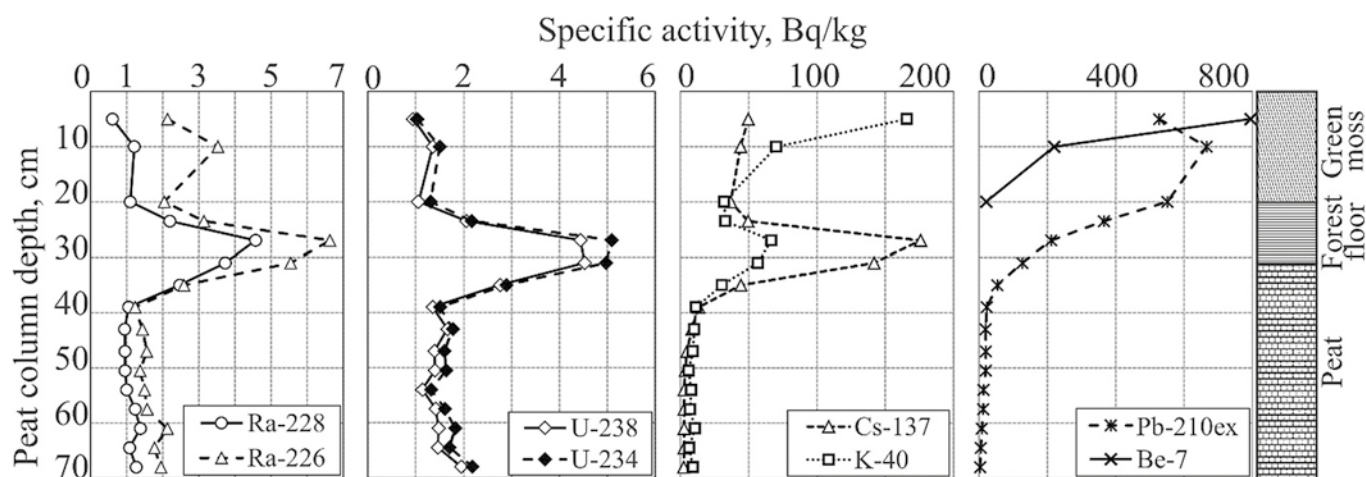
Figure 1. Measured (1) and calculated (2) distribution of ^{222}Rn along sections of the adsorption column (sorbent VSK-5, 2.0 l/min, exposition 50 min, temperature 61 °C)

REDISTRIBUTION OF RADIOACTIVE ELEMENTS IN THE NEAR-SURFACE LAYER OF THE SHERSTOBITOV PEAT RAISED BOG

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The vertical distribution of natural ^{238}U , ^{234}U , ^{226}Ra , ^{228}Ra , ^{40}K radioactive elements and man-made ^{137}Cs in the near-surface layer of the Sherstobitov raised peat bog was studied. A similar distribution pattern is observed for all elements. There is a pronounced peak in concentrations corresponding to the forest floor layer and the upper peat horizon.



The upper part of the litter (20–25 cm) is a peatogenic horizon, where organic matter (OM) is not yet peat. Below (25–35 cm), the OM of the sphagnum begins to transform actually into peat. This leads to changes in the degree of decomposition and humification, as well as compaction and chemical changes in the organic and mineral component. Therefore, this section may represent a geochemical barrier where chemical elements (Cs, K, Ra, and U) may accumulate. It should be noted that this interval (25–35 cm) corresponds to the level of maximum standing of bog water in the spring-summer period¹. This contributes to the concentration of chemical elements dissolved in bog waters in peat material.

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RADIOLYSIS SUPPRESSION IN THERAPEUTIC RADIOPHARMACEUTICALS

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The corpuscular radiation of the radionuclide, which is a part of a finished dosage form (FDF) of a therapeutic radiopharmaceutical (RP), is the cause of continuous generation of radical particles in the volume of the formulation. Particles interaction with components of the formulation leads to a decrease in the quality of the radiopharmaceutical due to the gradual accumulation of autoradiolysis products of the radioconjugate, which are often significantly different by its pharmacokinetics. To stabilize the radiopharmaceutical and increase its shelf-life, various antioxidants (radioprotectors) are introduced into the composition of FDF. The choice of pharmaceutically suitable radioprotectors, which are inert towards the main components of the radiopharmaceutical is an important stage of pharmaceutical development of therapeutic RPs.

In this work, the efficacy of different stabilizers was evaluated on the example of the compound [^{177}Lu]Lu-PSMA-617 used for prostate cancer therapy in comparison with the most popular today gentisic and ascorbic acids (GA and AA). The effectiveness of stabilizers (cysteine, vanillin, methionine, adenine, dobesilic acid, thymine, uracil, nicotinamide, meglumine and mannitol) was estimated in terms of radiochemical purity (RCP) decrease of the radiopharmaceutical, which was monitored by HPLC and TLC methods.

On the example of cysteine and *meso*-dimercaptosuccinic acid it was shown that thiol-containing compounds exhibit high activity in terms of radiolysis suppression. The features and limitations of their use in the composition of FDF RP were also noted. Promising results for use of unsaturated cysteine derivatives such as alliin, allylcysteine, S-allylmercaptocysteine (S-AMC) were shown. The introduction of S-AMC into the FDF of [^{177}Lu]Lu-PSMA-617 (all other conditions being equal) maintains RCP at $\geq 95\%$ for 1.4–1.5 times longer compared to an equivalent amount of GA. The application of these substances will allow to avoid some negative aspects related to oxidation of other radioprotectors (e.g. gentisic and ascorbic acids, vanillin): coloration, formation of phenolic and benzoquinone derivatives.

The study was carried out with the financial support of the Federal Medical Biological Agency of the Russian Federation, № 122031100121-4.

APPROACHES TO HANDLING IRRADIATED REACTOR ZIRCONIUM MATERIALS USING THE EXAMPLE OF IRRADIATED FUEL CHANNELS OF RBMK REACTORS

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During the operation of zirconium alloys in the core of thermal reactors, β and γ -emitting radionuclides ^{54}Mn , ^{60}Co , ^{94}Nb , ^{95}Zr , ^{95}Nb , ^{182}Ta , as well as purely β -emitting radionuclides ^3H , ^{14}C , ^{35}S , ^{36}Cl , ^{45}Ca , ^{93}Zr , ^{93}Nb and ^{93}Zr (long-lived radionuclides with $T_{1/2} > 30$ years)¹.

The main radioactivity of RBMK's (99,2%) zirconium pipes is determined by the activity of long-lived ^{94}Nb , while its volume fraction is only about 2%.

For zirconium pipes, the specific activity reaches $8.1 \cdot 10^6$ Bq/g, which corresponds to high level radioactive waste and should be carried out to deep disposal sites for radioactive waste. At the same time, during operation, oxide deposits of complex composition are formed on the inner surface of the channels, which do not allow direct compaction and subsequent transfer to disposal.

A similar problem exists when handling process pipes (Zr – 2.5 Nb) of Candu and IPHWR reactors.

The method for handling zirconium solid radioactive waste was proposed. Selective electrolytic separation of zirconium from a fragment of a spent channel (irradiation period – 30 years) was carried out in melts based on an equimolar mixture of NaCl-KCl with additions of chlorides of alkali and rare earth metals. Zirconium obtained in metallic form. The achieved degree of zirconium extraction is 90%, the purification factor is 10^3 in one stage. Additionally, operations are proposed to handle products and bring them to the acceptance criteria for long-term isolation.

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Pd-Te PHASE IN SPENT NUCLEAR FUEL: AIR OXIDATION AND ACID DISSOLUTION BEHAVIOR

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The development of closed nuclear fuel cycle technology implies the use of fast neutron reactors to produce energy and reproduce nuclear fuel. It is known that one of the features of the spent fuel from such reactors is the high content of fission products, in particular palladium. One of the forms of palladium in the oxide fuel in this case will be a Pd-Te alloy with a composition close to the $\text{Pd}_{20}\text{Te}_7$ intermetallic compound. During fuel reprocessing, the presence of both palladium and tellurium can complicate the process. In particular, palladium can actively pass into the organic phase during extraction, and tellurium is capable of forming volatile oxygen compounds during fuel oxidation in voloxidation process. Thus, in this work, we studied the behavior of the Pd-Te alloy during oxidation in air and during dissolution in nitric acid in order to establish possible reaction products.

An intermetallic compound of composition $\text{Pd}_{20}\text{Te}_7$ was chosen as a simulator of the Pd-Te alloy, which was synthesized by the reaction of stoichiometric amounts of starting substances in an evacuated ampoule at a temperature of 1000 °C for 48 hours. The resulting product was characterized using powder X-ray diffraction (PXRD) and scanning electron microscopy.

Preliminary data on the oxidation of the alloy in air were obtained using thermogravimetry – differential scanning calorimetry measurements in the temperature range 40–1500 °C. Next, the phase composition of the products was clarified at different temperatures using PXRD with sample heating. Finally, to determine the distribution of volatile oxidation products along the temperature gradient, thermochromatography was used with sample heating at 1000 °C in an air flow.

It was found that $\text{Pd}_{20}\text{Te}_7$ samples are completely dissolved in 8M HNO_3 at 90 °C within an hour. The resulting brown-red solutions were further examined using spectrophotometry. Dry products formed during the evaporation of solutions were studied using IR spectroscopy and PXRD.

ANODIC DISSOLUTION OF URANIUM ALLOYS CONTAINING PALLADIUM AND NEODYMIUM IN MELTS BASED ON A EUTECTIC MIXTURE OF LITHIUM AND POTASSIUM CHLORIDES

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To achieve the closure of the nuclear fuel cycle, it is necessary to create a technology for reprocessing spent nuclear fuel (SNF), which allows to isolate target components and reduce the volume of radioactive waste, one of the main potential technological operations of which is the electrofining of metallized SNF. To carry out refining conversion, it is necessary to determine the parameters of anodic dissolution of alloys modeling the product of metallized spent fuel.

This paper presents the results of a study of the processes of anodic dissolution of model U-Pd and U-Pd-Nd alloys with different concentrations of palladium and neodymium in melts based on 3LiCl-2KCl- UCl_3 (10.1 wt. % UCl_3) at 550 °C, performed using a complex of various electrochemical methods.

The conducted studies allowed us to conclude that the increase in the content of Pd and Nd in alloys from 1.0 to 10.0 wt. % may affect the course of anodic dissolution of alloys. It is shown that palladium does not transfer to the electrolyte in significant quantities, and neodymium accumulates in the melt only when refining an alloy with a content of 10.0 wt. % Nd.

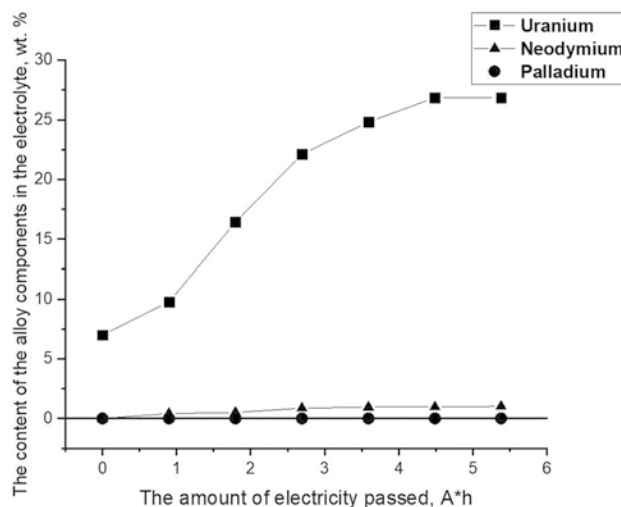


Figure 1. Change in the concentration of uranium, palladium and neodymium in the melt 3LiCl-2KCl- UCl_3 (10.1 wt. % UCl_3) during anodic dissolution of the U-Pd (1.5 wt. %)-Nd (10.0 wt. %) model alloy at 550 °C and a current density of 0.35 A/cm²

ELECTROFINING OF METALLIZED MODEL NUCLEAR FUEL IN ELECTROLYTES CONTAINING REE CHLORIDES

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Electrolytic refining of metallized spent nuclear fuel (SNF) in molten salt electrolytes is one of the main stages of pyrochemical processing of SNF. The main task of this operation is to separate uranium from fission products (noble metals and rare earth elements (REE)). To achieve this goal, experiments on the electrolytic separation of uranium from a model alloy simulating SNF in melts containing REE chlorides were performed in this work.

It has been demonstrated that the method of electrorefining a model metallized spent nuclear fuel makes it possible to obtain high-purity uranium cathode precipitates. The noble metals in the bulk accumulate in the anode sludge, however, under certain conditions, there is a slight transition of silver and palladium into the electrolyte, which entails the appearance of these elements in the cathode sediment. Despite the presence of palladium and silver ions in the electrolyte, as well as the addition of rare earth element chlorides to the electrolyte, the accumulation of which occurs during the cyclic refining process, this method allows to achieve high purification coefficients of uranium.

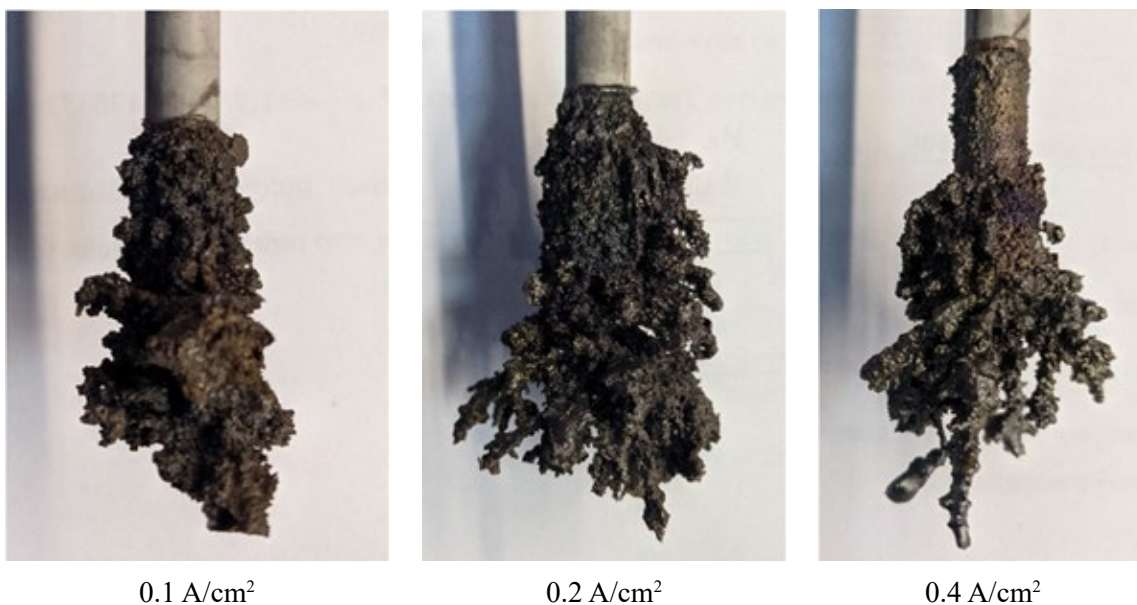


Figure 1. Cathode deposits of uranium obtained during electrolytic separation from an alloy of metallized model spent nuclear fuel at various initial cathode current densities in an electrolyte with a concentration of UCl_3 10.1 wt. %, temperature 550 °C, specific amount of electricity 1 A·h/cm²

EXPERIMENTAL AND THEORETICAL XANES INVESTIGATION OF UO_x AND UN SYSTEMS: HIGH-RESOLUTION MODELING RESULTS

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X-ray Absorption Spectroscopy (XAS) is currently one of the leading methods for studying the structure of substances and electronic states. Both structural and electronic properties of actinides are of fundamental interest for describing intra-molecular interactions. Using laboratory spectrometers, it is possible to obtain not only information about the oxidation state of the studied materials but also structural and electronic information using various theoretical approaches (Fig. 1).

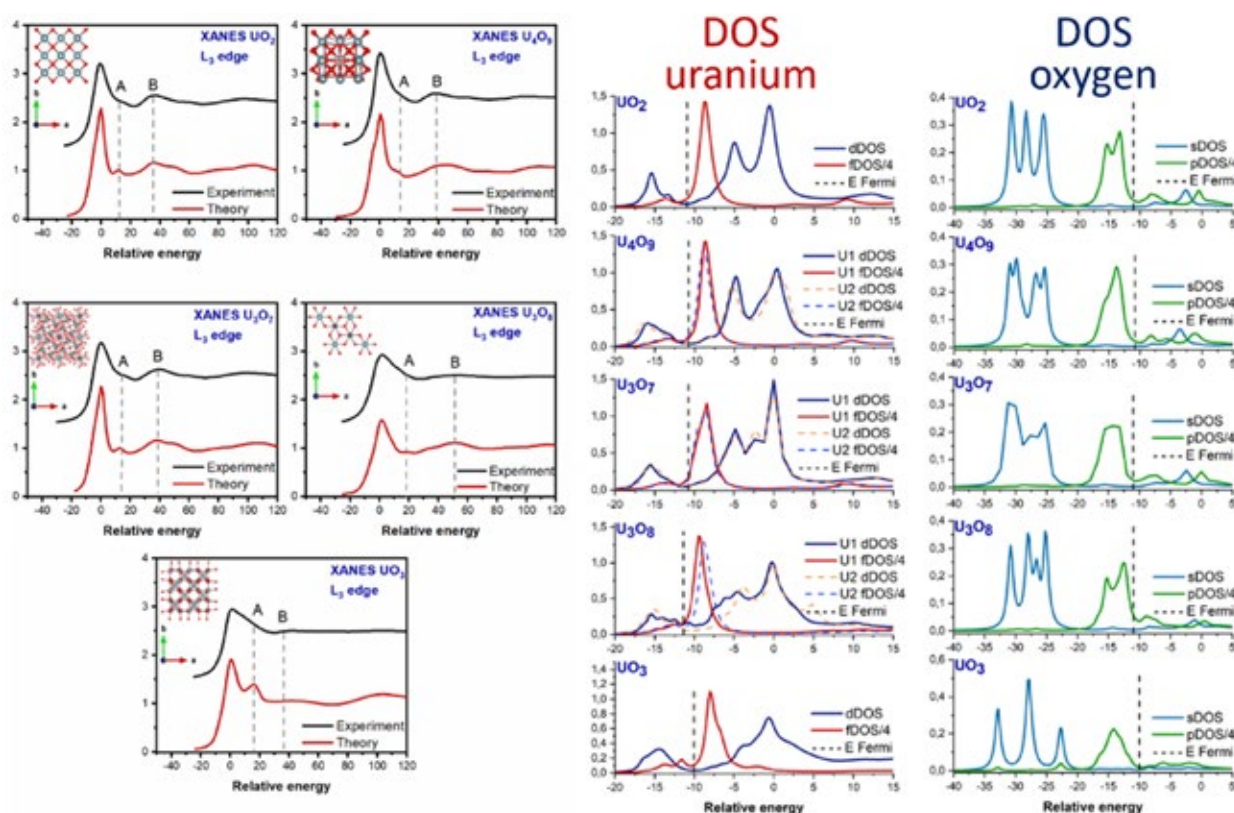


Figure 1. Experimental and theoretical X-ray absorption spectra of UO_2 , U_4O_9 , U_3O_7 , U_3O_8 , UO_3 , as well as electron density of states of uranium and oxygen

Using theoretical approaches to model XANES spectra of various uranium oxides allows for the estimation of local density of electronic states (DOS). DOS helps identify potential transitions and spectral lines observed in experiments, which is crucial when considering the behavior of UN systems and their potential use as nuclear fuel for energy production.

This work was supported by the Russian Science Foundation, grant 23-73-30006.

STUDYING NEW SUBTYPES OF NON-COVALENT INTERACTIONS BY THE HIRSHFELD SURFACE METHOD IN RHENIUM AND TECHNETIUM COMPOUNDS

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In this work, four classes of compounds were obtained and structurally characterized: Tc(V) coordination compounds, Tc(VII) and Re(VII) salts with guanine, with histidine, and with pyrazole.

Using the Hirshfeld surface method, it was shown that hydrogen bonds play the main role in the nonvalent interactions of Tc(V) and Tc/Re(VII) compounds. In compounds containing an aromatic moiety, anion- π , π -stacking, and CH- π interactions appear. In compounds with halogen and chalcogen atoms, typical and already well-described halogen and chalcogen bonds appear.

For the first time, anion \cdots anionic (M-O \cdots M) interactions were discovered in pertechnetates and perrhenates using the example of newly synthesized and structurally characterized three compounds of pertechnetate and perrhenate with a guaninium cation. In the case of a compound with singly protonated guanine, an unusual new anion \cdots anion interaction was found for the first time, in which the metal atom of one tetroxide anion is bonded to the oxygen atom of another and vice versa. It is proposed to call the new type of interaction: "double lock". The work shows that the first described $\text{Re}_4\text{O}_{15}^{2-}$ anion exists only in the *cis* conformation, which is apparently due to the presence of intramolecular Re \cdots O stabilizing nonvalent interactions, characteristic of molecules of similar geometry.

In L-histidinium perrhenate, a new type of anion \cdots anion interaction of C-O \cdots Re with a carboxylate group with an O \cdots Re distance of 2.97 Å was described for the first time. This type of interaction was discovered in other Re and Mn compounds, but it is absent for Tc. The work demonstrates the importance of weak non-covalent bonds for the structures of the resulting compounds, even those with identical structures, and opens the possibility of separating closely related elements (such as Tc and Re).

The work was carried out with the financial support of the Russian Science Foundation, project No. 23-73-01068.



RADIATIONAL-THERMAL STABILITY OF NITRIC ACID SOLUTIONS OF CARBOHYDRAZIDE

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In the radiochemical technology of spent nuclear fuel reprocessing, organic reducing agents and complexing agents are used during the stage of reductive re-extraction. One such compound is carbohydrazide (CH). The danger of mixing the reducing agent with nitric acid is the occurrence of exothermic processes, which can proceed at high speed and be accompanied by the intensive release of heat and gases. This can lead to deformation of the apparatus or release of its contents into the environment. The objective of this work was to investigate the impact of irradiation on the thermal stability of CH solutions in nitric acid.

For non-irradiated solutions with increasing nitric acid concentration, the temperature of exothermic reaction onset decreases with a simultaneous increase in heat release. The onset temperatures of exothermic reactions in irradiated solutions increase slightly up to 100 and 250 kGy. At a dose of 500 kGy, the value of T_{st} increases to 145 for 3 mol/L HNO_3 solutions and to 137 °C for 7 mol/L HNO_3 solutions. The values of specific heat release in 3 mol/L HNO_3 solutions are close at all irradiation doses. In 7 mol/L HNO_3 solutions, the heat release decreases and at 500 kGy is 24 J/g, which is more than 5 times less than the heat release of the unirradiated solution.

Irradiation of nitric acid solutions of CH therefore reduces their thermal stability. The first exothermic effect corresponds to the exothermic reaction in the unirradiated sample, at the end of which there is a second exothermic reaction associated with the decomposition of nitration products of CH, some of which are explosive¹.

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SORPTION PROPERTIES OF ACTIVATED CHARCOAL WITH ALKALINE-EARTH METAL IODIDES AND TEDA IN RELATION TO RADIOACTIVE METHYL IODIDE

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Activated charcoals are widely used for the localization of radioactive iodine compounds at nuclear power plants. They are impregnated with various chemical reagents to enhance the sorbents affinity for radioiodine, such as triethylenediamine (TEDA) and specific metal iodides. The addition of these additives enhances the adsorption efficiency of methyl iodide by establishing specific dispersion interactions with TEDA and forming stable ammonium salts that are securely trapped inside the porous charcoal structure. The interaction mechanism is presumably explained by physical reversible and chemical irreversible adsorption occurring simultaneously.

The purpose of this study was to compare the sorption properties of activated charcoal loaded with alkaline earth metal iodides and TEDA in relation to radioactive methyl iodide.

The research work proposed a potential chemical reaction between alkaline earth metal iodides (Ba, Sr, Ca) and TEDA based on the results of gravimetric and X-ray phase analyses. A significant decrease in the influence of the gas flow humidity on the sorption capacity of sorbents loaded with both metal iodide and TEDA was found, compared to the values obtained for sorbents only impregnated with TEDA. The study demonstrated the significant impact of short-term heat treatment on charcoal impregnated with TEDA. Subjecting this sorbent to heat treatment for 24 hours results in a reduction in the effectiveness of radioiodine sorption. However, sorbents with a combined impregnant do not lose their sorption capacity under the same conditions. Research has demonstrated that when more than 10^6 column volumes of air are passed through sorbents with introduced barium iodide, it results in a decrease in the sorption rate by 40% due to atmospheric air poisoning. Moreover, for sorbents with a combined impregnant, the decrease in efficiency is not so significant. The proposal suggests utilizing more cost-effective calcium iodide rather than barium iodide for the impregnation of commercial iodine sorbents. This approach takes into account that the capacity and efficiency of these impregnated activated carbons are practically identical, falling within the range of error.

MONTMORILLONITE AS RADIONUCLIDE CARRIER AGENT FOR NUCLEAR MEDICINE PURPOSES

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At present, a significant amount of research in the field of nuclear medicine is devoted to the development of new radiopharmaceuticals (RPs) that provide a target delivery of the emitting radioisotope. At the same time, researches explore the possibilities and determination of the conditions for the use of nano- and micro-sized radionuclide carriers as a part of new RPs generation¹.

One of these promising carrier agents is montmorillonite (MMT), a natural mineral, various forms of which are widely studied as a drug delivery system with controlled release. The high adsorption capacity of MMT contributes to increasing drug intercalation and then its sustained release²⁻⁴. Bentonite clay of Bentonite Company deposits consists of the high content of MMT (up to 95%).

MMT prospects for the PRs development are due to the high sorption capacity of cations and anions from water solutions as well as the purpose for obtaining samples with the required aggregate sizes (nm, mkm), biocompatibility, non-toxicity and radiation resistance. Despite these advantages, there are no research results of MMT as a carrier agent for radionuclides in the medical field to date.

Our work presents the results of the first studies on the development of prototype RPs based on MMT. The sorption kinetics of promising radionuclides for therapeutic applications has been studied on various MMT samples at different pH and temperature conditions. The influence of the ratio of solid and liquid phases and temperature on the degree of sorption has been determined. The sorption capacity of MMT samples has been found for the studied radionuclides. Thermodynamic data have been obtained under the study conditions. Promising MMT samples have been found for further *in vivo* studies.

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PROBLEMS AND METHODOLOGICAL APPROACHES TO DETERMINATION OF ACTINIDE CONTENT IN GRAPHITE: RADIOCHEMICAL METHOD

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One of the significant problems in the decommissioning of some uranium-graphite reactors (UGRs) in the world is the presence of nuclear fuel fragments spillage in the graphite stacks. In Russian Federation according to rough estimates, about 5% (~3000 tons) of graphite contains a significant amount of long-lived actinides of “fuel” origin (isotopes Am, Cm, Np, etc.). Actinide content levels in graphite have a significant impact on the choice of graphite handling approaches. Thus, the accuracy of actinide determination in graphite is important. The most effective method for actinides determination is radiochemical ones, which involves the separates actinides out from graphite with their subsequent analysis on spectrometric equipment. In this case, the other actinides determination is carried out after their chromatographic separation (Fig. 1).

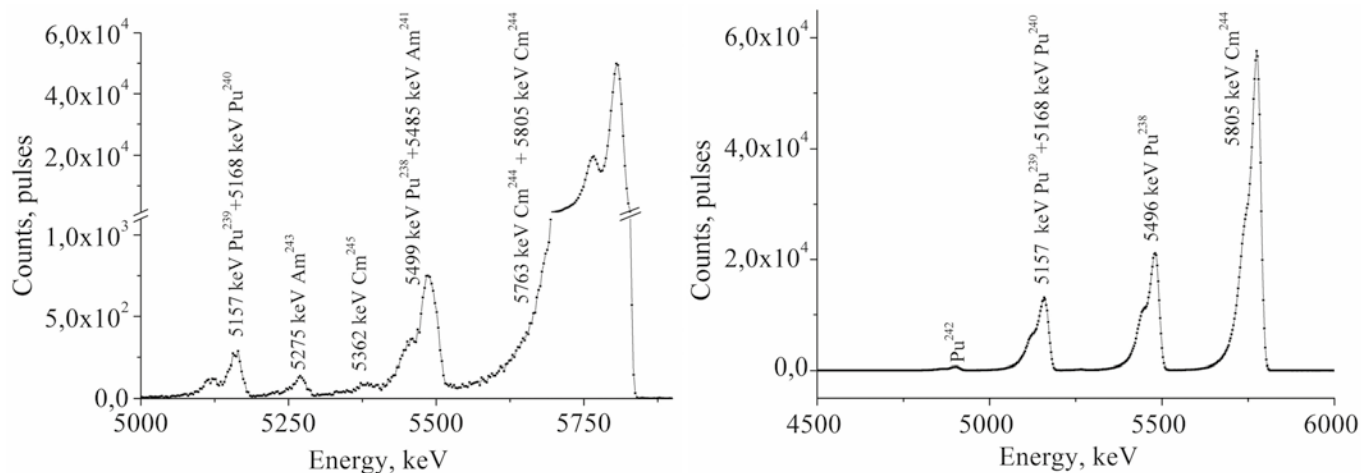


Figure 1. Characteristic alpha-radiation spectrum of actinides separated from a graphite sample out using a radiochemical method: initial spectrum (left) and after separate out Am and partially Cm (right)

As can be seen (Fig. 1), of all actinides, ²⁴⁴Cm has the highest alpha activity. The research results showed a significant non-uniformity of actinides in irradiated graphite, exceeding the uncertainty (error) of the measurement technique. The report presents methodological approaches to reduce the influence of this effect and improve the measurement quality.

APPROACHES TO DEFINING THE GRAPHITE RADIOACTIVE WASTES CLASS

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As the experimental results of irradiated graphite sample studies on C-14 content ($2,0 \times 10^4$ – $1,6 \times 10^6$ Bq/g) have shown, individual graphite stack of RBMK-1000 LNPP are divided between 2nd and 3rd class (Fig. 1) approximately equally¹. According to the average value of C-14 content ($\sim 7.5 \times 10^5$ Bq/g) the graphite stack of RBMK-1000 as a whole belongs to 3 class¹.

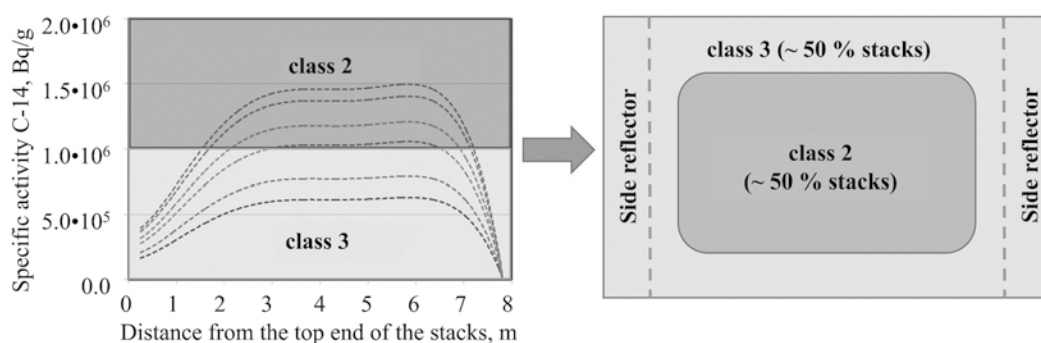


Figure 1. Classification of radioactive waste in the form of RBMK-1000 graphite stack for determination of possible disposal options

The obtained results allow, in case of orderly dismantling of RBMK-1000 graphite stacks subject to the condition of optimisation algorithms application for placing the blocks into containers, to ensure the average content of C-14 in containers less than $1,0 \times 10^6$ Bq/g, which will allow classifying the contained radioactive waste as class 3 and, accordingly, significantly reduce disposal costs.

Currently, work is underway to improve the methodological basis for determining the content of actinides (^{244}Cm , $^{241,243}\text{Am}$, $^{239,240,241}\text{Pu}$, etc.) in RBMK graphite, which also significantly affect the classification of graphite radioactive waste.

The report presents conventional and promising methods, including radiochemical ones, for determining the key (class-defining) radionuclides, as well as approaches and problems of graphitic radioactive waste classification, taking into account the specifics of Russian and international legislation.

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SYNTHESIS AND CHARACTERIZATION OF $M_{0.5}Zr_2(AsO_4)_x(PO_4)_{3-x}$ (M – Sr, Ba AND Cd) KOSNARITE-BASED CERAMICS FOR NUCLEAR WASTE IMMOBILIZATION

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The mineral-like ceramics with the structure of kosnarite ($KZr_2(PO_4)_3$) or the related compound $NaZr_2(PO_4)_3$ (NZP) are studied as potential matrices for immobilization of high-level waste¹. An important problem is the immobilization of soluble components in an insoluble stable structure. Sr^{2+} , Ba^{2+} (a decay product of cesium) and Cd^{2+} (a strong thermal neutron energy absorber) are highly soluble and must be reliably solidified. Arsenic is a component of chemical weapons that must be disposed of.

In this work we have studied the synthesis and characterization of phosphates $M_{0.5}Zr_2(AsO_4)_x(PO_4)_{3-x}$ immobilizing radioactive (M=Sr, Ba, Cd) and technological (Zr) components of radwaste, and the effect of the isomorphic substitution $P^{5+} \leftrightarrow As^{5+}$ on their structure and properties.

A sol-gel method was used to synthesize the desired materials by combining the appropriate metal salts and acids, followed by drying, heating and treatment steps. XRD results indicate that the crystalline $M_{0.5}Zr_2(AsO_4)_x(PO_4)_{3-x}$ (M – Sr, Ba, Cd) solid solutions of the NZP structure ($0 \leq x \leq 3$) were formed at 800°C. The results of Rietveld refinement showed that the framework is formed by ZrO_6 octahedra and mixed AsO_4/PO_4 tetrahedra connected by vertices; Sr, Ba or Cd cations are located in extra-framework positions.

Thermal expansion from –100 to +200 °C and hydrolytic stability of the representatives were studied. Ceramics can be classified as moderately expanding materials with average linear thermal expansion coefficients of $(8.5–9.0) \cdot 10^{-6} \text{ } ^\circ\text{C}^{-1}$. The hydrolytic stability of $Sr_{0.5}Zr_2(AsO_4)_{1.5}(PO_4)_{1.5}$ ceramics has been studied in a Soxhlet extractor (90 °C). The strontium leaching rate for 28 days, equal to $1.6 \cdot 10^{-5} \text{ g}/(\text{cm}^2 \cdot \text{day})$, and the XRD data of the sample before and after the dynamic test indicate a high hydrolytic resistance of the material.

Single-phase multicomponent crystalline $M_{0.5}Zr_2(AsO_4)_x(PO_4)_{3-x}$ ceramics containing Sr, Ba, Cd, Zr, As and P cations in various combinations in both cationic and anionic structural sites remain thermally stable in the temperature range of –100 to 1000 °C. Thermal expansion and the behavior in aqueous media demonstrate their suitability as matrices for radioactive waste.

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The present work was supported by the RSF, project No. 23-23-00044.

PENTAVALENT NEPTUNIUM BEHAVIOUR IN CARBONATE-RICH SOLUTIONS IN THE PRESENCE OF Ca^{2+} AND Mg^{2+} CATIONS

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Nuclear power creates long-term radioactive waste, requiring secure storage for centuries. Understanding radionuclide behaviour in solutions is vital for safety in deep geological disposal. ^{237}Np presents a significant long-term radiotoxic hazard in nuclear waste, increasing waste activity over thousands of years due to the decay of ^{241}Am . Understanding the composition and properties of solubility-controlling neptunium phases is crucial for predicting the maximum mobilization of Np through aqueous pathways from a waste repository. The study aims to examine Np(V) behaviour in solutions with carbonate anions and alkaline earth metal cations. The interaction between Np(V) and Ca^{2+} and Mg^{2+} cations is fascinating because of a substantial gap in the literature regarding Np(V)–Ca and Np(V)–Mg carbonates systems.

Double Np(V) carbonates were synthesized through chemical precipitation from a carbonate-containing Np(V) (10^{-3}M) solution in the presence of Ca^{2+} or Mg^{2+} cations. Cation exchange between solid $\text{NaNpO}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}$ and Mg^{2+} or Ca^{2+} in solution was also carried out. The resulting solids were analyzed using X-ray diffraction and scanning electron microscopy (SEM/EDX). The resulting compounds $\text{Ca}_{0.5}\text{NpO}_2\text{CO}_3$ or $\text{Mg}_{0.5}\text{NpO}_2\text{CO}_3$ were found to have a layered structure, where the anionic layer $[\text{NpO}_2\text{CO}_3]^-$ has an orthorhombic structure similar to the $\text{NaNpO}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}$ phase¹.

Double Np(V) carbonate dissolution was studied by immersing solids in NaClO_4 (0.01M or 0.1M) at pH 6–10. The dissolved Np, Ca or Mg concentrations were determined periodically. The concentration of neptunium in the solution was found to be dependent on the pH value and had a U-shaped curve that passed through a minimum of $3 \cdot 10^{-5}\text{M}$ at pH=9. According to UV-vis spectroscopy, Np existed in the solution in the pentavalent state during the dissolution process. The data obtained was used to calculate $\text{Ca}_{0.5}\text{NpO}_2\text{CO}_3$ and $\text{Mg}_{0.5}\text{NpO}_2\text{CO}_3$ solubility products.

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HIGH TEMPERATURE TREATMENT OF NITRIDE SPENT NUCLEAR FUEL

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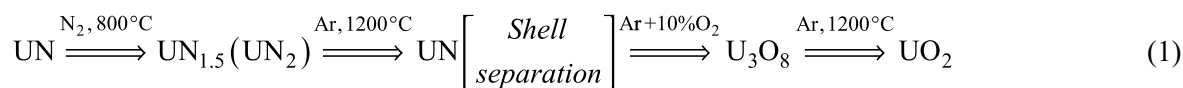
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High temperature treatment (HTT) of nitride spent nuclear fuel (SNF) is a series of key technological operations in the pyrochemical scheme of SNF reprocessing.

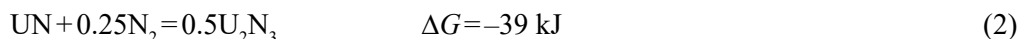
The main objectives of HTT include:

1. separation of fuel from the fuel element shell;
2. release and capture of volatile fission products (Cs, Rb, I, Cd);
3. conversion of nitrides into oxides (UO₂, PuO₂, ZrO₂, La₂O₃, CeO₂, Nd₂O₃ etc.) suitable for further processing.

The most complete scheme of nitride SNF HTT consists of nitriding, denitration, shell separation, UN oxidation to U₃O₈ and subsequent reduction to UO₂. It is presented below in the form of sequence (1):



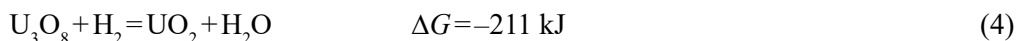
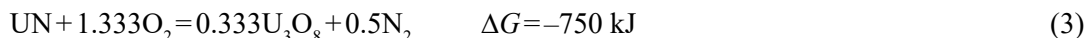
At the first stage, nitride SNF is maintained in nitrogen at 800–850 °C. In this case, the reaction proceeds:



The UN FCC lattice is replaced by the BCC one of α-U₂N₃, and the fuel volume increases by about 30%. This leads to deformation of the shell and crushing of the fuel. All this significantly facilitates the release of volatile fission products from SNF.

The second stage is denitration, i.e., a reverse transition of U₂N₃ → UN. The volume of fuel decreases during this operation which can contribute to SNF separation from the shells. Some mechanical agitation is needed to ensure maximum separation.

The fourth and fifth stages are the oxidation of UN to UO₂. Uranium is very easily oxidized to U₃O₈, so the production of UO₂ requires two stages (3) and (4):



The result of the SNF HTT is UO₂, that is suitable for the next reprocessing stages.

SORPTION AND SPATIAL DISTRIBUTION OF RADIONUCLIDES ON MINERALS OF THE NIZHNEKANSKY MASSIF ROCKS IN CONDITIONS OF FUTURE RW DISPOSAL

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The concept of isolation of radioactive waste (RW) containing long-lived and heat generating radionuclides in the deep crystalline rocks of Nizhnekansky massif (Krasnoyarsk region) is realized in Russia. To provide a safety assessment of the future repository, it is necessary to carry out forecast modeling of radionuclide behavior in the environment of host rocks. Obtaining of quantitative parameters of radionuclides retention by crystalline rocks is essential for forecast modeling¹. The retention parameters are affected by the composition of the groundwater solution due to its contact with both the host rock itself and engineered safety barriers, including the matrix with conditioned RW, bentonite buffer and stainless container.

The present work is aimed at determination of parameters of radionuclides retention by crystalline rocks of the future repository under different conditions, such as pH of solutions, temperatures and ionic strength. The ionic strength of the solutions is due to groundwater contact with both host rock and engineered safety barriers, including the RW immobilization matrix and clay buffer. In our experiments the groundwater model solutions and solutions after leaching of magnesium-potassium-phosphate (MPP) matrix were chosen. MPP matrix is currently considered as a promising material for RW conditioning in Russia². The influence of potassium and magnesium cations, as well as the temperature and pH of solution on the ¹³⁷Cs, ⁹⁰Sr, ²⁴¹Am, ²³⁷Np, ²³⁹Pu sorption by rock samples was established.

The quantitative spatial distribution of studied radionuclides on mineral phases of rock samples was evaluated using the technique based on the comparative analysis of digital radiography and SEM-EDX data. It was shown that the distribution of radionuclides on the mineral phases of the host rock surface is not influenced either by the ionic strength of solutions or by temperature.

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INTERACTION OF PLUTONIUM AND ITS ANALOGS WITH MINERALS AND NATURAL ORGANIC MATTER: FROM SPECIATION TO THERMODYNAMIC MODELING

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Understanding the principles underlying the behavior of long-lived actinides in the environment is necessary to create reliable and safe radioactive waste storage facilities and remediate contaminated areas. The chemistry of actinides is complex and unique, and plutonium has a special place on this list due to its redox reactions. Pu sorption was first observed to be accompanied by a redox reaction in the early 1980s. Almost simultaneously, several studies reported that Pu can be stabilized in the tetravalent state on the surface of iron oxide/oxyhydroxides. However, despite such a long and seemingly exhaustive study, the mechanism of the redox reaction upon sorption remains unclear. In addition, unlike other radionuclides, numerical modeling of Pu sorption reactions has not been developed, although is necessary from a practical point of view. The aim of these study is understanding sorption of behaviour of plutonium together with creation of a model account for redox reactions upon sorption.

The redox reactions occurring during sorption on the redox of inactive minerals are difficult to describe thermodynamically because there is no obvious electron source for the reaction. In this work we conducted experiments in a wide range of redox conditions (from anaerobic reduction conditions to highly oxidizing conditions) to create a model that will work for different systems. Varying mineral surfaces such as goethite, anatase, smectite, illite bernessite with or without adding of natural organic matter (NOM) can help highlight the role of chemical interactions in sorption for ongoing reactions. The use of elements-analogs such as cerium, americium and neptunium will, on the one hand, simplify the systems under study, since all cerium, americium and neptunium are not characterized by so many possible degrees of oxidation. For the characterizing speciation od sorbed atoms X-ray absorption spectroscopy (XANES and EXAFS) was used. PHREEQC code was used to model sorption. The MOUSE code was used for optimization of sorption constants in this system.

This work was supported by the Russian Science Foundation (project 21-73-20083)

PRODUCTION OF PROMETHIUM-147 FROM THE IRRADIATED NEODYMIUM OF NATURAL ISOTOPIC COMPOSITION

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Promethium-147 has a wide scope of application such as manufacture of light compositions for control devices, measurement of air dustiness, thickness and density of materials. Usually Pm-147 is produced by its extraction from a mixture of fission fragments of heavy nuclei. The cumulative yield of Pm-147 during the U-235 fission is 2.25%. The alternative way of the radionuclide production is Nd irradiation with the nuclear reactor neutrons when Pm-147 is produced by the $^{146}\text{Nd} (n, \gamma) ^{147}\text{Nd} (\beta^-) ^{147}\text{Pm}$ reaction. Both ways provide for production of non-carrier added Pm-147. However, the second way is less labor consuming and more environmentally friendly as it doesn't involve the irradiated nuclear fuel handling.

Neodymium of natural isotopic composition was experimentally irradiated in the reactor to test the calculation methods, practice radiochemical technologies and produce the test batch of Pm-147. The target with Nd oxide of 466.5mg (399.2mg neodymium by metal) was irradiated in the SM reactor neutron trap cell.

Besides the target Pm-147, the irradiated Nd of natural isotopic composition contains other Pm radionuclides such as Pm-148m and Pm-148, as well as isotopes of Nd, Sm, Eu, Gd. The possibility of chromatographic extraction of Pm isotopes from irradiated Nd of natural isotopic composition was experimentally tested. The radionuclide composition of the produced Pm-147 chemical is given. The coefficients of Pm-147 purification from impurity radionuclides were determined.

The good correlation between the calculated (8.14GBq Pm-147) and experimental results (8.4GBq Pm-147) is shown, which indicates the correctness of the calculation methods used.

SELECTIVE EXTRACTION OF ^{249}Bk FROM EUROPIUM NITRIC ACID SOLUTIONS AS A CURIUM SIMULATOR IN PRESENCE OF KBrO_3

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When RIAR processes the irradiated material (composition of Cm oxide and metallic Al), Al component of the composition is initially diluted by alkaline. Under these conditions, Cm oxide is insoluble and nitric acid with the concentration of 4–8 mol/l is used to dissolve it. It is assumed, that the obtained TPE nitic solution contains Al up to 10% of the initial amount (each irradiated target contains around 30 g of Al). The experiments were aimed to test the effect of macro-components (Eu as a Cm simulator, as well as Al) on the sorption of Bk and Ce radionuclides as a chemical analogue of Bk on AXIONIT 9S cation exchange resin with D2EGFC sorbent on the inert carrier (Teflon).

Studied was the possibility of chromatographic separation of a mixture of micro-quantities of ^{249}Bk , ^{144}Ce and Eu macro components at concentration of 4.36 g/l (in terms of content in mol/l equivalent to a concentration of ^{244}Cm 7g/l) and of Al 6g/l in nitric acid medium on the sorbents AXIIONIT 9S and D2EGFC-Teflon.

Determined were the sorption characteristics of AXIONIT 9S and D2EGFC-Teflon in relation to radionuclides ^{144}Ce , ^{152}Eu , ^{244}Cm , ^{249}Bk , ^{95}Zr , ^{95}Nb , ^{106}Ru , ^{249}Cf in the $\text{HNO}_3 - \text{KBrO}_3$ medium.

The obtained results enable to conclude that the selective ion exchange and chromatographic extraction of Bk from solutions with gram amounts of stable Eu as a Cm simulator is possible.

THE TECHNETIUM ISOTOPES PRODUCED BY PROTON IRRADIATION OF MOLYBDATES AQUEOUS SOLUTIONS

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Technetium isotopes are of great interest for medical and analytical research.

To study the possibility of generation technetium from molybdenum stable isotopes¹ were done irradiations of molybdate aqueous solutions of natural isotopic composition with protons 11 MeV². Then the target radionuclide was isolated from the target substance and radionuclide impurities.

Experiments were performed on cyclotron Siemens RDS-111 and use of a standard target device for ¹³N radionuclide. The results were analyzed on a γ -spectrometer and showed the presence pronounced γ -lines. γ -lines corresponded to technetium isotopes obtained from reactions ⁹⁴Mo(p,n)^{94g,m}Tc; ⁹⁵Mo(p,n)⁹⁵Tc; ⁹⁶Mo(p,n)^{96g,m}Tc; ¹⁰⁰Mo(p,2n)^{99m}Tc.

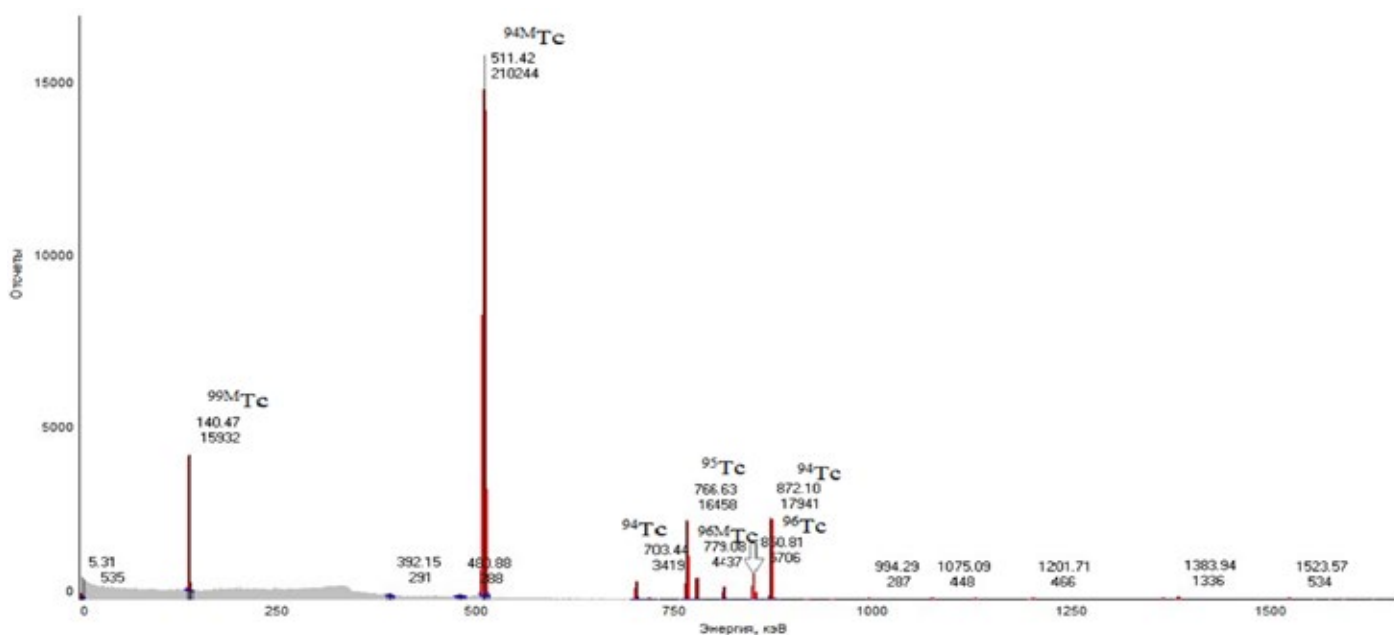


Figure 1. γ -Spectrum with decoding of radionuclides

The method is shown to be fundamentally promising for producing Tc-94m for PET diagnostics, and Tc-95 as a label for monitoring the yield of analytical procedures involving the isolation of Tc from natural objects.

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ENERGY TRANSFER FROM SOLVENT TO SOLUTE IN RADIATION-CHEMICAL TRANSFORMATIONS OF EXTRACTANT BASED ON SOLUTIONS OF DCH18C6 IN 1,1,7-TRIHYDRODODECAFLUOROHEPTANOL

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The dicyclohexano-18-crown-6 (DCH18C6) / 1,1,7-trihydrododecafluoro-heptanol system is a potential strontium-selective extractant for the reprocessing of spent nuclear fuel. In this work, the structure of the main radical intermediates of radiation-chemical transformations in this system was determined for the first time using the electron paramagnetic resonance (EPR) method under model conditions (at low temperatures). Based on the data obtained, a probable mechanism for the formation and subsequent transformations of radicals is proposed.¹ The formation of macrocyclic radicals due to the interaction of crown ether with the products of radiolysis of the solvent indicates a significant contribution of processes of indirect action of radiation on crown ether molecules, which should be taken into account when predicting the radiation resistance of such systems.

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UNDERSTANDING OF PROCESSES BEHIND SEQUENTIAL EXTRACTION OF Am (III) FROM ENVIRONMENTAL SAMPLES

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The long-term storage of accumulated radioactive waste poses an important challenge in the field of nuclear power, since the release of technogenic radionuclides into the environment could lead to an environmental catastrophe. One such element is americium having alpha emitter isotopes with a long half-life. Also it is therefore important to study not only the chemical properties of americium, but also its forms of presence in relevant environmental objects. On the basis of this information mobility and bioavailability can be predicted and the problem of radioactive element recovery in already existing contaminated sites can be solved.

One of the methods suitable for determination of radionuclide forms in natural objects, mainly soils/sediments, is sequential extraction. The results of such studies provide information on possible mechanisms of radionuclide interaction with components of soils. Sequential extraction consists in the stepwise interaction of the sample with reagents in the order of increasing exposure conditions (change of pH, reagent concentration, etc.). In the previous work¹ using such procedure together with spectroscopic and microscopic methods it was shown that the main state of uranium in bottom sediments is U(VI) in a readily available form.

In this work sequential extraction of ²⁴¹Am was performed using four different procedures, differs on number of stages and used reagents. In order to better understand the results of sequential extraction, model samples in which Am (III) were sorbed onto different minerals (goethite, bentonite, birnessite, etc) and humic acids were analysed. The results obtained were compared with data for bottom sediments from liquid radioactive waste reservoirs ("Mining and Chemical Combine", Zheleznogorsk, Russia). According to the results turned out that depending on the procedure, the fractionations of americium activity and the main fraction differed. The fraction distributions according to the Schultz method refused to be approximately the same for all model and wasted samples, which indicates the insufficient selectivity of the method. According to the results of other procedures common for all objects was the minimum content of americium activity in the residual fraction, except for the birnessite.

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PRODUCTION OF CARRIER FREE LUTETIUM-177 RADIONUCLIDE BY THE TANDEM METHOD

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Today, methods of radionuclide diagnostics (RND) and radionuclide therapy (RNT) have become an important part of modern medicine, where radionuclides in the form of various radiopharmaceuticals (RFP) are the fundamental elements of these techniques. Carrier free Lutetium-177 is one of the promising radionuclides with optimal nuclear physical characteristics for the diagnosis of prostate cancer and neuroendocrine tumors using various RFPs, by labeling amino acid peptide ligands with PSMA-617, PSMA-11, DOTA-TATE, DOTA-TOC DOTA-NOC

In this regard, the demand on the world market for this nuclide is increasing every year and to meet the needs it is necessary to separate ^{177}Lu from large attachments of the ytterbium-176 target material. On the other hand, to obtain ^{177}Lu carrier free radionuclide with high radionuclide and chemical purity in large quantities, the use of a single ^{177}Lu separation method does not lead to the desired result.

This research presents the results of experiments on the extraction of carrier free lutetium-177 radionuclide, with high chemical and radionuclide purity from the ytterbium-176 target material by tandem electrochemical and ion exchange chromatographic methods.

The electrochemical separation of lutetium-177 radionuclide is based on the discharge of the main mass quantities of the target material onto the mercury cathode by electrochemical reduction $^{176}\text{Yb}^{3+}$ up to $^{176}\text{Yb}^0$, with the formation of $^{176}\text{Yb}/\text{Hg}$ amalgam. Potassium citrate was used as an electrolyte in the range of pH 6–7 and temperature 0–2 °C. Under such electrolysis conditions, in 2 hours, more than 97% of ytterbium is restored and passes into the mercury cathode.

The ion exchange chromatographic method was used for the final purification of ^{177}Lu from residual amounts of ytterbium-176 and other chemical impurities. The DOWEX 50x8, 200–400 mesh, in NH_4^+ form has been used as an ion-exchange resin, as well as alpha-hydroxyisoacetic acid as a complexing reagent. Elution of ^{177}Lu и ^{176}Yb in the gradient mode of the eluent with a pH of 4.5 was carried out.

A technology for the production of carrier free lutetium-177 radionuclide, with high radionuclide and chemical purity has been developed.



TECHNETIUM PENTACARBONYL HYDRIDE

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Technetium pentacarbonyl hydride, $[\text{H}^{99}\text{Tc}(\text{CO})_5]$, was discovered in 1962 and characterized only by IR-spectroscopy.¹ Recently we prepared $[\text{H}^{99}\text{Tc}(\text{CO})_5]$ in trace amounts during hydrolysis of $[\text{H}^{99}\text{Tc}(\text{CO})_6]^+$.² In this study a new straightforward synthesis of $[\text{H}^{99}\text{Tc}(\text{CO})_5]$ by reduction of $[\text{H}^{99}\text{TcBr}(\text{CO})_5]$ with NaBH_4 in presence of water and simultaneous extraction of the product in toluene was developed. Yield is 88.2%. IR (ν , cm^{-1} , toluene): 2021.3 (s, $\nu(\text{C}\equiv\text{O})$), 682.8 (w, $\delta(\text{Tc}-\text{H})$). NMR (toluene- d^8 , δ , ppm): ^1H : -5.50 ; ^{99}Tc : -2501.83. EI mass spectrum M^+ , m/z : calculated 239.97 measured 239.9.

Reactivity of $[\text{H}^{99}\text{Tc}(\text{CO})_5]$ were studied. We found that in presence of water neat $[\text{H}^{99}\text{Tc}(\text{CO})_5]$ is rapidly transformed into the trinuclear complex $[\text{H}^{99}\text{Tc}_3\text{H}(\text{CO})_{14}]$, whereas in solution the complex is significantly more stable. $[\text{H}^{99}\text{Tc}(\text{CO})_5]$ exhibits weak hydridic properties: it reacts only with strong acids such as F_3CCOOH and HClO_4 to give $[\text{H}^{99}\text{Tc}(\text{F}_3\text{CCOO})(\text{CO})_5]$ and $[\text{H}^{99}\text{Tc}(\text{ClO}_4)(\text{CO})_5]$ respectively, but does not react with HCOOH . It is readily oxidized with I_2 and atmospheric oxygen on heating to form $[\text{H}^{99}\text{TcI}(\text{CO})_5]$ and $^{99}\text{Tc}_2(\text{CO})_{10}$, respectively. In an inert atmosphere $[\text{H}^{99}\text{Tc}(\text{CO})_5]$ is resistant to substitution of its carbonyl groups but in presence of oxygen it reacts with nitrogen-containing heterocycles (2,2'-bipyridine and 1,10-phenanthroline) with formation of unusual technetium carbonyl complexes, $[(\mu_3-\text{CO}_3)(^{99}\text{Tc}(\text{bipy})(\text{CO})_3)_3]^{99}\text{TcO}_4$ and $[\text{H}^{99}\text{Tc}(\text{phen})_2(\text{CO})_2]^{99}\text{TcO}_4$.

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METHOD OF GAMMA SPECTROMETRY FOR PLUTONIUM CONCENTRATION DETERMINING IN THE FLUORIDE MELTS BASED ON LiF-NaF-KF

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The characteristics of the molten salt reactor-burner of minor actinides significantly depend on the physicochemical properties of the fuel composition, in particular, on the concentration of actinides in the salt solvent. The fluoride salt based on LiF–NaF–KF is considered as a candidate salt solvent¹. The purpose of this study is to investigate a possibility of plutonium concentration determination in the fluoride melts by gamma spectrometry method.

The determination of the mass of plutonium in solidified melt samples weighing 10...20 mg was carried out by recording background radiation of ²³⁹Pu using a laboratory gamma spectrometer with a coaxial detector made of high-purity germanium. Concentrations of plutonium fluoride in melt samples were 5% mol., 10% mol., and 15% mol.

The data were processed out using the calculated analytical dependence of the gamma quantum yield from a melt sample in the form of a ball with a radiation source evenly distributed over its volume, taking into account attenuation due to photoabsorption and incoherent scattering of photons. Gamma-ray quanta of eight energies (129, 203, 332, 345, 375, 414, 423, 451 keV) were considered. For these energies the constants of the interaction of photons with melt components were used from the EPDL library². According to the measurement results minimal attenuation is observed for gamma quanta with energies of 375 and 414 keV.

The using of the entire set of gamma-ray background radiation ²³⁹Pu energies in the processing of measurement results and the consistency of the results obtained for them provided an increase in the reliability and accuracy of determining the mass of plutonium in melt samples. The error of the plutonium fluoride concentration measurement does not exceed 8% in the range of up to 15% mol.

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METHODS OF SEPARATION AND DETERMINATION OF THE CONCENTRATION OF ACTINIDES, FISSION PRODUCTS AND CORROSION PRODUCTS IN FLUORIDE MELTS BASED ON LiF-NaF-KF

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As part of the study of the physico-chemical properties of the fuel compositions of the the molten salt reactor-burner of minor actinides based on fluoride salt LiF-NaF-KF as a candidate fluoride salt¹, it is necessary to determine their chemical composition, including the concentration of actinides, fission products and corrosion products.

Laboratory studies of the method for determining fuel compositions were carried out on systems simulating target ones, the main components of which were plutonium, uranium, neodymium and nickel fluorides as simulators of actinide fluorides, fission products and corrosion products.

Analytical control of uranium in melt samples was carried out by atomic emission spectrometry with inductively coupled plasma (ICP-AES). Uranium and plutonium were preliminary separated by ion exchange and extraction chromatography methods on a resin system (SPS-SBA(4)-150)-UTEVA in a nitric acid medium with a concentration of 7.2 mol/l.

Analytical control of neodymium and nickel in melt samples was carried out by the ICP-AES method with preliminary separation of uranium and plutonium by ion exchange and extraction chromatography on the resin system (SPS-SBA)-UTEVA. In the process of the neodymium and nickel determination concomitant americium was separated using extraction chromatographic resins TEVA² and TRU in a nitric acid medium with a concentration of 4 mol/l and 2 mol/l, respectively.

Analytical control of plutonium was carried out by alpha spectrometry after selective separation of plutonium from americium and uranium (if available) by ion exchange chromatography method using anion exchange resin SPS-SBA(4)-150 with the addition of a radioisotope indicator ²⁴²Pu and stabilization of the valence state of plutonium.

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THE FEATURES OF Cs(I) AND Sr(II) SORPTION ONTO SOILS

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^{137}Cs and ^{90}Sr are one of the main fission products that can enter the environment, soil and water as a result of nuclear accidents or leaks from radioactive waste storage facilities. These isotopes have relatively short half-life (30.1 and 28.9 years), can accumulate in soil and be transported through the food chain. However, long-lived ^{135}Cs (a component of spent nuclear fuel) may also become important with time.

The mobility of radionuclides in soils depends on various parameters, such as mineral composition, chemical properties of soils, acid-base conditions presence of organic matter and other. The method of sequential removal of organic matter and non-silicate iron compounds from the soil before the sorption experiment was applied to understand the interaction mechanisms with individual soil components. The investigation results of sorption regularities and the strength of Cs(I) and Sr(II) fixation by various soil horizons are presented in the work.

Experiments were carried out on 4 horizons of peaty-podzolic-gleyic and 4 horizons of floodplain soddy-gleyic soils from the Central Forest State Natural Biosphere Reserve (Nelidovsky district of the Tver region). The sorption experiments were performed by 2 scenarios – with 100 g/L soil suspensions in 0.01 M NaClO_4 at room temperature, and 1.7g/L of soil in distilled water at a constant temperature of 8 °C to simulate incubation conditions. To evaluate the strength of Cs(I) and Sr(II) binding the sequential extraction were carried out according to the Tessier procedure.

It was shown, that peaty-podzolic-gleyic soils effectively sorb Cs(I). The experiments with a Cs(I) concentration of 10^{-6} M and trace concentrations showed similar sorption regularities for the samples from different soil horizons. Based on results of sequential extraction we can suggest that Cs(I) sorbed on the functional groups of organic matter is fixed less strongly than Cs(I) attached to the specific sites of illites and vermiculites. The strength of Cs(I) fixation is affected by the type of sorption site and the time of interaction. Contrary to Cs(I), Sr(II) sorbes unquantitatively on studied soils, and sorption reduces with organic matter removal. The sorption of Sr(II) varies strongly with pH. The results of sequential extraction revealed that Sr(II) binds tightly with soils, but the strength of the binding increases when the organic matter is removed.

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INVESTIGATING THE PROPERTIES OF LOW-MELTING BOROSILICATE GLASSES FOR A SMALL-SIZED MELTER DESIGNED BY MAYAK

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Approximately in 2028 Mayak is planning to launch a new vitrification complex that is capable of solidifying LRW of any composition.

The developed concept of the new vitrification complex suggests using a removable small-sized direct electric heating borosilicate-glass melter designed by Mayak. This work is aimed to develop a low-melting composition of borosilicate glass that will allow incorporating an acceptable degree of high level waste. The glass composition should meet the requirements¹, and an operating drain temperature (viscosity range) should be from 1000 to 1150 °C.

This temperature range is determined by stability of structural materials of the melter (for example, melting point of the electrode and the drain pipe materials is 1200 °C).

Designing an experiment using a simplex method² is one of the most effective techniques, which for a relatively small number of experiments allows obtaining a mathematical model in the form of a so-called reduced polynomial reflecting the dependence of the studied property of the mixture on its components content.

To solve this problem, the fourth-order simplex lattice design is used to further obtain a polynomial reflecting dependence of the studied property of the mixture on the content of its components.

Using mathematical models the authors have designed domains presenting dependence of characteristics of melted borosilicate glasses on their composition and have transferred them to the simplex.

The authors have determined areas of borosilicate glass compositions that comply with the requirements¹ and ensure the operability of the removable small melter designed by Mayak.

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COMPARATIVE ANALYSIS OF THERMAL CONSOLIDATION METHODS OF NaY FAUJASITE ZEOLITE FOR IMMOBILIZATION OF ^{137}Cs RADIONUCLIDES

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To solve the problem of long-term immobilization of high-energy ^{137}Cs radionuclides, it is optimal to use zeolite of the NaY Faujasite structural type as a material for ceramic matrix compounds. The global scientific community has proposed various methods for the consolidation of ceramic materials of this kind: cold pressing-sintering (CPS), hot pressing (HP), microwave sintering (MS) and spark plasma sintering (SPS). As part of this work, a comparative analysis of the parameters of hydrolytic stability, physical and mechanical properties, as well as the crystalline parameters of ceramic matrices based on NaY zeolite, sintered by various methods was performed (Table 1). Overall data obtained indicates the optimality of the spark plasma sintering process.

Table 1. Comparative analysis of various methods of consolidation of ceramic matrices for the immobilization of cesium radionuclides

Consolidation method	Sintering time	T, °C	ρ , g/cm ³	Leaching rate R(Cs ⁺), g/cm ² ·day	Microhardness, HV
CPS	1 h	1000	2.6594	$1.8 \cdot 10^{-6}$	479
	3 h	1000	2.6559	—	380
	5 h	1000	2.7129	—	389
MW	30 min	1000	1.5189	—	294
	1 hour	1000	2.6488	$1.6 \cdot 10^{-6}$	385
HP	5 min	1000	2.0198	$2.1 \cdot 10^{-6}$	587
SPS	5 min	1000	2.7210	$2.3 \cdot 10^{-8}$	619

The work was carried out within the framework of the state assignment of the Ministry of Science and Higher Education No.FZNS-2023–0003, the topic “Fundamentals of chemical engineering of new functional materials adaptive for nuclear and radiation technologies”.



MECHANISMS OF NEPTUNIUM SORPTION ONTO PEATY-PODZOLIC-GLEYIC AND FLOODPLAIN SODDY-GLEYIC SOIL

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Commercial nuclear reactor operation poses a problem regarding highly radioactive waste, of which ^{237}Np is an important component due to it being a long-lived alpha-emitter, with activity only growing overtime as a result of ^{241}Am decay. Because Np is a dangerous pollutant most likely to be present in aerobic conditions in a highly mobile form (NpO_2^+), its interaction with environmental objects, such as soils, is of interest for understanding and modeling possible migration. The purpose of this work was to identify mechanisms of neptunium sorption onto soil horizons with different properties.

Np(V) interaction with soil horizons was studied in two variations: “sorption” and “incubation”. “Sorption” aimed to obtain regularities of Np fixation with time in solutions differing in pH values (1–8) and ionic strength (0.01–0.5M). The objective of “incubation” was to study sorption in conditions resembling natural ones (8 °C, wetting and drying alternating in two-week cycles for the duration of 3 months). Information on Np speciation in the samples was obtained by X-ray absorption spectroscopy and sequential extraction following modified Tessier¹ procedure.

Soil horizons studied in this work are classified as peaty-podzolic-gleyic (PPG: H, ELih, ELg, ELBcn, IIBGg) and floodplain soddy-gleyic (FSG: O, AY, Bg, BDg) soils². It was established that on the two lowest horizons of both PPG and FSG Np sorbs in a similar pattern: sorption is pH-dependent, growing with increasing pH, steady-state is reached within a week. This is consistent with Np(V) forming inner-sphere complexes with illite and iron (hydro)oxide minerals, which are more prevalent in the lower horizons. Sorption profiles for ELg and AY horizons also show pH-dependence, but with slower kinetics and to a lesser extent, maximum 50–70% sorption reached gradually within a month. Upper soil horizons (H, O, ELih) are similar to each other in the sense that their high organic matter content dictates higher sorption values (up to 100%) in less than a week with almost no pH-dependence present. For these horizons Np(V) reduction to Np(IV) was confirmed by XANES and sequential extraction results.

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CONTROL OF Cs-137 REMOVAL IN WATERS OF MONITORING WELLS OF RADIOACTIVE WASTE STORAGE AND BURIAL SITES

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The safety of radioactive waste storage and burial sites is a critical measure for the sustainable development of regions and the prevention of radionuclide intrusion into natural bodies of water and groundwater. For ensuring environmental and radiation safety it is necessary to control the removal of artificial radionuclides into underground aquifers from the territories of radioactive waste storage and burial sites. Therefore, samples of sewage, surface and groundwater are taken on the territories, in sanitary protection zones and surveillance zones of such facilities. In order to control Cs-137 in radioactive waste burial sites, regulatory documents set the detection limit of 0.001 Bq/l. To ensure the required detection limit it is necessary to develop express highly sensitive methods of radionuclide determination.

A variant method for detection of Cs-137 in natural and waste waters based on concentration of the radionuclide by selective ferrocyanide sorbents under dynamic conditions and subsequent measurement of the concentrate by gamma-spectrometry is proposed. The developed method of detection allows achieving the required detection limit of 0.001 Bq/L. The influence of the sorbent type on the conditions of Cs-137 concentration from aqueous samples and the registration efficiency of the concentrate is shown.

The content of Cs-137 in samples of natural waters and waters of the monitoring wells of radioactive waste storage and burial sites was detected using the developed method. In all surface water samples the Cs-137 concentration did not exceed the established intervention level for drinking water¹, and in the waters of monitoring wells – the required standards.

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DETERMINATION OF IMPURITY ELEMENTS IN URANIUM-CONTAINING MATERIALS

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Quality control of uranium-containing materials involves the determination of the content of impurity elements. Currently, it is promising to use a highly sensitive inductively coupled plasma mass spectrometry method for these purposes.

Uranium has an overwhelming effect on the analytical signals of the elements being determined during the measurement process. In this regard, preliminary separation of uranium from impurities is necessary. The method of solid-phase extraction chromatography has a number of advantages: high selectivity, high productivity and simplicity of hardware design.

It was of interest to compare the sorption characteristics in relation to uranium of foreign and Russian sorbents: UTEVA (USA)¹ and TVEX-TBP (JSC GP Smoly, Moscow)². The study showed that both resins, within the limits of their sorption-capacitance characteristics, meet the requirements for the separation of impurities for subsequent measurement by inductively coupled plasma mass spectrometry. However, the capacity and equilibrium time for UTEVA resin are twice as high as for TVEX-TBP.

Taking into account the work done, optimal conditions for the chromatographic separation of uranium and impurities on a column using UTEVA resin were selected. As a result, the method of measuring the mass fraction of 23 impurity elements in uranium-containing materials by inductively coupled plasma mass spectrometry was certified. The measured mass fractions for most of impurity elements ranged from 0.0001% to 0.1000%, and the total error of determination does not exceed 30% relative to the lower limit of the range. The obtained accuracy indicators of the technique meet the existing requirements for quality control of uranium-containing materials.

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SENSORY METHODS FOR CONTROL DURING THE PRODUCTION OF RADIOPHARMACEUTICAL YTTRIUM-90

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The high potential of radiopharmaceuticals based on ^{90}Y is due to its unique properties. The high energy of beta particles makes it suitable for irradiating large tumors, and the tendency to form complex compounds allows one to obtain a wide range of radiopharmaceuticals.¹ In the generator we are creating, the parent radionuclide ^{90}Sr is part of the solid matrix and is firmly held there (Fig. 1). The daughter ^{90}Y is washed off from the matrix with an alkali metal carbonate solution and sent for yttrium separation into a cell with a yttrium-selective membrane. On the opposite side of the membrane, ^{90}Y is concentrated.

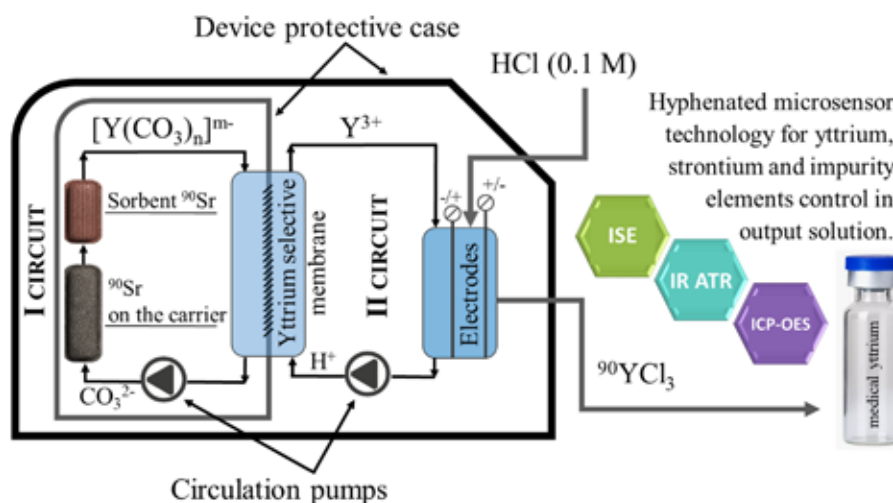


Figure 1. Yttrium-90 generator circuit with potentiometric and optical detection

In the second circuit of the generator, there is an electrochemical cell in which additional purification of ^{90}Y is carried out to obtain high-purity $^{90}\text{YCl}_3$ without a carrier. Control of the purity of the output product is one of the most important points and can be carried out using developed chemical sensors.²⁻³

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SEPARATION OF Ti-44 AND Sc-44 BY EXTRACTION AND EXTRACTION CHROMATOGRAPHY METHODS

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The theranostic approach in nuclear medicine involves the simultaneous use of radiopharmaceuticals for diagnosis and therapy. Scandium radionuclides are promising for theranostics because their isotopes have both diagnostic (^{43,44}Sc) and therapeutic potential (⁴⁷Sc).

The radionuclide ⁴⁴Sc (T_{1/2} = 4.0 h) can be produced from ⁴⁴Ti (60 yrs) via generator method. The long half-life of the parent ⁴⁴Ti implies its reuse. The ⁴⁴Ti/⁴⁴Sc generators developed on the basis of ion exchange (DOWEX 1x8¹) and extraction chromatographic resins (TEVA resin^{2,3}, Zr resin⁴) are designed according to the “direct” scheme, in which the parent radionuclide is retained on the sorbent and the daughter radionuclide is eluted. Following this approach, the subsequent regeneration of ⁴⁴Ti and the determination of the optimum generator lifetime are questionable.

The aim of this work is to develop generator schemes taking into account the reusability of ⁴⁴Ti. At the first stage, the separation of ⁴⁴Ti and ⁴⁴Sc by liquid-liquid extraction and extraction chromatography was studied. Data were obtained on the extraction of these radionuclides from HCl and HNO₃ solutions of different concentrations using the extractant Aliquat 336 (methyltriethylammonium chloride), organophosphorus compounds HDEHP (di(2-ethylhexyl)phosphoric acid), TBP (tributyl phosphate) and TOPO (tri-n-octylphosphine oxide). A comparative separation of ⁴⁴Ti and ⁴⁴Sc was performed on TEVA resin and LN resin, since the resins include Aliquat 336 and HDEHP as an extractant.

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SYNTHESIS OF NEW COMPOSITE MATERIALS BASED ON AMIDOXIMES FOR EXTRACTION OF NATURAL AND ANTHROPOGENIC RADIONUCLIDES FROM LIQUID MEDIA OF COMPLEX COMPOSITION

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Sorption materials with grafted amidoxime functional groups are currently a promising class of adsorbents used for selective removal of heavy metal ions from liquid mono- and multicomponent media. The efficiency of these sorbents largely depends on the choice of support matrix on which functional groups are immobilised. At the same time, the chemical composition and structural features of the matrix can significantly affect the sorption-selective characteristics and physicochemical properties of the sorbents as a whole.

In order to extract and concentrate radionuclides (U, Th, Ra, Pb, etc.) from liquid media of complex composition, a series of composite materials based on pure 4-aminofurazan-3-carboxamidoxime (43AF) and its Se-derivative (Se-43AF) were prepared. By polycondensation reaction of 43AF and SeO_2 , in the presence of matrix (silica gel, chitosan, cellulose, spherically granulated ionites), the composites were obtained, characterised by increased selectivity to radionuclides in low and highly mineralised solutions (up to 40 g/l) in a wide pH range. A comprehensive study of the dependence of radionuclide sorption efficiency on the peculiarities of amidoxime radical binding to the matrix has shown that: at ^{238}U extraction by composites on the basis of Se-43AF and silica gel/ionites the K_d values at pH 6–9 are 10^4 – 10^6 cm³/g (SEC= 600–800 mg/g); at ^{232}Th extraction by composites based on pure 43AF and cellulose/chitosan – K_d at pH 3–5 is 10^5 – 10^8 cm³/g (SEC=500–900 mg/g); at ^{99}Tc , Ba (Ra) extraction by composites based on Se-43AF and anionite, K_d values at pH 3–5 are $\geq 10^4$ cm³/g ($V/m=1000$).

The obtained results testify to the prospectivity of the obtained materials, which can be further recommended for use in the processes of extraction of radionuclides of different types, both for radioecological needs, tasks of purification of LRW, mine and ground waters, and for extraction of radionuclides as valuable components of raw materials.

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SORPTION OF CESIUM AND STRONTIUM ON BENTONITE CLAYS OF VARIOUS DEPOSITS

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To ensure safety of high-level radioactive waste (HLW) for hundreds of thousands of years it is necessary to create protective engineering barrier systems. As one of the barrier materials it is supposed to use bentonite clays having low water permeability and high sorption capacity towards a number of radionuclides. Isotopes Cs^+ and Sr^{2+} are fission products of uranium fuel and need to be investigated due to their high mobility in the environment and biotoxicity. For long-term safety justification of the HLW disposal site it is necessary to perform mathematical description of the sorption processes taking into account the peculiarities of the environment, implemented in geomigration models.

In this work we studied the interaction of Cs^+ and Sr^{2+} with clay minerals, as well as the factors affecting sorption: their concentration, mineral composition of samples and solution composition after contact. Experiments were carried out on clay samples from Russian and near abroad deposits (e.g. 10 Khutor, Dinosavrovoye, Zyryanskoye deposits), as well as well-known world deposits (MX-80, FEBEX, Kunipia-F). The obtained results formed the basis of thermodynamic modelling carried out with the help of computer codes PHREEQC¹ and MOUSE².

Both cesium and strontium are characterized by interaction with clay minerals by ion exchange mechanism. In addition, for strontium, interaction by the mechanism of complexation in alkaline media is possible. The data on sorption isotherms make it possible to calculate the number of sorption sites for each clay sample depending on its mineral composition.

The sorption data obtained in the experimental work were described using different approaches using both literature sorption constants and their optimization. Using a large set of experimental data, it is possible to determine the model that most adequately describes the processes taking place. The selected and optimized model for describing the sorption of Cs^+ and Sr^{2+} , can be further implemented in geomigration models.

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DETERMINATION OF OPTIMAL PARAMETERS FOR SEPARATION OF LUTETIUM-177 AND YTTERBIUM BY CHROMATOGRAPHIC METHOD

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Radiopharmaceuticals based on the ^{177}Lu isotope are widely used in nuclear medicine as a part of drugs for targeted therapy of neuroendocrine tumors¹, prostate tumors² and bone metastases³. One of the ways to obtain ^{177}Lu without a carrier is to irradiate an ytterbium target enriched in ^{176}Yb with a neutron flux. ^{177}Lu is isolated from the ytterbium target by chromatography. For the most complete isolation of lutetium-177 from an ytterbium target, it is necessary to determine the optimal parameters of the separation process.

To determine the optimal parameters for the separation of ^{177}Lu and ytterbium the distribution coefficients between the eluent and the ion exchange resin were determined for the Dowex 50WX8 system (200–400 mesh) in the NH_4^+ form – a-HIBA – H_2O . Distribution coefficients were also determined for the following systems: Dowex 50WX8 (200–400 mesh) in H^+ form – HCl – H_2O ; Dowex 50WX8 (200–400 mesh) in NH_4^+ form – HCl – H_2O .

To determine the distribution coefficients, radioactive indicators ^{177}Lu and ^{169}Yb , obtained by irradiating the corresponding oxides in the channel of the IRT-T nuclear reactor, were used. Distribution coefficients were determined by static and column methods. Under static conditions, the phases were mixed for 24 hours to establish equilibrium, and under the column method, until the concentrations of the initial solution and eluate were equal. The column method was used to determine low distribution coefficients.

An aliquot of each selected fraction (from the static or column method) was measured on a Canberra HPGe spectrometer with a GC2018 detector.

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DEVELOPMENT OF SHORT-LIVED ALPHA-EMITTER ^{226}Th GENERATOR FOR TREATMENT OF EPITHELIAL AND EASILY ACCESSIBLE TUMORS

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A new and rapidly developing field of nuclear medicine, targeted alpha therapy, is effective in the treatment of various types of cancer due to the unique property of alpha particles, which release a large amount of energy in a limited area of biological tissue. One of the promising radionuclides for this type of therapy is ^{226}Th ($T_{1/2} = 30.6$ min). Its nuclear properties are similar to ^{213}Bi , which is now widely studied for clinical use. ^{226}Th can be conveniently produced via a $^{230}\text{U}/^{226}\text{Th}$ generator. In turn, ^{230}U is separated from its parent ^{230}Pa , which is generated by irradiating natural thorium with protons.

To quickly obtain neutral eluate of ^{226}Th in citrate buffer, we developed an original generator system consisting of two consecutive chromatographic columns. In the first column, filled with TEVA resin (Triskem), the parent ^{230}U is fixed, while ^{226}Th is eluted with a 7M HCl solution and immediately adsorbed on the second column containing DGA or UTEVA resin (both from Triskem). ^{226}Th can be desorbed from the second column using a dilute citrate buffer solution. The entire milking process takes 5–7 minutes, with a yield of more than 90% of ^{226}Th in 1.5 mL of eluate (pH 4.5–5.0), which is suitable for direct use in radiopharmaceutical synthesis. The impurity level of ^{230}U is less than 0.01%. The proposed $^{230}\text{U}/^{226}\text{Th}$ generator has been tested for two months, including a second loading of ^{230}U additionally separated from ^{230}Pa .¹

The resulting ^{226}Th solution can be directly used in synthesis of radioimmunoconjugates for the therapy of epithelial and easily accessible tumors; we focused on Th-DTPA(DOTA)-Nimotuzumab, which is specific to EGFR-overexpressing carcinoma cells. We have developed a labeling procedure using the longer-lived ^{234}Th isotope, with a labeling yield of 45–50%. The effectiveness of these conjugates against epidermoid carcinoma cells, A431, has been demonstrated.²

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CHEMICAL RESISTANCE OF METAL PHASE SIMULANTS PRESENT IN IRRADIATED NUCLEAR FUEL TOWARDS OXIDATION IN AIR AND NITRIC ACID

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During nuclear reactor campaign a considerable amount of platinum group metals (PGMs) is produced. PGMs usually form independent metallic phases, also known as “white inclusions”. Five-component Mo-Tc-Ru-Rh-Pd alloy, known as ϵ -phase, is formed in oxide fuels, while intermetallic species $U(PGM)_3$ are discovered in nitride spent nuclear fuel (SNF). It is known that these SNF components are responsible for the precipitates formation during SNF dissolution process and can contain fissile materials.

The following aims were considered during this work: (1) synthesis of the simulants of ϵ -phase and $U(PGM)_3$ series, (2) research of their oxidation behavior in air in the range from 40 °C to 1500 °C, (3) research of their dissolution in 8M nitric acid, (4) surface investigation after electrochemical etching in nitric acid.

ϵ -phase and $U(PGM)_3$ simulants were prepared by arc-melting of mixtures of metals and following annealing under vacuum conditions in quartz ampoules with zirconium getter at 1000 °C for 96 hours. Two samples of ϵ -phase – $Mo_{0.2}Re_{0.1}Ru_{0.6}Rh_{0.05}Pd_{0.05}$, $Mo_{0.2}Tc_{0.05}Re_{0.05}Ru_{0.6}Rh_{0.05}Pd_{0.05}$ and four samples of $U(PGM)_3$ – $U(Ru_{0.66}Rh_{0.17}Pd_{0.17})_3$, $U(Ru_{0.17}Rh_{0.66}Pd_{0.17})_3$, $U(Ru_{0.17}Rh_{0.17}Pd_{0.66})_3$ and $U(Ru_{0.33}Rh_{0.33}Pd_{0.33})_3$ were prepared. All samples were characterized with powder X-ray diffraction (PXRD) and scanning electron microscopy (SEM) with micro energy dispersive X-ray spectroscopy (EDS).

To investigate oxidation behavior of alloys differential scanning calorimetry with thermal gravimetry (TG-DSC) in airflow was applied. The heating was conducted from 40 °C to 1500 °C with heating rate of 5 °C/min. To determine the intermediate oxidation products PXRD with in situ heating from room temperature to 1200 °C was applied to Tc-absent ϵ -phase and $U(Ru_{0.33}Rh_{0.33}Pd_{0.33})_3$.

Leaching of “white inclusions” in 8M nitric acid at 95 °C was conducted for several days. Probes were taken at least two times per day, the taken probe volume was replaced with fresh acid. Probe compositions were analyzed with inductively coupled plasma mass-spectrometry and liquid scintillation count (for Tc).

Electrochemical etching was conducted in two stages. On the first stage corrosion potentials in 8M nitric acid were determined, afterwards surface polishing and SEM was done. On the second stage samples were held in acid under determined corrosion potentials for one hour, followed by SEM-EDS of etched surface.



INFLUENCE OF Fe (II) ON Se (IV) IMMOBILIZATION IN NATURAL CLAY MATERIALS

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Mobile anionic forms of long-lived radionuclides are one of the actual issues for the burial of radioactive waste (RW) in deep geological formations. The challenge of immobilizing ^{79}Se with half-life of 3.27×10^5 years is associated with the high mobility of SeO_3^{2-} and SeO_4^{2-} anions in aqueous environments. Construction of clay based engineered barriers for the immobilization of the radionuclides is a common approach. Clays are effective sorbents for cationic forms of various radionuclides however they have a low sorption selectivity for anionic forms of radionuclides.

Identification of natural clay materials suitable for the effective immobilization of anionic selenium forms from aqueous solutions and estimation the role of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio in Se sorption on clays were purposes of this research.

Natural clays of various mineral compositions from the 10th Khutor, Zyryanskoe, Dash-Salakhly, Kornilovskoe, Saraibashskoe, and Biklyanskoe deposits were studied. A correlation between the sorption properties of clays towards SeO_3^{2-} and their composition were revealed. It was shown that the ratio of iron oxidation states affects selenium immobilization¹, thus the content of Fe^{2+} and Fe^{3+} in all the clay samples were studied by acid decomposition. In the presence of $\text{Fe}^{II}\text{SO}_4$, the sorption of Se(IV) exceeds 80% on all studied clay samples.

Biklyanskaya clay had shown the highest sorption ability (80%) towards Se(IV) out of all the studied clays. Therefore, Biklyanskaya clay can be used as part of the barrier material to reduce the Se(IV) migration.

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FEATURES OF THE C-14 AND Cl-36 LEACHING PROCESS FROM IRRADIATED GRAPHITE

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The degree of potential hazard of the bulk of graphite radioactive waste (~95%) is determined by the presence of predominantly long-lived radionuclides¹. The parameters characterizing the process of leaching of long-lived radionuclides from irradiated graphite are among the main ones for predictive assessments of the radiological hazard of burial of various types of graphite radioactive waste, which are in the form of whole parts, fragments and graphite chips.

The leaching process from graphite radioactive waste is characterized by a number of features that distinguish it from other types of waste. Unlike monolithic radioactive waste, for graphite the leaching process is determined by the pore system in the volume of graphite elements. The size of the graphite elements will determine the time of saturation of the pores and the delay time of the release of the radionuclide into the solution, determined by the rate of mass transfer of the leaching solution in the pores with the external volume of the aqueous medium. For the research, we used irradiated PUGR graphite (block – grade GR 220 and samples of crushed block graphite RBMK 1000 of Unit 2 of Leningrad NPP (grade GR 280), formed during the work to restore the resource characteristics of the masonry. The research results showed that the parameters characterizing the dynamics of the leaching process in within ~1.5 years for whole and crushed samples there are no significant differences in both C-14 and Cl-36. As the process of radionuclide transport from the depth of the sample reaches equilibrium, the intensity of leaching decreases by two orders of magnitude and the dynamics of the process has a slowly decreasing character. The contribution of the surface of open pores to the intensity of the leaching process will dominate compared to the contribution of the open surface of fragments and crumbs².

The results obtained indicate the possibility of burying irradiated graphite in the form of products (blocks, sleeves), their fragments and crumbs.

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SPECIATION OF ^{60}Co , ^{85}Sr , ^{137}Cs RADIONUCLIDES IN SPENT FUEL POOL MODEL SOLUTION

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Radionuclides come to media of spent fuel pool from fuel pin assembly surface and from the primary circuit media. During operation in spent fuel pool corrosion products are accumulated, which sorb part of the radionuclides. These contaminants hinder the operation of the spent fuel pool and noticeable complicate its decommissioning.

The spent fuel pool cleaning solutions used are typically based on ion exchange and microfiltration methods. At the same time, a number of radionuclides in the spent fuel pool media are in a non-ionic state and are not associated with large suspended particles, which lead to a relatively low degree of purification of the media. Determination of radionuclides speciation in the spent fuel pool media makes it possible to increase the efficiency of its purification.

Speciation of ^{60}Co , ^{85}Sr , ^{137}Cs radionuclides were investigated the ultrafiltration method in model solutions of spent fuel pool containing boric acid concentration 20 g/L and Fe(III) concentration 1 mg/L at different pH values. Ultrafiltration experiments were carried out in ultrafiltration cell Millipore 8200 with different membranes from regenerated cellulose Millipore Ultracel at 3 bar pressure.

Was demonstrated that retention of ^{60}Co hydrolysis particles does not depend on membrane molecular weight cutoff. At the same time retention of ^{60}Co in weakly acidic pH area decrease with increasing membrane molecular weight cutoff. Retention of ^{137}Cs , ^{85}Sr in pH range 4–11 weakly depend on membrane molecular weight cutoff which probably indicates the formation of pseudocolloidal particles in an aqueous solution of boric acid.

Fe(III) retention in the pH range 7–10 on a membrane with a molecular weight cutoff of 10 kDa is reduced compared to membranes with a lower molecular weight cutoff, which is likely due to the formation of Fe(III) polyborate complexes, the molecular weight of which is more than 5 kDa.

NICKEL RADIONUCLIDE SPECIATION IN HIGH-SALINITY SPENT DECONTAMINATION SOLUTIONS

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Nickel is one of the main components of corrosion-resistant alloys used in nuclear industry, including materials for the core and primary circuit of nuclear power plants. As a result of stable nickel isotopes activation of, long-lived radionuclides ^{59}Ni and ^{63}Ni are formed, which are transported through technological systems and form deposits on equipment surfaces. The radioactive waste generated during the decontamination of equipment elements is characterized by long periods of danger, largely due to the presence of nickel radionuclides.

In this work, by ultrafiltration and centrifugation methods, we determined the conditions of formation and the boundaries of existence of ionic and nonionic forms of $^{63}\text{Ni(II)}$ radionuclides in high-salinity solutions of NO_3^- , NH_4^+ , SO_4^{2-} , as well as in the spent electroplasma decontamination electrolyte, in the presence of Fe (III) in the pH range 4–9.

It was shown that the retention of $^{63}\text{Ni(II)}$ by the ultrafiltration membrane is 10–40% depending on the medium, with the maximum retention corresponding to pH 7–8, and at pH 9 a decrease in retention is observed. In the presence of Fe(III) in the electrolyte solution, the radionuclide retention increases to 90% at pH 8 and decreases to 60% at pH 9. The observed effects are associated with the simultaneous presence of both ionic and nonionic forms of ^{63}Ni in the solution, as well as the formation of mixed complexes Fe(III)-Ni(II)/

The revealed patterns of behavior of nickel radionuclides can be used to improve the efficiency of methods for purifying liquid radioactive waste generated during electroplasma decontamination of metal parts at nuclear and radiation facilities.

^{137}Cs , ^{85}Sr , AND ^{60}Co SORPTION KINETICS ON MODIFIED OIL SHALE SORBENTS FROM LRW MODEL SOLUTIONS

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A huge amount of liquid radioactive waste (LRW) is the result of nuclear facility functioning. In particular, ^{137}Cs , ^{90}Sr , and ^{60}Co make a significant contribution to the specific activity of NPP LRW. Sorption is a well-studied and widely used process for the low-salt LRW purification. The Republic of Belarus has reserves of natural materials that can be used as sorbents for cleaning LRW from radionuclides. The processing products of Lyuban and Turov oil shale may be promising sorbents. To assess the efficiency of sorption of radionuclides on sorbents, it is necessary to know how long it takes for sorption equilibrium to be established in the solution-sorbent system.

The time required for sufficient purification of model LRW of low activity ($\sim 10^5$ Bq/l) from cesium, strontium, and cobalt radionuclides was estimated based on changes in the sorption parameters of these radionuclides: sorption (S , %) and distribution coefficient (K_d , cm^3/g). The parameters were assessed at the following time points from the start of the experiment: 2, 5, 10, 20, 30, 40, 50 minutes, 1, 2, 3, 4, 6 hours, and 1, 2, 7 days. The samples of oil shale without pretreatment (A) and with treatment with live steam while heated to 420°C (B) were used.

Based on the data obtained, it can be stated that for ^{137}Cs , ^{85}Sr , and ^{60}Co radionuclides, sorption equilibrium under experimental conditions is established within 2 days. However, it cannot be said that the values of sorption and distribution coefficient established in 1 day differ significantly from those in 2 days or even in 1 week. For example, for the purification of liquid radioactive waste from ^{60}Co with sorbent A, the sorption parameters are as follows: $S_{24\text{h}} = 71\%$ and $S_{1\text{w}} = 83\%$, $K_{d\ 24\text{h}} = 4,2 \cdot 10^3 \text{ cm}^3/\text{g}$ and $K_{d\ 1\text{w}} = 5,3 \cdot 10^3 \text{ cm}^3/\text{g}$, for sorbent B – $S_{24\text{h}} = 94\%$ and $S_{1\text{w}} = 97\%$, $K_{d\ 24\text{h}} = 2,0 \cdot 10^4 \text{ cm}^3/\text{g}$ and $K_{d\ 1\text{w}} = 3,4 \cdot 10^4 \text{ cm}^3/\text{g}$.

Thus, the duration of the experiment for the evaluation of the efficiency of sorption of radionuclides by sorbents based on modified oil shale, equal to 24 hours, allows the experiment to be carried out without loss of efficiency of liquid radioactive waste treatment.

APPLICATION OF VERMICULITE AND ZEOLITE ADDITIVES TO IMPROVE THE SORPTION PROPERTIES OF BENTONITE CLAY

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Long term safe disposal of radioactive waste is achieved by creating a multi-barrier approach.¹ Clays with good waterproof properties and high sorption capacity can be used in a construction of protective barriers. Clays containing montmorillonite are considered to be the most promising materials for this purpose.² In this study the sorption capacity towards Sr-90 and Np-237 by bentonite clay of the Saraybashskoe deposit was investigated.

The strontium sorption degree on the studied clay was sufficiently high – 85–90%, which corresponds to $(1,5-3) \cdot 10^2 \text{ cm}^3/\text{g}$ of distribution coefficient values. At the same time significant part of sorbed strontium was fixed in mobile (water-soluble and ion-exchange) forms. In order to increase the content of firmly fixed forms of Sr-90, the clay of the Saraybashskoe deposit with zeolite additive is proposed to be used.

Neptunium sorption on the studied clay was less effective than strontium and was equal to 50–60% and distribution coefficient value was $(2-3,5) \cdot 10 \text{ cm}^3/\text{g}$. As compared with Sr-90, the sorbed Np-237 had lower content of mobile forms. However, the content of firmly fixed forms on the clay wasn't sufficient as well. The efficient sorption capacity and high retention can be achieved by using the clay of the Saraybashskoe deposit with zeolite and vermiculite additives.

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RETROSPECTIVE ESTIMATION OF THE POTENTIAL MOBILITY OF ARTIFICIAL RADIONUCLIDES (^{60}Co , ^{137}Cs , ^{152}Eu , ^{154}Eu , ^{241}Am , ^{238}Pu , $^{239,240}\text{Pu}$) IN BOTTOM SEDIMENTS OF THE YENISEI RIVER (SIBERIA, RUSSIA)

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The transformation of physicochemical forms of artificial radionuclides in bottom sediments (BS) of the Yenisei River 2–13 years after the shutdown of last nuclear reactor at the Krasnoyarsk Mining-and-Chemical Combine (MCC) was studied. Artificial radionuclides ^{60}Co , ^{137}Cs , ^{152}Eu , ^{154}Eu , ^{155}Eu , ^{241}Am , ^{238}Pu , and $^{239,240}\text{Pu}$ were recorded in samples of BS collected in the Yenisei River in 2012–2023. The potential mobility of radionuclides was estimated by sequential extraction of the radionuclides from samples of BS, as a result of which six fractions were obtained (exchangeable, carbonate, Fe and Mn oxides, organic, amorphous-silicate, mineral residue). A significant percentage of ^{60}Co (34–100%) and ^{137}Cs (72–97%), which continue to flow into the Yenisei with controlled radioactive discharges, was irreversibly associated with the mineral residue of BS. The ratio of relatively mobile forms of cobalt in BS varied significantly over the studied time-span. Controlled releases of europium into the Yenisei ceased after 2013, however low percentage of europium was present in the irreversibly bound form (5–27% for ^{152}Eu) in samples of BS, and various mobile forms of europium were recorded. Noticeable part of ^{152}Eu (up to 15.5%) was registered in the most mobile – exchange form. The forms of ^{154}Eu and ^{152}Eu were different, which can be explained by the different origins of these isotopes. The largest proportion of plutonium (41–92%) was irreversibly associated with the mineral residue of BS. However, a significant increase in the proportion of plutonium associated with the organic matter of BS was registered when plutonium releases into the river increased. The relationships between content of minerals and radionuclides in BS has been estimated.

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**RUSSIAN-CHINESE SYMPOSIUM
ON SELECTIVE TECHNOLOGIES
FOR SEPARATION OF
SUBSTANCES WITH SIMILAR
PROPERTIES**

CARBON DOTS: TARGET-ORIENTED SYNTHESIS AND TAILOR-MADE FUNCTIONS

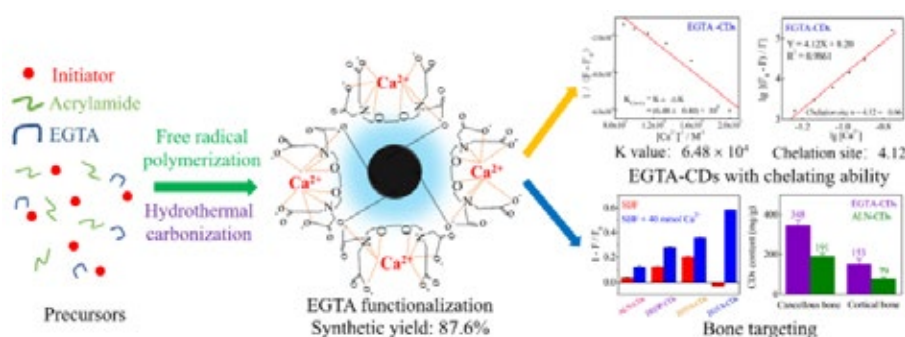
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Carbon dots hold metal ions sensitive fluorescent properties and biomedical applications¹. However, target-oriented synthesis of carbon dots with tailor-made functions are still the challenges. In this talk, carbon dots with high synthetic yield more than 85wt% was target-oriented synthesized via free radical polymerization in combination of hydrothermal carbonization². Various functional units including metal ions ligands, drug and chitosan were covalent linked on carbon dots. The metal ions affinity and nanozyme activity of ligand functionalized carbon dots and CDs-Metal was dominated by stability constant of ligand against to different metal ions³. Chitosan or drug derived carbon dots served as down-regulating ROS in living system for protection effect of oxidation stress⁴ and anti-senescence via dual pathway of anti-oxidative stress and mTOR⁵.



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MEMBRANE CHEMICAL EXCHANGE FOR SEPARATION OF LITHIUM AND LITHIUM ISOTOPES

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In the past decades, the global electric vehicle industry has undergone rapid development. Unexpected opportunities for the membrane separation to extract valuable resources, such as lithium, from challenging sources like Salt Lake brines, emerged and remained the great opportunity for researchers and engineers from both academia and industry. Despite significant advancements, the field remains divided between two distinct separation concepts: equilibrium separation based on affinity and non-equilibrium separation dependent on sieving, Donnan exclusion, and other molecular interactions.

Affinity separation offers very high separation factors and high enrichment but often is a slow process. In contrast, non-equilibrium separation is fast, but the separation factor is low. This presentation critically analyzes the pros-and-cons of two concepts from both theoretical and practical perspectives. The state-of-the-art research on extraction of lithium from brine and Lithium isotope separation will be presented. We emphasize the importance of utilizing chemical exchange in both applications. We also introduce an environmentally friendly membrane extraction technology as a potential separation technology for separation lithium and lithium isotopes.

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DESIGN OF SELECTIVE LIGANDS

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A method on the base of radii thermodynamic (RT) of metal ions and ensembles of regression models (ERM) was developed to predict the stability constants ($\log K$) of the ML complexes of 42 metal ions ($M = Ag^+, Al^{3+}, Am^{3+}, Ba^{2+}, Be^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Ga^{3+}, Hg^{2+}, In^{3+}, K^+, La^{3+}, Li^+, Mg^{2+}, Mn^{2+}, Na^+, Ni^{2+}, NpO_2^{2+}, Pb^{2+}, Sr^{2+}, Th^{4+}, UO_2^{2+}, VO^{2+}, Y^{3+}, Zn^{2+}$, and lanthanides from Ce^{3+} to Lu^{3+} excluding Pm^{3+}) with various organic ligands (L) in water. The method is used to design ligands with a desired complex stability and ion selectivity, applying the chemical editors EdiSDF and EdChemS to generate combinatorial virtual libraries of compounds^{2,3}. Using the known $\log K$ of 8269 complexes of 42 metal ions with 1990 organic ligands in water, it has been shown^{1,4,5} that the metal ion can be described by a single parameter called the thermodynamic ionic radius r , and the stability constants of the two ions M_i and M_j with ligand L are related by the simple relationship $\log K_j = (r_i/r_j) \cdot \log K_i$. The predictive performance of this relationship was tested on external test sets. The accuracy of TR-based $\log K$ estimates is comparable to that of the QSPR and DFT methods^{1,4}. The TR approach was combined with ERM derived from QSPR modelling using machine learning. The modelling was performed using the largest $\log K$ arrays for 416 (Cd^{2+}), 396 (Co^{2+}), 883 (Cu^{2+}), 612 (Ni^{2+}) and 568 (Zn^{2+}) complexes, which contributed to the high reliability of the predictions and wide applicability domain of ERM. The modelling was performed using the ISIDA QSPR software package². Based on the combined approach, the program StaCoRT - a predictor of the stability constants of the ML complexes was developed².

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THEORY AND PRACTICE OF SELECTIVE SEPARATION OF REE BY SYNERGETIC MIXTURES OF EXTRAGENTS

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In conditions of a limited range of industrially produced extractants for the separation of elements with similar properties, the use of synergistic mixtures based on them is of particular importance for increasing selectivity. Synergistic mixtures of extractants allow, first of all, to increase the extraction of the distributed element from an aqueous solution into the organic phase. Another important property is the increase in the selectivity of the distributed component, which is quantitatively characterized by the separation coefficient.

This report focuses on the use of synergistic mixtures based on industrially produced extractants of various classes for the selective separation of rare earth elements (REE) from low-acid nitrate solutions. The use of solutions with low concentrations of HNO_3 as an aqueous medium is dictated by economic factors. Increasing the HNO_3 content above 10-12 g/l can make the entire process unprofitable.

The work examines the selective properties of synergistic mixtures of methyltri-n-octylammonium nitrate (TOMAN) and tri-n-butyl phosphate (TBP), industrial grades of extractants, for the separation of mixtures of light rare earth elements (Ce(III), La, Pr, Nd) and medium group (Sm, Eu(III), Gd) into individual elements. Mixtures of TOMAN with the ammonium salt of di-2-ethylhexylphosphoric acid (AS-D2EHPA) and/or the ammonium salt of carboxylic acid Versatic-10 are also considered for the separation of medium and heavy REE groups along the Gd/Tb line and the separation of some elements of the heavy group (Tb, Dy, Ho, Er) into individual elements.

Using the examples of the extraction systems listed above, it is shown that selectivity in the separation of rare earth elements by synergistic mixtures is determined, first of all, by the difference in the compositions of the extracted compounds, which in turn is determined by the molar ratios $\text{Ln}(\text{NO}_3)_3$: TOMAN : TBP (AS-D2EHPA, AS-Versatic-10), the ratio of the concentrations of separated REEs in the aqueous phase and the composition of the synergistic mixture in the organic phase. An important factor influencing the synergistic properties of mixtures and their selectivity is the hydration of all components in the organic phase, which reduces the thermodynamic activity of the extractants of the mixture in accordance with their degree of hydration and the water activity of the equilibrium aqueous phase.

EXTRACTION OF HEAVY RARE EARTH ELEMENTS AND YTTRIUM FROM CHLORIDE SOLUTIONS USING MIXTURES OF P507 AND CYANEX 272

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The extraction of rare earth elements (REEs) from chloride solutions after leaching REE carbonate concentrate (Apatit Cherepovets, Cherepovets, Russia, Vologda region) with solutions of the mixtures of P507 (2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester) and Cyanex 272 (bis(2,4,4-trimethylpentyl)phosphinic acid) (1:1) at various concentrations was experimentally studied. It was shown that the distribution ratios of all REEs decrease with the increasing concentration of these metals in the initial solution, which is associated with the loading of the organic phase. The most significant improvement in the extraction is observed for the heavy group of rare earth elements. The extractability of REEs increases with the increasing atomic number of the element, as is typical for the extraction of these metals with acidic organophosphorus extractants.

The results obtained show that the separation factors of adjacent rare earth elements decrease slightly with the increasing concentration of metals in the initial aqueous solution. Increasing the concentration of the extractant mixture does not have a significant effect on the values of the adjacent REE separation factors. The data obtained on the distribution ratios and separation factors made it possible to propose a flow sheet for the separation of rare earth elements with the production of Y, Ho, Tb and Dy. The flow sheet consists of 5 cascades with total number of separation stages is equal to 253.



SELECTIVE LITHIUM EXTRACTION BY NEW BINARY EXTRACTANTS BASED ON ORTHO-SUBSTITUTED PHENOLS

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Currently, there is a clear trend towards the development of lithium-selective technologies, which allow to significantly reduce the energy intensity of the stages of brine concentration and removal of interfering/companion ions. Methods of liquid extraction, sorption and various membrane processes are being actively developed. The most promising is the development of liquid extraction methods due to their high productivity, low cost and scalability. However, the range of lithium-selective extractants is limited, so the actual task is to search for new lithium-selective extractants with low cost and allowing to organize a highly efficient environmentally friendly process of lithium extraction without its preliminary concentration.

In this work, based on the structural similarity of ortho-substituted phenols with the enolic form of 1,3-diketones, we predicted and confirmed their propensity to selectively extract lithium. A systematic study of the extraction of Li, Na and K from alkaline media using various ortho-substituted phenols has been carried out. The compositions of extractable complex compounds were determined and possible mechanisms of lithium, sodium, and potassium extraction by ortho-substituted phenols were proposed; thermodynamic parameters of extraction processes were determined. Laboratory modeling of lithium extraction process on the background of extremely high concentrations of sodium and potassium was carried out using new extractants. The principal possibility of realization of the technological process of lithium extraction with a high degree of concentration and purification from alkali metals was shown.

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SELECTIVE SYSTEMS FOR EXTRACTION AND SEPARATION OF ACTINIDES FROM CARBONATE MEDIA

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In parallel with the improvement and modification of the standard PUREX aqueous technology for reprocessing spent nuclear fuel (SNF), alternative carbonate and alkaline hydrometallurgical schemes for reprocessing of SNF, various types of liquid and solid radioactive waste (RW) are actively developing in Japan (JAERI), the USA (LANL, PNNL), South Korea (KAERI) and the China (CIAE).

An original carbonate solvent extraction scheme (CARBEX process) has been developed in Russia, which includes the extraction and purification of uranium and transuranic elements from carbonate solutions of oxidative dissolution of SNF using solvent mixtures based on quaternary ammonium bases (QAB).

The use of solvent extraction processes at the refining stages of fissile materials in the CARBEX process ensures the achievement of high purification factors of uranium and plutonium, at the level of 10^6 - 10^8 , and the production of their suitable compounds for the fabrication of mixed oxide or nitride uranium-plutonium nuclear fuel.

The paper summarizes, systematizes the results of scientific research and presents the achievements of Russian researchers in the field of development and improvement of carbonate systems for the processing of SNF and RW, increasing the selectivity of separation, efficiency of separation and purification of uranium, plutonium, minor actinides and fission products in carbonate solvent extraction systems using QAB salts.

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MOLECULAR IMPRINTED POLYMER SORBENTS FOR PREPARATIVE EXTRACTION OF LOW-MOLECULAR-WEIGHT BIOLOGICALLY ACTIVE SUBSTANCES

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Selective polymer sorbents are used in various fields affecting human life, such as ecology, industry and medicine. The mechanism of such sorbents action is based on the selective binding of molecules of the extracted substance from a multicomponent aqueous medium. Therefore, selectivity is a fundamental factor in their effectiveness.

Molecular imprinting has become a method for creating highly selective sorption centers that mimic natural receptors. It consists in carrying out polymerization in the presence of molecules of the target object (template). Due to the preservation of the "molecular memory" embedded in the crosslinked polymer mesh, the imprinted cells are able to re-embed the target molecule. Non-covalent molecular imprinting is most widely used in practice due to the relative simplicity of the process itself, which is based on non-covalent intermolecular interactions.

Using this method, polymer sorbents have been developed for the selective extraction of low-molecular-weight biologically active substances (erythromycin, glucose, cholesterol, etc.) from liquid media. The study of the obtained sorption materials by liquid adsorption methods made it possible to determine the binding nature of the target molecules and showed an improvement in the permeability of imprinted polymers compared to non-imprinted analogues. The conditions for the formation of homogeneous sorption centers were identified, the limiting mechanism of binding kinetics of target objects and the conditions for the implementation of a regular sorption regime were determined. It was found that polymer imprinting, regardless of the nature of the target molecules, improves the selectivity of sorption systems and the implementation of a quasi-equilibrium sorption regime, which makes it possible to scale the developed sorption processes for extracting biologically active substances to semi-preparative and preparative scales.

BIOINORGANIC SORBENTS BASED ON IMPRINTED PROTEINS

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Major number of modern analytical methods are based on natural (biological) receptors like antibodies, enzymes, DNA, etc. Among different bioreceptors are used in analytical devices (test-systems and sorbents), antibodies are prevalent. Devices based on antibody-antigen interactions are characterized by high specificity that has resulted in their wide application at science, medicine, environmental and food control. However, there are few disadvantages of immunoreceptors devices like production via laboratory animals, low chemical, and physical stability, losing of receptor affinity due to immobilization at carrier surface. In this connection, there are different ways to address these shortcomings, and one of them is synthetic receptors. Molecular imprinting is one of the most widespread techniques of synthetic receptors syntheses. The polymeric materials obtained by molecular imprinting are called molecular imprinted polymers (MIPs).

Currently MIPs successfully are used for separation and determination of low and high molecular weight substances. Analytical performance of MIPs based devices could be the same or higher than common commercially available immunochemical kits.¹ Unfortunately "common" MIPs have several disadvantages for example biocompatibility and recycling degree, uneven distribution of binding sites and inability to predict structure of imprinted polymer. In that case imprinting of proteins is one of the promising ways to obtained MIP without described shortcomings².

In this study, we present the approach for obtaining bioinorganic sorbents based on imprinted bovine serum albumin and glucose oxidase, with a specificity against zearalenone. The zearalenone was successfully extracted from model solutions and artificially contaminated wheat samples.

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PHOSPHORYL KETONES: COMPLEXING AND EXTRACTION PROPERTIES, PRACTICAL APPLICATION

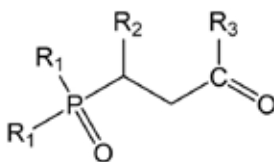
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This work summarizes the results of studies of the complexing and extraction properties in relation to actinides and lanthanides of neutral organophosphorus compounds of the class of phosphoryl ketones:



The data obtained make it possible to determine the direction of the design of promising extractants for the effective and selective extraction of actinides and lanthanides in the group of phosphoryl ketones to solve various technological problems. The structures of highly effective extractants of the phosphoryl ketone class have been developed. A comparison of the extraction ability of these compounds with commercially available organophosphorus extractants showed their clear advantages. The possibility of using extractants of the phosphoryl ketone class for the effective extraction of valuable target components (actinides, zirconium, scandium and collective REE concentrates at the Nd-Sm boundary) from eudialyte ore concentrate and phosphogypsum leaching solutions within one technological stage of the extraction process has been demonstrated. The results obtained can become the basis for a new industrial technology in the production of rare and rare-earth metals from mineral and technogenic raw materials, as well as in the field of radioactive waste conditioning.

INFLUENCE OF THE PARAMETERS OF THE EXTRACTION SYSTEM ON THE SELECTIVITY OF EXTRACTION Ln(III), Am(III) AND Cm(III) BY N,N,N',N'- TETRABUTYLDIGLYCOLAMIDE

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The diglycolic acid diamides are the perspective extractants for the recovery of minor actinides, such as Am and Cm, from the spent nuclear fuel. In the present work the influence of the different extraction systems parameters on the selectivity of Eu(III), Am(III) and Cm(III) extraction by N,N,N',N'-tetrabutyl diglycolamide (TBDGA) from the nitric acid media was studied.

Extraction systems with several types of diluents were considered in the work: saturated hydrocarbons (the mixture of n-dodecane with decanol-1 (v:v 90:10, DD+Dec-1)), aromatic hydrocarbons with the electron withdrawing groups (nitrobenzene (PhNO₂), m-trifluoromethylnitrobenzene (F-3)), and without them (benzene, toluene (PhMe) and pseudocumene (PC)) and chlorinated hydrocarbons (CCl₄, CHCl₃, 1,2-dichloroethane (DCE) and 1,1,2,2-tetrachloroethane (TCE)). The extraction of HNO₃, the influence of the nitric acid concentration in the aqueous phase on the distribution ratios of Eu(III), Am(III) and Cm(III), the compositions of the extracted compounds and the thermodynamic parameters of the extraction reactions were studied for all the systems investigated.

The extraction capacity of TBDGA towards the listed metals increased in the following order of the diluents: PhNO₂, F-3 > DD+Dec-1, CCl₄, PhH > PC > PhMe, DCE, TCE > CHCl₃. Systems with F-3 in the region of high HNO₃ concentrations in the equilibrium aqueous phase and systems with PC in the region of medium acid concentrations exhibited significant Eu(III)/Am(III) pair partition coefficients (6 - 10) and proved suitable for the separation of minor actinides and light lanthanides from medium and heavy lanthanides. Significant Am(III)/Cm(III) pair partition coefficients (1.8 - 2.2) were obtained for systems with PhNO₂ in the region of low HNO₃ concentrations in the equilibrium aqueous phase.

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COMPLEXATION AND EXTRACTION PROPERTIES OF 1,3-BIS(DIPHENYLPHOSPHORYL)-2-OXAPROPANE TOWARDS RARE EARTH ELEMENTS

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It is well known that 1,3-bis(diphenylphosphoryl)-2-oxapropane ($L - Ph_2P(O)CH_2OCH_2P(O)Ph_2$) has a high complexation ability towards various metal ions, including rare earth elements (REE), due to the presence of phosphoryl groups. This podand extracts yttrium subgroup of REE much better than cerium subgroup. To explain the reasons for this selectivity we studied the complexation of L with REE.

The stability constants of L complexes with REE nitrates from the beginning, middle, and end of the REE series (Ce^{3+} , Tb^{3+} , Lu^{3+}) were determined by spectrophotometric titration. It has been found that $M^{3+}L$ and $M^{3+}L_2$ complexes are formed in the acetonitrile. Their stability increases through the REE series.

The extraction of individual REE (Ce^{3+} , Tb^{3+} , Er^{3+} , Lu^{3+}) with L in the presence of ionic liquids methyltriocetyl ammonium nitrate and bis[(trifluoromethyl)sulfonyl]imide 1-butyl-3-methylimidazolium was studied.

The ion-selective properties of L towards REE were tested. Podand exhibits potentiometric selectivity to the lutetium cations.

We synthesized 20 new complexes of L with ions of all metals from the REE series. Their composition and structure were characterized by X-ray diffraction and elemental analysis, IR and NMR spectroscopy. The resulting compounds are 2D and 3D metal-organic frameworks. By TGA method, it was found that heating leads to the activation of porous in the frameworks.

The work was carried out with the financial support of the Russian Science Foundation, project No. 22-13-00051.

ESTIMATION OF THE SELECTIVITY OF ORGANOPHOSPHORUS COMPOUNDS TOWARDS s-, d- AND f-ELEMENTS

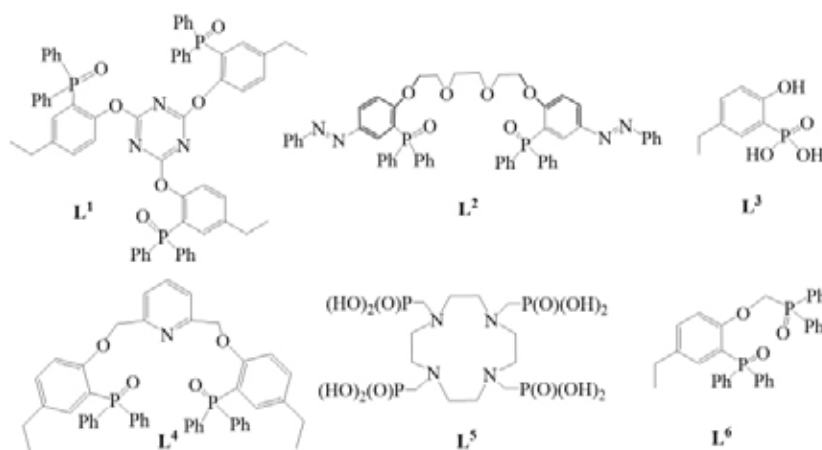
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It is known that polydentate organophosphorus compounds can bind cations of alkali, alkaline-earth, transition metals and rare earth elements. Qualitative and quantitative changes in coordinating centers, conformational rigidity of the molecule and variation of substituents at the P=O group make it possible to find compounds selective for various cations. This report provides examples of the design of organophosphorus compounds with selectivity towards lithium (L^1 , L^2), copper (L^3), cadmium (L^4), gallium (L^5) and rare earth (L^6) cations. The synthesized compounds can be used as active components of plasticized polymer membranes of ion-selective electrodes, effective extractants and potential anti-inflammatory drugs and radiopharmaceuticals. The selectivity was estimated by determining the stability constants of ion metal complexes with L^1 – L^6 using spectrophoto- and potentiometry.



The work was financially supported by the Russian Science Foundation, project No. 22-13-00051.



PROSPECTS FOR THE SELECTIVE EXTRACTION OF LITHIUM FROM NATURAL HYDROMINERAL SOURCES BY MACROCYCLIC EXTRACTANTS

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Hydromineral sources (salt lake brines, formation waters of oil production, hydrothermal waters, etc.) are known to constitute up to 70% of all natural lithium reserves.¹ To date, industrial technologies for lithium extraction exist exclusively for the processing of salt lake brines, and are almost completely lacking for other sources of hydromineral raw materials with a relatively low lithium content. Liquid-liquid extraction has a number of advantages (process rate, operational stability and simplicity of regeneration) compared to precipitation, ion-exchange, membrane and electrochemical methods for separation of lithium from multicomponent solutions. It was previously shown that extractants based on 14-membered macrocyclic polyethers provide the selective extraction of lithium from solutions with a high Me/Li⁺ ratio (where Me – Na⁺, K⁺, Mg²⁺).²

By using original methods, the individual stereoisomers of dicyclohexano-14-crown-4 (DCH14C4) were synthesized and characterized by FTIR, NMR spectroscopy and synchronous TGA/DSC analysis. The extractants based on solutions of DCH14C4 stereoisomers demonstrated a high resistance to macrocycle transfer into aqueous phase ($K_D^{DCH14C4} \sim 2 \cdot 10^5$) and Li⁺ extractability. The extraction isotherms of LiCl, NaCl and KCl from single-component and multicomponent solutions showed the high selectivity of the ligand with respect to Li⁺ cations. Moreover, the stereoisomerism of the macrocycle played a key role in the process. The results of this work demonstrate the high potential of the system based on DCH14C4 for the development of the process for the selective extraction of lithium from hydromineral sources.

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CHEMICAL ISOTOPE EXCHANGE BETWEEN HYDROGEN AND WATER IN CONTACT DEVICES WITH TUBULAR MEMBRANES

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Traditionally, chemical isotope exchange (ChIE) between hydrogen and water is carried out in vertical packed columns with layer-by-layer or mixed loading of a hydrophilic packing and a hydrophobic catalyst. However, such columns have low throughput - the linear velocity of the vapor-gas flow does not exceed 0.3 m/s¹. At Mendeleev University, a membrane-type contact device (MCD) was developed, in which the catalyst is separated from the flow of liquid water by a membrane impermeable to gas and permeable to water². In such devices there is no requirement for the hydrophobicity of the catalyst.

The paper presents the results of determining the mass transfer characteristics of the process of isotope exchange between hydrogen and water in MCD with tubular membranes. Figure 1 shows the dependence of the mass transfer coefficient on the linear velocity of the vapor-gas flow.

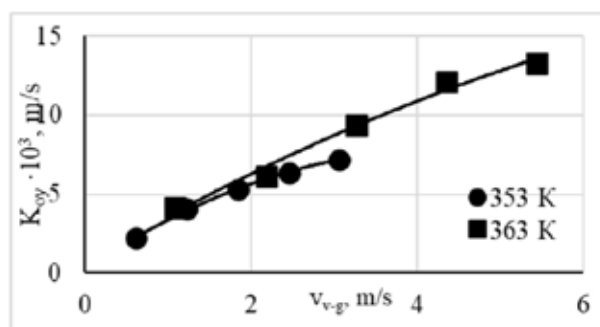


Figure 1. Dependence of the chemical transfer coefficient between hydrogen and water in MCD with tubular membrane on the linear velocity of the vapor-gas flow.

From Figure 1 it can be seen that the MCD with a tubular membrane has approximately 20 times greater throughput compared to traditional packed columns.

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APPLICATION OF DIGLYCOLAMIDES IN THE SCANDIUM SELECTIVE SOLVENT EXTRACTION PROCESSES

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Scandium is a scattered element with no deposits of its own. The processes for extracting scandium are complicated and multi-step, which explains the high cost of scandium products. The solvent extraction method, characterized by high selectivity and performance, in our days is one of the most effective for organizing of the scandium extraction, concentration and purification processes.

In the present work, N,N,N',N'-tetraoctyldiglycolamide (TODGA) is proposed as an extractant for the selective recovery of Sc from the multicomponent solutions.

The possibility of scandium extraction from hydrochloric, nitric and sulfuric acid media was considered. The extraction of scandium was increasing with the increased of the acid concentration in the equilibrium aqueous phase.

The metal:TODGA ratios in the extracted compounds were obtained for scandium, yttrium and rare earth elements (REE) by the slope analysis method. Scandium is co-extracted with the heavy RRE group, ratio metal:extractant in the extracted compounds is close to 3.

Complexes of scandium nitrate and chloride with N,N,N',N'-tetraethyldiglycolamide (TEDGA) have been isolated in the crystalline form. The complex of scandium nitrate with TEDGA consists of $[\text{Sc}(\text{TEDGA})_3]^{3+}$ cations, out-sphere nitrate anions and the molecules of the crystalline water. In the case of scandium chloride, both of $[\text{Sc}(\text{TEDGA})_3]^{3+}$ and $[\text{Sc}(\text{TEDGA})_2(\text{H}_2\text{O})_2]^{3+}$ cations were observed.

The values of enthalpies of extraction reactions were obtained in the magnitude of the temperature of 25-80 °C for Sc, Y and RRE during their extraction with the solution of TODGA in the mixture of dodecane-decanol from the hydrochloric, nitric and sulfuric acid solutions. The extraction reactions were exothermic for all elements; the values of enthalpies were in the range of -95 – -40 kJ/mol.

This work was supported by the Ministry of Science and Higher Education of Russia [grant agreement № 075-15-2024-534]

EXTRACTION CHROMATOGRAPHY RECOVERY OF RARE EARTH ELEMENTS IN RECYCLING PROCESS OF NdFeB MAGNETS

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End-life NdFeB magnets are promising secondary sources of rare earth elements (REE)¹. When processing these magnets, the main difficulty is the separation of Fe(III) and REE². To solve this problem, the extraction chromatography method using impregnated resins turned out to be the most effective.³ A new approach to the separation of REE and Fe(III) in solutions obtained during processing of NdFeB magnets using resins impregnated with TODGA is proposed. At the first stage, Fe(III) and the sum amount of REE are separated by elution of the resin with solution of 3 M NH₄NO₃, then Pr(III) and Nd(III) are separated by passing through the column solution of 3 M NH₄Cl, after that Dy(III) is stripped with distilled water. The chromatogram obtained under these conditions is shown in Figure 1.

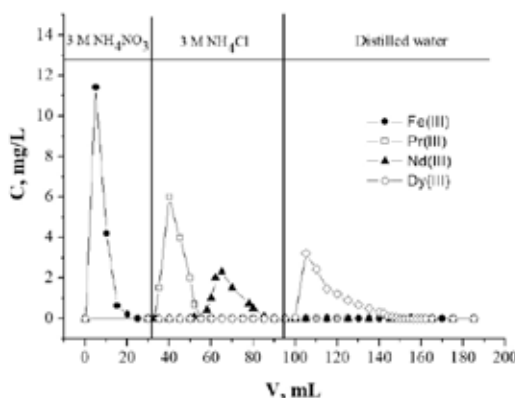


Figure 1. Separation of Fe(III), Pr(III), Nd(III) и Dy(III) using resin impregnated with TODGA

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DENSITY AND DIELECTRIC PERMITTIVITY OF SOLUTIONS OF LANTHANOIDES OF MIDDLE-HEAVY GROUP IN AQUEOUS SOLUTIONS AND EXTRACTS P507 AND CYANEX 272

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The densities of mixed solutions of rare-earth elements of the medium-heavy group with NaCl were determined by the pycnometric method. Aqueous solutions of NaCl with a concentration of 10,50,100,150,200, 220 g/dm³ containing lanthanoides chlorides of the medium-heavy group with a concentration range from 0.05 mol/dm³ to 1.73 mol/dm³ at pH = 1.5 were studied.

143 mixed solutions were studied at a temperature of 25°C. Using the Nonlinear Matrix Fit method using the Poly2D model using the Origin program, the parameters of formula (1) were calculated depending on the density of the NaCl and LnCl₃ components:

$$\rho = z_0 + a \cdot x + b \cdot y + c \cdot x^2 + d \cdot y^2 + f \cdot x \cdot y \quad (1),$$

where ρ -density of the test solution, g/ml;

x-concentration of LnCl₃, mol/dm³; y- concentration of NaCl, g/dm³.

Dielectric permittivity of solutions with the concentration of the total REE in the aqueous phase from 0.05 mol/dm³ to 0.75 mol/dm³ and NaCl concentration equal to 150 g/dm³ was measured in the frequency range from 0.5 to 110 MHz. Solutions were obtained from carbonate concentrate (Apatit, Cherepovets, Russian Federation, Vologda region) REE composition: Ce – 1,79 %, Sm – 15,23 %, Eu – 5,13 %, Gd – 18,4 %, Tb – 2,38 %, Dy – 8,78 %, Y – 44,13 %, La – 0,77 %, Nd – 3,17 %, Pr – 0,15 %.

Using the dielcometry method, the dependence of the dielectric constant of LnCl₃ solutions in aqueous solutions and in extracts containing a mixture of extractants P507 and CYANEX 272 at different frequencies was obtained. Empirical formulas and dependences of the dielectric constant on the composition of the aqueous and organic phases of extraction systems were obtained.

An empirical equation connecting the density of a solution with the concentration of NaCl and the concentration of the total REE allows to calculate the concentration of sodium chloride with an accuracy of 0.1-0.5% from the density and concentration of the total REE. The empirical formula for the dependence of the concentration of the total REE (C_{LnCl_3}) on ε allows to calculate C_{LnCl_3} at a NaCl concentration of 150 g/dm³ from the value of ε with an accuracy of 3%.

NEW ENVIRONMENTALLY BENIGN TECHNOLOGIES FOR THE PRODUCTION OF PLATINUM METALS

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The use of aqueous biphasic polymer-salt extraction system for selective extraction of Pd(II) and Pt(IV) from chloride technological solutions was proposed by the authors of this report for the first time¹. The extraction process of metal separation in laboratory conditions can be realized using rotating coiled columns (RCC) or laboratory centrifugal reactors, and using a cascade of commercially available centrifugal reactors in industrial conditions.

The principal novelty of the proposed approach consists in the possibility of multistage extraction process and the absence of the need to add any specific reagents for targeted binding of metals. The use of polyethylene glycol-1500 (PEG-1500) as a stationary phase allows to recover 96-100 % of Pd(II) and Pt(IV) from chloride solutions containing copper and nickel². To obtain individual solutions of the target metals, it is sufficient to change the composition of the salt-rich phase at the re-extraction stage, in particular, the salt concentration and pH value. The final purity of target metal fractions obtained after their extraction from model technological solutions is $\geq 99.9\%$. Subsequent electrochemical separation of metals is promising.

The components of the aqueous biphasic systems are utilizable, non-toxic, available and widespread in laboratory and technological practice. The scheme of multistage separation of platinum metals is tested with the use of RCC. The possibility of using traditional extraction equipment is demonstrated.

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PREDICTING THE STABILITY CONSTANT OF METAL COMPLEXES USING A GRAPH NEURAL NETWORK

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Effective extraction separation of metal cations with similar properties requires the selection of ligands providing strong and selective binding to one of the cations to be separated. The experimental search for such ligands involves multiple determinations of the complex stability, which requires significant resources. Therefore, the problem of theoretical prediction of the stability constants of metal complexes with organic ligands seems relevant.

Graph neural networks have been successfully used to solve various chemical problems^{1,2}. This work explores the possibility of using a similar architecture (Fig. 1) to predict the stability constants of 1:1 metal-ligand complexes. The proposed model was trained on complexes of lanthanides, some actinides and other metals. The coefficient of determination (R^2) of the final model on the validation set for most cations exceeded 0.9, which indicates the good predictive ability of the model.

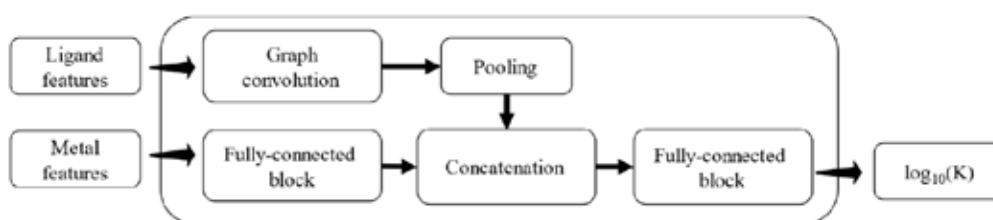


Figure 1. Neural network architecture proposed

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The work was carried out using the equipment of the Center for Shared Use of Ultra-High-Performance Computing Resources of M.V. Lomonosov Moscow State University.

EXTRACTION OF RARE METALS WITH A STOICHIOMETRIC BINARY MIXTURE OF ACID PHOSPHORYL PODANDUM AND QUATERNARY AMMONIUM NITRATE

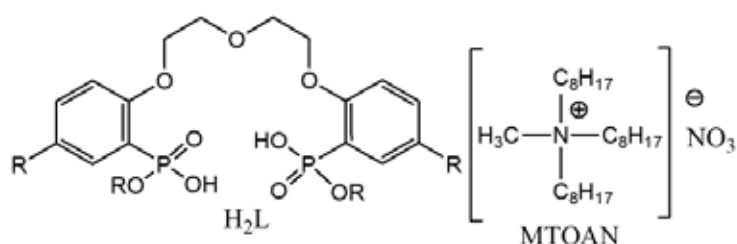
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Along with traditional extractants, stoichiometric binary mixtures of extractants of various natures are used for the extraction and separation of rare metals, which under certain conditions form salts classified as ionic liquids:



The patterns of extraction of different groups of rare metals with stoichiometric binary mixtures of acidic phosphoryl podands and quaternary ammonium bases have been determined.

The extraction of cesium with a stoichiometric binary mixture of 1,5-bis[o-(hydroxyethoxyphosphoryl)phenoxy]-3-oxapentane and trioctylamine from various media was studied. It has been shown that the extraction ability of the organic salt $[(\text{NHR}_3)^+][(\text{L})^{2-}]$ in carbonate and nitric acid (up to 0.1 M HNO_3) media is significantly higher compared to dibenzo-18-crown-6 and dtertbutyldicyclohexano-18-crown-6. The extraction of rare metals with a stoichiometric binary mixture of acidic phosphoryl podands and quaternary ammonium bases from eudialyte ore concentrate leaching solutions was studied. Using this mixture, uranium(VI), thorium(IV), zirconium(IV), hafnium(IV), scandium(III) and titanium(III) are quantitatively extracted from eudialyte ore concentrate leaching solutions, while rare earth elements are concentrated in the raffinate.

ZrCl₄ AND HfCl₄ VAPOR PRESSURE ABOVE KCl-AlCl₃-MeCl₄ MELTS

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Zirconium and its alloys are reliable structural materials for thermal nuclear power plants. One of the most important issues of the use of zirconium in the nuclear industry is the requirement for purification of metal from impurities of hafnium, that is geochemically accompanies zirconium and has a noticeably higher thermal neutron capture cross section.

The extractive rectification method can be used to purify zirconium from hafnium. The rectification process makes possible to separate ZrCl₄ and HfCl₄ at pressure near 1 atm in course of their direct contact with a low-melting KCl-AlCl₃-based melt. The optimal parameters for extractive distillation can be found from the data on the vapor pressure of zirconium and hafnium tetrachlorides at different temperatures over chloroaluminate melts that contain ZrCl₄ and HfCl₄.

In the present study the dependence of the vapor pressure of ZrCl₄ and HfCl₄ on temperature was investigated when constant AlCl₃/KCl molar ratio in the salt system and various of zirconium and hafnium tetrachlorides concentration were applied. The results of the experiments with a molar ratio of aluminum to potassium of 1.02 are shown in Figure 1. The obtained data clearly indicate, that temperature and ZrCl₄ and HfCl₄ concentrations increase lead to increase the vapor pressure of zirconium and hafnium tetrachlorides. However, the vapor pressure of hafnium tetrachloride in the entire range of measured concentrations is always higher than the vapor pressure of zirconium tetrachloride in case of their equal values content.

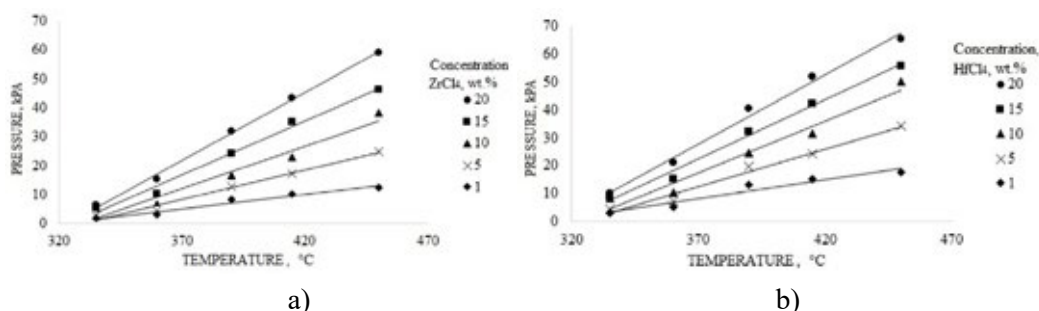


Figure 1. temperature influence on ZrCl₄ (a) HfCl₄ (b) vapor pressures, molar ratios of aluminum to potassium are equal to 1.02 in the both cases

SYNTHESIS, CRYSTAL STRUCTURE AND SPECTRAL PROPERTIES OF NEW COMPLEXES OF DIETHYL(2-HYDROXY-3-NITRO-5-ETHYLPHENYL)PHOSPHONATE WITH U(VI) AND Np(VI)

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The search for new organic ligands (extractants) for selective binding of f-elements in the reprocessing of spent nuclear fuel (SNF) is currently a pressing task. Identifying structural regularities of organic ligands and their complexes with industry-required elements can help develop effective extractants for practical hydrometallurgical applications.

Since in the PUREX process actinides are extracted in the form of AnO_2^{2+} ions obtained after dissolution of SNF in nitric acid, in this work, we investigated the complexation of U(VI) and Np(VI) nitrates with diethyl(2-hydroxy-5-ethylphenyl)phosphonate (L^1), an organic ligand that has not been extensively studied, in acetonitrile at room temperature. The crystal structure of L^1 was determined for the first time and coordination compounds of the nitro derivative diethyl(2-hydroxy-3-nitro-5-ethylphenyl)phosphonate (L^2) with UO_2^{2+} and NpO_2^{2+} were obtained and characterised by X-ray diffraction analysis (fig.1) and electron spectroscopy.

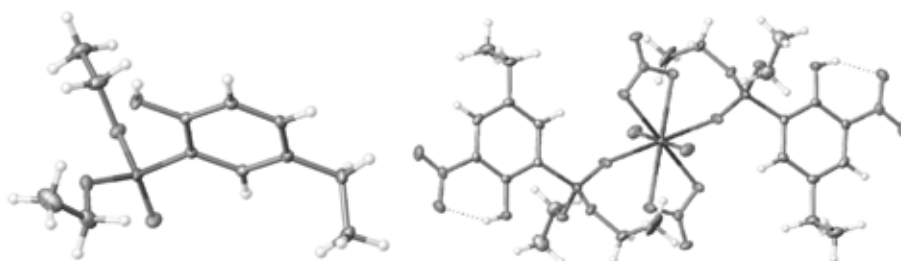


Figure 1. Fragment of the structure of L^1 (left) and a fragment of the structure of the complex L^2 with $\text{UO}_2(\text{NO}_3)_2$ (right).



COMPLEXATION AND EXTRACTION PROPERTIES OF 1,3-BIS(DIPHENYLPHOSPHORYL)-2-OXAPROPANE TOWARDS RARE EARTH ELEMENTS

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It is well known that 1,3-bis(diphenylphosphoryl)-2-oxapropane ($L = \text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{OCH}_2\text{P}(\text{O})\text{Ph}_2$) has a high complexation ability towards various metal ions, including rare earth elements (REE), due to the presence of phosphoryl groups. This podand extracts yttrium subgroup of REE much better than cerium subgroup. To explain the reasons for this selectivity we studied the complexation of L with REE.

The stability constants of L complexes with REE nitrates from the beginning, middle, and end of the REE series (Ce^{3+} , Tb^{3+} , Lu^{3+}) were determined by spectrophotometric titration. It has been found that $\text{M}^{3+}L$ and $\text{M}^{3+}L_2$ complexes are formed in the acetonitrile. Their stability increases through the REE series.

The extraction of individual REE (Ce^{3+} , Tb^{3+} , Er^{3+} , Lu^{3+}) with L in the presence of ionic liquids methyltriocetyl ammonium nitrate and bis[(trifluoromethyl)sulfonyl]imide 1-butyl-3-methylimidazolium was studied.

The ion-selective properties of L towards REE were tested. Podand exhibits potentiometric selectivity to the lutetium cations.

We synthesized 20 new complexes of L with ions of all metals from the REE series. Their composition and structure were characterized by X-ray diffraction and elemental analysis, IR and NMR spectroscopy. The resulting compounds are 2D and 3D metal-organic frameworks. By TGA method, it was found that heating leads to the activation of porous in the frameworks.

The work was carried out with the financial support of the Russian Science Foundation, project No. 22-13-00051.

SURFACE MODIFICATION OF ION EXCHANGE MEMBRANES WITH CERIUM OXIDE

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Membrane separation processes are widely used in modern industry. In recent years, a great attention has been paid to methods for separating ions of the same sign but of different valence. The introduction of hydrogen cerium phosphate into membranes can increase their monovalent ion selective transport. The purpose of this work was the surface modification of industrial heterogeneous cation exchange MC-40 membranes and anion exchange MA 41 membranes with cerium oxides, including those containing phosphoric acid groups.

The modified membranes were characterized by scanning electron microscopy, TGA, IR spectroscopy, voltammetry. Their conductivity in various ionic forms, the transport numbers of cations (for MC-40) and anions (for MA-41), as well as selective permeabilities for singly and doubly charged cations/anions during water desalination by electrodialysis were determined.

Modification of MC-40 membranes with ceria leads to an increase in selectivity to doubly charged ions. There is no negative effect on the cation transport numbers in the obtained membranes upon modification. The conductivity of membranes in the Na^+ -form decreases slightly with the ceria introduction, while for the modified membranes in the Ca^{2+} -form its change is insignificant. Membranes modified by ceria with phosphoric acid groups are less prone to fouling than the pristine MC-40 membrane.

Modification of MA-41 membranes with ceria has almost no effect on the conductivity of the resulting materials, but leads to an increase in their selectivity to singly charged anions (chloride and nitrate ions in relation to sulfate ions). The stability of the prepared materials during the separation of singly and doubly charged anions was shown.

Thus, the prepared composite membranes are capable of separating singly and doubly charged ions quite effectively. Moreover, such important parameters as conductivity and transport numbers do not change or their change is insignificant.

The work was funded by the Russian Science Foundation, grant No 23 43 00138, <https://rscf.ru/project/23-43-00138/>.



SYNTHESIS OF NANOSTRUCTURED SILICA FOR SORPTION PRECONCENTRATION AND SEPARATION OF POLYPHENOLIC SUBSTANCES

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The complexity of natural objects and low content of substances in them require the search for new methods and materials for sample preparation. One of the most promising sorbents are ordered mesoporous silica, characterised by high surface area and homogeneous pore size. The aim of the work is to compare the parameters of sorption concentration and separation of polyphenolic substances by varying the structure and nature of sorption sites of ordered mesoporous silica.

Ordered mesoporous silica was synthesized by varying the composition of the reaction mixture, including in the presence of potential sorbates (quercetin and dihydroquercetin). The sorption of flavonoids from individual and binary acetonitrile solutions was studied by the breakthrough curves method.

Flavonoid	Sorbent	Q, mkmol/g	Kk _{conc}
Quercetin	S1	0,5	0,8
	QS1	1,2	2,8
Rutin	S1	2,8	6,4
	QS1	10,8	22

Table 1. Parameters of sorption preconcentration of flavonoids

It was noted that the addition of flavonoids in the synthesis of silica (sorbent QS1) increased the selectivity towards quercetin and other polyphenols with similar structure. At the same time, the concentration coefficients increased by 3,5 times (Table 1) in comparison with the sorbent synthesised without addition of target substances (S1).

The work was supported by the Ministry of Science and Higher Education of the Russian Federation within the framework of the state assignment to universities in the field of scientific activity for 2023-2025, project FZGU-2023-0009.

The background is a dark, almost black, space filled with intricate, glowing patterns of particles. These particles, in shades of bright blue and vibrant orange, form complex, swirling, and branching structures that resemble mineral deposits, molecular models, or perhaps the paths of subatomic particles. The overall effect is one of dynamic energy and scientific exploration.

DEVELOPMENT OF THE MINERAL RESOURCES FOR RUSSIA'S TECHNOLOGICAL SOVEREIGNTY



DEVELOPMENT OF MODELS OF MINERAL FORMING SYSTEMS: THE WAY TO DEVELOP MINERAL RESOURCE BASE

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The development of the mineral resource base requires persistent replenishment of the extracted volumes of metals, i.e. discovery of new sources of ore and, consequently, improvement of criteria for predicting perspective territories and discovery of new deposits, sometimes of genetic types unconventional for the country. It seems important to answer two questions: 1) forecast, search for ore deposits and the doctrine of ore formation processes: WHERE and HOW can these branches connect? and 2) how can basic science contribute to the development of the mineral resource base? In order to choose the right criteria, it is necessary to understand which of the geological characteristics reflect the processes that led to the formation of the deposit or metallogenic provinces. The choice of a promising province is a critical, most important step, which creates enormous risks and possible financial losses if large deposits are not discovered. The main goal of the forecast and search is decrease of the study area until the discovery of the ore deposit.

The selection of areas is based on their features that are easy to identify and then use in field works. The main requirement for forecasting and prospecting criteria is that they should reflect not only spatial relationships, but indicate the genetic connection of geological structures with ores! Therefore, the development of genetic models of mineral-forming systems is a necessary stage of the strategy for forecasting and searching for perspective territories and deposits. Model can be empirical (descriptive) or theoretical (genetic). The first one contains those characteristics that are considered typical for a group of deposits, even if the relationships between these characteristics are unknown. In the second, the characteristics are interconnected through some fundamental phenomenon. The concept of “Mineral-forming systems” is based on the recognition of fundamental processes that occur in the earth’s interior and lead to the accumulation of metals in a relatively small block of the earth’s crust, and not just on the scale of the ore deposit itself. The model of mineral-forming systems includes the geodynamic conditions for the origin of systems, the geological structure, the source of magmas and fluids, the causes and paths of their migration, the conditions for the transfer of metals and the reasons for the deposition and preservation of ores.

PROSPECTS FOR THE APPLICATION OF BIOHYDROMETALLURGY FOR THE EXTRACTION OF STRATEGIC METALS

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Currently, microbially-assisted technologies for bioleaching of sulfide ores and concentrates, sulfates and heavy metal ion removal from wastewaters, as well as destruction of cyanides and thiocyanates are successfully used. The beginning of the active development of biohydrometallurgy coincided with the discovery of the first known acidophilic iron-oxidizing bacterium *Acidithiobacillus ferrooxidans* in the 50s of XX century. In recent decades, based on microbiological and molecular biological studies of the metabolism and genomics of microorganisms, it has been established that representatives of bacteria and archaea participate in bioleaching, the diversity of their physiological properties allows performing technological processes in a wide range of conditions. Biohydrometallurgical technologies are used to process copper ores and refractory gold concentrates around the world. According to recent estimates, biooxidation accounts for about 5% of global gold production. In the Russian Federation, the Polyus Company created and implemented the BIONORD technology at the Olimpiada gold-sulfide deposit, based on the use of bacteria of the genera *Leptospirillum*, *Acidithiobacillus* and archaea of the genus *Ferroplasma*. The Olimpiada plant has been the largest gold mining plant in the Russian Federation for a long time and is one of the 5 largest gold mining plants in the world and still holds the lead among plants, which use biooxidation.

In addition, technologies based on the use of sulfate-reducing bacteria and neutrophilic thiobacilli for removal metal ions, as well as thiocyanates and cyanides from metallurgy wastewaters, respectively, have been developed and implemented. Such technologies are actively used mainly abroad, while in Russia their use is limited.

In general, an analysis of the mineral resource base of Russia and the existing problems of the mining and metallurgical complex show that for our country the development and implementation of biohydrometallurgical technologies is a promising direction and may be in demand in the near future.



TECHNOLOGIES FOR DEVELOPMENT OF MINERAL RAW MATERIALS OF THE KOLA PENINSULA: HISTORY AND PROSPECTS FOR ADAPTATION AND IMPLEMENTATION

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The large-scale development of the mineral resource base of the USSR could not but affect the development of reserves of the Khibiny massif of the Kola Peninsula, where the Kola Branch of the USSR Academy of Sciences was being created as part of a number of scientific institutes with experimental industrial buildings. The modern Kola Scientific Center of the Russian Academy of Sciences, having an accessible mineral resource base, carries out a range of high-tech developments aimed at its development together with companies in the mining industry in the region. The main directions of development of the Federal Research Center KSC RAS are conducting comprehensive science-oriented research and applied developments along the entire chain of reserves development from the search for promising deposits, the development of methods for opening and processing mineral raw materials to the production of basic intermediates and final products based on deep chemical processing. Among the examples of the most promising current projects in the development of the mineral resource base by the Federal Research Center KSC RAS is the development of the Kolmogorskoye lithium deposit, within the framework of which, after conducting an exhaustive chemical and mineralogical analysis and determining the composition of the delivered samples, approaches were proposed for lump pre-enrichment of ore using the flotation enrichment method to obtain concentrates for optimized hydrometallurgical sulfuric acid technology for opening spodumene concentrate. The second example is solving problems of improving the quality of products at AO «Apatit» in conditions of variability in the mineral composition of apatite-nepheline ores. The third is a project with AO «Apatit» to identify the prospects for commercial production and the sales market for products obtained by processing the enrichment of apatite-nepheline ore, as well as their volumes based on the results of the economic forecast.

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UNIQUE MARINE ECOSYSTEMS IN THE ORE-BEARING SEABED AREAS

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Currently, deep-sea research of the World Ocean has been developing dynamically because of the fast development of underwater robotics and bottom sampling technologies. Unexpectedly, high biodiversity has been found on continental slopes, abyssal plains and even in hadal trenches, and many hundreds of new species have been described from these deep-sea environments.

Our previous ideas on resources of the World Ocean are also being revised. Its biological, mineral and energy resources are increasingly considered as a determining factor in the future sustainable development of our civilization. With their rational use, they can cover the needs of all mankind for hundreds of years to come, providing future generations with practically inexhaustible sources of energy, mineral resources for industrial development, high-quality food and medicines.

The Northwestern Pacific is one of the most interesting regions of the World Ocean in terms of the landscape's diversity, biotope's variety and communities inhabiting them. It is also one of the most productive regions with the richest biological resources. Huge mineral deposits are also concentrated there: gas hydrates, barites, ferromanganese crusts and nodules, cobalt-rich manganese crusts, and deep-sea polymetallic sulfides.

For many years, NSCMB FEB RAS has conducted integrated field studies of deep-sea ecosystems in the Northwestern Pacific, including potentially ore-bearing seabed areas.

A comprehensive study of biological diversity in deep waters has led to the most interesting discoveries, forcing us to significantly reconsider our ideas about the quantitative and qualitative composition of deep-sea biota. A change in ideas about deep-sea biodiversity, including areas where mineral deposits are concentrated, has given rise to one of the urgent problems of modern deep-sea oceanology – the search for a scientifically based compromise between the extraction of valuable mineral and energy resources, the development of fisheries and the conservation of deep-sea ecosystems with their huge biological diversity ¹.

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INNOVATIVE PROCESSES OF STRATEGIC MINERAL RAW MATERIALS COMPLEX ORES BENEFICIATION AND DEEP PROCESSING

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Trends in the Russia's mineral resource industry development are largely determined by the transition to the nature-like technologies implementation. They can reproduce systems and processes of living nature in the form of technical systems and technological processes integrated into the natural environment and natural resource turnover (Strategy <http://publication.pravo.gov.ru/document/0001202402280003>); safe and resource-saving extraction of natural resources, as well as the need to involve in industrial processing refractory ores and technogenic resources, which are characterized by low content of valuable components, low-sized dissemination and comparable technological properties of mineral complexes. In this regard, it seems relevant to create innovative processes of concentration and processing of strategic mineral raw materials on the basis of various methods development for studying mineral substances, scientific substantiation and elaboration of methods for increasing the minerals technological properties contrast by creating a new class of selective reagents and the use of energy methods of impact on raw materials for selective disintegration and separation of mineral raw materials. The main deposits of rare (RM) and rare-earth (REM) minerals are systematized from the point of view of the main components and concentrator minerals content, and the main beneficiation methods. Technological ways of technogenic and poor raw materials engaging in processing in order to recover strategic metals are considered. The possibility of quantitative assessment of the influence of physical and energetic exposures on ore and processed products on the basis of interpretation of the results of thermogravimetric study, as well as by analyzing structural, phase and chemical transformations is substantiated. The directions of improvement for the selection methodology of technological solutions in flotation to choose selective reagents of directed action and topology of technological schemes are presented. Innovative technological solutions for combined technology of ore processing for some deposits of strategic mineral raw materials are given. Some aspects of application of digital technologies and artificial intelligence in beneficiation and processing are shown.

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MICROBIAL ECOLOGY OF SULFIDE CONCENTRATE BIOOXIDATION REACTORS AND THE POSSIBILITY OF OPTIMIZING BIOHYDROMETALLURGICAL TECHNOLOGIES

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The practical application of bioleaching (biooxidation) of sulfide ores and concentrates demonstrates that biohydrometallurgical technologies provide effective processing of mineral raw materials with relatively low costs and environmental risks. Biohydrometallurgical processes are performed by microbial communities, which include representatives of extreme acidophilic bacteria and archaea (genera *Acidithiobacillus*, *Leptospirillum*, *Sulfobacillus*, *Ferroplasma*, and *Acidiplasma*). Microbial communities that carry out the processes of reactor biooxidation of sulfide concentrates are currently actively studied. Modern molecular biological methods make it possible to study adaptive changes in microbial communities of bioreactors when shifting the conditions of technological processes.

In our studies, we investigated adaptive changes in the microbial population during the biooxidation of pyrite-senopyrite gold-bearing concentrate under different conditions: different temperature (from 40 to 50°C), different pulp densities, and the use of different additional carbon sources (carbon dioxide and molasses). It was shown that the use of carbon dioxide and molasses made it possible to neutralize the effects of such factors unfavorable for the biooxidation process as an increase in temperature and pulp density. Analysis of microbial populations of bioreactors using high-throughput sequencing of 16S rRNA gene fragments showed that when microbial communities of bioreactors adapted to different biooxidation conditions, qualitative and quantitative adaptive changes in the composition of communities were observed, including the predominance of poorly studied uncultivated groups of microorganisms under some conditions.

Further studies will make it possible to identify patterns of adaptive changes in the composition of microbial communities of bioreactors to regulate the activity of biooxidation processes.

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HYDROMETALLURGICAL PROCESSING OF LOW-GRADE CONCENTRATES OF NONFERROUS METALS

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Flotation beneficiation of sulfide ores is currently the main approach to obtain concentrates of nonferrous metals. At the same time, there are two main methods of flotation beneficiation: bulk and selective flotation. The first method includes predominantly intermediate steps of beneficiation, while selective flotation is used to obtain final products suitable for subsequent metallurgical processing. The increasing complexity of the composition of ores, ore mineralogical features (impregnation and intergrowth of minerals), as well as the similarity of the flotation properties of sulfide minerals, cause difficulties in separating sulfides and obtaining standard concentrates of nonferrous metals.

Promising methods of metallurgy, which can simplify ore flotation beneficiation schemes and increase the economic efficiency of production, are based on the processing of bulk sulfide concentrates. Biohydrometallurgy based on the biochemical activity of microorganisms is one of these methods. The role of microorganisms is to generate sulfide oxidants, to “clean” the surface of minerals from the formed reaction products, as well as to provide better access of the oxidant to the sulfide and high concentrations of the oxidant at the cell-mineral interface.

The efficiency of (bio)leaching is determined by the properties of sulfide minerals and the interaction during the formation of galvanic pairs in the reaction mixture, in particular. Thus, sphalerite (ZnS), pentlandite ($(\text{Ni,Fe})_9\text{S}_8$), violarite (FeNi_2S_4), and nickel-bearing pyrrhotite (FeS) are relatively readily destroyed in ferric sulfate solutions, while chalcopyrite is one of the most refractory minerals in these media. Selective oxidation of easily degradable minerals can be one of the promising areas of biohydrometallurgy, which allows complete extraction of one of the components (particularly, zinc and nickel) from a bulk concentrate. While most of the chalcopyrite remains in the leach residue, a high-grade selective concentrate (in particular, copper concentrate) can be obtained.

RESOURCE-SAVING METHOD FOR EXTRACTION OF LITHIUM FROM ORE MATERIALS AND LIQUID ENVIRONMENTS

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A new method has been developed for the extraction of lithium from pegmatite spodumene-containing ores and highly mineralized brines using sequential cyclic chemical processes with recovery of the leaching reagent in each cycle. This approach is important for the development of hard-to-reach deposits, where large costs are required for transporting raw materials or leaching reagents. For example, to obtain 1 ton of lithium carbonate from raw materials from the Kolmozerskoe deposit (Russia), 1.26 tons of concentrated sulfuric acid and more than 10 tons of feedstock are required. The possibility of using ammonium bisulfate instead of sulfuric acid, the consumption of which can be hundreds or thousands of times less, has been shown. This is due to the fact that one of the products of the interaction of ammonium bisulfate with aluminosilicates is ammonium sulfate, which, when heated, turns back into ammonium bisulfate. The results of laboratory experiments are presented for various stages of the process, from leaching to the final product. The proposed approach can also be effectively used to extract lithium from natural brines using sorbents or precipitants based on aluminum hydroxide. The cyclic bisulfate process makes it possible to maintain the selective properties of aluminum hydroxide in the working cycles of the process due to the dissolution of spent aluminum hydroxide and its return release in the form of freshly prepared aluminum hydroxide without the cost of imported reagents.



DEVELOPMENT OF METHODS FOR STRATEGIC METALS EXTRACTION FROM ORES AND PLACERS OF MAFIC- ULTRAMAFIC INTRUSIONS (PRIMORYE TERRITORY, RUSSIA)

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Within Primorye Territory a new promising type of mineral sources has been identified in Late Mesozoic mafic-ultramafic intrusions, in which strategically important metals (Ti, Au and Pt) are the main industrial components, and a wide range of high-tech elements (V, Nb, Nd, Co, Hf, Ce, Y, etc.) are the associated components. For critical metals extraction the methods of pyro-hydrometallurgy were applied. Thus, for placer objects, ammonium sulfate was used to isolate titanium dioxide, the most popular titanium-containing product on the world market, from a magnetic concentrate. Gold was extracted from a non-magnetic concentrate using leaching thiourea-thiocyanate solutions. The sludge produced by these reagents on the bulk material was used to isolate highly deficient metals. Finally, the use of pyro-hydrometallurgical processing techniques made possible the maximal extraction of the entire range of useful components without significant damage to the environment.

HYDROTHERMAL ACID LEACHING OF RARE METAL ORES OF THE CHUKTUKON DEPOSIT

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The Chuktukon deposit of rare metal ores is located in Siberia, 110 km north of the city of Kodinsk, Krasnoyarsk region. This deposit is unique. The basis of the ores are oxides of iron (~50%) and manganese (~10-15%). REMs are contained in phosphate forms. Their average content of oxides is about 4%, in some areas of the deposit it reaches 7%. The ores are extremely finely dispersed, the minerals are intergrown, which makes their enrichment impossible.

ICCT has developed a process for deep extraction of rare earth metals and dephosphorization of solutions by direct hydrothermal nitrate leaching of ores. The main leaching process is carried out at temperatures of 180-210°C with a solution of nitric acid. Under these conditions, iron(3+) oxides (hydroxides) remain in the sediment, rare earth metals are extracted into solution by 95-98%, phosphorus is reprecipitated to form poorly soluble iron phosphates. A technological scheme for processing ores with the extraction of rare earth metals and manganese has been developed.

In order to establish the mechanism of the main stage of REM leaching, a study of the process was carried out on model systems. REM phosphates (monazite) in the presence of iron(3+) oxides (hydroxides) were leached with hydrochloric, sulfuric and nitric acids. The process was carried out at different temperatures and acid concentrations. It was found that only nitric acid can be used for direct hydrothermal processing of iron-containing monazite ores. For this acid, quantitative recovery of lanthanides into solution can be achieved. Deep dephosphorization of solutions (phosphorus concentration less than 10 mg/l) is achieved due to the formation of poorly soluble giniite at temperatures above 180°C. It was found that giniite is formed along two routes: sorption of phosphoric acid on iron (3+) oxides (hydroxides) and precipitation from solution during the thermal decomposition of iron (3+) nitrate. Hydrothermal transformations are accompanied by the transition of iron (3+) oxides (hydroxides) into hematite, which is more stable in nitric acid.

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TECHNOLOGIES FOR RECOVERING OF LITHIUM FROM DOMESTIC MINERAL AND HYDROMINERAL LITHIUM RAW MATERIALS

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Recently, the world has seen a rapid increase in the demand for lithium associated with its use in lithium-ion batteries. This sets the country the task of searching and developing new mineral resources, creating new competitive technologies for extracting lithium from domestic raw materials. The history of the development of lithium production in Russia is closely connected with the history of the Institute of Solid State Chemistry and Mechanochemistry (ISSCM) SB RAS. In the 50s, Sc.D. Lileev I.S. developed a lime method for processing spodumene concentrate to produce lithium hydroxide. The technology was mastered at the Krasnoyarsk Chemical and Metallurgical Plant. Russia's growing need for lithium arouses interest in technologies for extracting lithium from hydromineral raw materials, the reserves of which in the form of formation waters from oil fields in the country are quite large. In the 1980s, fundamental work was carried out at the ISSCM SB RAS to study the processes of interaction of crystalline aluminum hydroxide (hydrargillite) with solutions of lithium salts. It has been shown that the interaction occurs due to the selective intercalation of lithium salts between hydrargillite layers with the formation of anionic derivatives of double aluminum-lithium hydroxide (DALH-An) [1], and DALH-Cl is capable of undergoing intercalation-deintercalation cycles. Based on DALH-Cl, a selective lithium sorbent was developed from lithium-bearing brines of calcium chloride and/or magnesium type. The Institute created a pilot plant for the processing of natural brines self-flowing into the quarry of the Udachnaya pipe, Yakutia. Scientific developments formed the basis of the sorption enrichment technology developed by Ecostar-Nautech company [2]. This process was later industrialized by a Chinese company to produce lithium carbonate from lake brines Dabsan Nur (Qinghai Province, China). The enterprise has been operating since 2012 and produces about 10 thousand tons of lithium carbonate per year.

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PROBLEMS AND PROSPECTS OF COMPLEX RARE METAL RAW MATERIALS OF MURMANSK REGION FOR THE PRODUCTION OF FUNCTIONAL MATERIALS

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Murmansk region is considered as one of the country's main raw material bases for the production of strategic materials containing titanium, niobium, tantalum, rare earth elements (REEs) and other rare metals. Most of the region's raw materials are complex, non-traditional types. This makes them difficult for their reprocessing. This report discusses titanium-rare metal raw materials, primarily loparite, perovskite and sphene. Their processing will help meet the needs of the domestic industry for modern functional materials.

The deposits exploited in the region are the following: apatite-nepheline ores (Khibiny - the main rock-forming minerals are apatite, nepheline, titanite, titanomagnetite, but only apatite and a small part of nepheline are extracted); loparite ores (Lovozero, only loparite is extracted). The Afrikanda deposit of perovskite-titanium magnetite ores (compounds of titanium, REEs, niobium and tantalum) has been prepared for development. The presence in the region of a developed infrastructure, innovative technologies for the extraction, dressing and processing of complex raw materials developed at Kola science center create favorable conditions for organizing the production of scarce and imported substitute products.

The main products from these raw materials include pigment and special grades of titanium dioxide, sulfate titanate salts as environmentally friendly tanning agents for leather, titanium-containing sorbents and catalysts, compounds of niobium, tantalum, REEs for various purposes and components of welding electrode coatings, building materials based on raw material processing waste. Rational conditions for processing raw materials and obtaining batches of target products for testing from potential consumers are being worked out in the project of the Kola chemical technology cluster implemented at Kola Science Center. This helps speed up the development and implementation of new technologies.



MINERAL-RESOURCE BASE OF URANIUM

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Currently, there are 38 power units in operation in Russia with a total installed capacity of about 30 GW and more than 30 reactors of domestic design are available, are being built or are planned to be built abroad. If one VVER-1000 reactor consumes about 20 tons/year of fresh nuclear fuel (enrichment of about 4-5% in U-235), then about 1000 tons are needed for 50 reactors. In terms of natural uranium, this amounts to 7500-8000 t/year, but less than 3000 t/year is mined, and about 5000 t/year comes from other difficult to replenish sources.

The balance reserves of uranium in Russia as of January 1, 2022 amounted to 707.7 thousand tons and, according to a number of indicators, we have one of the largest mineral resource bases (MRB) of uranium in the world. However, an analysis of reserves for the main geological and industrial types of deposits shows that about a quarter of the total volume is in operation, and the resources have an extremely high production cost or uranium is an associated element in complex rare earth ores (Ulug-Tanzegskoe, Katuginskoe, Stepnoe, Shargadykskoe, etc.).

The reproduction and development of the uranium MRB requires new approaches to improving the forecasting and prospecting complex, which is associated with the depletion of easily discovered near-surface objects and the need to direct geological exploration work to identify “hidden” deposits, including unconventional types, as well as with the assessment of the mineral resource potential of the territories of the Far East and the Arctic zone with very difficult landscape and climatic conditions.

It is proposed to identify and justify prospecting areas on the basis of multi-scale forecasting and mineragenic studies using a mineral systems approach that implements the “source → transport → deposition” paradigm. It is focused on creating genetic models of deposits (models of uranium mineral systems) with an emphasis on the genesis, composition and properties of ore-bearing fluids. In this case, a complex of methods of remote sensing of the Earth, GIS modeling and neural network technologies is used. This approach to forecasting and prospecting activities opens a new page in the reproduction of the uranium MRB and creates good prospects for the sustainable development of the domestic nuclear industry.

MINING TECHNICAL SYSTEMS OF THE FULL CYCLE DEVELOPMENT DEPOSITS SOLID MINERALS

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The mining complex in the Russian Federation (RF) and the world is one of the main sources raw materials for most industries. At the same time, it is currently forming the main negative effects on the human environment (atmosphere, hydrosphere, lithosphere). For example, more than 100 billion tons of solid waste alone have already been accumulated in the country's dumps, sludge and tailings dumps. About 10 thousand hectares of land suitable for agriculture are annually alienated for landfills. The storage of mining waste, in Russia as a whole, occupies over 500 thousand hectares of land, and the negative impact of waste on the environment is manifested in an area exceeding this area by 10-15 times. The activities of enterprises related to the extraction minerals form 93% the total volume waste in the Russian Federation.

One of the promising, ecologically balanced directions for the development of geotechnologies in the mining complex is the creation of mining engineering systems with a full cycle integrated subsoil development providing for the creation fundamentally new quality management systems for mineral flows natural and technogenic raw materials during their formation, movement, technogenic transformation and utilization in the developed space of quarries and mines with a combination of geotechnologies - open, underground, open-underground, physico-chemical.

The report shows methodological and theoretical approaches to the creation of full-cycle mining systems with the formation material and energy balances and minimizing the environmental impact on the environment using specific examples.



APPROACHES TO STIMULATE BIOLEACHING OF METALS

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Modern industry and economy depend on the availability of metals. The bottleneck is the extraction of critical metals, including valuable and rare earth metals (REM).¹ For their extraction, hydrometallurgical methods are used, including bioleaching from low-grade ores and waste from the mining and metallurgical industry.

Large-scale use of leaching microorganisms has technical difficulties associated with the preparation of biomass and their activation during the process. Recently, it has been shown that performance can be enhanced by using stimulating supplements as additional energy substrates for autotrophic bacteria or oxidizers.^{2,3}

An additional approach is to select microorganisms by analysis of their genomes. It allows to measure resistance of the selected strains to limiting conditions before any scalable testing.⁴

The most difficult stage in the targeted production of critical metals, primarily rare-earth metals, is their separation from the mixture. The most successful selective separation of rare earth metals is performed using specific proteins.⁵ At the same time, we have begun work that allows microbial separation of metals using cheaper methods - at the cell level.⁶

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MICROBIOLOGICAL TREATMENT OF CYANIDE AND RHODANIDE-CONTAINING EFFLUENTS OF MINING INDUSTRY

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Currently, methods of biological treatment of recycled waters and effluents of gold recovery plants for removal of rhodanides and cyanides have been developed both abroad and in Russia. The species composition of associations of microorganisms performing biodegradation of cyanides and rhodanides in industrial waters are actively studied. Special attention is paid to the technical support of the biodegradation process, which allows to intensify the process by reducing the oxidation time, increasing the adaptive resistance of the association of microorganisms to the increased content of rhodanides and cyanides in industrial waters. Applied association of microorganisms allow reducing the concentration of rhodanide in circulating waters from 1400 mg/l to 0.02 mg/l, and the concentration of cyanides from 20 mg/l to 0.01 mg/l. At the same time, water purified from rhodanides and cyanides can be used as process water in production. A retention time of about 1 d allows to remove 99.9% of rhodanide and cyanide. The main microorganism in these association is the bacterium *Thiobacillus thioparus*, capable of destroying the rhodanide ion [1].

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SPECIFIC ASPECTS OF GOLD EXTRACTION FROM PYRRHOTITE-CONTAINING MATERIALS

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Cyanidation is still one of the most common ways to extract gold, despite stricter environmental standards.

About 25% of all gold in the world is represented by persistent ores (difficult to cyanidation), including gold-sulfide ores with a high sulfur content.

Gold ore deposits are characterized by a variety of material compositions. The search for a profitable method of processing gold-bearing ores is associated with study the composition of ore, the forms of finding useful components, as well as the influence of impurity elements on the process of direct extraction of gold, or ore enrichment.

Technologies for conditioning (preparation) of raw materials before cyanidation, which include operations of ultra-fine grinding, oxidative atmospheric opening, roasting, bacterial and autoclave oxidation, as well as combining these operations, have found active application in industry.

The report examines the peculiarities of the behavior of pyrrhotite under conditions of pre-treatment and cyanide leaching, and highlights well-known technical solutions to suppress the negative impact of this mineral. The results of studies aimed at studying the characteristics of the material composition are presented, as well as experimental data obtained when assessing the influence of the following factors on the cyanidation process: the level of pH, the addition of lead-containing compounds, and the use of preliminary air treatment.

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NEW PARADIGM FOR ORE DEPOSIT FORECAST

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One of the most pressing problems of ore prospecting geology is the problem of forecasting ore deposits, or, in other words, the problem of allocating new areas for the search for ore deposits.

Since most of the easily accessible deposits lying on the surface or close to the surface have already been discovered, the identification of new promising areas cannot be carried out using traditional geological methods. Geophysical and geochemical methods come to the fore within the framework of the forecast, making it possible to identify the structural features and elemental composition of the earth's crust characteristic of areas with anomalous grade of useful components. Such features include, first of all, anomalies associated with the energy supply of the processes of redistribution, accumulation and transport of ore matter, as well as with its sources and "trap" structures¹.

According to the established concept, geophysical and geochemical data are interpreted by geologists, and geological interpretations are considered in terms of available models of ore districts and deposits. For near-surface accumulations, this approach makes sense, since the uncertainty (ambiguity) of interpretation is reduced taking into account the available geological observations, however, for hidden and buried areas and deposits, the direct use of geophysical and geochemical criteria for prediction purposes would be more preferable. To do this, it is necessary, first of all, to determine and geometrize such criteria for data that ensure uniform coverage throughout the entire forecast area.

As a rule, magnetic, gravimetric, and gamma spectral survey data, as well as satellite data, meet the uniformity condition. Geochemical, electrical prospecting, and seismic data can play, rather, a supporting role, since, as a rule, they do not meet the requirement of uniform coverage of the territory. The issues of geometrization of criteria and the association of ore objects with them were previously resolved in various ways.²

To move in this direction, it is necessary to determine an organization that will purposefully collect and process geophysical and geochemical data for the purpose of identifying areas promising for ore deposits.

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DEVELOPMENT OF TECHNOLOGY FOR PROCESSING COPPER-NICKEL ORES ENRICHMENT STELLAR TAILINGS, ADAPTED TO THE CLIMATIC CONDITIONS OF THE RUSSIAN FEDERATION ARCTIC ZONE

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Interest in sulfide-containing enrichment waste, in addition to the possibility of recovering non-ferrous metals, is due to the need to reduce the environmental impact, since during waste storage, heavy metals are converted into water-soluble salts and transferred to adjacent ecosystems. For the processing of substandard raw materials, the heap leaching method seems promising. However, to process enrichment tailings, it becomes necessary to granulate the material to increase the heap filtration properties. In difficult climatic conditions, it is advisable to granulate the tailings before a long period of below-zero temperatures, store the dump in the winter and leach it during the warm period of the year. The use of nitrogenous compounds as an oxidizing agent can intensify the recovery of non-ferrous metals¹.

The tailings were granulated using a 10% sulfuric acid solution as a binder, varying the solid:liquid (S:L) ratio. The resulting granules were irrigated with an oxidizing agent – a 0.5% solution of sulfuric acid (S:L = 10:1) containing the addition of NaNO₂ in an amount of 2 g/l. The final oxidizing agent was nitrous acid. The granules were stored for 90 days at -15 °C, and then heap leaching was simulated with distilled water (15 days) and a 2% H₂SO₄ solution (15 days) in laboratory columns (S:L = 1:5) at temperature about +20 °C. In the process of simulating heap leaching, 52.3% of nickel was recovered from granules prepared at a S:L ratio of 6:1; the maximum copper recovery was achieved at a ratio of 5:1 and amounted to 47.8%.

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PRODUCTION OF NICKEL, COBALT AND LITHIUM SALTS FROM RAW MATERIALS OF THE ARCTIC REGION FOR THE SYNTHESIS OF BATTERY MATERIALS

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Currently, Russia faces the task of organising the production of battery materials from its raw materials, which would eliminate dependence on the purchase of imported reagents. However, even though lithium, nickel and cobalt salts are mainly used in materials synthesis for lithium-ion batteries, their production from domestic raw materials is either absent or these salts are obtained in limited amounts. At the same time, there are large deposits of nickel, cobalt and lithium in the Arctic zone of Russia, and the necessary infrastructure exists to organise the production of the required salts from semi-products of Kola MMC and ore from lithium deposits on the Kola Peninsula.

The work aimed to obtain nickel and cobalt salts from products produced at JSC Kola MMC and lithium compounds from spodumene concentrate from the Kolmozersky deposit.

Pure nickel and cobalt sulphates were obtained by two methods. By the first method, extraction conversion methods based on extraction of the base metal with cation-exchange extractant from sulfate-chloride solution or after extraction from chloride-ion solution¹⁻² were used, which provided obtaining sulfate salts of reactive purity.

By another method, battery-grade sulphates were obtained by electrochemical dissolution in sulfuric acid of cathode nickel and cobalt, and the use of cathode trimmings and substandard metal made it possible to reduce production costs considerably.

Lithium salts were obtained by sulfuric acid processing of spodumene concentrate from the Kolmozersky deposit containing 5.6% lithium. Tests showed the possibility of extracting more than 96% of lithium from the concentrate, with subsequent production of lithium carbonate from the solution, successfully used in solid electrolyte synthesis.

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PROSPECTS FOR APPLYING THE BIOLEACHING METHOD FOR PROCESSING SULPHIDE RAW MATERIALS IN ARCTIC

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Currently, the issue of depleting reserves of copper-nickel ores suitable for processing by traditional enrichment methods is extremely relevant. Technogenic sources are becoming considered as a significant reserve of non-ferrous and precious metals for the mineral resource base promotion. Bioleaching is considered as a promising pathway for processing such raw materials, since it does not require high capital and operating costs and is successfully used to recover copper, zinc, nickel, and uranium from sulfide ores¹.

In our work, we studied the possibility of bioleaching of a number of useful components included in substandard and technogenic raw materials using a mesophilic culture of microorganisms isolated in the Murmansk region². The possibility of using a combined method for processing technogenic raw materials, including low-temperature roasting with ammonium sulfate, water-leaching of the roasted mixture and subsequent biological after-leaching of the residue, was investigated. The object of the research was a sample of industrial sands, which formed by washing out of copper-nickel ore tailings, as well as the dust of Minor Smelter and Nickel Plants (Norilsk, Krasnoyarsk Territory). The sample contained 0.32% Ni and 0.22% Cu. During water leaching of a mixture of industrial sands and ammonium sulfate roasted at a temperature of 400 °C, more than 70% of non-ferrous metals were recovered into the solution. Subsequent biological leaching of the residue made it possible to increase the total recovery of non-ferrous metals up to 90%.

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VIMS EXPERIENCE IN THE DEVELOPMENT OF INNOVATIVE TECHNOLOGIES FOR PROCESSING COMPLEX ORES OF STRATEGIC METALS

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VIMS has developed a combined technology for processing lithium-containing ores with a variable approach to their processing depending on the material composition: large-scale enrichment (radiometric enrichment/heavy-medium separation), deep enrichment (flotation/magnetic separation), chemical and metallurgical processing of spodumene concentrate (preliminary mechanical activation, sulfatization/thermochemical treatment/autoclave leaching), processing of a lithium-containing solution, a cycle for the production of lithium compounds of battery quality.

New flotation reagents have also been tested for processing beryllium-fluorite ores to produce high-quality fluorite concentrates and beryllium concentrates of the highest grade.

Non-standard technological approaches have been proposed for processing complex tantalum-niobium ores of various geological and industrial types (chemical conditioning of enrichment concentrates, extractive and thermobaric acid leaching¹) to produce commercial products: high-grade pyrochlore concentrate, tantalum and niobium oxides, collective rare earth concentrate, Sc_2O_3 , TREO, uranium chemical concentrate.

A rational technology for the enrichment of high-alumina chrome ores² has been developed, combining radiometric methods with roasting-magnetic refinement of chrome concentrate suitable for pyrometallurgical conversion.

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MECHANOCHEMICAL CONCENTRATING AND INCREASING THE SOLUBILITY OF RARE EARTH ELEMENTS FROM COALS AND ASH AND SLAG WASTES

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The use of mechanochemical treatment of coal is widespread across industries such as energy¹, carbon chemistry, pharmaceuticals², and agriculture, which includes the manufacturing of feed additives and plant growth stimulants³. These technologies align with the principles of green chemistry by being efficient and capable of streamlining processes, reducing temperature requirements, and minimizing solvent use. One of the promising directions of application of mechanochemical treatment of coal and its combustion products is concentration and increase of solubility of rare and rare-earth elements. Brown coal is a recognized alternative source of rare metals, which are dispersed irregularly between the organic and mineral fractions of coals. The aim of the work was to study the processes occurring during mechanochemical treatment of coal to find conditions for conversion of REEs into soluble form.

The potential for mechanochemical concentrating rare-earth elements in the organic component of brown coal is demonstrated. In the case of coal from the Azeyskoye deposit, which has a total REE content of 970 g/t, the method developed enables the transfer of 93% of REEs into the humic acid fraction of the coal, with an initial distribution of REEs between the mineral and humic fractions at 60/40

It was discovered that fly ash samples from the Novosibirsk region's two largest thermal power plants exhibit exceptionally high levels of gallium, exceeding 2000 grams per ton. Through mechanochemical processing of fly ash with humic acids, it has been demonstrated that a product with a water-soluble gallium content of 220 g/t can be obtained. Treatment of fly ash with the addition of humic acid yields a product containing dissolved gallium, strontium, barium, sulfur, and potassium in the aqueous extract. The development of electrolytic, chromatographic, biotechnological and sorption methods for the extraction of pure metallic gallium from such a solution seems promising.

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NOVEL REAGENTS OF NATIONAL ORIGIN FOR APATITE-CONTAINING ORES FLOTATIONAL ENRICHMENT

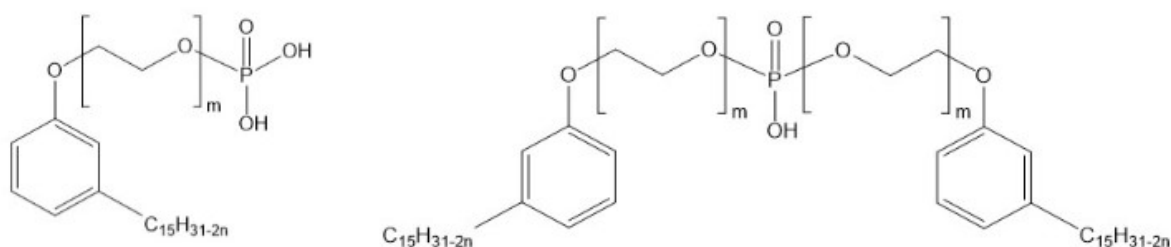
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Flotation takes one of the leading places among mineral processing methods. The flotation method is used in the processing of non-ferrous, noble, rare metal ores, apatite, fluorite and other ores. In this regard, expanding the range of nationally produced reagents is of great relevance from the point of view of both import substitution and the creation of new specimens.

In recent years, due to the deterioration of the apatite-containing ores qualitative composition, the Phospholan PE-65 reagent (Nouryon) has become widely used. A collector based on natural raw materials, an oxyalkylated cardanol phosphates namely was developed by PAO "Uralchimplast":



where $n=0,1,2,3$, $m=5-45$

Cardanol produced from the natural liquid obtained by cold extracting or pressing the shells of cashew nuts. Such reagents with $m=5,10,30,40$ and 45 being used as a part of a collecting mixture instead of Phospholan PE-65 showed their high efficiency and good foam-forming properties in laboratory testing. A closed cycle flotation of apatite-nepheline ore containing 14.1% of P_2O_5 resulted to an apatite concentrate with P_2O_5 content above 39% and recovery of 96.2-96.5% with their use.

The effect of said reagents was checked in industrial scale trials. With the use of the FE-10 reagent with $m=10$ as a part of the collecting mixture a standard apatite concentrate with a P_2O_5 recovery of 95% was obtained. The foam in the main flotation and cleaning operations was good loaded and easily destroyable.



CHEMISTRY OF NATIVE GOLD AND THERMODYNAMIC STUDIES OF GOLD-BEARING SYSTEMS

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One of the most important fundamental tasks of the theory of ore formation is the development of physicochemical models for the formation of gold-ore deposits. Although gold can form natural compounds with metals (Ag, Cu, Hg, Tl, Sn, Pb, Pd), chalcogenes (Te, S, Se) and metalloids (As, Sb, Bi) (41 minerals, <http://rruff.info/ima>), it occurs mainly as native metal in ores. Analysis of data on the chemical composition of native gold showed that it contains impurities of Ag, Hg, Cu and Pd. These elements form continuous or limited solid solutions with Au. Intermetallics of Au with Hg, Cu, Pd are known.

Thermodynamic studies of gold-bearing systems are typically conducted taking into account that gold is formed as a pure metal. In our calculations, which model the formation of pyrite-bearing ores in hydrothermal conditions, the origin of Au-Ag continuous solid solution was considered. This allowed us to prove that high-fineness gold is typical of gold-ore deposits of green-schist belts and Carlin type. Formation of electrum along with high-fineness gold was observed for alunite-quartz and Au-Cu-porphyry, and Au-skarn, Au-As, Au-Sb and Au-Te deposits. Electrum, kustelite and native silver are typical of Au-Ag adularia-quartz deposits.

Taking into account the chemistry of gold, we have estimated the standard thermodynamic properties of solid solutions in the systems Au-Cu, Au-Ag-Cu, Au-Hg, Au-Ag-Hg, and Au-Ag-Cu-Hg. On the example of Au-Hg-Sb from the Kyuchyus deposit (Yakutia), hypogene and hypergene models of formation of mercury gold. Scenarios of formation of Au-Cu intermetallics and solid solutions in Au-Ag-Cu-Hg system were modeled for some gold-ore deposits (Zolotaya Gora, Urals; Aitik, Sweden; Wheaton Creek, Canada).

The detailed study of the composition of mineral associations from the epithermal Au-Ag deposits in the Okhotsk-Chukot volcanogenic belt (Rogovik, Valunistoe, Korrida, Pepenveem, etc.) and results of thermodynamic modeling allowed us to reconstruct the main physicochemical parameters (T , fS_2 , fSe_2 , fO_2 , pH) controlling ore formation at these objects. The influence of these physicochemical parameters, as well as fTe_2 , on the mobilization, transport, deposition of Au and Ag and the composition of Au-Ag mineralization in epithermal deposits of Kamchatka was studied.

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MINERALOGICAL CRYSTAL CHEMISTRY OF RARE EARTH ELEMENTS: CONNECTION WITH THE PROBLEM OF ASSESSMENT OF THEIR DEPOSITS

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The raw material base of rare earth elements (*REE*) in Russia is specific; exploration and assessment of many deposits requires an original approach. In particular, it is important to have a good knowledge of the crystal chemical characteristics of *RE* minerals. The structural chemistry of *REE* has been well-developed on synthetic compounds, but the mineralogical crystal chemistry of *REE* has some specific features, of which three are important. 1) REE^{3+} occur in minerals not individually, but as a group, and each structure type has a special selectivity with respect to one or another *REE* subgroup. 2) *REE* are regularly distributed between minerals of different structural types, which makes it necessary to perform a crystal chemical analysis of their parageneses and evolution series. 3) Minerals in different natural systems demonstrate different features of the isomorphism of REE^{3+} with Ca, Na, Sr, Th and U^{4+} . The subordinate relationship between *REE* and Ca is effectively realized in Ca-enriched agpaitic silicate rocks; Thus, in the Khibiny massif, *REE* are mainly dispersed as an isomorphic admixture in apatite and titanite. In the Ca-poor Lovozero massif, *REE* show isomorphism with Na and are distributed between loparite and eudialyte. In the “rigid” loparite structure, REE^{3+} are included in the large-volume position, which determines its strict selectivity towards Ce and La. As a result: the *REE*-rich Lovozero massif will remain an industrial source of only *LREE* until an effective technology for processing eudialyte ores is created. In carbonatite systems, even rich in Ca, the relationship between *REE* and Ca is different due to the crystal chemical features of carbonates with these cations: calcite and dolomite are associated with *REE* carbonates without Ca or with $REE \geq Ca$. In Russia, small rich deposits in alkaline-ultrabasic massifs are typical, where carbonatites are enriched in Na, and *REE* substitute Sr (burbankite and ancylite carbonatites of Vuoriyarvi, Seblyavr, etc.). An important for Russia type of *REE* deposits (*Y* and *HREE*) is related to alkaline granites (Katugin, Ulug-Tanzek, Western Keivy objects). Their ores are typically polymineral, and the distribution of *REE* between minerals is contrasting, and an understanding of its patterns is important. For deposits in weathered carbonatites (Tomtor, Chuktukon, Belaya Zima), it is important to identify phosphates of the monazite, rhabdophane and churchite groups, which are similar in properties in aggregates, but differ in their affinity for certain *REE* subgroups.



PROSPECTS FOR THE USE OF BLASTING INJECTION OXIDATION AND ORE LEACHING IN THE DEVELOPMENT OF DEPOSITS OF STRATEGICALLY IMPORTANT MINERAL RAW MATERIALS

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The effectiveness of underground leaching of valuable components from ores is determined by the formation of a system of microcracks in ores during blasting preparation and the intensity of mass transfer processes during subsequent irrigation with leaching solutions. It is proposed to increase the development of leaching solution-filtrating microcracks in blasted ore and the level of oxidation of ore minerals by combination of blasting disintegration of ores and their treatment with high-temperature vapors of oxygen-containing reagents penetrating through the forming microcracks under the pressure of explosive gases into the blasted ore mass. This solution is implemented by placing of containers with aqueous solutions inside the borehole charges. Reagent places in boreholes under the thermobaric influence of explosive gases, transform into a plasma state with the formation of highly active oxidizers of ore minerals: ions, radical ions and oxygen radicals (O^{2+} , O^{\cdot} , O^* , $O^{\cdot*}$) and its compounds with hydrogen (HO_2 , OH^*). Subsequent leaching of ores prepared using this technology is more effective, the extraction of valuable components from them increases significantly (table 1).

Table 1. Results of blasting experiments with reagent addition and subsequent leaching

Recovery of precious component, %	Characteristics of model material		
	Molybdenum ore Gitche-Tyrniauz	Cemented gold- bearing flotation tailings, Darasun mine	Cement-sand mixture with evenly distributed copper powder
Standard blasting and subsequent leaching	43,8	63,5	11,0
Blasting with reagent addition (injection blasting) and subsequent leaching	76,5	85,6	94,3

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ONTOGENESIS OF NATIVE GOLD IN BROWN COALS

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We have studied the morphostructural features and chemical composition of micron and submicron particles of native gold from brown coals and overcoal sediments of the Yerkovetskoe Deposit Zeya–Bureya Sedimentary Basin (East Russia). The samples of coals and host rocks in the form of thin sections, as well as coal particles and grains of native gold obtained during the process of dispersion and fractionation of loose and crushed samples divided according to size and density, were analyzed using the scanning electron microscopy in combination with X-ray microanalysis involving various visualization modes.

It was revealed that native gold is syngenetic with the mineralization of brown coals, and microphases dispersed in the minerals of overcoal loose and sandy-clay sediments were the source of native gold. In coals, gold is accumulated at the stages of formation (alluvial and eolian, including terrigenous and ionogenic subtypes) and diagenesis of coal deposits (ground-infiltration subtype). A significant part in the mineralization process of coals and formation of microparticles of native gold was contributed by descending water infiltration of polycomponent colloid solutions. During the dehydration, hydrogels are transformed into iron hydroxysiliconized xerogels, mineral phases are formed which have a varying composition, floccular structure and encapsulate submicron gold particles. The shell that covers all microparticles of gold has identical origin and composition. Coal beds that border host rocks are an open system with constant inflow of substance, which leads to the gradual formation of polycomponent aggregated particles in micro cavities. Part of gold in coals occurs as sulfur-bearing complexes dissolved in pore water.

The key factor in the migration and deposition of gold in coals is the role of inorganic substance involved in the processes of coal mineralization. Organic substance plays a more passive role and has medium-forming (colloid, molecular and ionic sieves) and accumulation functions.

This research was carried out within the framework of the state assignment of IGNM (FEB, Blagoveshchensk) (No 224022000193-7) and IGM (SB, Novosibirsk) (No. 122041400237-8) of the RAS.



LITHIUM DEPOSIT TYPES, THEIR DISTRIBUTION IN GEOLOGICAL TIME AND SPACE, ROLE IN THE MODERN RAW MATERIAL BASE

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Currently, 6 types of lithium deposits are of economic importance: pegmatite, granite, clay, salar, geothermal, oil-and-gas fields. A brief description of them is given, the distribution of their resources in geological time (Fig.) and by geological structures is shown, and the role of each type in the explored resource base and in global production is demonstrated.

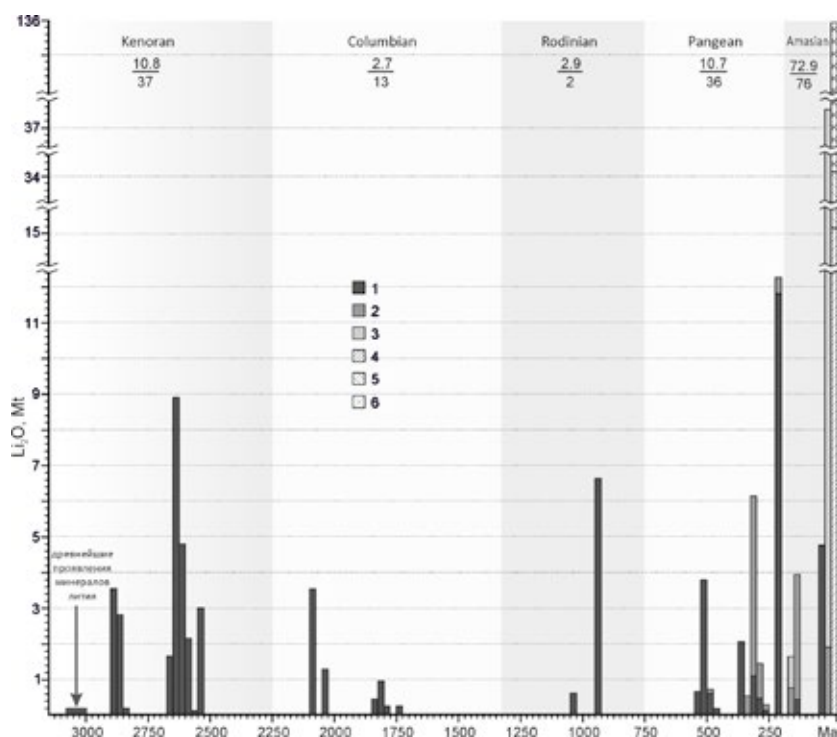


Figure. Distribution of resources of different types of lithium deposits on the geological time axis. Numbers under the names of supercontinent cycles: numerator – the share of a corresponding cycle deposits in the total resources of the entire sample (%), denominator – the number of deposits. Symbols for deposit types: 1 – pegmatite, 2 – granite, 3 – clay, 4 – geothermal, 5 – oil-and-gas fields, 6 – salar.

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STRATEGIC METALS IN THE ORES OF THE URAL DEPOSITS

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An overview of the problem of strategic and critical minerals of the Russian Federation, a significant proportion of which is contained in folded belts, the largest of which is the Urals, is made. The focus is on high-tech minor elements and by-product components of ores extracted in non-ferrous metallurgy – Co, In, Ga, Ge, Re, Tl, Te, Cd, Se. There is a high and growing demand for most of them in the world, but their accounting in the Russian Federation, in fact, has not been established. As a rule, the products of the mining and metallurgical complex are not analysed along the production chain, including intermediates and waste (and these elements are not only valuable, but also toxic).

The paper considers the problem of minor elements – the forms of their occurrence and ways of extraction: Re – in porphyry deposits; In, Co, Cd, Ga, etc. accumulator and energy metals – in pyrite, copper-skarn and Au-sulphide deposits. The sulphides of VMS ores are especially enriched with scattered elements, these are Co, Cd, In, Ga, Ge, Sb, Se, Te, sometimes Tl and Bi (tens and hundreds of ppm, up to thousands of ppm), the contents of which vary widely depending on the paleotectonic environment of ore deposition, which determines the typification of the deposits.

Global development and scientific and technological progress are intensifying the use of mineral raw materials – the necessary basis for the production of high-tech products. Russia, like other advanced manufacturing countries of these products (USA, EU, etc.), is in dire need of various raw materials that are “critical” for its economy. The State needs to ensure stricter accounting and stimulate the growth of the complexity of processing and encourage the extraction of associated components. In the field of mineral extraction and its use, it is necessary to reduce the dependence of the domestic economy on imports. Expanding self-sufficiency should become a priority of the long-term strategy of the Russian Federation in the field of mineral resources.

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SUSTAINABLE LIQUID EXTRACTION PROCESSES FOR RECYCLING OF MINERAL RAW MATERIALS AND WASTES

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Hydrometallurgical processes for the extraction, separation and purification of substances are an integral part of most technologies for processing mineral raw materials and wastes. In this regard, the development of technological processes for separating the components of liquid mixtures is a task whose relevance is increasing every year. One of the most accessible, universal and effective methods for the extraction, separation and purification of substances is liquid-liquid extraction and hybrid processes based on it.

To date, a significant scientific background has been formed in terms of the development of promising extraction systems based on ionic liquids and deep eutectic solvents, which provide new degrees of freedom in controlling the selectivity of extraction separation¹⁻³. The implementation of these approaches to solve production problems requires modern hardware^{4,5} and solutions to problems associated with scaling these processes.

The presented report will examine the key issues of using extraction and hybrid methods based on them in hydrometallurgical chemical-technological processes for the extraction, separation and purification of substances, which is of paramount importance in solving the problems of forming the technological sovereignty of the Russian Federation.

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BISMUTH: RAW MATERIAL BASE AND CONCENTRATE PROCESSING TO OBTAIN HIGH PURITY BISMUTH AND ITS COMPOUNDS

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Russia takes one of the leading positions in the world in the reserves of bismuth. The main bismuth ore regions are North Caucasus, Far East, Ural, the Altai Territory, and the Chita Region.

Bismuth consumption in the world is currently 21 thousand tons per year, with annual average growth rate 5,8%. In these circumstances, 77% of bismuth is used in the form of its compounds¹. Bismuth compounds are synthesized from Bi 1 grade metal (Bi not less than 98%), which is obtained by pyrometallurgical processing of lead, copper, tin, and molybdenum-tungsten concentrates containing bismuth at a level of 0,1–2,0%. The lead-bismuth alloy containing 6–40% bismuth is obtained at the initial stage of processing.

The reasonableness of lead-bismuth alloy processing according to the hydrolytic technology is demonstrated, resulting in the formation of high-purity bismuth compounds omitting the complicated stages of electrolysis and refinement, which are connected with obtaining metal bismuth of Bi 1 grade. The method is based on alloy dissolution in nitric acid and subsequent purification of the lead-containing solution from bismuth by its precipitation within pH range 1,0–1,5 in the form of basic nitrate having the composition $[\text{Bi}_6\text{O}_4(\text{OH})_4](\text{NO}_3)_6 \cdot \text{H}_2\text{O}$.

It has been determined that high-purity bismuth compounds can be obtained in the interaction of basic bismuth nitrate $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$ with the solutions of acids: citric, gallic, tartaric, oxalic, as well as nitric, hydrochloric and sulfuric.

The possibility to obtain bismuth of Bi 0000 grade (not less than 99,9999% Bi) by adding high-purity bismuth oxide and sulfur to sodium hydroxide melt at a temperature of 500 °C is demonstrated.

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SYNERGISM OF ETHOXYPHOSPHATE AND SODIUM OLEATE MIXTURE IN AQUEOUS SOLUTION

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Aqueous solutions of anionic surfactants are widely used in the practice of flotation enrichment of non-sulfide ores. At the same time, there is a lack of information on the physicochemical patterns of action for the compositions currently used in manufacturing.

The study of the mixture of mono- and diisononylphenol ethoxyphosphoric esters and sodium oleate demonstrates the occurrence of synergism in aqueous solutions (Table 1), as well as the improvement of apatite flotation characteristics¹ (Figure 1).

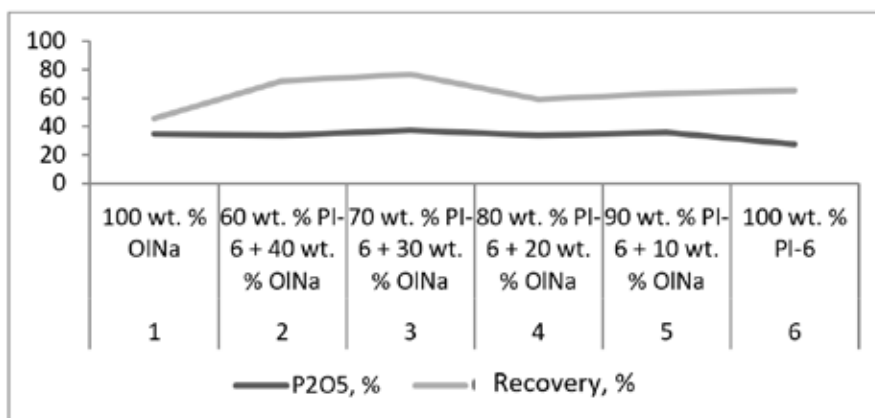


Figure 1. Dependence of recovery rate and P2O5 content in concentrate during froth flotation of apatite from apatite-nepheline ore

Table 1. Thermodynamic parameters of surfactant micelles in aqueous solution

m_{pl}/m_{ol}	α_{ol}	C_{ol-pl}	x_1^m	β_m	f_{ol}	f_{pl}	$\Delta G_m, \text{ kJ/mol}$
1:1	0,75	$7,14 \cdot 10^{-5}$	0,042	-10,58	$6,0 \cdot 10^{-5}$	0,98	-17,68
7:3	0,63	$5,73 \cdot 10^{-5}$	0,17	-14,59	$3,5 \cdot 10^{-5}$	0,65	-16,20

The obtained experimental data allow us to recommend the mixture for industrial use.

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ELECTROCHEMICAL CULTIVATION OF ACIDOPHILIC MICROORGANISMS – PROSPECTS FOR INTENSIFICATION OF BIOHYDROMETALLURGICAL PROCESSES

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Bacterial oxidation of gold-bearing sulfide minerals is currently considered as one of the promising methods used for gold dissection. At the same time, the concentration of microorganisms often becomes the main limiting factor of the bacterial process. One of the approaches to obtaining high concentrations of bacteria on iron solutions is reactors developed at the Institute of Biophysics SB RAS for growing large concentrations of iron-oxidizing bacteria with conjugated electrochemical reduction of iron, allowing to grow up to 15-20 g/l of biomass *A. ferrooxidans* in continuous operation [1].

The following areas of application of biomass of iron-oxidizing microorganisms grown in an electrochemical reactor are possible. Use in the mining industry, in heap, underground and vat bacterial leaching of ores, tailings, dumps and concentrates of non-ferrous and precious metals. In case of heaps, it is an extension of the time of seasonal work on heaps due to an early start in the spring and a late end in the autumn. Due to the high concentrations of microorganisms, the lag phase of starting the pile and the more intensive oxidation of its sulfide part decreases. During underground leaching, the intensification of oxidation processes is due to the high concentration of microorganisms. At stirred-tank reactor, it accelerates the output of BIO workshops to design indicators, faster restoration of the process, in case of its technological failure.

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PROCESSING PROSPECTS OF WASTES FROM MINERAL PROCESSING PLANTS OF EPITHERMAL DEPOSITS

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Recently, worldwide has begun to pay great attention to solving environmental issues and comprehensive use of non-renewable resources, including resources of “primary” mineral deposits through the processing of technogenic mineral raw materials contained in mining waste. The most relevant objects of research are tailings dumps, represented by products of processing of volcanogenic massive sulfide, base-metal, gold and alluvial deposits.

Ore bodies of epithermal deposits contain from 1-3% to more than 20% of ore minerals (mainly sulfides: pyrite, chalcopyrite, sphalerite, galena, arsenopyrite), depending on the genetic subtype of the object and the characteristics of the host rocks.¹ In the “primary” ores of such deposits gold (native gold, sulfides, tellurides and selenides of gold) is often observed as finely dispersed dissemination in a predominantly quartz vein matrix, and also as inclusions in sulfides.

The main technology for extracting precious metals from ores of epithermal deposits is cyanidation, as a result of which up to 90% of gold is extracted. But in the case of the refractory ores (fine gold or inclusions of gold minerals in sulfides) presence at the deposit, cyanidation is characterized by even lower amounts of extraction of precious metals.² As a result, metal residues that are not sufficiently extracted from the ore end up in tailings, where further migration of gold and associated elements occurs from primary ores to supergene ones, with superimposed anthropogenic specifics.

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RESEARCH OF THE PROPERTIES OF MINERAL SORBENTS

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Due to its high thermal stability, mechanical strength and chemical inertness, natural materials are widely used in various industries. On the territory of Astrakhan, there are large reserves of opoka and marl minerals, creating promising objects for solving modern environmental problems¹. This study is devoted to the study of the properties of opoka and marl.

The results of electron microscopic images (SEM Hitachi TM3030) allow us to note that marl and opoka are mesoporous materials, but differ in their morphological characteristics. In opoka, layered prismatic elements predominate and the surface is heterogeneous, containing many impurities, the pore size varies from 8 to 20 nm. Marl is characterized by lamellar stratification; the size of the visible pores is 4 to 10 nm. X-ray diffraction patterns show that the main crystalline phase of opoka is silicon dioxide. The marl peaks correspond to calcite and quartz.

Information obtained with an energy dispersive spectrometer (EDX Quantax 70) on the local elemental composition and the distribution of elements on the sample surface according to SiO_2 content confirms that opoka belongs to the diatomite type and the marl belongs to the class of montmorillonite. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of marl is 13, that of opoka - 26, indicating the presence on the surface of strong acid centers that exhibit the greatest activity in the cation exchange process.

Structural characteristics were evaluated by the material's specific surface area and its porosity using the BET method based on nitrogen adsorption data (Gemini VII 2390 (V1.02t), Micromeritics) at 77 K. It has been established that the specific area of the flask ($S_{\text{ar}} = 94 \text{ m}^2/\text{g}$) is 9 times larger than that of marl ($S_{\text{ar}} = 11 \text{ m}^2/\text{g}$); the same pattern is observed in terms of volume and pore area (volume is 7.5 times larger, and the area is 20 times).

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ADVERSE OXIDATION-REDUCTION REACTIONS DURING DIRECT ALKALINE EXCESS OF TOMTOR ORES

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The Tomtor deposit is a unique raw material source of rare earth elements and niobium in terms of their content and reserves in ores. The main rare metal minerals of the ores are monazite ((Ce, La, Y)(PO₄)) and strontium-barium pyrochlore ((Sr, Ba)(Nb₂O₆)). In the same time, due to the fine particles and strong mutual splice of mineral particles, these valuable mineral components cannot be extracted and purified by enrichment methods, and the processing of ores requires their direct chemical decomposition.

When carrying out hydrothermal alkaline opening of Tomtor ore (a common method of monazite extraction), active gas formation and the formation of stable foam filling the reactor, unusual for this process, were found, which significantly complicates the technological process. It is shown that the resulting gas is hydrogen, formed due to occurrence of oxidation-reduction reactions of sodium hydroxide solutions with gangue minerals. During the research, data were obtained on the effect of process temperature and sodium hydroxide concentration on the rate of hydrogen evolution and the depth of the process. It was established that for the studied sample of a representative sample of ore, the volume of hydrogen produced is approximately 6-7 liters per kg of ore. Studies of these systems have shown that the main reason for the formation of hydrogen is the oxidation-reduction decomposition of highly dispersed pyrite by an alkaline solution. Under these conditions, siderite decomposes to form iron(2+) hydroxide when the process is carried out in an inert atmosphere or hematite - the process is carried out in an oxygen atmosphere.

Preliminary studies have been carried out to identify the causes of the formation of persistent foam. It is assumed that its stability is due to the formation of a structural-mechanical barrier due to the adsorption of ultradisperse hydrophobic particles at the interface between the aqueous and gas phases. Taking this into account, conditions for smooth alkaline leaching of Tomtor ore without side foam formation were found.

The study was carried out with the financial support of the Russian Science Foundation, project No. 23-63-10017.

APPLIED GEOCHEMISTRY OF THE FEDOROVA-PANA PLATINUM-BEARING COMPLEX

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The Fedorova-Pana layered ultramafic-mafic Complex (FPC) in the center of the Kola Peninsula is the main part of the Kola Platinum-bearing Province, the second largest in terms of reserves of platinum group elements (PGE) in the Russian Federation¹. The distribution of reserves between poor and rich mineralization, with a sharp predominance of the former, prevents the start of exploitation of the province's deposits. This distribution does not coincide with the usual proportions for layered intrusions², when rich reef-style PGE mineralization prevails, which suggests further prospecting for this type of mineralization. The FPC contains seven reef-style horizons³, among which three PGE deposits were discovered and put on the state balance sheet. The idea of mineral magmatic systems (MMS) of the FPC, based on the similarity of geochemistry of layered strata and reef-style mineralization located within them, should contribute to the success of prospecting. Four MMS^{4,5} can be distinguished in the FPC: 1) Pd/Pt=8–12 (South Reef); 2) Pd/Pt=4–6 (North and A reefs); 3) Pd/Pt=2–3 (B and FT-1 reefs); 4) Pd/Pt<1 (C and FT-2 reefs). The second (main) MMS, including the North and A reefs with a total length of about 35 km, is the most promising in terms of growth of rich mineralization reserves. Only one third along the main MMS has been studied in detail at depth. This third includes the Kamennik and Kievev deposits in the North Reef, which are 5 and 6 km long, respectively. Reefs from minor systems have rather complicated structure, but the example of the third MMS (Pd/Pt=2–3) with the 1-km-long East Chuarvy deposit discovered in the B Reef indicates the possibility of ore bodies formation in such conditions⁴. Thus, the sum of geochemical data on PGE mineralization of the FPC allows outlining a prospecting strategy aimed at a discovery of a large and rich PGE deposit.

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EXTRACTION OF CRITICAL METALS FROM INDUSTRIAL WASTES OF COAL COMBUSTION

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Solid waste from coal combustion is characterized by large volumes of formation and the need for disposal. From a processing point of view, dry selection ash, or fly ash (also known as fly ash), is of greatest interest. Analysis of the composition of ash (Table 1) showed that it can be a technogenic source of scarce metals - aluminum, titanium, zirconium, rare and noble metals. Due to the increased content of heavy metals concentrated in it during combustion and disposal, ash can be classified as a higher hazard class (IV) than ash and slag waste in general (V). Therefore, it is advisable to process this ash separately.

Table 1. Contents of main (%) and *valuable (g/t)* elements in the ash sample

Si	Al	Fe	C	Ca	Ti	Zr	Co	V	Y	Ce	La	Ga	Ag
27,1	11,3	2,6	2,4	1,5	0,7	429	276	154	51	50	43	30	18

Complex processing of dry fly ash with the extraction of valuable metals is relevant due to the classification of aluminum, zirconium, titanium, manganese, vanadium, cobalt as critical types of mineral raw materials, as well as the presence of impurities of rare earth elements in the ash (including critically important yttrium and neodymium).

In order to increase the efficiency of extracting valuable metals from ash, a combined scheme for the extraction of aluminum and other scarce metals has been proposed and effective modes of magnetic separation, sintering with alkaline reagents, and acid leaching with ultrasonic intensification have been substantiated.

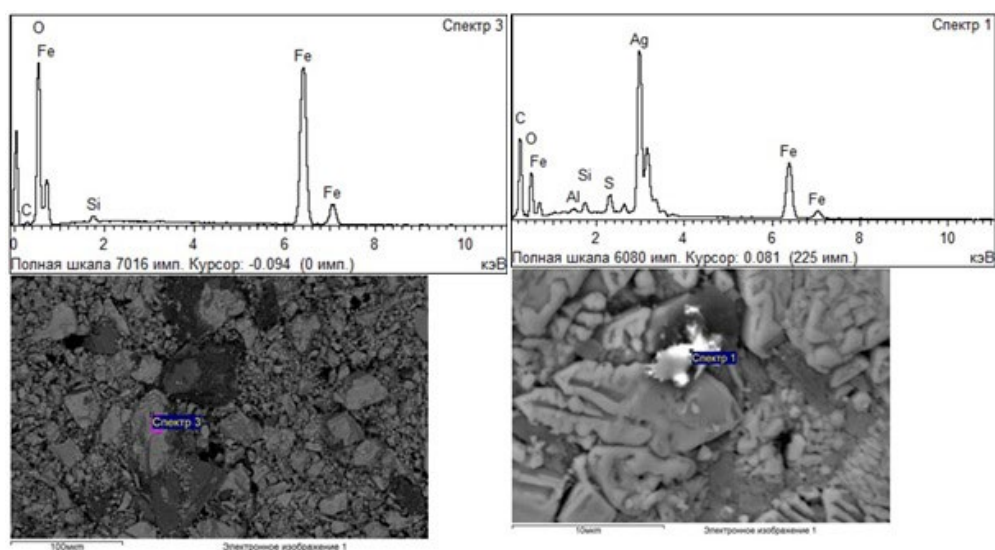
Increasing the completeness of the opening of the refractory mineral phases of the ash is achieved by converting some of the leaching-resistant mineral forms into more soluble ones under the developed firing conditions, as well as by using a combination of acidic reagents during leaching with the formation of strong oxidizing agents (peroxodisulfuric acid) and ultrasonic intensification. As a result, an almost complete 99% recovery of aluminum, lanthanum, cerium, cobalt, 63% of vanadium, 61% of zirconium, 57% of yttrium was achieved.

THE CHANGES OF STRUCTURAL IN IRONIC QUARTZITES UNDER THE IMPACT OF LASER RADIATION

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Currently, methods for the effect of energy fluxes on matter are becoming increasingly interesting¹. The article presents the results of a study of ferruginous quartzites during pulsed laser processing. One of the promising directions is the laser treatment of finely dispersed mineral media². Electron microscopic examination revealed the identification of silver in ferruginous quartzites.



Drawing of a sample of the initial ferruginous quartzite and after laser treatment

Surface structuring is necessary both for the analysis of mineral raw materials and as one of the ways to improve technological solutions for the extraction of valuable components.

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APPLICATION OF PHYSICO-CHEMICAL MODELING IN THE DEVELOPMENT OF WASTE (USING THE EXAMPLE OF GOK, MURMANSK REGION)

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The need to develop and implement technology for processing secondary REE resources is caused by the intensive growth of global consumption of them as critical components for many high-tech industries¹. A promising source of REE can be attributed to the tailings of Lovozersky GOK, which are waste products resulting from the production of loparite concentrate and contain on average up to 1% TR₂O₃. The purpose of the work is to study the effect of temperature and concentration of nitric acid on the forms of finding and concentration of REE and other elements using physico-chemical modeling² with boundary conditions of the model - 100 g of rock, 2.4 and 7.2 M HNO₃, T= 80-130°C, P = 1 bar, the degree of interaction “rock-solution” - from -7 to 0. The simulation results at the specified temperatures and concentrations of nitric acid showed the transition into solution of all elements contained in the rock and their forms: Al³⁺, SiO₂, Zr⁴⁺, La³⁺, Ce³⁺, UO₂²⁺, Li⁺, Fe³⁺, Ca²⁺, Na⁺, Ba²⁺, Cd²⁺, Zn²⁺, Ni²⁺, Cu²⁺, HSeO₃. An increase in the acid concentration has a significant effect on the leaching process.

The presence of Al³⁺ and SiO₂ in the system indicates the degree of decomposition of aluminosilicates, which causes gelation in solution, which complicates technological processes.

The use of modeling makes it possible to clarify the forms of elements in solution, which should help optimize the leaching process in order to extract REE and recycle waste.

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The work was carried out with the financial support of the Russian Science Foundation, project 24-17-00114.

DIRECTED CONCENTRATION OF USEFUL COMPONENTS BY NATURE-LIKE UPWARD FILTRATION MASS TRANSFER IN ANTHROPOGENIC OBJECTS

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The new technology of upward capillary mass transfer of useful components fluids within the framework of a new paradigm in subsoil development “field cultivation” includes a full cycle of the sequence of natural processes directly in the array: transition into solution; directed filtration through the array capillaries to the surface; concentration of useful components compounds on physical and geochemical barriers in the near-surface zone of the array; accumulation and formation of concentration zones. The upward movement of solution through the capillaries of the array is due to the natural mechanism of capillary movement of solutions in the array with possible strengthening of the pressure gradient for directionality and control. The technology allows extracting useful components from arrays of both natural and anthropogenic origin after their orderly immobilisation in the near-surface zone. Capillary upward movement of the solution provides the most complete and constant contact of the liquid with the massif material when passing through capillaries and guarantees extraction and mass transfer of the useful component as part of the productive solution to the surface. Formation takes place in the massif at the place of occurrence due to natural geological processes. The greatest values of substance concentration have a layer on the surface.

The processes of formation of new ore bodies have been experimentally substantiated and variants of technological solutions have been proposed. The proposed direction makes it possible to radically increase the resource base of the country through the involvement in profitable development of small deposits (ore occurrences) and wastes of enrichment and metallurgical production. The proposed approach is economically efficient and environmentally safe.

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ISOTOPE-GEOCHRONOLOGICAL MARKERS OF ORE PROCESSES IN DEPOSITS OF STRATEGIC TYPES OF MINERAL RAW MATERIALS IN THE NORTH-WESTERN SECTOR OF THE RUSSIAN ARCTIC (MURMANSK REGION): NEW APPROACHES AND PROSPECTS

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Studies of isotope-geochronological and isotope-geochemical characteristics of ore deposits in the Kola region represent a relevant area of scientific research due to the region's significant potential for mineral resource extraction. The use of modern methods of isotope analysis to determine the age and isotopic parameters of the genesis of ore formations, including the use of ore minerals-geochronometers, allowed to clarify the history, conditions of formation of deposits and the place of ore genesis in the evolution of ore-magmatic systems of the region.

Using complex (U-Pb for zircon and baddeleyite + Sm-Nd for rock-forming and ore minerals) dating, the main boundaries of the formation of the main Cu-Ni-PGE deposits of the Fennoscandinavian Shield were established and confirmed: syngenetic oreogenesis 2.53-2.48 billion years, hydrothermal-metasomatic ore formation at 2.47 billion years, introduction of additional portions of ore-bearing magmas at the 2.45-2.44 billion years stage, and late metamorphic reworking of rocks with formation of redeposited ores at the 2.0-1.9 billion years stage. As a result of Sm-Nd isotope dataset analysis of data on ore minerals from a number of Cu-Ni-PGE, Fe-Ti-V deposits and Mo-ore occurrences in the Karelian-Kola region, promising isotope-geochemical markers were found, which provide information on the nature of ore-forming fluid during secondary processes and are applicable for reconstruction of the sequence of sulfide mineral formation. The presented approach has been tested and has prospects for application in other regions of the country and the world, which contributes to the development of isotope research methodology aimed, among other things, at optimizing efforts in the mining industry.

The work was carried out within the framework of the research project of Geological Institute of the Kola Science Centre of the Russian Academy of Sciences No. FMEZ-2024-0004.

THE POTENTIAL OF HELIUM PRODUCTION IN THE OIL AND GAS CONDENSATE FIELDS OF THE REPUBLIC OF SAKHA (YAKUTIA) TO ENSURE THE SOVEREIGNTY OF THE RUSSIAN FEDERATION IN STRATEGIC RAW MATERIALS

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Helium is a unique strategic raw material, which is commercially contained only in natural gas. 22 oil and gas condensate fields containing helium in industrial concentrations have been discovered on the territory of Yakutia, which makes it possible to consider the territory of Yakutia as the basis for the integrated development of the Russian helium industry. Currently, natural gas production in the region is carried out without the release of helium as a separate commodity product. If measures are not taken to create a system for collecting, transporting and storing helium, then within 20 years the total loss of helium can reach 1 billion m³. The market potential of helium in Yakutia is estimated at more than 40 billion rubles.

In this regard, the implementation of a new infrastructure project for the helium extraction and the collection of helium concentrate at oil and gas production sites with the creation of a product pipelines system and storage facilities is becoming highly relevant in terms of increasing the economic efficiency of natural gas production, rational use of natural resources, and import independence of the Russian economy.

The research presents the analysis and selection of geological objects with the prospect of helium concentrate long-term storage near the developed deposits to preserve the helium resource. The advantages and disadvantages of storing helium concentrate by reverse injection of helium into formations, in salt caverns, in isolated deposits of depleted oil and gas condensate fields have been determined. The sites on the territory of the Republic of Sakha (Yakutia) suitable for these types of storage have been allocated.

When solving the problem of reducing helium losses during pipeline transportation of helium-bearing natural gas and helium concentrate in a cold climate, it is important to develop frost-resistant polymer materials with high sealing ability. The work presents the technology of plastic deformation of polymer blanks based on polytetrafluoroethylene (PTFE). The materials were tested for helium permeability.



OBTAINING BARITE FROM TECHNOGENIC DEPOSITS OF THE SALAIR RIDGE

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Issues of ensuring technological sovereignty and import substitution of critical raw materials are the most pressing tasks facing Russian science. Barite mineral raw materials are of particular importance, the main consumers of which are the chemical and oil industries¹. In this regard, work on the search and evaluation of barite deposits is relevant and significant. When solving this problem, special attention should be paid to the possibility of developing technogenic deposits to obtain commercial barite.

The purpose of the study is to study the prospects of tailings of polymetallic deposits of the Salair Ridge (Kemerovo region), as potential sources of barite raw materials, with the study of: the mineralogical and geochemical characteristics of stored waste, assessment of the resource potential of tailings, assessment of the possibility of enrichment to obtain standard barite concentrates. The conducted studies showed the possibility of obtaining barite concentrates from tailings materials: Ursk, Dyukov Log, Talmovskie Sands (Kemerovo region)².

Table 1. Comparison of the obtained barite concentrates

Parameters/Samples	Ursk	Dyukov Log	Talmovskie Sands
Barite content, %	84	79	71
pH	7.2	4.8	5.6
Content of water-soluble salts, %	<0.1	<0.1	<0.1

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The research was carried out with funds from the Russian Science Foundation grant №23-27-00340

MAINTENANCE AND STORAGE OF MICROORGANISMS AFTER BIOLEAGING OF METALS IN BIOTECHNOLOGY

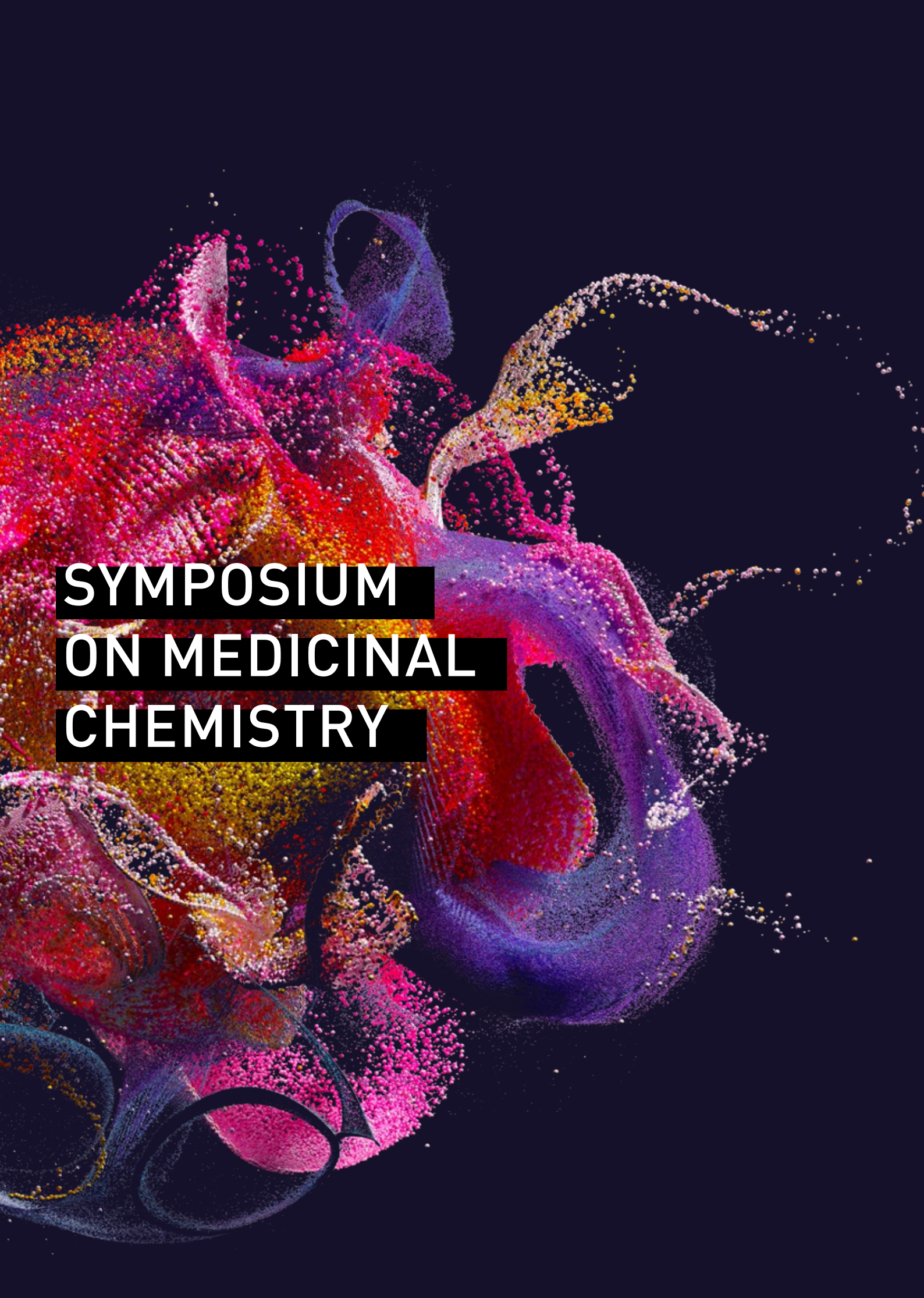
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The use of iron-oxidizing and sulfur-oxidizing microorganisms in the process of processing mineral raw materials has led to the successful development of biohydrometallurgy. There are the following methods for storing iron-oxidizing and sulfur-oxidizing microorganisms: cryo-freezing, drying from a frozen state, drying after cultivation in liquid nutrient media. It is important to maintain cultures of microorganisms during long-term storage. However, the preservation of microorganisms can be complex due to their species composition, varying nutrient requirements and environmental conditions¹. To maintain microorganisms important for hydrometallurgy, methods of sowing and reseedling on nutrient media are used to obtain enrichment cultures, thus regular monitoring of the physicochemical parameters of nutrient media, such as pH, Eh, temperature, density of solutions and the concentration of necessary elements in them, allows maintaining optimal conditions for the growth of microorganisms. Existing methods make it possible to preserve the viability of microorganisms, the biochemical activity of cells, morphological and cultural properties for a fairly long period of time, but there are also disadvantages associated with the costs and risks of preserving cultures². Optimal storage conditions may vary depending on the specific species of iron-oxidizing and sulfur-oxidizing microorganisms³.

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An abstract, vibrant, and complex structure composed of numerous small, colored particles (red, orange, yellow, green, blue, and purple) arranged in a swirling, organic pattern against a dark background. The structure resembles a molecular model or a dynamic system of particles. The text is overlaid on the central part of this structure.

SYMPOSIUM ON MEDICINAL CHEMISTRY

WAY2DRUG PLATFORM: FROM BIOLOGICAL ACTIVITY PREDICTION TO SYSTEMS PHARMACOLOGY

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The global chemical space is extremely vast, and finding a molecule with the required pharmacotherapeutic properties is a challenging task. Starting with the analysis of large chemical and biological data obtained *in silico*, *in vitro*, *in vivo* and *in clinics*, it is necessary to finish with a single pharmacological substance satisfied a set of criteria for safety and efficacy. Using information carefully selected from available data sets on active/inactive compounds and applying AI/ML tools, researchers are shifting from the global to the local scale of pharmaceutical research and development, which can significantly reduce the costs of developing new pharmaceuticals and the risks of negative results.

Way2Drug (<https://www.way2drug.com/>) is a fast-growing web portal focused on integrating popular tools for *in silico* drug discovery. Way2Drug currently provides services to predict the biological activity (PHARMA), toxicity (TOX), metabolism (META) and physicochemical characteristics (ADME) of drug-like compounds. All tools are freely available for non-commercial academic research.

Along with predictive web services, the Way2Drug portal presents information resources, including the WWAD database (World-Wide Approved Drugs, <https://www.way2drug.com/wwad/>), a database on phytocomponents of official medicinal plants of Russia Phyto4Health (<https://www.way2drug.com/p4h/>), host gut microbiota metabolism xenobiotics database HGMMX (<https://www.way2drug.com/hgmmx/>).

The study was performed in the framework of the Program for Basic Research in the Russian Federation for a long-term period (2021-2030) (No. 122030100170-5).

INNOVATIVE SMALL MOLECULE DRUGS INTRODUCED ON THE RUSSIAN MARKET

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The dramatic period experienced by our country and the world is affecting many aspects of our life, including the processes of development and implementation of innovative drugs. There are several significant factors influencing these processes in the Russian Federation in modern conditions. Firstly, it is the strengthening of the demand of the state and society for the appearance of innovative drugs of national development. Secondly, it is the termination in the Russian Federation from the beginning of 2022 of phase III regulatory clinical trials of innovative drugs registered in the USA, EU, Japan and other unfriendly countries, which actually marks the gradual withdrawal of the most modern medicinal products from the Russian market. Thirdly, it is the moral and economic crisis of the generic pharma business model that has defined the domestic industrial landscape for the last three decades. All this is accompanied by a number of objective problems, such as the absence or underdevelopment in Russia of some critical technologies in the field of drug development; problems of interaction between academic/university science and business; disbalances in the development of basic and applied components in science; the phenomenon of the “death valley” as a complex gap between early research and clinical/production stages, etc.

In this regard, the experience of domestic scientific and industrial groups, which have managed in this difficult situation to ensure the development and successful introduction of their own innovative drug products on the Russian market, is of particular interest. From the point of view of medicinal chemistry, these products are based on modern conceptual and methodological approaches, providing relevance for health care and effective market introduction. Modern Russian practice provides examples of innovative compounds of the “first-in-class” type, effective solutions of the “next-in-class” type, repositioned drugs.

The report reviews examples of innovative small molecule drugs developed and introduced in the Russian Federation in the last few years, focusing on medchem aspects. In-depth analysis and development of this best practice can ensure the technological sovereignty of our country in the field of pharmaceutical drug development.

PHYSICOCHEMICAL METHODS FOR SEARCHING AND ESTABLISHING MECHANISMS OF ACTION OF ANTIVIRAL DRUGS

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The COVID-19 pandemic has made the task of finding effective methods to combat viral infections quite urgent. Vaccination can prevent infection, but rapid mutation of viruses reduces the effectiveness of vaccines and requires a fairly long time to develop new variants. In this regard, the search for antiviral drugs comes to the fore. The small number of structural proteins of viruses makes it possible to establish the general mechanisms of their activity and model the various stages of the process of viral infection of a cell.

In this work, we have shown how, by combining methods of structural biology, biophysical techniques and computer modeling methods, it is possible to establish the functional role of various viral proteins, search for their active centers, as well as search for candidate molecules for antiviral drugs and test the activity of various existing drugs. Using the example of the influenza A virus, we demonstrated that the study of the fusion of single viruses with model lipid membranes using fluorescence microscopy in combination with computer molecular modeling proves the activity of the antiviral drug Triazavirin and its derivatives in relation to the stage of virus penetration into the cell, and also predicted optimal modifications of the drug molecules to increase its effectiveness. Using small-angle X-ray scattering and atomic force microscopy in combination with molecular modeling, we demonstrated the functional activity of the influenza A virus M1 matrix protein, found its active site, and predicted a group of molecules with potential antiviral activity. Overall, our comprehensive approach allows us not only to establish mechanisms of action for antiviral drugs, but also to search for new promising molecules.

The work was carried out with the financial support of the Russian Foundation for Basic Research, project 20-54-14006.

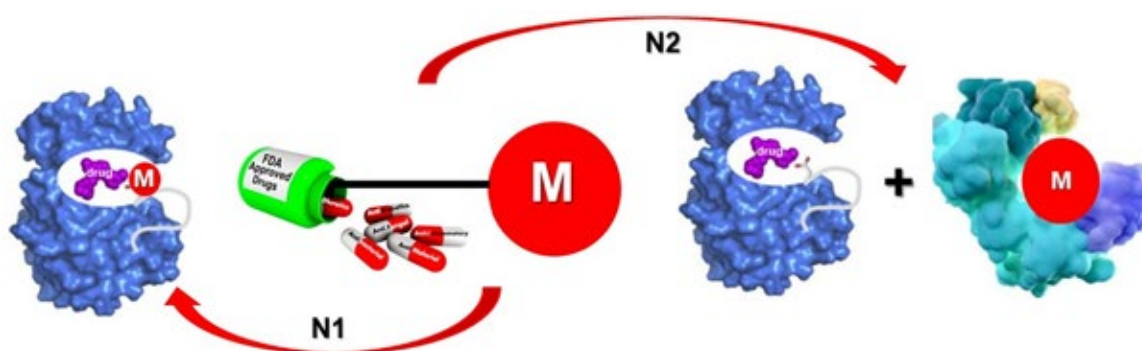
METAL-BASED DRUG CANDIDATES WITH MULTIMODAL MODE OF ACTION

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The field of metal-based drugs nowadays expands the pharmaceutical market and opens the possibility to treat some diseases that are not cured by organic medicines.¹ The current clinical arsenal of metal compounds operates via a limited number of mechanisms, whereas new putative compounds explore alternative mechanisms of action, which could potentially bring new chemotherapeutic approaches into the clinic.

In this review, a novel approach to create metal-based drug candidates is discussed. It is based on combination of two moieties in one molecule – a known organic drug and metal atom with a confirmed pharmacological activity. Organic drug might serve as a delivery agent to its target improving thereby the activity by the presence of metal (path N1). On the other hand, the dissociation of metal complex guides both metal and organic drug to different targets which provides multimodal mode of action (path N2).



The target-focused synthesis, physico-chemical properties and physiological activity of various metal complexes (Pt, Sn, Au, Fe, Co, Ni, Cu, Zn, Ga, In, Ce, La) with non-steroidal anti-inflammatory and antiandrogenic drugs, cytoprotectors and antioxidants *in vitro* and *in vivo* will be discussed.²⁻⁴

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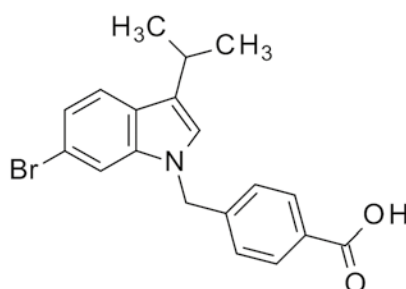
Financial support of RSF (grant 22-63-00016).

(HETARYLMETHYL)BENZOIC ACIDS: FROM EXPERIMENTAL INHIBITORS OF BACTERIAL CYSTATHIONINE- γ -LYASE TO A NEW CLASS OF ANTI-BIOTIC ADJUVANTS

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Bacterial cystathionine- γ -lyase (CSE) is an attractive biological target for the development of new antibiotic adjuvants. This enzyme plays an important role in the synthesis of endogenous hydrogen sulfide, a molecule that helps to protect bacterial cells from oxidative stress. We have identified several potential inhibitors of CSE, and based on biological testing, the most promising compound appears to be 4-(6-bromo-3-isopropyl-1*H*-indol-1-yl)methylbenzoic acid:



This substance, in the form of a water-soluble sodium salt, effectively inhibited bacterial (but not human) cystathionine- γ -lyase, and also showed high efficacy during *in vivo* tests on models of pneumonia and sepsis caused by a polyresistant strain of *Pseudomonas aeruginosa*, as well as wound infection caused by a methicillin-resistant strain of *Staphylococcus aureus*. Based on the results obtained, this compound is considered a promising candidate for further preclinical and clinical studies.

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DESIGN OF NEUROPROTECTIVE COMPOUNDS: AMPA RECEPTOR MODULATORS

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Positive allosteric modulators (PAMs) of AMPA-type ionotropic glutamate receptors are considered as promising neuroprotective compounds. The intense ionic current caused by the action of such modulators on AMPA receptors, followed by depolarization of the postsynaptic membrane, triggers the gene expression mechanism responsible for the synthesis of NGF (nerve growth factors) and BDNF (brain-derived neurotrophic factor). In addition, AMPA receptor PAMs have a significant impact on the processes of learning and memory formation. Therefore, drugs that act on AMPA receptors in this way may be effective in the treatment of neurodegenerative diseases¹.

In this report we discuss the approaches to computer-aided molecular design of AMPA receptor modulators based on the molecular dynamics simulation studies of the agonist-receptor-modulator complexes for different modulator binding sites in the receptor. The mechanisms of action of AMPA receptor ligands responsible for the manifestation of various therapeutic effects are considered. The most promising compounds were synthesized and studied *in vitro* and *in vivo*. The simulation results are confirmed by experimental data. A number of new promising compounds with picomolar activity, a unique combination of properties, and low toxicity have been found.

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CHEMISTRY, PHARMACOLOGY, AND TECHNOLOGY OF LAPPACONITINE AND ITS DERIVATIVES

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Plant diterpene alkaloids are a promising class of natural compounds for fundamental and applied research.

A screening of 50 species of alkaloid-bearing plants was conducted, from which more than 200 diterpene alkaloids (DA) related to C-20-diterpene, C-19-nor-diterpene, and C-18-bis-nor-diterpene bases were isolated. Among them, lappaconitine is of particular importance – a representative of C-18 diterpene alkaloids with a wide range of pharmacological activities, used in medical practice under the name “allapinin.” Lappaconitine is found in many plants of the genus *Aconitum*. It is known that acid hydrolysis of lappaconitine leads to N-deacetylappaconitine, and alkaline hydrolysis leads to lappaconine.

Previously, studies by the Department of Pharmacology and Toxicology of the Institute of Chemical Radiology of the Academy of Sciences of the Republic of Uzbekistan established a high antiarrhythmic effect of lappaconitine. After a single intragastric administration of lappaconitine (allapinin) in doses of 1–2 mg/kg, the antiarrhythmic action (PAD) lasts for 18–20 hours, while the duration of action of reference antiarrhythmics such as quinidine, novocainamide, rhythmilene, etmozine, and mexitol (50–100 mg/kg) is not determined after 4–6 hours. The disadvantage of using lappaconitine is its side effects and relatively high toxicity.

In collaboration with the Xinjiang Technical Institute of Physics and Chemistry and the Shanghai Institute of Medical Materials (PRC), 128 new derivatives of lappaconitine were synthesized, and the antiarrhythmic activity of 92 compounds was determined. The relationship between structure and antiarrhythmic activity was analyzed. Seven substances with higher antiarrhythmic activity and significantly lower toxicity than lappaconitine were selected. Among these substances, the most promising were identified: CAM-68 and CAM-74.

Most modern studies of the pharmacological activity of lappaconitine and its derivatives globally focus on analgesic, anti-inflammatory, antitumor, and antiarrhythmic effects. Among DA, substances were found that advantageously combine pronounced PAD with antispasmodic, analgesic, anti-inflammatory, local anesthetic, sedative, or psychostimulating effects. Thus, plant diterpene alkaloids are a promising class of natural compounds for expanding fundamental chemical, pharmacological, and technological research, including studying their mechanisms of action, clarifying structure-activity relationships, and chemical modifications to create new drugs.

INHIBITORS OF VIRUSES CAUSING PARTICULARLY DANGEROUS INFECTIONS

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The past century has been marked by numerous achievements and innovations that have improved the quality and longevity of life of people all over the world. However, these same advances have led to a dramatic increase in vulnerability to rapidly evolving outbreaks of infectious diseases as a result of population growth and mobility, climate change, increasing interdependencies and inequalities.

Diseases with epidemic potential such as avian influenza, filovirus infections (Ebola and Marburg), and diseases caused by orthopoxviruses herald a new era in which outbreaks with widespread impact and potentially high rates of spread will become more frequent and more difficult to suppress. “Disease X” is an extremely dangerous infectious or viral disease that could emerge in the future and cause a significant number of casualties. “Disease X” is a reflection of the knowledge that a serious international epidemic could be caused by a pathogen that is currently unknown.

The report reviews the results of the successful search for novel inhibitors of viruses causing highly dangerous infections using naturally occurring compounds as starting molecules.

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DESIGN OF INNOVATIVE TARGET ORIENTED AGENTS – GENERATORS OF ENDOGENOUS TRANSMITTER MOLECULES FOR THE TREATMENT OF SOCIALLY SIGNIFICANT DISEASES

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Since the discovery of nitrogen monoxide (NO) as an endogenously generated effector molecule, tens of thousands of papers have been published on its chemistry and biology. No other area of biomedical researches has experienced such a stunning explosion in such a short period of time¹. This discovery was a paradigm shift in biological signaling and suggested the possibility that other small freely diffusible molecules (HNO² and H₂S³) might be synthesized endogenously as active molecules and played equally significant roles in the regulating of wide range of functions both normally and in pathology. In this regard, the development and application of new compounds – generators of these endogenous transmitters, as an innovative strategy for searching for medicines for the treatment of socially significant diseases with fundamentally different mechanisms of action, has received rapid development in the last years.

Results of fundamental studies on the design of new pharmacologically active multitarget of nitrosyl ferredoxins mimetics obtained at the FRC PCP MC RAS in 2019–2024 as potential medicinal agents for NO therapy of tumor⁴ cardiovascular⁵ and infectious diseases^{6,7} will be presented.

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ARTIFICIAL NEURAL NETWORKS OF DIFFERENT ARCHITECTURE IN THE SEARCH OF PHARMACOLOGICALLY ACTIVE COMPOUNDS

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The effectiveness of using artificial neural networks of three different architectures for constructing relationships between several types of pharmacological activity and the structure of chemical compounds, represented by parameters of various physico-chemical meanings, is shown.

A multi-target model of RAGE-inhibitory activity with the architecture of the feed-forward neural network in the form of a multilayer bottleneck perceptron was built. This model was based on the description of the chemical structure of 183 known experimentally studied compounds by a spectrum of minimum docking energies into specific binding sites of 34 relevant target proteins. The accuracy indicators of the most valid model were $Acc=95.6\%$, $Sens=94.2\%$, $Spec=97.5\%$, $ROC=0.956$; significance of the model $p < 1 \cdot 10^{-15}$.

A multi-target model of anxiolytic activity with the architecture of the convolution neural network was built. This model was based on variables derived from the correlation convolution of multiple docking energy spectra across the entire volume of 22 relevant protein targets for 537 known experimentally studied compounds. The accuracy indicators of the most valid model were $Acc=91.2\%$, $Sens=91.3\%$, $Spec=91.2\%$, $ROC=0.944$; significance of the model $p < 1 \cdot 10^{-15}$.

A multi-descriptor model of antimicrobial activity against *S. aureus* with the architecture of the fully connected correlation neural network was built. This model was based on describing the structure of known 3699 experimentally studied compounds by a set of fragment QL-descriptors, quantum chemical parameters of molecular orbitals and physico-chemical parameters. The Goodman-Kruskal correlation coefficient for the resulting model was $R\gamma=0.443$; significance of the model $p < 1 \cdot 10^{-17}$.

The work was carried out within the framework of the state assignment of the Ministry of Health of the Russian Federation No. 23022400009-9 "Development of a methodology for computer search for multi-target pharmacologically active compounds based on multiple docking and technology of convolutional neural networks of different architectures".

PHOTOREGULATED TRANSPORT OF BIOLOGICALLY ACTIVE AND NATURAL OCCURING MOLECULES USING HETEROCYCLIC FLUOROPHORES

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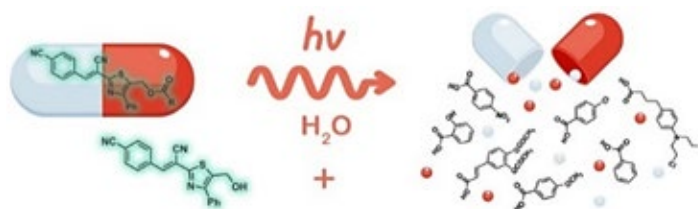
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Photocleavable protecting groups (PPGs) (photocages, photocouriers, photocontainer) are photoactive compounds used as safeguard for a temporal masking of the functional (either chemical or biological) activity of a molecule.¹ PPGs were object of intensive investigations in a plethora of domains of applications in organic syntheses and in the study of processes in chemistry, in materials science, in biological and medical research fields, diagnostic and for temporally and spatially controlled delivery of bioagents.

Exposure to light induces the breaking of the covalent bond between PPG and the caged biomolecule (cargo), leading to the restoration of the biomolecule's activity. In this way, a spatial and temporal control of the substrate bioactivity can be achieved, making PPGs powerful tools for the study of small molecules, short-living particles, or therapeutic agents, such as pharmaceuticals, signaling agents, neurotransmitters, ions in living organisms.

We have synthesized a series of new fluorophores based on an arylidenethiazole framework and studied the prospects for their use as a photocontainer for the targeted delivery of drugs, diagnostic agents, or natural compounds containing a carboxyl group.



The mechanism of photorelease of biomolecules was studied using spectral studies, HPLC-HRMS and quantum mechanical calculations. Biological experiments have shown the biocompatibility of the hybrids and the selectivity of their intracellular localization in the endoplasmic reticulum, lipid droplets and mitochondria.

Reference

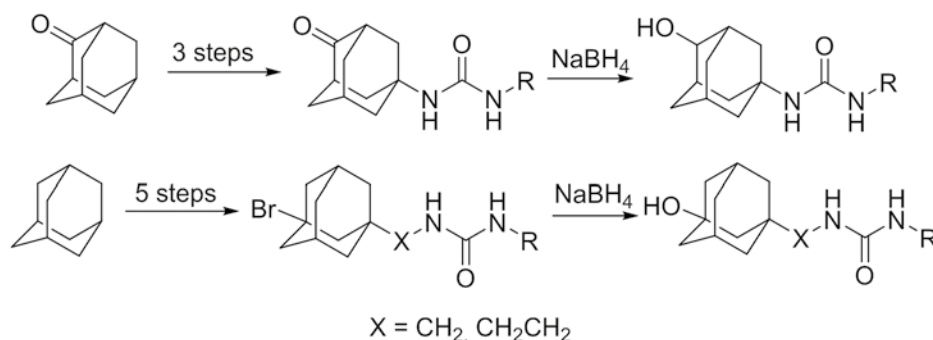
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APPROACHES TO INCREASING THE WATER SOLUBILITY OF SOLUBLE EPOXIDE HYDROLASE INHIBITORS

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1,3-Disubstituted ureas containing adamantyl moiety are effective inhibitors of soluble epoxide hydrolase (sEH) and have strong analgesic activity. Currently, compounds capable of inhibiting sEH in subnanomolar concentrations have been synthesized, but the water solubility of such compounds remains insufficient. In this regard, we have proposed a number of approaches to modification of the adamantyl fragment of the molecule with oxo and hydroxy groups.



The study of solubility in water was carried out by the turbidity method at a wavelength of 600 nm, which was additionally validated by the HPLC-MS method. The introduction of a hydroxy group into the nodal position of adamantyl fragment increases water solubility up to 10 times, and the introduction of an oxo group into the bridge position up to 15 times. The introduction of a bromine atom into a node position also has a positive effect on water solubility (up to 1.7 times). Thus, the developed methods for modification of the adamantyl fragment of 1,3-disubstituted ureas and their precursors can significantly increase their water solubility. For the first time, 1,3-disubstituted diureas, which have inhibitory activity in subnanomolar concentrations due to the formation of additional, previously undescribed hydrogen bonds in the active center of the enzyme, were studied as inhibitors of soluble epoxide hydrolase.

This work was carried out with financial support from the Russian Science Foundation (project № 19-73-10002).

DIARYLMETHYLPHOSPHONATES CONTAINING STERICALLY HINDERED PHENOL: SYNTHESIS, SWITCH FROM ANTIOXIDANT ACTIVITY TO ROS GENERATION AND INDUCTION OF APOPTOSIS

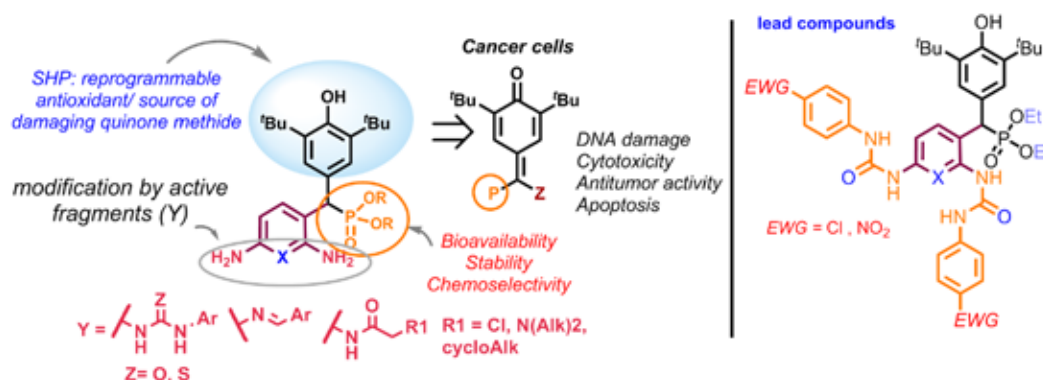
Gibadullina E.M.^a, Nguyen H.B.T.^b, Neganova M.E.^{a,c}, Aleksandrova Y.R.^{a,c}, Lyubina A.P.^a, Voloshina A.D.^a, Burilov A.R.^a, Sinyashin O.G.^a, Alabugin I.V.^a

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The utility of sterically hindered phenols (SHPs) in drug design is based on their chameleonic ability to switch from an antioxidant that can protect healthy tissues to highly cytotoxic species that can target tumor cells. A library of new hybrid molecules combining SHPs with an activating phosphonate motif in the benzyl position with various functionally substituted fragments was synthesized. To determine the antitumor potential of the compounds and to understand their mechanisms of action, we studied the biological activity and identified molecules with a high cytotoxic activity towards tumor cell lines.¹⁻³



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The research was supported by the Ministry of Science and Higher Education of the Russian Federation at FRC Kazan Scientific Center (grant No. 075-15-2022-1128).

SULFUR-, SELENIUM-CONTAINING HYDROPHILIC ANTIOXIDANTS: SYNTHESIS AND INFLUENCE ON OXIDATIVE PROCESSES IN LIVING SYSTEMS

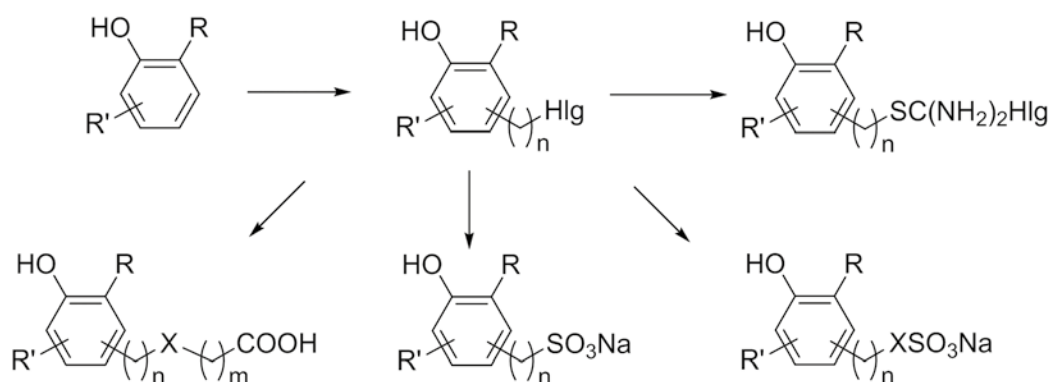
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The significant role of free radicals in the pathogenesis of a wide range of common diseases (oncological, cardiovascular, endocrine, neurodegenerative) forms the need for the creation of drugs with antioxidant action, including in infusion and injection forms.

Based on commercially available phenols through the corresponding haloalkyl-substituted derivatives, we synthesized sulfur- and selenium-containing compounds with hydrophilic properties:



R, R' = H, Alk; Hlg = Cl, Br, I; X = S, Se; n = 1-4; m = 1, 2

Kinetic experiments and *in vitro* demonstrated the presence of antiradical and antiperoxide activity in the synthesized compounds. *In vivo*, the compounds exhibited pronounced anti-inflammatory, antitumor, hepato-, cardio- and neuroprotective properties. It has been established that the pharmacological activity of a number of compounds is inextricably linked to their ability to activate the expression of antioxidant defense enzyme genes through the redox-sensitive Keap1/Nrf2/ARE.

CREATION OF FUNCTIONAL BLOCKS OF COORDINATION COMPOUNDS WITH VARIOUS TYPES OF BIOLOGICAL ACTIVITY: SYNTHETIC APPROACHES, MEDICAL-BIOLOGICAL TESTS, PROSPECTS FOR IMPLEMENTATION

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In the modern world, where the rate of emergence of new strains of viruses and bacteria leading to epidemics is high, where already known microorganisms develop new types and mechanisms of resistance, and chemotherapeutic agents are powerless against aggressive types of cancer, synthetic chemists are involved in the design of new molecules that can affect new targets in pathogen cells and alternative pathways leading to inactivation of pathogens. The key condition for a coordination compound to acquire biological activity is the correct selection of the combination of metal(s) and M–L ligands, which will provide the “needed” physicochemical properties to the future pharmaceutical composition and, subsequently, the drug.

Homo- and heterometallic carboxylate complexes of transition metals, acting as substrates, have proven themselves to be both labile fragments capable of quite easily rearranging the metal oxide fragment, and ions sensitive to the coordination of various N-donor bases (Zn^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Mn^{2+} and etc.). Such lability can be important in bioisosteric modifications (replacement of pivalate anions Piv^- with other carboxylate groups (furan / thiophene / indole, etc.) with the acquisition of biological activity by the final complex. Methods for the synthesis of mononuclear complexes Cu(II), Zn(II), Co(II), Fe(III) with furoic acids anions and a number of N-donor ligands, showing high activity against mycobacteria (*M. smegmatis*, *M. tuberculosis*). It has been recorded that a number of {M–L} combinations are capable of causing only a bacteriostatic, but also a bactericidal effect (complete suppression of the vital activity of strains). The results of the tests made it possible to select cations to which mycobacteria are sensitive, as well as N-donor ligands that can significantly enhance biological activity. In addition, a number of Fe(III) and Co(II) showed high antiproliferative activity with simultaneously low toxicity towards healthy cells.

The work was carried out with the financial support of the Russian Science Foundation, project 22-13-00175.

DEVELOPMENT AND STUDY OF THERAPEUTIC AND DIAGNOSTIC CONJUGATES BASED ON PSMA LIGANDS

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Beloglazkina E.K.¹, Majouga A.G.³**

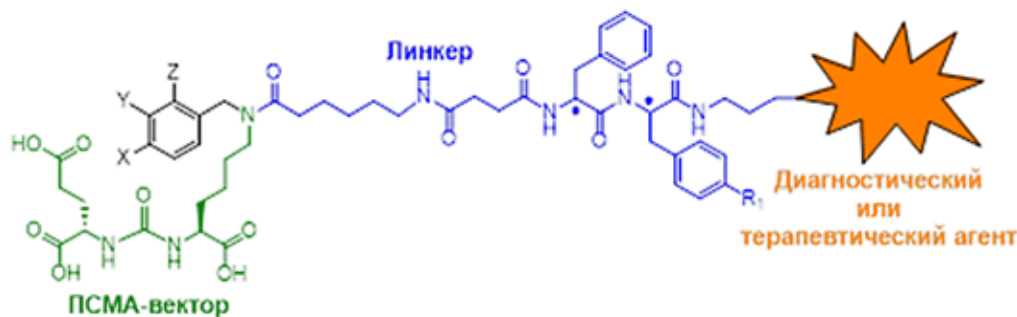
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Prostate cancer is one of the most common oncologic pathologies among the male population, according to world statistics for 2021. One of the approaches to the development of modern therapy or diagnostics of this disease can be targeted delivery directed to the protein target – PSMA. In this regard, the design of new high-affinity PSMA ligands and the creation of conjugates based on them, with subsequent study of their biological activity is an urgent task.^{1,2}



The presentation will detail approaches to the design and synthesis of PSMA ligands, allowing the development of diagnostic and therapeutic conjugates based on them, both small-delivery molecules and radioisotopes. The results of biological in vitro and in vivo tests of these conjugates will also be discussed.

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ANTITUMOR PLATINUM AND RUTHENIUM COMPOUNDS WITH TARGETING ACTION

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Clinically used platinum (II) drugs for the treatment of malignant tumors have proven to be highly effective in the battle against cancer. However, the lack of selectivity, a significant number of side effects, and the development of resistance to these drugs are becoming increasingly difficult obstacles to their widespread use. Platinum (IV) coordination complexes, as well as ruthenium coordination and organometallic compounds, are currently being investigated as an alternative to classical platinum-based drugs, as they may overcome some of the drawbacks associated with these traditional agents.

We have proposed a novel approach for the development of innovative anticancer drugs that combines two pharmacophores into one molecule.^{1,2} This molecule contains Pt(IV), Ru(III), and Ru(II), as well as a targeted ligand that can interfere with the cellular processes specific to malignant cells, or increase the protection of normal cells from the toxic effects of non-biogenic metals.

The new compounds exhibit high activity against cancer cell lines in in vitro studies. The mechanism of action of these compounds has been investigated, and leading compounds with high selectivity towards malignant tumors have been identified.

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DEVELOPMENT OF HETEROBIFUNCTIONAL PROTAC-TYPE MOLECULES TO OVERCOME DRUG RESISTANCE OF CANCER CELLS

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Drug resistance is one of the causes for the ineffectiveness of antitumor therapy and the development of tumor relapses and metastases¹. It is believed that the greatest contribution to drug resistance is made by enhanced expression of ABC family transport proteins, which are responsible for the efflux of various xenobiotics².

Despite the prospects of ABC transporters as a therapeutic target for overcoming resistance, there are no effective approaches to the development of efflux inhibitors. We previously used AMP mimetics to inhibit the ATP-dependent efflux process³. In this work, we propose to use PROTAC-type molecules to stimulate the release of the transporters from the membrane and, consequently, to reduce their transport activity.

We chose P-glycoprotein as a target as it is the most studied of all transporters of the ABC family. A detailed study of its structure allowed us to identify the most promising site for targeting the chimeric molecule. Screening of commercial and in-house compound libraries identified pyrazolopyrimidine structures as selective ligands for the site considered. Chemical synthesis of PROTAC structures was carried out based on MDM2 inhibitors previously developed in our laboratory. Studies of the resulting series of compounds on cell lines and resistance models allowed us to evaluate the prospects of the proposed approach for combating drug resistance mediated by the activity of transport proteins.

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KNOWLEDGE-DRIVEN SEARCH FOR SMALL MOLECULE ANTIVIRALS

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An important problem of contemporary medicinal chemistry is the discovery and development of pharmacological instrument for prevention of the consequences caused by the emergence of highly dangerous viral infections, a striking example of which was the COVID-19 pandemic. At the same time, due to climate change in the Russian Federation, the endemic regions of tick-borne encephalitis and West Nile fever are expanding. Vaccination is an effective way to prevent viral infections, but it can only be carried out by qualified medical personnel and does not allow for post-exposure prophylaxis. In addition, the development of vaccines is possible only after isolation and biological characterization of the pathogen. The design of small molecule drugs with a broad spectrum of direct antiviral action is an alternative approach, the key advantage of which is the ability to quickly optimize previously discovered molecules.

In this presentation we will discuss examples of the authors' use of the most important approaches of searching for new antivirals: direct repositioning, big data driven selection of promising compounds, as well as screening of privileged structure classes. Based on our own experimental data, we analyze the advantages and limitations of each of these approaches in the early development of small molecule compounds that act on viruses of varied nature, such as tick-borne encephalitis virus, SARS-CoV-2, enterovirus A71, etc.

The work was carried out with financial support from the Ministry of Education and Science of the Russian Federation (state research program no. FNZG-2024-0005).

NOVEL BIOLOGICALLY ACTIVE NITROGEN-, SULFUR-, AND OXYGEN-CONTAINING HETEROCYCLIC COMPOUNDS WITH MULTITARGET ACTIVITY

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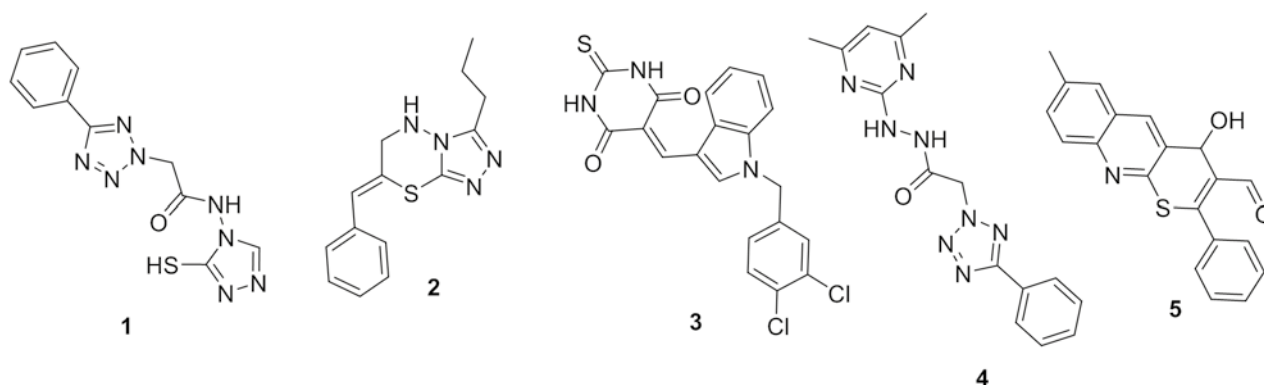
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Development of rational synthesis methods for active ingredients of original medicines with multitarget action is one of the most important tasks in modern medicinal chemistry and pharmaceutical industry¹.

In this study, we conducted *in silico* (PASS, molecular docking, scoring) prediction of biological activity and synthesis of non-annulated and annulated heterocyclic ensembles – polynuclear derivatives of 1,2,4-triazole, tetrazole, pyrimidine, pyrimidinone, 1,3,4-thiadiazine and thiopyrano[2,3-*b*]quinoline.



Based on the *in vitro* and *in vivo* data, compounds **1–5** exhibit antiviral, antimicrobial, antifungal, and antidiabetic activities.

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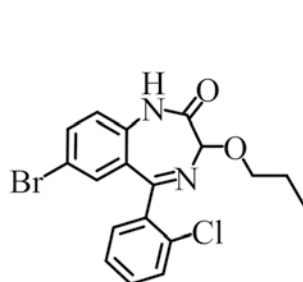
This work was supported by the Russian Science Foundation (RSF), Project No. 23-13-00224.

DEVELOPMENT AND IMPLEMENTATION OF INNOVATIVE ANALGESICS BASED ON 1,4-BENZODIAZEPIN-2-ONES

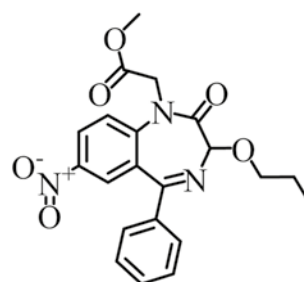
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The search and creation of original safe analgesics is one of the urgent problems of medicinal chemistry. Based on new derivatives, two innovative derivative analgesics, 1,4-benzodiazepin-2-one, have been developed and are at different stages of clinical trials. **Propoxazepam** [1–2] and **PAV-0056** [3–4].



Propoxazepam



PAV-0056

Propoxazepam is a complete CBDR agonist and bradykinin B₁ receptor antagonist, exhibits potent analgesic effect at a dose of 0.03 mg/kg with anticonvulsant effect beginning to appear at doses greater than 1.5 mg/kg LD₅₀ > 2000 mg/kg.

PAV-0056 has no affinity to CBDDR and PBDR, is an antagonist of bradykinin B₁ receptors, exhibits a powerful analgesic effect at a dose of 0.01 mg/kg LD₅₀ > 2000 mg/kg and does not exhibit psychotropic properties. Both compounds can be used for the treatment of pain of different etiology, while the analgesic effect is realized not through CBDD and not through opioid receptors.

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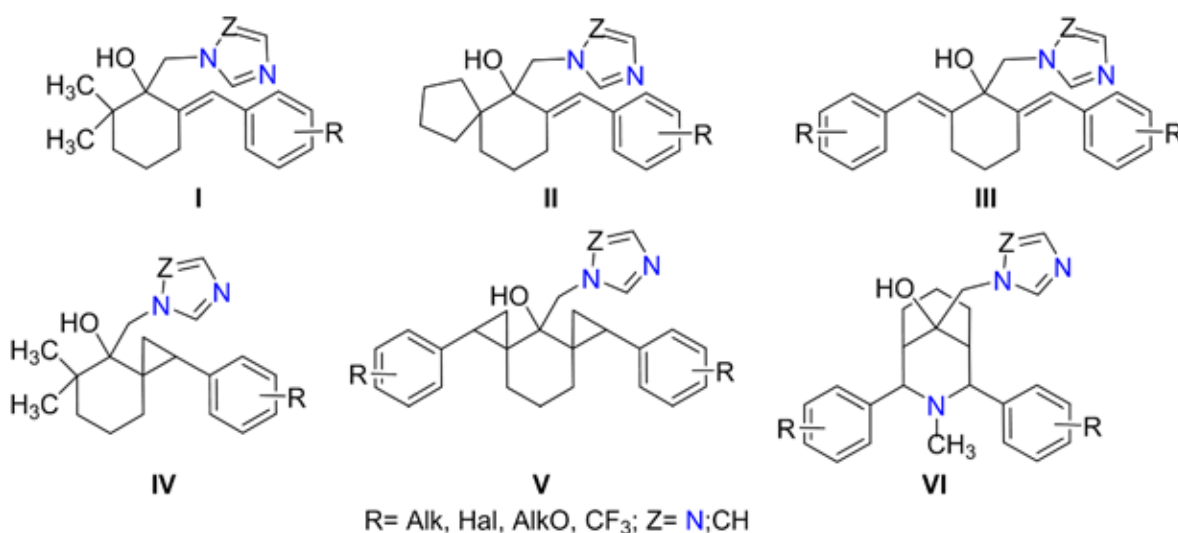
This research was supported by the Ministry of Science and Higher Education of the Russian Federation (project no. FSWW-2023-0008), and the Tomsk Polytechnic University Development Program.

SYNTHESIS, ANTIFUNGAL AND ANTIMYCOBACTERIAL ACTIVITY OF AZOLYLMETHYL-CYCLOHEXANOLS AND 3-AZABICYCLO[3.3.1]NONANE-9-OLS

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The most significant subclass among systemic fungicides and antimycotic drugs are monosubstituted 1,2,4-triazoles and imidazoles¹. Recently, substituted azolymethylcyclopentanols such as metconazole and triticonazole have entered the agricultural fungicide market. In order to obtain drugs for both agricultural and medical purposes, cyclohexane analogues of triticonazole, azolymethylarylidencyclohexanols (**I**) have been synthesized. By modifying their structure spiro[4.5]decanols² (**II**), bis-arylidencyclohexanols (**III**), spiro[2.4]octanols³ (**IV**), dispiro[2.1.2.3]decanols⁴ (**V**), 3-azabicyclo[3.3.1]nonan-9-ols (**VI**) were synthesized.



Leader compounds of series **I** with MIC <0.1 µg/ml were identified as a result of fungicidal tests *in vitro* and showed superior activity to standards (amphotericin B, triadimenol). When tested for antimycobacterial activity (*Mycobacterium tuberculosis* H37Rv) the same series of compounds were identified with MIC of <10 µg/ml.

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PREDICTION OF ADMET PROPERTIES OF DRUGS USING ARTIFICIAL NEURAL NETWORKS: RELIABLE MODELS AND NOVEL APPROACHES

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The Artificial Neural Networks (ANN) have long been employed in medicinal chemistry and chemoinformatics as an invaluable tool that helps one to elucidate complex relationships between the important properties and chemical structures of drugs and drug-like compounds by deriving reliable predictive models. This approach proved especially fruitful for the prediction of ADMET (absorption, distribution, metabolism, excretion, toxicity) properties in diverse chemical space.¹ The fragmental (substructural) molecular descriptors based on occurrence counts of simple structural fragments provide a uniform, content-rich representation of the structures resembling a kind of a “structural hologram”. Coupled with the classical feed-forward back-propagation ANN architectures, they have allowed us to predict important ADMET endpoints such as human intestinal absorption, blood-brain barrier permeability,² hERG-mediated cardiac toxicity, mutagenicity, etc. Similar methodology can also be applied to model the cell wall permeability of *Mycobacterium tuberculosis* and other bacterial pathogens.³ In recent years, to enhance the predictivity and applicability domain of the models, we have used the Big Data sources, deep network models, and multi-task learning architectures.

In addition, a number of alternative approaches have been proposed and explored. One of them goes beyond the “flat descriptor vector” representation, aiming to capture various chemically relevant relationships between the fragmental descriptors in more reliable and informative models. Another approach is based on the specialized graph neural network architectures adapted to the ADMET prediction tasks.

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SYNTHESIS AND ANTIMICROBIAL PROPERTIES OF S-, O-, N-, F-CONTAINING MONOTERPENOIDS

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One of the classes of membranotropic substances capable of changing the properties of cell membranes, in particular their permeability, are natural terpene compounds. The terpenoids are known to be able to integrate into the cell membrane by immersing their hydrophobic hydrocarbon moiety in it and binding to the non-polar chains of phospholipids. Therefore, the introduction of a compact lipophilic monoterpene fragment into the molecules of biologically active substances affects their binding to the cell membrane and facilitates the membrane transport of these molecules, allowing us to expect an increase in the biological activity of new compounds, as well as an appearance of multitarget effect.

Chemical modification of terpenes makes it possible to obtain new polyfunctional compounds in which the biological activity caused by the terpene fragment is combined with the properties of the introduced pharmacophore groups.

We have developed new methods for the synthesis of chiral biologically active S-, O-, N-, and F-containing compounds based on semi-synthetic terpenoids and antibacterials of various groups (beta-lactams, fluoroquinolones, sulfen/sulfinimines, sulfonamides, disulfides, and a few derivatives of chloramphenicol and metronidazole) and identified the factors influencing the course and stereoselectivity of reactions. The antibacterial activity of the synthesized compounds was assessed *in vitro* on the main pathogenic strains of bacteria and, additionally, *in vitro* tests for cytotoxicity against normal somatic animal cells were carried out. As a result, we have obtained the new conjugates of terpenoids with fluoroquinolones and cephalosporins that possess pronounced activity against *Staphylococcus aureus* strains, including methicillin-resistant ones.

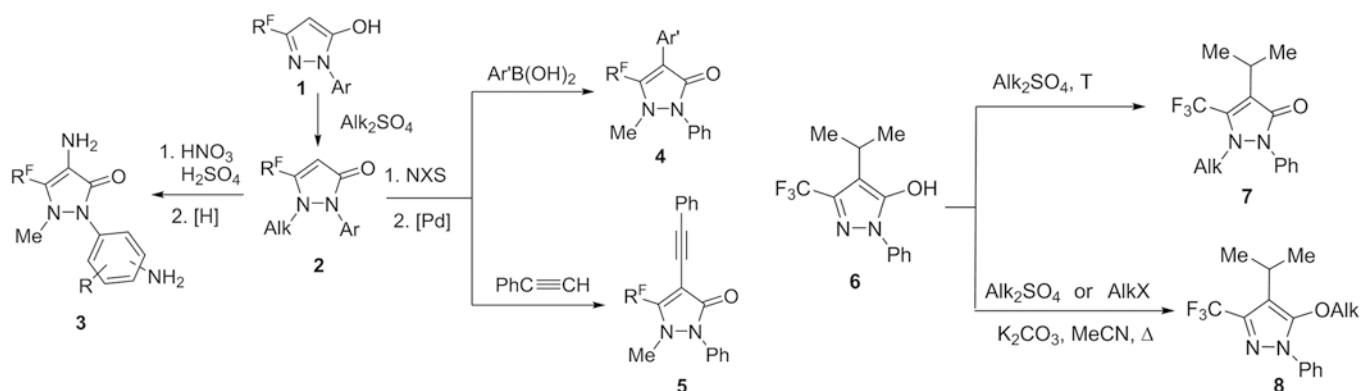
The study was financially supported by the Ministry of Science and Higher Education of the Russian Federation (State task No. 122040600073-3). The analysis of the synthesized compound was performed using facilities of the Shared-Use Equipment Center "Khimia" (Institute of Chemistry, FRC, Komi Science Center, Ural Branch, RAS).

DESIGN OF BIOACTIVE COMPOUNDS BASED ON 5-POLYFLUOROALKYL-SUBSTITUTED ANTIPYRINES

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Methods for the synthesis of perspective structures for biological testing based on 5-polyfluoroalkyl-substituted antipyrines were discussed. To obtain R^F -antipyrines **2**, selective N-alkylation of 3- R^F -pyrazol-5-ols **1** were used. It was found that heterocycles **2** could not involve into a nitrosation reaction owing to the deactivating effect of the polyfluoroalkyl group, but the treatment of compounds **2** with a nitrating mixture led to a series of 4-nitroantipyrines, the subsequent reduction of which yields to 5- R^F -4-aminoantipyrines **3**. In addition, 5- R^F -antipyrines **2**, after preliminary introduction of a halogen atom into position 4, can be involved in Pd-catalyzed cross-coupling reactions. It allowed us to obtain a great number of 4-aryl-5- R^F -antipyrines **4** and 5- R^F -4-(phenylethynyl)-antipyrines **5**¹.



Based on the cyclization of phenylhydrazine and 4,4,4-trifluoro-3-oxo-2-(propan-2-yl)butanoate, *iso*-propylpyrazole **6** was synthesized. Its alkylation led to fluorinated analogues of propyphenazone **7** and its 5-alkoxyl derivatives **8**².

The report provides data on the biological activity of the synthesized compounds, including promising analgesic and antiviral properties.

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The study was carried out with the financial support of RSF (project 24-13-00427).

ROLES OF COMPUTER MODELING IN CHEMISTRY TO SUPPORT INNOVATION DEVELOPMENT

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The use of computer modeling at different levels has become an integral practice in both engineering and scientific research. A traditional justification for it, being both rational and sound, is the replacement of long time and/or expensive natural experiment, as well as the systematization and partial automation of processes. In science, modeling is often considered as a less demanding means to obtain numerical estimation of important quantities, as well as clear illustrations. However, the role of modeling in organization of thought process and systematization of hypotheses remains far less covered.

In a presentation it will be shown that the underestimated roles of modeling could be split into two directions. The first role consists in supporting the thought process itself helping to formulate, systematize and check hypotheses. The second role consists in providing means to support and guide high-tech (science intensive) projects, which being put in business terms is best described as risk management. The first role is more related to the fundamental components of scientific research, whereas the second role is more relevant for fast obtaining the results of applied researches in conditions of limited resources and time, which is typical for innovation process. The conceptual findings are demonstrated using the area of drug discovery and several other fields, related to chemistry and technology. In particular, it will be shown that artificial intelligence (AI) in its current form is inherently capable of playing only a supporting role in innovative development.

Wide application of modeling approaches both at the conceptual level – to reveal the most crucial factors of the phenomenon under study – and at the project level – to rationally manage project risks – will help speed up and systematize the innovation development of Russian Federation to achieve the technological sovereignty.

ADD-ONS TO MOLECULAR MODELING METHODS: IMPROVEMENT IN ACTIVITY PREDICTION

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The basic task of molecular modeling consists of several parts:¹

- Development and application of molecular modeling methods as the first stage of directed synthesis, allowing (a) to predict the structures of products of directed synthesis, (b) to establish reaction mechanisms and (c) to determine key electronic and spatial effects that control the synthesis process and determine the activity of individual molecules, and active classes of compounds and complexes.

- practical validation of predictive modeling methods by obtaining substances with properties specified during modeling.

Methods and practical results of research:

1. FEP (Free Energy Perturbation):

- Syk kinase inhibitors. A set of new Syk kinase inhibitors (non-Hodgkin lymphoma and rheumatoid arthritis) in the submicromolar concentration range was modeled and synthesized;²

- selective inhibitor of ABL tyrosine kinases PF-114. PF-114 inhibits T315I and other mutant forms of the BCR/ABL protein (resistant forms of chronic myeloid leukemia).³

2. Searching for active sites for a specific ligand on the entire protein surface⁴ allows one to determine both the implicit active site of the protein and previously undetected secondary activity. An inhibitor of the main protease COVID-19 has been identified⁵ as a secondary activity of a known drug.

3. QM-cluster methodology (quantum chemical methods): a method for calculating the affinity of bioisosteres has been developed.⁶

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HOW TO PREPARE A NEW POWERFUL ANTISEPTIC

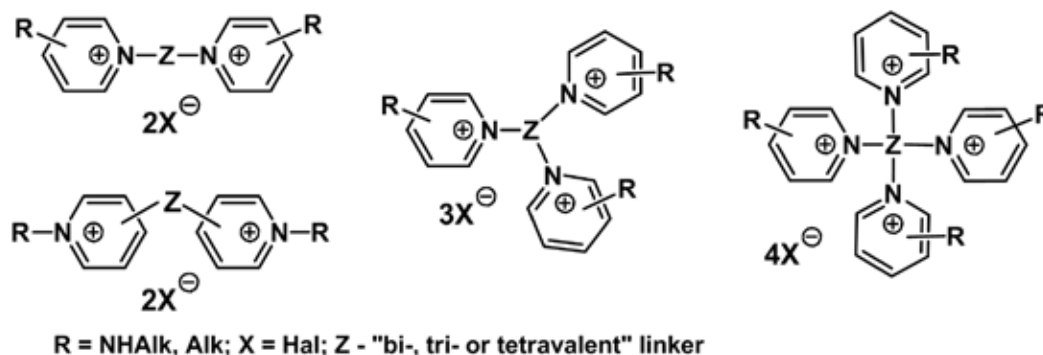
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It is known that various strains of bacteria, including pathogenic ones, develop resistance to antimicrobial drugs over time. A significant number of chronic infections are caused by bacteria growing in the form of biofilms. Antibiotics, which are the mainstay of treatment for bacterial infections, are virtually ineffective against microbes that grow as biofilms. The development of new highly active antibacterial drugs is an urgent and socially significant task.

This work proposes an original approach to the synthesis of new types of bis- tris- and tetra-quaternary ammonium compounds (QACs), which possess antibacterial and antifungal activity and are superior in activity to known antiseptics.¹⁻³ The resulting compounds are effective against both planktonic cells and biofilms.

General structure of bis-, tris- or tetra- QACs



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This work was supported by the Russian Science Foundation (grant № 24-13-00307).

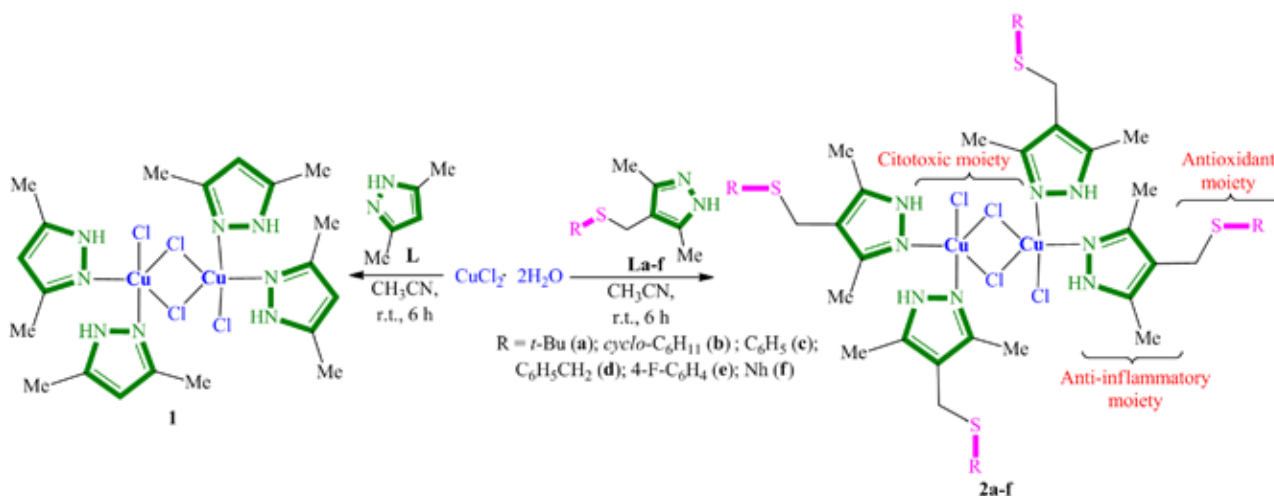
DRAG DESIGN OF NOVEL LOW-MOLECULAR BINUCLEAR CU-CONTAINING SULFANYL AZAHETEROCYCLES

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Currently, the share of metal-containing drugs in the chemotherapy of malignant tumors is growing. However, existing problems – drug resistance of cancer cells and severe side effects contribute to the search for new anticancer drugs¹. Taking into account the previously obtained results², we designed novel binuclear tetraligand complexes Cu(II) **1** and **2a-f** with 1*H*-pyrazole ligands **L** and 4-methylsulfanylpirazole ligands **La-f** in order to impart multifunctional properties to them (see scheme)³.

The report will discuss the results of the synthesis, structural features, thermal stability in solid form and in solution, as well as data from primary *in vitro* screening of fungicidal activity and cytotoxic action (using the example of neoplastic cell cultures Jurkat, MCF-7, THP-1 and conditionally normal HEK293 cells) target complexes **1** and **2a-f**.



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The work was carried out in accordance with the research plans of the INC UFRC RAS on the topic FMRS-2022-0074, 2022–2024.

BIOCOMPATIBLE NANOSYSTEMS BASED ON SULPHO-DERIVATIVES OF PILLAR[5]ARENE AND ANTITUMOR DRUGS OF PROTEIN AND PEPTIDE NATURE: SYNTHESIS AND SUPRAMOLECULAR SELF-ASSEMBLY

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The use of protein and peptide drugs in an individual form has a number of limitations associated with a high toxicity, rapid inactivation and side reactions as antigenicity, allergenicity, etc. Thus, the design of new supramolecular systems for non-covalent immobilization of anticancer protein drugs is one of the urgent problems in medical diagnostics and therapy of oncological diseases.

In this work, new water-soluble derivatives of pillar[5]arene, containing both sulfo groups and a fluorescent label in their structure, were obtained by targeted synthesis. The structure of all synthesized macrocycles was characterized by a set of physical methods: IR, ^1H , ^{13}C NMR spectroscopy, MALDI and ESI mass spectrometry.

The interaction of the macrocycles with proteins (bleomycin, binase, lysozyme) with high association constants and stoichiometry 1: 2 (macrocycle: protein) was investigated by UV-vis spectroscopy. According to dynamic light scattering (DLS) data, the pillar[5]arenes with binase and lysozyme at pH=7.4 formed stable monodisperse aggregates, the morphology of which is ordered spherical nanoaggregates with an average diameter of 200 nm. In the fluorescence spectra of aggregates of the pillar[5]arene with binase, the flare-up of fluorescence at the wavelength of the fluorescent fragment of the macrocycle ($\lambda_{\text{ex}}=485$ nm) was observed with an increase in the binase concentration in the system.

Additionally, we studied the cytotoxicity of the obtained associates, antiproliferative, apoptosis-inducing properties in relation to A549 cells using colorimetric methods and flow cytometry. It is important to note that the cytotoxicity of nanoaggregates (the pillar[5]arene/binase) is lower than that of RNase itself

Thus, the obtained new biocompatible water-soluble macrocyclic receptors on the pillar[5]arene platform can be used to stabilize and prolong the action of antitumor drugs of a protein nature.

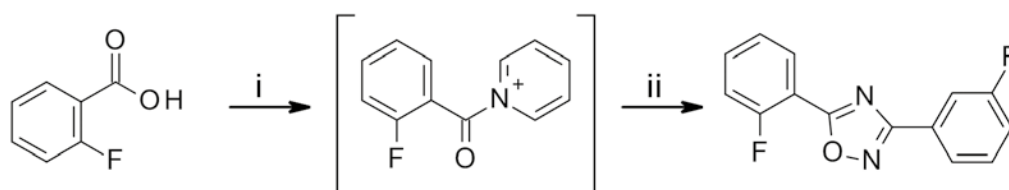
This work was supported by the Russian Science Foundation (project № 22-73-10166), <https://rscf.ru/project/22-73-10166/>

SYNTHESIS OF 1,2,4-OXADIAZOLE DERIVATIVES USING 1-ACYLPYRIDINIUM SALTS PREPARED *IN SITU*

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For the first time, the use of 1-acylpyridinium salts prepared *in situ* was proposed as starting compounds for the synthesis of 1,2,4-oxadiazoles. The interaction of the latter with amidoximes of various structures in anhydrous pyridine allowed to obtain target functional derivatives of 1,2,4-oxadiazoles by a one-reactor scheme, which is illustrated by the following examples:



R = H (**3**), CH₃ (**4**), C(O)OCH₃ (**5**);
i = S(O)Cl₂, Py, 0 °C; ii = 3-RC₆H₄C(NH)NHOH, Py, 0 → 115 °C

The target compounds were obtained in 87–93% yield from theory and high purity without additional purification. The chemical structure of the obtained substances was confirmed by NMR spectroscopy and high-resolution mass spectrometry. The purity of the obtained compounds was proved using TLC and HPLC-UV-MS analyses. Among the obtained compounds, two derivatives of 1,2,4-oxadiazole (**4**, **5**) can be considered as synthetic precursors^{1–4} for obtaining the substance of the drug Ataluren used in the clinic for the treatment of Duchenne muscular dystrophy.

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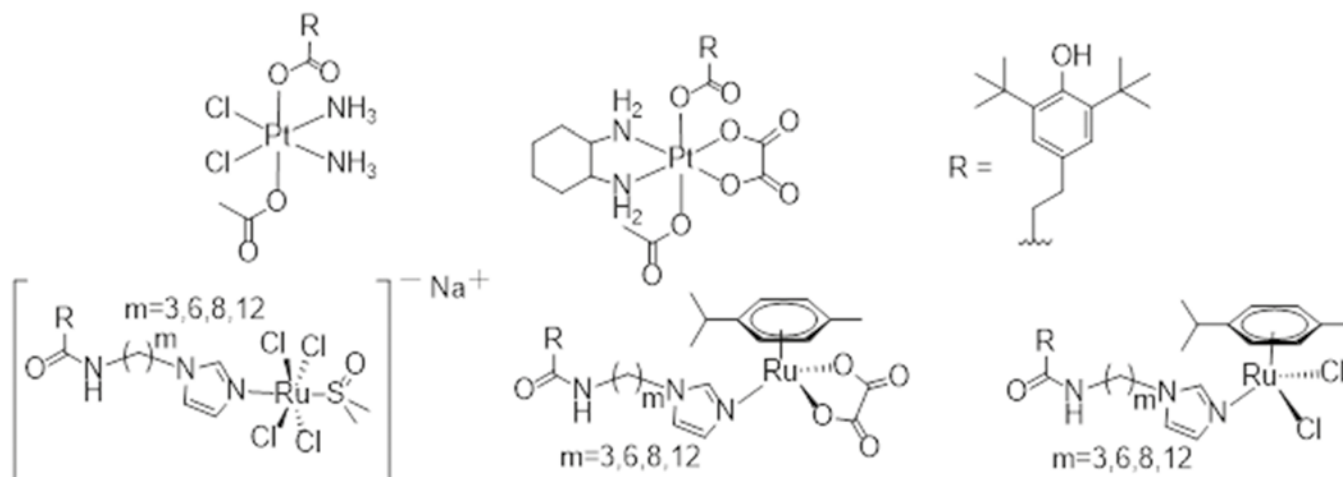
This work was supported by Russian Science Foundation (project No 23-90-04000).

ANTIPROLIFERATIVE AND ANTIOXIDANT ACTIVITY OF RUTHENIUM AND PLATINUM COMPOUNDS WITH PHENOSANIC ACID BASED LIGANDS

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One notable drawback of metal-based antitumor agents is their high toxicity. A prospective strategy for the development of novel compounds involves incorporating an antioxidant moiety into complex structures, thereby potentially mitigating the toxicity towards healthy cells. In this study, a series of Pt(IV), Ru(II), and Ru(III) compounds with ligands based spatially hindered phenol – phenosanoic acid, were synthesized and investigated.



The obtained compounds underwent comprehensive characterization employing NMR spectroscopy, mass spectrometry, and elemental analysis.

Evaluation of their antiproliferative activity revealed a noteworthy superiority of platinum complexes over the standard cisplatin. Additionally, ruthenium compounds exhibited half-inhibition concentrations (IC_{50}) within the micromolar range. Further mechanism of action investigations indicated high potential of these compounds as antioxidants.¹

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This work was supported by RSF project № 22-63-00016.

BISPIDINE-BASED LIGANDS AS POTENTIAL AGENTS FOR TUMOR DIAGNOSTICS

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Copper-64 radioisotopes are widely used in therapeutic, diagnostic and theranostic purposes. Despite having a short half-life time, they have great potential for tumor diagnostics visualization and imaging using positron emission tomography technique.

In this work we present novel chelators for copper (II) based on bispidine functionalized with 1,2,3-triazoles, carboxylic groups, and combined side chains (Fig. 1).

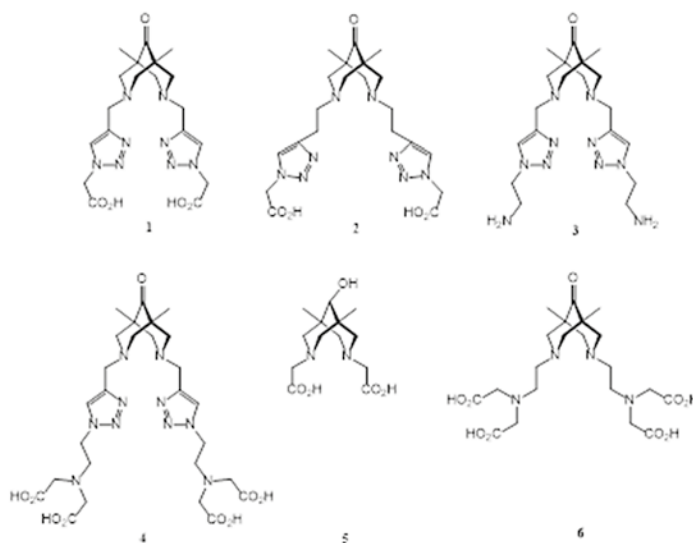


Figure 1. Structures of ligands 1–6 which are investigated in this work

We assessed the stability of formation constants of copper(II) complexes. It was found that insertion of triazole fragments with monocarboxylic units prevents the chelation of ⁶⁴Cu. However, insertion of di- and tetraacetic acid moieties allowed to increase the stability of radioactive-labeled compounds in biological fluids, which was demonstrated with *in vivo* experiments on mice.

PRINCIPLES OF CREATION OF TRIBOLOGICAL POLYMER COMPOSITIONS WITH QUASI-CRYSTALLINE FILLER FOR USE AS MATERIALS FOR MEDICAL PURPOSE

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Hip replacement surgery is one of the most popular in orthopedics. Endoprostheses are made from biocompatible materials: titanium, ceramics, ultra-high molecular weight polyethylene (UHMWPE). The bowl is usually made of titanium, and in the “head-liner” pair (friction unit), the liner is most often made of UHMWPE. The liner wears out first. Therefore, an urgent task is to create a material with high wear resistance and low friction coefficient.

The report presents the results of approaches to creating compositions based on polymers (UHMWPE, PTFE) with a quasicrystalline filler (Qc) Al-Cu-Fe with high tribological properties. The addition of Qc significantly increases wear resistance (for example, for a composite with 16 vol.% filler, the wear resistance of a composition with PTFE increased by 3000 times¹). However, with simple mechanical mixing, the adhesion of the filler and matrix is low, and spalling of the Qc is observed.

The following methods are considered: polymerization filling of UHMWPE with KK2; joint mechanical activation; silanization of CC particles with vinyltriethylethoxysilane to increase adhesion to PTFE.

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The work was carried out within the framework of the state assignment of the National Research Center “Kurchatov Institute”

PHARMACOKINETIC STUDY OF PREDNISOLONE PHOSPHATE'S LIPOSOMAL FORMS

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The liposomal formulation of prednisolone (Pred, synthetic glucocorticoid widely used in clinics) improves the drug efficacy and selectivity due to optimization of its pharmacokinetics and biodistribution profile¹. Therefore, evaluation of the influence that the technological parameters used in the preparation of liposomes might exert on their biological performance is important for the successful development of such formulation. The purpose of this study was to compare the pharmacokinetic parameters of two liposomal formulations of the prednisolone prodrug prednisolone phosphate (PredP) when administered intravenously to rats in comparison with free drug.

The PredP liposomal formulations were prepared by the method of microfluidic flow focusing and the method of thin film hydration followed by extrusion. Both types of liposomes had similar physicochemical parameters (average particle size was about 170 nm, PDI 0.2). The pharmacokinetics of both types of liposomes administered intravenously to healthy rats at a dose of 5 mg/kg (PredP) was studied in comparison with free form of prednisolone phosphate. The main PK parameters were calculated by the model independent method using the PKSolver add-in software for Microsoft Excel.

The sample preparation technique developed in this study ensured a high degree of PredP extraction from blood plasma over the selected concentration range (HPLC method with diode array detection). It was shown that the preparation method exerted the noticeable influence on the PredP PK profile in plasma. In this case, the liposomes prepared by the method of thin film hydration followed by extrusion exhibited the lower initial release and conversion of PredP in plasma *in vivo*, as compared with the liposomes obtained by microfluidic flow focusing.

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The research was carried out within the state assignment of Ministry of Science and Higher Education of the Russian Federation (project FSSM-2022-0003).

TARGETED CONJUGATES BASED ON MESO-ARYLPORPHYRINS AND TYROSINE KINASE INHIBITOR FOR ANTITUMOR PDT

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Photodynamic therapy (PDT) based on the using of non-toxic agents – photosensitizers (PS) and laser radiation, has successfully established itself in the clinical practice of oncological diseases. The development of targeted PSs allows to enhance antitumor effects mediated by PDT.¹

Among characterized cancer targets, epidermal growth factor receptors (EGFRs), which belong to the family of tyrosine kinases receptor, have attracted the most attention due to their overexpression in a wide range of tumors. Combining the high selectivity of tyrosine kinase inhibitors (TKIs) to tumor cells with the therapeutic activity of PSs through their conjugation allows to achieve significant progress in treatment of oncology by PDT.²

In this work we synthesized conjugates of meso-arylporphyrins with a low-molecular-weight tyrosine kinase inhibitor, erlotinib, located near the macrocycle under copper-catalyzed azide-alkyne cycloaddition conditions. A modified Schotten-Baumann reaction was used to create conjugates with TKI separated from the macrocycle by an aliphatic spacer.

Confocal microscopy revealed that the compounds are able to be internalized by A431 cells and localized in mitochondria. MTT-test data indicate high photoinduced cytotoxicity of cationic conjugates against cell lines characterized by EGFR overexpression, 50 times exceeding dark toxicity.

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The work was financially supported by RSF, project 22-73-10176.

DYNAMICS OF IN VITRO DEGRADATION OF POLYMER COMPOSITE GRANULES FROM CHITOSAN, CARBOXYMETHYLCELLULOSE, PHOSPHATES AND CALCIUM SILICATES IN A MODEL BIOLOGICAL ENVIRONMENT

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The research and development of new reparative materials for the restoration of damaged or lost bone tissue are important tasks of modern medical science¹. For a more effective and uniform recovery, it is necessary to select combinations of drugs with different rates of resorption. From the point of view of accelerating the process of osteogenesis, drugs based on mixtures of phosphates and calcium silicates are promising.

In this work, the in vitro degradation rate of composite spherical granules (4 mm) consisting of a mixture of hydroxyapatite (HA) and wollastonite (W) (HA/W) was studied 0/100, 20/80, 40/60, 60/40, 80/20, 100/0) in combination with biodegradable polymers – chitosan and carboxymethylcellulose (CMC). Tris buffer (pH=7) was selected as a model biological medium and isotonic solution (0.9% NaCl). The experiments were carried out under thermostatically controlled conditions at a temperature of 37 °C. The kinetics of degradation and dissolution were evaluated by 1, 2, 3, 5, 7, 14 and 21 days. Concentrations of Ca^{2+} , PO_4^{3-} , and SiO_3^{2-} ions were spectrophotometrically determined at specified time intervals, and changes in the pH of the solution were evaluated. Kinetic parameters were graphically calculated.

It was found that granules containing wollastonite retain their shape throughout the experiment, slowly dissolving. In contrast, samples made of pure hydroxyapatite are destroyed almost instantly. The maximum content of calcium ions in solutions is reached on the 5th day of the experiment, and phosphate ions on the 2nd. A greater value of silicate ions was noted in the isotonic solution. The maximum rate of dissolution is observed on the third day. An increase in the content of hydroxyapatite in the granules affects a decrease in the overall dissolution rate. Thus, the combination of substances with different solubility can provide the necessary kinetics of bone resorption and consolidation.

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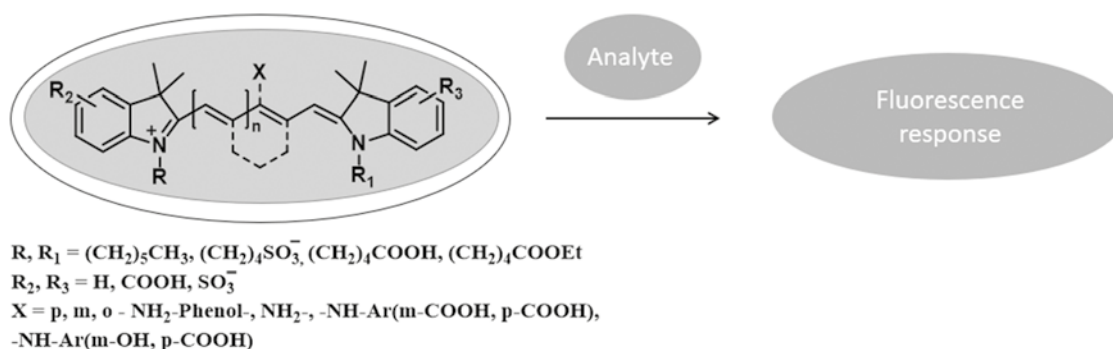
DEVELOPMENT OF SYNTHETIC RECEPTORS BASED ON CARBOCYANINES WITH IONOGENIC GROUPS FOR SELECTIVE BINDING AND DETERMINATION OF LOW MOLECULAR WEIGHT ORGANIC COMPOUNDS

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The development of simple analytical methods for visualization of low molecular weight organic compounds has attracted considerable attention nowadays. Synthetic receptors allow selective binding and high sensitivity determination of low molecular weight organic compounds in objects of complex composition by optical methods.¹ Previously, we have used reactive carbocyanines for the detection of drugs.²

In the present study, we derive synthetic carbocyanine-based receptors with ionogenic groups contained in different parts of the molecule that allow binding of target analytes. Different combinations of such groups allow fine tuning of analyte binding and fluorimetric response of the dye. This concept can be implemented, in particular, for the determination of antibiotics of different types (cephalosporin, phenothiazine, penicillin and other series).



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SYNTHESIS OF NEW BORON-CONTAINING BIOLOGICALLY ACTIVE COMPOUNDS FOR BORON NEUTRON CAPTURE THERAPY FOR CANCER

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Currently, due to the prevalence of cancer, the urgent task is to create new effective drugs for their therapy. Boron neutron capture therapy (BNCT) of cancer¹, which is based on the selective accumulation of isotope ¹⁰B in cancer cells and subsequent treatment with a stream of thermal neutrons, which allows selectively destroying tumor cells without affecting the surrounding healthy tissue, seems to be one of the promising methods of treating tumors. One of the ways to solve this fundamental problem is the synthesis of polyhedral boron hydrides containing BODIPY, capable of fluorescing and tracking the accumulation of boron in tumor cells for further treatment by the BNCT method. Therefore, the development of effective methods for the synthesis of new conjugates of polyhedral boron hydrides with BODIPY is an urgent task. The report will present our recent results on the preparation and design of various boron clusters with BODIPY (Fig. 1).

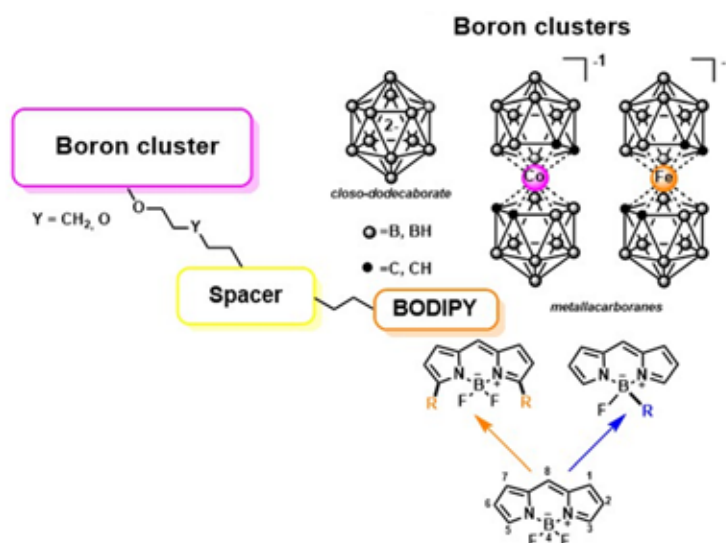


Figure 1. Polyhedral boron hydrides based on BODIPY

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This work was supported by the Russian Science Foundation (RSF), project 24-73-10090.

SYNTHESIS OF NEW PHOSPHORYLATED QUATERNARY AMMONIUM SALTS AND THEIR DERIVATIVES

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As a result of gradual mutation of bacteria, viruses and fungi, susceptibility to drugs is lost, making it difficult to treat infections and increasing the risk of disease spread. Therefore, there is an urgent need to obtain more effective antimicrobial and antiviral drugs with a broad and long spectrum of action.

We have previously shown that α -phosphorylated quaternary ammonium salts exhibit high antibacterial activity against human and animal pathogens¹⁻². Continuing our work in this area, we developed a method for the synthesis of a series of β -phosphorylated derivatives of quaternary ammonium salts (Fig. 1)³:

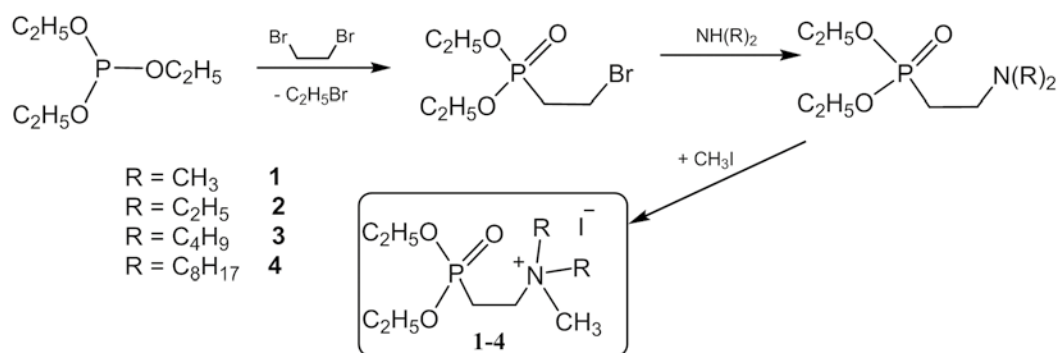


Figure 1. Scheme for the synthesis of β -phosphorylated quaternary ammonium salts

β -aminoethylphosphonates were reacted with iodinated alkyls to give the target products 1–4: the reactions were carried out at room temperature in benzene. All obtained products were isolated from the reaction mixture, the structure was proved by a complex of physical methods: ³¹P, ¹H, ¹³C NMR, IR spectroscopy.

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The work was carried out at the expense of the Kazan (Volga Region) Federal University Strategic Academic Leadership Program ("Priority-2030").

SEARCH FOR CYTOTOXIC AGENTS AMONG MIXED-LIGAND COPPER(II) COMPLEXES WITH FERROCENE AND 1,10-PHENANTHROLINE / 2,2'-BIPYRIDINE DERIVATIVES

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The search for effective drugs for antitumor therapy is an urgent challenge in medicinal chemistry. Since the copper(II) complex with 1,10-phenanthroline $[\text{Cu}(\text{phen})_2]^{2+}$ has nuclease activity¹, the design and synthesis of compounds based on it can lead to the production of cytotoxic agents. The coordination of additional ligands to the copper ion leads to a change in the physicochemical properties (increased solubility, stability in solutions, lipophilicity, etc.), as well as the cytotoxic profile of the complexes. Ferrocene derivatives possess various types of biological activity and low toxicity², and therefore are promising for the synthesis of potential cytotoxic agents.

In this work, ferrocenylmethylethionine³ and based on it mixed-ligand copper(II) complexes with 1,10-phenanthroline and 2,2'-bipyridine were obtained and characterized. The cytotoxic activity of the synthesized coordination compounds was studied on several human tumor cell lines. To assess the selectivity of the complexes, the non-tumor cell line MRC-5 was used.

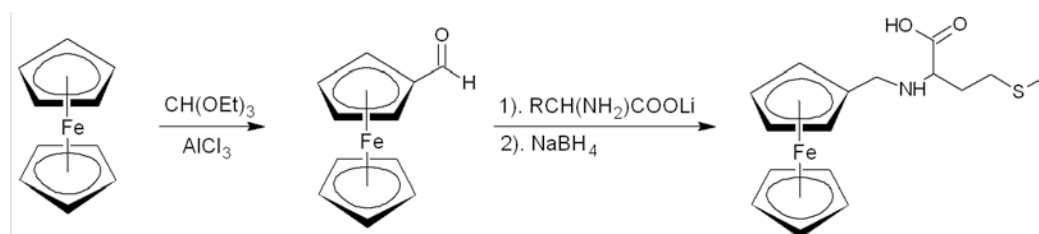


Figure 1. Scheme for the synthesis of ferrocenylmethylethionine

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MICELLAR FORMS OF OLEYLHYALURON FOR THE DESIGN OF NANOSCALE THERANOSTICS

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Oleic acid hydrophobized hyaluronic acid (HA-C18), (15kDa, degree of substitution 9%) is an amphiphilic polymer with the ability to self-assemble into micellar structures in aqueous media. This property is used for solubilization of hydrophobic drugs. The possibility of developing theranostic systems based on HA-C18 micellar structures as a polymeric nanoscale carrier has been studied. HA-C18 micelles were loaded with drugs (etoposide (ETP), its prodrug 4-O'-benzyloxycarbonyl derivative (ETP-Cbz), paclitaxel (PTX)), MRI contrast agent (superparamagnetic iron nanoparticles, SPION) and a clozo-decaborate complex (2-(dioctylsulfonio)-clozo-decaborate 1-butyl-3-methylimidazolium, CDB) as a neutron-capture agent. A conjugate of HA-C18 with the fluorescent dye cyanine 5 (Cy5) was also prepared. Thin film methods, ultrasonic homogenization followed by removal of organic solvents by evaporation or dialysis were used to obtain the structures. Parameters of the obtained structures are given in the table:

Form composition	Size, nm	PDI	ζ - potential, mV	CMC, mg/ml	Inclusion (%)
HA-C18/SPION	186,4 \pm 1,7	0,096 \pm 0,012	-53,4 \pm 1,8	0,004	88,2
HA-C18/CDB	246,2 \pm 2,8	0,041 \pm 0,008	-46,9 \pm 1,1	0,037	87,4
HA-C18 – Cy5	555,9 \pm 38,1	0,346 \pm 0,064	-30,7 \pm 2,8	0,038	< 1
HA-C18/ETP	232,4 \pm 30,5	0,340 \pm 0,070	-46,4 \pm 0,1	0,04	74,1
HA-C18/ETP-Cbz	268,2 \pm 47,5	0,250 \pm 0,101	-39,8 \pm 2,6	–	82,2
HA-C18/PTX	350,4 \pm 2,7	0,120 \pm 0,007	-40,4 \pm 0,3	–	65,0

Transmission electron microscopy was used for visualization, the stability of the structures was evaluated by determining the critical micelle formation concentration (CMC). The obtained structures can be considered as a platform for the design of theranostics.

This work was financially supported by RSCF, project 23-25-00194.

FORWARD SYNTHESIS PLANNING BASED ON MONTE-CARLO TREE SEARCH

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We introduce i-Synthesis – a new forward synthesis planning (reactants-to-products) tool based on the Monte-Carlo tree search algorithm. The algorithm iteratively applies reaction transformations to a set of initial compounds and generates synthetic routes leading to a target molecule or similar compounds. The objective function of forward synthesis planning is typically related to a specific property or activity of a target molecule. In this work, we chose structural similarity between intermediate products and the target molecule as an objective function for the search algorithm, as it allows us to compare its performance with available retrosynthesis planning tools.

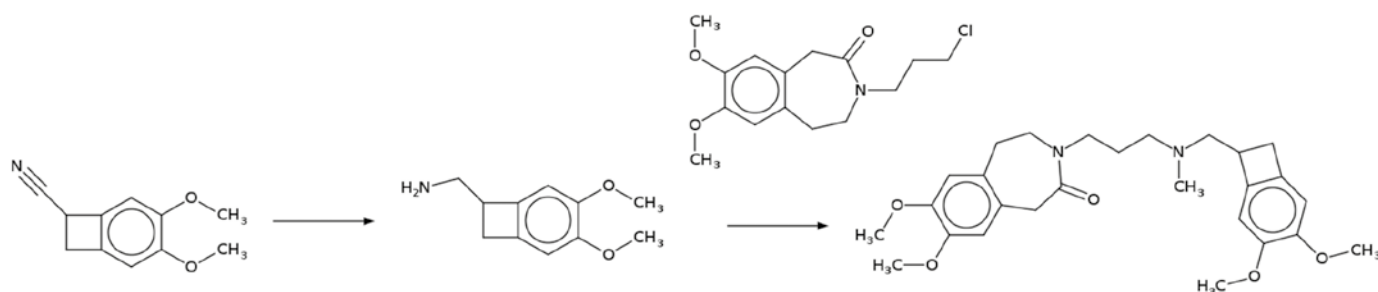


Figure 1. Predicted synthesis pathway for ivabradine, an antianginal drug

Current implementation of i-Synthesis is based on a collection of 604785 commercially available building blocks from ZINC database and 2597 reaction transformation templates automatically extracted from the USPTO reaction database. We have performed a benchmark of i-Synthesis and AiZynthFinder¹ to find synthetic routes for 15 popular drugs. i-Synthesis found synthetic routes for 9 exact target molecules (same as AiZynthFinder), while suggesting routes for similar compounds in other cases.

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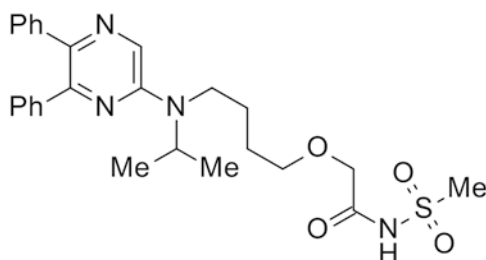
This work was funded by the subsidy allocated to Kazan Federal University for the state assignment in the sphere of scientific activities FZSM-2024-0002.

DEVELOPMENT OF A NEW APPROACH TO OBTAINING A KEY INTERMEDIATE FOR THE SYNTHESIS OF THE ACTIVE PHARMACEUTICAL SUBSTANCE OF THE DRUG SELEXIPAG

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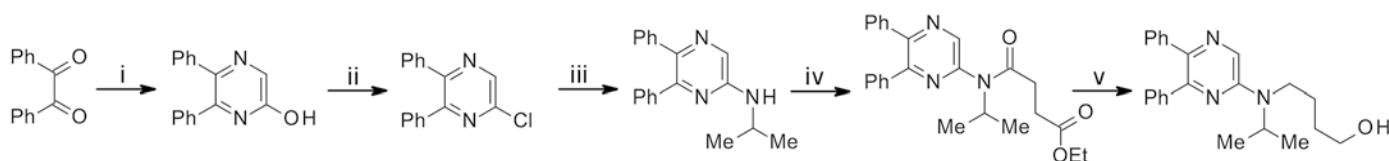
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Selexipag is a highly selective agonist of prostacycline receptors of a non-prostanoid nature:



It finds application in the clinic for the treatment of pulmonary arterial hypertension and is marketed by the pharmaceutical company Janssen under the trade names *Uptravi*[®] and *Apbravi*[®]. There is no production of the active pharmaceutical substance and the drug Selexipag in Russia.

As a part of the implementation of the import substitution program in the field of pharmaceuticals for the treatment of orphan diseases, we have developed an effective, brand new synthesis scheme for the key intermediate of the synthesis of the substance of the drug Selexipag – 4-[(2,3-diphenylpyrazine-5-yl)(isopropyl)amino]butanol. The key stage of this scheme is the acylation of 2,3-diphenyl-5-(isopropylamino)pyrazine chlorangidride of succinic acid monoethyl ether with subsequent reduction of the resulting product:



i = $\text{H}_2\text{NCH}_2\text{C}(\text{O})\text{NH}_2 \cdot \text{HCl}$, EtOH, NaOH, further – HCl, H_2O ; ii = PCl_5 , $\text{P}(\text{O})\text{Cl}_3$; iii = Me_2CHNH_2 , Me_2SO ;
iv = $\text{ClC}(\text{O})\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OEt}$, $[(\text{Me}_2\text{CH})_2\text{NEt}]$; v = AlCl_3 , $\text{Na}[\text{BH}_4]$, THS, further – NaOH, H_2O

The proposed approach makes it possible to obtain a target intermediate with a good yield and purity sufficient for subsequent conversion into the target substance of Selexipag.

This study was supported by RSF (project 23-90-04000).

SYNTHESIS, PHYSIO-CHEMICAL AND MICROBIOLOGICAL EVALUATION OF SURFACTANTS SYNTHESIZED FROM NAPHTHALENE AND PYRIDINE MOIETIES

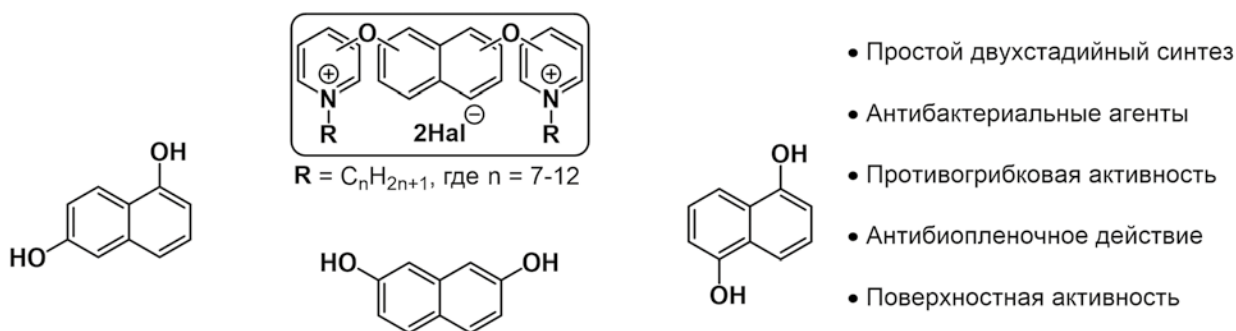
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The naphthalene moiety is an important building block in the synthesis of biologically active molecules used as anticancer, antimicrobial, anti-inflammatory, antiviral, antidiabetic, anticonvulsant and other agents¹. In turn, quaternary ammonium compounds (QACs) are a class of surfactants that are widely used in everyday life as disinfectants due to their detergent properties and antibacterial action².



In the presented work, we synthesized broad-spectrum biocides by incorporating a naphthalene moiety into bis-QACs through a simple two-step synthesis from dihydroxy-naphthalene derivatives. The results obtained indicate a high potential for using the developed molecules as antiseptics and/or disinfectants.

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CHEMICAL KNOWLEDGE OF LARGE LANGUAGE MODELS IN THE MOLECULE DESCRIPTION GENERATION TASK

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Language models in chemistry are used to generate molecules and predict reactions. However, do language models react more to the similarity of strings, or are they able to interpret these strings as some chemical structures? The paper explores various methods of augmentation of string representations of SMILES¹ molecules in order to understand how modern language models such as MolT5² and Chem+Text T5³, respond to these changes. Augmentation methods for changing SMILES strings while maintaining the same molecular structure include: using canonical SMILES strings, adding hydrogen, converting to Kekule SMILES strings, and renumbering cycles.

Our results using the CHEBI-20⁴ dataset of 3,300 pairs of SMILES-description show that for each augmented sample, there is an average drop in metrics of 15% and 11% for MolT5 and Chem+Text T5, respectively. Adding hydrogen changes the string the most, so the metrics in this sample drop the most (minus 21–29% of quality). The renumbering of cycles, on the contrary, causes the minimal changes in the row presented, and on this test set the drop in metrics is insignificant (minus 1–9% of quality).

The probing method showed the instability of the models to changes in the molecular string. The results indicate that the differences in metrics are more related to the processing of linguistic data than to deep representations of chemistry. In future studies, we plan to study these representations in detail on different layers of models.

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SEARCHING FOR BIOLOGICALLY ACTIVE MOLECULES IN CHEMICAL SPACE GENERATED BY THE SUZUKI REACTION

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The search for biologically active molecules is a key task in the field of cheminformatics today. One of the methods for solving this problem is the combinatorial generation of molecules or the generation of molecules with specific properties using neural networks¹. Using this approach, it is possible to find hit molecules, but researchers may face the difficulty of synthesizing the generated molecules.

The algorithm that was developed in this work allows to consider the synthetic availability of compounds for searching biologically active molecules. For the generating procedure the Suzuki–Miyaura cross-coupling reaction was used. The open database eMolecule was used as available for purchase reactants for generation pipeline. This approach makes it possible to obtain potentially synthetically accessible molecules. In the course of our work, we developed an algorithm for searching for JAK2 Janus kinase inhibitors among the chemical space generated using the Suzuki–Miyaura reaction.

During the generation, it was shown that despite the use of one type of reaction, we obtained a huge chemical space in the amount of 18709599 molecules. To filter the chemical space and search for potentially active molecules for Janus kinase, we used the QSAR model we developed. As a result of filtration, 6815092 active molecules against JAK-2 were obtained, representing 36% of the generated chemical space. Thus, among the generated space, molecules potentially active towards JAK-2 kinase were found, which can be further studied using more accurate models and methods of computational chemistry.

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This work was funded by the subsidy allocated to Kazan Federal University for the state assignment in the sphere of scientific activities FZSM-2024-0002

COMPLEXES OF CALCIUM (II) IONS WITH AMINO ACIDS: STRUCTURE, STRUCTURE AND STABILITY

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Knowledge of complexes of amino acids with metals and their derivatives has important pharmaceutical implications, for example, they can be used in multidrug resistance to cancer researches.

At the same time, studies in this area are complex due to the nature of the analyzed objects, and there are not too many reliable data in the literature on the interaction between calcium (II) ions and organic ligands. Most of them belong to the second half of the 20th century, and the constants values were obtained only by one method themselves.

The stability constants of Ca^{2+} complexes with 19 amino acids different in composition and structure in aqueous solutions at $T = 298 \text{ K}$ were determined using the methods of potentiometric titration and spectrophotometric determination using mathematical processing of experimental data. The stability constants are placed in the range $\lg K = 0.39\text{--}4.33$.

Based on experimental data, three main groups of formed complexes of amino acids with Ca^{2+} are proposed: unstable, weakly stable and relatively stable. The nature of stability sequence of Ca^{2+} complexes with amino acids is explained. Molecules of the most stable amino acids consist of a smaller number of carbon atoms and do not have bulky and branched CH_3 substituents, which can be a steric obstacle in the coordination of free s-orbitals of Ca^{2+} complexing ions and electron pairs of ligands.

The work was carried out within the framework of the state assignment of the Ministry of Science and Higher Education of RF (№. 075-03-2023).

MULTIDESCRIPTOR NEURAL NETWORK MODEL OF DEPENDENCE WITH ACTIVITY AGAINST *S. AUREUS* OF CHEMICAL COMPOUNDS STRUCTURE

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The aim of the work was develop with artificial intelligence methods a multidescrptor model dependence of antimicrobial activity against *Staphylococcus aureus* on the structure of chemical compounds with different physico-chemical descriptors.

The training set included data of 3,699 known compounds: code, three levels of antimicrobial activity, 156 descriptor variables. The structure of was represented by 124 fragmented QL-descriptors of 1st rank (87 structural, 19 lengths and 18 links; calculated in IT Microcosm)¹, 20 quantum-chemical parameters (energies 10 HOMO and 10 LUMO, calculated by PM7 method in the HiperChem), as well as 12 physico-chemical parameters (calculated in DruLiTo).

The training of neural networks was carried out using the Statistica according to the two-step scheme described in the work². A two-layer perceptron MLP $k-m-2$ with a bottleneck was chosen as the initial architecture of the neural network. Here, k is the number of input neurons, in this case, 156, according to the number of physico-chemical parameters; m is the number of hidden neurons, set by the program from 3 to 155, since $2 < m < k$.

When training networks on a random sampling for level Moderate of antimicrobial activity was obtained optimum precision neuronetwork with next architecture and predictive characteristics: MLP 156-24-2 (Tanh, Softmax) Acc=93,5%, Sens=64,3%, Spec=98,2%, ROC=89,2%. The use of fixed sampling options for training improved the prediction accuracy of active compounds: MLP 156-15-2 (Logistic, Softmax) Acc=93.6%, Sens=74.1%, Spec=96.8%, ROC=91.3%.

Thus, the use of multidescrptor descriptions allowed to build a highly accurate neural network model of the dependence of antimicrobial activity on the chemical structure of compounds of *S. aureus*.

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COPPER(II) COMPLEXES BASED ON TETRAZOLE AND 1,10-PHENANTHROLINE / 2,2'-BIPYRIDINE DERIVATIVES: SYNTHESIS, *IN VITRO* AND *IN VIVO* TOXICITY ASSESSMENT

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Copper(II) complexes with 1,10-phenanthroline and 2,2'-bipyridine are of particular interest as candidate molecules for the therapy of malignant neoplasms. Within the framework of this study, mixed-ligand 1,10-phenanthroline / 2,2'-bipyridine based copper(II) complexes with tetrazole derivatives (5-phenyl-1H-tetrazole (HL¹), 5-(4-chlorophenyl)-1H-tetrazole (HL²)) have been synthesized. The compounds obtained have been characterized by elemental and powder X-ray diffraction analyzes, EPR and IR spectroscopy, thermogravimetry, single-crystal X-ray diffraction analysis. It has been shown that the resulting series of complexes with the general formula [Cu₂(L^{N-N})₂(L¹/L²)₄], as a rule, has a binuclear structure due to the bridging function of the (L¹)⁻ or (L²)⁻ ligands.

In vitro cytotoxic activity has been tested against several human tumor cell lines using the IN Cell Analyzer 2200. The complexes have been shown to have pronounced cytotoxic activity in the concentration range of 0.5–50 μM. When assessing the activity of the complexes on the non-tumor MRC5 cell line, 1,10-phenanthroline-5,6-dione (phendione) based compounds have been found to exhibit selectivity towards tumor cells (selectivity indexes vary from 4 to 7).

For the most promising complex [Cu(phendione)(L¹)₂], an assessment of acute toxicity *in vivo* has been carried out; white laboratory mice have been selected as experimental animals. The median lethal dose LD₅₀ has been found to be 145 mg/kg, which is significantly higher than the LD₅₀ value of cisplatin (13 mg/kg).

For a number of synthesized compounds, the possible mechanisms of action have been studied: the ability of the complexes to damage the main target of metal-based antitumor drugs – DNA, the possibility of reactive oxygen species generation, the effect of compounds on the mitochondrial membrane potential.

This work has been supported by the Russian Science Foundation, project № 20-73-10207.

COMPLEXES OF GOLD, RUTHENIUM, AND IRIDIUM WITH GLUCOSE-BASED BICYCLOPHOSPHITE LIGANDS AS PROMISING ANTITUMOR AGENTS

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The search for an alternative to platinum in metal-containing antitumor drugs is one of the significant tasks in modern medicinal chemistry. Promising compounds are Ru, Au and Ir, which are not biogenic metals and are not involved in metabolism, but are toxic, and the kinetics of complexes of these metals, like platinum, is within the time frame of the cell cycle.

The purpose of this work is to obtain compounds of iridium, gold, and ruthenium with glucose-based phosphite ligands, as well as to study their physicochemical and biological properties to select these complexes for potential drugs. New complexes of iridium, gold, and ruthenium with a fragment of a biologically active substance – bexarotene – were obtained and their antiproliferative activity and stability in aqueous solutions were studied.

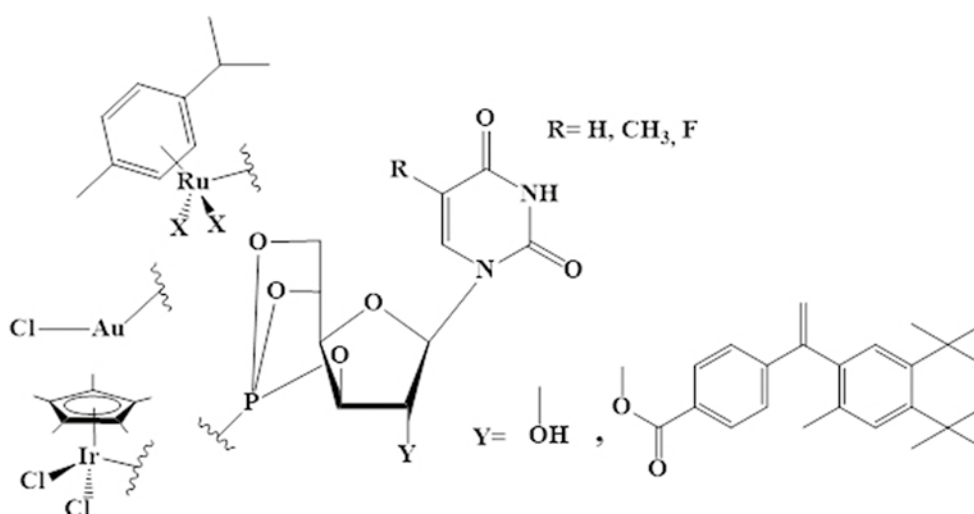


Figure 1. General scheme for the molecular design of new Ru(II), Ir(III) and Au(I) compounds

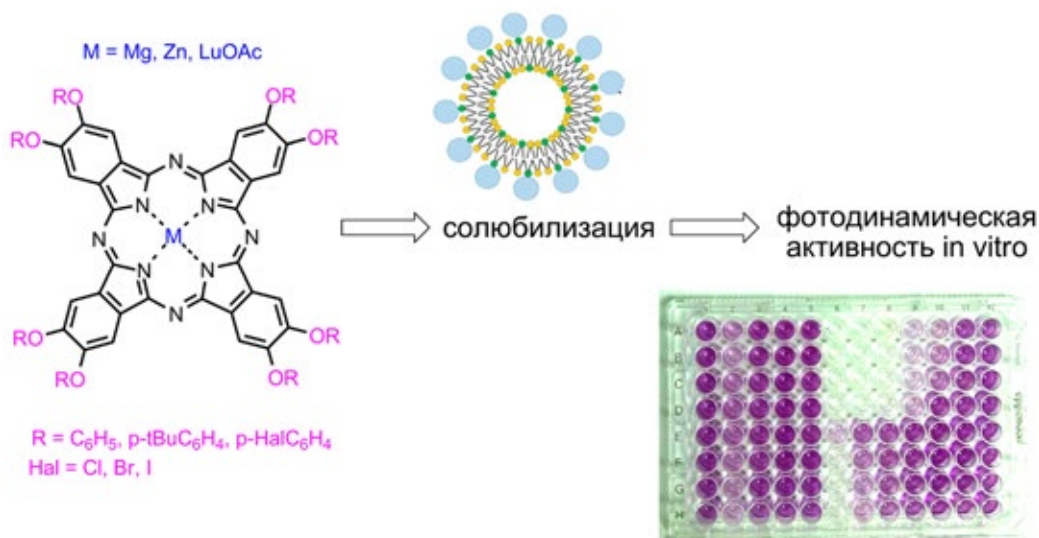
The work was carried out with financial support from the Russian Foundation for Basic Research, grants No. 20-33-90081 and No. 19-53-12042.

ARYLOXYSUBSTITUTED PHTHALOCYANINES: SYNTHESIS, SOLUBILIZATION, PHOTOCHEMICAL PROPERTIES

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As part of this work, a series of photosensitizers based on new aryloxy-substituted phthalocyanine complexes was obtained. The ability of target photosensitizers to generate two reactive oxygen species: singlet oxygen and superoxide anion radical has been demonstrated. In the case of halogen-substituted complexes, when going from chlorine to iodine, an increase in the generation yield of singlet oxygen and a decrease in the efficiency of superoxide anion radical generation were observed.



Water-soluble complexes of phthalocyanines with cyclodextrins of a 1:1 composition were obtained. These solubilized forms demonstrated a photodynamic effect *in vitro* for the WI38, HCT166, MCF7 and A431 cell lines. The iodine-substituted complex showed the greatest activity; the IC₅₀ after irradiation was 7 μ M. The presence of a heavy atom (iodine) leads to an increase in the population of the triplet level of the photosensitizer and an increase in the $^1\text{O}_2$ generation activity.

The work was carried out with the financial support of the Russian Science Foundation, project 23-73-10076.

NEURAL NETWORKS ON GRAPHS FOR PREDICTION OF LIPOPHILITY OF COMPOUNDS

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Among the properties of ADMET, lipophilicity, which is defined as the partition coefficient between octanol and water (logP), is a key parameter in early drug discovery studies. However, it is not always possible to measure logP experimentally, resulting in a lack of reliable experimental data for a large number of compounds.

The most modern computational approach for calculating lipophilicity, with optimal performance and accuracy, are methods based on the use of deep neural networks¹. This paper presents a graph deep neural network model predicting logP as well as a confidence interval. Among the various molecular representations that underlie the architecture of neural networks, graph-based representations have the highest performance. The model was trained on a concatenated data set composed of 8 published papers, the data was subjected to a cleaning procedure, duplicates and stereoisomers were removed. The total number of compounds is 55,000 for each of the known experimental logP values. The resulting model has greater performance in predicting lipophilicity with $r^2=0.96$ and $rmse=0.43$ log units than previously published models with $r^2=0.94$ and $rmse=0.45$ log units and trained on 17603 compounds².

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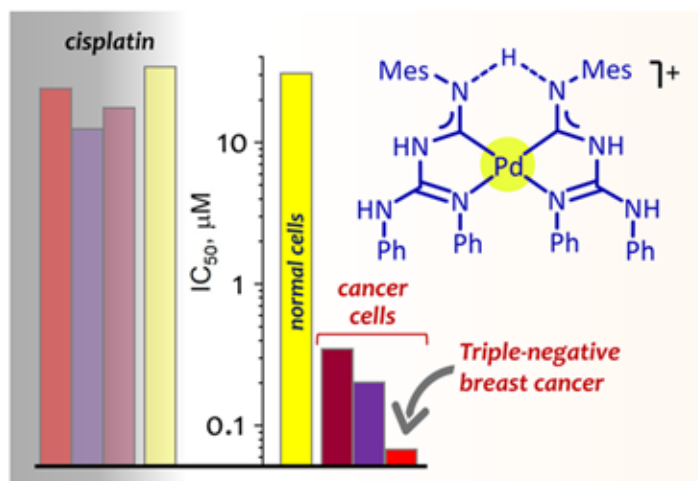
This work was funded by the subsidy allocated to Kazan Federal University for the state assignment in the sphere of scientific activities FZSM-2024-0002

METAL-(ACYCLIC DIAMINOCARBENE) COMPLEXES DEMONSTRATE NANOMOLAR ANTIPROLIFERATIVE ACTIVITY AGAINST TRIPLE-NEGATIVE BREAST CANCER

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Breast cancer is the most commonly diagnosed malignant cancer worldwide amongst women and is the leading cause of cancer-related fatalities. Triple-negative breast carcinoma (TNBC) is an extremely aggressive and metastasizing form of breast cancer that has a poor prognosis. This talk will report the discovery of a novel class of hydrolytically stable Pd^{II} species with biguanide-like C,N-chelated ligands, which exhibit excellent antiproliferative activity for TNBC cells *in vitro* (IC₅₀ <0.1 μM) together with effective inhibition of tumor growth model in mice.¹ The lead candidate caused profound caspase-mediated cell death accompanied by strong lipid peroxidation in triple negative breast cancer MDA-MB-231 cells at low nanomolar concentrations and was at least 300 times more active than cisplatin *in vitro*. It retained its antiproliferative activity under hypoxic conditions, demonstrating its ability to overcome the hypoxia-induced mechanisms of multi-drug resistance developed by TNBC tumors and affecting the efficacy of drugs currently used in the clinic. The facile one-pot metal-mediated synthesis from commercially available precursors and their encouraging biological activity *in vitro* and *in vivo* make them good candidates for further evaluation as potential antineoplastic agents.



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FORMATION OF PHARMACOLOGICALLY ACTIVE COPPER(II) AND COBALT(II) COMPLEXES

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The rise of multidrug-resistant bacteria has generated a great challenge to treat infections caused by bacteria with the available antibiotics. According to WHO, about 700 thousand people die annually from infections caused by resistant strains. Therefore, there is a need to develop new antimicrobial drugs with alternative mechanisms of action. Possible solutions include complexes with essential metals, such as copper and cobalt, which are essential trace elements and perform important functions in living organisms.

Due to their good solubility, which is an important criterion for future drugs, carboxylate complexes are increasingly attracting the attention of researchers. In this regard, the purpose of the presented work was to develop a method for the synthesis of Cu(II) and Co(II) complexes with furan / thiophene / indolecarboxylic acids and polypyridines as N-donor ligands, determine the structure, study the physicochemical properties and biological activity.

According to X-ray diffraction data, the resulting complexes can be divided into three groups: mono-[M(An)₂L(H₂O)_x] (M = Cu, Co; L = bpy, 1,10-phen, neoc, nphen; x=0, 1), bi-[Cu₂(An)₄L₂] (L = 1,7-phen, nphen, bpy, 1,10-phen) and trinuclear [Co₃(An)₆L₂] (L = phen, neoc). The purity of the compounds was confirmed by X-ray diffraction and elemental analyses, stability in solutions of DMSO and 0.9% NaCl was assessed by UV-spectroscopy and quantum chemical calculations.

Results of *in vitro* antibacterial activity of the obtained compounds against *M. smegmatis*, *M. tuberculosis*, ten G(+) and G(-) bacterial strains and antiproliferative effectiveness on tumor cell lines: HCT116 (intestinal cancer), A549 (lung cancer), SKBR3 (breast cancer), SKOV3 (ovarian cancer), as well as the non-tumor line HDF (dermal fibroblasts) as a control, showed high biological activity of the resulting compounds; The most promising for further testing are cobalt complexes, which demonstrate low toxicity while simultaneously being highly active.

The work was carried out with the financial support of the Russian Science Foundation, project 22-13-00175.

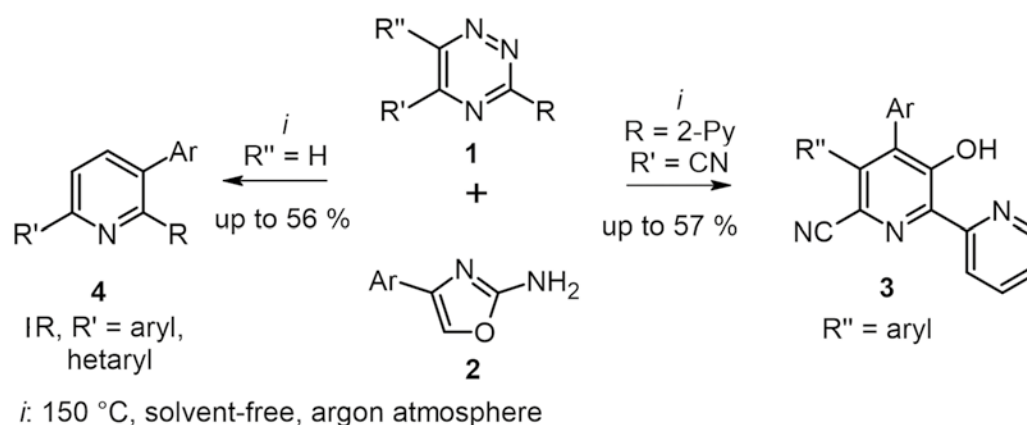
A NEW APPROACH TO SUBSTITUTED (2,2'-BI) PYRIDINES BASED ON THE REACTION BETWEEN 2-AMINO OXAZOLES AND 1,2,4-TRIAZINES

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A new approach to the preparation of multisubstituted (bi)pyridines has been developed, based on the reaction of 1,2,4-triazines **1** with 2-amino oxazoles **2** under heating in solvent-free conditions.¹⁻²



The structure of the products was confirmed by NMR spectroscopy, mass spectrometry, and X-ray diffraction data for a series of compounds. The key advantages of this approach are the availability of starting compounds and the production process in the absence of a catalyst and solvents.

The resulting 3-hydroxy-2,2'-bipyridines **3** demonstrate promising photophysical properties. In addition, these compounds are structural analogues of some natural antibiotics.

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This work was supported by the Ministry of Science and Higher Education of the Russian Federation, Agreement № 075-15-2022-1118 dated 29.06.2022.

MIXED LIGAND ESSENTIAL METALS COMPLEXES AS PROMISING CANDIDATES FOR ANTI-TUMOR THERAPY

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The design strategy for new drugs is the modification of existing drugs that are known to have a clinically significant antitumor effect. One class of compounds currently in clinical trials is the *Casiopéinas*[®] series. In development of this direction, work is underway to obtain mixed ligand complex compounds of a number of essential (vital) metals (Cu(II), Zn(II), Mn(II), Ni(II), Co(II)) with tetrazole, pyridine and phenylphosphine derivatives. All compounds undergo primary characterization using a set of physicochemical methods. The crystal structures of the most complexes were established using X-ray diffraction analysis.

To study the possibility of biomedical application, the behavior of complexes in biocompatible solutions was studied using electric field sputtering mass spectrometry, electronic absorption spectroscopy, EPR spectroscopy of frozen complexes' solutions, and conductometry.

Screening of the cytotoxic properties of the complexes was carried out *in vitro* using IN CellAnalyzer 2200 (GE Healthcare, UK) using the method of double staining of cells with fluorescent dyes, which makes it possible to assess the percentage of living, apoptotic and dead cells. Several human tumor cell lines were used in the work: Hep-2 (larynx carcinoma), MCF-7 (breast adenocarcinoma), HepG2 (hepatocarcinoma), as well as non-tumor HEK293-A (embryonic kidney cells) and MRC-5 (fibroblasts) for assessing the selectivity of the studied complexes. It was shown that the complexes have pronounced cytotoxic activity in the concentration range of 0.5–50 μ M, and a number of compounds with high selectivity were isolated.

Acute toxicity *in vivo* was assessed for the most promising complexes. It was shown that the semi-lethal dose LD₅₀ for all studied compounds is significantly higher than that for cisplatin.

The work was supported by the Russian Science Foundation (Project № 20-73-10207).

NANOMETRIC CYTOACTIVE MATERIAL “LITAR” AND TISSUE REGENERATION

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One of the main conditions for the existence of a biological system (this includes the human body) is the regeneration of the tissue(s) of this system, which (regeneration) occurs constantly throughout the entire life cycle of an individual representative, which ensures the inviolability of this system¹. The provision or course of regeneration is carried out by the action of crystals of hydroxylapatite (calcium hydroxophosphate) or simply apatite on human stem cells². In the body, these crystals have sizes of 35–37 nm, and in the “LitAr” material they were obtained with sizes of 3–4 nm and 50 nm. The process was controlled by laser ablation³. At the same time, the implantation material provided regeneration, for example, of bone tissue, in approximately the same time (3–4 months), when the biodegradation time of “LitAr” with apatite crystals of different sizes was 20–25 days. If the size of the crystals is the same in the native bone, then in the material it exists in two phases 3 ÷ 4 and 25 ÷ 50 nm. At the same time, it was not possible to obtain crystals with small and large sizes separately – they were formed simultaneously. It is possible that it is not the size of apatite that is essential in starting regeneration, but its ability to undergo hydrolysis in the stem cell, changing the pH from 3.5 to 7–8.

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QUANTUM MECHANICAL-CLUSTER APPROACH TO SOLVE THE BIOISOSTERIC REPLACEMENT PROBLEM IN DRUG DESIGN

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Bioisosteres are molecules which differ in substituents having very similar shapes. Bioisosteric replacements are ubiquitous in modern drug design, where they are used to alter metabolism, change bioavailability, or modify activity of the lead compound. Prediction of bioisosteres relative affinities with computational methods is a long-standing task; however, the very shape closeness makes bioisosteric substitutions almost intractable for computational methods which use standard empirical force fields.

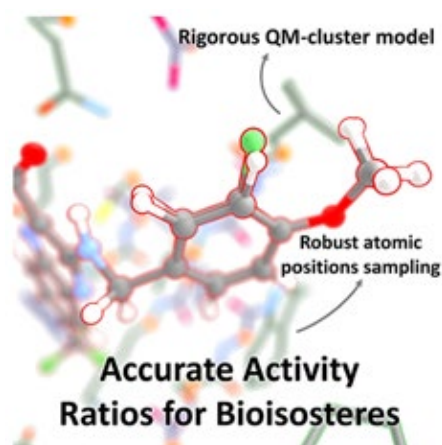


Figure 1. Visual scheme of our approach

Here, we design a QM-cluster approach based on GFN2-xTB semi-empirical method and apply it to a set of H→F bioisosteric replacements. Our QM-cluster methodology based on few steps: extract ligand and the protein residues, which have at least one atom within 4 Å from the ligand, building convex hull and add residues penetrating it, move each atom (except for the fixed one) by 0.03(3) Å to create 101 different structures and find lowest energy during geometry optimization and finally calculate relative affinity. Finally, we estimate computational errors using bootstrap method.

The proposed methodology enables advanced prediction of biological activity change upon bioisosteric substitution of –H with –F, with the standard deviation of 0.60 kcal/mol, surpassing the ChemPLP scoring function (0.83 kcal/mol), and making QM-based $\Delta\Delta G$ estimation comparable to ~0.42 kcal/mol standard deviation of in vitro experimental measurement. The speed of the method (~5 hours on a laptop) and lack of tunable parameters makes it affordable in current drug research.

T.V.L. and M.G.M. are grateful to the Russian Science Foundation for financial support (grant #22-73-10124).

EFFECT OF NITROSYL IRON COMPLEXES ON THERAPEUTIC TARGETS OF CARDIOVASCULAR DISEASES

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One of the factors in the development of cardiovascular diseases (CVD) is aberrant production of nitric monoxide (NO)¹. In medical practice, exogenous NO donors are utilized to compensate for its deficiency.

The purpose of this work was to study the effect of a number of promising compounds, nitrosyl iron complexes (NICs), with aromatic thioligands on therapeutic targets for the treatment of CVD. The NO-donating activity of NIC was studied using the Griess reaction. Soluble guanylate cyclase (sGC) is a direct enzymatic target of NO-dependent signaling². Also important enzymes in the regulation of the cardiovascular system are adenylate cyclase (AC) and phosphodiesterase (PDE). Activation of sGC and AC results in the increased synthesis of cyclic nucleotides, while PDE converts them into an inactive non-cyclic form. Since inflammation (eg, of the lining of arteries) is often an important risk factor for the development of CVD, the enzyme cyclooxygenase (COX-2) may be an interesting therapeutic target to consider. The effect of NICs on AC and sGC was assessed by changes in the level of cyclic nucleotides using the ELISA method, and on PDE and COX-2 – by model enzymatic reactions.

It was shown that all complexes with aromatic thiols had an effect on the enzymatic targets discussed above.

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The study was supported by Russian Science Foundation № 22-73-10049, <https://rscf.ru/project/22-73-10049/>

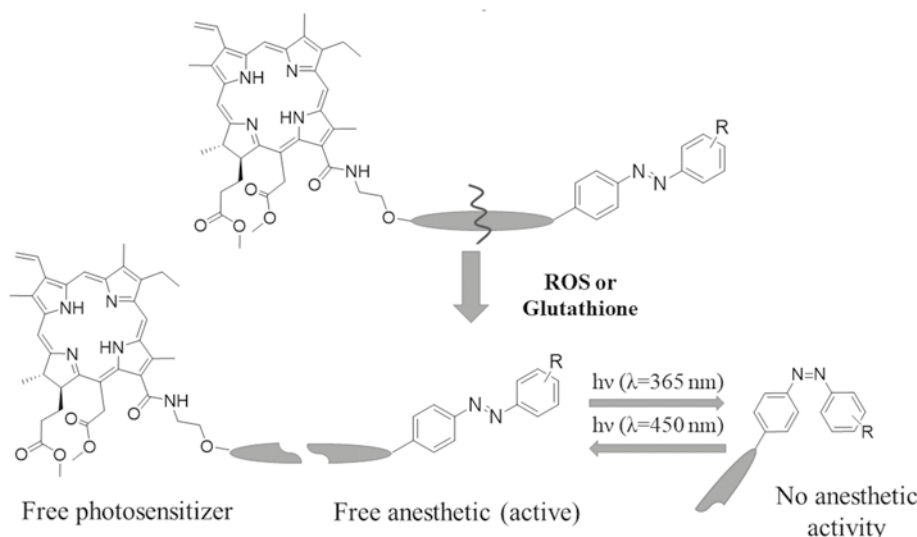
CONJUGATES OF AZOBENZENES WITH NATURAL CHLORINS AS PROTOTYPES OF LIGHT-CONTROLLED ANTICANCER AND ANTIBACTERIAL DRUGS WITH ANESTHETIC ACTIVITY

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Photodynamic therapy (PDT) is an effective way to treat both bacterial infections and cancer, since the reactive oxygen species generated by photosensitizers effectively destroy tumor and bacterial cells. At the same time, both bacterial infections and the PDT procedure are associated with pain, most of the anesthetics used having low selectivity of action.¹ Conjugation of natural chlorins with photo-switchable analogues of known anesthetics will allow PDT or antibacterial therapy to be performed simultaneously with selective anesthesia.



In this work, conjugates of natural chlorins with ethercaine-based anesthetics were obtained, and their antibacterial, antitumor and analgesic activity were studied.

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DEVELOPMENT OF LOW MOLECULAR P-GLYCOPROTEIN INHIBITORS BASED ON 18-B- GLYCYRRHETIC ACID DERIVATIVES

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Overexpression of P-glycoprotein (P-gp) is one of the key mechanisms underlying multidrug resistance (MDR) in tumor cells. This transporter ensures the removal of various xenobiotics from cells, including anti-tumour drugs, making it a promising therapeutic target. Modern P-gp inhibitors display a number of side effects that limit their clinical use and require new strategies for the development of such compounds. Natural metabolites are considered a promising platform for their design.

In the present study two semisynthetic triterpenoids, N,N-dimethylamine-containing soloxolone amide (1) and meta-pyridine-containing oxadiazole GLA (2), were identified as effective inhibitors of P-gp transport activity in human cervical cancer KB-8-5 cells and mouse lymphosarcoma RLS40 (by measuring the intracellular accumulation of rhodamine-123 (Po-123) and doxorubicin (Dox)). In addition, the lead compounds had an MDR-reversing effect due to their ability to synergistically increase the sensitivity of KB-8-5 cells to the cytotoxic effect of Dox. The observed effects of triterpenoids were not due to a decrease in P-gp expression, but were mediated by their direct interaction with the transmembrane domain of P-gp, as confirmed by RT-PCR, Western blot and molecular modeling. The pronounced anti-P-gp activity of compound (1) was further verified in vivo in the murine lymphosarcoma RLS40 model.

Thus, the identified compounds can be considered as drug candidates for the adjuvant therapy of tumors with an MDR phenotype associated with overexpression of P-gp.

This research was supported by the Russian Science Foundation, grant No. 23-14-00374.

NEW COMPLEXES OF Ba^{2+} AND Ca^{2+} WITH CHELATED DERIVATIVES OF BENZODIAZACROWN COMPOUNDS

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Studying the complexing properties of macrocyclic ligands is an important area of modern research. Complexes of crown ether derivatives with alkaline earth metal cations are subjects of great interest nowadays. They are effectively used in medicine as part of radiopharmaceuticals, fluorescent sensors, and probes.

Azacrown compounds form a class of ligands capable of forming strong complexes with a wide range of metal cations. Their distinctive features are possibility of complexation in both organic and aqueous media, the presence of a pre-organized macrocyclic cavity and capability of modifying ligand properties by introducing various coordinating groups. The complexing ability of azacrown esters is influenced by the rigidity and size of the macrocycle, the nature and properties of donor atoms, and the presence and characteristics of chelating groups. In this regard, our work is aimed at developing and studying the complexation of a series of 18-crown-6 and 21-crown-7 diazacrown derivatives with Ca^{2+} and Ba^{2+} cations. Diazacrown compounds contain a rigid aryl fragment, a combination of oxygen and nitrogen atoms in a macrocycle and additional coordinating carboxylate and picolinate groups in their structure.

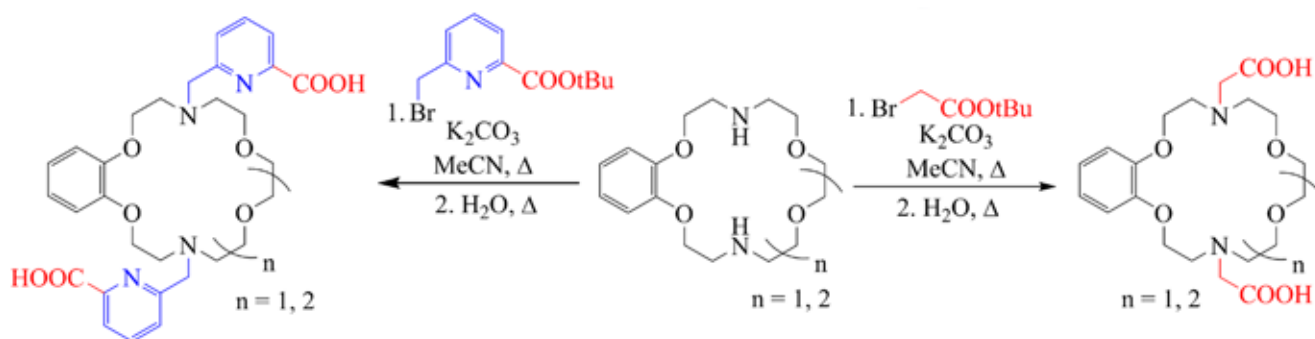


Figure 1. Synthesis of benzodiazacrown derivatives

It was found that all the studied ligands are capable of binding calcium and barium cations in aqueous solution. The most durable complex for barium is formed by a 21-membered macrocycle with picolinate groups, and for calcium is by an 18-membered macrocycle with carboxyl groups.

The work was carried out with the financial support of RSF No. 23-73-01270.

SYNERGETIC EFFECT OF SILVER COMPLEXES WITH ARSINE LIGANDS ON THEIR BIOLOGICAL ACTIVITY

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Silver compounds and its complexes, stabilized by various ligands, are capable of exhibiting powerful antimicrobial, antiviral, and anticancer effects in ionic form.¹ On the other hand, the biological activity of arsenic compounds also is well known.

Various complexes of silver nitrate and tetrafluoroborate with cyclic arsines were synthesized (Fig. 1) and their cytotoxicity against the cell lines M-Hela, HuTu 80 and Chang Liver, as well as antimicrobial activity against gram-positive and gram-negative bacteria were studied.

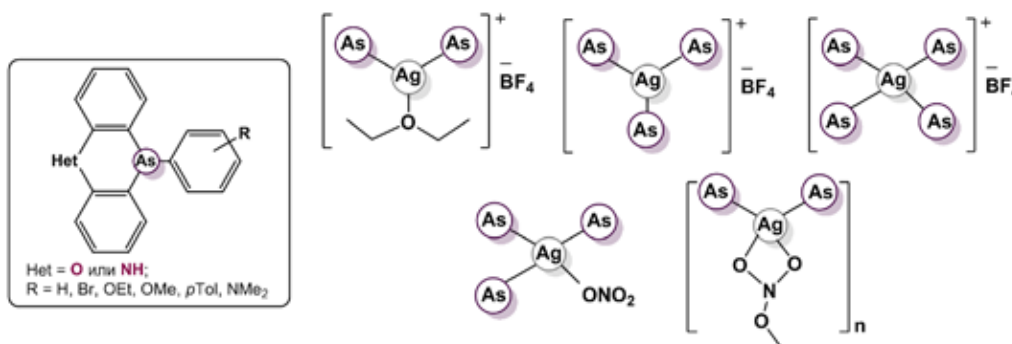


Figure 1. Types of synthesized silver complexes

Arsine ligands and AgBF_4 have moderate cytotoxicity towards cancer and normal cells, comparable to 5-fluorouracil (IC_{50} 50–90 μM). AgNO_3 is noticeably more toxic to cancer cells (IC_{50} 11–16 μM) with a high selectivity index for normal Chang Liver cells (SI is 15). Silver complexes with arsine ligands in all cases exhibit a synergistic effect, in which the IC_{50} decreases in the case of M-Hela by 2.5–4 times, and for HuTu80 by 25–50 times.

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The work was carried out with the financial support of the Russian Science Foundation and the Cabinet of Ministers of the Republic of Tatarstan within the framework of scientific project No. 23-23-10072.

SYNTHESIS OF POLYFLUORINATED 1-BENZYLISATINS FOR CREATION OF ANTICANCER AGENTS

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Despite advances in diagnosis and treatment, cancer remains one of the leading causes of death worldwide. The search for new effective antitumor agents is an urgent task of modern medicinal chemistry and practical oncology. It is known that isatin and its derivatives have a wide range of biological activity¹, including antitumor activity, therefore this class of chemical objects is used in the creation of drugs. One of the promising approaches to the chemical modification of substances is the introduction of a fluorine atom into the target molecule, which often leads to a significant increase in biological activity².

In this work, a series of fluoroisatins 3a–f were synthesized by a simple alkylation reaction of the sodium salt of 5-fluoroisatin 2, obtained in situ, with fluorinated benzyl halides (Fig. 1).

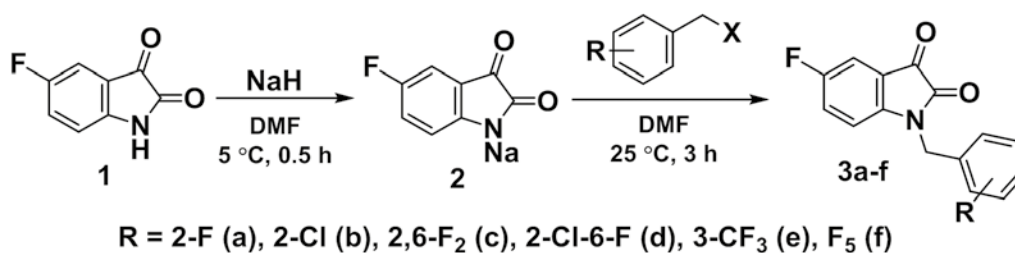


Figure 1. Two-step synthesis of polyfluorinated 1-benzylisatins

The resulting compounds have the potential to be used as a basis for the creation of antitumor agents with a known mechanism of action. It has been shown that the most cytotoxic derivatives are capable of inducing the production and accumulation of reactive oxygen species by disrupting the normal functioning of mitochondria and dissipation of the mitochondrial membrane, which leads to the triggering of apoptosis.

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The work was carried out with the support of the Ministry of Higher Education of the Russia at the Federal Research Center “Kazan Scientific Center” (grant No. 075-15-2022-1128).

SYNTHESIS OF NOVEL IODINE-CONTAINING AZOLOAZINE DERIVATIVES IN THE DESIGN OF ANTIVIRAL AGENTS

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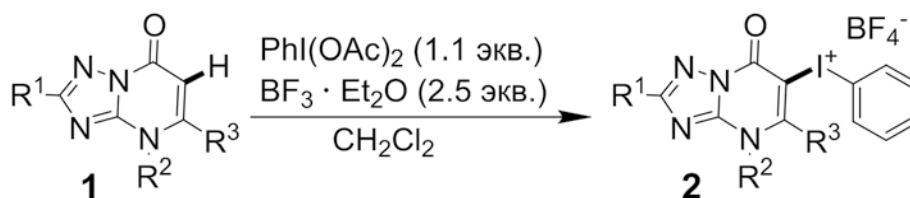
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The development of antiviral drugs has traditionally attracted much attention from researchers due to the emerging viral mutations, resistance to existing drugs, and the appearance of new viruses. As far as drug development with regard to RNA viruses is concerned, azoloazine-type heterocycles have proven to be of particular interest here, being considered as structural analogues of natural nucleic bases. One of the well-known commercially available drugs of this class is riamilovir (trade name Triazavirin®).¹

We recently found that azolopyrimidine analogues of riamilovir containing an aromatic thioether substituent at the azine ring are able to exhibit activity against SARS-CoV-2, as shown by both *in vitro* and *in vivo* experiments.² To expand the scope of suchlike compounds and further investigate their bioactivity, we came to design some potentially reactive synthons based on iodonium salts. The corresponding compounds (**2**) were obtained in yields of up to 90% as a result of the reaction of azolopyrimidines **1** with (diacetoxy)iodobenzene and BF₃OEt₂.



The ongoing research in this field is aimed at the further functionalization of the obtained compounds **2**.

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This research was funded by the Ministry of Science and Higher Education of the Russian Federation (Agreement No. 075-15-2022-1118).

TRANSITION-METAL-FREE C-H FUNCTIONALIZATION OF 2H-IMIDAZOLE N-OXIDES IN THE SYNTHESIS OF BIOACTIVE MOLECULES

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Currently, the development of effective methods for the synthesis of biologically active compounds is one of the top priorities of modern organic chemistry. At the same time, azaheterocyclic compounds are part of many chemical and pharmaceutical drugs. One of the effective ways to modify nitrogen-containing heterocycles is the method of C-H functionalization which has been successfully applied in the design of phenol-¹ and thioarylated² imidazolic derivatives.

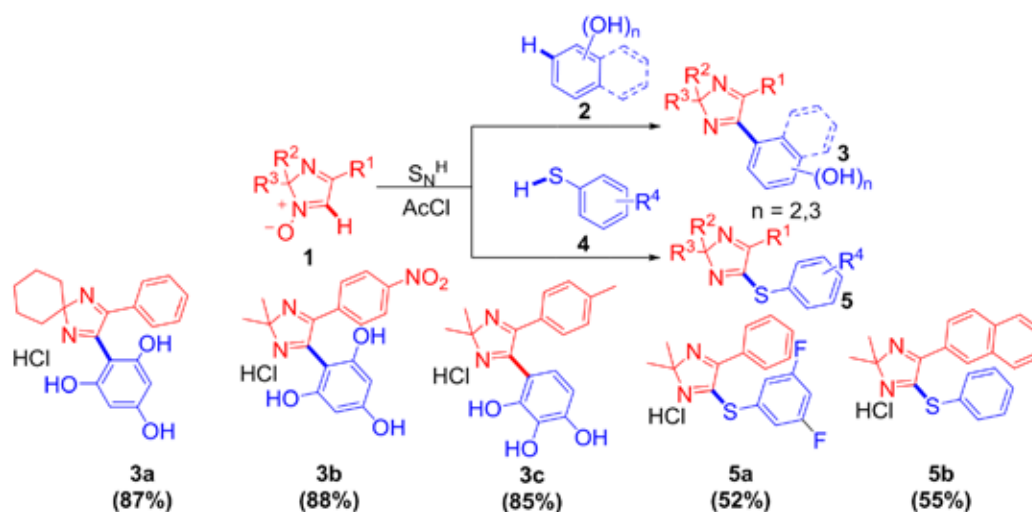


Figure 1. C-H functionalization of 2H-imidazole N-oxides

It is worth noting that some specific synthesized molecules have shown valuable endothelium-protective properties in *in silico/in vivo* experiments. Besides, phenol-containing compounds have shown effective antiradical activity (quenching up to 5 radical oxidative chains).

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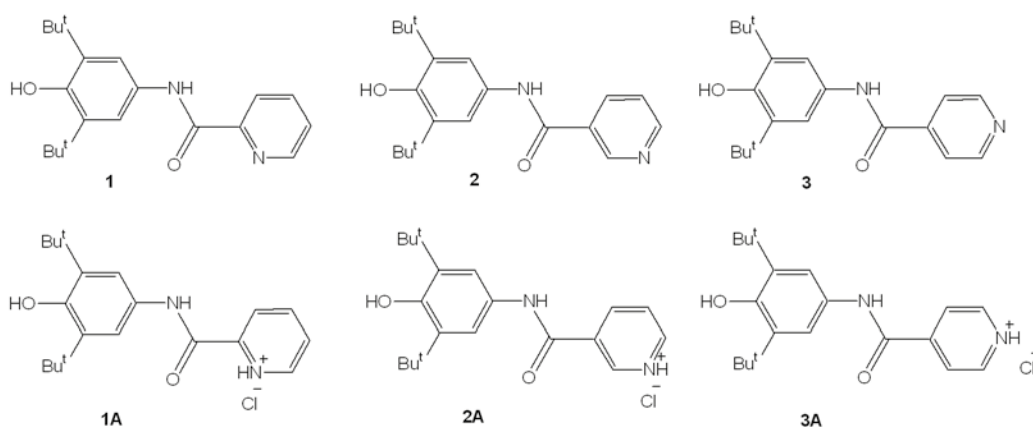
The study was carried out with the financial support of the Russian Science Foundation as part of a research project № 23-63-10011, <https://rscf.ru/en/project/23-63-10011/>

RADIOPROTECTORS BASED ON PYRIDINECARBOXYLIC ACIDS WITH A FRAGMENT OF STERICALLY HINDERED PHENOLS

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The development of means for protection against ionizing radiation is an important task. It is known that antioxidants are able to interrupt chain radical processes that occur in cells under the influence of radiation, and thereby protect the biological substrate. Sterically hindered phenols are known for their antioxidant properties and are widely used. A series of pyridinecarboxylic acid derivatives **1–3** containing a fragment of 2,6-di-*tert*-butylphenol and their hydrochlorides **1A–3A**, were synthesized. The compounds were characterized by IR and ^1H , ^{13}C NMR spectroscopy and elemental analysis.



The compounds showed pronounced antioxidant activity *in vitro*, they are effective one-electron reducers, as confirmed by the CUPRAC-test and free radical scavengers, as assessed by the DPPH-test. Hydrochlorides **1A–3A** were tested in a system using ionizing radiation and cholesteric liquid crystal dispersions (CLCDs) and proved to have radioprotective properties. The data obtained allow us to propose the resulting compounds as promising radioprotective agents.

The work was carried out with the financial support of the Russian Science Foundation, project 23-23-10030.

REACTIONS OF NITROSYL IRON COMPLEXES WITH MUCIN AND PROSPECTS FOR THEIR ORAL DELIVERY

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Nitrosyl iron complexes (NICs) are coordination compounds, potential new generation prodrugs for the treatment of socially significant diseases, including neutral NO groups, which, upon dissociation, spontaneously go into solution. The use of complexes in the form of a solid dosage form orally is the most promising way to administer NICs, since it does not require their preliminary dissolution.

This work shows that NICs and their decomposition products are able to penetrate through the gastrointestinal tract into the bloodstream: the EPR signal standard for nitrosyls is observed in all organs studied, including the brain. The complexes are stabilized on the mucin surface due to weak intermolecular interactions. As a result of studying the decomposition of NICs in simulated gastric fluid without pepsin (SGF) at pH 1.2, it was shown that an acidic environment will not have a significant effect on the rate of their decay. Dosage forms (tablets) containing NICs were obtained, for which the optimal kinetic profile of NO release was determined using the Griess test. It is provided by the composition of tablets containing albumin as an excipient.

Thus, with the intragastric method of delivery, NICs and their decomposition products retain their NO-donor properties, are successfully absorbed into the bloodstream and distributed throughout the organs. The developed dosage form provides an expansion of the arsenal of medicinal agents, long-acting NO donors used for the treatment of socially significant diseases.

The study was supported by Russian Science Foundation, № 22-73-10049, <https://rscf.ru/en/project/22-73-10049/>.

MECHANISM OF THE REACTION OF LIGAND EXCHANGE FOR GLUTATHIONE IN THE THIOSULFATE NITROSYL IRON COMPLEX

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Of particular interest for medicine and pharmacy are nitrosyl iron complexes with functional sulfur-containing ligands (NICs), exogenous donors of nitrogen monoxide (NO). They are low molecular weight structural analogues of the active centers of nitrosylated iron-sulfur proteins. It is assumed that NICs and their decomposition products *in vivo* can react with Fe- and SH-containing proteins, as well as low-molecular-weight thiols, in particular with reduced glutathione (GSH), which is widespread in cells and tissues.

This work describes the interaction of the binuclear NIC with thiosulfate ligands $\text{Na}_2[\text{Fe}_2(\text{S}_2\text{O}_3)_2(\text{NO})_4] \cdot 4\text{H}_2\text{O}$ (complex 1) with GSH. Using UV spectroscopy, the Griess reaction, and quantum chemical modeling, it was shown that the original thiosulfate ligands of complex 1 are replaced by GS^- to form a new binuclear nitrosyl complex with two glutathione ligands. The mechanism of this reaction has been described, which is as follows: at the initial stage, two glutathione molecules are attached to complex 1, then thiosulfate ligands are sequentially cleaved off, and the process is not accompanied by the formation of mononuclear NICs. The rate of NO release is two orders of magnitude lower than that of the original complex 1: $k_{\text{ef}} = (1,8 \cdot 0,1) \cdot 10^{-3} \text{ s}^{-1}$ and $k_{\text{ef}} = (2,9 \cdot 0,9) \cdot 10^{-5} \text{ s}^{-1}$ for the reaction without and in the presence of GSH, respectively. The resulting product generates NO over a prolonged period. Thus, the inclusion of GSH in the metabolism of this promising drug can significantly affect its NO-donating properties and vasodilating activity.

This work was performed in accordance with the state task, state registration No 124020500019-2.

APPLICATION OF A CONVOLUTIONAL MULTITARGETED NEURAL NETWORK MODEL BASED ON MULTIPLE DOCKING TO PREDICT THE ANXIOLYTIC ACTIVITY OF AMIDES AND AMIDINES OF THE ADAMANTANE SERIES

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The anxiolytic activity of chemical compounds is mediated by their effect on a variety of target proteins, with complex interactions between them. In this study, a forecast of the anxiolytic activity of adamantane amides and amidines was made using a convolutional multi-target neural network model based on multiple docking and validation of the forecast results was carried out in an experiment. According to the scheme presented in work¹, 22 target proteins relevant to anxiolytic activity were selected. Multiple docking of new compounds and the comparison drug ethifoxin was performed using MSite² and AutoDock Vina³ programs. Using the CorrConv program, a correlation convolution of the energy spectra of multiple docking was performed. The training of the convolutional neural network model was carried out in the Statistica⁴ program. Using the constructed model, a forecast of the anxiolytic activity of four new substances was made. An experimental test in the Open Field test showed that one compound is comparable in activity to the comparison drug ethifoxin, which is consistent with the results of the in silico prognosis.

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The work was performed within the framework of the state task of the Ministry of Health of the Russian Federation No. 23022400009-9 “Development of a methodology for computer search for multi-target pharmacologically active compounds based on multiple docking and convolutional neural network technology of various architectures”.

REACTIONS OF NITROSYL IRON COMPLEXES WITH BLOOD PROTEINS

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Nitrosyl non-heme iron complexes (NICs) are a stable depot of NO, a signaling molecule involved in the regulation of many physiological processes. Their synthetic analogues, low-molecular-weight NICs with functional sulfur-containing ligands, spontaneously generate NO upon dissociation and are effective vasodilators¹. Moreover, depending on the structure of the ligand, the complexes have cytotoxic, antimetastatic, antidiabetic and other activities².

NICs and their decomposition products will react with heme- and SH-containing proteins when introduced into the bloodstream. In this work, the mechanisms of the interaction of NICs with aliphatic and aromatic thiols with bovine serum albumin and hemoglobin were studied using experimental (UV, EPR, fluorescence spectroscopy, Griess reaction, etc.) and theoretical methods (quantum chemical modeling). It has been established that the structure of the ligands included in the composition of NICs has a significant influence on the process of their decomposition. *In vivo* experiments confirm that these proteins bind NICs. Thus, the complex study carried out makes it possible to predict the main pathways of decomposition of promising NICs *in vivo*.

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The study was supported by Russian Science Foundation, No 22-73-10049, <https://rscf.ru/en/project/22-73-10049/>.

NITROSYL IRON COMPLEXES WITH THIOUREA DERIVATIVES: DECOMPOSITION, NO-DONOR ACTIVITY AND EFFECT ON Ca^{2+} -ATPASE OF SARCOPLASMIC RETICULUM

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Nitrosyl iron complexes (NICs) with functional sulfur-containing ligands are a class of promising exogenous NO donors which, during dissociation in aqueous solutions, release NO and biologically active thiol ligands. In this work, NICs with thiourea derivatives $[\text{Fe}(\text{SC}(\text{NH}_2)(\text{NHC}_2\text{H}_5))_2(\text{NO})_2]\text{Cl}$, $[\text{Fe}(\text{SC}(\text{NH}_2)(\text{NHC}_2\text{H}_5))\text{Cl}(\text{NO})_2]$ and $[\text{Fe}(\text{SC}(\text{NH}_2)_2)_2(\text{NO})_2]\text{Cl} \cdot \text{H}_2\text{O}$, which have therapeutic potential for the treatment of socially significant diseases, were studied. The decomposition of NICs in buffer anaerobic solutions was studied using absorption spectroscopy, amperometry, quantum chemical and kinetic modeling. A reaction scheme for the decomposition of complexes was proposed and the rate constants were calculated.

The effect of NICs on the activity of the enzyme Ca^{2+} -ATPase of the sarcoplasmic reticulum (SR), which regulates the level of Ca^{2+} in the cell, was also assessed. Inhibition of its activity prevents the formation of blood clots and the adhesion of metastatic cells to the capillary endothelium. It was found that in the studied concentration range (0.1–0.001 mM) NICs affect the transport and hydrolytic functions of the enzyme; in the highest concentration they completely inhibit the activity of the enzyme. The data obtained make it possible to predict the antihypertensive, antimetastatic and vasodilator activities of the studied compounds.

This work was performed in accordance with the state task, state registration No 124020500019-2.

ANALGETIC AND ANTI-INFLAMMATORY ACTION OF BIFARMACOPHORIC PRODRUGS BASED ON PYRIDOXINE

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Nonsteroidal anti-inflammatory drugs (NSAIDs) are one of the most commonly used types of worldwide medications. NSAIDs act directly at the site of inflammation by blocking the synthesis of prostaglandins. One of the most powerful non-opioid analgetics is ketorolac (superior all known NSAIDs). Unfortunately, ketorolac has many serious side effects: erosive and ulcerative lesions of the gastrointestinal tract, impaired renal function, metabolic acidosis etc.

Based on our systematic studies of the synthesis and biological activity of pyridoxine derivatives¹ in this work new biparmacophore derivatives containing fragments of pyridoxine and ketorolac (NPVS-7 and NPVS-8) were synthesized. Anti-inflammatory, analgetic and toxicity properties of the obtained compounds were studied *in vivo* (on Wistar rats). It was found that in the “hot plate” test NPVS-8 has higher analgesic activity (16.7 ± 0.6 sec.) compared to ketorolac (12.1 ± 0.8 sec.). In the formalin test NPVS-8 showed anti-inflammatory activity comparable to ketorolac. And finally, the safety profile of the studied compounds be considerably superior to ketorolac (in an acute toxicity study for NPVS-7 and NPVS-8 $LD_{50} > 2000$ mg/kg in comparison with ketorolac $LD_{50} = 189$ mg/kg). Thus, the synthesized compounds may be of interest as promising drug candidates with an improved safety profile compared to known NSAIDs.

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The study was supported by the Russian Science Foundation grant No. 24-23-00350, <https://rscf.ru/en/project/24-23-00350/>

SUPRAMOLECULAR PARTICLES BASED ON VIOLOGEN CALIX[4]RESORCIN AND SODIUM ALGINATE AS DRUG NANOCONTAINERS

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Nanoscale particles for drug delivery to cancer cells and tissues have become very popular in modern medicine due to their ability to penetrate various biological barriers. In this work, we studied the co-aggregation of sodium alginate (Alg) and viologen calix[4]resorcinols with alkyl chains of different lengths at the lower rim (VR-Cn, Fig. 1). Due to the joint action of electrostatic and hydrophobic interactions in VR–Alg mixed solutions, nanoparticles spontaneously form, the size and properties of which depend on the length of alkyl substituents in the VR structure and the ratio of components in the mixed system. The obtained aggregates are able of both solubilizing hydrophobic substrates and the hydrophilic anticancer drug doxorubicin. These particles prolonged release of doxorubicin in acidic medium, which is optimal for its delivery to tumor tissues. Thus, supramolecular interactions between viologen calix[4]resorcinols and sodium alginate lead to the spontaneous formation of supramolecular polymeric nanoparticles. These aggregates show potential as nanocontainers for drug binding and controlled release.

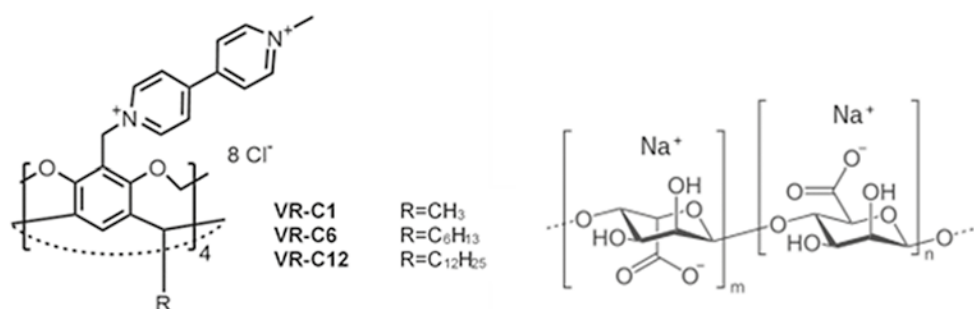


Figure 1. Structure of viologen calix[4]resorcin and sodium alginate

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COLLOIDAL QUANTUM DOTS FOR BIOLOGY AND MEDICINE

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Over the last decade, great attention of researchers has been focused on a 0-dimensional quantum objects based on semiconductor materials, which called QDs, due to increasingly technology-relevant applications^{1,2}. QDs obtained by using techniques of organic and inorganic chemistry are used in various fields such as electronics, optics, catalysis, energy production and storage. Medicine and biology are an area where colloidal QDs have promising applications in detection, study, treatment of individual cells and entire organisms.

In the present work, simple synthesis methods were developed to meet all modern requirements of green chemistry. Water was used as a solvent to produce colloidal nanoparticles. Non-toxic or bioactive organic molecules attached to semiconductor core served to stabilize, minimize possible toxicity, and functionalize QDs simultaneously.

The chemical and physical properties of QDs were studied by using SEM, TEM, optical absorption and luminescence³. Dynamic light scattering were used to study the hydrodynamic diameter DH, size distribution and colloidal stability of water solution QDs were investigated.

The stages of QDs penetration into the cell have been established. The result of conjugation depends on the concentration of the colloidal solution, the type of cell culture, and the time of conjugation. The cytotoxicity of colloidal QDs was carried out in vitro on cultures of human dermal fibroblasts and the cancer HeLa line.

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This work was supported by the Russian Science Foundation (project 19-73-20012-II, <https://rscf.ru/en/project/19-73-20012/>) and was performed at the Institute of Solid State Chemistry UB RAS, using Physics Technological Infrastructural Complex of the Institute of Metal Physics UB RAS.

SYNTHESIS AND ANTIHYPOXIC ACTIVITY OF 1-SUBSTITUTED 5-SULFONYLTETRAZOLES

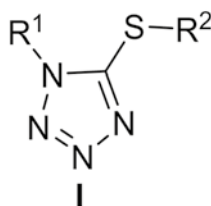
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It is known that heterocyclic compounds containing an exocyclic sulfur atom can have antihypoxic and antioxidant activity.¹ Antihypoxants are a group of drugs that increase the body's resistance to oxygen deficiency, often resulting from a variety of pathological processes. In this regard, substances exhibiting antihypoxic activity can be used to treat various diseases.¹ For this reason, the search for new compounds with antihypoxic and antioxidant activity is an urgent task.

We found that tetrazole derivatives with the general formula **I** exhibit high antihypoxic activity in models of normobaric hypoxia with hypercapnia, histotoxic hypoxia, and hemic hypoxia.



R1=Alk, Ar; R2=Alk

Also, the obtained compounds showed high anti-ulcer activity.

The report examines the synthesis of the studied compounds, as well as the analysis of the relationship between the activity of compounds and their structure.

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SYNTHESIS AND ANTIBACTERIAL ACTIVITY OF BIS-, TRIS- AND TETRAKIS-AMMONIUM COMPOUNDS BASED ON VITAMIN B₆

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Quaternary ammonium compounds (QACs) are the most important class of antiseptics and disinfectants. In the previous works of our group was produced and successfully passed preclinical study the bis-ammonium compound **KFU-05**, which has high antimicrobial properties and low toxicity *in vivo* (Fig. 1).¹

As part of further study of the “structure-biological properties” relationships, more than 150 QACs were synthesized. The parameters that were varied included the number and position of ammonium fragments, the lipophilicity of the compounds, and the use of a pentaerythritol scaffold. As a result, several lead-compounds with antibacterial activity comparable to **KFU-05** were identified.

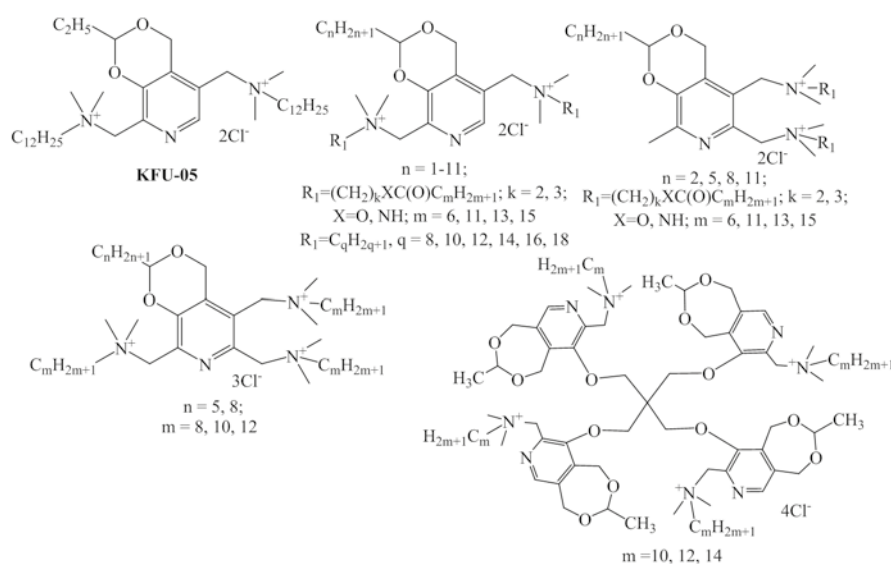


Figure 1. QACs based on pyridoxine derivatives

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COPPER(II) COMPLEXES WITH DIPHENYLPHOSPHINIC ACID AND 1,10-PHENANTHROLINE / 2,2'-BIPYRIDINE DERIVATIVES: SYNTHESIS AND CYTOTOXIC PROPERTIES

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Due to the major side effects and chemotherapy resistance of the clinically approved metal-based antitumor drugs (cisplatin and its derivatives), the search of novel medications bearing endogenous metal ions is carried out. Mixed-ligand 2,2'-bipyridine, 1,10-phenanthroline based copper(II) complexes are actively considered as potential anticancer agents, and one of the compounds registered as Mark Title Casiopeínas® has even reached the clinical phase I¹.

In the present study, five mixed-ligand copper(II) complexes with diphenylphosphinic acid (HL) and 1,10-phenanthroline or 2,2'-bipyridine derivatives (L^{N-N}) were synthesized. Obtained compounds were characterized by elemental and powder X-ray diffraction analyses, IR and EPR-spectroscopy, all the molecular and crystal structures were established by single-crystal X-ray diffraction analysis. In most of the experiments the composition of mixed-ligand copper(II) complexes can be described by the general formula [Cu(L^{N-N})(H₂O)L₂].

The cytotoxic activity of the complexes was investigated on tumor (Hep2, HepG2, MCF-7) and non-tumor (MRC-5) human cell lines using 2D and 3D (HepG2 spheroids) cell culture models in 0,1–100 μM concentration range. The cytotoxicity of 1,10-phenanthroline based compounds is superior to that of cisplatin. The level of reactive oxygen species generation in Hep2 cells has been shown to increase after incubation with complexes.

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ANTIBACTERIAL AND ANTIFUNGAL ACTIVITY OF ALPHA HYDROXYPHOSPHONATES

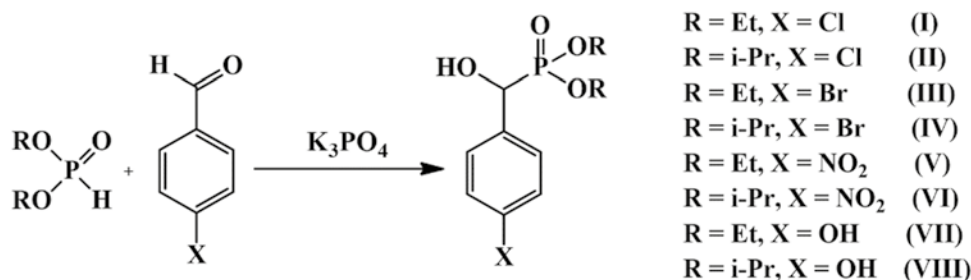
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Organophosphorus compounds, and in particular alpha-hydroxyphosphoryl compounds and their derivatives, have long established themselves as promising enzyme inhibitors, herbicides, antibiotics and fungicides^{1,2}. Recent studies have shown that phosphonates containing substituents at the α -carbon atom have high herbicidal, antibacterial, antifungal effects, and exhibit antioxidant and antiviral activity³.

In the present study, a wide series of α -hydroxyphosphonates were obtained using the Abramov reaction in order to study them for antimicrobial and antiviral properties.



The reactions took place at room temperature, without solvent, for 15 minutes in the presence of potassium phosphate as a catalyst. The structure of the compounds was confirmed by a combination of ³¹P, ¹³C, ¹H NMR, IR spectroscopy and X-ray diffraction. It has been established that some of the obtained compounds exhibit an antimicrobial effect against a number of pathogenic microorganisms of humans and animals and fungi of the genus Candida.

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THE SYNTHESIS AND ANTIMICROBIAL POTENTIAL OF A NEW GENERATION OF BIS-QUATERNARY AMMONIUM COMPOUNDS

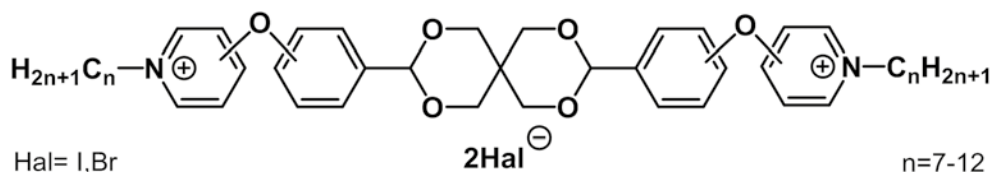
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One of the promising approaches to combat resistant microorganisms and biofilms is the development of novel biologically active compounds with a broad spectrum of antimicrobial activity. Quaternary ammonium compounds (QACs) are highly effective disinfectants with a powerful biocidal effect, even at low concentrations, excellent cleansing properties on hard surfaces and are relatively low in toxicity, making them suitable for use on human skin.¹



As part of the study, we report on the synthesis and microbiological evaluation of new bis-pyridinium compounds based on a pentaerythritol linker. The synthesized compounds were tested on a wide range of pathogenic microorganisms of the ESCAPE group, including biofilms and highly resistant clinical isolates. This approach allowed us to create a new generation of effective antimicrobial agents from readily available reagents.

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METRONIDAZOLE LOADING IN MIL-101(Fe) AND INVESTIGATION OF RELEASE IN VARIOUS BODY FLUIDS

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Metal organic frameworks (MOF) are new classes of highly porous materials. Crystal lattice of these frameworks is built by coordination bonds between central metal ions and organic ligands with chelating functional groups, which form a bond with the metal by the donor–acceptor mechanism.^{1,2} These polymers are promising candidates for target drug delivery and controlled drug release.³ We synthesized MIL-101(Fe) by hydrothermal method. MIL-101(Fe) has low toxicity and biodegradability.⁴ Metronidazole was encapsulated (10 wt. %) in synthesized MOF. The created MOF and composite were characterized by the methods of powder X-ray diffractometry, porosimetry and scanning electron microscopy. We confirmed the encapsulation of the drug and demonstrated the absence of its effect on the MOF structure. In addition, we conducted a study of the release of metronidazole from this MOF in various biological fluids such as saliva and blood serum and compared the profile of its release in deionized water. The selectivity of metronidazole release from MIL-101(Fe) in various media was revealed. The data obtained may be useful for using MIL-101(Fe) for targeted drug delivery and delayed release.

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PHOTOACTIVE WATER-SOLUBLE CLUSTER COMPLEX $[\{\text{Mo}_6\text{I}_8\}(\text{S}_2\text{O}_3)_6]^{8-}$, HAVING A CYTOSTATIC EFFECT

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Octahedral metal cluster complexes with the general formula $[\{\text{Mo}_6\text{X}_8\}\text{L}_6]^n$ (X is halogen; L is a terminal ligand of organic or inorganic nature) have a number of properties that are attractive from the point of view of various biomedical applications. Such compounds have a radiopaque $\{\text{Mo}_6\text{X}_8\}$ core, pronounced phosphorescence in the red/near-IR region of the spectrum, and are capable of photosensitizing the process of generation of reactive oxygen species under UV or X-ray radiation. In addition, most of the studied molybdenum cluster complexes have low dark and high phototoxicities in *in vitro* models. All these properties allow us to consider octahedral molybdenum halide clusters as potential theranostic agents in the fight against cancer.

Primary biological screening of our recently obtained cluster complex with the composition $\text{Cs}_3\text{Na}_5[\{\text{Mo}_6\text{I}_8\}(\text{S}_2\text{O}_3)_6]$ (Fig. 1) showed that, in addition to the above-described properties, $[\{\text{Mo}_6\text{I}_8\}(\text{S}_2\text{O}_3)_6]^{8-}$ has a pronounced cytostatic effect. This fact allows us to consider it as a potential anticancer drug with combined action.

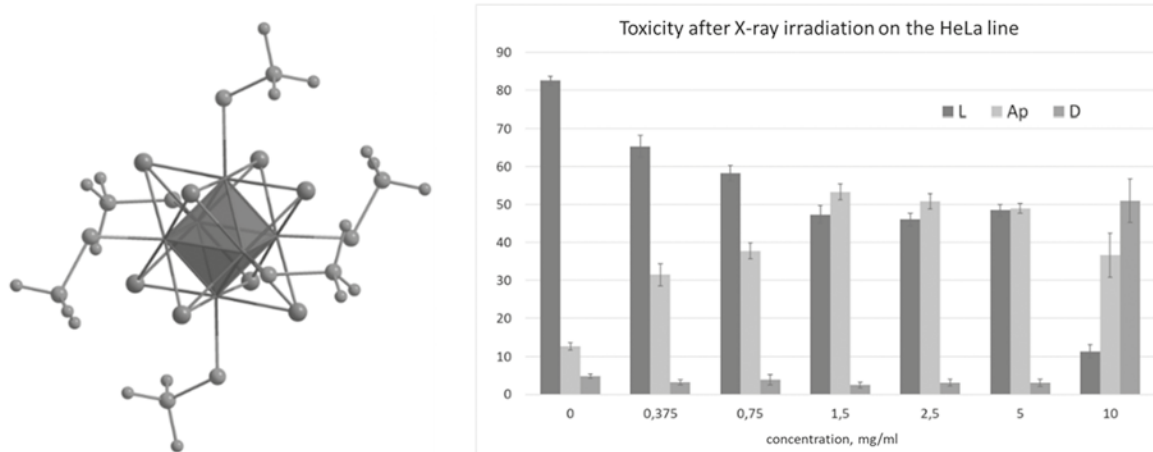


Figure 1. Structure of $[\{\text{Mo}_6\text{I}_8\}(\text{S}_2\text{O}_3)_6]^{8-}$ (left);
X-ray induced toxicity on HeLa cells (L – live, Ap – apoptotic, D – dead) (right)

The work was carried out with the financial support of the Russian Science Foundation, project 19-73-20109.

SYNTHESIS AND MULTI-PURPOSE BIOLOGICAL ACTIVITY OF “HYBRID” TETRAZOLE-CONTAINING COMPOUNDS

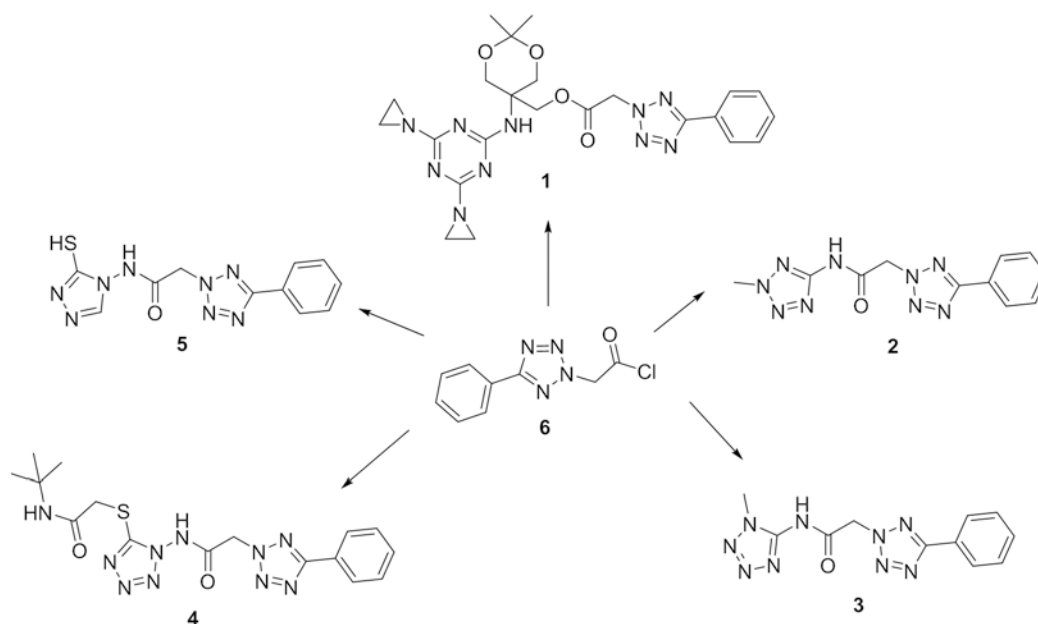
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The active pharmaceutical ingredients of tetrazole-containing drugs are “hybrid” systems containing several heterocyclic moieties¹. It is for such “hybrid” assemblies that multipurpose biological activity should be expected.

In this study, we conducted *in silico* (PASS, molecular docking, scoring) prediction of the biological activity of non-annulated polynuclear derivatives of compounds obtained by acylation of triazole-, tetrazole- and triazine-containing substrates with 5-phenyltetrazol-2-ylacetic acid chloride.



Based on the *in vitro* and *in vivo* data, compounds **1–5** exhibit antiviral, antitumor and antidiabetic activities.

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This work was supported by the Russian Science Foundation (RSF), Project No. 23-13-00224.

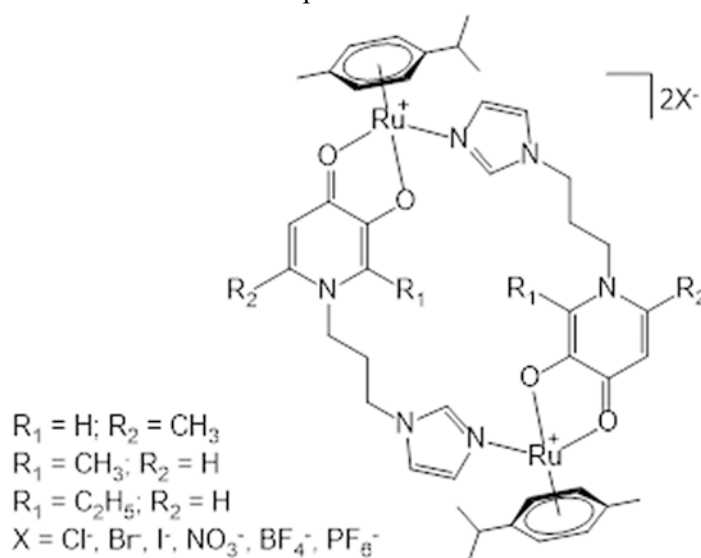
BEHAVIOR AND ANTITUMOR ACTIVITY OF RUTHENIUM METALLACYCLES WITH PYRIDONE LIGANDS

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As a promising replacement for antitumor platinum compounds, the most widely studied and described in the literature are ruthenium compounds. In 2021, the FDA approved the first ruthenium complex, BOLD-100, as an orphan drug. In addition, relatively recently, metallacycles were identified as a separate class of compounds and are of interest as macrocyclic compounds.

In this work, a series of ruthenium metallacycles with pyridone ligands were obtained, which are highly soluble in water and demonstrate promising antitumor activity *in vitro* tests on human cancer cell lines. The structure-activity relationship was studied for the obtained series of compounds.



The behavior of the resulting compounds in solutions was studied by NMR spectroscopy and quantum chemical calculations. The mechanism of cell death was determined by flow cytometry.

This research was funded by Russian Science Foundation, grant number 23-73-01076.

DESIGN OF MOLECULES WITH DESIRED PROPERTIES AND PREDICTION OF THE ROUTE OF THEIR SYNTHESIS

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Current methods for creating and optimizing molecules are often expensive and time-consuming. To address this challenge, mathematical models and algorithms have gained popularity in recent years, as they enable the prediction of molecular properties and optimization of their structures.

In this work, we present a tool for predicting the synthesis path and optimizing the desired property of a target chemical compound, as well as molecules similar to the target. Our approach is based on a virtual reactor that generates synthesis paths for molecules using predefined reaction rules and the structure of the target molecule. We utilize a genetic algorithm for optimization, which is inspired by the biological principle of natural selection. Through selection, crossover, and mutation of chromosomes, the algorithm identifies the optimal sequences for obtaining the desired molecule.

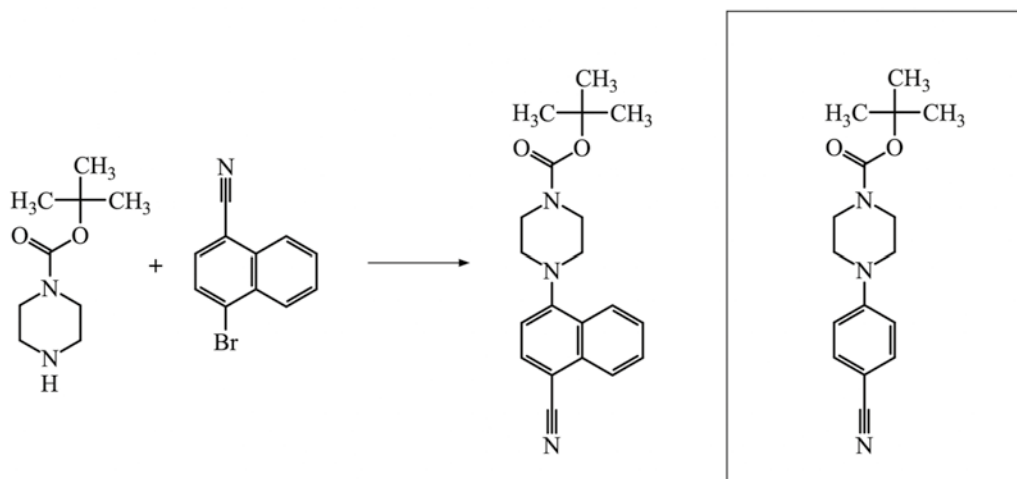


Figure 1. Predicted synthesis path of an analogue of the target molecule SCHEMBL2471189 (in the box) with a Tanimoto similarity coefficient=0.92

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This work was funded by the subsidy allocated to Kazan Federal University for the state assignment in the sphere of scientific activities FZSM-2024-0002.

NANOPARTICLES BASED ON POLYSACCHARIDES WITH DIFFERENT STRUCTURES FOR DRUG DELIVERY AGAINST BRAIN DISEASES

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Modern methods of therapy of hard-to-treat diseases are associated with the use of drugs that even in minimal concentrations have harmful effects. Methods of drug delivery to cancerous brain tumors are divided into local and systemic¹. In the second case, the delivery is carried out through the bloodstream and passes through the blood-brain barrier (BBB) and is the safest. Nanoscale particles with positive surface charge can cross the BBB. Biopolymeric nanoparticles can self-configure the conditions around tumor cells, promoting better entrapment of drug-loaded delivery vehicles².

Nanoparticles in this work were prepared by ionic gelation method based on oppositely charged polysaccharides chitosan and pectin. The morphology of nanoparticles was studied. Their mechanical properties, size and surface charge were evaluated. The structural features were determined by IR spectroscopy and the efficiency of sorption and desorption of antitumor drugs was determined by UV-visible spectrophotometry. The cytotoxicity of nanoparticles was evaluated for U87-MG.

In this way, nanoparticles with sizes ranging from 50 to 500 nm were obtained with different compositions. It was found that the kinetics of drug sorption and desorption depended on the ratio of polymer concentrations in the initial mixtures. Preliminary data showed that the introduction of nanoparticles loaded with drugs reduced the proliferative activity of tumor cells.

The obtained nanomaterials may be of potential practical interest for use as means of drug delivery to the brain, including therapy of oncologic diseases.

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This work was supported by the Russian Science Foundation (grant No. 22-73-10172).

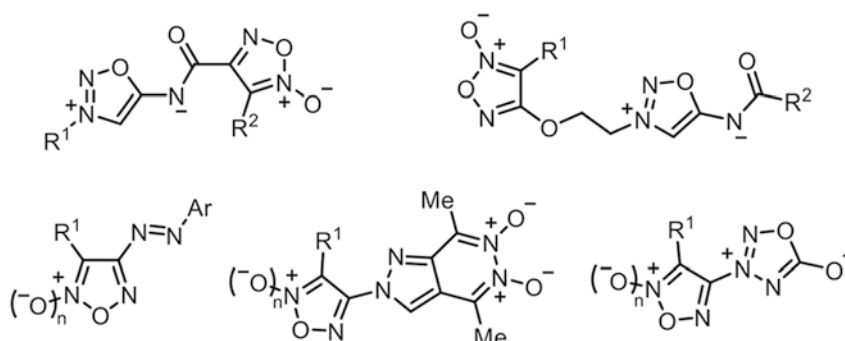
ASSEMBLY OF NEW HYBRID HETEROCYCLIC NO-DONORS

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Nitric oxide (NO) donors are important therapeutic agents among the realm of pharmaceuticals introduced into clinical practice to date. NO-donors are referred to as substances from the class of nitrogen-oxygen molecular systems capable of releasing nitric oxide in the human body. NO plays a multimodal role and is one of the essential and universal regulators of cellular metabolism, having a key effect on a variety of physiological processes. However, NO-donor drugs currently introduced into medical practice have a number of disadvantages. Their long-term use leads to tolerance development and side effects associated with severe vasodilation. Therefore, a search for new selective NO-donors with an optimal rate of nitric oxide generation and a wide spectrum of action remains relevant.

Herein, we present the latest achievements of our laboratory in the development of new methods for the synthesis of polynitrogen-oxygen heterocyclic structures with an ability to donate NO. Over the past 5 years, we created promising synthetic strategies for the assembly of heterocyclic systems of this kind, including 1,2,5-oxadiazole 2-oxides (furoxans), mesoionic sydnonimines and azasydnones, pyridazine di-*N*-oxides, as well as hybrid combinations derived thereof. Practically useful properties of the synthesized heterocyclic assemblies and the prospects for their use as NO-donors will also be presented in the report.



USING THE GAS DISCHARGE VISUALIZATION METHOD TO ASSESS THE STRUCTURAL ORGANIZATION OF AQUEOUS SOLUTIONS OF DRUGS

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The possibilities of using the gas discharge visualization¹ (GDV) method to assess the structural organization of aqueous solutions of drugs have been studied^{2,3}. Pictures of the angular distribution of electrons that passed through the studied liquid media and escaped into the air were studied by the sliding gas discharge they caused in the air and recorded in the GDV chamber. GDV images were a set of maxima corresponding to the directions (channels) of facilitated electron movement. To interpret data on the angular and energy distributions of kilovolt electrons passing through such media and providing visualization of the structural organization of solutions, data on the channeling of electrons through liquids with different types of ordering of micellar associates were used. The results obtained were used to evaluate the biological effect provided by agonists and antagonists of potassium and calcium channels of erythrocytes, as well as on changes in short-range order in ordered solutions.

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SYNTHESIS AND PROPERTIES OF ESTERS BASED ON OXYMETHYL-1,3-DIOXACYCLOALKANES

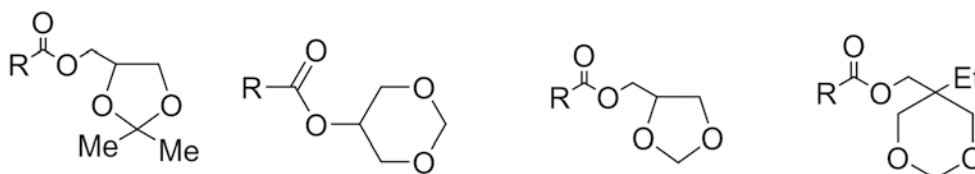
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Currently, 1,3-dioxacylane derivatives are widely used as fuel additives in the petrochemical industry. This is due to the availability of initial reagents: olefins, dienes, ethylene glycol, glycerol, amines, and the widespread use of these compounds in the synthesis of solvents, surfactants, additives to oils and polymers, corrosion inhibitors, plasticizers, biologically active drugs, etc.¹⁻³

The present paper presents the results of research on the development of a selective method for the synthesis of carboxylic acid esters containing a 1,3-dioxacylane moiety under the conditions of the Garegg-Samuelson reaction.

The synthesis of new esters containing a cycloacetal group based on benzoic, salicylic, p-hydroxybenzoic, phenoxyacetic, 2,4-dichlorophenoxyacetic, adamantanecarboxylic, monochloroacetic, maleic and fumaric acids and natural diterpenic acids has been carried out.



Their cytotoxic, antimicrobial, anticoagulation and antiplatelet activity have been studied.

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SYNTHESIS OF NEW 3-CINNAMYLTHTIO-1,2,4-TRIAZOLES WITH FUNGICIDAL AND ANTHELMINTIC ACTIVITY

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Azoles are one of the most studied and widespread classes of antimycotics with high efficacy and low toxicity to humans and animals¹. In recent years, it has been revealed that the introduction of an additional heterocyclic fragment into the historically formed chemotype of azole preparations increases fungicidal activity¹ (Fig. 1). However, the effect of the sterol-emulating fragment is significant.

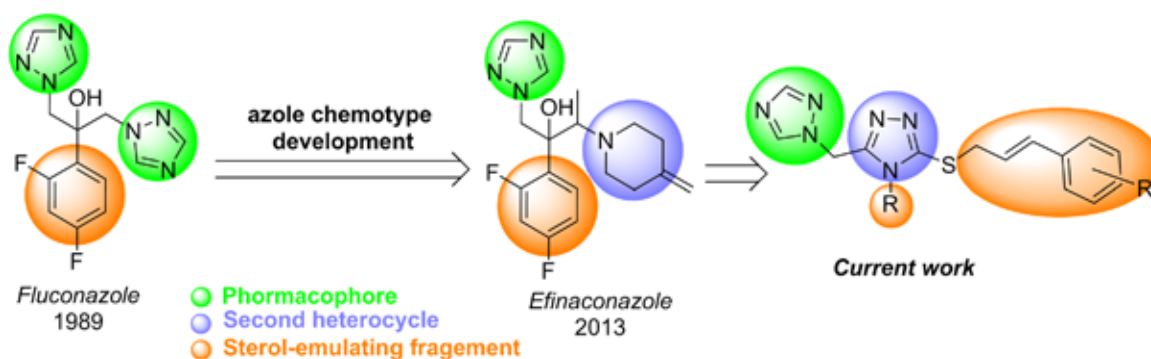


Figure 1. The historical development of the chemotype of azole preparations and the general structure of synthesized compounds

This work is devoted to the methods of synthesis and the study of the fungicidal and anthelmintic activity of 3-cinnamylthio-5-(1,2,4-triazole-1-ylmethyl)-1,2,4-triazoles² in *in vitro* and *in vivo* tests.

The simplicity of the production and the high biological activity of 3-cinnamylthio-1,2,4-triazoles are a useful base for exploratory research of new low-toxic antimycotic and anthelmintic drugs.

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QUANTUM DOTS IN MODERN RESEARCH: MEDICINE, DIAGNOSTICS, ECOLOGY

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The development of systems for the hypersensitive detection and diagnosis of oncological and infectious diseases, highly dangerous infections, the development of express diagnostic systems that allow simultaneous registration of numerous biomedical parameters are directly related to the development and investigation of the next-generation biomarker technology for various fields of clinical diagnosis^{1,2}. Quantum dots (QDs) representing fluorescent semiconductor nanocrystals include chemical elements of groups I and VI, II – VI, IV, III and V12) of the Mendeleev’s Periodic Table of Chemical Elements. They have a structure consisting of a core and an outer shell covered with ligands. The size of QDs ranges from 2 to 10 nm. By adjusting the size of QDs, it is possible to adjust the fluorescence of quantum dots in a wide wavelength range of 400–4000 nm, which allows measurements in the ultraviolet, visible and near-infrared ranges. The family of carbon nanomaterials ranges from sp³-enriched nanostructures such as nanodiamonds to sp²-enriched graphene nanosheets and graphene quantum dots (GQDs). Carbon nanoparticles (CNPs) involve a wide group of nanomaterials, including carbon black, amorphous carbon, carbon dots (CDs) and core-shell nanocarbons². Recent advances in the field of nanomaterials have helped researchers expand the use of graphene quantum dots and carbon quantum dots, which have proved particularly attractive for detecting tagless microorganisms. The report focuses on new aspects of QD investigation for medicine and clinical diagnosis of oncological diseases, including theranostic research and bioimaging^{1,2}. Methods to limit the use of GDs associated with the manifestation of toxicity are considered in detail.

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DETERMINATION OF ACUTE TOXICITY OF CISTANCHE MONGOLICA PLANT EXTRACT IN MICE

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In our time, when medicine is developing, it is important to study the properties of medicinal substances isolated from plants.

Cistanche is widely used throughout the world, especially in Chinese traditional medicine. The official pharmacopoeia of China includes preparations derived from the species *Cistanche Herba*, *Cistanche Deserticola*, *Cistanche tubulosa*. The above plants are widely used in a number of diseases, namely, kidney failure, impotence, depression, female infertility, pathological discharge in women, metrorrhagia, senile constipation^{1,2}.

Goals and objectives of the study: To determine the acute toxicity and pharmacological activity of the extract of the upper and lower parts of the *Cistanche mongolica* plant.

Acute toxicity of the aboveground and underground extracts of the *Cistanche mongolica* plant was carried out on male white mice. During the experiments, the test substance was administered orally at doses ranging from 1,000 mg/kg to 10,000 mg/kg, then for the first 3–4 hours and 7–14 days. Virtually no side effects were observed at low doses. The results of the experiments are presented in Table № 1 below.

Table 1. Acute toxicity results of *Cistanche mongolica* plant extract in white mice

№	Substance	Dose mg/kg	Number of animals	Number of dead	Number of survivors	% Number of survivors
1	<i>Cis-mongolica</i>	1000	10	0	10	100
2	<i>Cis-mongolica</i>	3000	10	0	10	100
3	<i>Cis-mongolica</i>	7000	10	0	10	100
4	<i>Cis-mongolica</i>	10000	10	0	10	100

From this we can conclude that the average lethal dose of acute toxicity of the herbal extract of *Cistanche mongolica* LD₅₀ when administered orally as a result of the experiments was found to be above 1000 mg/kg. Class V for acute toxicity of the substance is practically harmless.

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DEVELOPMENT OF METHODS FOR THE SYNTHESIS OF CONJUGATES OF AMPHIPHILIC PHOTSENSITISERS WITH GLYCOLYSIS INHIBITORS

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Photodynamic therapy (PDT) is a minimally invasive method of cancer treatment. The combination of a photosensitizer (PS), light with a certain wavelength and molecular oxygen leads to local photodamage, which triggers cell death mechanisms. The main disadvantage of most PS is insufficient selectivity against tumors, which leads to undesirable side effects.

Increased levels of glycolysis are observed in a variety of cancers. This unique metabolic profile of cancer cells provides a biochemical basis for the development of novel chemotherapeutic strategies targeting the glycolysis pathway in cancer cells. Therefore, hexokinase enzymes, which provide the conversion of glucose to glucose-6-phosphate in the first step of glycolysis, can be targeted.

2-Deoxy-D-glucose is able to reduce tumor growth by inhibiting glycolysis, and induces autophagy and apoptosis of cancer cells. 3-Bromopyruvate is able to inhibit hexokinase II, thereby reducing ATP production.

In this work, new conjugates of meso-aryl porphyrins with glycolysis inhibitors on the periphery of the macrocycle were obtained. Porphyrins of structural types A4 and A3B were synthesized by monopyrrole condensation according to the Lindsey method. Conjugates with 2-deoxy-D-glucose were synthesized using a copper-catalyzed click-reaction, and PSs with 3-bromopyruvate were obtained via amide bond formation.

The target conjugates were characterized by modern physicochemical methods of analysis, including 2D-NMR spectroscopy. The PS molecules were included in polymeric micelles to enhance solubility. Biological tests of the target compounds are currently underway.

The work was financially supported by RSF, project № 22-73-10176.

PREPARATION OF IRON(III) HYDROXIDES WITH HUMIC MACROLIGANDS USING THE SALTING-OUT METHOD

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Humic substances (HS) are natural multifunctional compounds that are nontoxic across the entire range of natural concentrations. The macroligand properties of HS allow them to form complexes with Fe(III), which could be promising for the development of iron replacement therapy drugs for the treatment of iron deficiency anemia (IDA)¹. The absence of side products is of great importance for the production of medicinal drugs. By using the salting-out method, quantitative extraction of organic complexes of Fe(III) from aqueous matrices with low concentrations of inorganic salts can be achieved.

The aim of this study was to develop a method for synthesizing Fe(III) complexes with humic substances with increased iron content. The two-stage synthesis method of Fe(III) compounds with humic substances involves the precipitation of freshly formed Fe(OH)₃, the hydrolysis of Fe(III) in the presence of HS in an alkaline medium, followed by drying the precipitate under reduced pressure². In this study, salting-out of the hydrophobic fraction of the target product was carried out using organic solvents with different polarities (ethanol, isopropanol, acetone) prior to the drying stage of the preparation, followed by centrifugation of the precipitate. Fulvic acids from peat and humic acids from coal were used as HS, and FeCl₃ was used as the iron source.

The composition, structure, particle size, and physicochemical properties of the obtained preparations were confirmed by ICP-AES, powder X-ray diffraction, and dynamic light scattering. The application of the salting-out method ensured high efficiency in purifying the obtained Fe(III) compounds with humic macroligands from salt impurities. All samples contain less than 11% sodium, while the iron content varies from 13% to 33%.

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The work was carried out within the framework of the State Assignment 121021000105-7.

SYNTHESIS OF FLUORESCENT DIAGNOSTIC CONJUGATES BASED ON LIGANDS OF PROSTATE SPECIFIC MEMBRANE ANTIGEN

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Prostate tumors are one of the leading causes of cancer deaths in men. Histological analysis and intraoperative surgery are among the leading ways to diagnose and treatment of this disease. In both cases, it is important to visualize the diseased areas against the background of healthy tissue. Fluorescent dyes modified with targeted vectors are used for selective staining of malignancies. In the case of prostate cancer, the protein marker is prostate specific membrane antigen (PSMA). Urea-based ligands have been widely used as PSMA inhibitors.

High-affinity to PSMA ligands based on urea with a dipeptide linker modified for different conjugation methods (azide-alkyne cycloaddition, peptide synthesis, etc.) were used as a vector platform in this work¹. On their basis, new fluorescent conjugates with functionally substituted carbocyanines were obtained, which are promising imaging agents². Depending on the type of carbocyanine in the conjugate structure, its physicochemical properties and selectivity to the target protein may change. The work will present a comparison of synthetic approaches to synthesis of such conjugates, their advantages and disadvantages. The results of biological studies *in vitro* will also be presented.

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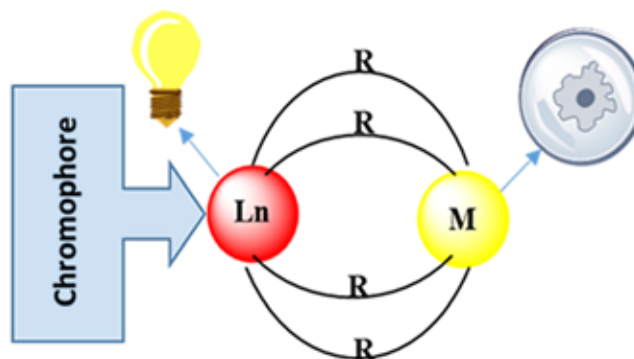
The research was supported by the Russian Science Foundation grant No. 23-23-00297, <https://rscf.ru/en/project/23-23-00297/>.

CHEMICAL DESIGN OF BIOLOGICALLY ACTIVE HETEROMETALLIC COMPLEXES OF TRANSITION METALS

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The search for synthetic approaches to the production of heterometallic compounds continues to be an urgent task of modern coordination chemistry. Heterometallic compounds obtained by combining functional biologically active blocks may have unique multi-target biological properties (antibacterial, antiproliferative, antiparasitic, etc.)¹. Heterometallic *d-f* complexes in which a biologically active d-block is associated with a luminescent lanthanide fragment acting as an optical label can have a therapeutic effect and detect the localization of compound².



This paper presents methods for the directed synthesis of heterometallic compounds with metallostyle Zn_2Ln_2 ($Ln = Gd^{III}, Eu^{III}$), as well as M_2Mn_4Fe ($M = Cu(II), Co(II), Ni(II)$). The study of the biological properties of the obtained complexes *in vitro* showed high antibacterial activity against the non-pathogenic *M. smegmatis* strain and a selective antiproliferative effect in the test line of ovarian cancer *SKOV3*.

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The work was carried out with the financial support of the Russian Science Foundation, project 24-23-00188.

NUCLEOPHILIC POST-FUNCTIONALIZATION IN THE SYNTHESIS OF ARYLTHIOFLUORINATED IMIDAZOLES

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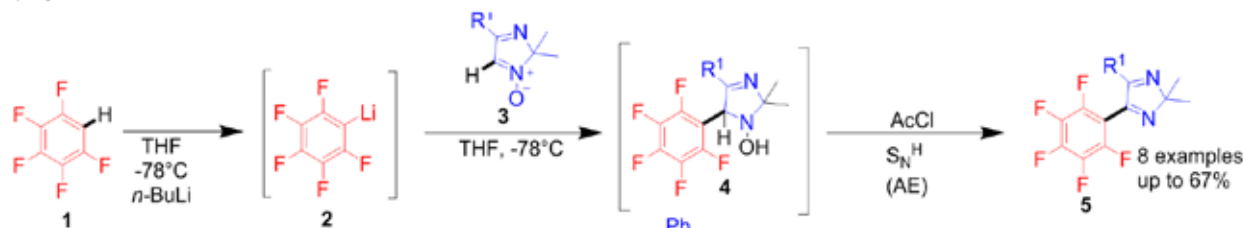
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Currently, fluorine-containing compounds are widely used due to their increased bioavailability, photophysical properties, and resistance to undesirable degradation processes. On the other hand, thioether derivatives find application in medicine and can be used as antituberculosis and anti-HIV agents, for the therapy of rheumatoid arthritis, granulomatosis and other pathologies. Thus, the development of effective approaches to the synthesis of original molecules containing both (poly)fluorine and thioaryl moieties may be of particular interest for organic and medical chemistry.

The present work deals with the studying of the possibility for further modification of pentafluorophenylated imidazoles using thioaryllating agents, proceeding by the mechanism of nucleophilic substitution of fluorine (S_N^{Ar}).

a) Synthesis of Pentafluorinated imidazoles



b) Arylthiolation of pentafluorinated imidazole

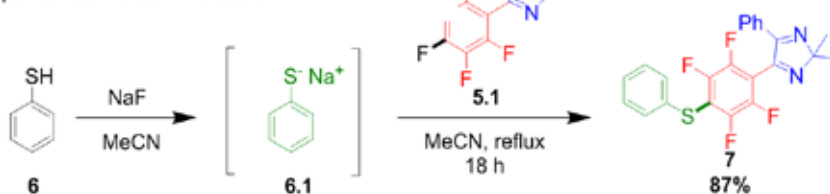


Figure 1. Synthetic route to arylthiofluorinated imidazoles

It is worth noting that compounds possessing a similar structure to molecule 7 have shown promising results in *in silico* experiments against biotargets associated with the pathogenesis of cardiovascular diseases.

The study was carried out with the financial support of the Russian Science Foundation as part of a research project № 23-63-10011, <https://rscf.ru/en/project/23-63-10011/>

NUCLEOPHILIC C-H FUNCTIONALIZATION IN THE SYNTHESIS OF CARBONITRILE DERIVATIVES OF IMIDAZOLES

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The imidazole fragment is a common heterocycle in the structure of many bioactive compounds and molecules with valuable photophysical characteristics. At the same time, the CN-group can be considered as a valuable pharmacophore block and a functional group for further transformations.

This work deals with the application of an effective method of cyanation of imidazole-containing substrates in the design of promising molecules for medicinal chemistry, as well as the future development of effective approaches to the modification of carbonitrile-substituted imidazoles.

Thus, the reaction of nucleophilic substitution of hydrogen (S_N^H) in imidazole-N-oxide systems of various structures (2*H*-imidazole and 1*H*-imidazole) was successfully applied to obtain nitrile derivatives in 74–80% yields. Further research is focused on transformations of the nitrile group into active pharmacophore blocks (amines, amides, tetrazoles, carboxylates, etc.).

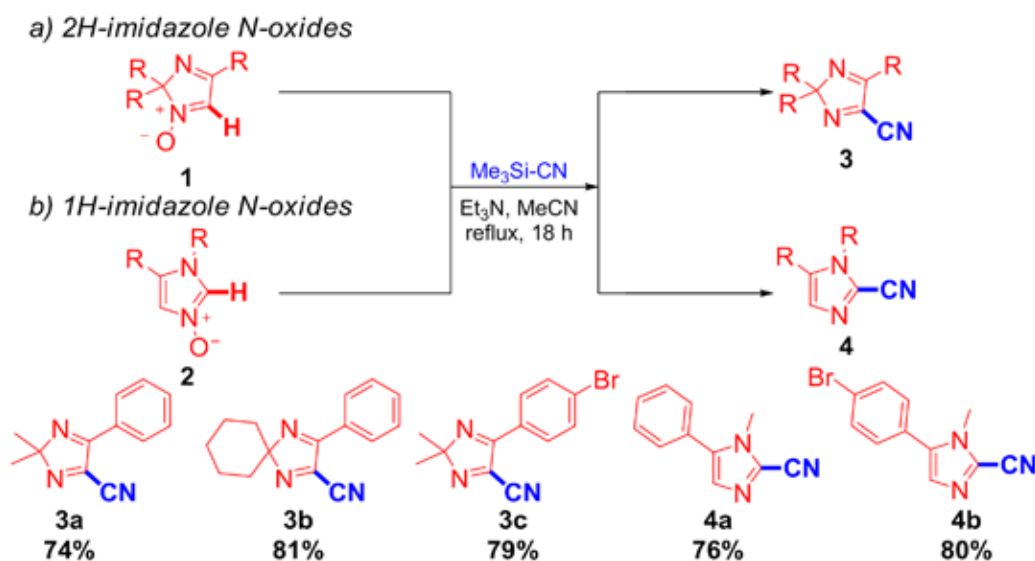


Figure 1. Synthesis of carbonitrile-imidazoles and further prospects for their modification

The study was carried out with the financial support of the Russian Science Foundation as part of a research project № 23-63-10011, <https://rscf.ru/en/project/23-63-10011/>

DEVELOPMENT OF LC-MS/MS METHODS FOR THE ASSESSMENT OF ADME PROPERTIES OF A NEW POTENTIAL INHIBITOR OF BACTERIAL CYSTATHIONINE γ -LYASE

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The LC-MS/MS methods that are used to support ADME studies in early drug discovery and candidate selection were developed. In vitro ADME studies were performed to evaluate the solubility, permeability, stability, P-glycoprotein inhibition, lipophilicity, and plasma protein binding of a new potential inhibitor of bacterial cystathionine γ -lyase (bCSE) that exhibits antibacterial activity against MRSA.

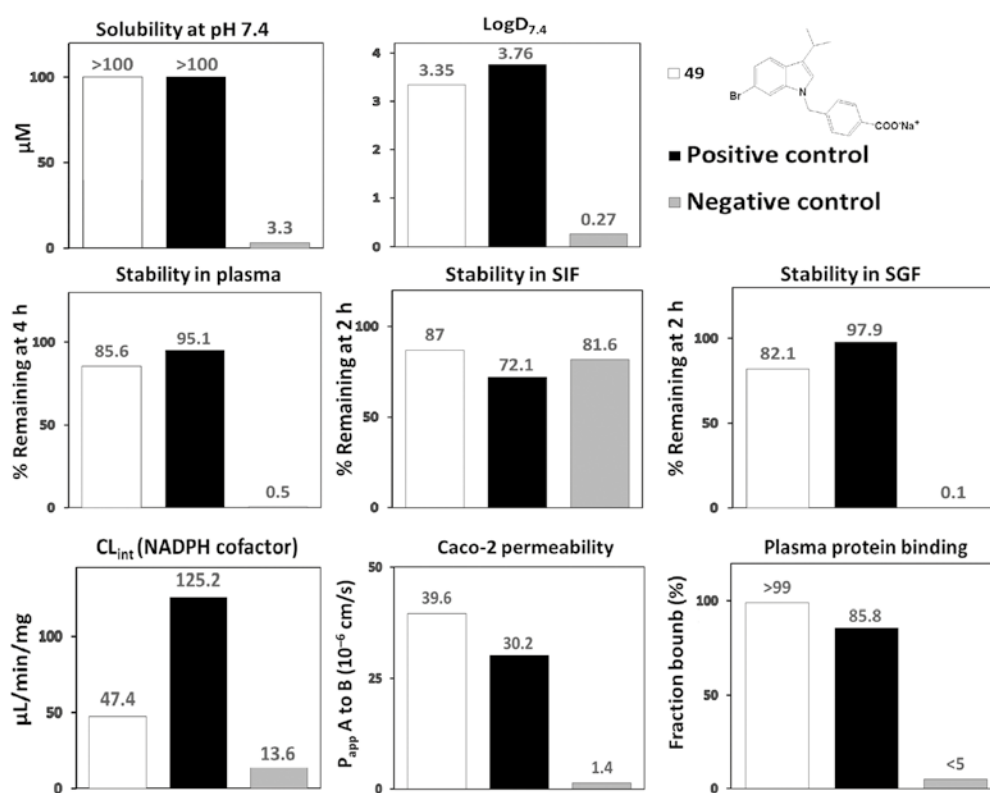


Figure 1. ADME properties of a new potential inhibitor of bCSE (compound 49)

CAPABILITIES OF MOLECULAR MODELING DURING THE DESIGN OF NEW ANTIVIRAL AGENTS

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A serious problem in the development of antiviral drugs is the development of drug resistance. Thus, the vast majority of circulating variants of influenza A viruses are currently resistant to the action of rimantadine, a blocker of proton transport through channels formed by the M2 protein of the virion envelope. Recently, for N-(1-(adamantan-1-yl)ethyl)isonicotinamide, we discovered antiviral activity against the resistant influenza virus A/PR/8/34 and low toxicity, and also obtained interesting *structure – activity* relationships for close analogues of this compound¹.

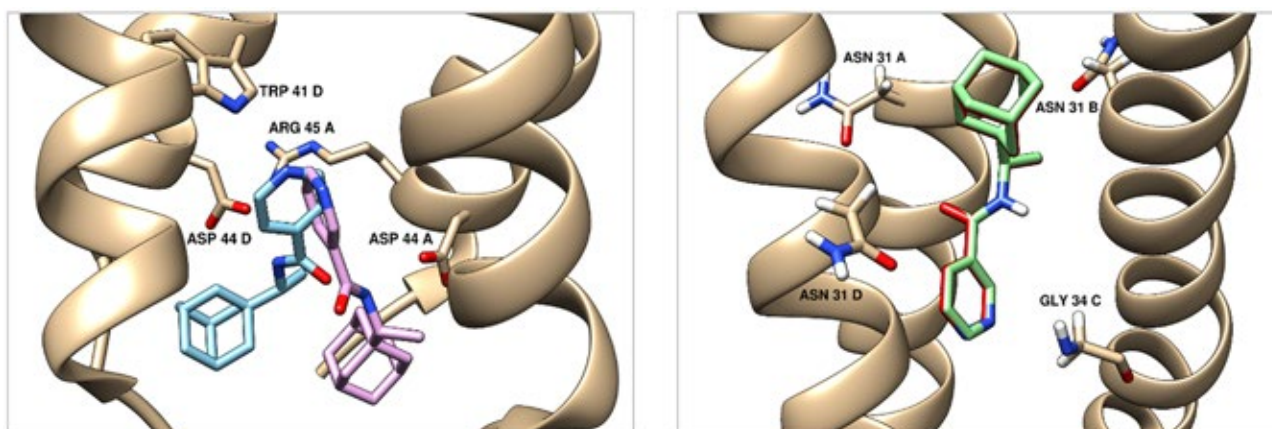


Figure 1. Fragments of the M2 channel with the S31N mutation of the influenza A virus (PDB ID: 2LY0): complexes of substances obtained in the work in the peripheral (left) and main (right) binding sites of rimantadine. Of the C-subunit, only the Gly34C residue is shown

The report discussed the results of molecular modeling of all stereoisomers of the obtained compounds into the model of the M2 channel with the S31N mutation (see example in Fig. 1). These results are in accordance with the conclusion of the authors of² about the role of various sites of the M2 channel in providing activity against rimantadine-resistant influenza virus.

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The research was carried out under financial support of Russian Science Foundation, project 23-75-01013.

SYNTHESIS OF ^{57}Fe -LABELED IRON HYDROXIDE COMPLEXES WITH HUMIC SUBSTANCES FOR PRECLINICAL STUDY

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Iron deficiency anemia (IDA) affects over 2 billion people worldwide, posing a serious public health challenge. One promising approach is the use of iron (III) preparations stabilized with polysaccharides, but they have side effects such as anaphylactic shock. To address this, natural humic substances (HS) were used as ligands to increase iron (III) bioavailability and reduce side effects.

In the study, coal-derived humic acids (CHA), peat-derived fulvic acids (PFA), along with the isotope ^{57}Fe and natural iron were used. Equal proportions of ^{57}Fe and natural iron were ground in a mortar and dissolved in excess HCl, then oxidized with hydrogen peroxide to form FeCl_3 , which was used in further synthesis according to the methodology from the patent application. Two labeled complexes were synthesized, CHAFe (8% ^{57}Fe /16% Fe) and PFAFe (9% ^{57}Fe /18% Fe). Iron presence in an amorphous nanoscale state was confirmed by X-ray diffraction, electron microscopy, and dynamic light scattering. Mössbauer spectroscopy confirmed the presence of iron in the (III) oxidation state in an octahedral oxygen environment.

Thus, the use of natural humic substances to stabilize iron (III) hydroxides appears to be a promising approach to address the issue of iron deficiency anemia, as it allows stabilizing the nanocrystalline size of iron hydroxide crystals. Further preclinical studies in this area may contribute to the development of new methods for the treatment and prevention of iron deficiency conditions.

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The work was carried out with financial support from state budget theme 121021000105-7.

ANALYSIS OF THE COMPOSITION OF FATTY ACIDS OF BIOLOGICALLY ACTIVE ADDITIVES

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Currently, dietary supplements obtained from both animal and plant resources are widely represented. By the nature of their origin, they initially have a different composition with a certain ratio of fatty acids, therefore they are unequal sources of a variety of polyunsaturated fatty acids. In addition, some fatty acids do not participate in human metabolism, but are always present in food products, so their additional entry into the human body with dietary supplements is extremely undesirable.

The purpose of our work was to study the detailed qualitative composition of fatty acids and lipids of dietary supplements from various manufacturers and forms.

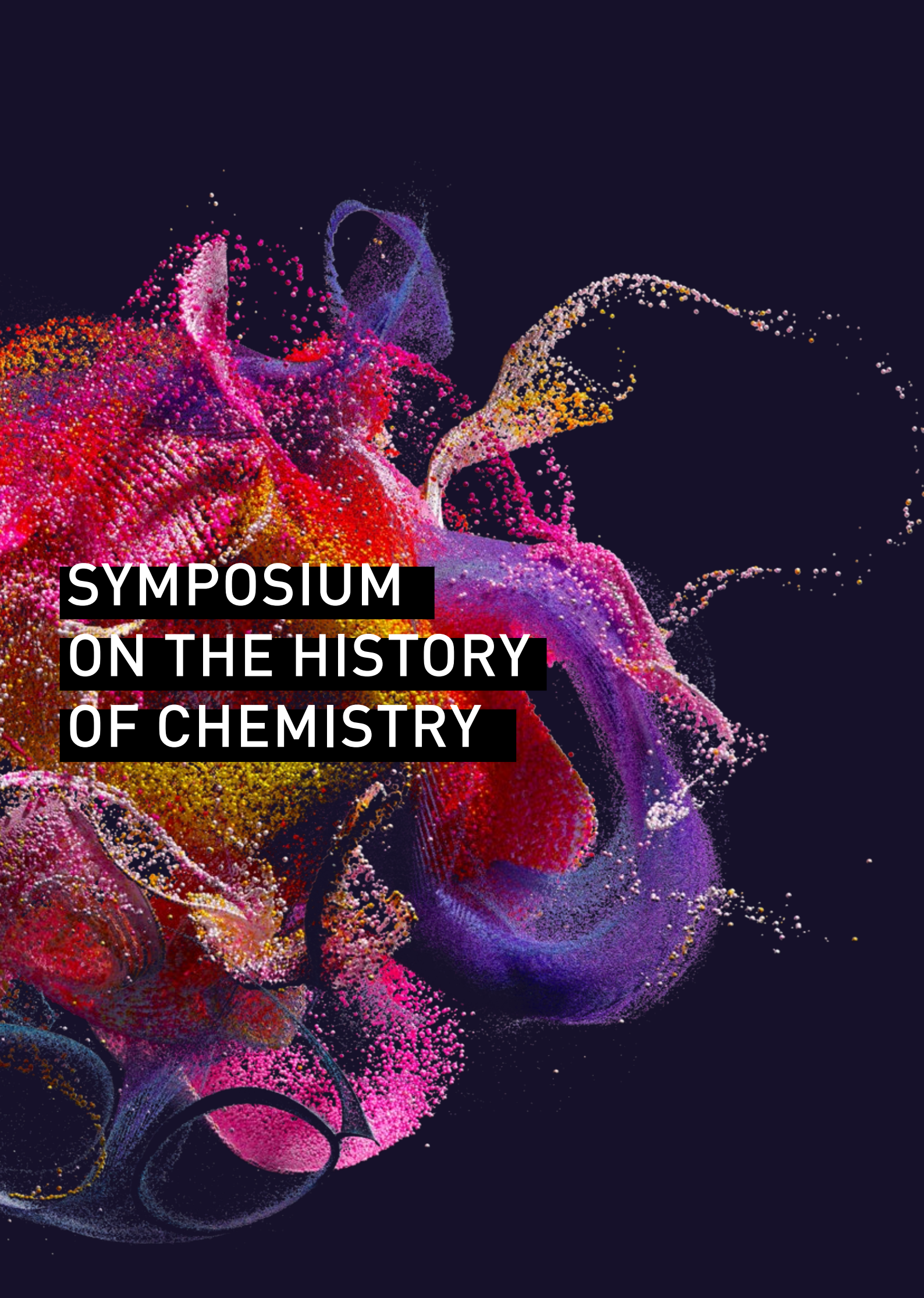
All studied samples were divided by source into three groups. Methyl esters of fatty acids were obtained according to the method we described earlier. Identification of fatty acid methyl esters was performed using GLC-MS. For MS identification of individual species of fatty acid methyl esters during their GLC fractionation, an extended package of built-in operating programs MSD ChemStation G1701EA E.02.00.493 with a NIST spectral library was used, and the degree of correspondence between the mass spectrum of the sample and the mass spectrum in the database was 98–99%.

To assess the level of unsaturation of fatty acids in lipids of dietary supplements, the unsaturation index was calculated.

Statistical processing of the data was carried out using one-way analysis of variance. Experiments for each sample were performed in triplicate with three independent biochemical runs each.

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An abstract, vibrant visualization of particle dynamics, possibly a molecular simulation or a complex fluid flow. The image features swirling, ribbon-like structures in shades of magenta, pink, red, orange, and purple, set against a deep black background. These structures are composed of numerous small, bright particles, giving them a textured, granular appearance. The overall effect is one of dynamic energy and complex, interconnected patterns.

SYMPOSIUM ON THE HISTORY OF CHEMISTRY

THE LEDENTSOV SOCIETY: THE FIRST RUSSIAN SCIENCE SUPPORT FOUNDATION

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The year 2024 marks the 115th anniversary of the founding of the H.S. Ledentsov Society for the Assistance in the Advances in the Experimental Sciences and their Practical Applications. This society, named after H.S. Ledentsov and rightfully called the first Russian scientific research foundation, was established in 1909 by Khristofor Semyonovich Ledentsov, the famous Vologda merchant and philanthropist. On May 17, the first meeting of the Society took place, where 123 prominent scientists were appointed as its members, including 13 chemists and materials scientists. For the next 9 years, the society had provided comprehensive assistance to Russian researchers in various fields, including natural and technical sciences such as chemistry and chemical engineering. The research activities of such outstanding chemists as A.E. Chichibabin, N.D. Zelinsky, I.A. Kablukov and L.A. Chugaev was made possible thanks to the support of the Ledentsov Society^{1,2}, which provided them with everything they needed to conduct their work: laboratories, equipment, instruments and reagents.

In addition to providing comprehensive assistance to individual researchers, the members of the society had also contributed to major State strategic projects. Since 1910, the Society had published "Vremennik", which contained unique information such as excerpts from meeting minutes, scientific reports, and application reviews, which reflected the history of Russian research institutions and some lesser-known milestones in the development of science and technology in our country.

The activities of the Ledentsov Society, in accordance with the vision of its founder, had contributed to the development of Russian innovation infrastructure. This included the system for expert evaluation of applications, the principles for project financing, and the rules for interaction with specialized scientific institutions aimed at conducting scientific research in experimental laboratories using modern equipment.

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METAL COMPLEX CATALYSIS – THE GREATEST ACHIEVEMENT IN XXTH CENTURY CHEMISTRY

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The second half of the 20th century is significant for catalytic chemistry with the intensive development and effective use in the chemical industry of homogeneous metal complex catalysts, which have become the most important tools of modern synthetic organic chemistry. According to the academician I.I. Moiseev, metal complex catalysis (MCC) is one of the attributes of the scientific and technological revolution¹. Despite the fact that the first reactions catalyzed by metal complexes were discovered at the end of the 19th century (S. Friedel and D.M. Crafts, M.G. Kuchеров, G.J. Fenton), MCC as a full-fledged scientific direction was formed as a result of development and thanks to outstanding achievements in organometallic and coordination chemistry, chemical kinetics of complex reactions, the emergence and improvement of new instrumental research methods. The most important contribution to understanding of the patterns of MCC reactions was made by the possibilities of studying them *in situ* (use of NMR, EPR spectroscopy, etc.) that arose by this period, as well as by electrochemical and isotope methods. The first attempts to apply quantum chemical approaches date back to the same period.

A significant contribution to the formation and development of MCC as an independent branch of catalytic chemistry belongs to Soviet and Russian scientists, in particular:

- kinetics and mechanism of olefin oxidation in solutions of PdCl_2 (I.I. Moiseev et al., 1959-1963);
- kinetics and mechanism of addition HX molecules to acetylene (R.M. Flid, O.N. Temkin, D.V. Sokolsky, 1952-1963);
- reduction of molecular nitrogen to ammonia (M.E. Volpin, V.G. Shur, 1964) и гидразина (A.E. Shilov et al., 1965-1970).

MCC today is the most “advanced” type of catalysis and, thanks to a combination of purely chemical, instrumental and theoretical methods and approaches, has a positive impact on the understanding and development of other areas, including more technologically advanced heterogeneous catalysis.

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AT THE ORIGINS OF SOVIET POLAROGRAPHY

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2022 marks the 100th anniversary of the publication of the first paper on the polarographic method by the Czech scientist Jaroslav Heyrovský. In 1931, at the 1st All-Union Conference on Electrochemistry and Chlorine in Leningrad, Heyrovský's former student E. Varasova introduced the advantages and characteristics of the new method to the scientific community of our country. In 1932, V. Vernadsky visited Heyrovský's laboratory and recommended the polarographic method to interested scientists and industrial and medical practitioners. It was agreed to translate Heyrovský's monograph into Russian. The monograph, translated by Varasova, was published in 1937. Our examination of the handwriting showed that the first part of the manuscript was translated by I. Smoler (one of the thirteen immigrants from the Russian Empire who worked in Heyrovský's laboratory),^{1,2} and edited by Varasova. Heyrovský participated in the Mendeleev Congress dedicated to the 100th anniversary of the birth of D. Mendeleev in 1934. In 1935 the first Soviet review on polarography, written by Varasova, was published. At the same time, the first Soviet polarograph was designed under the direction of I. Starik (Varasova acted as a consultant), the production of polarographs began in Odessa, and the first courses of polarographic analysis were held under the direction of E. Burkser, to which chemists from all over the country were invited. As early as 1936-1937, Soviet scientific journals published articles by scientists who had participated in these courses, namely Y. Gokhshtein, N. Komar, E. Burkser, S. Mikhlin, P. Pavlov, G. Pavlenko, Y. Usatenko, Y. Lyalikov, E. Kronman, A. Dymov, and T. Kryukova.³ The first years of research in the field of polarography in the USSR were spent searching for conditions for the determination of elements, studying the behaviour of elements on a mercury drop cathode, and using polarographs to study physical and chemical phenomena.

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CHEMISTRY AND CHEMICAL TECHNOLOGICAL IN HISTORY OF THE KAZAN NATIONAL RESEARCH TECHNOLOGY UNIVERSITY

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Famous chemists of Kazan: M.Ya. Kittari, A. M. Zaycev, Ya.V. Bogorodsky, A.E. Arbuzov, – actively collaborated with Stearin-soap, glycerin and chemical plant of the Krestovnikov brothers, including the practice of students^{1,2}. In 1930 the Kazan Chemical Institute was established. Nowadays, after a series of renamings, it is the Kazan National Research Technological University (KNRTU).



Group of the best builders of the main building of the Kazan Institute of Chemical Technology. 1939 (from the family archive of professor A.V Gerasimov)

The history of the system-forming departments of KNRTU shows the impact of scientific research on the creation of new technologies and vice versa – the impact of industrial technology problems on the formation of new scientific directions. These are the fields of electrochemistry, colloidal chemistry, organic and inorganic synthesis, chemistry of high molecular compounds and elastomers, composite materials, fluid technologies, petrochemicals, pharmacology, biotechnology and analytical chemistry (as a universal technology for science and practice)^{2,3}. In the scientific and educational environment of KNRTU all directions are connected by studies of the history and methodology of chemistry, technology and science in general^{2,3}.

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CHEMICAL DISCOVERIES AND CHEMISTS ON COINS

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Numismatics is a highly valuable source of knowledge about the development of human society and the declared priorities in a society. It affects the values and ideals translated by the state, and therefor depicted on the coins and banknotes.^{1,2}

The analysis of numismatic material of XVIII-XXI centuries will be presented, consisting circulating and commemorative coins, these are depicting renowned chemists of the past and their discoveries. The data will be arranged by issuing countries, depicted scientists and coin mintage numbers. It will be analyzed the contribution to the chemical science of chemists minted on the coins.^{3,4}



Figure 1. Revers of 3 ruble coin from year 2000, as an example of the commemorative coin, highlighting the important chemical discovery – periodic table.

Finally, the data will be provided on the coins dedicated to chemical discoveries and chemists from 19 issuing countries with total mintage over 38.000.000 pieces (Fig. 1).

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EVOLUTION OF THE NOMENCLATURE OF OPTICAL ACTIVE SUBSTANCES: AMINO ACIDS AS A CASE STUDY

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Optical active substances are capable of rotating the plane of polarization of plane-polarized light. This ability was first discovered in quartz crystals (Arago, 1811) and a little later in various organic compounds and their solutions (Bio, 1815). This property is associated with the special structure of molecules or a crystal lattice: such molecules or crystals do not have mirror-rotational axes of symmetry. With the discovery of the phenomenon, it became necessary to describe the presence of this property in substances and indicate the direction of rotation of the plane of polarization - to the right or left (clockwise or counterclockwise). And with the discovery of optical isomers that have the same composition but rotate the plane of polarization of plane-polarized light in different directions (due to different arrangements of atoms in space), the need to clearly designate such isomers in writing has also appeared. The report describes how different generations of researchers solved this problem, what symbols were used at different periods of time to indicate the sign of rotation of the plane of polarization, and how various systems of nomenclatures for optically active compounds emerged and developed. Particular attention is paid to the case of amino acids. This example shows how nomenclature based on the sign of rotation of the plane of polarization ((+)/(-) or *d/l*) was replaced by nomenclature based on the relative (D/L) and then on the absolute configuration of molecules (R/S, Cahn-Ingold-Prelog rules). It is discussed why a large number of researchers, when designating optical isomers of amino acids, still prefer the rational nomenclature proposed by the editors of the *Journal of Biological Chemistry* in 1947 (D/L)¹ over the Cahn-Ingold-Prelog rules.

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PAGES OF HISTORY OF TEACHING PHYSICAL CHEMISTRY: ONE OF THE OLDEST DEPARTMENTS IN RUSSIA

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Understanding of modern trends in the development of physical chemistry as a science and an academic discipline is impossible without knowledge of its history. The concept of physical chemistry as well as ideas about its essence and problems were first formulated by the Russian scientist M.V. Lomonosov, who in 1752-1753 gave a special course of lectures on this subject to the students of the Academic University in Petersburg¹. However, separation of physical chemistry into an independent field of research and education began only more than 100 years later, in the second half of the 19th century. Although the world centers of physical chemistry at that time were universities in Germany, where such prominent scientists as F.W. Ostwald, J.H. Van't Hoff and others worked, the development of this branch of chemical science in Russia proceeded at an accelerated pace^{1,2}. Since the late 1800s it started to be taught at Kazan and Moscow Universities, Electrical Engineering and Mining Institutes in St. Petersburg, but separate departments providing systematic training of specialists in this field were not organized immediately.

The oldest one in Russia is the Department of Physical Chemistry of the Institute of Fine Chemical Technologies named after M.V. Lomonosov (ITHT) RTU MIREA. It became the successor to the Laboratory of Physical Chemistry and Quantitative Analysis of the Moscow Higher Women's Courses, where, on the initiative of N.D. Zelinsky, teaching physical chemistry as a separate subject began in the 1903/04 academic year. The first Head of the laboratory and subsequently of the specialized department was S.G. Krapivin, the former student of N.D. Zelinsky and V.F. Ostwald³. Later effective approaches to education were developed by other talented scientists and teachers of ITHT, among whom Ya.K. Syrkin⁴ played a prominent role.

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THE DEVELOPMENT OF OPIOID CHEMISTRY AND THEIR ANTAGONISTS

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The isolation and pharmacological description of morphine (*Principium somniferum*), performed in 1805-1817 by Friedrich Wilhelm Adam Serturner¹, became the basis for the formation of modern European pharmacology and stimulated the development of chemical sciences. The advent of narcotic painkillers has revolutionized medicine, but their use continues to pose a significant risk to human life.

For the first time, the fundamental possibility of controlling the dangerous manifestations of opioid analgesics was shown in the period of 1915-16 and was based on the discovery of a chemical reaction of tertiary amines splitting (von Braun reaction), which allowed to obtain *N*-demethylated derivatives of natural opioids, and subsequently to carry out their functionalization².



The study of pharmacological antagonism of morphine and *N*-allylnorcodeine led to the formulation of the idea of the existence of related targets for them³ and became an important milestone in the formation of the doctrine of receptors and, subsequently, led to the discovery and structural description of the family of opioid receptors.

Practical success in creating the first drug based on opioid antagonists was achieved in 1941, but given the developing public health crisis in North America, known as the "opioid epidemic", the evolution of opioid chemistry and their antagonists continues to follow the evolution of science and society into a new era⁴.

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PETROCHEMICAL SCIENTIFIC SCHOOLS USPTU

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The report provides a historical analysis of the main topic and discusses the most important results of computational, experimental and applied research carried out by teams of scientific schools of the Ufa State Petroleum Technical University (until 1993, the Ufa Petroleum Institute) in petrochemistry, which were formed by 1980: D.L. . Rakhmankulov “Chemistry and technology of linear and cyclic acetals and their N-, S-, Si-containing analogues”; B.K. Marushkin - scientific school in the field of improving mass transfer equipment of oil refining industries; M.A. Tanatarov “Theoretical research to increase the stability of industrial oil refining catalysts”; Z.I. Sunyaev and R.N. Gimaev “Improving the technology for producing petroleum coke”; J.F. Galimov “Improving catalytic processes and catalyst production”; A.F. Akhmetov “Improving the technology for producing high-octane fuels.”

The authors of the report substantiate promising directions for the development of scientific research aimed at producing high-octane gasoline, petroleum coke and other carbon materials, and improving the quality of diesel fuel. A comparison is made of the level of petrochemical work of scientific schools of UNI-USPTU with foreign research, and factors that can expand the use of achieved results in practice are identified.

VIRTUAL MUSEUM OF CHEMISTRY. FIRST RESULTS AND PERSPECTIVES

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The years 2022-2031 have been declared the Decade of Science and Technology by decree of the President of the Russian Federation. One of the key initiatives of this decade is the "Work with Experience", initiative designed to collect, systematize and use the accumulated experience of science, as well as actively popularize the history of science.

In 2023, the N.S. Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences began, within the framework of this initiative and with the support of the Commission on the History of Chemistry at the Division for Chemistry and Materials Science of RAS, the implementation of the project "Virtual Museum of Chemistry", which provides for the creation of a thematic popular science media.

During the project's first year, it is planned to create and place on the website a database of memorable dates of Russian and World chemistry, place digitized popular science materials on chemistry of the past centuries, as well as create and place at least 200 topics about:

Biographies of outstanding chemists of Russia and in the world;

The history of the discovery and study of individual substances;

A New Popular Library of Chemical Elements;

Chemistry on the map of Russia (reports from chemical and science museums, memorial houses of outstanding chemists);

The history of the Russian chemical institutes;

Chemists everyday life (history of chemical vessels, devices and devices, principles of their operation and use in a modern laboratory).

It is also planned to create a "chemical" layer on Yandex maps with a marker of memorable places related to chemistry.

The report by the editor-in-chief of this project outlines the first results of the museum, as well as suggests further ways of its development.

The project is being implemented with the financial support of the Ministry of High Education and Science of the Russian Federation within the framework of the federal project "Popularization of Science and Technology" № 075-15-2024-508

PROFESSOR D.L. RAKHMANKULOV SCIENTIFIC SCHOOLS

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In 1971, Dilius L. Rakhmankulov became the head of the Department of General and Analytical Chemistry at the Ufa Petroleum Institute (UNI). A unique scientific school founded under his leadership at the department to study the properties, transformations and reaction mechanisms of cyclic and linear acetals and their nitrogen-, sulfur- and silicon-containing analogs¹. In the 1980 – 1990s, Rakhmankulov expanded researches in this direction at the laboratories of the Research Institute of Fine Organic Synthesis and the Research Institute of Low-Tonnage Chemical Products and Reagents.

New knowledge obtained in result of the fundamental research of the scientific school in the field of chemistry of cyclic and linear acetals and their heterocyclic analogs. The research of the scientific school was also of great industrial importance for the production of new effective solvents, metal corrosion inhibitors, plant protection products, reagents for flotation and oil production and other products in demand in the industry.

In the 1990s, D.L. Rakhmankulov founded the scientific direction «Modern problems of the history of natural science in the field of chemistry, chemical technology and petroleum business» at our university. The purpose was to preserve the scientific heritage and history of industrial enterprises, research organizations, educational institutions of the Republic of Bashkortostan and the Russian Federation. The research resulted in a lot of monographs and international scientific conferences².

D.L. Rakhmankulov schools students and co-workers became prominent scientists, heads of department of universities, research institutes, industrial enterprises and business projects. Many of them continued to develop the ideas of scientific schools. Among them are the academician of the AS of the RB U.B. Imashev, corresponding member S.S. Zlotzky and V.V. Zorin, Prof. E.A. Kantor, D.E. Bugai, A.I. Gabitov and many others.

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CHEMISTRY AT ST. PETERSBURG STATE ELECTROTECHNICAL UNIVERSITY

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The discipline "Chemistry" has been taught at St. Petersburg Electrotechnical University "LETI" since its foundation. In 1891 prof. A.A. Krakau organized a chemical department, which since 1898 has offered courses in electrochemistry and physical chemistry. The latter was read by the founder of physical and chemical analysis – Academician N.S. Kurnakov, who organized in 1899 physico-chemical laboratory. In 1906, along with the electrical engineering faculty, an electrochemical faculty was formed and a number of chemical departments were organized, where both teaching and scientific activities were carried out. The departments were headed by prominent scientists – prof. N.A. Pushin (later corresponding member of the Serbian Academy of Sciences), academician I.V. Grebenshchikov, prof. M.S. Maksimenko – creator of domestic electrometallurgy, corresponding member USSR Academy of Sciences P.F. Antipin, corresponding member USSR Academy of Sciences K.K. Khrenov. Employees and graduates of the faculty participated in the creation of such industries as electrometallurgy of light metals, electrolytic production and refining of heavy non-ferrous metals, production of chemical power sources, etc.

In 1930, due to the reorganization of higher education, the electrochemical faculty was liquidated, all departments except general chemistry were closed, the chemical direction ceased to graduate, famous chemists left, and the range of scientific activities narrowed. All this led to the loss of connections in the science-education-production chain and, as a consequence, to the decline in the field of general chemical education.

A certain renaissance of chemistry at LETI was observed with the arrival of prof. B.F. Ormont (1960-1972). Scientific activity was activated, the department was named physical chemistry. The next leap in the development of the department of physical chemistry begins with the arrival of the head of the department in 2009 corresponding member RAS V.V. Gusarov. During this period, scientific work resumed, young active teachers appeared, and the department regained its graduating status.

Using the example of the history of chemical education at St. Petersburg Electrotechnical University "LETI", the decisive role of the close connection between educational and scientific activities in the development of departments. It is shown that for the stable and positive development of departments it is necessary that they be graduating.



D.I. MENDELEEV AND MINING INSTITUTE

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In 2019, the XXI Mendeleev Congress was held on the basis of St. Petersburg University. The fundamental foundations of scientific knowledge laid down by the outstanding scientist Dmitry Mendeleev are relevant for many areas of science and industrial industries and they are traditionally discussed every 5 years. Many years of cooperation connects Dmitry Mendeleev with the Mining Institute. For example, in search of material for his research, including while working on the Periodic Law, he repeatedly applied to the Mining Museum. The greater connection of the great scientist began with the 100th Anniversary of the Mining Institute in 1873, when he personally congratulated the first technical university in Russia. On the other hand, the mineralogical collection helped Mendeleev to conduct a predictive assessment of elements for the future Periodic System. Artifacts and documents stored in the library, archives and the Mining Museum as well as the modern activities of scientists indicate the enormous importance and contribution of the Mining University to practical activities, and the scientific heritage of D.I. Mendeleev. The new book "D.I. Mendeleev and the Mining University. Stages of development of Russia" prepared and published at this year 2024. In this work have been proven the facts of the scientific and historical connection between Dmitry Mendeleev and the Mining University in St. Petersburg. The study of archival documents of the Mining Museum, the Department of General Chemistry and the Main Library of the Mining University made it possible to restore the history of scientific cooperation with the great scientist. With special respect from scientists and professors of St. Petersburg Mining University of Empress Catherine II which keeps the memory of many years about cooperation with the great Russian scientist and following his example of selfless service for the benefit of domestic science.

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THE ROLE OF V.B. ALESKOVSKII'S "FRAMEWORK" HYPOTHESIS IN THE DEVELOPMENT OF SOLID STATE CHEMISTRY

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Considering the history of the chemical science development, especially since the second half of the XX century, it is impossible not to note the attention of scientists to the chemistry of solids. It was during this period that the first monographs in this field appeared, but the authors of such works were often physicists who presented their ideas about solid compounds from the standpoint of solid-state physics¹. V.B. Aleskovskii was one of the first who began to consider solids and the ways of their transformations from the chemist perspective.

He analyzed a huge amount of research in the field of both classical chemistry and its section related to solids, presented in the framework of famous

discussion between C.L. Berthollet and J.L. Proust, in the works of leading chemists (D.I. Mendeleev, N.S. Kurnakov, S.A. Shchukarev, N.A. Shilov, A.A. Balandin, etc.), which allowed him to propose a chemical model of solids. It is based on the "framework" hypothesis formulated by V.B. Aleskovskii². Its essence is that any solid body, regardless of its composition, nature (organic or inorganic), structure (crystalline or amorphous), can be represented in the form of a framework, on the surface of which there are some or other functional groups (FGs). As a consequence, two main directions of transformations of solids are possible: due to interaction with the elements of the framework and a more reactive reaction direction with FGs on the solid surface. The experimental substantiation of these views was reflected in the molecular layering (ML) method³

developed by him together with S.I. Kol'tsov. On the ML method principles the chemical nanotechnology, which is currently one of the most dynamically developing areas in micro- and nanoelectronics, was created.

The report considers the stages of development and the current state of the methods of obtaining a wide range of materials for various functional purposes, based on the approaches of V.B. Aleskovskii.

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SOLUTIONS CHEMISTRY AT THE IPI-ISUCT INORGANIC CHEMISTRY DEPARTMENT

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In the history of Russian chemical science and chemical education, 1918 can be called a landmark date to a certain extent. This year, on the basis of the Riga Polytechnic Institute in Ivanovo-Voznesensk, the first technical university of Soviet Russia¹ is being created at the Faculty of Chemistry of which (later IICT-IACH-ISUCT) the Department of General Chemistry² headed by its first head, Nikolai Petrovich Peskov³, becomes a key functional unit. In the 1920s, a series of works by N.P. Peskov "Solution, suspension, colloid. Theoretical and experimental research". These studies will be the harbinger of a new scientific school that will appear at the department in a few decades.

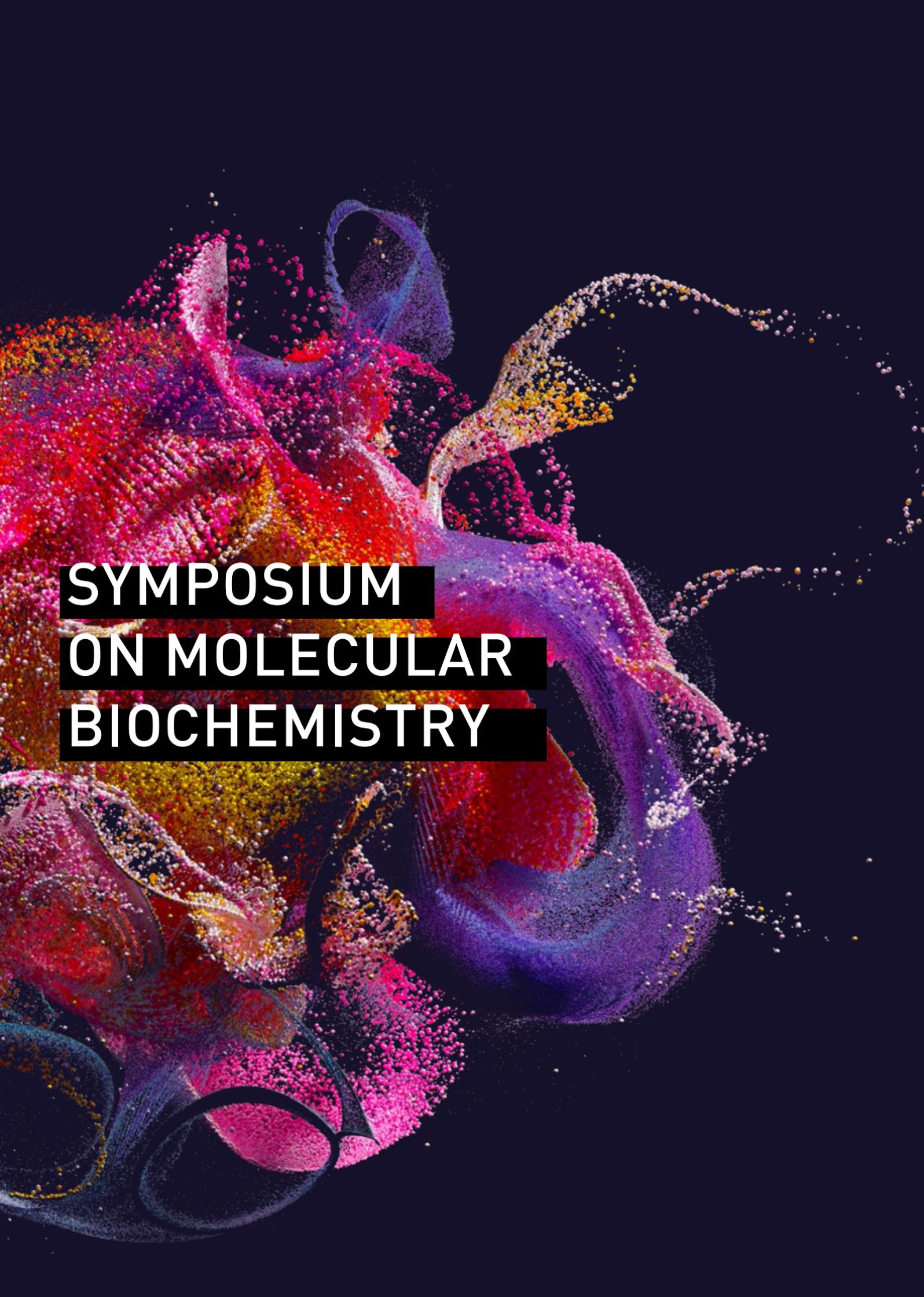
In 1918 - 1930, the training of chemical students at IvPI was aimed at the needs of textile and dyeing production, where the role of solution chemistry is quite large. However, the fundamental problems of solution chemistry were not solved systematically enough at that time.

Since 1962, under the leadership of Prof. G.A. Krestov (later a corresponding member of the USSR Academy of Sciences), the formation of a scientific school of solution chemistry⁴ began in Ivanovo. In the period from 1962 to 1994, when preparing students in general and inorganic chemistry, separate sections of theoretical and experimental chemistry of solutions were introduced, which later (in the 1990s) were transformed into separate lecture courses.

In the late 1970s, a workshop on solution chemistry began. In 1978, the achievements of the Department of Inorganic Chemistry were noted by Academician N.M. Zhavoronkov, Director of the IGIC of Academy of Sciences of the USSR. The USSR Academy of Sciences is raising the issue of organizing a new institute on mortar topics, which will be opened in Ivanovo in early 1981.

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An abstract, colorful visualization of a molecular structure, possibly a protein or a complex molecule, rendered in a point cloud or particle-based style. The structure is composed of numerous small, colored spheres (pink, red, orange, yellow, purple, blue) that form a complex, interconnected network. The background is a solid dark blue. The text "SYMPOSIUM ON MOLECULAR BIOCHEMISTRY" is overlaid on the structure in white, bold, sans-serif font, with each word on a separate line and a black rectangular background for each word.

**SYMPOSIUM
ON MOLECULAR
BIOCHEMISTRY**

NEW ANTIMICROBIAL AGENTS BASED ON MODIFIED NUCLEOSIDES

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Antimicrobial resistance (AMR) is one of the most serious global health problems and contributes significantly to morbidity and mortality worldwide. According to WHO, in 2019, bacterial AMR was associated with 4.95 million deaths worldwide, and was the direct cause of death in 1.27 million cases. It is estimated that by 2050, resistant microorganisms will claim 10 million lives per year - more than cancer.

Promising candidates for the role of new antibacterial agents are nucleoside derivatives. Currently, analogs and derivatives of nucleic acid components are important elements of anticancer and antiviral therapy. At the same time, among representatives of natural nucleosides and their synthetic analogues, antibacterial activity was discovered relatively recently, and this area is actively developing.

In recent years, our laboratory has obtained a significant number of nucleoside derivatives and screened their biological activity. Antibacterial activity has been shown in some gram-positive bacteria, such as *B. subtilis*, *L. mesenteroides*, *S. aureus* and a number of mycobacteria.

The most significant results were obtained with *M. tuberculosis*. A number of compounds inhibited the growth of Mtb at concentrations comparable to currently used therapeutic drugs, and these concentrations were the same for both the laboratory ("wild") strain H37Rv and the multidrug-resistant strain MS-115. The compounds were not toxic to eukaryotic cells.

An electron microscopic study of the interaction of the resulting compounds with Mtb demonstrated a few morphological changes in the cells, which resulted in partial and/or complete destruction of the three-layer cell wall of the bacteria.

Thus, the use of nucleoside derivatives and analogues as bacterial growth inhibitors is of significant interest in microbiology, biochemistry, medicinal chemistry and pharmacology.

SYNTHETIC OLIGOSACCHARIDES RELATED TO O-ANTIGENS OF KLEBSIELLA PNEUMONIAE AS A PLATFORM FOR VACCINE DEVELOPMENT

Krylov V.B.

Antimicrobial resistance (AMR) is a global health threat with a steadily increasing number of associated deaths that are expected to reach 10 million by 2050. Vaccination is considered by experts as a means of preventing the development of drug resistance, making the creation of new types of vaccines against hospital infections an urgent task.¹

Synthetic oligosaccharide ligands structurally related to cell wall polysaccharides of infectious agents are a convenient basis for the creation of appropriate specific vaccines and diagnostics. In this communication, the main stages of development of 3-rd generation carbohydrate vaccines are considered on the example of the bacterial pathogen *Klebsiella pneumoniae*. Original stereospecific methods of oligosaccharide synthesis developed in our laboratory made it possible to obtain spacers corresponding to immunodeterminant fragments of *K. pneumoniae* polysaccharides. Thus, using pyranoside-furanoside rearrangement we obtained oligosaccharides related to *K. pneumoniae* LPS O-chains of the main clinically significant serotypes: O1, O2, O2ac, O3.²⁻⁴ Using these oligosaccharides we designed conjugated candidate vaccines that induce protective antibodies preventing infection with antibiotic-resistant strains of the pathogen.

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PROCESSING AND PRESENTATION OF ANTIGENS: FROM FUNDAMENTAL ASPECTS TO SPECIFIC THERAPY

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Human leukocyte antigen (HLA) genes encode proteins presenting thousands of self and foreign peptides, which play a critical role in the immune responses against pathogens and tumor cells as well as those resulting in autoimmunity. Here we report how antigen presentation either by HLA class I or class II may modulate the pathogenesis of autoimmune and viral diseases. Our data revealed that HLA-DRB1*01:01 may kinetically discriminate between viral peptides and endogenous myelin-derived peptides. We showed that myelin peptides encapsulated into the mannosylated liposomes, referred as Xemys, suppress development of experimental autoimmune encephalomyelitis (EAE), and furthermore successfully passed the Phase II of clinical trials. We demonstrated that exposure to the Epstein-Barr viral antigen LMP1 induces myelin-reactive antibodies *in vivo*. We thus reasoned that antibodies induced against LMP1 during EBV infection might act as inflammatory trigger by reacting with myelin, suggesting molecular mimicry in the mechanism of MS pathogenesis. Here we report the novel third class of ubiquitin-independent degrons, which promote efficient engagement of MBP by REG α or REG β -capped immunoproteasomes. These immunoproteasomes generate significantly enhanced amounts of MBP-derived immunodominant peptides, which being presented by MHC class I on the surface of oligodendrocytes attract cytotoxic lymphocytes, thus suggesting that immunoproteasomes equipped by REG $\alpha\beta$ heptamers became deadly machines coordinating autoimmune attack on the myelin sheaths *ab intra*. Finally, our data read that mutations in the hACE2-binding region RBD496-513 of Omicron B.1.1.529 strain results in a dramatic increase of proteasome-mediated release of two public HLA class I epitopes, which might be one of the key factors that forced the SARS-CoV-2 to cross back the red line of the pandemic status.

Study was supported by Russian Science Foundation grants 24-74-10107 and 23-74-00053.

COMPUTER MODELING OF THE MOLECULAR MECHANISMS OF ANTIBIOTIC RESISTANCE

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The study of molecular mechanisms of biochemical reactions is an important fundamental problem of applied importance for biomedical and biotechnological research. Modern methods of computer molecular modeling allow more precise detailing than experimental methods, namely, to obtain structural and functional data with atomic resolution for all elementary steps of the process.

The work significantly expands the methodologies used to create new pharmaceuticals and determine the molecular mechanisms of substrate specificity of hydrolases. The proposed approach involves the joint use of combined quantum mechanics/molecular mechanics methods to calculate the cross sections of the potential energy surface and molecular dynamic trajectories, followed by an analysis of the characteristics of the electron density in the active site of the enzyme. Bacterial enzymes, penicillin-binding proteins and beta-lactamases, belong to the class of hydrolases and are responsible for the manifestation of resistance caused by the formation of unstable covalent adducts and inactivation of antibiotics, respectively. The application of the developed technique made it possible to propose a mechanism for the occurrence of antibiotic resistance due to mutations in genes encoding penicillin-binding proteins of bacteria; to determine the mechanism of formation of inhibitors of bacterial metallo-beta-lactamases in their active sites from organic boronic acids; to interpret the differences in the observed rates of hydrolysis of cephalosporin compounds by metallo-beta-lactamases; to identify structural features that determine the different composition of carbapenem products in metallo-beta-lactamases from different classes; to propose a molecular mechanism of drug repurposing of the unithiol drug to inhibit metallo-beta-lactamases.

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NOVEL ENZYMES CATALYSING THE CONVERSION OF FUCOIDANS

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Fucoidans are sulphated heteropolysaccharides from brown algae that have anticoagulant, immunomodulatory, antitumour and antiviral effects and are currently being proposed as potential drugs. Despite the widespread popularity of these polysaccharides, the question of the relationship between biological activity and chemical structure has not been resolved, as the structures of fucoidans have not been fully elucidated. There is also the well-known problem of standardisation of polysaccharide preparations. The language of polysaccharides is much more complex than that of genes or proteins. While genes use only four "letters" and proteins use twenty, the sugar alphabet has more than twenty "letters" that can be modified with different substituents, secondly, the "letters" can be linked in different ways, and finally, they can form branched structures. This makes the analysis of the structure of polysaccharides incredibly difficult. Even the use of NMR spectroscopy and mass spectrometry does not always allow us to determine the structure of complex polysaccharides with sufficient accuracy.

Important tools for structural studies of polysaccharides are enzymes with established specificity and mechanism of action. Fucoidanases and sulfatases with different specificities are currently used to study fucoidans. With the help of these enzymes it is possible not only to determine the structure of fucoidans but also to "edit" their structure to obtain fragments with a given biological activity. The parameters of the enzymatic reaction can be easily controlled, the yield of the target products is usually high and their structure is constant, which is not achieved when reactions take place in the absence of enzymes. In addition, the enzymatic transformation of polysaccharides opens up the prospect of obtaining new standard drugs with higher biological activity.

NON-VIRAL DELIVERY SYSTEMS: HOW THE STRUCTURE OF LIPID COMPONENTS AFFECTS THE EFFICIENCY OF NUCLEIC ACIDS TRANSPORT

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Liposomes and lipid nanoparticles are attractive delivery systems for therapeutic nucleic acids due to their biocompatibility, modularity, and ability to transport nucleic acids of various sizes. However, the effectiveness of liposomes in biological environments is often reduced due to interaction with numerous extra- and intracellular barriers.¹ In the extracellular environment, liposomes are adsorbed by blood components and immune system proteins, which can destabilize them and cause earlier release of the nucleic acid. The main intracellular barriers for lipid delivery systems are the endosomal and nuclear membranes.

The effectiveness of nucleic acid delivery is determined by the type of components used to form lipid nanoparticles. As part of the study, effective methods for the synthesis of polycationic amphiphiles,² targeted lipoconjugates,³ and PEG lipids⁴ were developed. For example, increasing the length of the PEG reduces the liposomes' ability to transfect cells *in vitro*, but increases their circulation time in the bloodstream and enhances the activity of immunostimulatory RNAs *in vivo*.

Transfecting activity screening of lipids *in vitro* allowed us to create liposomal delivery systems capable of transfer mRNA and siRNA *in vivo*.^{5,6}

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INHIBITORS OF HYDROGEN SULFIDE SYNTHESIS ENZYMES AS ANTIBIOTIC POTENTIATORS

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Most antibiotics used to treat infectious diseases are aimed at inhibiting essential bacterial proteins. However, the effectiveness of traditional antibiotics decreases as pathogenic bacteria acquire resistance to their action, which necessitates increasing the concentrations of antibiotics used for therapy, combining them, and searching for new antibacterial drugs. As an alternative approach, the effect of traditional antibiotics, which cause bacterial damage through oxidative stress, can be enhanced by further blocking bacterial enzymes that produce H₂S and the resulting production of H₂S and glutathione. Recently, cystathionine-γ-lyase (CSE) has been proposed as such a target.¹ In many pathogenic bacteria (for example, *Staphylococcus aureus* or *Pseudomonas aeruginosa*), CSE is the main producer of H₂S and is involved in their mechanisms of antibiotic resistance. In silico and in vitro screening identified three leaders among CSE inhibitors, which were distinguished by high activity, selectivity and low toxicity. The chemical synthesis of these compounds was optimized, which made it possible to obtain them in gram quantities. Based on the structures of the leading compounds, their derivatives with improved potentiating activity against antibiotics were obtained.

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WHAT FOR DO YOU NEED THREE COPPER IONS IN THE REACTION OF NUCLEOPHILIC SUBSTITUTION

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Thiocyanate dehydrogenases (TcDH, EC 1.8.2.7) is a newly discovered family of copper-containing enzymes harboring a unique three copper cluster and catalyzing the transformation of thiocyanate into cyanate and sulfur. Combination of the biochemical, kinetic, spectral (ESR), structural and modeling (QM/MM) studies resulted in the formulation of the detailed molecular mechanism for the initial stage of the enzymatic reaction – the nucleophilic attack of the substrate, the thiocyanate, by a water molecule. The 3D structures of thiocyanate dehydrogenases from various sources in the free state and in complexes with inhibitors (thiourea) and substrate analogs (selenocyanate) were determined up to atomic resolution that enabled to visualize the important reaction intermediates and verify the suggested molecular mechanism of TcDH action. During the catalytic cycle TcDH undergoes profound conformational changes that affects the position of the constituent copper ions and results in the activation of the attacking water molecule.

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ROLE OF SMALL OPEN READING FRAMES IN CELL FUNCTIONING

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The basic dogma of molecular biology postulated that in eukaryotic cells one gene encodes one protein, but progress in genome, transcriptome, and proteome analysis has allowed the boundaries of coding potential to be expanded.

Telomerase is a ribonucleoprotein complex that completes telomeres in actively proliferating cells. Telomerase activity is ensured by two main components: telomerase reverse transcriptase and telomerase RNA, the presence of which is necessary for the functioning of the enzyme. Telomerase RNA is present in all cells throughout the entire life cycle of an organism. We have demonstrated the coding potential of the human telomerase RNA precursor. The hTERP protein, encoded by telomerase RNA, is involved in the mechanisms of regulation of cell survival and death, and activation of autophagy.

Analysis of the distribution of ribosomes along the RNA of a eukaryotic cell has revealed the accumulation of translating ribosomes in regions previously considered non-coding; for example, the 5'-untranslated regions (5'-UTRs) of many mRNAs accumulate ribosomes. We used a library of lentiviral particles to deplete 977 small reading frames using the CRISPR/Cas9 genome editing system to search for regions involved in maintaining cell proliferation. Studying the mechanisms of functioning of some targets identified during screening will make it possible to determine their role in the life of the cell.

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MICE GENOME EDITING AS A TOOL FOR FUNCTIONAL GENOMICS AND PERSONALIZED MEDICINE

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Genome editing gives us unprecedented possibilities. Despite significant functional advances in genomics, thousands of mammalian genes remain unexplored. To fully understand how the genome determines the structure and function of an organism, we need to understand the functional role of all genes. Our group at Moscow State University is specialized in the editing of mouse genome.

Over the course of several years, our group has studied a number of genes whose function was previously unknown¹⁻³. A number of new mitochondrial proteins responsible for the assembly of the mitochondrial ribosome have been found. Several genes are being studied, the products of which interact with RNA and carry out their function by influencing different types of RNA.

In addition to fundamental scientific interest, editing the mouse genome opens the way to the creation of personalized models of human genetic diseases. This approach will allow us to better understand the causes of the development of genetic diseases and open the way to the development of individual therapy for such diseases. We will cover a number of examples of such work.

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MICRORNA-TARGETED DRUGS: MIRNASES VS ANTISENSE OLIGONUCLEOTIDES

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With the expansion of genomic and molecular biological research methods, short non-coding RNAs, microRNAs (miRNAs), have gained indisputable recognition as an important element of cellular regulatory systems. Any disturbances in miRNA expression lead to a global pathological restructuring of extensive networks of molecular interactions, and as a consequence, the initiation and development of many human diseases, including cancer. Among all the drugs developed to date that regulate the level of miRNA, antisense oligonucleotides and miRNases have shown the greatest activity.

Antisense oligonucleotides are short synthetic modified oligonucleotides 15-20 nt long, complementary to the selected miRNA. The undoubted advantages of miRNA-targeted antisense oligonucleotides are their record nuclease resistance and the ability to cause target degradation through the recruitment of RNase H, an enzyme that causes RNA cleavage within the RNA-DNA heteroduplex.

miRNases are conjugates of antisense oligonucleotides that ensure binding to a specific miRNA target and a short catalytic peptide that can cleave it. The exceptional characteristics of miRNases are the combination of high intrinsic catalytic activity and synergistic action with RNase H, leading to quantitative cleavage of miRNAs in a truly catalytic mode.

The report will present a detailed comparison of these approaches in regulating the level and activity of oncogenic miRNAs, consider the consequences of the use of miRNases and anti-miRNA oligonucleotides on cellular and tumor models in vivo, and also propose ways for further development of these strategies for miRNA-mediated suppression of carcinogenesis processes.

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MYCOBACTERIUM TUBERCULOSIS NON-CODING RNAs AS REGULATORS OF HOST-PATHOGEN INTERACTION

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The centuries-long co-evolution of *Mycobacterium tuberculosis* and its host provided the pathogen with a set of strategies that can effectively combat the host's defense systems. Small non-coding RNAs of intracellular pathogenic bacteria can not only adapt the bacterial transcriptome to changing conditions, but also interact with the infected organism, thereby interfering with the processes of antibacterial defense.

We performed a comprehensive study of MTS1338 and MTS0997, the small *M. tuberculosis* RNAs, in pathogenesis of tuberculosis, for which we created the mutant strains with deleted MTS1338 and MTS0997 genes, and characterized them in vitro (in a liquid medium), in infected macrophage-like cultures, primary macrophages, as well as in mouse models of infection. We demonstrated for the first time that the small RNAs MTS1338 and MTS0997 are virulence factors of *M. tuberculosis*, triggering molecular cascades to dampen immune processes, such as, antigen presentation, immunoproteasome formation, phagosome maturation, synthesis of proinflammatory cytokines and type I interferons. Also, we found secretion of MTS1338 into the cytoplasm of infected macrophages and its interaction with components of the immune system.

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THERAPEUTIC STRATEGIES WITH CHEMICALLY MODIFIED SMALL INTERFERING RNAs

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Small interfering RNAs (siRNAs) are the most effective agents for targeted suppression of gene expression and are promising drugs for personalized medicine. SiRNA-cholesterol (Ch) conjugates enable the delivery of siRNA into cells without the use of transfection agents. A study of the effectiveness and duration of action of Ch-siRNA with “light” and “heavy” modification patterns differing in the length and location of the linker on the biological activity of siRNA allowed us to identify the most effective designs. Suppression of MDR1 gene expression by 78% in KB-8-5 tumors in mice demonstrates the advantage of fully modified (2'F, 2'OMe, PS) Ch-siRNAs.

A new type of RNAi inducer has been developed, which is convenient for synthesis and opens up possibilities for modifications. It was shown for the first time that Ch-supramolecular complexes with 2'F, 2'OMe, and LNA, containing from three to eight antisense chains, exhibit interfering activity. 4 days after i.v. administration of Ch-containing monomers and supramolecular trimers reduced *MDR1* mRNA levels in xenograft tumors in mice by 85% and 68%, respectively. The formation of supramolecular structures with three or four antisense chains equipped with terminal PS modifications enhances their accumulation in the liver and causes a decrease in *Ttr* mRNA levels by 67%.

The mesyl modification (μ) is a promising analogue of the phosphorothioate modification (PS), as it provides greater nuclease resistance and does not exhibit toxicity. Modification patterns containing up to 26 μ modifications that retained high biological activity and improved the pharmacological properties of siRNA were created.

The developed strategies were tested in an *in vivo* model of LPS-induced acute lung injury in mice to suppress the expression of the *Timp1* and *Il6* genes. Leader siRNAs significantly reduced the levels of target mRNAs, infiltration by inflammatory cells, and the severity of destructive changes in lung tissue after intranasal instillation into mice with acute lung injury.

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GENETICALLY ENGINEERED PROTEIN NANOCONTAINERS FOR BIOMEDICAL APPLICATIONS

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Encapsulins (nanocompartments) are high-molecular-weight capsid-like protein complexes consisting of a shell and a cargo protein. Due to their extraordinary stability, lack of toxicity and biodegradability, these unique structures, first discovered in bacteria in 1994, appear to be a promising alternative to popular nanoplateforms based on inorganic and/or polymeric nanoparticles^{1,2}.

We have shown that stable expression of encapsulin encoding genes can be achieved in mammalian cells. At the same time, various cargo proteins, both native and exogenous, can be encapsulated into the shell. For example, the cargo protein of *Quasibacillus thermotolerans* encapsulins is an enzyme with ferroxidase activity, which oxidizes Fe^{2+} to Fe^{3+} with the formation of magnetic nanoparticles. This allows cells to be tracked using MRI or non-linear magnetization (MPQ)¹. We also introduced a photoactivatable form of the mCherry protein as an exogenous cargo into *Myxococcus xanthus* encapsulins, which allowed them to be used as a label for super-resolution microscopy.

We have developed two encapsulin-based vector nanocontainer systems chemically modified with human transferrin. The targeting of the systems was confirmed by determining the content of intracellular iron and optical methods. Both approaches clearly demonstrated that nanocarriers selectively bind to transferrin receptors (TfRs) on cell surfaces, followed by internalization via receptor-mediated endocytosis pathway. The developed nanosystems can be used for targeted delivery of gene and chemotherapy drugs into cells with high TfR expression level.

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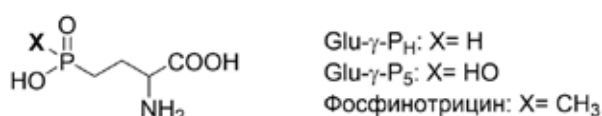
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PHOSPHORUS-CONTAINING ANALOGUES OF GLUTAMIC ACID: SYNTHESIS, INTERACTION WITH THE ENZYMES AND BIOLOGICAL ACTIVITY

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Replacement of the distal carboxyl group of glutamic acid with a phosphorus-containing fragment leads to the analogues having different spatial geometry and ionization constants.



Among these analogues, the most well-known and studied is the commercial herbicide phosphinothricin, which phosphorus-containing group mimics the intermediate tetrahedral state of the carboxyl group in the glutamine synthetase reaction. This similarity leads to irreversible and highly effective inhibition of the enzyme¹.

Singly charged phosphorus-containing group of Glu- γ -PH is an oblate tetrahedron, which may mimic a planar singly charged HOOC-group. Having penetrated in the cell, Glu- γ -PH may inhibit corresponding enzymatic reactions as such or undergo substrate-like transformations, leading to new biologically active phosphorus-containing metabolites. The interaction of phosphorus analogues of glutamic acid with enzymes², as well as the antibacterial activity of their derivatives^{3,4}, including the inhibition of the growth of clinical isolates of multidrug-resistant *Klebsiella pneumoniae* are discussed.

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NEW ANTIMICROBIAL AGENTS BASED ON MODIFIED NUCLEOSIDES

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Antimicrobial resistance (AMR) is one of the most serious global health problems and contributes significantly to morbidity and mortality worldwide. According to WHO, in 2019, bacterial AMR was associated with 4.95 million deaths worldwide, and was the direct cause of death in 1.27 million cases. It is estimated that by 2050, resistant microorganisms will claim 10 million lives per year - more than cancer.

Promising candidates for the role of new antibacterial agents are nucleoside derivatives. Currently, analogs and derivatives of nucleic acid components are important elements of anticancer and antiviral therapy. At the same time, among representatives of natural nucleosides and their synthetic analogues, antibacterial activity was discovered relatively recently, and this area is actively developing.

In recent years, our laboratory has obtained a significant number of nucleoside derivatives and screened their biological activity. Antibacterial activity has been shown in some gram-positive bacteria, such as *B. subtilis*, *L. mesenteroides*, *S. aureus* and a number of mycobacteria.

The most significant results were obtained with *M. tuberculosis*. A number of compounds inhibited the growth of Mtb at concentrations comparable to currently used therapeutic drugs, and these concentrations were the same for both the laboratory ("wild") strain H37Rv and the multidrug-resistant strain MS-115. The compounds were not toxic to eukaryotic cells.

An electron microscopic study of the interaction of the resulting compounds with Mtb demonstrated a few morphological changes in the cells, which resulted in partial and/or complete destruction of the three-layer cell wall of the bacteria.

Thus, the use of nucleoside derivatives and analogues as bacterial growth inhibitors is of significant interest in microbiology, biochemistry, medicinal chemistry and pharmacology.

SEARCH FOR APPROACHES TO IMPROVE SURFACTIN PRODUCTION EFFICIENCY IN *BACILLUS SUBTILIS* CELLS

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Surfactin is a cyclic lipopeptide with high surface activity and a promising synthetic surfactants analogue. Production of surfactin is limited due to the low efficiency of biosynthesis performed by natural producers, main of which are *Bacillus subtilis*. Development of superproducer strains will solve the problem of the high cost of surfactin and increase its production level for many various applications. We assume the idea that small non-coding 6S RNA (6S-1 and 6S-2) take part in surfactin biosynthesis in *B. subtilis*, as it was mentioned in scientific papers.

Impact on efficiency of surfactin biosynthesis in *B. subtilis* of 6S-1 and 6S-2 RNA is the purpose of this research. Bacterial microorganisms *B. subtilis* natural strain NCIB 3610 are considered as the research object. Deletion of 6S-1 RNA, not the 6S-2, leads to the increasing in the mRNA level of all the genes of the *srfA* operon encoding surfactin synthetase in the late stationary growth phase. Nevertheless, deletion of 6S-1 RNA doesn't have effect on surfactin production efficiency increasing. It is probably caused by parallel transcription activation of *rocG* gene responsible for glutamate catabolism, the latter is a part of surfactin molecule.

Mutations in *spxH* gene in the strain NCIB 3610 with 6S-1 gene deleted was shown by performing the nanopore sequencing. This might affect the Spx protein accumulation, that is the transcription negative regulator of *srfA* operon encoding the surfactin synthetase.

The work was carried out with the financial support of the RSF, project 24-24-00193.

DISCOVERING COMPOUNDS THAT POSSESS ANTIBACTERIAL ACTIVITY. ESTABLISHING THE MECHANISM OF ACTION FOR ANTIBACTERIALS THAT HAVE BEEN IDENTIFIED

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The coronavirus crisis has demonstrated the vulnerability of humanity to pathogens. Apart from the direct harm caused by the virus, there is also a significant increase in bacteria's resistance to the antibiotic drugs used.

Our laboratory has developed the pDualrep2 reporter system, which enables high-performance sorting of antibiotics based on their mechanism of action. This reporter system allows for the detection of inhibitors of protein biosynthesis and inducers of the SOS response in bacterial cells. In our laboratory, we conducted a large-scale screening of chemical molecules for antibiotic activity, testing more than 60 thousand compounds. Additionally, a search for antibiotics from natural sources was conducted, and several thousand potential producers were tested.

During these screenings, several natural inhibitors of protein biosynthesis were discovered and investigated, such as altiomycin and tetracenomycin X. Additionally, a new inhibitor of protein biosynthesis, auraplanin, was also discovered.

This study was funded by the Ministry of Science and Higher Education of the Russian Federation (Agreement No. 075-15-2021-1085).

MODERN APPROACHES TO STUDYING INTERACTIONS OF VARIABLE CARBOHYDRATE CHAINS OF GLYCOSAMINOGLYCANS WITH PROTEIN RECEPTORS

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Glycosaminoglycans (GAGs), sulfated polysaccharides of proteoglycans of the extracellular matrix of mammals, are involved in physiological processes in health and disease through interactions with protein macromolecules. The significant variability in the distribution of sulfate groups along the linear backbone, which is regulated in situ in the matrix, challenges studies of the structural complementarity of GAGs and their protein receptors^{1,2}.

In this report, the current approaches in studying the interactions of GAGs with proteins will be discussed. A database of GAG–protein complexes will be presented³. The possibilities of applying artificial intelligence methods to identifying new protein receptors will be considered. An integrative approach combining experimental and computational methods for determining the structural and thermodynamic characteristics of the interactions between GAGs with their protein receptors will be illustrated⁴.

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DEVELOPMENT OF INHIBITORS TARGETING GLIAL-MESENCHYMAL TRANSITION OF GLIOBLASTOMA MULTIFORME CELLS BASED ON SEMISYNTHETIC TERPENES: FIRST STAGE PROGRESS

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Glioblastoma multiforme (GBM) is a highly aggressive cancer with a low median survival (15 months). One of the key processes associated with the high aggressiveness of GBM is glial-mesenchymal transition (GMT), in which GBM cells acquire a highly invasive phenotype and resistance to chemotherapy.

In the present work, three series of chemical derivatives of isoalantolactone (a sesquiterpene lactone) and soloxolone (a pentacyclic triterpenoid) were screened for their ability to block key GMT-associated processes in GBM cells and leptin-stimulated neuroblastoma cells. Three hits (compound 19, soloxolone tryptamide (STA), soloxolone methyl (SM)) were identified that effectively blocked the clonogenicity, motility and invasiveness of tumor cells and modulated their adhesion properties. In addition, the ability of STA to inhibit spheroidal growth of GBM cells and high synergistic cytotoxic effect of STA and 19 with temozolomide were demonstrated. The pronounced anti-GBM activity of STA was verified in a mouse xenograft model of U87 glioblastoma, where a 7-fold intraperitoneal injection of STA (20 mg/kg) resulted in a 6-fold suppression of tumor growth and depletion of the network of immature thin-walled vessels and connective tissue fibers in GBM tissue. Using network pharmacology methods, we found that the revealed properties of compound 19, STA and SM may be related to their direct interaction with Hsp90, EGFR and SOS/MEK1/ERK2, respectively.

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PROTEIN AND COMPOSITE NANOPARTICLES FOR INTRACELLULAR DRUG DELIVERY

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Proteolytic hydrolysis, poor membrane permeability and weak tissue penetration of proteins hamper compensation therapy and targeted delivery. Protein nanoparticles (NP) could enhance protein stability, provide cellular uptake and induce innate immunity. NP were fabricated from enzymes (nucleases, proteases, lipase, catalase, horseradish peroxidase and lysozyme), antibodies, cytokines, linear and multiple antigenic peptides by nanoprecipitation from their solutions in fluoroalcohol with subsequent alcohol evaporation at 58°C and reduced pressure. Protein NP retained the catalytic and ligand-binding properties of original proteins. They appeared to be stable during storage at +4°C for 3 years. These NP could penetrate into human blood leukocytes, embryonic and cancer cells by means of unspecific endocytosis with their accumulation in endosomes and lysosomes with maximum in 2 days posttreatment with subsequent gradual degradation. The entry of foreign protein NP induced interferon α , β and λ gene expression.

To avoid lysosomal entrapment and proteolytic hydrolysis the protein NP were wrapped with cellular membranes and phospholipids using thin layer hydration approach. Phospholipids forming a complex with ammonium ferrothiocyanate were measured colorimetrically¹. Ultraviolet spectroscopy at 280 nm was used to determine protein concentrations in the composite NP. Structures of the composite NP were confirmed by fluorescent microscopy and scanning transmission electron microscopy (STEM). The composite NP consisting of protein core and membrane shells provided intracellular delivery by means of both membrane fusion and endocytosis.

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NEW ENZYMES FROM LACTOBACTERIA. PROSPECTS OF USE

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There is evidence in the literature that when bacteria of the genus *Lactobacillus* are cultivated in the presence of cells of the genus *Klebsiella*, lactobacilli secrete a number of proteins that help suppress the growth of *Klebsiella*¹. Among the proteins synthesized only in response to the presence of *Klebsiella*, peptidases, enzymes that hydrolyze nucleic acids, and various metabolic proteins were found.

Our laboratory conducts a systematic study of the key proteins of lactobacilli in order to understand the mechanism of their action, as well as to study the antagonistic effect of lactobacilli on pathogenic microorganisms. Currently, ribonucleoside hydrolase C (RihC), L-lactate dehydrogenase (L-LDH) and cysteine synthase A (CysK) genes have been cloned from *Limosilactobacillus reuteri* LR1. (strain *L.reuteri* LR1 was kindly provided by the All-Russian Scientific Research Institute of the Dairy Industry (VNIMI). RihC, L-LDH and CysK were obtained in active and soluble form and their basic properties were studied.

The structure of RihC was solved and the main features of the active site were determined. A study of the antibacterial activity of RihC and L-LDH showed that the addition of these proteins to a medium containing pathogenic organisms resulted in decreased biofilm growth for some pathogen species. The study of such enzymes opens up broad prospects for their use in the creation of new antibacterial drugs. In addition, RihC can be used to obtain high purity nitrogenous bases and their derivatives.

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MOLECULAR IMAGING IN IN VIVO ENZYMOLOGY

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Each living organism is individual. Firstly, there are genetic, epigenetic and transcriptomic factors (genotyp), and secondly, there are proteomic and metabolomic parameters, which refer to the set of variable phenotypic traits that cannot be predicted based on genotype analyses. The meaning of imaging systems is to collect signals and generate images, which are analyzed to obtain spatiotemporal characteristics of certain molecular processes occurring in the organs and tissues of a living organism, characterized by a high degree of heterogeneity both within a living organism and between different individuals. Up to a certain level of organization of biological structures, their behavior is described by the laws of statistical physics, but starting from the cellular level, determinism appears. At the same time, specific structures formed by cells appear at the tissue level, which determine the tissue characteristics of cell transport and transformation. To assess the influence of intracellular viscosity, the method of fluorescence correlation microscopy (FCS) using photoconvertible fluorescent proteins was used¹. At the early stage of apoptosis, when there are still no morphological changes in the cell structure, we observe activation of caspase-3 with a simultaneous increase in viscosity in individual cellular compartments², possibly due to the formation of a complex with PARP. Caspase-3 is well known for its role in programmed cell death. However, when moving to the system level of a living organism of a laboratory animal, a number of new factors arise. Raw fluorescence lifetime data measured in living animals should be classified as “probability data” (or “apparent data”)³. In order to obtain true parameters, it is necessary to use methods of anatomical and morphological analysis, for example, magnetic resonance imaging using light guides⁴, supplemented with new computing capabilities, built on artificial intelligence algorithms, and taking into account the real physical picture of the processes occurring in living organisms.

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RECOMBINASE POLYMERASE AMPLIFICATION IN COMBINATION WITH MEMBRANE IMMUNOCHROMATOGRAPHY FOR RAPID DETECTION OF PATHOGENIC BACTERIA *SALMONELLA ENTERICA* AND *LISTERIA MONOCYTOGENES*

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The monitoring and control of the pathogenic bacteria presence in food products are the keys to prevent contamination and to ensure biosafety. This study has been developed and presented the test systems of molecular genetic and immunoanalytical methods of assay for rapid detection of the pathogenic bacteria *Salmonella enterica* and *Listeria monocytogenes* in milk. The test systems combine isothermal recombinase polymerase amplification (RPA) of pathogen DNA and rapid lateral flow assay (LFA) on test strips. In RPA, a fragment of the *invA* gene for *S. enterica* and a fragment of *bsh* gene for *L. monocytogenes* are amplified to form 190 bp and 177 bp amplicons. The reaction takes 15 minutes and is carried out at a temperature of 40 °C. In LFA, the resulting amplicons are detected due to biotin and fluorescein residues at opposite ends of the oligonucleotide. Thus, the biotin binding protein streptavidin is immobilized on the analytical zone of the test strip and a monoclonal antibody to fluorescein labeled with gold nanoparticles is used in the liquid phase. Test strips provide rapid testing within 7 minutes and allow subsequent visual recording of the result. It has been established that the detection limits of genomic DNA of *S. enterica* and *L. monocytogenes* in the test systems were 0.5 fg and 1.0 fg respectively. The developed bioanalytical systems have been shown broad specificity for various serotypes of *Salmonella enterica* subspecies *enterica* and *Listeria monocytogenes*. The detection limit of salmonella in artificially contaminated samples of milk was $8 \cdot 10^2$ cells/ ml. After the enrichment by culturing for 6 hours this parameter was $2 \cdot 10^0$ cells per 25 g of milk. Thus, the presented test systems can become the basis for practical kits of reagents for rapid detection of pathogenic bacteria in food products.

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NUMEROUS SMALL OPEN READING FRAMES AFFECT PROLIFERATION OF HUMAN CELLS

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Although the human genome has been fully read, the full set of functional open reading frames (ORFs) remains unclear. Among them, identifying functional small ORFs consisting of less than 100 codons poses a major scientific challenge.¹ Of the many small ORFs, the upstream ORFs, which are located in the 5' untranslated regions of messenger RNAs (mRNAs), have attracted particular attention. Upstream ORFs may regulate translation *in cis* and also encode small functional proteins (microproteins). About half of mammalian mRNAs contain upstream ORFs, but their functions remain largely poorly understood.²

Ribosome profiling data allowed us to select nearly a thousand highly conserved upstream ORFs in human mRNAs. We performed extensive selection of upstream ORFs for cell proliferation using the CRISPR/Cas9 system. We confirmed the translation of several upstream ORFs through endogenous tagging, including a target in the *PRPF19* gene. Subsequent experiments indicate that the upstream ORF in *PRPF19* may encode a microprotein or regulate the translation of *PRPF19* mRNA.

Selection of upstream ORFs allowed us to identify a number of targets that play important roles in proliferation of human cells. The selected targets may regulate gene expression at the translational level or encode functional microproteins.

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NEW CATIONIC LIPOSOMES BASED ON CARBOHYDRATE-CONTAINING AMPHIPHILES FOR DELIVERY OF NUCLEIC ACIDS INTO EUKARYOTIC CELLS

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Cationic liposomes are used for nucleic acid (NA) delivery into eukaryotic cells for the treatment of inherited or acquired diseases. One of the strategies for creating targeted NA delivery systems is the design of cationic amphiphiles covalently bound to a targeting ligand, which simultaneously ensures both NA binding and its delivery into target cells¹.

In this work, we synthesized carbohydrate-containing amphiphiles including a spermine residue necessary for NA compactization and binding, a diglyceride involved in the formation of lipid aggregates, and carbohydrate residues (lactose or D-mannose), which improves the hydrophilic-lipophilic balance of the molecule. In addition, the lactose residue can serve as a targeting ligand for the NA delivery into hepatocytes, and the mannose residue can serve for specific interaction with lectin receptors of dendritic cells and macrophages. Based on the compounds obtained and the helper lipid DOPE, cationic liposomes were formed, their cytotoxicity was studied, and the ability to deliver various NA into eukaryotic cells was assessed.

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SCREENING FOR COMPOUNDS SELECTIVELY INHIBITING THE GROWTH OF TUMOR CELLS: ANTI-TUBULIN DIARYLISOXAZOLE DERIVATIVES

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During the screening of drugs against tumor cells in cocultures with cell lines of non-tumor etiology (FCCT [1]) and according to Mosman, an effect on tubulin was predicted for a number of found compounds. Compound 92518, structurally related to colchicine, acted on cells in the early micromolar range. Between the verubulin analogues with an aliphatic ring 1,2-annulated with a pyrimidine moiety substituted at positions 2 and 4, the most active compounds were comparable in *in vitro* activity to classical verubulins. Substance 07018 was selective against tumor cells and being similar to the dimer of combretastatins, but it did not affect tubulin polymerization. 3,4-diarylisoaxazoles bearing various substituents in the fifth position of the isoxazole ring and bioisosteres to the methoxy substituent in ring B turned out to be the most selective and acted in nanomolar concentrations [2]. They demonstrated antitubulin properties *in vitro*. It turned out that 5-Cl substituted 43, which is significantly less cytotoxic than CA-4p, led to complete remission in mice with models of murine leukemia and slowed down the growth of HCT-116 mouse xenografts (66-74%), which was also slightly superior in efficiency combretastatin A4-phosphate.

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METABOLOMIC CHANGES IN THE BLOOD AND BRAIN OF OXYS RATS – A MODEL OF ALZHEIMER'S DISEASE

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Using the method of metabolomic profiling using an analytical platform based on NMR spectroscopy, a comparative quantitative analysis of metabolites in the brain and blood of OXYS rats, a model of premature aging, one of the manifestations of which is the development of a complex of signs of Alzheimer's disease (AD), was carried out. The study was performed on animal tissue samples taken in the “preclinical” period preceding the development of signs of AD (at the age of 20 days), during the period of their manifestation (3-4 months) and active progression (16-18 months). Wistar rats of the same age were used as controls. The use of chemometric and statistical analysis methods made it possible to identify the main metabolic patterns during aging and the development of disease symptoms. Among the many metabolites whose interstrain differences in concentrations were identified, special mention should be made of scyllo-inositol, the concentration of which in the hippocampus of OXYS rats was significantly increased in all age groups studied. Based on the data obtained, it was suggested that the accumulation of scyllo-inositol in the brain even at an early age allows us to consider it as a predictor and potential biomarker for the development of signs of AD in OXYS rats and, possibly, in humans.

It has been shown that taking the drug melatonin has a positive effect on the metabolomic profile, while the effect is more pronounced in the blood serum than in the cerebral cortex. For most metabolites, differences in metabolite concentrations were leveled off: with drug administration, the concentrations of metabolites in the tissues of OXYS rats become close to the concentrations of metabolites in the tissues of Wistar rats. The therapeutic effect of the drug melatonin is confirmed by data measuring the content of A β amyloid in the cerebral cortex of rats.

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SYNTHESIS OF HEPARINOID FRAGMENTS FOR BIOLOGICAL AND CONFORMATIONAL STUDIES

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Heparin and heparin sulfate are representatives of the glycosaminoglycan (GAG) class of polyanionic polysaccharides, which are essential to a variety of regulatory processes from tissue growth to blood clotting. GAG-like structures are not exclusive to mammals: we previously reported on newly isolated heparinoid preparations from the starfish *Lysastrosoma anthosticta* and *Lethasterias fusca*, which contain highly unusual monomers: 3-*O*-sulfated and 2,3-*O*-disulfated iduronopyranoside units, which do not occur in human heparinoids, however both preparations were found to be biologically active, affecting blood clotting and hematopoiesis^{1,2}. In order to explore the effect this unusual sulfation might have on the polysaccharide chain and its protein interactions, we have synthesized a series of eight iduronopyranosides, covering all possible patterns of sulfation, and analyzed their conformational behavior by means of NMR spectroscopy and *ab-initio* computational studies. We found that increased substitution shifts the idopyranoside ring's conformation from ⁴C₁ towards ¹C₄, and that the conformational equilibrium includes the ¹S₃ conformer³.

Expanding upon this work we have synthesized a series of sulfated di- and trisaccharides, representing human (2S-IdoA) and starfish (2,3S-IdoA) structures. The iduronic acid residue in these structures is flanked by 6SGlcNS residues in order to more accurately model the polysaccharide chain, and observe in more detail the effect of substitution has on iduronopyranoside ring conformation and heparinoid biological activity.

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STUDY OF THE STRUCTURE OF LIPOOLIGOSACCHARIDE OF THE MARINE GRAM-NEGATIVE BACTERIUM *KANGIELLA JAPONICA* KMM 3897

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Extremophiles are organisms that can live and reproduce in conditions that are considered destructive to many other life forms. For some extremophile microorganisms, the ideal habitat is water bodies with high salt content, including seawater. Currently, marine bacteria represent a promising source of new metabolites with a wide range of biotechnological applications.

The outer membrane of the cell wall of Gram-negative bacteria is usually composed of lipopolysaccharides (LPS), which are amphiphilic macromolecules anchored in the phospholipid bilayer. The amphiphilic nature of LPS is defined by three distinct covalently linked structural domains: hydrophilic O-specific polysaccharide, core oligosaccharide, and lipid A. The structure of LPS, especially lipid A and core oligosaccharide, plays an important role in the integrity, flexibility, and fluidity of the cell wall of Gram-negative bacteria and is crucial for normal physiology and microbial growth.

This work presents the results of a structural study of lipooligosaccharide (LOS) from the marine Gram-negative bacterium *K. japonica* KMM 3897. It is shown that 11:0(3-OH) and 11:0 fatty acids are the main ones for LOS and that lipid A is a mixture of hexa-, penta-, and tetraacylated isoforms bearing one or two phosphate groups at canonical positions. The core oligosaccharide is a trisaccharide constructed from residues of 2-amino-2-deoxy-D-glucose, D-glycero-D-manno-heptose, and 3-deoxy-D-manno-oct-2-ulosonic acid phosphorylated at the O-4 position. Taking into account the peculiarities of the structure, LOS may potentially have antagonistic properties against the LPS of pathogenic microorganisms and inhibit the activation of the signaling cascade mediated by the TLR4/MD-2 receptor complex.

SEARCH FOR EVOLUTIONARILY NEW MCE-18 STRUCTURAL SCAFFOLDS OF COMPOUNDS THAT ARE SELECTIVELY CYTOTOXIC AGAINST TUMOR CELLS

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In silico compound prefiltration and high-throughput screening are widely used to search for new structural scaffolds for antitumor compounds. New compounds can be selected using, for example, the MCE-18 descriptor. Via this descriptor, a library of 4992 evolutionarily novel compounds was obtained for high-throughput analysis.

In order to evaluate selectivity of compounds *in vitro*, we analysed cells cocultures of tumorr (A549, MCF7) and non-tumour (VA13, MCF10A) etiology, which were marked by the expression of fluorescent proteins (eGFP and Katushka2S, respectively)¹. The high-throughput analysis identified 162 compounds demonstrating selectivity.

For FCCT-selective compounds, clustering was performed using the structural similarity parameter FragFp with a threshold value of 0.7. 8 clusters were found, for 5 clusters the effect was confirmed in the Mosman test, while 4 of them belonged to oxadiazole derivatives. Compounds F835, L115, L234, L700, M950 can be mentioned separately. They are derivatives of pyrazolo[1,5-d][1,2,4]triazin-4(5H)-one (F835), thieno[3,2-d]pyrimidin-4(3H)-one (L115), 1,2,4-oxadiazole (L234&L700), 5-(5-cyclopropyl-1,3,4-oxadiazol-2-yl)-2,4-dimethyl-3-pyrrolesulfonamide (M950). In terms of selectivity for VA13/MCF7 cells, cluster 835 had the best value, clusters 115, 234, 700 showed low selectivity, and compounds comprising cluster 950/952 did not show selectivity in the Mosman monoculture assay, however, they had effective concentrations in the nanomolar range.

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SYNTHESIS OF OLIGOSACCHARIDES RELATED TO CRYPTOCOCCUS NEOFORMANS GALACTOXYLOMANNAN FRAGMENTS

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Cryptococcus neoformans is a fungal human pathogen that causes severe disease in immunocompromised patients (especially those with HIV/AIDS).¹ This fungus can infect the brain, causing cryptococcal meningitis, a disease that is fatal if not treated properly. In recent years, there have been serious concerns about the increasing incidence of cryptococcal meningitis among people with normal immune system function.^{2,3} Also of concern is the ever-expanding endemic area of this pathogen.

One of the main virulent factors of *C. neoformans* is its bulk polysaccharide capsule. The minor capsular polysaccharide, galactoxylomannan (GalXM), is structurally conserved for all serotypes of the fungus that makes it a promising diagnostic marker and also a target for vaccine development. Our work presents an approach for the stereospecific synthesis of GalXM-related oligosaccharides consisting of an α -(1 \rightarrow 6)-galactopyranose chain of various length bearing β -galactofuranose residues at O-2 or/and O-3 of some links.⁴ The presented compounds were obtained as conjugates with biotin and BSA and will be applied to study the immunobiological role of corresponding GalXM fragments for the purpose of creating diagnostic kits and vaccine against *C. neoformans*.

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STUDY OF THE EFFECT OF NUCLEOTIDE DISTRIBUTION ON THE FUNCTIONALITY OF DNA AND RNA COMPLEXES

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Theoretical and computational approaches to modeling nucleic acid complexes are widely used to study their behavior in biology and nanotechnology. DNA objects can be functionalized with potential applications from nanomedicine to nanoelectronics¹.

Optimization of the parameters of oligonucleotide complexes through sequence selection is a crucial task. The work investigates structural transitions in different types of oligonucleotide complexes and shows that the transition temperature is dependent on the size of complementary nucleotide blocks. By using the basin-hopping optimization method, a methodology is developed to control the melting point of different types of nucleic acid structures².

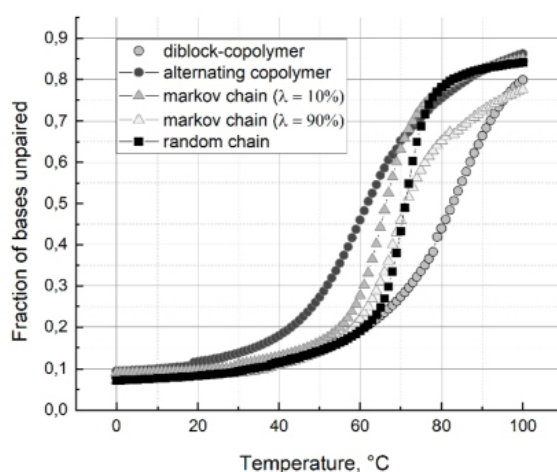


Figure 1. Dependence of the fraction of bases unpaired on temperature

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RESEARCH ON BERBERINE DERIVATIVES FOR SELECTIVE CYTOTOXICITY AGAINST TUMOR CELLS AND ANALYSIS OF POSSIBLE MECHANISMS

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Cancer is one of the leading causes of mortality worldwide. In combating the disease, significant attention is devoted to the development of antitumor drugs among low molecular weight compounds¹.

In the study, over a hundred compounds of various chemical structures were analyzed for their cytotoxic effects on co-cultures of cancerous and non-cancerous cells. Compounds of the SHE group, derivatives of berberine, demonstrated selective cytotoxicity against tumor cells.

Berberine is an active substance found in certain plants of the Berberidaceae family. Some studies indicate the potential anti-tumor effect of berberine².

Derivatives of SHE were investigated for their selective toxicity to tumor cells using the MTT assay. Substituting the methoxy group at C₉ of berberine with hexylamide (SHE-196) exhibits comparable selectivity to the parent compound but at lower concentrations. Substituting the methoxy group with an acetamide group bearing two unsubstituted aryl fragments (SHE-11) reduces selectivity compared to SHE-196, and substitution of halogens in this fragment leads to loss of selectivity ($SI_{VA13/MCF7}(\text{Berberine}) = 9,2$; $SI_{VA13/MCF7}(\text{SHE-196}) = 7,3$; $SI_{VA13/MCF7}(\text{SHE-11}) = 3,5$).

Possible mechanisms of action were considered for selectively acting molecules. The compounds exhibited an antimyochondrial effect as revealed by the JC-1 assay. Using the ethidium bromide displacement assay for these derivatives, it was shown that they act as DNA intercalators.

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EFFECT OF MESENCHYMAL CELLS (MSCS) AND NANOSCAFFOLD ON WOUND HEALING IN IRRADIATED RATS

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Repetitive exposure to radiation has many disadvantages such as delayed wound healing. Different treatment modalities were found to enhance normal wound healing or accelerate delayed wound healing. Aim of study: investigate the efficacy of MSCs combined with nanoscaffold in accelerating wound healing. Sixty-four male rats were selected for the study. Rats were randomly divided into four equal groups A, B, C and D. All rats received 6 Gy Gamma radiation and were subjected to a circular incision having the diameter of 1.5 cm. group1(irradiated group): received no treatment ,group2(stem cells): injected with 1 million cells of MSCs subcutaneously, the amount of the injected material was equally distributed along the margin of the wound with uniform space between each injection, group 3 (nano-Scaffold) in the form of circle sheet with diameter 1.5 cm was placed on the surgical incision, group 4: (MSCs and nano-Scaffold) was injected with 1 million cells of (MSCs), and nanoscaffold in the form of circle sheet with diameter 1.5 cm was inserted over the surgical incision. The rats in each group were further randomly subdivided into two subgroups (8 rats for each) according to the date of sacrifice 7 and 14 days after inducing wounding. On the third day post irradiation, surgical procedure was performed under general anesthesia. Results: The three treated groups showed acceleration in wound healing when compared to the control group, regarding mRNA analysis, histologically and clinical wound closure. The healed tissues using MSCs with nano-scaffold showed the least number of inflammatory cells, the most well organized mature collagen fibers without scar formation and the better healing after assessment of changes in the gene expression of TGFβ-1 during mRNA analysis. There is a significant difference in acceleration of wound healing using MSCs with nano-scaffold when compared to other groups.

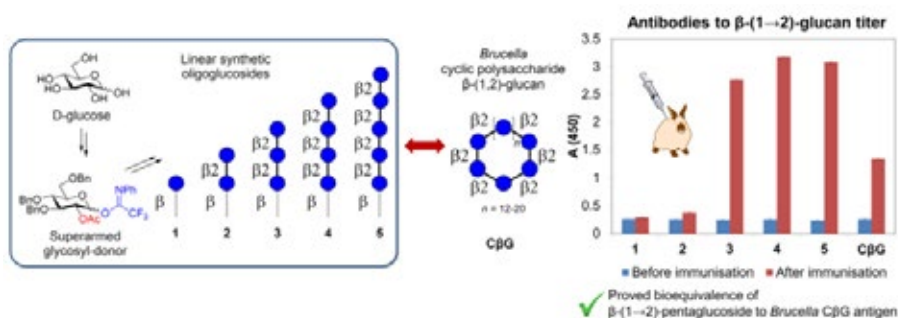
LINEAR OLIGOSACCHARIDE FRAGMENTS OF BRUCELLA CYCLIC β -(1 \rightarrow 2)-GLUCAN: SYNTHESIS, NMR AND IMMUNOCHEMICAL INVESTIGATION

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Brucellosis is zoonotic infection caused by *Brucella* spp. bacteria. Infection afflicts cattle and humans widely across the globe. Current veterinary standards of brucellosis eradication in livestock require culling of cattle that hugely impacts economy. Modern problems with brucellosis diagnostics, treatment and prevention cause the necessity for interdisciplinary studies of bacterial surface antigens, such as carbohydrates. One of the *Brucella* polysaccharides, cyclic β -(1 \rightarrow 2)-glucan (C β G), still has controversial opinions about its applicability in diagnostics and immunization against brucellosis. Herein, the full synthesis of its linear fragments and their conjugates is described for the first time. For carrying out the full synthesis of oligosaccharides acetimidate donor was obtained. Although the desired

β -(1 \rightarrow 2)-linked di- and trisaccharides can be easily obtained using standard methods, the synthesis of longer chains has appeared to be challenging. Effective glycosylation reactions was achieved only in toluene, but not in DCM commonly used for glycosylation.



NMR-studies revealed pentasaccharide as minimal size fragment for modeling C β G polysaccharide properties. It was used for ELISA screening of human donors sera experiments. To confirm the bioequivalence of the synthetic fragment and native C β G, antibodies against β -(1 \rightarrow 2)-pentaglucoside were raised by serial immunization of rabbits with the corresponding bovine serum albumin conjugate. Importantly, the antibodies obtained recognized not only linear synthetic oligoglucosides but also the natural C β G produced by *Brucella*. These results open new opportunities for veterinary and clinical diagnosis of brucellosis.

This work was supported by the Russian Science Foundation (grant 19-73-30017-P).

COMPARISON OF STRUCTURAL CHARACTERISTICS AND ANTICANCER ACTIVITY IN VITRO OF FUCOIDAN FROM *F. EVANESCENS* AND THEIR DERIVATIVES OBTAINED BY CHEMICAL AND ENZYMATIC HYDROLYSIS

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Sulfated polysaccharides of brown algae, fucoidans, have great potential for use in medicine, pharmacology and cosmetology due to their wide range of biological activities¹. However, there are difficulties in standardizing these structurally complex compounds. It is relevant to obtain low molecular weight derivatives of fucoidans because they can be standardized, which is necessary for the development of drugs. It is also assumed that the resulting derivatives may exhibit increased biological activity compared to the native polymer due to their enhanced absorption in the intestine and increased concentration in the blood vessels.

The application of existing chemical methods for obtaining of products of fucoidan depolymerization often leads to the elimination of sulfate groups from α -L-fucose residues, which are one of the main monosaccharides from which the fucoidan molecule is built, and, as a consequence, a decrease in the biological effects exhibited by fucoidans². The use of fucoidanases, enzymes that specifically catalyze the hydrolysis of O-glycosidic bonds in fucoidans and fucan sulfates, is promising.

This work is devoted to the study and comparison of the structural characteristics of fucoidan derivatives from the brown algae *F. evanescens*, obtained using enzymatic and chemical hydrolysis, as well as comparison of their antitumor activity *in vitro* against various types of cancer cells.

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MACHINE LEARNING METHODS APPLIED TO PROTEINS RECOGNIZING GLYCOSAMINOGLYCANS

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Glycosaminoglycans (GAGs) are negatively charged, unbranched polysaccharides that play a vital role in cell-cell communication. They are components of glycoproteins and are responsible for binding to intercellular host proteins. This interaction is critical for signal transduction, pathogen recognition, and tissue structure formation. In addition, GAGs influence the development and morphology of cells, both in health and diseases. The wide range of functions of GAGs indicates the importance of studying the molecular basis of protein recognition of these polysaccharides. However, obtaining experimental information on in vitro protein-GAG interactions is limited by difficulties in the synthesis of the target carbohydrates, which is translated into a scarce of structural information on their complexes¹.

The implementation of bioinformatical tools and in silico design may help clarify the structural prerequisites for the substrate specificity of GAG-binding proteins. In this report, we present the results of machine learning approaches for the prediction of protein specificity to GAGs. The efficiency of the xgboost model (an algorithm included in the family of gradient boosting models) exemplified by the case of heparan sulfate is revealed by high balanced accuracy and supported by the comparison with complexes available in the GAG-DB database¹.

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ESTABLISHING OF THE RED FLUORESCENT PROTEIN TAGRFP'S MUTANTS WITH REDUCED IMMUNOGENICITY

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Over more than twenty years of using tumor models based on cells expressing fluorescent proteins (FP), it has become obviously that FB¹, initially considered as immunologically inert, may actually not be such inert mice². The impact of the host immune response to tumor cell expressing FBs may introduce uncertainty into the evaluation of antitumor therapy's effect, for example, leading to an overestimation of the number of dead tumor cells and/or an underestimation of the metastatic potential of a fluorescent tumor.

Using the Internet resource NetMHC-4.0^{3,4}, the possibility was assessed that parts of the amino acid sequence of the TagRFP protein may represent epitopes of T cells of BalB/C mice (alleles K2-Dd, Ld, Kd). Then, the alanine scanning⁵ was performed for high-affinity sequences to estimate the change in affinity at amino acid substitution. Among the epitopes, those located in the α -loops and the C-terminus of the FP outside the β -barrel were selected to minimize the effect of the substitution on protein folding and fluorophore maturation.

Based on these calculations, site-directed mutagenesis of the TagRFP protein was carried out at positions 224, 225, 228. The chromatographic purification technique was optimized for the resulting proteins.

An enzyme-linked immunosorbent assay technique was also developed and optimized to determine the binding of antibodies to the TagRFP protein (WT and mutants) to TagRFP (WT) adsorbed in the microplate wells.

This technique was applied to the blood sera of BalB/C mice obtained by multiple immunization of animals with mutants of the TagRFP protein with potentially reduced immunogenicity.

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PREDICTION OF THE FULL-SIZE STRUCTURE OF THE PARP1 REPAIR PROTEIN USING MACHINE LEARNING AND HOMOLOGICAL DESIGN METHODOLOGY

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Prediction of the full-length tertiary structure of proteins is one of the important and ambitious tasks of molecular modelling. At present, not all spatial structures of therapeutically relevant proteins are deciphered by experimental methods. For instance, the full-length structure of the DNA repair enzyme poly(ADP-ribose) polymerase 1 (PARP1) remains incompletely annotated. Only individual domains of proteins are represented in the Protein Data Bank.

To select the optimal prediction method and determine an accurate structure well-known tools (AlphaFold2, RoseTTAFold, IntFOLD5, I-TASSER) were used to predict the tertiary structure of PARP1 in this study. The geometric parameters of the obtained proteins were subjected to molecular dynamics simulations for 300 ns in an NPT ensemble with the OPLS4 force field. To validate the predicted secondary structures of individual PARP1 domains were compared with the structures of domains deciphered by experimental methods. As a result of the investigation using molecular modelling methods, the full-length tertiary structure of PARP1 was annotated and the optimal method for predicting similar enzymes was determined.



Picture 1. PARP1 structure predicted by AlphaFold2: Zn²⁺ cations are shown as grey balls.

ENANTIOMER-SPECIFIC INTERACTION OF LIPOPHILIC POLYAMINES WITH CELLULAR TRANSPORTERS

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The study of molecular mechanisms underlying the inhibition of proliferative activity in tumor cells is a key direction for the development of new highly effective targeted antineoplastic agents. Within the context of this research direction, data have been obtained indicating a significant role of polyamines in the processes of proliferation and differentiation of cells. The concentration of polyamines in tumor cells is significantly higher than in healthy ones. According to the results of recent scientific studies, the SLC3A2 protein, responsible for the transport of polyamines, is critically important for the process of carcinogenesis, which justifies its potential as a target for the development of polyamine transport inhibitors. Based on this hypothesis, a series of works aimed at the rational design of low-molecular-weight inhibitors of the SLC3A2 receptor has been carried out.

In the framework of laboratory studies, a series of lipophilic polyamines with a racemic glycerolipid fragment was synthesized (Figure 1). The compounds demonstrated cytotoxic activity in the micromolar range of concentrations and did not cause hemolysis of erythrocytes. Significant interest, in the context of this research, was aroused by optically active glycerolipids. Namely, the ability of their enantiomers to interact differently in chiral biological systems, allowing the modulation of their target activity.

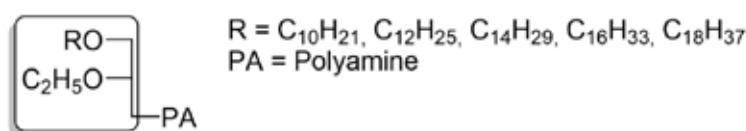


Figure 1: Lipophilic polyamines with different long-chain alkyl substituents

This aspect became the basis for a detailed study of the molecular metadynamics of the stereoisomers of the synthesized compounds with the SLC3A2 transport protein. The study of free energy surfaces revealed that both isomers have high binding energy values in the active site ($\Delta G = -130$ kcal/mol), indicating their high affinity for the protein's active site. However, the S-isomer overcomes an increased energy barrier when penetrating the cell membrane from the outside, whereas the R-isomer, on the contrary, after penetrating the cell, demonstrates a reduced ability to be released into the intercellular space. The presented data highlight the influence of stereochemical factors on the level of biological activity and the efficiency of compound binding in the active cavity of SLC3A2, providing an opportunity for fine optimization of ligands' target activity in the process of rational design for their further use as components of therapy for malignant neoplasms. The results of the calculations require further confirmation by biological experiments.

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INCREASING THE THERMOSTABILITY OF TERMINAL DEOXYNUCLEOTIDYL TRANSFERASE FOR SYNTHESIS OF SINGLE-STRANDED DNA

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Terminal deoxynucleotidyl transferase (TdT) - is an enzyme that catalyzes the addition of triphosphate nucleotides to single-stranded DNA, which has found wide application in the preparation of aptamers, biosensors, and for de novo enzymatic DNA synthesis [1].

In this work, we expressed a eukaryotic enzyme TdT in *Escherichia coli* and were able to obtain it in a soluble form by using the fusion partner SUMO, which increases proteins solubility.

The wild-type polymerase we obtained turned out to be insufficiently thermostable for use in enzymatic synthesis technology. To address the issue of thermostability, various three-dimensional structures of TdT and other family X polymerases were analyzed by using the B-Fitter program to find the most mobile amino acids. The most promising sites for saturating mutagenesis have been identified.

As part of rational design, a number of promising replacements have been developed using the FoldIt program. A technique for obtaining saturating libraries and individual mutants has been developed. All obtained substitutions were confirmed by Sanger sequencing.

To test the thermostability of a large number of mutants without isolating the protein, a screening technique was developed in cell supernatant using FAM-labeled primers.

More than 8 thermostable variants of TdT have been discovered, with denaturation temperatures reaching 50 oC. A TdT variant without the Loop2 loop was obtained and it was shown that the mutant has greater processivity [2].

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The work was carried out on the basis of the reference center of synthetic biology of the SBM Research Institute.

SOLOXOLONE PARA-METHYLANILIDE AS AN INHIBITOR OF INVASIVENESS AND STEMNESS IN GLIOBLASTOMA

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The median survival of patients with glioblastoma multiforme is limited to 15 months due to the low effectiveness of therapy. Glioblastoma cells undergoing glial-mesenchymal transition (GMT) increase invasion into brain tissues, making tumor resection difficult. In addition, tumor stem cells with increased drug resistance mediate a weak response of glioblastoma to temozolomide therapy, which leads to the development of tumor relapse.

Previously, we developed 9 amide derivatives of the triterpenoid soloxolone, capable of crossing the blood-brain barrier and inhibiting the growth of glioblastoma both *in vitro* and *in vivo*. Here, we screened these compounds, resulting in the identification of the potential GMT inhibitor soloxolone para-methylanilide (SpMA): SpMA increased adhesiveness but decreased motility and expression of mesenchymal markers (N-cadherin, fibronectin, and Slug) in glioblastoma cells by blocking the TGF- β 1/Smad2/3 pathway through direct interaction with T β RI/II. Additionally, SpMA suppressed the stemness of glioblastoma cells by inhibiting their clonogenicity, spheroid growth, and aldehyde dehydrogenase (ALDH) activity. SpMA was shown to enhance the cytotoxic effect of temozolomide against glioblastoma cells *in vitro* (synergy score $\delta = 15$), which was further verified in a mouse xenograft model, where SpMA demonstrated high therapeutic efficacy without systemic toxicity.

Taken together, SpMA is an inhibitor of the invasiveness and stemness of glioblastoma cells and a promising candidate for inclusion in combination treatment regimens for glioblastoma.

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CONJUGATES OF PEPTIDES AND HYALURONIC ACID BINDING VASCULAR ENDOTHELIAL GROWTH FACTOR

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Age-related macular degeneration and diabetic retinopathy are the most common eye diseases that significantly degrade the quality of life, also it's the main cause of age-related vision loss^{1,2}. The main pathological process underlying these diseases is neovascularization associated with excessive activity of vascular endothelial growth factor (VEGF).

The main disadvantage of currently existing medicines is the necessity for frequent intravitreal injections.

The actively developed direction of solving this problem is the production of conjugates of VEGF inhibitors with hyaluronic acid. It is a prospective carrier, because hyaluronic acid is one of the main components of the vitreous body.

In this work, we use anti-VEGF peptides earlier developed in our research group as angiogenesis inhibitors. Structural formulas: Aib2 (VUPNc[CDIHVnLWEWEC]FERL-NH₂), kv114* (KUKKc[CDIHVnLWEWEC]FERL-NH₂).

By now, the drug's effectiveness has been demonstrated *in vitro* experiments, including using special cell lines. Animal experiments were also carried out, which confirmed the high effectiveness of the developed conjugates in reducing induced neovascularization in the eyes of rabbits.

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OPTIMIZATION OF LIPOSOMAL COMPOSITIONS FOR MRNA DELIVERY

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The clinical applications of therapeutic nucleic acids (TNAs) are rapidly expanding within the medical field. The delivery of TNAs into living cells and organisms requires specialized transport systems such as cationic liposomes, which protect TNAs from nucleases and other factors within biological fluids. An ideal delivery system should exhibit flexibility to accommodate various types of TNAs on diverse types of cells and tissues, enabling rapid and cost-effective drug development through simple replacing the nucleotide sequence. However, practical implementation usually requires optimization of the liposomal composition and/or method of its preparation to achieve maximum effectiveness.

Previously, we developed liposomal compositions based on polycationic amphiphiles 2X3¹ and 2X7², which showed high efficiency of pDNA and siRNA delivery into eukaryotic cells. This study aimed to evaluate the effectiveness of these liposomal compositions for mRNA delivery. Preliminary studies showed the insufficient effectiveness of previously developed compositions, so they were optimized by assessing the size, heterogeneity of liposomes and their complexes with mRNA. The newly optimized liposomal compositions were further studied for the efficiency of mRNA binding and the dynamics of reporter protein accumulation in HEK293T cells upon delivery of mRNA over a 40-hour period.

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THE DISCOVERY OF NEW GH141 STRUCTURAL FAMILY ENZYMES OF THE FUCOIDAN-DEGRADING LOCUS OF THE MARINE BACTERIUM *WENYINGZHUANGIA FUCANILYTICA* CZ1127^T

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The cell wall matrix of brown algae contains fucose-containing sulfated polysaccharides, which are known as fucoidans¹. These polysaccharides are of great interest to researchers due to the wide range of biological activities they exhibit. Fucoidans may differ in their monosaccharide composition, type of glycosidic linkages between α -L-fucose residues and other monosaccharides, arrangement of sulphate groups, and the presence of various side branches¹. The observed biological effects of these polysaccharides are probably related to subtle elements of their structure. To determine this relationship, it is most relevant to utilise a variety of enzymes with established specificity and mechanism of action. This would allow selective implementation of various subtle modifications of glycans under mild conditions. However, enzymes involved in the transformation of fucoidans are poorly characterized, and many have not yet been discovered.

A gene cluster potentially involved in the degradation of fucoidans was previously identified in the genome of the marine bacterium *Wenyngzhuangia fucanilytica* CZ1127T². This cluster encodes approximately 30 enzymes belonging to different glycoside hydrolase (GH) families². Analysis of the functional activity of the enzymes encoded by these genes allowed us to determine their involvement in fucoidan depolymerisation. Among the enzymes studied, we characterised for the first time the fucoidan-degrading representatives of the GH141 structural family.

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A TEST SYSTEM FOR EVALUATING THE EFFECTIVENESS OF ABC TRANSPORTER INHIBITORS

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The activity of breast cancer resistance protein BCRP and P-glycoprotein, transmembrane proteins of the ABC family, provides the release of antitumor drugs from cells and formation of chemoresistance by cancer cells. To overcome chemoresistance of tumors is possible by the treatment with transporter inhibitors. Since the normal activity of both BCRP and P-glycoprotein is insufficient to accurately quantify the effectiveness of such inhibitors, the use of special tools is clearly necessary.

The aim of the work was to create a cell test system to evaluate the ability of compounds to reduce the transport activity of ABC transporters. For this purpose, wild-type HCT116 cells were used; the chemoresistance properties of these cells were induced by long-term exposure to the cytostatic drug taxol, the most widely used anticancer drug of natural origin. As a result of this exposure, ABC transporter-mediated resistance was formed not only to taxol, but also to other drugs with a different mechanism of action. The contribution of transporters to chemoresistance of cells was assessed by the ratio of cell accumulation of BCRP and P-glycoprotein dye substrates. Overexpression of transport proteins was confirmed by immunocytochemistry. The developed test system was used to evaluate the effectiveness of ATP mimetics¹, potential inhibitors of ABC transporters.

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SYMPOSIUM GLASS AND CERAMICS"

POROUS OXIDE MATERIALS IN CATALYSIS

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Heterogeneous catalysts, which are composite materials, are used in most large-scale catalytic processes. Such catalysts consist of a porous oxide matrix with supported active metal-containing component. Most often, porous materials based on aluminum and silicon oxides or their compounds act as an oxide matrix.

The report presents the results of the development of scientific and technological bases for the production of porous oxide materials, the synthesis of heterogeneous catalysts based on them, and data on the relationship between the properties of catalysts and the characteristics of porous oxide materials.

The main results are related to the development of an environmentally safe method for the production of nanodispersed aluminum hydroxide, the synthesis of porous aluminum oxide materials with a developed surface (up to 300 m²/g) based on it and following preparation of catalysts for key refining processes (hydrotreating and hydrocracking of petroleum fractions).

For a number of catalytic processes, silicon dioxide acts as a porous matrix – the support for the active component. The report also presents methods for the synthesis of such materials with a surface ranging from 10 to 1000 m²/g within the framework of a single technological approach.

For deep processing of heavy oil fractions, composite materials consisting of aluminum oxide, silica-alumina or synthetic micro/mesoporous zeolite act as porous supports. The results of using the recrystallization method to control the mesoporous structure of zeolite and an analysis of the use of newly synthesized catalysts in the hydrocracking process have been presented.

As a result of systematic research, a technological platform has been developed for the production of porous oxide materials and the synthesis of a wide range of highly efficient catalysts for oil refining processes on their basis.

ADDITIVE TECHNOLOGIES FOR FUNCTIONAL GRADIENT MATERIALS PRODUCTION

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An important step for parts design is parts adaptation for the manufacturing process. It should be noted that optimization of the part configuration, the location of structural zones, thin-walled and mesh elements, and chemical composition using digital design is a key direction in the development of additive technologies, which will make it possible to find solutions that are unattainable with traditional design and construction. Integrating design, optimization and manufacturing into a single system forms a new approach to digital manufacturing¹.

This process of creating products is called functional-gradient additive manufacturing. The implementation of this process involves optimizing products for specific operating conditions².

It is important to note that the key direction in the development of additive technologies is the design of not only the configuration of products, but also the properties of the materials from which this product is made. In one part, for example, a working blade, burner or other parts, a situation arises of uneven thermal fields (a part of detail operates at low temperatures, other part - at high temperatures), uneven loads (unidirectional in one zone, cyclic in another). Thus, the formation of a certain structure is advisable in each individual element of a detail based on the results of operating conditions analysis using advanced software.

Thus, a voxel model is obtained where each voxel has a certain structure and properties, and the whole product can operate under the existing difficult operating conditions³⁻⁴. The use of additive technologies will make it possible to create functionally graded materials with the required properties in each element in one technological cycle⁵.

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CURRENT STATE AND PROSPECTS FOR THE DEVELOPMENT OF RESEARCH IN THE FIELD OF CERAMIC AND GLASS -LIKE MATERIALS IN THE FAR EAST

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The report presents current research results and scientific-technical solutions in the field of ceramic and glass-like materials development along the key areas of the Strategy for Scientific and Technological Development of the Russian Federation. This is a systematized experience of Far Eastern scientists, specialists in the fields of chemistry, physics, and materials science, representing the Far Eastern Branch of the Russian Academy of Sciences and key universities of the Far Eastern Federal District – members of the Far Eastern Section of the Scientific Council of the Russian Academy of Sciences on Ceramic Materials.

The scientific results include original approaches in chemical synthesis, composition design, structural engineering, and formation of key performance characteristics and properties of ceramic and glass-like materials, presented in the form of: composite bioceramics (ZrO_2 , TiO_2 , Al_2O_3 , CaSiO_3 , $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) and bioglasses of the "45S5 Bioglass" type for osteoplastic surgery; radionuclide ceramics and glass-ceramics for immobilization of high-energy isotopes ^{137}Cs , ^{90}Sr , ^{60}Co (structures of the pollucite, perovskite, anorthite, wollastonite types, etc.); heat-resistant ceramics for extreme operating conditions (SiC , HfB , TiC , HfCxNy); magnetic ceramics containing rare-earth elements (NdFeB) for technical devices; solid-state phosphors in the form of biphasic ceramics $\text{Al}_2\text{O}_3\text{--Ce:YAG}$ and $\text{Al}_2\text{O}_3\text{--Ce:(Y,Gd)}$ AG for energy-efficient compact and high-power (ultra-bright) LED systems; scintillation ceramics of the $\text{Lu}_3\text{Al}_5\text{O}_{12}$ (Ce:LuAG) composition for high-precision X-ray detectors; ceramics of the CaCoSiO_3 composition based on boron-containing mineral raw materials and processing wastes for the construction and energy industries; heterostructured electrodes ($\text{Mo}_2\text{C}/\text{Mo}_3\text{Co}_3\text{C}$) and solid-state electrolytes ($\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$) for fuel cells; polymer-ceramics based on UHMWPE for components with improved tribological characteristics; hard wear-resistant alloys based on metallic and non-metallic carbides, and others. Attention is paid to the development of prototypes and products based on these materials, promising for practical applications.

CERAMIC MATERIALS BASED ON CHALCOGENIDES OF RARE EARTH ELEMENTS

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Simple and complex chalcogenides of rare earth elements (REE) are a synthetic class of materials that exhibit properties ranging from dielectrics to superconductors¹. Methods for the preparation of powders, the following simple and complex chalcogenides of rare earth elements are discussed: Ln_2X_3 , Ln_3X_4 , LnX , $\text{Ln}_2\text{O}_2\text{X}$, LnFX , CaLn_2X_4 , SrLn_2X_4 , SrLnCuX_3 , EuLnCuSe_3 , CuLnX_2 ($\text{Ln} = \text{REE}$, $\text{X} = \text{S}, \text{Se}$). Ln_2X_3 powders were obtained from oxides by the action of CS_2 , H_2S , and H_2Se gases. Temperature intervals for the preparation of $\text{Ln}_2\text{O}_2\text{S}$ by the reaction of $\text{Ln}_2(\text{SO}_4)_3$ with H_2 , H_2S have been determined. Regularities in 15 series of state diagrams of $\text{MX-Ln}_2\text{X}_3$ (M - metal) systems as a technological basis for ceramics production have been considered. The dependence of characteristics of ceramic materials on pressing pressure under standard conditions and annealing temperature has been established.

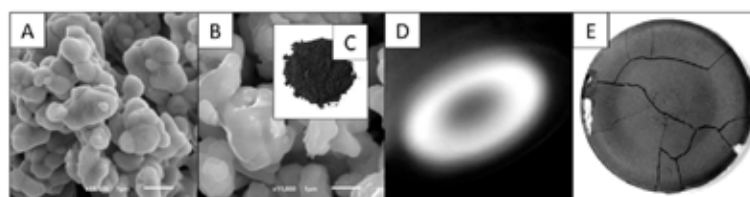


Figure 1. A - scanning electron microscopy (SEM) image of $\gamma\text{-Sm}_2\text{S}_{2.98}$ particles, B – SEM image of SmS particles, C - photograph of SmS powder, D - magnetron discharge over SmS target, E - photograph of SmS target after long-term use.

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EFFECT OF ELEMENTAL COMPOSITION OF OPTICAL AND RADIATION-RESISTANT GLASSES ON THEIR QUANTITATIVE CHARACTERISTICS OF ATTENUATION OF X-RAY AND GAMMA RADIATION

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The linear coefficient of X-ray and gamma radiation attenuation (LCRA) is one of the most important characteristics of optical and radiation-resistant glasses when operating optical elements from them under conditions of high radiation loads. The mass coefficients of radiation attenuation (MCRA) with the energy of quanta, E , from 0.2 to 3.0 MeV were calculated for oxides which are the main components of these glasses. The sum of the products of the oxides mass fractions in the glass compositions by the corresponding MCRA values, multiplied by the density of glasses, gives their LCRA values.

It was shown that MCRA values of SiO_2 , B_2O_3 , Na_2O , K_2O , Al_2O_3 , CaO and ZnO (glasses of K and TK types) slightly decrease when E varies in the specified range, practically coinciding with each other. When complicating glass compositions (STK, F, TF, STF, BF), such oxides as PbO , Ta_2O_5 , Gd_2O_3 , La_2O_3 , BaO , CdO , Nb_2O_5 , ZrO_2 , Y_2O_3 have strong impact (in decreasing order) on their LCRA in the field of E values from 0.2 to about 1.0 MeV whereas at $E > 1.0$ MeV both MCRA of oxides, and LCRA of glasses change approximately equally at increase E .

Based on the effect of the elemental composition of radiation-resistant glasses on their characteristics of ionizing radiation attenuation, a method for selecting glass types and their thicknesses for the design of observation radiation-shielding windows (ORSW) for "hot chambers" is proposed which is characterized by a high attenuation rate of radiation (up to $10^5 - 10^6$) with quantum energy from 0.2 to 3.0 MeV, acceptable transmission capacity of the ORSW at high radiation loads and the minimum possible total thickness of all glass plates in the ORSW design.

According to the totality of these requirements, firstly, a recommendation was made to design two alternative ORSW versions: the first one dedicated for both X-ray and gamma radiation with E from 0.2 to 1.0 MeV, and the other version - only for gamma radiation with E from 1.0 to 3.0 MeV. Secondly, 2 acceptable variants of the ORSW designs were proposed for the entire range of quantum energies from 0.2 to 3.0 MeV: a crown-flint variant based on a pair of TKN1- TF200 glasses and a pure crown type based on TKN1 glass.

GRAIN BOUNDARY DIFFUSION IN OXIDES. THEORY AND APPLICATIONS

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A significant number of works have been devoted to the problem of diffusion in oxide ceramics, but a unified concept that allows describing a wide range of observed experimental phenomena has not yet been formed.

The first part of the work is devoted to a detailed analysis and systematization of experimental data on grain boundary diffusion in pure ceramics and the influence of small additions of impurities on the diffusion properties of grain boundaries. Factors that influence the diffusion properties of grain boundaries are the size of the ions, the effective charge, the limiting solubility at the temperature of the diffusion process, as well as the distribution coefficient, which characterizes the degree of interaction of the impurity with the grain boundaries.

In the second part of the work, a model is presented that is based on the ideas of the theory of nonequilibrium grain boundaries developed for metals, significantly supplemented by ideas reflecting the specifics of ceramics. One of the key parameters of the model is the value of the free volume of grain boundaries, which can increase or decrease depending on the concentration and type of impurity ions arriving at the boundary. A change in the free volume of grain boundaries leads to a change in the activation energy of the grain boundary diffusion process. A significant influence on the activation energy of diffusion is also exerted by such a thermodynamic quantity as the specific energy of the liquid-crystal interface, which is influenced by the temperature and thermodynamic parameters of low-melting eutectics in the ceramic-impurity system.

An important feature of grain boundaries in ceramics (as opposed to grain boundaries in metals) is the dependence of the width (thickness) of the grain boundary on the impurity concentration, the size of the impurity ions and their effective charge. Taking this factor into account makes it possible to describe the complex patterns of the influence of small additions of impurities on the diffusion permeability of grain boundaries in oxide ceramics.

SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS OF STRUCTURAL CERAMICS: FROM SOLID SOLUTIONS TO HETEROPHASE COMPOSITIONS

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A review is provided in the field of synthesis of ultra high-temperature materials (UHTM) [1]-[3]. Using the example of $(\text{Zr}_{1-x}\text{Ta}_x)\text{B}_2$, $(\text{Hf}_{1-x}\text{Ta}_x)\text{B}_2$, $(\text{Zr}_{1-x}\text{Nb}_x)\text{B}_2$, $(\text{Hf}_{1-x}\text{Nb}_x)\text{B}_2$, the mechanisms of combustion and structure formation were considered. A combination of SHS and hot pressing produced UHTM with high hardness, thermal conductivity, oxidative and thermal resistance. The structure and properties of carbides $(\text{Ta,Zr})\text{C}$, $(\text{Ta,Hf})\text{C}$, $(\text{Nb,Zr})\text{C}$, $(\text{Ta,Nb,Zr})\text{C}$ have been studied. The possibility of producing ultrafine-grained (UFG) ceramics based on eutectics HfB_2 - HfC , ZrB_2 - ZrC , $(\text{Hf}_{1-x}\text{Zr}_x)\text{B}_2$ - $(\text{Hf}_{1-x}\text{Zr}_x)\text{C}$, et al. has been demonstrated. Each particle of such SHS powder consists of UFG and nanosized grains, and their formation is facilitated by rapid crystallization in combustion wave and the absence of mutual solubility of carbides and borides. The hierarchical structure combines the advantages of micron powders and nanostructures, which made it possible to produce samples with high crack resistance. To ensure the completeness of chemical transformations and synchronization of phase formation in the combustion wave, the mechanical activation was used, expanding the range of applications of coarse-grained powders.

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OPTICAL GLASSES AND GLASS-CRYSTALLINE MATERIALS FOR PHOTONIC APPLICATIONS: CURRENT STATE AND PROSPECTS FOR DEVELOPMENT

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An overview of the current state of science and production of optical glasses and glass-ceramics is presented, and the prospects for their development are also considered. The work provides an answer to the question of "What glasses and glass-ceramics will be in demand in the 21st century, i.e. what materials will provide new trends in the development of optics and photonics?" Several key directions can be identified, including the development of glasses and glass-ceramics for:

- 1) miniaturization of optical and photonic elements, devices and systems in order to reduce their weight and size characteristics, energy consumption and control actions;
- 2) hybrid and monolithic integration of optical and photonic elements and systems on a single substrate;
- 3) ultra-fast (fs) signal switching and creation of "all-optical" control devices;
- 4) photonic systems with low energy level of control signals (fJ);
- 5) elements and devices of fiber communication lines and photolithography based on ultrapure materials with record low losses and a special dispersion pattern;
- 6) micro-structured and photonic crystal optical fibers, including activated ones, for fiber lasers and sensors;
- 7) large-sized optical elements of high optical quality for laser thermonuclear fusion, photolithography, and astronomy;
- 8) ultra-light optical elements for avionics, space based on hybrid materials such as "glass-polymer";
- 9) ultra-strong optical elements for avionics, deep-sea and spacecraft;
- 10) ultra-thin large-sized panels for displays, solar panels, flexible and roll optics;
- 11) micro-optics elements based on materials with low melting, forming, and molding temperatures and a special dispersion pattern;
- 12) elements and devices operating in the mid- and far-IR spectral range, as well as the THz region.

The work was carried out with the financial support of the Russian Science Foundation, project 24-43-20020.

ADVANCED CAPABILITIES OF ELECTROPHYSICAL SINTERING FOR FUNCTIONAL CERAMICS AND DEVICES

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The pursuit of modern technologies for producing functional ceramics and devices of superior operational quality is a critically important direction for the advancement of science and industry. Scientific and technological research emphasizes contemporary and unconventional methodologies. Among such promising techniques is the class of electrophysical sintering methods, encompassing electric current-activated sintering (ECAS), spark plasma sintering (SPS), flash sintering (FS), and others. These technologies are geared towards the sintering of dispersed materials, as well as solid-state *in-situ* synthesis.

Accordingly, this work presents research findings on the capabilities of spark plasma sintering in obtaining mineral-like ceramic matrices for the immobilization of radionuclides and active zones of radioisotope sources based on them, uranium oxide fuel compositions, bone-ceramic biomaterials, neutron and X-ray absorbing shielding screens, high-temperature and functionally graded composites, chemoceramics, permanent magnets, optoceramics and scintillation detectors, wear-resistant ceramics for industrial tooling, and more. The results are novel and hold fundamental and applied significance.

This research was conducted within the framework of the state assignment from the Ministry of Science and Higher Education of the Russian Federation, topic No. FZNS-2023-0003.

SYNTHESIS OF A NEW MATERIAL BY THE REACTION-DIFFUSION TURING PROCESS AND STUDY OF THE PROPERTIES OF THE DIAMOND-SILICON CARBIDE COMPOSITE

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Diamond particle-based materials are of great interest to industry. The reaction sintering method (impregnation of porous samples with silicon melt) is actively developing, leading to the formation of a structure consisting of diamond particles and SiC.

For the first time, using the example of diamond–silicon carbide composites, under certain conditions (concentration of components, faceting of diamond particles, impregnation temperature, medium pressure, etc.), a material with a regular microstructure forming thrice periodic surfaces of minimum energy was obtained for passing the reaction-diffusion Turing mechanism. Micron SiC grow on the surface of diamond particles when diamond particles are impregnated with silicon melt, forming a Turing «patterns» (Fig. 1a). This leads to filling the space between the diamond particles with dense layers of synthesized SiC and obtaining a monolithic diamond–silicon carbide material («Ideal») (Fig. 1b), having the highest mechanical and dynamic characteristics, compared with standard materials based on corundum, silicon carbide and boron (Table 1).

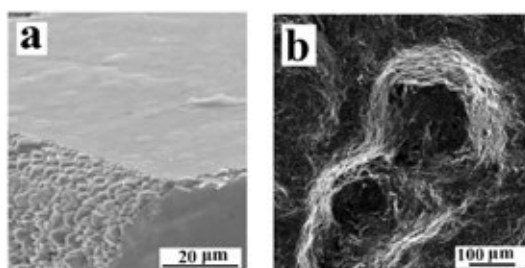


Figure 1. Turing «Patterns» (a), the structure of the diamond-silicon carbide material (b)

Material	ρ , g/sm ³	E , GPa	v_{sound} , km/s	σ_b , MPa	K_{IC} , MPa·m ^{1/2}	HV , GPa
«Ideal»	3,35-3,40	720-780	15,0	420	4,7	63-68
SiC	3,05-3,10	380-410	10,2	380-400	3,5-4,0	20-21
B ₄ C	2,60-2,65	380-420	11,8	350-380	3,2-3,5	28-30

Table 1. Properties of «Ideal», silicon carbide and boron carbide

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ADDITIVE TECHNOLOGIES FOR THE FABRICATION OF CERAMIC PRODUCTS

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Currently, additive technologies are rapidly developing towards the use of plastics, metals and alloys. The use of 3D printing for the manufacture of ceramic products has a number of difficulties and limitations.

The most developed method of 3D printing with ceramics is photopolymer printing with pastes based on ceramic particles and polymer solutions. The method provides high accuracy and high surface quality. A limitation of the method is the impossibility of manufacturing products of significant thickness, because a necessary stage of the technology is burning out the binder from the workpiece. To prevent sedimentation, small particles must be used. Also quite common is the method based on the use of powders and spraying liquid glue (binder jetting). Quite large powders are used, so the resulting products are difficult to consolidate to a state of low porosity. There are examples of using the method of selective laser sintering (SLS) of ceramic powders, but in this case there are problems with insufficient laser energy to melt the ceramics and its cracking during cooling.

The authors proposed using the "core-shell" approach to improve additive technologies. For the SLS process, a "ceramic core – metal shell" powder technology has been developed, which will make it possible to print ceramic products with such powders due to the interaction of the shell material with the core when heated, as well as metal-ceramic, for example, carbide steels. The application of shells also increases the technological properties of powders - fluidity, absorption of laser radiation, corrosion resistance.

The work was supported by the Russian Science Foundation grant No. 21-73-30019.

MECHANICAL PROPERTIES OF CHALCOGENIDE GLASSES AND THE INFLUENCE OF METALLOPHILIC INTERACTIONS ON THEM

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Mechanical properties are one of the most important performance characteristics of glasses in general and chalcogenide glasses (CG) in particular. The most well-studied mechanical property of CG is microhardness (H_v). It is important to know not only H_v at room temperature, but also its temperature dependence - $H_v(T)$. A method is proposed for calculating $H_v(T)$ from absolute zero to glass transition temperature.

Another important characteristic of mechanical properties is ductility. Ductility is discussed in articles devoted to glassy materials, but its numerical values are not given. The report discusses the possibility of using the Milman equation to calculate the ductility of glasses, using experimental values of H_v and ultrasound speed as initial data. This method is convenient for glassy materials, since for many of them the indicated properties have been studied and presented in publications.

CG are formed by covalent bonds, which, due to their characteristics, determine the semiconductor properties and low plasticity of CG. To improve the performance characteristics of CG, it is desirable to increase their ductility while maintaining semiconductor properties. A possible solution to this problem is the formation of non-directed metallophilic bonds in a glass network in addition to directed covalent bonds. Metals that are prone to forming metallophilic bonds and, at the same time, can be included in the chemical composition of CG in significant quantities include silver and copper. Numerous results of studying the structure of CG, available in the literature, indicate that at a high concentration of silver chalcogenides, its atoms are located in each other's first coordination sphere at a distance less than twice the van der Waals radius. This, along with their low effective charge, indicates the formation of metallophilic bonds. The results of a study of changes in the mechanical properties of CG with an increase in the content of silver chalcogenides in their composition are analyzed. It is shown that in this case a multiple increase in their plasticity is observed.

The work was carried out with the financial support of the Russian Science Foundation, project 24-23-00140.

FUNCTIONAL OXIDE MATERIALS FOR ELECTRONICS, INCLUDING PRINTED ONE

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The issue of improving the efficiency of electronic devices, including increasing speed, reducing energy consumption, and minimizing dimensions, remains highly relevant at present. The enhancement of optical and electron-beam lithography through silicon technology can solve these challenges. An economically and technologically justified alternative is the implementation of additive printing of electronic components. Existing technological methods can use powders and suspensions as the raw material for such components. The first step in addressing this complex issue should be the creation of fine, including nanosized, powders of functional materials. Semiconductor materials of the specified size, promising for printing active electronic components (for example, transistors, diodes), as well as power supply elements will have the greatest scientific novelty. The most suitable class of such materials is the InGaZnO system. Furthermore, In-Sn-O, In-Zn-O, ZnO oxides, In_2O_3 , CuO, Cu_2O , SnO systems can also be prospective.

To facilitate the translation of the created fundamental results into the development of prospective semiconductor oxide materials in practical applications in the field of active electronic element printing, it is necessary to achieve the following material characteristics: the average size of the created powders - 150 nm; the bandwidth - up to 2.0 eV; for wet printing the stable state of suspension - not less than 90 days.

In addition to the above-mentioned active elements, the attention of professionals in this field is directed towards creating sensors and memory elements using printing methods. As research and analytical review data shows, solid solutions based on ferrites, including magnetoplumbite ($\text{AFe}_{12}\text{O}_{19}$) and spinel (AFe_2O_4) structures, serve as promising materials for fast (THz) memory elements. Partial or full replacement of cations of one of the sub-lattices with cations with electrical and magnetic properties different from the original matrix allows the characteristics of these materials to be modified and adjusted to the requirements of specific applications. Creating materials with a high entropy of mixing allows radical changes to the properties of such materials while preserving the type of the original crystal structure. The combination of these two trends (doping/substitution and high entropy materials) allows the creation of materials with a wide continuous range of variable characteristics. Thus, the authors of the group have experience in ensuring the variation of the Curie temperature of materials from -50 to 800 °C, which is in demand at present when developing some types of sensors. A combination of the properties of these materials (primarily, electrical and magnetic) allows they're tuning even in the finished product by applying an external magnetic or electric field.

There is a acute need for such adjustable materials in areas of electronics where it is necessary to solve tasks related to the generation, conversion, or absorption of electromagnetic waves. Examples of such applications can be information and telecommunication systems (land and space communication, radar, radio navigation), elements of new electronic component base for terahertz, sub-terahertz, microwave, and shortwave ranges (filters, phase shifters, gates, generators), radio photonics devices, inductive position sensors, and others.

Acknowledgements

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STRUCTURE FORMATION OF POROUS GLASS MATERIALS AND PROSPECTS FOR THEIR APPLICATION

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Porous glass materials are a new and promising type of insulation. Their production is based on the ability of silicate masses to gradually reduce viscosity and form a plastic mass in a certain temperature range. The formation of pores occurs when compounds are introduced into the charge that release gases when heated. Further sharp cooling ensures hardening of the material and fixation of the porous structure. The materials obtained in this way have all the advantages of traditional glass (inertness, non-flammability, etc.), as well as low density and high thermal insulation characteristics, which allows their use in almost all types of construction.

The most famous material from this class is foam glass. For its production, a mixture of glass powder with pore-forming additives is used, the first of which was calcium carbonate, which decomposes when heated, releasing CO_2 . However, obtaining a high-quality fine-porous structure when using it is very difficult. Currently, it is achieved by using specially welded glasses and nanodispersed carbon pore-forming agents. Foaming is ensured by the oxidation of carbon by oxygen and glass components.

At the same time, technological solutions are known that make it possible to obtain a material with a uniform fine-porous structure using more accessible raw materials. One such solution is the use of broken sheet glass and organic blowing agents. Foaming is ensured both by their combustion and by the decomposition of nanodispersed carbon formed during their pyrolysis. The hydrate foaming method, based on the dehydration of hydrosilicates formed by the interaction of alkaline hydroxides with silicate raw materials, has also become widespread. It makes it possible to significantly expand the raw material base for the production of porous silicates, however, obtaining a uniform structure requires additional technological operations.

The work was performed as part of the project under an agreement on the provision of grants from the federal budget in the form of subsidies in accordance with paragraph 4 of Section 78.1 of the Budget Code of the Russian Federation, Agreement # 075-15-2022-1111 from June 29, 2022, topic "Carbon-neutral technologies for recycling large-tonnage fuel energy waste with the production of functional geopolymer materials".

DIFFUSION IN THE TWO-PHASE SOLID MATERIAL ASSUMING PERCOLATION THEORY

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Solid-phase synthesis of ZnS-based luminescent material enclosing the associative luminescence centers formed by the dopant atoms of copper and bromine $\text{Cu}'_{\text{Zn}}-\text{BrS}^\bullet$ is discussed. Annealing the powder mix of ZnS, CuCl and NH_4Br in reducing atmosphere provides the diffusion and volume distribution of Cu^+ and Br^- ions in the matrix.

It was stated experimentally in five series of the synthesized phosphors that $\text{ZnS}:\text{Cu},\text{Br}$ forms the combined sphalerite-wurtzite crystal structure and the intensity of radioluminescence given by the $\text{Cu}'_{\text{Zn}}-\text{BrS}^\bullet$ associates sharply increases at certain content of the wurtzite phase in ZnS structure.

The description of this phenomenon can be provided by the percolation theory instruments. Forming of the long interphase boundary between sphalerite and wurtzite phases in the phosphor grain of ZnS matrix as a percolation infinite cluster analogue, results in the grain-boundary diffusion rate increasing and improving luminescence centres forming ability.

The computer modeling of the diffusion process in discussed system was made and the descriptive model of structure defects migration through the two-phase phosphor structure was developed.

The application of this approach in solid state physical chemistry provides an additional tool for controlling the structure and properties of functional materials.

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THE RELATIONSHIP BETWEEN THE STRUCTURE AND PROPERTIES OF THE GLASSES OF THE SYSTEM $\text{Na}_2\text{O}-\text{BaO}-\text{B}_2\text{O}_3$

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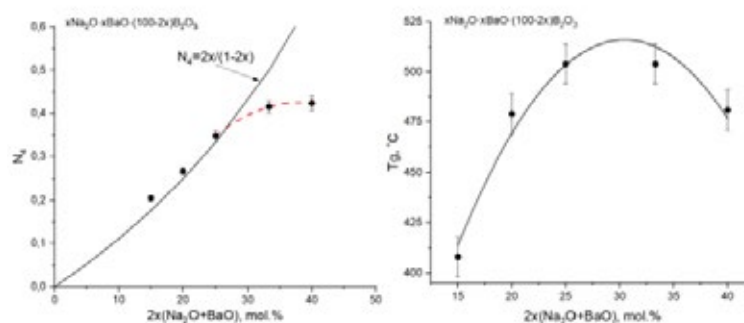
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Borate glasses are of great interest for research due to their wide glass transition interval with rare earth oxides¹ and the reduced processing temperature compared to silicate systems, which is especially important in the field of immobilization of radioactive waste. However, the low chemical and thermal resistance of borate and alkali borate glasses² requires the creation of a foundation for further development of materials based on such glasses with increased stability.

In the present work, the short-range order structure of mixed glasses of the system $\text{Na}_2\text{O}-\text{BaO}-\text{B}_2\text{O}_3$ was studied, the composition of glasses was displayed by the formula $x\text{Na}_2\text{O}x\text{BaO}(100-2x)\text{B}_2\text{O}_3$, where the parameter x changed in the range $7.5 \leq x \leq 20$ mol. %

The short-range order structure was expressed in terms of the fraction of the tetrahedral boron N_4 . It is shown that the glass structure in the concentration range of $15 \leq 2x \leq 25$ mol. % obeys the theoretically calculated dependence $N_4=f(2x)$ and correlates with an increase of the glass transition temperature. Further, this correlation is disrupted due to the dominant role of the formation of groupings with non-bridge oxygen atoms and to the shift of the equilibrium $\text{B}\text{O}_3(\text{B}\text{O}_4^-) \leftrightarrow \text{B}\text{O}_2\text{O}-(\text{B}\text{O}_2^-, \text{BO}_3^-)$ to the right.



Graph. 1. The dependence of tetrahedral boron fraction N_4 (left graph.) and the glass transition temperature (right graph.) on the total concentration of modifier oxides.

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CERAMIC MATERIALS IN $\text{Ca}_3(\text{PO}_4)_2$ - $\text{Ca}_{2.5}\text{Na}(\text{PO}_4)_2$ SYSTEM FOR APPLICATION IN TISSUE ENGINEERING

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The choice of a method for creating bioresorbable materials for bone tissue reconstruction is an important task of modern materials science and engineering. Biphasic ceramics based on high-temperature phases of tricalcium phosphate (TCP) and mixed calcium-sodium phosphate are promising for such application because we can control its dissolution rate in the body environment by varying the content of components in the composition. In order to find the optimal conditions for obtaining ceramics with a preassigned (Ca+Na)/P ratio, it is necessary to refine the quasi-binary section of the phase diagram of this system in the high-temperature region. Thus, the aim of this work was to study the phase equilibria in the system $\text{Ca}_3(\text{PO}_4)_2$ - $\text{Ca}_{2.5}\text{Na}(\text{PO}_4)_2$ to obtaining of biocompatible ceramic materials.

To clarify the quasi-binary section of the phase diagram of the $\text{Ca}_3(\text{PO}_4)_2$ - $\text{Ca}_{2.5}\text{Na}(\text{PO}_4)_2$ system in the high-temperature region from 1000 to 1400°C, mixtures based on β -TCP and the «A» phase of $\text{Ca}_{2.5}\text{Na}(\text{PO}_4)_2$ were fabricated in 10 mol. % (11 compositions), which were subjected to heat treatment at temperatures 1000 – 1400°C with slow cooling and quenching. As a result, the limits of existence of the two-phase region of β -TCP and «A» phase were determined, which lies in the range from 20 to 100 mol. % of «A» at temperatures from 1000 to 1150°C. In this regard, to obtain dense ceramics based on β -TCP and «A» phase (β -TCP content of 30, 50 and 70 mol. %), multistage heat treatment with heating at 1300°C with long holding time followed by cooling to 1100/1030°C was carried out to get into this region of compositions. Increasing the «A» phase content from 30 to 70 mol. % in the composition of such ceramics results in density increases from 83 to 92%. For compositions containing 40 to 60 mol. % of «A», the formation of α -TCP and «A» phase was found in the high-temperature region from 1200°C. It was decided to produce ceramics based on the combination of high-temperature phases in the middle of this region (50 mol. % «A») by quenching at 1300°C. As a result of this heat treatment, it was possible to obtain ceramics with a density of up to 97 %.

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BIORESORBABLE CERAMICS BASED ON MAGNESIUM PHOSPHATES OBTAINED BY AEROSOL PYROLYSIS METHOD

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Magnesium phosphate-based ceramics is a promising material in terms of creating bioresorbable implants because of its high solubility and biocompatibility. The method of aerosol pyrolysis produces finely dispersed and highly active powder precursors, which can be used to create fine crystalline ceramics with high strength. Therefore, the aim of this work is to obtain compositions in the $\text{Mg}_3(\text{PO}_4)_2$ – $\text{Mg}_2\text{P}_2\text{O}_7$ system using the aerosol pyrolysis method for the fabrication of bioresorbable ceramics.

For pyrolysis, 0.1 M solutions containing $\text{Mg}(\text{NO}_3)_2$ and NH_4HPO_4 in different ratios were poured into the container of the inhaler in order to obtain $\text{Mg}_3(\text{PO}_4)_2$, $\text{Mg}_2\text{P}_2\text{O}_7$ and $3\text{Mg}_3(\text{PO}_4)_2/2\text{Mg}_2\text{P}_2\text{O}_7$ (eutectic composition) as end products. Aerosol droplets with a diameter of up to 3 μm were heated to 600°C in the quartz reactor, where nitrates were decomposed and amorphous powder was formed, which was subjected to further heat treatment.

According to SEM, the aerosol pyrolysis method produces spherical-shaped particles with bimodal distribution: the first mode corresponds to particles from 100 to 500 nm, the second mode – from 500 nm to 1.5 μm , which is confirmed by dynamic light scattering. According to the dilatometric analysis of the compositions obtained after pyrolysis, the shrinkage of the materials starts at 800°C and reaches 15% at 1100°C. Based on the obtained data, two heat treatment modes were selected: sintering at 1100°C for 3 hours and at 930°C for 5 days. The use of the first mode leads to cracking of materials based on magnesium orthophosphate and pyrophosphate, which can negatively affect the mechanical characteristics. In the case of eutectic composition, cracking is practically not observed, and a density of 85% can be achieved. The second heat treatment mode avoids cracking and increase in crystallite size, and the density reaches 83%.

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CESIUM-CONTAINING HIGH-SILICA GLASSES

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High-silica glasses containing cesium are a promising material for use in medicine, optics, and as model glasses as containers for disposal of liquid radioactive waste^{1,2}. To synthesize high-silica glasses (QS) containing cesium, porous glasses (PG) were used, which were obtained by acid etching of two-phase glass (composition according to analysis, mol.% 6,8Na₂O · 22,1B₂O₃ · 70,4SiO₂ · 0,19P₂O₅ · 0,52F³). The high adsorption capacity of PG with respect to metal ions from aqueous solutions of their salts made it possible to use the method of impregnating PG with a CsNO₃ solution to vary the content of cesium ions in the QG. After impregnation with PG, they were heat treated at temperatures not higher than 900°C⁴. The paper presents the results of a comprehensive study of the properties of QG: morphology (SEM, TEM, XRF), optical properties (optical density and refractive index) and functional composition of the surface (method of selective adsorption of acid-base indicators⁵).

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INFLUENCE OF SINTERING ADDITIVE ON DENSITY OF SAMPLES BASED ON MAGNESIUM ALUMINATE SPINEL

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Vacuum firing in the presence of sintering additives is an alternative method for obtaining high-density ceramics based on magnesium aluminate spinel¹⁻². This method allows to obtain the required structure without the use of hot pressing. The additives introduced into the material contribute to lowering the sintering temperature, slowing down the growth of grains, which entails the removal of porosity from the material³.

In this work, gallium oxide in the range from 1 to 3 mol. % is considered as a sintering additive. Gallium oxide is able to form a cubic solid solution with the main compound, MgAl_2O_4 , which provides at the sintering stage to achieve a density close to theoretical⁴. Firing of disk-formed samples is carried out at 1780°C in a vacuum furnace.

According to the data obtained from X-ray phase analysis, all the studied samples had a single phase – magnesium aluminate spinel, which may indicate the dissolution of the additive in the sublattice of the basic material. Optimal values of average and relative density are observed in samples containing 2.0 mol% of the additive (Table 1). There is no open porosity in all samples.

Additive concentration, mol. %	1,0	1,5	2,0	2,5	3,0
Average density, g/cm ³	3,52	3,52	3,57	3,50	3,51
Relative density, %	98,3	98,3	99,7	97,8	98,0

Table 1. Material density values

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POLYMER GLASSES IN ENGINEERING AND MEDICINE

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In this work, polyimides, polyamidoimides and polyimidourethanes having high glass transition temperatures with covalently attached azochromophoric groups were synthesized and the second harmonic generation coefficients, d_{33} , were measured for corona-poled films of these polymers. The highest d_{33} values (>50 pm/V) were obtained for polymers with covalently attached 3,4-dicyanoazobenzene groups. For some polyimides, the frequency dependences of the d_{33} values were measured, and it was shown that they are red-shifted with respect to the absorption spectrum. Therefore, there is a frequency region in which the polymer is almost transparent, and the d_{33} value is still high (Fig. 1).

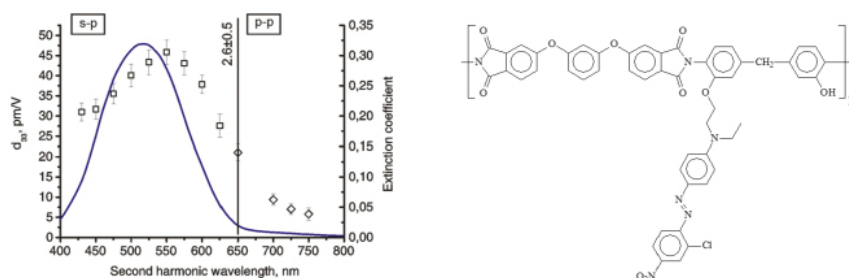


Figure 1. Dispersion of the quadratic nonlinearity coefficient, d_{33} , (left) for polyimide of the presented structure (right) in s-p (squares), and p-p (diamonds) configurations. The absorption spectrum is shown as a solid line. The vertical line corresponds to the wavelength at which the d_{33}/d_{31} ratio was determined.

Cell-graft-PMAA molecular brushes with a cellulose (Cell) backbone and polymethacrylic acid (PMAA) side chains were synthesized by the ATRP method. It has been shown that the luminescence intensity of cyanoporphyrine (PF) derivatives increases when they are incorporated into Cell-graft-PMAA, due to restrictions on their mobility by the glassy polymer matrix. *In vitro* and *in vivo* experiments demonstrated the high photodynamic activity of Cell-graft-PMAA/PF nanoparticles. It was shown that the obtained biocompatible Cell-graft-PMAA brushes provide high selectivity for the delivery of PF to tumor cells.

THE TECHNOLOGY OF SmS CERAMICS PRODUCTION, Sm₂S₃-SmS-Sm₂O₂S SYSTEM

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The phase diagram of the Sm₂S₃-SmS-Sm₂O₂S system is of technological importance and was constructed for the first time¹. The composition of the ternary eutectic was determined by the methods of secant planes and Schoeffe polynomials. The established coordinates of nonvariant points in the Sm₂S₃-SmS-Sm₂O₂S system and the absence of noticeable solid solutions are of technological importance in the production of samarium monosulfide ceramics. For example, the appearance of eutectics in the samples will noticeably lower the sintering temperature of SmS ceramics. This study allows us to predict the phase equilibria in the unstudied systems Ln₂S₃-LnS-Ln₂O₂S (Ln - lanthanide).

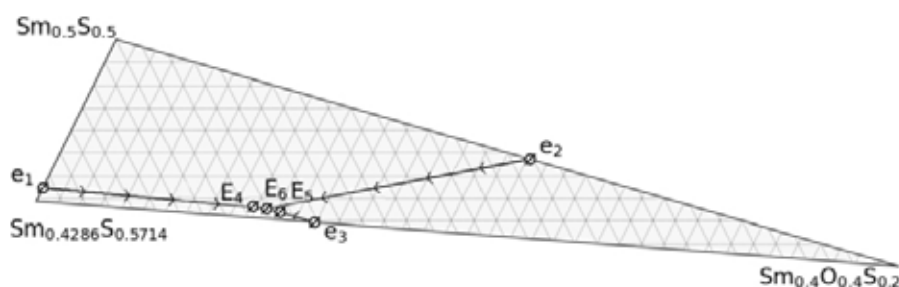


Figure 1. Sm₂S₃-SmS-Sm₂O₂S region from the ternary diagram of the S-Sm-O system.

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Экологические проблемы планеты становятся все более значимыми и тревожащими, поэтому инновации, которые помогали бы эти проблемы решить, не просто привлекают интерес, а приобретают поистине глобальную актуальность. Сохранение окружающей среды и природных ресурсов для будущих поколений – суть новой этики прогресса.

ПРОГРЕСС, БЕЗОПАСНЫЙ ДЛЯ ПРИРОДЫ

Компания «ФосАгро» – лидер российской химической промышленности выступила с инициативой создания фонда для финансовой и научной поддержки перспективных ученых-химиков, в сферу интересов которых попадают охрана окружающей среды, здравоохранение, продовольствие, повышение энергоэффективности и рациональное использование природных ресурсов.

В 2013 году между ЮНЕСКО, Международным союзом теоретической и прикладной химии (IUPAC) и компанией «ФосАгро» было подписано соглашение о партнерстве в создании программы грантов для ученых, занимающихся так называемой «зеленой химией». Предметом этого направления в науке является создание производственных технологий и материалов, безопасных для природы и человека.

Так родился проект «Зеленая химия для жизни», помогающий талантливой молодежи не только материальными средствами для

продолжения исследовательской работы и реализации проектов, но и плодотворным общением со старшими коллегами – видными современными химиками, и организацией информационного обмена в научной среде. Это первый проект в истории ЮНЕСКО и ООН, реализуемый за счет средств российского бизнеса. ФосАгро выделила более \$2,5 млн на развитие и реализацию проекта.

ТРИНАДЦАТЬ МУДРЕЦОВ

Отбор заявок на участие в проекте – обязанность компетентного жюри, в которое входят 13 ученых из 11 стран. Проект-победитель должен соответствовать нескольким критериям. Оцениваются его научная новизна, глобальная и локальная значимость, соответствие принципам «зеленой химии», компетентность молодого ученого и его команды, оснащенность института и лабораторий, в которых предполагается вести проект. Качество работ очень высокое, и членам жюри приходится порой вступать в длительные диспуты по той или иной кандидатуре.

НАУЧНЫЙ ПОИСК БЕЗ ГРАНИЦ

В 2016 году был учрежден специальный грант за исследования в области применения фосфогипса. В 2019 году в штаб-квартире ЮНЕСКО в Париже в рамках открытия Года Периодической таблицы химических элементов было принято решение продлить грантовую программу «Зеленая химия для жизни».

Проблемы экологического характера, к сожалению, есть во всем мире, и во всем мире есть ученые, которые предлагают решения для многих из этих проблем методами и технологиями «зеленой химии». Это наглядно демонстрирует география проекта «Зеленая химия для жизни». За время реализации программы на рассмотрение жюри поступило более 1000 заявок, 55 грантов было присуждено молодым ученым из 33 стран. Самый главный результат грантовой программы – практическое применение разработок молодых исследователей.



ЖИЗНЬ ПОСЛЕ ГРАНТА

Дважды за первые 10 лет существования проекта победителями конкурса становились ученые из России. Одна из них – Галина Калашникова, заведующая лабораторией синтеза и исследования минералоподобных функциональных материалов Центра наноматериаловедения ФИЦ КНЦ РАН. В 2019 году грант «Зеленая химия для жизни» был присужден проекту «Разработка универсального и экологичного метода гранулирования синтетических титаносиликатных материалов (сорбентов, катализаторов, регенерируемых матриц), полученных на основе отходов региональных горно-обогатительных и металлургических производств».

Галина Калашникова:

– В рамках проекта удалось опробовать 5 разных методов грануляции для новых материалов с широким функционалом свойств (сорбенты, катализаторы для органического синтеза, керамические матрицы), которые мы синтезируем именно в нашей лаборатории. Мы смогли выбрать наиболее подходящий метод получения гранул для каждого из них, а также приоритетные нетоксичные связующие. Полученные гранулы были опробованы в качестве сорбентов для очистки жидких радиоактивных отходов от радиоизотопов 137-цезия и 90-стронция совместно с лабораторией хроматографии радиоактивных элементов и станцией переработки радиоактивных отходов Института физической химии и электрохимии им. А. Н. Фрумкина РАН.

Работа по проекту продолжается, несмотря на окончание действия гранта. Все полученные средства были потрачены только на выполнение основной задачи, благодаря чему мы приобрели необходимое оборудование, получили хороший опыт в работе с зарубежными коллегами и выстроили приоритетные направления дальнейшей совместной работы со многими научно-исследовательскими организациями.

Хочется пожелать организаторам конкурса еще больше новых проектов, которые были бы направлены на самые острые вопросы взаимосвязи экологии и современной промышленности.



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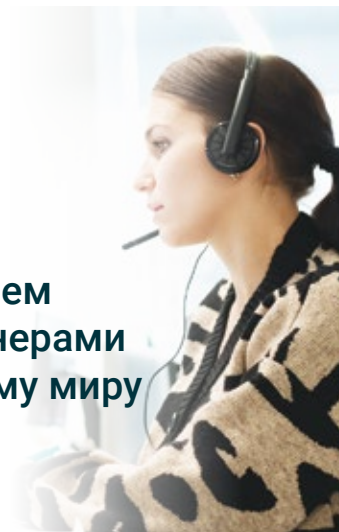
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