APPROVED at a meeting of the Scientific Council NJSC «Al-Farabi KazNU». Minutes No.10 dated May 23, 2022.

The program of the entrance exam for applicants to the PhD for the group of educational programs D108 - «Nanomaterials and nanotechnologies»

## 1. General provisions.

- 1. The program was drawn up in accordance with the Order of the Minister of Education and Science of the Republic of Kazakhstan dated October 31, 2018 No. 600 "On Approval of the Model Rules for Admission to Education in Educational Organizations Implementing Educational Programs of Higher and Postgraduate Education" (hereinafter referred to as the Model Rules).
- 2. The entrance exam for doctoral studies consists of writing an essay, passing a test for readiness for doctoral studies (hereinafter referred to as TRDS), an exam in the profile of a group of educational programs and an interview.

Block	Points
1. Essay	10
2. Test for readiness for doctoral studies	30
3. Exam according to the profile of the group of the educational program	40
4. Interview	20
Total admission score	100/75

3. The duration of the entrance exam is 4 hours, during which the applicant writes an essay, passes a test for readiness for doctoral studies, and answers an electronic examination. The interview is conducted on the basis of the university separately.

#### 2. Procedure for the entrance examination.

- 1. Applicants for doctoral studies in the group of educational programs D108 «Nanomaterials and nanotechnologies» write a problematic / thematic essay. The volume of the essay is at least 250-300 words.
  - 2. The electronic examination card consists of 3 questions.

# Topics for exam preparation according to the profile of the group of the educational program.

Discipline "Fundamentals of nanotechnology"

# Basic concepts and definitions of the science of nanosystems and nanotechnology

The history of the development of nanotechnology and nanomaterials. Basic terms and concepts. Objects and methods of nanotechnology. Fundamentals of the classification of nanomaterials. Examples of nanoobjects and nanosystems, their features, properties and applications. Fullerenes, fullerites, graphenes, nanotubes, nanofibers, aerogels - structure, physical properties, applications. Principles and prospects for the development of nanotechnology. Carbon nanotubes. Single-walled and multi-walled nanotubes. Properties of carbon nanotubes depending on chirality.

# Nanomaterials, nanoparticles and their classification.

Inorganic and organic functional nanomaterials. Hybrid (organic-inorganic and inorganic-organic) materials. Biomineralization and bioceramics. Nanostructured 1D, 2D and 3D materials. Mesoporous materials. Molecular sieves. Nanocomposites and their synergistic properties. Structural nanomaterials. Types of nanoparticles. Quantum dots, quantum wires. Techniques for obtaining and stabilizing nanoparticles.

## Basic principles of the formation of nanosystems.

Physical and chemical methods. Methods for obtaining nano-objects "from top to bottom". Methods for obtaining nano-objects "from bottom to top". Mechanical activation and mechanosynthesis of nanoobjects. Nanoobject synthesis technologies (chemical vapor deposition (CVD), physical vapor deposition (PVD)). Nucleation processes in gaseous and condensed media. Heterogeneous nucleation, epitaxy and heteroepitaxy. Chemical homogenization methods (coprecipitation, sol-gel method, cryochemical technology, aerosol pyrolysis, solvothermal treatment, supercritical drying).

# Formation mechanisms of spherical and tubular nanoparticles.

Dislocation model, vapor-liquid-crystalline (VLC) growth mechanism, carbide mechanism. Models of the formation and growth of nanoparticles. Sears dislocation model. Steam-liquid-crystalline (VLC) -Wagner-Alice mechanism. Carbide mechanism, limiting stages. Quataron model of particle formation. Magnetic mechanism of nanotube formation

## Colloidal chemistry of nanoobjects. Capillarity and wetting.

Surface energy and surface tension. Drops on solid and liquid surfaces. Complete and incomplete wetting. Surface (electrostatic and molecular) and capillary forces. Contact angle hysteresis: the role of chemical heterogeneity and roughness. Superhydrophobic surfaces. Dynamics of wetting and spreading.

# **Application of nanomaterials**

Historical aspect in the field of the use of nanomaterials. The use of carbon black with hydrophobic properties. Structural nanomaterials. Nanosorbents and their application. Application of nanoscale catalysts. Scopes of graphene, carbon nanotubes and fullerenes.

# Discipline "Physical and chemical foundations of obtaining nanomaterials and nanostructures"

#### Basic technologies for obtaining nanomaterials.

Classification of methods for obtaining nanomaterials. Technologies based on chemical processes. Technologies based on physical processes. Powder metallurgy method. Surface technologies. Methods of severe plastic deformation. Complex synthesis methods. Synthesis of nanodispersed materials. Synthesis of nanostructured composites.

## Methods of nanolayer synthesis.

Atomic molecular epitaxy, molecular and chemical assembly, Langmuir-Blodgett molecular layering. Methods for the synthesis of nanostructured materials: vacuum-plasma and chemical synthesis of fullerene-like materials, carbon nanotubes, multilayer nanocomposites. Sol-gel technology. Synthesis of polymers and polymer compositions.

# Methods for the synthesis of carbon nanotubes.

Arc method for producing carbon nanotubes. Laser ablation method. Preparation of CNTs by CVD. Pyrolytic method for the synthesis of CNTs. Synthesis of CNTs in a flame. Electrochemical synthesis of nanotubes. Formation of carbon nanotubes in flames. Effect of an electric field on the mechanisms of synthesis of carbon nanotubes in a flame.

# Methods for the synthesis of fullerenes.

Gas-phase synthesis. Arc discharge synthesis. Thermal catalytic decomposition of hydrocarbons. Pyrolytic method. Synthesis of heterofullerenes. Methods for obtaining endo- and exo-fullerenes. Fullerene synthesis in a flame. Influence of the electric field on the mechanisms of fullerene synthesis. Synthesis of fullerene-containing soot.

# Synthesis of hydrophobic materials and coatings.

Types and classification of hydrophobic materials and coatings. Synthesis of superhydrophobic soot in a flame. The mechanism of soot formation. The influence of the electric field and catalysts on the properties of superhydrophobic soot.

# Methods for obtaining nanopowders, nanofibers.

Mechanochemical synthesis of nanomaterials. Self-propagating high-temperature synthesis (SHS). Gas-phase synthesis. Plasma chemical synthesis. Formation of the carbon phase during the catalytic cracking of hydrocarbons. Techniques for carbonization and carbonization of samples. Non-carbon nanotubes.

# Obtaining nanoparticles.

Physical methods of synthesis. Obtaining using molecular beams. Plasma chemical method. Evaporation-condensation method. Pulsed radiolysis method. Chemical methods: recovery from solutions, sol-gel transition, cryotechnology. Synthesis in porous media, microemulsions and micelles. The structure and properties of clusters. Fractal and close-packed clusters. Types of chemical reactions involving clusters. Theoretical cluster model.

## Fundamentals of the process of obtaining nanoparticles in liquid media.

Features of obtaining nanomaterials in liquid media. Nucleation and growth of nanoparticles. Homogeneous and heterogeneous nucleation. Influence of various system parameters on the nucleation rate and kinetics of nanocrystal growth. Critical nucleus size, dependence on system parameters. Kinetics of nanoparticle growth. Growth rate, influence of supersaturation, ionic equilibrium. Stabilization of nanoparticles.

# Synthesis of nanoparticles by deposition methods.

The main chemical reactions leading to the synthesis of nanoparticles in liquid media and their controlled release from solutions. Obtaining gold nanoparticles. Synthesis of nanoparticles of silver, platinum, palladium and other noble metals. Methods for stabilizing nanoparticles in solutions are electrostatic, adsorption, chemisorption. Kinetic control of nanoparticle growth. The main factors affecting the size of nanoparticles. Application of deposition methods for the synthesis of nanoparticles consisting of an alloy of metals, with a core-shell structure, multilayer structures. Synthesis of nanoparticles of metal oxides and nanocomposites.

## Modification of the surface of solids.

Features of the surface properties of solids of various chemical nature. Influence of the chemical state of a surface on the physical and chemical properties of solids. Methods of surface modification: physical (alloying, ion implantation, application of thin films and coatings) and chemical (change in the functional cover) modification.

#### Mechanisms of formation of spherical and tubular nanoparticles.

Sears dislocation model. Steam-liquid-crystal (VLC) -Wagner-Alice mechanism. Carbide mechanism, limiting stages. Quataron model of particle formation. Magnetic mechanism of nanotube formation.

## Discipline "Experimental methods of research of nanomaterials and nanostructures"

## General characteristics and classification of methods.

Interaction of radiation with matter. Absorption, emission, scattering. Spectroscopic and diffraction methods. Energy characteristics of various spectroscopic methods. Sensitivity and resolution. Method characteristic time.

## Research methods for nanoscale systems

General ideas about the methods of studying the physical, chemical, biological properties of nanosystems. Microscopic research methods. Basic principles, directions and objects of research. Resolution. Elements of optoelectronic devices. Basic principles of operation of electron microscopes High resolution transmission electron microscopy. Probe scanning microscopy (scanning, tunneling, atomic force, near-field optical). The principle of operation of probe microscopes. Scanning electron microscopy. Application of electron microscopy in nanotechnology. Additional capabilities of probe microscopy: atomic manipulation and lithography.

# Vibrational spectroscopy methods. IR spectra and Raman scattering

Possibilities of IR spectroscopy and Raman methods, their application in chemistry. Selection rules and intensity in IR and Raman absorption. Frequencies and forms of normal vibrations of molecules. Taking into account the symmetry of the molecule. Analysis of normal vibrations of a molecule based on experimental data. Comparison of IR and Raman spectra and conclusions about the symmetry of molecules. Technique and techniques of IR spectroscopy and Raman spectroscopy. IR spectroscopy equipment. Raman spectroscopy equipment, advantages of laser excitation sources. CARS method. Comparison of IR and Raman spectroscopy methods, their advantages and disadvantages.

## Electron spectroscopy methods. UV spectroscopy

Emission UV spectroscopy as a method for studying diatomic molecules. Visible absorption spectroscopy. Technique and technique of absorption spectroscopy in the visible and UV regions. Test samples. Sensitivity of the method, its advantages and disadvantages.

# Method of electron paramagnetic resonance EPR

Physical bases of the phenomena of electron paramagnetic (spin) resonance and nuclear magnetic resonance (EPR and NMR). Spins and magnetic moments of nuclei and electrons. g-factor and its value. Anisotropy of the g-factor. Spin-orbital coupling. Removal of the degeneracy of spin states in a constant magnetic field. EPR condition. Population of energy levels, saturation, relaxation processes and signal width. Line shape. Hyperfine splitting of the EPR signal in the interaction of an electron with one or several nuclei. Number of multiplet components, intensity distribution. STS constants. Block diagram of an EPR spectrometer, experimental features, advantages and limitations of the method.

#### **NMR** method

NMR condition. Relaxation processes. Chemical shift and spin-spin splitting in NMR spectra. Kernel shielding constant. Relative chemical shift, its definition and use in chemistry. Spin-spin interaction of nuclei, its nature, number of multiplet components, intensity distribution, sum rule. Analysis of first and non-first order NMR spectraProton magnetic resonance, 13C NMR and other nuclei. Double resonance method. Technique and methodology of the experiment. Block diagram of an NMR spectrometer, types of spectrometers. The nature of the samples. Structural analysis. Study of complexation processes. Study of fast processes. Comparison of the NMR method with other methods, its advantages and limitations. Principles of laser magnetic resonance spectroscopy (LMR).

#### Gas chromatography method

Physical and chemical foundations of chromatographic processes. Classification of chromatographic methods. Chromatographic peak parameters. Gas chromatography options. Block diagram of a chromatograph.

Influence of temperature on the chromatographic process. Using methods of programmed temperature change. Types of detectors. Methods for qualitative and quantitative chromatographic analysis.

## **Method of mass spectrometry**

Mass spectrometry versus other physical research methods. Classification of devices. The principle of operation of the mass spectrometer, the main characteristics. Types of mass analyzers: time of flight; radio frequency; quadrupole; ion-cyclotron resonance, etc. Block diagram of a mass spectrometer with a magnetic mass analyzer. Methods for introducing samples into a mass spectrometer. Combination with a gas chromatograph. Molecular beams. Effusion cells. Direct injection of solid samples.

# X-ray spectroscopy. Physical foundations of the X-ray method of analysis.

X-ray diffractometry. Types and characteristics of tubes and X-ray detectors. Diffractometry (recording and calculation of diffractograms). Identification of matter (phases of matter) by interplanar distances and measurement of cell parameters. X-ray filing cabinets. Optical systems, crystal lattice diffraction. Wolfe-Bragg equation.. Features of modern equipment for studying the phase composition and structure parameters of semicrystalline materials, including thin films, coatings and nanoscale powders.

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- 3. Poole Ch., Owens F. Nanotechnology. Moscow: Technosphere, 2004.
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