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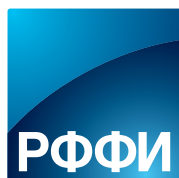
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***Dear readers!***

The year of 2019 is marked by the jubilee data that is extremely important for all the world of science: the 150<sup>th</sup> anniversary of the Periodic Law of Chemical Elements discovered by Dmitry Mendeleev, the great Russian scientist. This year is named the International Year of Periodic Table of Chemical Elements by the UN and celebrated under the auspices of the UNESCO and International Union of Pure and Applied Chemistry (IUPAC). The XXI Mendeleev Congress on General and Applied Chemistry of the Mendeleev Russian Chemical Society (MRCS) to be held in September 2019 in St. Petersburg, Russia, will be one of the key events to celebrate the jubilee.

Therefore, it is not by coincidence that the Editorial Board of “Russian Foundation for Basic Research Journal” (“RFBR Journal”) decided to devote two journal issues to this remarkable event. Chemistry is one of the natural science fields determining the development of many allied disciplines that need new materials, reagents, molecular probes, and other chemicals and procedures for special studies.

I would like to note that “chemical sciences” form a large topical block of scientific studies actively supported by the Russian Foundation for Basic Research. Only within the recent five years, more than 5,800 grant applications were filed, and the best of them were supported by about 2.7 billion rubles. In addition, considerable support was granted to the chemically oriented basic research (“ofi” contest) and interdisciplinary projects (“mk” contest), which received more than 2.3 billion rubles during the same years. Funding of researches in chemistry was also provided for the projects born in the frames of the regional and international programs.

The support of young scientists by the RFBR should be specially mentioned. We managed to frame the systematic and comprehensive approach to involve the young into science and to support their scientific activities. Let me mention just one example. Maxim Nikitin, chemist, the winner of the Russian Federation President Prize in Science and Innovations, was supported by the RFBR in 2014 under the “My first grant” program. In 2015, he received the RFBR grant under the contest of research projects carried out by the leading youth scientific teams. In 2017, Maxim Nikitin was awarded the RFBR grant under the “Eureka! Idea” program and the President Prize. Thus, being initially supported by the RFBR, the talented young chemist became the scientist famous in the whole country.

An increase in the overall budget of the RFBR also provides the development of forms and volumes for the support of fundamental chemical studies. The RFBR experts evaluate the most important, “break-through” fields of research. Among them there is the support of the so-called “green chemistry” studies, i.e., the improvement of processes and reactions in chemistry to make them environmentally friendly and, ideally, exert a positive effect on the Nature at all their stages. These innovative technological schemes are urgent for large-tonnage chemical productions and, hence, of pronounced practical use. It is also important that the use of green chemistry principles decreases production expenses due to the deletion of several very expensive and “dirty” stages of annihilation or processing of harmful by-products.

RFBR pays particular attention to studies in the field of polymer materials. Nowadays polymers compose the most important class of modern materials widely used in all areas of technology, as well as in agriculture and for private use.

Capabilities of the modern chemistry are clearly illustrated in the articles included into these two topical issues of “RFBR Journal”.

*Vladislav Ya. Panchenko  
Chairman of the Board of the Russian Foundation for Basic Research,  
Editor-in-Chief of “RFBR Journal”*



## About the Editor of the Themed Section RAS Corresponding Member, Professor N.E. Nifantiev



- *Head of the Laboratory of Glycoconjugate Chemistry N.D. Zelinsky Institute of Organic Chemistry RAS*
- *Bureau member of the Division of Chemistry and Material Sciences of RAS*
- *Deputy-chair of RAS Scientific Council on Organic Chemistry, member of other four RAS Scientific Councils*
- *Member of editorial boards of journals: Herald of the Russian Academy of Sciences; Russian Chemical Bulletin; Bioorganic chemistry; Journal of Carbohydrate Chemistry (USA)*
- *Vice-President (President-elect) of the Division of Organic and Biomolecular Chemistry of the International Union of Pure and Applied Chemistry (IUPAC), Chair of IUPAC "Organic Synthesis" Sub-committee*
- *RAS contact person in the International Science Council (ISC, former ICSU)*
- *RAS M. Shemyakin Prize (2013), Leninsky Komsomol Prize in Science and Technology (1988)*

Nikolay Eduardovich Nifantiev was born on October 12, 1958, in Krasnoyarsk. In 1980, he received his B.Sc. in organic chemistry from the Department of Chemistry in Lomonosov Moscow State University and was enrolled in a postgraduate program in N.D. Zelinsky Institute of Organic Chemistry of the USSR Academy of Sciences (IOC USSR AS). In 1984, he received his Ph.D. in organic chemistry from N.D. Zelinsky IOC USSR AS, and in 1995 he received his D.Sc. in bioorganic chemistry, and chemistry of natural and physiologically active compounds.

In 1994, N.E. Nifantiev founded the research group for chemistry of glycoconjugates, IOC RAS, which in 2004 grew into the laboratory of glycoconjugate chemistry. Current research focuses on the synthesis, structural and conformational analysis of oligo- and polysaccharides, investigation of mechanisms of glycosylation reactions, rational design of pharmaceutical preparations, the development of conjugated carbohydrate vaccines

and diagnostic test systems for detection of fungal and bacterial infections.

Since 2011, Professor N.E. Nifantiev is a Corresponding Member of the Division of Chemistry and Material Sciences of RAS. He is the Head of the Conjugated Carbohydrate Vaccines Integrative Program of Scientific Research (IPSR), which works within the Strategic Research Program of the Technological Platform "Medicine of the Future".

Professor N.E. Nifantiev has published about 400 scientific papers and reviews in leading Russian and International journals, and he is the co-inventor in more than 30 Russian and foreign patents dedicated to the development of drugs and vaccines.

## Abstract of the Themed Section

*N.E. Nifantiev*

United Nations Organization (UN) proclaimed the 2019 to be the International Year of the Periodic Table of Chemical Elements (IYPT2019). The leading organization on its implementation is the United Nations Educational, Scientific and Cultural Organization (UNESCO). The International Union of Pure and Applied Chemistry (IUPAC) played a serious role in advancing the 150<sup>th</sup> anniversary of the discovery of the Periodic Law of chemical elements by great Russian scientist D.I. Mendeleev as the topic of the International Year of the UN and in organizing events dedicated to the IYPT2019. One of the main events on celebrating the IYPT2019 in Russia will be the XXI Mendeleev Congress on General and Applied Chemistry of the Mendeleev Russian Chemical Society (MRCS), which will be held in St. Petersburg in September 2019.

That is why, the first and second issues in the present year of the “Russian Foundation for Basic Research Journal” (“RFBR Journal”) are devoted to these events that are very important for chemist-researchers.

When preparing these two special issues of the Journal, we aimed at reporting on the IYPT2019, MRCS, and the forthcoming and previous Mendeleev Congresses. All the three topics are considered in the article “Periodic Law, Mendeleev Society and Mendeleev Congresses” written by Academician A.Yu. Tsivadze.

The history of the Russian Chemical Society (RCS) started in November 1868 when the Ministry of Enlightenment of Russia approved the Charter of the RCS, one of the Founding Members of which had been Dmitri Mendeleev. The first report on Mendeleev Periodic Table of Chemical Elements was delivered during a meeting of the RCS in March 1869. Therefore 1869 is considered by the world science as the

year of discovery of the Periodic Law and formulation of the Periodic Table of Chemical Elements. Year 2019 is the 150<sup>th</sup> anniversary since Dmitry Mendeleev discovered the Periodic System, and the United Nations proclaimed this year to be the International Year of the Periodic Table of Chemical Elements.

After a series of transformations, in 1992 the RCS became the Mendeleev Russian Chemical Society. In 2019, the RCS is holding anniversary events; the extraordinary Mendeleev Congress on General and Applied Chemistry is one of them. It will be held in Saint Petersburg in September 2019 and will host approximately 3,000 foreign and Russian participants. English-speaking symposia, conferences and round tables on current issues of strategic development of science and technology are planned in the framework of the Congress.

Professor M. Poliakoff (School of Chemistry, University of Nottingham) told about the global significance of the Periodic Law of chemical elements for mankind in his report “The Periodic Table: Icon and Inspiration”. Since Dmitry Mendeleev published the initial concept of the Periodic Law in 1869, the table has been continuously updated with newly discovered elements, and figuratively speaking, today it serves both as an icon and as an inspiration for modern chemists. Its image is so easily recognizable all around the world that it has become a symbol for science. This paper highlights just a few of the varied forms that the Table can take, such as an infographic, which can convey the shortage of certain elements with great impact.

The article by Academician V.V. Lunin and PhD (Chemistry) E.A. Baum “Russian Contribution to the Periodic System” also concerns the history of the Periodic Table creation and describes the Russian contribution to it: the elements discovered in Russia. For 50 years, scientists around the world have been searching for the relationship between the mass of atoms and the properties of elements, until the Russian scientist D.I. Mendeleev, having created the Periodic Table and formulated the Periodic Law, did complete this search. The discoveries of new chemical elements predicted by D.I. Mendeleev had soon followed and confirmed the fundamental importance of his Periodic Law as the basic law of natural sciences. The works on the synthesis of transuranium and superheavy elements with serial numbers 113–118 have been carried out by the scientists of the Joint Institute for Nuclear Research (JINR, Dubna, Russia) during the past 50 years, and are the



indisputable evidence for the validity of the Law of Periodicity of Chemical Elements and the proof of the Russian science triumph.

The process of IYPT2019 organization and accepting the corresponding decision by the UN supported by the IUPAC and many national chemical unions is considered in the article “International Year of the Periodic Table of Chemical Elements” by RAS Corresponding Member N.P. Tarasova. The role of the UNESCO in performing the IYPT2019 is described in detail in the article written by PhD (Jurisprudence) N.A. Tsivadze (coworker of the Natural Science Sector of the UNESCO) “UNESCO Leading Role in the Celebration of the International Year of the Periodic Table of Chemical Elements (IYPT 2019)”.

The International Year of the Periodic Table of Chemical Elements in 2019 is of basic significance for the entire world. The IYPT2019 draws the world community attention to the development of fundamental sciences, to deepening and expansion of education for sustainable development, to global problems that cannot be solved without active use of achievements of modern green chemistry. The quality of everyday life of present and future generations is directly connected with the progress and achievements of chemical science and technology.

In 2019, the large-scale events dedicated to D.I. Mendeleev and his scientific heritage will take place both in Russia and throughout the world. The International Year of the Periodic Table once again emphasizes the importance of the systematicity in our chaotic world. The System gives an opportunity to understand the idea of regularity and thus arms human beings with the ability to predict.

In accordance with the United Nations General Assembly resolution, the year 2019 was proclaimed the International Year of the Periodic Table of Chemical Elements, and the UNESCO was designated as the leading organization for its implementation. At the present day, the UNESCO is the largest UN specialized agency with broad competence in providing interstate collaboration in the area of science, capable of playing a unique role for promotion of peace and sustainable development. The establishment of UN observances stimulates interest in the activities and programs of the organization in these areas and also contributes to the intensification of activities at the international level. The proclamation of 2019 as the International Year of the Periodic Table is a recognition of the important role of the basic sciences, in particular, achievements in the field of chemistry and physics, in addressing the numerous development challenges that the world is currently facing in implementing the United Nations “2030 Agenda for Sustainable Development”. The International Year under the auspices of UNESCO provides an opportu-

nity to mobilize all interested parties around the topic of science for peace and development – from government officials to media representatives and schoolchildren.

I would like to note that had no chance to read previously any articles about the organization of such significant international events and, therefore, the articles by N.P. Tarasova and N.A. Tsivadze seem to be unique and informative for both wide readership and possible future organizers of other “International Years” in the framework of the UN.

The first themed issue of the “RFBR Journal” is completed by the articles on achievements of the modern chemistry. Academician Yu.Ts. Oganessian writes about the experimental synthesis and study of the properties of new superheavy elements in the article “Synthesis and Study of the New Superheavy Elements of D.I. Mendeleev Periodic Table of Elements”.

In the sixties of the XX century, the possibility of existence of the region of increased stability of superheavy nuclei in the vicinity of  $Z \approx 114$  and  $N \approx 184$  was proved. For the first time a successful synthesis of superheavy elements was carried out at the Flerov Laboratory of Nuclear Reactions of the JINR. Superheavy elements of D.I. Mendeleev Periodic Table of Elements with atomic numbers 114–118 were synthesized in the fusion reactions of the nuclei of the transuranic elements with calcium-48 nuclei.

The article by Yu.Ts. Oganessian deals with the choice of reactions for the synthesis of new elements, methods of studying their nuclear physical and chemical properties. The experimental complex “Factory of superheavy elements” founded at the JINR and prospects of further research development are described.

The article by Professor A.A. Lutovinov “Stars from Cradle to Grave: Powerful Factories of Chemical Elements” is devoted to the synthesis and transformations of chemical elements in the outer space.





The first elements of the Periodic Table – hydrogen, helium and partly lithium – appeared within the first seconds after the birth of the Universe. The first stars “gathered” from these materials are the natural factories of the synthesis of heavier elements not only throughout their lives, but even during their death process, during Supernova explosions. Supernova explosions, in their turn, are powerful factories for the production of heavy elements. Modern instruments allow scientists not only to register such events, but also to determine how many different chemical elements were formed during these events. The recent discovery of the merging neutron stars and subsequent studies of their afterglow allowed us to clarify the process of formation of superheavy elements in the Universe up to the gold and uranium. Thus, astrophysical observations give scientists the most important information about the “production rates” of elements in the nature and their abundance in the Universe.

Academician V.A. Stonik and Professor T.N. Makarieva in the article “Mendeleev’s Periodic Table and Marine Biomolecules” tell about a wide variety of chemical elements in structures of organic compounds extracted from sea sources. This mini-review highlights the involvement of some

elements of Mendeleev Periodic Table into marine biogenic compounds and these elements participation in the metabolism of marine organisms. Accumulation of some metals by marine invertebrates and the metal complexation by highly structurally diverse secondary metabolites are discussed. In addition, examples of the covalent bonds formation in marine bioorganic molecules with a number of non-metals are considered.

Academician Yu.A. Zolotov in the article “Analytical Chemistry of the 21<sup>st</sup> Century: New Face of the Science” characterizes the general state of analytical chemistry and marks changes in trends of its development, a substantial growth, on the one hand, of the volume of complexity of the solved problems and, on the other hand, of its potential. The position that the analytical chemistry occupies among other sciences is briefly considered, and its instrumentation improvement is noted.

Author focuses on the Russian scientists’ advances in this sphere, particularly those whose investigation were supported by the Russian Foundation for Basic Research. Examples of the new analytical methods creation, the original analytical approaches development and the important applied tasks solution in spheres of medicine, environmental protection and the food and medicines quality and safety control are given. The prospects of analytical chemistry development for the next 10–15 years are evaluated in the first approximation.

The authors of all articles of this issue of the “RFBR Journal”, paying their respect to the great discoveries of scientists, past and present, forecast wide prospects of investigation development in the area of pure and applied chemistry in the XXI century.

## Periodic Law, Mendeleev Society and Mendeleev Congresses

*Aslan Yu. Tsivadze*

In November 1868, the Ministry of Enlightenment of Russia approved the Charter of the Russian Chemical Society (RCS), one of the Founding Members of which had been Dmitri Mendeleev. The first report on Mendeleev Periodic Table of Chemical Elements was delivered during a meeting of the RCS in March 1869. Therefore 1869 is considered by the world science as the year of discovery of the Periodic Law and formulation of the Periodic Table of Chemical Elements. Year 2019 is the 150<sup>th</sup> anniversary since Dmitry Mendeleev discovered the Periodic System, and the United Nations proclaimed this year to be the International Year of the Periodic Table of Chemical Elements (IYPT2019).

After a series of transformations, in 1992 the RCS became the Mendeleev Russian Chemical Society. In 2019, the RCS is holding anniversary events. The extraordinary Mendeleev Congress on General and Applied Chemistry is one of them. It will be held in Saint Petersburg in September 2019 and will host approximately 3,000 foreign and Russian participants. English-speaking symposia, conferences and round tables on current issues of strategic development of science and technology are planned as a part of the Congress.

**Keywords:** Dmitri Mendeleev, Periodic Law, International Year of the Periodic Table of Chemical Elements, Mendeleev Congress.

The Periodic Law discovered by Dmitry Mendeleev is one of the most significant achievements not only in chemistry, but for science in total as well. The Periodic Table of Chemical Elements is the most famous and praised among all scientific charts. In terms of appreciation and versatility, the Periodic Table could only be comparable with the multiplication tables and the alphabet. It is different though, in that ever since its discovery it has been expanding and adding on new elements and scientific data. It is a permanent source of inspirations, discoveries and inventions. The grandeur and recognition of Mendeleev as the author of the Periodic Law and Periodic Table of Chemical Elements has been growing over time. However, Mendeleev's Periodic Law and the Periodic Table were not receiving much acknowledgement at first. Therefore, the story of recognition of Mendeleev's discovery has been subject to study, discussion and heated debate. This also was foreseen by Dmitry Mendeleev. Regarding this prospective he once wrote: "For the Periodic Law – the future is not threatening with dismounting, but holds promises to build and develop upon it" [1].

On February 8, 1869, Dmitry Mendeleev turned 35 years old. By that time and on the day of his 35<sup>th</sup> birthday, he had not yet made public his formulation of the Periodic Law, but apparently the work

had been prepared for submission. Today it is common knowledge that the year of discovery of the Periodic Law is 1869. To confirm this, the UN General Assembly's Decision of December 20, 2017, declares the year 2019 as the International Year of the Periodic Table of Chemical Elements in commemoration of the 150<sup>th</sup> anniversary of its discovery by Mendeleev. While this fact raises no doubts, there are disputes and contradictory reasoning about the very date of discovery, i.e. when exactly the Periodic Law was proposed for the first time and the Periodic Table of Chemical Elements was presented. This problem is addressed in the recent article of Igor Dmitriev "The Discovery of Periodic Law in the Interpretation of Soviet Historians of Science (1950–1980)" published in the book "History of Biology and Chemistry in the Twentieth Century: Contribution of Russian Historians of Science to the Study of Chemical and Biological Disciplines" (Moscow, 2018,



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The image shows a handwritten manuscript page from 1869, titled "Опыт системы элементов, основанной на их атомных весах и сходстве химических свойств" (An Experience on the System of Elements Based on Their Atomic Weights and Chemical Similarity). The page contains a table of elements with their atomic weights and names in Russian. The table is organized into columns and rows, with some elements highlighted in red. There are handwritten notes and signatures around the table.

**Fig. 1.** The Table from the manuscript “An Experience on the System of Elements Based on Their Atomic Weights and Chemical Similarity” accepted for publication in February 17 (March 1), 1869.

pp. 105–120) [2]. Dmitriev reasonably believes that “the first to be named among the most detailed historical and scientific research in this area are the works of Boniface Mikhailovich Kedrov (1903–1985) and above all his monograph «The Day of One Great Discovery»” [3]. According to Kedrov, Dmitry Mendeleev discovered the Periodic Law on February 17, 1869. In his opinion, by that time Mendeleev had finished the first three chapters of his book “Principles of Chemistry” [4] and was thinking intensely at the continuation of the work, resulting from which he made a draft central part of the Table, and with that “the discovery of the Periodic Law entered its decisive phase” [3]. According to Kedrov, that version of the Table was sent by Mendeleev to the printing house in the evening of February 17. Besides, that version was printed in Russian and French – 150 and 50 copies, respectively. According to D.N. Trifonov [5], the date of February 17, 1869, should be considered the “day of completing

one great discovery” rather than beginning it. Comparing the versions of Kedrov and Trifonov, I.S. Dmitriev identifies three stages of making the great discovery:

- 1) The Initial phase – from the midday of February 15 until the morning of February 17;
- 2) The Defining phase – from the second half of February 16 until the morning of February 17;
- 3) The Final phase – the evening of February 17.

Despite the fact that these versions have emerged from a deep event-against-time analysis, Dmitriev rightly believes that the resulting process of discovery was pressed into one day. This makes an impression that the decisive event was the revelation during a day-dream, and the discovery was more a result of successful placement of cards with inscribed atomic weights of chemical elements rather than of hard work and meditating over the physics and the chemistry of nature. In fact, Mendeleev had been approaching this result during a long period. His famous textbook “Principles of Chemistry” was conceived and built on the basis of his thoughts about the Periodic Table [6].

Whichever story is correct, it is evident that on February 17, 1869, according to the old style (March 1, according to the new style), Dmitry Mendeleev submitted to N.A. Menshutkin the article entitled “An Experience on the System of Elements Based on Their Atomic Weights and Chemical Similarity” which was printed as a separate paper. The article was meant for publication in the Journal of the Russian Chemical Society (RCS) and for making a report at the upcoming meeting on the discovery of the Periodic Law (Fig. 1). In addition, after reviewing the proof, Mendeleev sent the article to many domestic and foreign chemists. The report on Mendeleev’s Periodic Law was heard at the meeting of the RCS on March 6, 1869. The Periodic Law was formulated by Mendeleev as follows: “The physical and chemical properties of elements, which manifest themselves in the properties of simple and complex bodies they form, are periodically dependent on their atomic weight”. As for the Table, in February 1869, Mendeleev provided the so-called “short form” and only on December 3, 1870, at an RCS meeting presented the “Natural System of Elements” which most closely resembled today’s Periodic Table of Chemical Elements.

Although the systematization of the properties of chemical elements involved many prominent chemists of the time, the Periodic Law proposed by Dmitry Mendeleev was interpreted by his contemporaries ambiguously, and most of the reviewers expressed mistrust and sharp objections. Still, some of Mendeleev’s predecessors did find certain consistent patterns reflecting upon the similarity of properties of chemical elements arranged in series and their respective rows. Among these patterns the Law of Octaves by J. Newlands (1865),

the Law of the Triads by I. Döbereiner (1829) and the Rule of A. Chancourtois (1862) [6] should be highlighted. However, those laws were of a local character and wouldn't lead to a generalizing law. Closest to the discovery of Dmitry Mendeleev was the approach of the famous German scientist Lothar Meyer [7], who presented in 1870 a sort of periodic table, but his rationale was different from that of Mendeleev. In particular, he wrote: "It would be premature to change the widely accepted atomic weights on the basis of such a fragile starting point" and further: "The idea that those chemical elements that have not yet been decomposed are truly indecomposable at the present time seems highly unconvincing, to say the least". Later, some of the predecessors would claim the priority of the discovery. At the same time, L. Meyer himself acknowledged Mendeleev's priority in an expressly clear manner: "In 1869, before I made public my thoughts about the periodicity of the properties of elements, there appeared a summary of Mendeleev's article, which stated: 1) There is a step change in the properties of elements, put in the order that follows the increase of atomic weights; 2) The value of atomic weights determines the properties of the elements; 3) Atomic weights of some elements require correction; 4) There must be some elements that have not yet been discovered... All of this was published by Mendeleev before me and for the first time in general. I openly admit that I did not have enough courage for such far-sighted assumptions, which Mendeleev stated with confidence". Indeed, the great scientific courage, persistence and confidence of Mendeleev were needed in order to arrange the chemical elements in accordance with the Periodic Law and to build such a table. These traits distinguished the great Russian scientist from all his predecessors. Moreover, Dmitry Mendeleev was so sure that the properties of elements change periodically according to the law proposed by him, that he did not look for contrived explanations whenever contradictions were detected. He insistently and with a stout heart predicted the properties of elements not yet known, leaving empty cells in the Periodic Table and predicting the discoveries of the corresponding elements. To the surprise of many, his predictions came true quite quickly in the historical aspect. The historical facts of subsequent findings of the predicted elements clearly and distinctly speak for the greatness of the genius of Dmitry Mendeleev.

The fact draws attention that Mendeleev's Periodic Law provided its author with an immediate tool for the step-by-step correction of the atomic weights of 11 out of the 63 then-known elements. Just a little later, in 1875, the French chemist Paul Emile Lecoq de Boisbaudran discovered Gallium, which turned out to be the predicted by Mendeleev "Eka-Aluminium".

This impressed even the most die-hard skeptics. Moreover, in 1879, Lars Fredrik Nilson discovered a new element named Scandium, which turned out to be the "Eka-Boron" predicted by the author of the Periodic Law. In 1885, K. Winkler discovered another new element, Germanium, which turned out to be the predicted "Eka-Silicon". Thanks to all that, Dmitry Mendeleev appeared as some sort of magician who without having in his hands even a single grain of those previously unknown elements gave surprisingly precise descriptions of their basic properties. When he found some differences in the properties of the predicted "Eka-Aluminium" against the properties of Gallium described by P. Lecoq de Boisbaudran, Mendeleev strongly stood on his grounds. Lecoq de Boisbaudran rechecked his experimental data and acknowledged the rightness of the Periodic Law author. These historical facts were the triumph of Dmitry Mendeleev. With the discovery of noble gases in the 1890s, new evidence in support of the law of periodicity was obtained. Mendeleev predicted the existence of these gases as early as in 1869. Leaving the "empty" cells between Thorium and Uranium, Mendeleev contributed to the discovery of Polonium and Radium by Maria Skłodowska-Curie and Pierre Curie.

Later on the discoveries in physics followed that gave quantum-mechanical substantiation for the Periodic Law. Meanwhile, the process of discovering new artificial elements continued. Element No 101 was named "Mendelevium" in honor of the great Russian scientist. In recent times, three new elements have been discovered – the 116<sup>th</sup>, 117<sup>th</sup> and 118<sup>th</sup>. Element No 118 was found by the famous Russian physicist, Yuri Oganessian and was named "Oganesson" in his honor. On December 20, 2017, the General Assembly of the United Nations declared the year 2019 as the International Year of the Periodic Table of Chemical Elements to celebrate the 150<sup>th</sup> anniversary of discovery of Men-

deleev's Periodic Law. This decision was a response to the initiative from the Russian Chemical Society named after Mendeleev. The initiative was supported by the Russian Academy of Sciences, the Ministry of Science and Higher Education of the Russian Federation, the Ministry of Foreign Affairs of the Russian Federation, UNESCO, IUPAC and other international and scientific organizations and chemical societies in more than 80 countries of the world. On January 29, 2019, the opening ceremony of the International Year took place at UNESCO headquarters in Paris. This ceremony confirmed the absolute recognition of the discovery made by the brilliant Russian scientist as one of the greatest discovery in the history of mankind. At the same time, the opening ceremony in Paris demonstrated the special significance of the contribution to scientific and technical progress on the part of Russian researchers.

Dmitry Mendeleev began his way in science in St. Petersburg at a time when a whole constellation of future prominent Russian chemists appeared. Among them were Nikolay Menshutkin, Alexander Voskresensky, Alexander Borodin, Nikolay Zinin, Nikolay Beketov, Alexander Butlerov

and others. In September 1860, the first International Congress of Chemists was held in Karlsruhe. Young Mendeleev, at the age of 26, took part in that important congress. Along with him A. Borodin, N. Zinin and other Russian scientists attended the event. That was the time of emerging national chemical societies all over the world. In 1863, Mendeleev wrote: "Our chemical meetings are held once every two weeks, they attract more and more people and we think to come out into the light, forming a society..." It is noteworthy that the meetings were held in the personal apartments of scientists and most often in Mendeleev's quarters. On January 4, 1868, the first Congress of Russian Naturalists and Doctors was held. During this event, a statement by chemists was announced: "The chemical section declares a unanimous desire to unite in the Chemical Society to communicate between the already established entities of Russian chemists". At the same time, the formation of national chemical societies took place in various European countries. The London Chemical Society was established in 1841, and the French Chemical Society – in 1857. A bit later – in 1867 – the German Chemical Society was formed, followed by the Czech Chemical Society (1870). The American Chemical Society was established in 1876. In consideration of those events, the issue of launching a national chemical society in Russia in the 60s of the nineteenth century became very topical. Mendeleev was one of the most active initiators of organizing the Russian Chemical Society. A draft charter of the RCS was prepared. A handwritten version of the draft charter, personally written by D.I. Mendeleev (Fig. 2) has survived to these days. The charter was officially approved by the Ministry of Education of Rus-

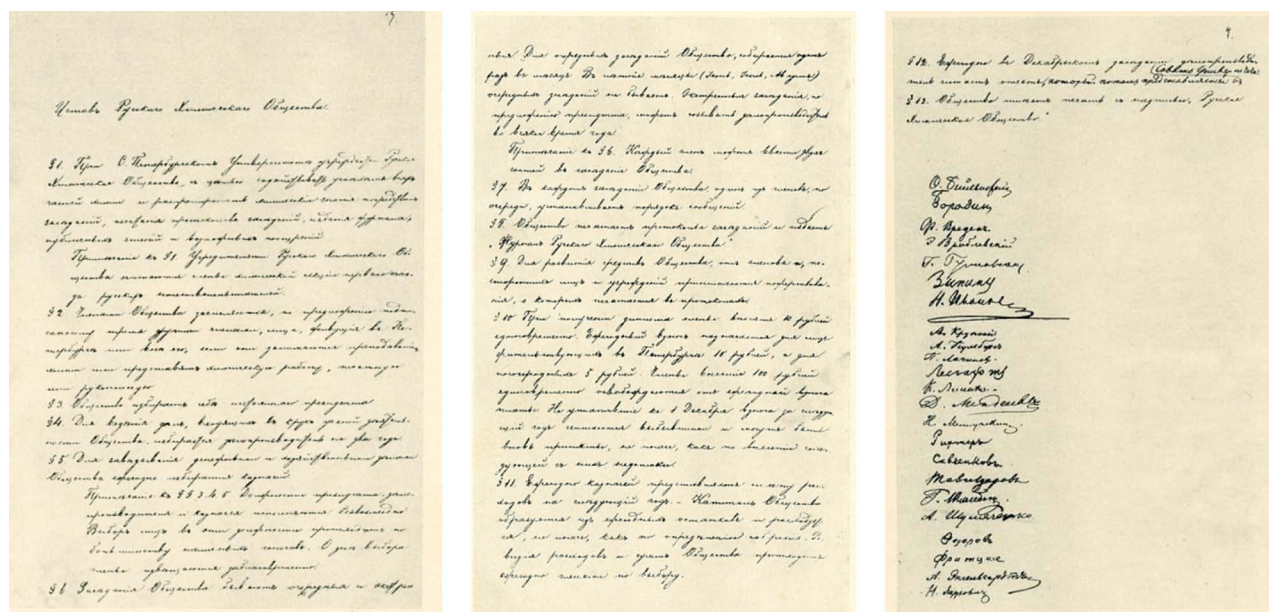


Fig. 2. The draft Statute of Russian Physical Chemical Society hand-written by Dmitri Mendeleev and approved by the Ministry of Public Education with minor changes in October 28, 1868.

sia on October 28, 1868, with introduction of very little changes. In 1876, at the suggestion of Mendeleev, the Russian Chemical Society was transformed into the Russian Physical-Chemical Society through merging with the Russian Physical Society. Through the period of 1868 to 1897, Dmitry Mendeleev had made 90 reports at the meetings of the Russian Chemical Society and the Department of Chemistry of the Russian Physical-Chemical Society (RPCS). He had delivered 35 keynote speeches at the meetings of the Physical Society and the Department of Physics of the RPCS through 1872 to 1887. More than 150 original memos from Dmitry Mendeleev were printed in the Society's journal.

Mendeleev read his memo "Correlation of Properties and Atomic Weight of Elements" at a meeting of the Russian Chemical Society on March 6, 1869. That is why 1869 is considered the year of creating the Periodic Table of Chemical Elements and the year of the Periodic Law. In 1931, based on the Russian Physical-Chemical Society, the All-Union Chemical Society was founded and named after D.I. Mendeleev [8]. In 1992, the All-Union Chemical Society was transformed into the Russian Chemical Society named after D.I. Mendeleev. Hence, today's Russian Chemical Society is the successor of the first Russian Chemical Society and therefore in 2018 we celebrated the 150<sup>th</sup> anniversary of this organization.

On January 22, 2018, the Presidium of the Russian Chemical Society and the Bureau of the Department of Chemistry and Material Sciences of the Russian Academy of Sciences (DCMS RAS) held a joint extended meeting. Invited guests were Minister of Science and Higher Education of Russia Michael Kotyukov and his first deputy Grigory Trubnikov. Presentations were made by President of the Russian Chemical Society Aslan Tsivadze, IUPAC the Past-President Natalia Tarasova and Vice-President of the RCS Yulia Gorbunova. The meeting discussed the decision of the UN General Assembly to proclaim 2019 as the International Year of the Periodic Table in regard of the 150<sup>th</sup> anniversary of the Periodic Table of Elements. The participants took a decision for 2018 to plan events in commemoration of the 150<sup>th</sup> anniversary of the RCW, and in 2019 to hold anniversary events dedicated to 150 Years of the Periodic Table of Chemical Elements. The plan includes a large number of activities, and it is successfully implemented. One of the main events of the international jubilee year will be the Extraordinary XXI Mendeleev Congress on General and Applied Chemistry, which is scheduled for the period from September 9 to September 13, 2019, in St. Petersburg. About 3,000 participants will take part in the Congress, including more than 300 foreign participants. A significant increase in the number of foreign participants is a special feature of the upcoming Mendeleev Congress. Along with the tra-

ditional plenary and breakout sessions within the framework of the Congress, it is planned to hold 10 English-speaking international conferences, symposia and 12 round tables on topical issues of the strategic development of science and technology.

Mendeleev Congresses have always been noted for their interdisciplinary nature and a wide integral coverage of topical issues both in basic and applied science, as well as by the very representative range of participants. Today, the large-scale forums like this are especially in demand due to the new challenges facing the humankind. Mendeleev Congresses are held at intervals of 4–5 years in the main scientific and cultural centers of our country and determine the main directions of development in chemical science and industry. The scientific program of the upcoming XXI Congress provides for five plenary sessions, where the leading world scientists, including Nobel laureates, will deliver 20 plenary reports. The Congress will also include 10 sections on priority areas for the development of basic chemical science and technology; materials science; rational use of natural resources; countermeasures to anthropogenic disasters; processing industrial and agricultural wastes; ecology; education; etc. Many topical problems will be discussed at the meetings of 10 international English-speaking symposia on specific priorities of the field. The round tables will discuss important issues of interaction between science and business. There are plans for discussions on the history of chemistry and the problems of scientific diplomacy. There is no doubt that the successful holding of the XXI Mendeleev Congress on General and Applied Chemistry will contribute to scientific and technological progress throughout the world.

I would like to say special thanks to the Russian Foundation for Basic Research for the financial support in organizing and carrying out Mendeleev Congresses in Moscow (2007), Volgograd (2011) and Yekaterinburg (2016).

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# The Periodic Table: Icon and Inspiration

Martyn Poliakoff

Since Dmitry Mendeleev published the initial concept of the Periodic Law in 1869, the Table has been continuously updated with newly discovered elements, and figuratively speaking, today it serves both as an icon and as an inspiration for modern chemists. Its image is so easily recognizable all around the world that it has become a symbol for science. This paper highlights just a few of the varied forms that the Table can take, such as an infographic, which can convey the shortage of certain elements with great impact.

**Keywords:** Periodic Law, Mendeleev Table, chemical element.

I am deeply grateful to Academician V.Ya. Panchenko and RAS Corresponding Member N.E. Nifantiev for an invitation to write a paper for this special issue of “RFBR Journal” dedicated to the International Year of the Periodic Table of Chemical Elements, which is held in 2019 under the aegis of UN, and, as well, to the upcoming XXI Mendeleev Congress on General and Applied Chemistry (Saint Petersburg, September 9–13, 2019). Not in all countries, however, the Periodic Law is called after D.I. Mendeleev, although the Table is used all over the world.

My first Periodic Table [1] is shown in *Fig. 1*. It is quite amusing that my first inorganic chemistry textbook [2] did not include a periodic table at all. Like many of my contemporaries, I bought one which I proudly hung on my bedroom wall and still have in my office more than 50 years later.

After many years as an inorganic chemist, I still teach the subject but my research focus has moved to green chemistry, devising cleaner and more sustainable ways of manufacturing chemicals and materials [3, 4]. Much of the current work in green chemistry is aimed at finding non-petroleum feedstocks for organic chemicals [5], but we often overlook the fact that humanity is facing a potential shortage of many of the elements themselves. Unlike petroleum, the elements cannot run out, because, apart from helium which can escape into space and uranium which is fissile, the elements are essentially indestructible. Therefore, it is a question of human activity taking elements from relatively concentrated deposits and distributing them so thinly over the planet that they are no longer easily recoverable.

This shortage was once highlighted by Mike Pitts who produced one of the first periodic tables of “endan-

gered elements”. An updated version of this Table (*Fig. 2*) was recently prepared by David J. Cole-Hamilton and co-workers in the European Chemical Society in conjunction with the International Year of the Periodic Table of Chemical Elements [6]. It is quite a sobering table. Most chemists would not expect zinc to be more endangered than platinum in terms of supply. The whole problem is perhaps nicely embodied in recent discussions which concluded that there are probably more people in the world using mobile phones than are using toothbrushes [7]. The key point is that a toothbrush probably contains only five or six of the most abundant elements (H, C, O, N, Cl and possibly Si), whereas a modern mobile phone contains more than 40 elements, possibly even 50, many of them among the most endangered [8]. So, as highlighted in a recent Royal Society report [9], our planet is faced with a rising population and increasing consumption by that population. At the same time, we have a limited supply of elements to feed that consumption.

I have a second role, as Foreign Secretary and one of the Vice Presidents of the Royal Society. The Foreign Secretary’s post has existed since 1723, some 60 years longer than the Foreign



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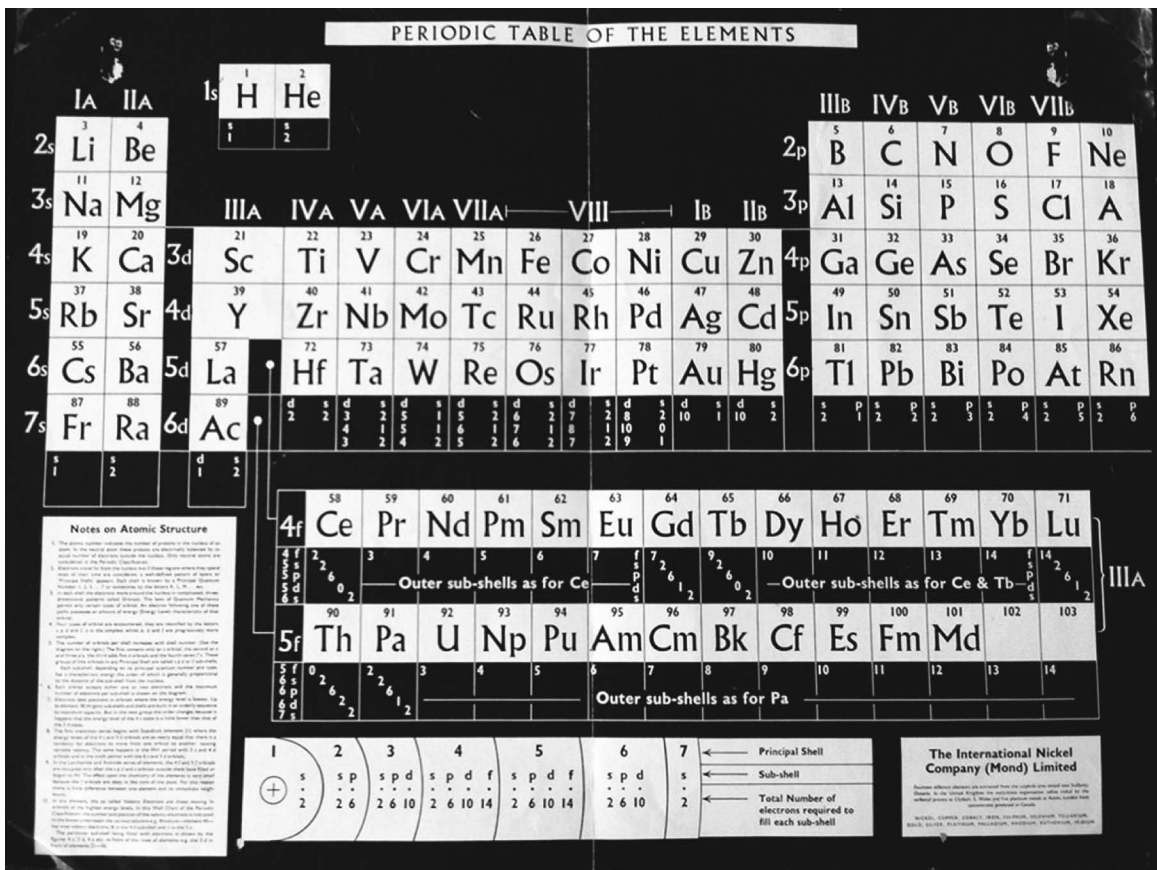


Fig. 1. My first Periodic Table. (Photo: Brady Haran).

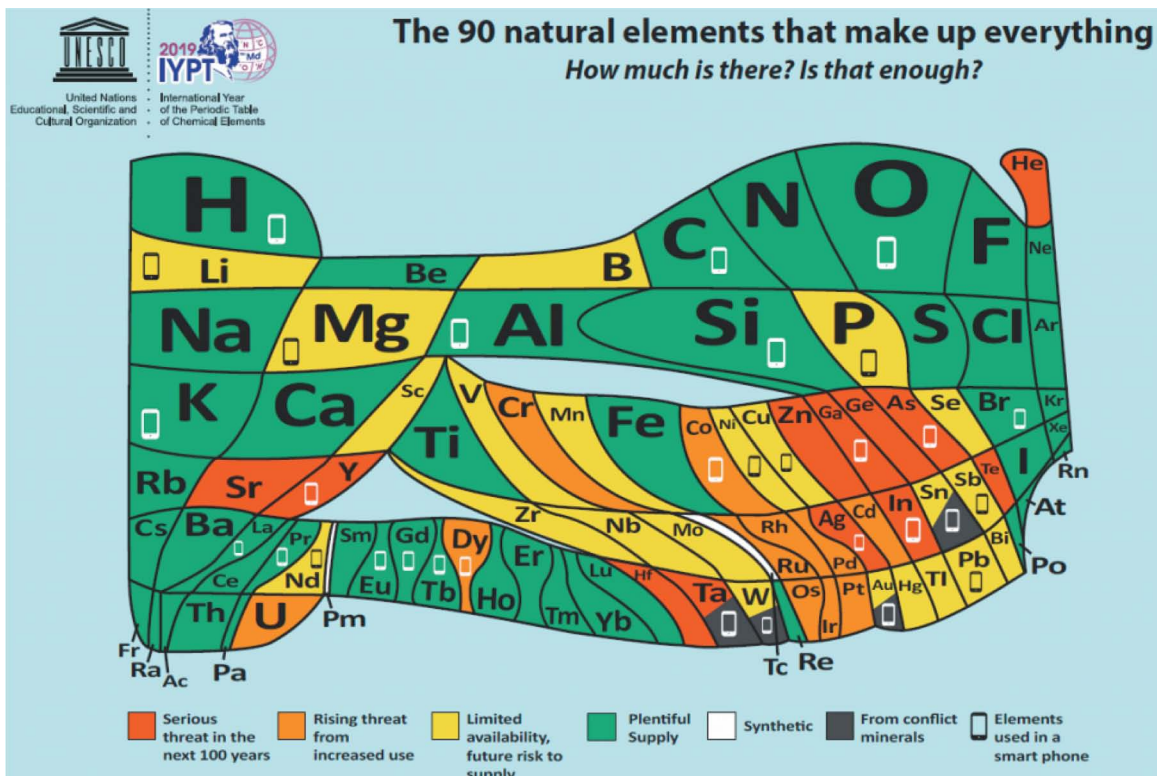


Fig. 2. The Periodic Table of “endangered elements”. Developed by David J. Cole-Hamilton and co-workers in the European Chemical Society (EuChemS) [6].



Fig. 3. The very necktie with symbols of the Periodic Table.

Secretary of the British Government. My predecessors include the polymath Thomas Young (inventor of Young's modulus and Young's slits and translator of Egyptian hieroglyphics) and the chemist Edward Frankland, propounder of the concept of valence and a founder of organometallic chemistry. The post is guided by an archaic mission statement to enjoy mutual intelligence and affairs with all manner of strangers and foreigners, in essence to be an ambassador for British science. Somewhat light-heartedly, I have adopted the Periodic Table as my badge of office and wear the Periodic Table tie whenever I am acting in my official role (Fig. 3).

It was, however, almost exactly 11 years ago that the Periodic Table began to change my life and those of several of my colleagues at the University of Nottingham. On 8 June 2008, we started collaborating with film-maker Brady Haran to make the "Periodic Table of Videos" (PTOV), a collection of YouTube videos, one for each of the 118 elements in the standard Periodic Table (Fig. 4) [10]. The project was scheduled to last a mere six weeks but, even before the filming was finished, there had been such an enthusiastic response from the public [11] that it became clear that we would

have to continue [12]. From the presenters' point of view, participating in PTOV has had several quite unexpected effects.

First, it has allowed us to learn about parts of chemistry to which we had never been exposed to before, for example seeing the extraordinarily beautiful purple colour of Pu(III) in solution [13] or how the platinum group metals are refined [14], and giving us access to priceless historical artefacts such as Joseph Priestley's spectacles [15] or Karl Claus's original samples of the element ruthenium at the University of Kazan<sup>1</sup> (one of the few elements originally discovered through the smell of one of its compounds) [16].

Second, we have been amazed to find how many people of all ages and walks of life are genuinely fascinated by the Periodic Table. Even the more abstruse points arouse real interest, for

<sup>1</sup> Kazan, the capital of the Republic of Tatarstan, was one of the birthplaces of chemistry in Russia, particularly organic chemistry with the schools of Zinin, Butlerov and Arbuzov. Kazan was also the place that aniline was synthesized for the first time by Zinin by reduction of nitrobenzene and his original sample, somewhat discoloured by age, is still displayed in the museum in the original chemistry building at the university.

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Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo
		*	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
		**	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

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**Fig. 4.** Screenshot of the Periodic Table of Videos (PTOV) website [10]. Now, on its eleventh birthday, PTOV involves 11 members of staff at the University of Nottingham and has 651 videos covering compounds as well as elements. The program has got >1.2 million YouTube subscribers and >198 million views.

example, a minor adjustment of the values of the atomic weights of some elements [17]. Viewers from across the world send us messages, ask us questions and even accost us in public places. Such enthusiasm is cheering when one often hears talk of younger generations thinking chemistry to be boring. Sometimes, it is very young viewers who are particularly enthusiastic. My family are visiting the UK this

summer, and my seven year old daughter asked if we could go to Nottingham because she is obsessed with the “Periodic Table of Videos”. Visiting the chemistry department and meeting some of the people in the videos would be more exciting for her than meeting the Disney princesses would be for the rest of her female classmates [18].

Third, it has been surprising to find how dynamic and changing the Periodic Table has been over the past 6 years. Seven “new” elements named copernicium (112), nihonium (113), flerovium (114), moscovium

**Periodic Table 1-172**

Period	18 Orbitals																					
1	1 H	2														13	14	15	16	17	18 He	1s
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne	2s2p			
3	11 Na	12 Mg	3	4	5	6	7	8	9	10	11	12	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar	3s3p			
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr	4s4d4p			
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe	5s4d5p			
6	55 Cs	56 Ba	57-71	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn	6s5d6p			
7	87 Fr	88 Ra	89-103	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113	114	115	116	117	118	7s6d7p			
8	119	120	121-	156	157	158	159	160	161	162	163	164	139	140	169	170	171	172	8s7d8p			
9	165	166											167	168				9s9p				

6	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	4f
7	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	5f
8	141	142	143	144	145	146	147	148	149	150	151	152	153	154	155	6f

8	121	122	123	124	125	126	127	128	129	130	131	132	133	134	135	136	137	138	5g
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Fig. 5. The extended Periodic Table up to element 172 as predicted by Pyykko [22]. It is interesting how the building-up principle for atomic orbitals appears for these elements with, for example, the 5g elements lying between groups 2 and 13 and the 6f elements between groups 14 and 3. (Image courtesy of P. Pyykko).

um (115), livermorium (116), tennessine (117) and oganesson (118) have been synthesized for the first time. The PTOV team attended the official naming ceremony for four of these elements [19]. In addition, PTOV has been privileged to visit the GSI in Darmstadt, and JINR in Dubna, the birthplaces of many superheavy elements [20, 21]<sup>2</sup>, to learn about their synthesis and chemistry.

Those who synthesize these superheavy elements are surprisingly upbeat about the possibility of obser-

ving elements with  $Z > 118$ , for example element 120 [22]. Therefore, it is of more than theoretical interest to consider what the structure of the Periodic Table might be beyond element 118. Pekka Pyykkö, one of the meeting's participants, has made a prediction for elements up to 172 (Fig. 5) [23]. This range not only covers the 6f block of

<sup>2</sup> At the start of PTOV, my knowledge of the superheavy elements was minimal, as demonstrated by our first video [29] on hassium, element number 108, which I showed at the end of my talk. The sound track is as follows:

Brady Haran: What is the next element?

Martyn Poliakoff: Hassium. I know nothing about hassium. Should we make something up? (Pause) Element 108 is hassium, I know absolutely nothing about it. However, the power of the Periodic Table is that, by looking at the Periodic Table, I can say: "Well its chemistry has got to be a bit like iron but it won't be exactly like iron because iron is a light element and, as the elements get heavier going down, their chemistry changes. They tend to have a larger number of so called oxidation states. And so what I would predict was that, if hassium was not radioactive, it would still be pretty poisonous and it might be an interesting catalyst. It would probably react with carbon monoxide and, if it was stable, it would have probably made a great addition to my doctoral thesis work!"

elements, but also the unprecedented 5g series. Cynics might dismiss such speculation as being somewhat philosophical but the PTOV viewers disagree; the video on Pyykkö's paper [24] attracted more than 56 000 views.

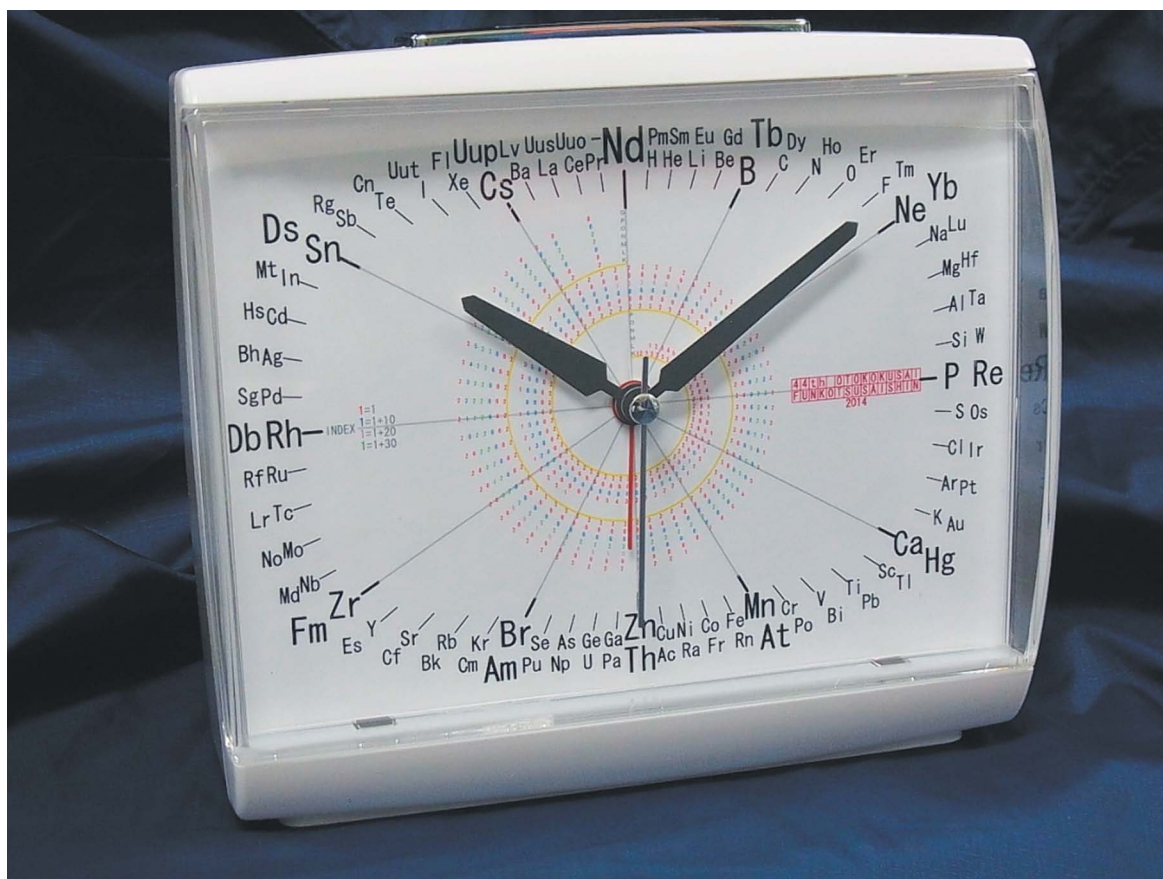
Working on PTOV has reminded us how the knowledge of most chemists is becoming increasingly focused and limited to their own particular area of chemistry. There are few chemists now who can claim the encyclopedic breadth of knowledge that Sadler [25] displayed in his inspiring presentation on the elements of life and medicines. This narrow focus is particularly sad, because, in the search for new more sustainable chemistry, few research chemists have familiarity with the more arcane chemistry of elements, knowledge which might for example open up new areas of catalysis. Hopefully, the International Year of the Periodic Table of Chemical Elements will re-excite chemists' imagi-

nations to the possibilities. In the longer term, there is reason for optimism. The Internet and Open Access are bringing chemistry to a much wider audience and, as in astronomy; one can easily imagine an increasing role for interested amateurs with sufficient free time to recognize patterns within chemical data which have been overlooked by overburdened professional researchers. Furthermore, we should not forget that, within research laboratories, the technicians often have a wider factual knowledge of chemical reactions than the more highly qualified and specialized researchers.

In recent years, the Periodic Table has become an advertising icon across the world (Fig. 6). Most chemists probably do not realize how fortunate our discipline is to have such a widely recognized symbol, something that physics lacks. For example, in the city of Oxford (UK), there are a taxi and a bus both decorated with the Periodic Table, which is particularly appropriate, because 2013 marked the centenary of the publication of Oxford physicist Moseley's [28] historic paper on X-ray spectra of the elements. That paper was the first definitive assignment of atomic number and helped explain anomalies such as the apparently reversed order of cobalt and nickel in terms of their atomic weights. Sadly, Moseley's premature death at



**Fig. 6.** The Periodic Table as an entertainment icon. This poster on a platform at Shibuya railway station in Tokyo (September 2012) introduces the "Science Department with Element Girls" as a club activity of the Japanese female pop group Sakura Gakuin (literally "Cherry Blossom Academy") [26]. The "element girls" are used as an unusual teaching aid in a book for teaching the Periodic Table [27]. (Photo: Morgan Thomas).



**Fig. 7.** Clock devised by chemistry teacher Nagayasu Nawa at Kurume University Fusetsu High School, Japan. It is an excellent example of how an unusual form of the Periodic Table can highlight particular features, in this case atomic number [30]<sup>3</sup>. (Photo courtesy of N. Nawa).

Gallipoli in 1915 prevented his winning the Nobel Prize for his outstanding achievement.

There is no single “true” Periodic Table, although probably only the standard “short form” is widely recognized by the general public. Unfortunately, the standard form does not make it easy to pick out the atomic number of a particular element without peering at the small print. By contrast, a recent “atomic clock”, designed by a Japanese schoolteacher makes the task very easy (*Fig. 7*). The clock exploits people’s almost instinctive ability to convert a position on the clock face into a number of minutes, for example enabling one instantly to see that neodymium has atomic number 60. So different arrangements of the elements can serve different purposes; novel forms of the Periodic Table can be useful for highlighting particular aspects of the elements. Let us hope, however, that no examiner gets hold of the Japanese clock because it has no less than 58 different pairs of ele-

ments, each with the associated opportunity of forcing unwilling pupils to compare and contrast their chemistry!

In conclusion, we are here to discuss the new chemistry of the elements. It is clear that the Periodic Table has become an icon of our profession as chemists, easily recognized by most people. However, it has also become an important tool for our research, constantly reminding us that there is still so much chemistry to be discovered and luring us to explore the chemistry of the less popular elements. Surely their time will come, giving us quite unexpected new materials, catalysts and reactions. So do not hesitate. Go and explore!

<sup>3</sup> “It has 118 atomic symbols – H to Uuo – on its dial in a double circle. Near the centre of the clock is a spiral line along which are written numbers that represent the electron configuration of each atom written on the outer circles. (Add 10, 20 or 30 to the number according to the colour index.) This clock was given as the prize to the winner of the finger-match games held in the chemistry room on 27 April 2014, when our school festival was held under the theme FUNKOTSUSAISHIN or do your best,” – N. Nawa. The clock unit used was MAG T-511WH manufactured by NOA Co., Ltd.

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# International Year of the Periodic Table of Chemical Elements

*Natalia P. Tarasova*

Year 2019, the International Year of the Periodic Table of Chemical Elements, is of special value for our country. 150 years ago, in 1869, the outstanding Russian scientist D.I. Mendeleev published the first scheme of the Periodic Table of Chemical Elements. The International Year of the Periodic Table of Chemical Elements draws the world community attention to the development of fundamental sciences, to deepening and expansion of education for sustainable development, to global problems that cannot be solved without active use of achievements of modern green chemistry. The quality of everyday life of present and future generations is directly connected with the progress and achievements of chemical science and technology. In 2019, the large-scale events dedicated to D.I. Mendeleev and his scientific heritage will take place both in Russia and throughout the world. The International Year of the Periodic Table once again emphasizes the importance of the systematicity in our chaotic world. The System gives an opportunity to understand the idea of regularity and thus arms human beings with the ability to predict.

**Keywords:** International Year of the Periodic Table of Chemical Elements, D.I. Mendeleev, International Union of Pure and Applied Chemistry (IUPAC).

On December 20, 2017, the 74<sup>th</sup> plenary meeting of the 72<sup>nd</sup> session of the United Nations General Assembly passed a resolution on science, technology and innovation for development. [«Science, technology and innovation for development (document A/72/422/Add.2)»] [1]. In paragraph 31 of this Resolution, the UN proclaimed “...the year beginning on 1 January 2019 the International Year of the Periodic Table of Chemical Elements to enhance global awareness of, and to increase education in, the basic sciences, with special attention to the countries of the developing world, to improving the quality of everyday life and, inter alia, for future advances in research and development...”, and invited “...the United Nations Educational, Scientific and Cultural Organization to serve as the lead agency for the International Year, in collaboration with other relevant agencies, within existing resources...”. The Resolution also calls upon “... the relevant organizations of the United Nations system, within their respective mandates and resources, to ensure that no one is left behind and no country is left behind in the implementation of the present resolution”.

The UN discussion was preceded by a discussion at UNESCO, whose General Conference on November 2, 2017, at its 39<sup>th</sup> session, recommended that the UN General Assembly adopt at its 72<sup>nd</sup> session the resolu-

tion declaring 2019 as the International Year of the Periodic Table of Chemical Elements.

The Explanatory Note [2] to the Resolution particularly emphasized that the proclamation of 2019 as the International Year of the Periodic Table of Chemical Elements will manifest the acknowledgement of the important role of basic science, especially chemistry and physics, in solving the many development tasks that Member States have to face in the implementation of the United Nations Sustainable Development Agenda until 2030. The celebration of this International Year will also provide an opportunity to see the true value of the recent discoveries in close international cooperation as well as the naming of the four super-heavy elements of Mendeleev’s Periodic Table with atomic numbers 113 (nihoniy), 115 (moscovium), 117 (tennessin) and 118 (oganeson).

It was emphasized that holding the International Year of the Periodic Table of Chemical Elements in 2019



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will mark the 150<sup>th</sup> anniversary of its creation by Russian scientist Dmitry Mendeleev, who is considered one of the founders of modern chemistry. The document also mentions that among the most important achievement by D.I. Mendeleev was the prediction in 1869 of the properties of five elements and their compounds, which had not been discovered by that time and for which he reserved cells in his Periodic Table.

The Explanatory Note stated that proclaiming of 2019 as the International Year of the Periodic Table of Chemical Elements would provide the International Basic Science Program (IBSP) with extensive opportunities to accomplish its task of promoting international cooperation in basic science for sustainable development, as well as science education and capacity building, in particular in the framework of the program on microscopic research devoted to the Periodic Table of Chemical Elements. This International Year should also facilitate the launch of a wide range of collective projects in the wake of the International Year of Chemistry and the International Year of Crystallography, which were held under the auspices of UNESCO in 2011 and 2014, respectively.

In light of the above, the UNESCO General Conference was invited to adopt the following resolution:

*“The General Conference,*

*Having examined* document 39C/60,

*Recognizing* the importance of chemistry and the advances in research and discoveries on the Periodic Table of Chemical Elements for sustainable development and for the benefit of humankind,

*Stressing* that the Periodic Table is widely used in vital spheres of scientific knowledge such as chemistry, physics, and biology,

*Considering* that the celebration of the 150<sup>th</sup> anniversary of the Periodic Table of Chemical Elements in 2019 will provide an unparalleled opportunity to highlight the continuous nature of scientific discovery in different con-

texts, with particular emphasis on promoting science education at all levels among young women and men, especially in developing countries, including in Africa,

*Noting* that the year 2019 coincides with the anniversaries of a series of important milestones in the history of the Periodic Table, specifically with the isolation of arsenic and antimony by Jabir ibn Hayyan circa 1,200 years ago; the discovery of phosphorus 350 years ago; the publication of a list of 33 chemical elements grouped into gases, metals, non-metals, and earths by Lavoisier in 1789; the discovery of the Law of Triads in 1829 by Döbereiner; the establishment of the Periodic Table by Mendeleev 150 years ago; and the discovery of francium by Marguerite Perey in 1939;

*Being aware* that the year 2019 provides the opportunity to observe the outstanding scientific achievements that humankind has made since the discovery of the Periodic System by Dmitry I. Mendeleev in 1869...

*Invites* the Director-General to support all efforts leading to the proclamation of 2019 as the International Year of the Periodic Table of Chemical Elements

*Recommends* that the United Nations General Assembly, at its 72<sup>nd</sup> session, adopt a resolution declaring 2019 as the United Nations International Year of the Periodic Table of Chemical Elements.”

Adoption of these resolutions was possible thanks to coordinated actions by scientists representing various fields of science, national and international scientific unions, diplomats and ordinary citizens. Tremendous work in this regard has been fulfilled through 2016–2017 by the International Union of Theoretical and Applied Chemistry (IUPAC), the Russian Chemical Society named after D.I. Mendeleev, Department of Chemistry and Material Sciences of the Russian Academy of Science, many Russian and foreign researchers [3]. The initiative to hold the International Year was strongly supported by the International Union of Theoretical and Applied Physics (IUPAP), the European Union of Chemical Societies (EuChemS), the International Astronomical Union (IAU), the International Union of History and Philosophy of Science and Technology (IUHPS), as well as by more than 70 national member organizations IUPAC, national science academies, chemical societies and research institutes

In the framework of the International Year of the Periodic Table of Chemical Elements, the celebration of the International Women’s Day in Science on February 11, 2019, played an essential role. A special international symposium named “Making Their Table: Women and the Periodic Table of Elements” was held at the University of Murcia, Spain [4]. Women chemists played an outstanding role in discovery of new chemical elements of the Periodic Table. Just to be mentioned among the many other prominent women in the his-

tory of chemistry are Marie Curie, who was awarded the Nobel Prizes in 1903 and 1911 for discovery of radium and polonium; Ida Noddak for discovery of rhenium (Re), Margarita Catherine Perey for discovery of francium.

The opening ceremony of the International Year of the Periodic Table of Chemical Elements was held at UNESCO headquarters in Paris on January 29, 2019 [5].

The year 2019 as the International Year of the Periodic Table of Chemical Elements will see many relevant activities [6, 7], including:

- The 53<sup>rd</sup> International Mendeleev Olympiad of Schoolchildren in Chemistry, St. Petersburg, April;

- Mendeleev-150: the 4<sup>th</sup> International Conference on the Periodic Table, under the auspices of IUPAC, St. Petersburg, July 2019;

- The 51<sup>st</sup> International Chemical Olympiad, Paris, July;

- The 5<sup>th</sup> European Conference on Inorganic Chemistry (EICC-5) under the auspices of EuChemS, Moscow, June;

- Celebrations on the occasion of the 150<sup>th</sup> anniversary of Mendeleev's Table of Chemical Elements within the framework of the 47<sup>th</sup> International Chemical Congress of IUPAC, including the special Symposium named "150 Years of Periodic Table", Paris, July.

The closing of the International Year of the Periodic Table of Chemical Elements will be held on December 5, 2019, in Tokyo.

The Russian Federation will commemorate the year of the 150<sup>th</sup> anniversary of the Periodic Table with large-scale events, dedicated to the outstanding scientist and his scientific heritage. Prime-Minister Dmitry Medvedev heads the Organizing Committee of the

Year. The plan of events includes various exhibitions, conferences, symposia, meetings with the participation of prominent scientists [8]. In September, St. Petersburg will host the central event of the Year in Russia – the XXI Mendeleev Congress, dedicated to the 150<sup>th</sup> anniversary of the Periodic Table and the similar sesquicentenary of the Russian Chemical Society.

The International Year of the Periodic Table of Chemical Elements as well as revealing and wording of the Periodicity Law by Dmitry Mendeleev are good reminders of how important consistency is in the modern chaotic world. After all, it is the concept of a system that makes it possible to understand the very idea of order and regularity, and therefore arms the mankind with the ability to foresee.

On a final note, let me quote from Mendeleev's "Cherished Thoughts": "Maybe I'm wrong, but I still believe that in the epoch of reassessing the values it is good to present what you consider a common value. Let people reevaluate it from time to time and get rid of their predetermination of seeing science among many other things, acquiring value only with the fall of the appraisal's hammer" [9]. This statement fully applies to the Periodic Table of Chemical Elements.

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## UNESCO Leading Role in the Celebration of the International Year of the Periodic Table of Chemical Elements (IYPT-2019)

Natalya A. Tsivadze

In accordance with United Nations General Assembly resolution, the year 2019 was proclaimed the International Year of the Periodic Table of Chemical Elements, and the United Nations Educational, Scientific and Cultural Organization (UNESCO) was designated as the lead organization for its implementation. At the present day, the UNESCO is the largest UN specialized agency with broad competence in providing interstate collaboration in the area of science, capable of playing a unique role for promotion of peace and sustainable development. The establishment of UN observances stimulates interest in the activities and programs of the organization in these areas, and also contributes to the intensification of activities at the international level. The proclamation of 2019 as the International Year of the Periodic Table is a recognition of the important role of the basic sciences, in particular, achievements in the field of chemistry and physics, in addressing the numerous development challenges that the world is currently facing in implementing the United Nations' "2030 Agenda for Sustainable Development". The International Year under the auspices of UNESCO provides an opportunity to mobilize all interested parties around the topic of science for peace and development – from government officials to media representatives and schoolchildren.

**Keywords:** International Year of the Periodic Table of Chemical Elements, Dmitry Mendeleev, UNESCO, sustainable development, Open Science.

In accordance with the resolution of the UN General Assembly, the year 2019 was proclaimed the International Year of the Periodic Table of Chemical Elements<sup>1</sup>, and the United Nations Educational, Scientific and Cultural Organization (UNESCO) was designated as the lead organization<sup>2</sup>.

In the light of the 65<sup>th</sup> anniversary of Russia's membership in UNESCO, this date is of particular importance. The President of Russia at the meeting with UNESCO Director General Audrey Azule during her official visit



to Russia said that UNESCO has always been a key international and intergovernmental organization creating and developing humanitarian ties over the world<sup>3</sup>. Russia is always ready to render active support to the efforts of UNESCO in this field<sup>4</sup>.

<sup>1</sup> The International Year of the Periodic Table of Chemical Elements was proclaimed by the UN General Assembly and approved by the UNESCO General Conference (A/RES/72/228, 39C/60, [https://www.un.org/en/ga/search/view\\_doc.asp?symbol=A/RES/72/228&Lang=R](https://www.un.org/en/ga/search/view_doc.asp?symbol=A/RES/72/228&Lang=R)).

<sup>2</sup> On the history of the promotion of the idea and the decision to proclaim the International Year of the Periodic Table, see the articles [1, 2].

<sup>3</sup> Meeting of the President of the Russian Federation V.V. Putin with the Director-General of UNESCO Audrey Azule, 06.03.2019, Moscow, the Kremlin. (<http://kremlin.ru/events/president/transcripts/59980>).

<sup>4</sup> Speech by the head of the Russian delegation A.I. Kuznetsov at the 206<sup>th</sup> session of the UNESCO Executive Board, Paris, 04/11/2019. (<http://www.unesco.ru/ru/??module=news&action=id&id=989>).



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The Jubilee year of the Periodic Table brings us back to addressing the role of natural sciences in the development of society. The genius of Dmitry Mendeleev once again draws our attention to the special relevance of this human activity in the present time, which is a difficult period in general in international relations, characterized by political tension and uncertainty in the economic sphere. The transition to the new technological and economic mainstay suggests major changes in the social structure of nations. How can we ensure a peaceful transition and at the same time the right of every person to access knowledge and new technologies? What should we do to prevent losing the advantages that knowledge gives us, and to use them for the benefit of all people on Earth?

One hundred and fifty years ago, the scientific community was immersed in the chaos of newly acquired knowledge and desperately needed to find a key, a general principle that would help the understanding of how this world is built, organized and put to action. Just like then, today we are in a search again, this time looking for a model for managing science. However, without understanding the meaning and role of science for society and its sustainable development, such a model can hardly be found. Here is how the authors of the publication titled “New World Order: 150 Years of the Periodic Table” describe the situation in science prior to Mendeleev’s discovery: “Despite the rapid pace of new findings, and maybe because of this, total chaos reigned in chemistry then. Chemists yet had to understand the meaning of the term «chemical element»... Despite the confusion and uncertainty, the accumulated knowledge of the various elements and their features was so great that someone had to clean up the mess and find the logic that would allow to understand the relationship between various elements, and perhaps the essence of the materials themselves” [3]<sup>5</sup>.

Will UNESCO be able to cope with a task of such a nature and complexity?

Today, UNESCO is the largest specialized UN agency with broad competence in building cooperation of states on education, science and culture, playing a unique role in strengthening peace and sustainable development. The proposal to study the feasibility of the Open Science Concept submitted for consideration of the Member States of the UNESCO Executive Board says that the leading role of the organization in the international arena should be further strengthened to secure “its comparative advantage over other international organizations” in matters of scientific cooperation and special responsibility for popularizing the internationally recognized right of a human to engage in science<sup>6</sup>. With the continuing status of the international platform with the largest representation of countries, UNESCO is undoubtedly capable of and must fulfill this role<sup>7</sup>. The example of discussing the regulations on the use of artificial intelligence, which is just another topical issue in the worldwide interaction of various countries, draws our attention to the exceptional role of UNESCO as an integrator of existing law-making initiatives by various international and regional institutions<sup>8</sup>. “Indeed, our Organization is the only one in which such a global consensus can be reached,” UNESCO’s Director General Azule said at the opening of the 206<sup>th</sup> session of the Executive Board<sup>9</sup>.

At the same time, UNESCO, just like other international structures has

<sup>5</sup> See also: “Dmitry Mendeleev, the Man Who Brought Law and Order to Chemistry”, UNESCO Courier, Paris, June 1971. (<https://en.unesco.org/courier/1971-7/dmitry-mendeleev-man-who-brought-law-and-orderchemistry>).

<sup>6</sup> A preliminary study of the technical, financial and legal aspects of adopting the recommendations of UNESCO on Open Science, UNESCO, Executive Board, 2019, 206th. ([https://unesdoc.unesco.org/ark:/48223/pf0000367018\\_rus](https://unesdoc.unesco.org/ark:/48223/pf0000367018_rus)).

<sup>7</sup> Currently the organization has 193 members and 11 associate members. ([http://www.unesco.org/eri/cp/ListeMS\\_Indicators.asp](http://www.unesco.org/eri/cp/ListeMS_Indicators.asp)).

<sup>8</sup> UNESCO conference on “Principles for AI: Towards a Humanistic Approach?” Remarks by Angel Gurría OECD Secretary-General, 04.03.2019, Paris, France, (<http://www.oecd.org/fr/apropos/secretairegeneral/unesco-conference-on-principles-for-ai-towards-a-humanistic-approach-march-2019.htm>).

<sup>9</sup> Speech by Director-General Audrey Azule at the 206th session of the UNESCO Executive Board, Paris, 08/04/2019. (<https://unesdoc.unesco.org/ark:/48223/pf0000367599?posInSet=1&queryId=N-e60a1195-a7e34d61-a515-c79dfed9bc1d>).

to operate in the context of the continuous crisis of the global economy, ongoing conflicts in various regions and grave natural disasters<sup>10</sup>. It is obvious that right now the world's development strategically depends on cooperation in the field of education, science and culture. When societies around the world face growing pressure of change and the international community faces new problems, the role of mechanisms ensuring dialogue and interaction between countries keeps increasing. This process is based on the definition and recognition of common values and aspirations of the humankind. This is why UNESCO takes up a special place in the system of specialized UN agencies. According to Article 1 of the Charter, UNESCO "assigns itself with the task of promoting peace and security, promoting the cooperation of peoples through education, science and culture in the interest of ensuring universal respect for justice, rule of law, human rights and fundamental freedoms enshrined in the Charter of the United Nations for all nations, without distinction of race, sex, language or religion"<sup>11</sup>. When outlining its scientific programs, UNESCO relies on the conclusions and recommendations of the World Summit on Sustainable Development<sup>12</sup>, as well as the World Conference on Science<sup>13</sup>, which confirmed the important role of science as a basis for making far-sighted

decisions and determining the right policy strategies for sustainable development. The Updated Sustainable Development Agenda until 2030 specifies the role of science, technology and innovation in ensuring sustainable development. UNESCO is part of the United Nations task force leading the global Technology Facilitation Mechanism (TFM), which began its work on September 26, 2015. The activities of this Mechanism are aimed at achieving the goals of sustainable development through stronger cooperation in matters of science, technology and innovation, and expanding access to the achievements in this field, as well as by encouraging the exchange of knowledge on mutually agreed terms<sup>14</sup>.

The spread of knowledge with the accelerated pace of science development and ever increasing number of new technologies applied in various aspects of human life becomes a determining factor for knowledge implementation. Society must understand the content and significance of the discoveries that have channeled the development of modern science, and information about new inventions should become asset to the widest range of people. It is this understanding that guides UNESCO in the efforts undertaken by this organization in various areas of its competence around the world, since the day it was founded.

The proclamation of 2019 as the International Year of the Periodic Table of Chemical Elements is a way of appreciating the important role of basic science, in particular the advances in chemistry and physics, in addressing the numerous developmental challenges facing the modern world while implementing the United Nations 2030 Agenda for Sustainable Development. The motivating part of the document, which gives grounds for imparting the status of an international date within the framework of the UN, refers to the Periodic Table of Chemical Elements as a comprehensive

<sup>10</sup> Complex relations between states are also reflected in the decisions of the United States and Israel to withdraw from UNESCO. (Les États-Unis et Israël quittent l'UNESCO. <http://www.lefigaro.fr/international/2018/12/31/01003-20181231ARTFIG00116-les-etats-unis-et-israel-quittent-l-unesco-celundisoir.php> Publié le 12/31/2018; Israel and US exit UNESCO (<http://en.rfi.fr/americas/20190101-israel-unitedstates-quit-unesco-palestine-west-bank>).

<sup>11</sup> Charter of the United Nations Educational, Scientific and Cultural Organization, adopted November 16, 1945. [4].

<sup>12</sup> Johannesburg Declaration on Sustainable Development. Adopted at the World Summit on Sustainable Development (Johannesburg, South Africa, August 26 – September 4, 2002). ([https://www.un.org/ru/documents/decl\\_conv/declarations/decl\\_wssd.shtml](https://www.un.org/ru/documents/decl_conv/declarations/decl_wssd.shtml)).

<sup>13</sup> The conference is organized by the Hungarian Academy of Sciences in collaboration with UNESCO, the International Scientific Council and the American Association for the Advancement of Science. Every two years, this forum brings together scientists, executives, as well as representatives of non-governmental organizations, educational and research institutions. This year, a special session in partnership with IUPAC and PhosAgro will be devoted to the International Year of the Periodic Table. (<https://worldscienceforum.org/>).

<sup>14</sup> The UNESCO World Science Report shows that scientific researches serve both an accelerator of economic development and a determining factor in building more sustainable and environmentally sound societies. [5].

scientific concept that functions as catalyst for international cooperation in the basic science and serves the basis for scientific discoveries and achievements<sup>15</sup>.

The practice of declaring special dates (days, weeks, years, and decades) by the United Nations on specific events, issues or topics is intended to draw attention to the objectives of the Organization and to intensify efforts to support their implementation. By establishing memorable dates, the United Nations stimulates interest in its programs and activities in the relevant areas, as well as contributes to revitalization of these activities at the international level. Within its competence, UNESCO is the initiator of a number of dates to which a special section of the official website is dedicated<sup>16</sup>. In natural sciences, the Organization has successfully held International Years and International Days devoted to chemistry, crystallography, light, and other scientific fields, but there were no dates devoted to scientific discoveries. The unique character and unprecedented unanimous support rendered by the international scientific community to the Russian initiative of declaring the International Year commemorating the great Mendeleev's discovery speak for the fundamental significance of the Periodic Law for all sciences<sup>17</sup>.

The opening of the International Year at UNESCO Headquarters in Paris (Fig. 1) received wide coverage in

the world media and social networks<sup>18</sup>. The significance of the discovery was marked by special issues of the leading scientific publications *Nature* and *Science*, which were devoted to the Periodic Table and the recognition of the outstanding role of Dmitry Mendeleev in the formulation of a universal law for all world science [6, 7].

The highlights of the Opening Ceremony<sup>19</sup> were the lectures of Nobel laureate in chemistry, Bernard Förling, on "Periodic Table for Society and the Future", as well as Sir Martin Polyakoff, Professor and the member of the British Royal Chemical Society. It is very important that on the Opening Day there were two magnificent lectures by Russian scientists (Fig. 2) – said the RAS President Alexander Sergeev, – namely the lecture about the recently discovered elements of the Periodic Table by RAS Academician Yuri Oganessian, Scientific Director of the Flerov Laboratory of Nuclear Reactions at the Joint Institute for Nuclear Research in

<sup>15</sup> Proposal for the United Nations to proclaim 2019 as the International Year of the Periodic Table of Chemical Elements. UNESCO, Executive Board, 2017, 202<sup>nd</sup>. ([https://unesdoc.unesco.org/ark:/48223/pf0000259063\\_rus](https://unesdoc.unesco.org/ark:/48223/pf0000259063_rus)).

<sup>16</sup> UNESCO: International Years. (<https://en.unesco.org/commemorations/international-years>).

<sup>17</sup> Mark Lorch, "International Year of the Periodic Table: 150<sup>th</sup> Anniversary of Dimitri Mendeleev's Genius Creation", 07.01.2019. (<https://www.newsweek.com/periodic-table-150-genius-iconic-symbol-science-1281821>): "The table of chemical elements can now be seen in almost any laboratory. ... The Periodic Table of Elements has become a **traditional, cult symbol of science**" (Highlighted by myself – N.Ts.).

Maria Gunther, Dagens Nyheter, "I Februari 1869 Fick Mendelejev Ordning på Kemin" ["In February 1869, Mendeleev brought order in chemistry"], 03.03.2019. (<https://www.dn.se/nyheter/vetenskap/ifebruari-1869-fick-mendelejev-ordning-pa-kemin>): "...A breakthrough in science is so significant that the UN General Assembly and UNESCO declared 2019 the International Year of the Periodic System to celebrate its 150<sup>th</sup> anniversary".

<sup>18</sup> We give here the selected headlines from the world mass media that show how significant this discovery is.: D. Linkoln, "150 Years Ago, Science Changed Forever", 20.02.2019, (<https://edition.cnn.com/2019/02/20/opinions/periodic-table-birth-year-opinion-linkoln/index.html>); E. Scerri, "Happy Sesquicentennial, Periodic Table! (The organizing scheme that revolutionized our understanding of the chemical elements turns 150 in 2019)", 22.01.2019, (<https://blogs.scientificamerican.com/observations/happy-sesquicentennial-periodic-table>); T. Pradeep, "The Table that Defines Chemistry Turns 150", 09.02.2019, (<https://www.thehindu.com/sci-tech/the-table-that-defines-chemistry-turns-150/article26224712.ece>); J. Rosen, "The Fascinating Backstory of the Periodic Table, Which is About to Turn 150 Years Old", 31.01.2019, (<https://www.latimes.com/science/sciencenow/la-sci-sn-periodic-table-150-birthday20190131-story.html>); A. Schiphorst, "The Periodic Table of Chemical Elements and Us", 11.02.2019, (<https://www.euroscientist.com/the-periodic-table-of-chemical-elements-and-us/>); CBC News, "O Mg! It's the Periodic Table's B Day!", 16.01.2019, (<https://www.cbc.ca/news/canada/ottawa/periodic-table-birthday-1.4979745>); D. Samson, "Iconic Periodic Table Now Turning 150 Years Old This Year", 02.02.2019, (<https://www.techtimes.com/articles/238258/20190202/iconic-periodic-table-now-turning-150-years-old-this-year.htm>).

<sup>19</sup> Broadcast of the Opening Ceremony of the International Year in Paris, UNESCO. (<http://webcast.unesco.org/live/room-01/ru>).



*Fig. 1. Opening of the International Year of the Periodic Table of Chemical Elements, speech by Audrey Azoulay, the Director-General of the UNESCO. UNESCO, Paris, January 29, 2019. (UNESCO Photos ©UNESCO/Christelle Alix).*

Dubna; and the other lecture by Professor Alexander Lutovinov, Deputy Director of the Space Research Institute, RAS, about the cosmic origin of chemical elements<sup>20</sup>.

As part of the opening ceremony, an agreement was signed between UNESCO and the Russian company PhosAgro to extend cooperation in the implementation of the program named “Green Chemistry for Life”. This project is being implemented jointly with the International Union of Pure and Applied Chemistry (IUPAC) and is an example of developing research potential in the field of “green chemistry”, the use of scientific results for protection of environment and introduction of environmentally friendly technolo-

gies. The project provides grants to young scientists from developing countries who are working on the use of up-to-date chemical technologies in areas like environmental protection, health care, food and the use of natural resources<sup>21</sup>.

The interactive chemical exhibition “Science for Everybody”, prepared by the All-Russian Science Festival “NAUKA 0+” with the support of the Art, Science and Sport Charity Foundation, caused great interest among the public, especially students and schoolchildren. It was properly timed to the opening of the Year. As part of improving the work in popularization of science, UNESCO’s strategy is not only to raise awareness of the Periodic Table of Chemical Elements, but to promote chemistry and science in general, too. The mobile international exhibition devoted to chemistry and its modern achievements was presented by participants from Russia, Great Britain, France, the Netherlands, the USA, Switzerland, China, and Japan.

<sup>20</sup> Report by the President of the Russian Academy of Sciences, Alexander Sergeev, on the role of the International Year of the Periodic Table of Chemical Elements in the development of chemical science in Russia and strengthening the image of Russian science in the world. Meeting of the Organizational Committee for the preparation and holding in 2019 of the International Year of the Periodic Table of Chemical Elements. (<http://government.ru/news/35651/>).

<sup>21</sup> UNESCO, PhosAgro and the International Union of Pure and Applied Chemistry join forces in support of green chemistry. (<https://ru.unesco.org/news>).



Fig. 2. The Russian delegation to UNESCO. (©Tatyana Dyakova).

At the exhibitors' booths, everyone could take part in chemical experiments; get familiar with the current results of leading research groups in chemistry and materials science, and talk with famous scientists and young researchers. The most popular venue of the exhibition was the molecular bar, where meals and drinks have been made by experienced bartenders using the laws of physics and chemistry. Also at the exhibition, it was possible to test chemical robots and find out the proportions of chemical elements in the body.

In her speech, UNESCO Director-General Audrey Azule thanked the Government of the Russian Federation and the partners in organizing the ceremony for their help. She expressed confidence in that the International Year would be an excellent opportunity to enhance international scientific and technical cooperation and create new forms of cooperation.

A new approach to presenting of a scientific discovery at UNESCO is a development of established traditions [8], and it lays the foundation for popularization

of science in various formats. It definitely gives a momentum to organizing events around the world. Among the many presentations of the Table within the framework of the exposition, visitors could see the new version of the Periodic Table, developed by Artemy Lebedev Studio. This work by itself was the opening of another international competition and won the Gold in the appropriate category<sup>22</sup>.

Popularization is the interface of science and society – said Sergei Kapitsa, the winner of Kalinga Prize for the art of popularizing science awarded by UNESCO since 1952. In the course of building bridges between science and society, UNESCO provides citizens with information about new trends in science, emphasizing the role of science,

<sup>22</sup> iF World Design Guide, Periodic Table of Elements. (<https://ifworlddesignguide.com/search?search=Lebedev#/pages/page/entry/259038-periodic-table-of-elements>). The “iF Design Award” is an award that annually selects the best samples of industrial, communication, packaging and other types of design. The award was founded in 1954, and during its existence it has become one of the most prestigious design awards in the world. Over the entire 60-year history, the Gold in the nomination was received by Russia only once before this. The Periodic Table, developed in the studio of Artemy Lebedev, is unique in that it is a customizable layout that the user adjusts to himself depending on the level of complexity he needs. A total of over 100,000 different Table options are available. This allows any student, scientist and teacher to find the ideal option for solving current problems. (<https://periodic.artlebedev.ru/>).





*Fig. 3. Opening of the International Year of the Periodic Table of Chemical Elements. UNESCO, Paris, January 29, 2019. (UNESCO Photos ©UNESCO/Christelle Alix).*

tists in expanding our understanding of how this world and life are built and how they interact. It is safe to count on significant improvement of this interface during the International Year of the Periodic Table. The International Year under the auspices of UNESCO provides an opportunity to mobilize all interested parties around the topic of “Science for Peace and Development” – from government officials to media representatives and schoolchildren. UNESCO strongly encourages everyone to join the celebration of the International Year by organizing their own events (Fig. 3).

Not only the meaning and the value of the Periodic Law invite to join such a movement, but the personality of Dmitry Mendeleev, too, inspires for the search of new forms and meanings. Mendeleev’s Periodic Table of Chemical Elements “...crowned the efforts of scientists from many countries to discover a meaningful system in the properties of basic substances”, G. Teterin and C. Terlon wrote in their article “This Chart on the Laborato-

ry Wall” [9] dedicated to Dmitry Mendeleev. He was a man thanks to whom “the study of chemistry stepped from the medieval movement by touch into modern science”. Great scientists and inventors always excite human imagination. It is said about Newton, that he discovered the law of gravitation after an apple fell on his head; and James Watt allegedly was prompted to create a steam engine by a pot of boiling water in front of him. They say that Mendeleev saw his Periodic Table during his daydream! To line up of these stories, the authors of the article note, that “people tend to forget that if scientific truth suddenly brightens up a person like lightning, then this scientist must have spent years studying this subject. Louis Pasteur loved to say: «Luck favors only the prepared minds»”.

The character, courage and the thoughts of the great researcher attract and entice people around the world to do science. The personality of Dmitry Mendeleev, the tasks he had set and the goals he had achieved, are the established criteria for evaluating decisions in the field of science, technology and education. Apart from his scientific work, Mendeleev was actively involved in economic and social affairs. He was the closest advisor to Chairman of the Committee of Ministers of the Russian Empire, Sergei Witte; he advised the Russian government on agriculture and trade agreements; he worked on introduction of customs duties and import taxes to protect the Russian economy. The scientist was also one

of the first to support academic education for women and contributed to the opening of lecture halls and courses for them.

The significance of the Periodic Table in the history of world science and the grandeur of its author's personality allows Russia, as the initiator of the International Year, to suggest that the annual celebration of the Periodic Law of Chemical Elements discovery be fixed in the UNESCO agenda. At a meeting of the Organizing Committee for the International Year of the Periodic Table of Chemical Elements held on February 6, 2019, the proposal of Alexander Sergeyev, President of the Russian Academy of Science, on the establishment (with support of UNESCO) of the International Mendeleev Prize for achievements in basic science, which would emphasize the interdisciplinary nature of his discovery<sup>23</sup>. Up to this day, 23 prizes have been instituted under the auspices of UNESCO, including 12 prizes in the field of science: five prizes in natural sciences and

seven prizes in social and human sciences.

There is no other phenomenon in science, which would be more relevant to the present time, and which would so thoroughly reflect the need of modern society in the establishment of balance, harmony and sustainable development. There is no other person in the history of world science, who would so convincingly embody the unity of science, education and art. It seems that the establishment of UNESCO's Dmitry Mendeleev Prize will be the best symbol and incentive to achieve the goals that the United Nations Educational, Scientific and Cultural Organisation has written down in its mandate.

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<sup>23</sup> The initiative to establish the Prize was supported by D.A. Medvedev: "It seems to me that this is absolutely correct. Moreover, if such an award is established, then it must be significant in every sense of the word". (<http://government.ru/news/35651>).

# Russian Contribution to the Periodic System

Elena A. Baum, Valeriy V. Lunin

For 50 years, scientists around the world have been searching for the relationship between the mass of atoms and the properties of elements, until the Russian scientist D.I. Mendeleev, having created the Periodic Table and formulated the Periodic Law, did complete this search. The discoveries of new chemical elements predicted by D.I. Mendeleev had soon followed and confirmed the fundamental importance of his Periodic law as the basic law of natural sciences. The works on the synthesis of transuranium and superheavy elements with serial numbers 113-118, been carried out by the scientists of the Joint Institute for Nuclear Research (Dubna, Russia) during the past 50 years, are the indisputable evidence of the validity of the Law of Periodicity of chemical elements and the proof of the Russian science triumph.

**Keywords:** Periodic System, Periodic Law, D.I. Mendeleev, ruthenium, transuranium elements, superheavy elements, G.N. Flerov, Yu.Ts. Oganessian.

## Creation of the Periodic Table and formulation of the Periodic Law

One hundred and fifty years ago, on February 17 (March 1), 1869, Dmitri Mendeleev first unveiled his Periodic Table of Chemical Elements, which finally positioned in due order the 63 elements, known by that time, putting them together according to their atomic weights and in the form of a table. A few weeks later, Mendeleev sent to his colleagues the first version of the Table (“An Experience on the System of Elements Based on Their Atomic Weight and Chemical Similarity”)<sup>1</sup>. The making of the “Natural System of Elements” by November 1870 completed the research work on the Periodic Law that the Russian scientist

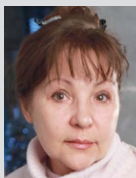
had engaged himself in for a year and nine months. In the article named “The Natural System of Elements and Its Use in Finding the Properties of Yet Undiscovered Elements”<sup>2</sup> Mendeleev proposed an improved version of the Table, noting in particular that certain facts did not fit into the framework of the earlier version that was compiled by March 1869: “Some cerite elements, uranium and indium, did not find a proper place in the system... <...> At present, such deviations from the periodic law... can be settled with a better detail” [2]. In the new Table, Dmitry Mendeleev reasonably chose the proper places for uranium, ceritic metals, indium, etc. By comparing the physical and chemical characteristics of the elements, the scientist gave grounds to placing within the Table of elements that were not yet found and suggested conditional names for them (*Fig. 1, 2, 3*).

With his discovery, Mendeleev finalized the 50-year search for the relationship between the mass of atoms and the properties of elements<sup>3</sup>. He proposed and sub-

<sup>1</sup> I.S. Dmitriev, Director of Mendeleev’s Museum and Archive at St. Petersburg State University, estimates this work as “making the first approximation to... a system of elements... and discovery of the conceptual core of the Periodic Law” [1]. The main statements of the discovery were also formulated by D.I. Mendeleev in his the article «The Correlation of Properties with the Atomic Weight of Elements», published in the Journal of the RCS (Russian Chemical Society) in May of the same year.

<sup>2</sup> Dmitry Mendeleev reported on it on December 3, 1870, at an emergency meeting of the RCS. “The Natural System of Elements” by D.I. Mendeleev was immediately entered into the second part of the first edition of “Principles of Chemistry” in 1871.

<sup>3</sup> Thus, finishing “Principles of Chemistry” at the beginning of 1871, he stated: “...The whole essence, the whole nature of the elements is expressed in their weight, i.e. in the mass of the interacting matter. <...> The physical and chemical properties of the elements, manifested in the properties of simple and complex bodies they form, are periodically dependent on... their atomic weight” [3].



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### ОПЫТЪ СИСТЕМЫ ЭЛЕМЕНТОВЪ

ОСНОВАННОЙ НА ИХЪ АТОМНОМЪ ВѢСѢ И ХИМИЧЕСКОМЪ СХОДСТВѢ

		Tl = 50	Zr = 90	? = 180.
		V = 51	Nb = 94	Ta = 182
		Cr = 52	Mo = 96	W = 186.
		Mn = 55	Rh = 104,4	Pt = 197,4.
		Fe = 56	Ru = 104,4	Ir = 198
		Ni = Co = 59	Pt = 106,6	Os = 199.
H = 1		Cu = 63,4	Ag = 108	Hg = 200
Be = 9,4	Mg = 24	Zn = 65,2	Cd = 112	
B = 11	Al = 27,4	? = 68	U = 116	Au = 197?
C = 12	Si = 28	? = 70	Sn = 118	
N = 14	P = 31	As = 75	Sb = 122	Bi = 210?
O = 16	S = 32	Se = 79,4	Te = 128?	
F = 19	Cl = 35	Br = 80	I = 127	
Li = 7	Na = 23	K = 39	Rb = 85,4	Cs = 133
		Ca = 40	Sr = 87,6	Ba = 137
		? = 45	Ce = 92	
		?Er = 56	La = 94	
		?Yt = 60	Di = 95	
		?In = 75,6	Th = 118?	

Д. Менделѣевъ

Fig. 1. The first printed version of the “An Experience on the System of Elements” (1869).

stantiated the concept that an element in the Periodic System is a “node of intersection” of regularly changing properties of elements, both horizontally and vertically (that is, within a series and a group). Thus, the place that an element is due to take in the Periodic System allows for a detailed description of its properties, and this

gives the great predictive power to the Table. Dmitry Mendeleev wrote about this in his work “Periodic Regularity for Chemical Elements”: “The system of elements is not only of pedagogical significance, nor it just facilitates the study of various facts, putting them in order and showing their connection. With all of the above-mentioned, it has pure scientific value as well, revealing analogies and pointing out new ways for study of elements” [4].

### L. Meyer and D.I. Mendeleev: priority disputes

In the 1860s, finding the link between atomic weights of the elements and their physical and chemical characteristics was also in the focus of research of the famous German chemist Julius Lothar Meyer (1830–1895), who was considered as the main “competitor” to Dmitry Mendeleev. Having attended the famous Congress in Karlsruhe (1860) and deeply impressed with the article of Stanislao Cannizzaro (1826–1910), L. Meyer began writing his textbook “Die Modernen Theorien der Chemie und ihre Bedeutung für die Chemische Statik” (“The Modern Chemical Theories and Their Meaning for Chemical Statics”), published in 1864<sup>4</sup>. In one of the chapters of his

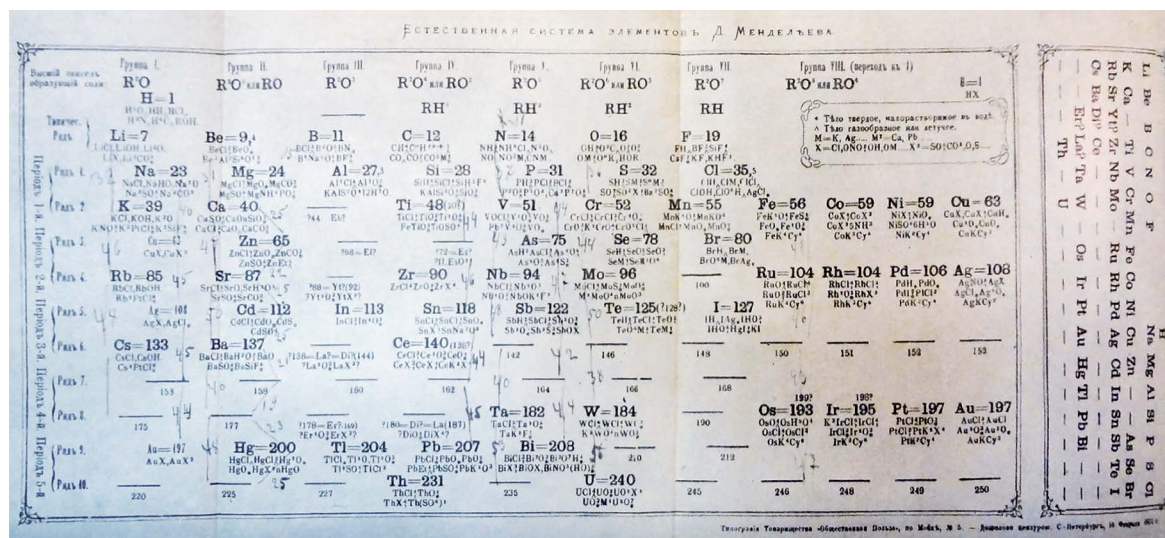


Fig. 2. Print of the “Natural System of Elements of D.I. Mendeleev” (1871). Such a table was presented at the beginning of the second part of Mendeleev’s “Principles of Chemistry”.

<sup>4</sup> His main goal was to eliminate the contradictions in the theories of atomic mass, atom, equivalence and molecule and develop a generalized chemical theory.

Высший окисель образующий соли:  
 Типичес. Рядъ  
 Періодъ 1-й  
 Періодъ 2-й  
 Періодъ 3-й  
 Періодъ 4-й  
 Періодъ 5-й

Группа I.	Группа II.	Группа III.	Группа IV.
$R^2O$ $H=1$ $H^2O, NH_3, HCl, H^3N, H^4C, ROH.$	$R^2O^2$ или $RO$	$R^2O^3$	$R^2O^4$ или $RO^2$ $RH^4$
<b>Li=7</b> LiCl, LiOH, Li <sub>2</sub> O. LiX, Li <sub>2</sub> CO <sub>3</sub>	<b>Be=9,4</b> BeCl <sub>2</sub> ; BeO. Be <sup>3</sup> Al <sup>2</sup> Si <sup>6</sup> O <sup>14</sup>	<b>B=11</b> BCl <sub>3</sub> ; B <sub>2</sub> O <sub>3</sub> ; BN. B <sup>4</sup> Na <sup>2</sup> O; BF <sub>3</sub>	<b>C=12</b> $CH_4, C^2H^{2+}, C^2H^{2-}$ CO, CO <sub>2</sub> ; CO <sub>2</sub> ; M <sub>2</sub>
<b>Na=23</b> NaCl, NaHO, Na <sup>2</sup> O Na <sup>2</sup> SO <sub>4</sub> ; Na <sup>2</sup> CO <sub>3</sub>	<b>Mg=24</b> MgCl <sub>2</sub> ; MgO, MgCO <sub>3</sub> MgSO <sub>4</sub> ; MgNH <sub>4</sub> PO <sub>4</sub>	<b>Al=27,3</b> Al <sup>2</sup> Cl <sub>3</sub> ; Al <sup>2</sup> O <sub>3</sub> KAIS <sup>2</sup> O <sup>8</sup> 12H <sup>2</sup> O.	<b>Si=28</b> SiH <sub>4</sub> ; SiCl <sub>4</sub> ; SiH <sup>2</sup> F <sup>6</sup> KAIS <sup>2</sup> O <sup>8</sup> SiO <sub>2</sub>
<b>K=39</b> KCl, KOH, K <sup>2</sup> O KNO <sub>3</sub> ; K <sup>2</sup> PtCl <sub>6</sub> ; K <sup>2</sup> SiF <sub>6</sub>	<b>Ca=40</b> CaSO <sub>4</sub> ; CaO; CaSiO <sub>3</sub> CaCl <sub>2</sub> ; CaO; CaCO <sub>3</sub>	?44=Eb?	<b>Ti=48(50?)</b> TiCl <sub>4</sub> ; TiO <sub>2</sub> ; Ti <sup>2</sup> O <sub>3</sub> FeTiO <sub>3</sub> ; TiOSO <sub>4</sub>
<b>Cu=63</b> CuX, CuX <sub>2</sub>	<b>Zn=65</b> ZnCl <sub>2</sub> ; ZnO, ZnCO <sub>3</sub> ZnSO <sub>4</sub> ; ZnEt <sub>2</sub>	?68=El?	?72=Es? ?11, EsO <sup>2</sup> ?
<b>Rb=85</b> RbCl, RbOH. Rb <sup>2</sup> PtCl <sub>6</sub>	<b>Sr=87</b> SrCl <sub>2</sub> ; SrO, SrH <sup>2</sup> O <sub>2</sub> SrSO <sub>4</sub> ; SrCO <sub>3</sub>	<b>89 Yt</b> ?88=Yt(92) ?Yt <sup>2</sup> O <sub>3</sub> ; YtX <sup>3</sup> ?	<b>Zr=90</b> ZrCl <sub>4</sub> ; ZrO <sub>2</sub> ; ZrX <sup>4</sup> .
<b>Ag=108</b> AgX, AgCl <sub>2</sub>	<b>Cd=112</b> CdCl <sub>2</sub> ; CdO, CdS. CdSO <sub>4</sub>	<b>In=113</b> InCl <sub>3</sub> ; In <sup>2</sup> O <sub>3</sub>	<b>Sn=118</b> SnCl <sub>4</sub> ; SnCl <sub>2</sub> ; SnO. SnX <sub>4</sub> ; SnNa <sup>2</sup> O <sup>2</sup>
<b>Cs=133</b> CsCl, CsOH. Cs <sup>2</sup> PtCl <sub>6</sub>	<b>Ba=137</b> BaCl <sub>2</sub> ; BaH <sup>2</sup> O <sub>2</sub> ; BaO BaSO <sub>4</sub> ; BaSiF <sub>6</sub>	<b>La Bg</b> ?138=La?= <sup>2</sup> Di?(144) ?La <sup>2</sup> O <sub>3</sub> ; LaX <sup>3</sup> ?	<b>Ce=140(1382)</b> CeCl <sub>3</sub> ; Ce <sup>2</sup> O <sub>3</sub> ; CeO <sub>2</sub> CeX <sub>3</sub> ; CeX <sub>2</sub> ; CeK <sup>2</sup> X <sup>6</sup>
153	158		
175	177	<b>Er 170</b> ?178=Er(169) ?Er <sup>2</sup> O <sub>3</sub> ; ErX <sup>3</sup> ?	<b>Di 175-190</b> ?180=Di?= <sup>2</sup> La(187) ?DiO <sub>3</sub> ; DiX <sup>4</sup> ?
<b>Au=197</b> AuX, AuX <sub>3</sub>	<b>Hg=200</b> HgCl <sub>2</sub> ; HgCl <sub>2</sub> ; Hg <sup>2</sup> O. HgO, HgX <sup>2</sup> ; nHgO	<b>Tl=204</b> TlCl <sub>3</sub> ; Tl <sup>2</sup> O, Tl <sup>2</sup> O <sub>2</sub> Tl <sup>2</sup> SO <sub>4</sub> ; TlCl <sub>3</sub>	<b>Pb=207</b> PbCl <sub>2</sub> ; PbO, PbO <sub>2</sub> PbEt <sub>4</sub> ; PbSO <sub>4</sub> ; PbK <sup>2</sup> O <sup>3</sup> ; V
220	225	227	<b>Th=231</b> ThCl <sub>4</sub> ; ThO <sub>2</sub> ThX <sub>4</sub> ; Th(SO <sub>4</sub> ) <sub>2</sub>

Фотокопия 29. Часть таблицы «Естественной системы элементов» с пометками Д. И. Менделеева

Fig. 3. Part of the table "Natural System of Elements of D.I. Mendeleev" with the author's marks.

book, the scientist touched upon the issue of "specific patterns" that he found in atomic masses, and compiled two tables, the first of which included twenty-eight elements, grouped by ascending atomic weight and valence, while the second contained the remaining twenty-two elements<sup>5</sup>. He identified some irregularities in the changes of atomic weights, so he urged his colleagues to put more efforts into their refinement, which he also began doing by himself in 1866. Due to transfer to a new place of work, Meyer postponed his research of chemical regularities and dependencies, although he continued to work on a new edition of the book, and by

1868 created a new table of elements, to a certain extent resembling the table proposed by Dmitry Mendeleev. In that edition, L. Meyer proposed an extended classification of fifty-two elements in fifteen vertical rows, while the sixteenth row was left empty. However, the table was not published at that time, since L. Meyer entrusted the project to one of his cohort, geologist Adolf Remele (1839–1915). As a result, both L. Meyer and D.I. Mendeleev designed their periodic systems in the form of two-dimensional tables independently of each other, when writing their textbooks in search for a new didactic introduction to the chemistry of elements.

At the end of 1869, Victor von Richter (1841–1891), a correspondent for *Berichte der Deutschen Chemischen Gesellschaft*, reported on interesting interrelationships in the system of elements published in Russia by D.I. Mendeleev [5]. He presented a fragment of the sys-

<sup>5</sup> Today, the elements of the first Table are known as elements of the main group, and those of the second – as elements of the secondary group.

tem and also mentioned a publication in *Zeitschrift für Chemie*, which described the content of Mendeleev’s innovations – the presence of a connection between the properties and the atomic weight of elements [6]. In fact, the main idea of D.I. Mendeleev was distorted in that translation of the Russian article in the mentioned journal: instead of periodicity of properties, the translator wrote about a stepwise change in the properties [7].

As a response to this message in 1870, an article by L. Meyer (manuscript dated by December 1869) was published, with the following heading: “Die Natur der Chemischen Elemente als Function ihrer Atomgewichte” (“Nature of Chemical Elements as Function of Their Atomic Weights”). The presented graph of dependence between atomic volumes and atomic weights showed some periodic dependence, about which L. Meyer spoke openly for the first time. But he undoubtedly derived the idea of periodicity from that very publication by Dmitry Mendeleev, which was misstated in the above German periodical. L. Meyer wrote in his article, “Thanks to a more accurate definition of atomic weights, it became possible to arrange all fairly well-known elements within one system. Recently, Mendeleev has shown that such an arrangement can be obtained by simply putting all atomic weights in a row without any arbitrary choice, and in the order of their increase, then breaking this row into segments

and joining them to each other without changing the order. The following table is essentially identical with that presented by Mendeleev” (cited from [8], p. 107).

In his article, L. Meyer gave an untitled table of the following form (Fig. 4) and supplemented it with a curve of atomic volumes of elements, which was at the time highly praised by Mendeleev for clarity.

His version of the elements table was very similar to the “Natural System” by D.I. Mendeleev, published by the Russian scientist only in 1871. According to historian of science I.S. Dmitriev<sup>6</sup>, “in the Meyer table, the future main and additional subgroups are clearly identified, which Mendeleev’s «An Experience on the System of Elements...», as a prototype of the long form of the System, actually lacked. But the main drawback of Meyer’s article was that he did not see the fundamental law of nature behind his table, and therefore did not dare to make detailed and clear predictions

I	II	III	IV	V	VI	VII	VIII	IX
	B = 11.0	Al = 27.3	—	—	—	In = 113.4	—	Tl = 202.7
	C = 11.97	Si = 28.0				Sn = 117.8		Pb = 206.4
			Ti = 48.0		Zr = 89.7			
	N = 14.01	P = 30.9		As = 74.9		Sb = 122.1		Bi = 207.5
			V = 51.2		Nb = 93.7		Ta = 182.2	
	O = 15.96	S = 31.98		Se = 78.0		Te = 128 ?		—
			Cr = 52.4		Mo = 95.6		W = 183.5	
—	F = 19.1	Cl = 35.3		Br = 79.75		I = 126.6		—
			Mn = 54.8		Ru = 103.5		Os = 198.6?	
			Fe = 55.9		Rh = 104.1		Ir = 196.7	
		Co =	Ni = 58.6		Pd = 106.2		Pt = 196.7	
Li = 7.01	Na = 22.99	K = 39.04		Rb = 85.2		Cs = 132.7		—
			Cu = 63.3		Ag = 107.66		Au = 196.2	
?Be = 9.3	Mg = 23.9	Ca = 39.9		Sr = 87.0		Ba = 136.8		—
			Zn = 64.9		Cd = 111.6		Hg = 199.8	

Fig. 4. Untitled table of elements presented by L. Meyer (1870).

<sup>6</sup> According to I.S. Dmitriev, if we discuss the issue of “priority at the level of the «tables», then Meyer, with all the shortcomings of his system, has good advantages. And if we talk about the discovery of the Periodic Law, then Mendeleev undoubtedly has a priority”. (From a conversation with I.S. Dmitriev in May 2019).



Fig. 5. Portrait of Karl Karlovich Claus.

of the properties of yet undiscovered elements and to correct the atomic weights of the known elements”.

The discoveries of new chemical elements predicted by Mendeleev soon followed (1875 – gallium, 1880 – scandium, etc.), which confirmed the fundamental importance of the Periodic Law formulated by the scientist. In the 1880s, there was a fierce dispute about the priority on the discovery. The dispute was maintained for some time on the pages of *Berichte der Deutschen Chemischen Gesellschaft* magazine.

The priority dispute demanded a new look at the results of a decade ago [9, 10]. In particular, L. Meyer regretted that he was able to submit only a short article in 1870, which made it impossible to compare the two tables in detail further. But in the end, he

admitted that Mendeleev was the first to reveal the periodic change in properties associated with atomic weights and the possibility of predicting the existence of elements not yet known to science. This very circumstance brought to triumph the law formulated by D.I. Mendeleev and over time led to oblivion of the German researcher’s contribution, as some modern historians of science like to believe<sup>7</sup>. Although in 1882, both researchers at the Royal Society of London were awarded the Devi Medal “for the discovery of periodic dependence on atomic weight”.

#### Ru – Ruthenium – Ruthenia – Russia

44 Ru  
Ruthenium  
Рутений  
101.07(2)

During the life of Dmitry Mendeleev, only one chemical element included in the Table was discovered in Russia. It was ruthenium, the metal belonging to the platinum group and discovered in 1844 by Karl Karlovich Claus (1796–1864)<sup>8</sup>, who served as Extraordinary Professor at Kazan University. On this occasion, Claus once wrote, “Wanting to get better knowledge of platinum metals and to prepare their main compounds for the chemical cabinet of Kazan University, I begged out of Mr. Sobolevsky 2 pounds of... [factory platinum] leftovers and in 1841 I got down to business” [12].

In the course of research, using the methods of platinum ore analysis developed by J.Y. Berzelius, the scientist found that osmiridium contains a new element, which he called ruthenium from the Latin naming of Russia – Ruthenia [13]. He studied the characteristic analytical reactions of the new element and obtained some of its compounds. Using the results of the quantitative analysis of salt  $K_2RuCl_5$ , Claus was able to determine the atomic weight of the element (104.2, which is close to the modern value of 101.07). In the autumn of 1844, he sent a letter with the message about his findings to Full Member of the Russian Science Academy G.I. Hess. The latter voiced this discovery at the meetings of the Petersburg Academy of Science in September and October of the same year. In 1845, Claus publishes a book about his discovery – “Chemical study of residues of Ural platinum ore and ruthenium metal”<sup>9</sup>,

<sup>7</sup> However, we would like to mention that in the foreign press there are still allegations to the Periodic Law as a joint discovery in two independent events. Some consider both L. Meyer and D.I. Mendeleev the authors of the Law. In particular, this can be seen in comments on the above-mentioned article “Die Natur der Chemischen Elemente als Function ihrer Atomgewichte” published by L. Meyer. They say, “...the first appearance in print... of a revolutionary classic article in which Lothar Meyer... for the first time fully expressed his ideas about the relationship between the atomic weight of elements and their properties – the Periodic Law. This law, which was discovered independently and almost simultaneously in 1868–1869 by the German chemist Lothar Meyer and the Russian Dmitry Mendeleev, can be expressed in the following words: the properties of elements are a periodical function (or periodic change) of their atomic weight” [11].

<sup>8</sup> K.K. Claus (Fig. 5), a Baltic German from Dorpat (now Tartu, Estonia), since 1837 taught at Kazan University, Professor of Pharmacy.

<sup>9</sup> Among the ruthenium satellites, Claus studied osmium and its compounds in particular ( $OsO_2$ ,  $Os_2O_3$ , etc.).

which received the full Demidov Prize (5,000 rubles) on April 17, 1846. In their review on the book G.I. Hess and Y.F. Fritzsche, the two Full Members of the Russian Science Academy, said: “Russia, due to this discovery, for the first time enjoys the honor of establishing in Chemistry a new simple body found in such domestic material, to which the very institution of awards in some way owes its origin” [14]. Later, D.I. Mendeleev, discussing the Periodic Law, also noted the important contribution by K.K. Claus into finding certain similarities of properties in the triads of platinum-group metals (“Claus noted that Os, Ir, Pt, with atomic weight of about 195, are similar to Ru, Rh, Pd, of which atomic weight is close to 105” [15]), which turned out to be significant for the systematics of elements before the discovery of Periodic Law.

The periodic system during the life of D.I. Mendeleev was already repeatedly modified following the new scientific data and discoveries. We should pay due to the intuition of its creator, who wrote about this in his *Fundamentals of Chemistry*: “The Periodic Law is not only waiting for new applications, but for improvements and detailed development as well... <...> For the Periodic Law the future is not threatening with dismounting, but holds promises to build and develop upon it” [3].

### **Expanding the boundaries of the Periodic System. Synthesis of transuranics**

Indeed, further development of the Periodic Law and the Periodic System is associated with accumulating experimental data in the field of atomic and nuclear physics. The discovery of radioactivity has changed our understanding of the Universe: the atoms were no longer viewed as the very immutable building blocks of the Universe. The value of atomic number was established, which numerically corresponded to the positive nuclear charge of each atom. With the introduction of quantum numbers, the Periodic Table has gained theoretical justification.

Further development of nuclear physics towards practical application of nuclear radiation as well as development of atomic projects in the USSR and the USA in the 1940s, became the driving force behind the creation of peaceful nuclear energy industry. The progress of science at that time allowed to expand the boundaries of the Periodic System with the synthesis of new elements beyond uranium – the transuranics (elements with atomic numbers from 93 to 101, 1940–1950s). Following the work of two US scientists – physicist E.M. Macmillan and chemist F.Kh. Eibelson, who du-

plicated E. Fermi’s experiments on obtaining elements heavier than uranium, and received the first transuranium element No 93, which they named neptunium<sup>10</sup>, – another group of researchers led by the famous American physicist G.T. Seaborg (1912–1999), who worked at Berkeley (University of California), came to tight grips with this problem. A year later, G. Seaborg and his staff discovered plutonium (atomic number 94). And then, over years of work, elements with serial numbers from 95 to 101 were synthesized. Such results could not have been achieved without the construction of charged particle accelerators and atomic reactors in which the synthesis of radioactive nuclei took place. Elements were obtained in the course of successive captures of neutrons by target nuclei. However, it was found that in transition to elements with a higher atomic number, the quantitative yield of each subsequent element decreased. That is why today’s plutonium reserves in the world amount to many hundreds of tons, while californium (atomic number 98) has been obtained only in a quantity of a few grams.

Synthesis of mendelevium (atomic number 101), of which in the first experiments several atoms were obtained<sup>11</sup>, confirmed the gaining ground conclusion of many scientists that using light particles (alpha-particles,  ${}^4_2\text{He}$ , deuterons  ${}^2_1\text{H}$ ) for bombarding targets was no longer productive. In the 1950s, physicists turned to new methods of synthesis – the fusion reactions involving heavy ions ( ${}^{12}\text{C}$ ,  ${}^{18}\text{O}$ ,  ${}^{22}\text{Ne}$ , etc.).

### **The triumph of Soviet science: obtaining elements with sequence numbers 102-105.**

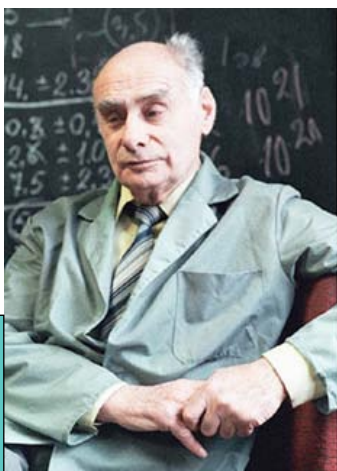
In order to carry out nuclear reactions with accelerated heavy ions, specialized accelerators were built, including the 1960’s U-300 cyclotron in

<sup>10</sup> Np was obtained in neutron bombardment of uranium (1940).

<sup>11</sup> Element  ${}^{256}\text{Md}$  (half-life of about 1 h) was first obtained at the Berkeley cyclotron (A. Giorso, B. Harvey, G. Schoppen, S. Thomson and G. Seaborg, 1955) under the action of  $\alpha$ -particles on Einsteinium atoms. The element is named after the creator of the Periodic Law.



**114 Fl**  
Flerovium  
Флеровий



**Fig. 6.** Georgy Nikolaevich Flerov; the element with atomic number 114 is named after him.

Dubna. The institute, where the accelerator belongs, was established in March 1956, under the name of Joint Institute for Nuclear Research (JINR)<sup>12</sup>. This unique cyclotron was designed in Leningrad based on the concept proposed by G.N. Flerov (Fig. 6), who headed the Laboratory of Nuclear Reactions (FLNR) at the Institute<sup>13</sup>.

Having synthesized many new elements and eventually over four hundred isotopes, this institute quickly gained a reputation as a world leader in nuclear research [18].

**102 No**  
Nobelium  
Нобелий

Just a few years after the institute was established, the first of new elements was made: an element with atomic number 102. V.A. Shchyogolev, one of the authors of this synthesis, carried out at the institute in the framework of FLNR, notes that obtaining elements with  $Z \geq 102$  was a very difficult experimental task. “The formation of the nuclei of these elements,” the researcher explains, “has to compete with the division of the compound nucleus, into which a lot of excitation energy is added (40–50 MeV). Therefore, these reactions were called

“hot fusion reactions”. For example, in the synthesis of the 102<sup>nd</sup> element in reaction  $^{238}\text{U} (^{22}\text{Ne}, 4n) ^{256}\text{No}$ , the ratio of division probability against the probability to obtain the desired core  $^{256}\text{No}$  is  $\sim 10^8$ . This means that in a few hours of the experiment, only about fifteen to twenty nobelium atoms can be obtained<sup>14</sup>. In addition to that, in various reactions of partial fusion of the target nucleus and the bombarding particle (the so-called nucleon transfer reactions), nuclei with  $Z < 102$  form in the region of Po – Ac. The probability of their formation is  $\sim 10^5$  times higher than the probability of formation of the desired nucleus...”, all of this creates a vast background, “...from which we have to isolate the effect of the radioactive decay of the new element’s nuclei” [19].

Actually, there were three groups simultaneously working on obtaining an element with  $Z \geq 102$ . The first international group included researchers from the Institute of Physics in Stockholm, the National Laboratory in Aragon (Georgia, USA) and the United Kingdom Atomic Energy Authority. The second team was from the Lawrence Berkeley Radiation Laboratory (USA), incorporating G. Seaborg and his coworkers. The third team was the JINR staff. The first group, in 1957, obtained an isotope with a mass number between 251 and 255, the second group, in 1958, registered the formation of an isotope with a mass number of 254. It was the combined Swedish-UK-US group that worked in the Nobel Institute in Stockholm, which first published the results of their work and gave the element the name of nobelium. However, the experimental data claimed by this group, and then by the group of G. Seaborg, were not confirmed by other researchers. In Dubna, in 1961, the researchers used the capacities of the just launched aforementioned cyclotron (Fig. 7), to once again address the problem of existence of element number 102. Resulting from this, a group of researchers (E.D. Donets, V.A. Shchegolev, V.A. Ermakov) by 1963 had synthesized the isotope of the 102<sup>nd</sup> element and reliably identified it with the mass number of 256. The discovery of Soviet scientists provoked further priority debate over discovery of the element with  $Z = 102$ , which lasted more than a decade. Russian priority was finally fixed, however fairly late: in the 1990s. But the attempt of Soviet scientists to name the element zholiomiy<sup>15</sup> in honor of F. Joliot-Curie had failed. The name of Nobelium has been fixed with that element (see [13], p. 223).

<sup>12</sup> From its very foundation, the Institute was positioned as an international scientific organization, uniting scientists from the socialist countries. The agreement on this organization was signed in Moscow by representatives of 11 states [16].

<sup>13</sup> Georgy Flerov (1913–1990), one of the founders of JINR. Permanent head of FLNR from 1958 to 1988. Full Member of the USSR Academy of Science since 1968 [17].

<sup>14</sup> The element was named Nobelium (see below).

<sup>15</sup> For quite long, the Soviet version of Mendeleev’s Table listed 102<sup>nd</sup> element Joliotium, while the US and European versions referred to it as Nobelium.

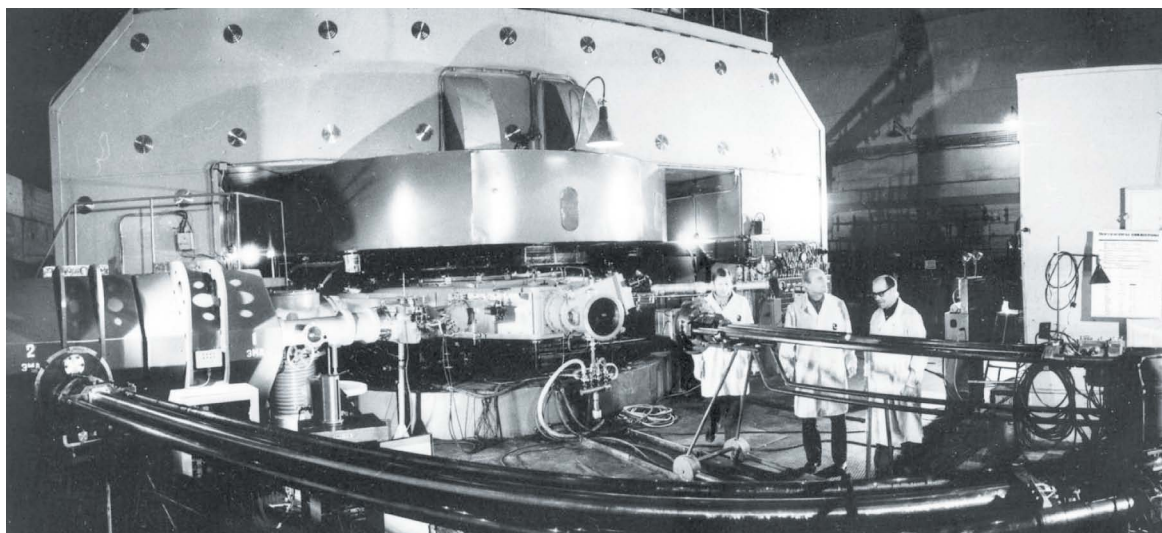


Fig. 7. Cyclotron U-300: the first accelerator of the Flerov Laboratory of Nuclear Reactions.

**103 Lr**  
Lawrencium  
Лоуренсий

**104 Rf**  
Rutherfordium  
Резерфордий

The discoveries of the 103<sup>rd</sup> and 104<sup>th</sup> elements also entailed a fierce debate about priority advantages. For the first time an attempt to synthesize element 103 was carried out in Berkeley in 1959–1961 (irradiating californium with boron ions). The researchers named the element Lawrencium (Lr) in honor of E. Lawrence, the inventor of cyclotron. However, as later stated by scientists from JINR, who dealt with a similar problem in the 1960s, there was no clear evidence of synthesis by the US counterparts. In 1965, a group of Soviet scientists under the leadership of G.N. Flerov reliably synthesized an element (in the process of bombarding americium with oxygen ions) and by its  $\alpha$ -decay identified the isotope with mass number 256<sup>16</sup>. As a result, in 1967, a group of FLNR researchers composed of: G.N. Flerov (laboratory director), I.I. Zvara, V.A. Druin and S.M. Polikanov, was awarded the Lenin Prize for synthesis and study of transuranic elements. Soviet researchers, however, could not defend the proposed name Rutherfordium (in honor of the Nobel laureate E. Rutherford, “the father of nuclear physics”, as he is often called) for the

element with  $Z=103$ . The International Union of Pure and Applied Chemistry (IUPAC) assigned the name of Lawrencium to the element.

**105 Db**  
Dubnium  
Дубний

In the USSR State Register of Discoveries, in 1964, an entry No. 37 was made, fixing the Soviet priority in detecting the 104<sup>th</sup> element<sup>17</sup>, for which the name of Kurchatovium was proposed (in honor of I.V. Kurchatov, the famous Soviet nuclear physicist). However, a few years later, the US competitors considered this discovery unproven, since they also synthesized the 104<sup>th</sup> element (Berkeley)<sup>18</sup>. The next round of “transfermium wars”<sup>19</sup> began, which also fell on the period of discovery of the 105<sup>th</sup> element. The latter was synthesized at JINR in 1969 by a group of researchers, which included: G.N. Flerov, Y.C. Oganessian, V.A. Druin, Yu.V. Lobanov et al. In 1970, the chemical and radioactive

<sup>16</sup> The Soviet achievement was recognized as a scientific discovery and entered into the USSR State Register of Discoveries under No 132 with a priority of April 20, 1965, in the following wording: “In experiment, a previously unknown element was formed with atomic number 103, the first isotope of which was synthesized by irradiation of americium-243 with ions of oxygen-18. It has a mass number of 256, a half-life of 35 s, and a complex energy spectrum of alpha-particles in the range of 8.3–8.6 mega-electron-volts” [20].

<sup>17</sup> The wording of the entry: “The phenomenon of generating an element with atomic number 104 was experimentally discovered in the process of irradiating a plutonium target with accelerated neon ions”. Authors: a group of researchers led by G.N. Flerov [20].

<sup>18</sup> In November 1969, at a conference in Texas, one of the members of the US group expressed doubts about the correctness of the data obtained by the Dubna group on the isotope with a mass of 260 for the 104<sup>th</sup> element.

<sup>19</sup> “Transfermium wars” is an established term for disputes between the US and Soviet scientists in the 1960–1990s on the priority in discovery of chemical elements beyond the 100<sup>th</sup> element.

properties of the new element were studied. Somewhat later, still in 1970, the element was obtained at Berkeley (when irradiating californium targets with nitrogen ions).

In the 1980s, IUPAC decided to resolve the issue of priority in the discovery of new elements. A joint decision with the International Union of Pure and Applied Physics created a working group of independent chemists and physicists to work out criteria for discovering new chemical elements and determining priorities in this area. As noted in [18], in 1995, the priority of Dubna in the discovery of elements with  $Z=102-105$  was recognized. In 1997, the 105<sup>th</sup> element was given the name “Dubnium” in recognition of the productive work by Dubna laboratory. In the same year, the aforementioned commission noted the great contribution of JINR to the detection of elements with  $Z=106-108$  (seaborgium, borium, meytnerium), although Berkeley (USA) and Darmstadt (Germany) scientific groups are generally recognized as their pioneers. Though analyzing the literature on this issue, one can see that there are still contradictions in assessing the contribution of various research teams to the discovery of elements with  $Z=102-105$  (for comparison we would redirect you to the well-known web resources of *Elementymology & Elements Multidict* at <http://elements.vanderkrogt.net/element.php?num=106>; or JINR at <http://www.jinr.ru/about/>; or the information presented in the popular encyclopedic publications [13]).

#### Achievements of research group headed by Yuri Oganessian: synthesis of superheavy elements from the 113<sup>th</sup> to the 118<sup>th</sup>

In 1974, in the town of Dubna, Yuri Oganessian proposed the method of “cold synthesis”, which has been successfully implemented by researchers in many countries to synthesize heavy elements, for almost 20 years. A prerequisite for this method is the use of “magic” nuclei  $^{208}\text{Pb}$  or  $^{209}\text{Bi}$ .

The method allows for advancing into the field of chemical elements with atomic numbers above 106. To proceed in this direction, a new cyclotron (U-400) was launched at JINR, which significantly expanded experimental capabilities of researchers both in terms of the “spectrum” of accelerated ions and in their physical characteristics. This method was used for the synthesis of elements with  $Z>106$  in Darmstadt and Dubna, in parallel. The JINR scientists directly participated in confirming an array of elements with atomic numbers above 106 (such as borium, copernicium, etc.).

However, it was a return to hot synthesis reactions using  $^{48}\text{Ca}$  ion as bombarding particles, that led Russian scientists to a number of impressive discoveries in the field of superheavy elements. Actinide isotopes (U, Np, Pu, Am, Cm, Cf) were used as the target material. The conducted experiments led to synthesis of six superheavy chemical elements in the region of  $Z=113-118$ , which completed the seventh period of Mendeleev’s Periodic Table. “In these studies,” the authors of these discoveries say, “...the properties of nuclear decay of more than 50 new isotopes of elements 104–118 with a large excess of neutrons were first obtained and determined. They have substantially replenished the chart of nuclides and expanded it to  $Z=118$ ... The results of synthesizing elements 112–118, obtained later in Dubna, were confirmed by GSI (GSI – Gesellschaft für Schwerionenforschung, Helmholtzzentrum für Schwerionenforschung GmbH) and LBNL (Lawrence Berkeley National Laboratory)” [21].

**$^{116}\text{Lv}$**   
Livermorium  
Ливерморий

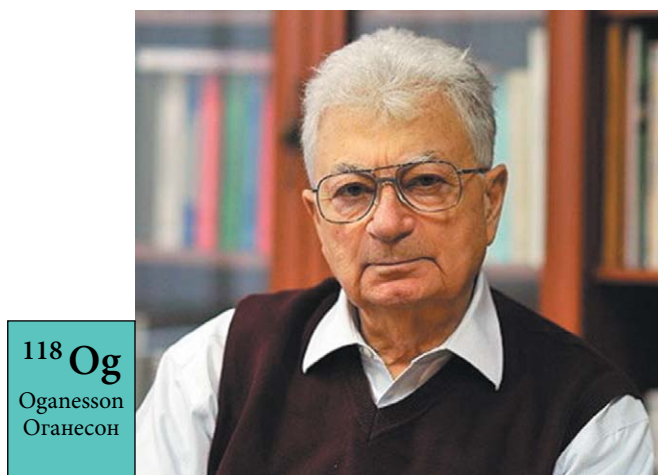
**$^{114}\text{Fl}$**   
Flerovium  
Флеровий

**$^{115}\text{Mc}$**   
Moscovium  
Московский

**$^{117}\text{Ts}$**   
Tennessine  
Теннессин

Based on the results of its work within a joint committee with the International Union of Theoretical and Applied Physics, IUPAC approved the priority for discovering elements with  $Z=114-118$  for Dubna. The 114<sup>th</sup> element Flerovium (Fl) and the 116<sup>th</sup> element Livermorium (Lv) were discovered, respectively, in 1999 and 2000 (JINR’s collaboration with Livermore National Laboratory, USA). Flerovium is named in memory of G.N. Flerov, the founder and long-time head of the JINR’s FLNR, which also bears his name. At the time, Georgy Flerov was a recognized leader in the field of synthesis of transuranic elements.

Livermorium was assigned its name in honor of the Lawrence Livermore National Laboratory, in collaboration with which the scientists from Dubna have fruitfully worked on synthesis of new elements for several decades. The 115<sup>th</sup> (2003) and 117<sup>th</sup> (2009) elements were synthesized according to IUPAC, thanks to the long-term cooperation of JINR scientists with two US laboratories, the aforementioned Liver-



**Fig. 8.** Yuri Tsolakovich Oganessian; the element with atomic number 118 is named after him.

more National Laboratory and Oak Ridge National Laboratory. Respectively, they received the names of: Moscovium for the 115<sup>th</sup> element (Mc), in honor of the Moscow region as a whole (the city of Moscow and the Moscow Region), it is where the studies were conducted on the synthesis of the element; and Tennessine for the 117<sup>th</sup> element (Ts), acknowledging the contribution of the state of Tennessee and several of its research laboratories, including Oak Ridge, into the study of superheavy elements. The 118th element, discovered in 2002, was named Oganesson and designated Og in honor of Yuri Oganessian, Scientific Director of JINR FLNR named after G.N. Flerov, for his innovations in the study of transactinoid elements (*Fig. 8*). The priority in discovery of this element was given to the collaboration of JINR and Livermore National Laboratory (USA). Oganesson became the second (after Seaborgium) element, named after a scientist of our day, who continues to work actively in science.

For several years, JINR researchers struggled for the recognition of their priority in obtaining the 113<sup>th</sup> element, which was actually registered for the first time in 2003 (in reaction of calcium-48 with americium-243). It was identified as a daughter product of the decay of an isotope of an element with  $Z=115$  and a mass of 288. The following was said on the JINR website on this occasion [22]: “A little later (in 2004), our colleagues from RIKEN (Japan), who make up the group headed by Professor K. Morita, carried out their first experiment on irradiating a bismuth-209 target with accelerated zinc-70 ions, wherewith the isotope of the 113<sup>th</sup> element with a mass of 278 and a lifetime of several milliseconds was registered. In general, the experiment lasted more than 10 years and a total of only 4 events of the synthesis of the new element have been recorded.

At the same time, about 100 events of element 113 formation have been recorded in Dubna through this period, and moreover, pioneering experiments were carried out to study its chemical properties. The fact of synthesis of isotope 113 with a mass of 284 was confirmed by the GSI (Germany) and Berkeley (USA)... We are happy for our colleagues from RIKEN, in particular because the supervisor of their studies, Professor K. Morita, to a certain extent is a coachee of Dubna... However, the method for synthesizing SHE, chosen by RIKEN scientists, has been completely played out”. Nevertheless, IUPAC in its press release dated by December 30, 2015, finally stated that the discovery of this element (nihonium) was recognized as achievement by the collaboration of the RIKEN Institute (Japan).

The JINR people see the prospect of further research on the synthesis of new elements with the creation at FLNR of the world’s first Superheavy Elements Factory (SHE Factory), based on the new heavy ion accelerator – the DC-280 cyclotron, launched in April 2019, which in terms of intensity outperforms any other similar facility in the world. This will allow for the soonest start of synthesizing new elements with atomic numbers 119, 120 and onwards, which will belong to the 8<sup>th</sup> period of the Periodic Table.

Indeed, the synthesis of elements 114–118 at the boundary of Mendeleev’s Table has substantially changed the ideas of scientific community about the limits of material space, becoming the first experimental confirmation of the existence of “stability islands” in the segment of superheavy elements. The studies carried out are of fundamental importance not only for nuclear physics, but for chemistry as well. They have provided yet another confirmation of Mendeleev’s fundamental Law of Periodicity in Chemical Elements and its prognostic capabilities.

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# Stars from Cradle to Grave: Powerful Factories of Chemical Elements

Alexander A. Lutovinov

The first elements of the Periodic Table – hydrogen, helium and partly lithium – appeared in the first seconds after the birth of the Universe. The first stars “gathered” from these materials are the natural factories of the synthesis of heavier elements, not only throughout their lives, but even during their death process, during Supernova explosions. Supernova explosions, in their turn, are powerful factories for the production of heavy elements. Modern instruments allow scientists not only to register such events, but also to determine how many different chemical elements were formed during such events. The recent discovery of the merging neutron stars and subsequent studies of their afterglow allowed us to clarify the process of formation of superheavy elements in the Universe up to the gold and uranium. Thus, astrophysical observations give scientists the most important information about the “production rates” of elements in the nature, and their abundance in the Universe.

**Keywords:** stars, evolution, thermonuclear reaction, supernova, merging of neutron stars.

...We are made of star stuff.

Carl Sagan, astrophysicist

## Formation of chemical elements in stars

$^1\text{H}$   
Hydrogen  
Водород  
1.008

$^2\text{He}$   
Helium  
Гелий  
4.0026

Immediately after the Big Bang, about 14 billion years ago, there were neither stars nor galaxies in the Universe. In order for the first space objects to form, the hot gas needed to cool down. This process took several hundred million years before the very first stars broke out in the Universe, which at that time consisted only of hydrogen and helium. Heavier elements have not yet formed. According to our ideas about the chemical processes occurring in gas, and the mechanisms of its cooling, the first stars should have been very massive. Recent calculations show that they could have a mass that is a hundred times the mass of the Sun. Take it for consideration that most modern stars are low mass objects with masses comparable to or less than solar. Stars light up as a result of nuclear fusion taking place in their depths. That it is the source of energy that supports their enormous luminosity. In the very first, longest phase of hydrogen combustion, helium is formed. As a result of a nuclear reaction, four protons (or hydrogen nuclei) merge to form a helium nucleus. In the subsequent burning stage, which constitutes only the last ten percent of the life of a star, the two helium nuclei (“ $\alpha$  particles”) turn into beryllium, which then captures another  $\alpha$  particle, turning into carbon in

the so-called triple  $\alpha$ -process. Through additional captures of  $\alpha$ -particles, carbon nuclei are converted into oxygen. Thus, resulting from nucleosynthesis processes, all elements of the Periodic Table are created, up to iron [1, 2].

Fusion of lighter elements into heavier ones leads to conversion of a small amount of mass into energy. For example, a helium nucleus is 0.7 percent lighter than four separate hydrogen nuclei. It is this difference in mass according to the Einstein’s law  $E = mc^2$  that maintains the luminosity of a star for a long period of time. However, as soon as an iron core is formed in the center of the star, its nucleosynthesis stops, since iron has the highest binding energy in terms of one nucleon. It becomes impossible to obtain energy through further nuclear reactions, and, thus, the star loses the source of energy necessary for its existence. As a result, the star can no longer maintain a state of equilibrium and begins to implode under its own gravity. Due to enormous pressure



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arising, the iron core turns into an extremely dense neutron star (for more details see below), and the star itself collapses, which is accompanied with a giant supernova outbreak. Such was the fate of the very first massive stars, and such is the fate of the massive stars in our day.

Maintaining the enormous luminosity of massive stars – tens or hundreds of solar masses – requires a significant amount of nuclear energy. Hydrogen burns out inside them much faster than in “lighter” stars. This is why their lifetime is limited to only a few millions or tens of millions of years, while the life of low-mass stars lasts billions of years. During a supernova explosion, all of the formed elements fall into the interstellar medium. The death of the first generation of stars became an important milestone in the evolution of the Universe, leading to its “contamination” with carbon, oxygen, nitrogen, iron and other elements. Thus, over time, the Universe has been increasingly enriched with elements heavier than hydrogen and helium, which astronomers call “metals.” All the stars in subsequent generations were formed from gas clouds containing metals, which were obtained from at least one generation of stars exploding in the form of supernovae. The appearance of metals in the early Universe changed the conditions for the subsequent star formation. Clouds of gas began to cool more efficiently in the presence of metals or dust, which allowed for the collapse of smaller clouds and, consequently, for the formation of smaller stars.

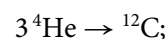
At the earliest stages of the Universe, massive stars exploding in the form of supernovae dominated the production of iron in the Universe. However, the situation has changed in about a billion years. Due to formation of stars with lower masses and a longer lifetime, a different way of iron production had occurred. At the end of their long life, stars with low mass turn into white dwarfs (objects consisting almost entirely of carbon with a small

admixture of oxygen and, possibly, neon, having a radius of several thousand kilometers and the maximum possible mass of 1.4 solar masses – the so-called Chandrasekhar limit). If a regular star and a white dwarf are in a binary system and there is sufficient flow of material from the star to the white dwarf, then the mass of the latter may at some point exceed the Chandrasekhar limit, which will lead to a collapse of the white dwarf and a thermonuclear explosion. A supernova of type Ia will flare up. Considering the predominance of low-mass stars in the modern universe, it is believed that iron is mainly produced via this process, rather than in explosion of massive stars as it was in the early Universe (see below for more details on registering supernova explosions and finding out the abundance of produced elements). Schematically, the evolution of stars with different masses is shown in *Fig. 1*.

As mentioned above, all elements, including iron, are created in nuclear fusion during the life of stars.

As an example, the following helium combustion reactions may be described:

– Three atoms of helium merging to form an atom of carbon:



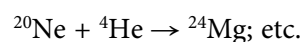
– One atom of carbon and one atom of helium merging to form an oxygen atom:



– One atom of oxygen and one atom of helium merging to form a neon atom:

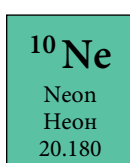
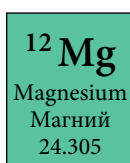
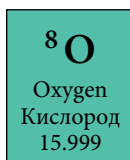
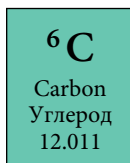
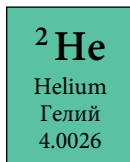


– One atom of neon and one atom of helium merging to form a magnesium atom:



But these elements (with atomic number  $Z < 30$ ) make up less than one third of the Periodic Table. Where do other elements with higher atomic masses come from, such as silver ( $Z=47$ ) and gold ( $Z=79$ ), or more exotic rare-earth elements, such as lanthanum ( $Z=57$ ) and europium ( $Z=63$ )?

As we know today from nuclear physics, elements heavier than iron are not created through synthesis processes, but through capturing of neutrons by seed nuclei (for example, iron nuclei). However, it is known that the neutron is unstable and subject to so-called  $\beta$ -decay ( $\beta$ -decay is a spontaneous decay converting one element to another while changing a neutron into a proton, which is accompanied with emission of an electron and antineutrino), therefore it is impossible to form a new



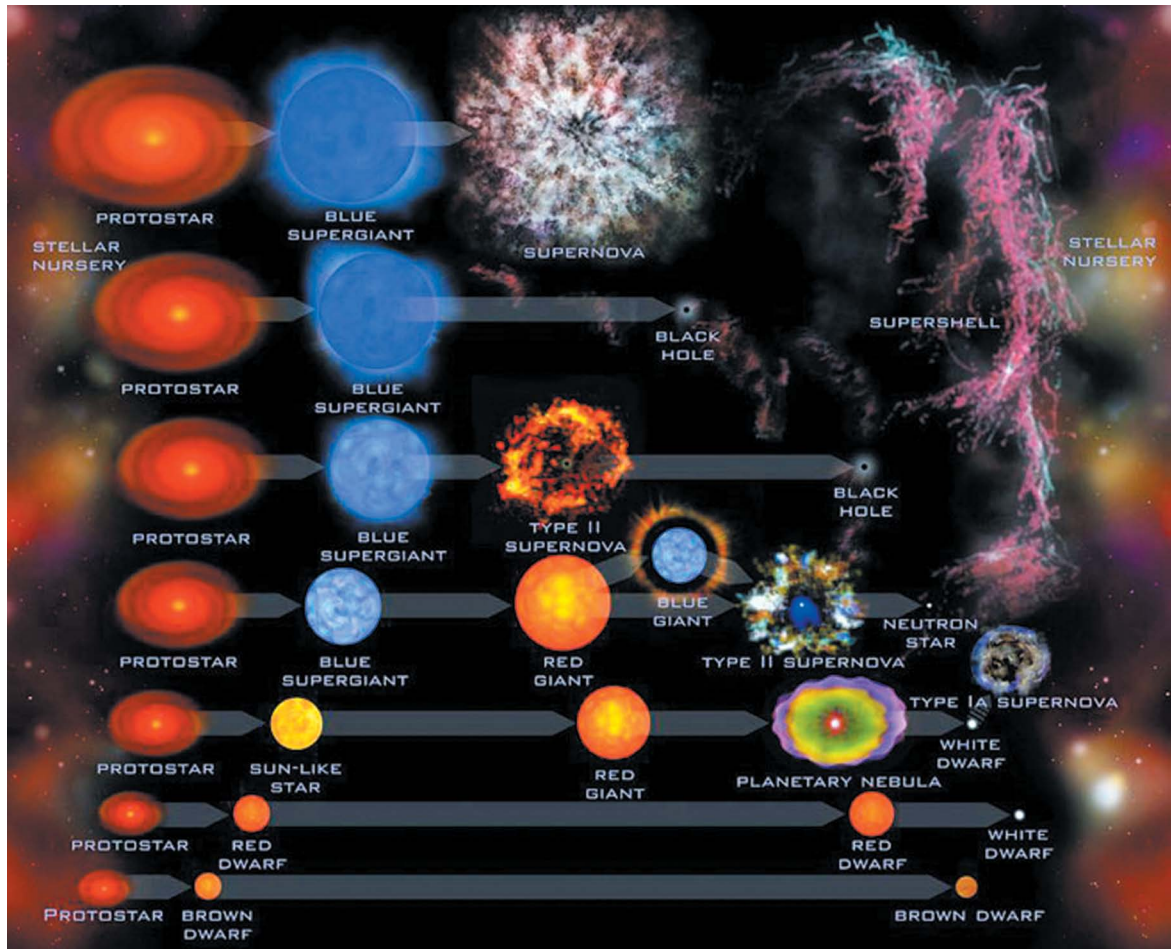


Fig. 1. Different stages of the stars evolution depending on their initial masses. (Credit: NASA / CXC / M. Weiss).

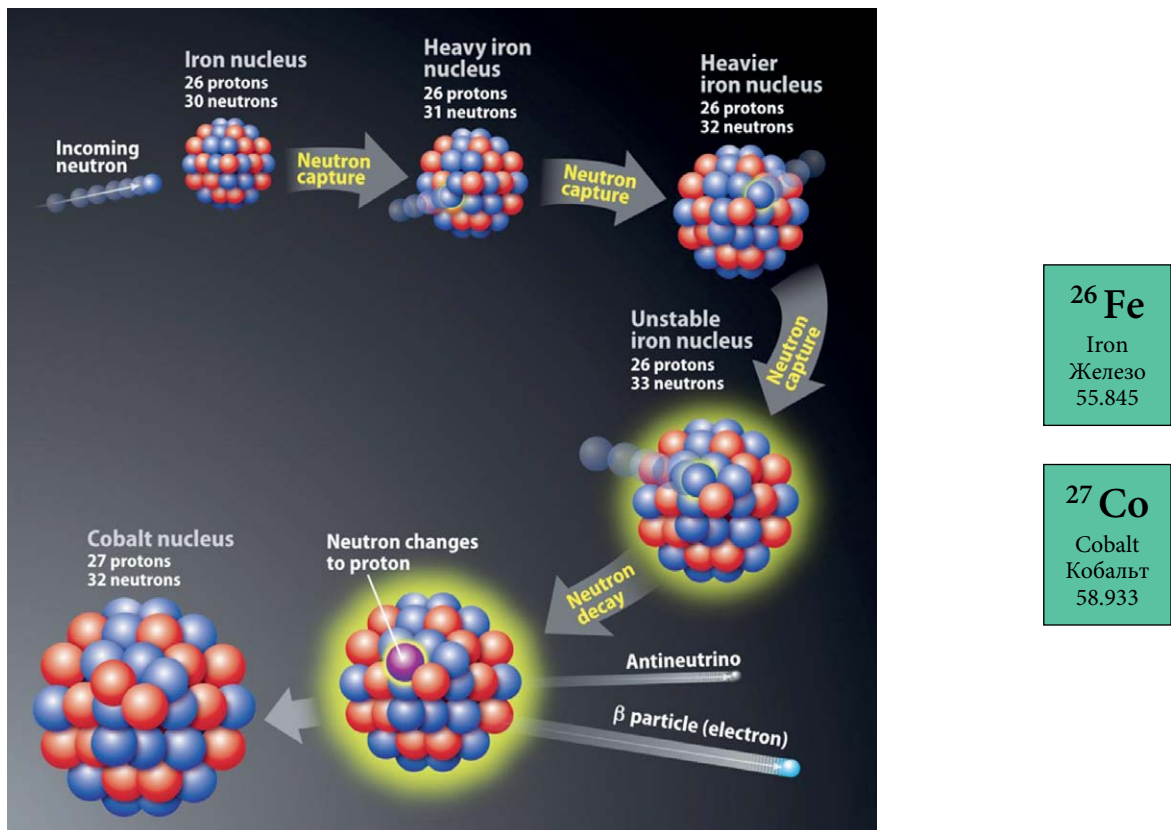


Fig. 2. The forming of a stable cobalt isotope from an iron by a few neutrons capture. (Credit: Astronomy Magazine).



nucleus and a new element through capturing a sole neutron. Nevertheless, if the medium is extremely rich with neutrons, the seed nucleus may have time to capture several neutrons before they disintegrate, and then the formation of a new stable nucleus with a large atomic number is possible.

It is believed that such conditions can occur in certain types of supernova explosions. For example, if iron nuclei are extremely rapidly bombarded with a large number of neutrons before the  $\beta$ -decay of nuclei, their nuclei capture more neutrons, creating heavy neutron-rich and unstable isotopes, which then turn into new and heavier elements. Because of the rapid bombardment this process is called the *r*-process. Approximately half of all stable isotopes of elements heavier than zinc are produced in this way. *Fig. 2* shows an example of the formation of a stable cobalt isotope from an atom of iron.

Another part of the isotopes of heavy elements is created in the so-called *s*-process, where slower neutron bombardment (taking longer time than the  $\beta$ -decay process) leads to consistent accumulation of heavy elements. This process occurs in the pulsating outer shells of stars – red giants with masses less than eight solar masses and high metallicity  $[Fe/H] > -3.0$  [2]. The latter indicates that the star was formed from a gas that already contained a small amount of iron atoms, which can play the role of seed nuclei. Thanks to the stellar wind, these elements end up in the interstellar medium.

Further we will describe exemplary observations of supernova explosions and fusions of neutron stars to show how nucleosynthesis of heavy elements in space is registered.

### Observations of supernovae in $\gamma$ -rays – direct quantitative measurements of the produced elements

Supernova explosion is the final stage of the star's existence, in which its core collapses under its own weight, and the energy released as a result of the collapse sweeps the

outer shell away in space, thereby throwing out the elements synthesized during the life of a star. It were supernovae that enriched the interstellar medium with silicon, calcium, iron and other elements thus making possible future formation of terrestrial planets and the birth of life. However, despite the much indirect evidence, we don't have much direct data in support of this concept. Among the most convincing are the registrations of optical, X-ray and  $\gamma$ -radiation from the radioactive decay of cobalt  $^{56}\text{Co}$  to iron  $^{56}\text{Fe}$  iron in the remnant of Supernova SN1987A in the Large Magellanic Cloud, the light of which reached the Earth 32 years ago, in 1987. It happened to be the only one close to us (160 thousand light years away) and bright supernova observed by mankind over the past 450 years. The observations of this Supernova became a priority in the early program of the Soviet X-ray Observatory ROENTGEN launched into orbit in March of the same year and mounted on the KVANT module of the MIR orbital station. The fact is that the shell formed by the explosion of a star with a total mass of more than 15 solar masses at first is so dense that it completely retains the X-rays. Next, since the shell scatters in all directions with enormous speeds, it gradually becomes transparent for X-rays and  $\gamma$ -rays. After the explosion, a decay chain occurs: the formed nickel turns into cobalt, which then decomposes into iron ( $^{56}\text{Ni} \rightarrow ^{56}\text{Co} \rightarrow ^{56}\text{Fe}$ ). As shown by theoretical calculations,  $\gamma$ -radiation caused by the decay of radioactive cobalt  $^{56}\text{Co}$  formed during the explosion should penetrate the expanding shell approximately six months after the explosion. On August 10, 1987, the instruments of the observatory first recorded hard x-rays from the Supernova region. It was a good proof of the idea that the radiation actually comes from the Supernova, and the measurement of its spectrum in a wide energy range (*Fig. 3*, [3]) was performed with high accuracy, which confirmed the earlier theoretical calculations. For the first time the available observational data had provided for the estimates of radioactive nickel and cobalt amounts produced during an outbreak of a supernova.

Twenty five years later, Supernova SN1987A again presented the Russian scientists with a discovery. This time, it was possible to register radiation in the decay lines of radioactive titanium  $^{44}\text{Ti}$  from the remnant of a supernova flare. It is believed that the decay of radioactive  $^{44}\text{Ti}$  gives energy for infrared, optical and ultraviolet radiation of supernova remnant after complete

**<sup>14</sup>Si**

Silicon  
Кремний  
28.085

**<sup>20</sup>Ca**

Calcium  
Кальций  
40.078

**<sup>28</sup>Ni**

Nickel  
Никель  
58.693

**<sup>27</sup>Co**

Cobalt  
Кобальт  
58.933

**<sup>26</sup>Fe**

Iron  
Железо  
55.845

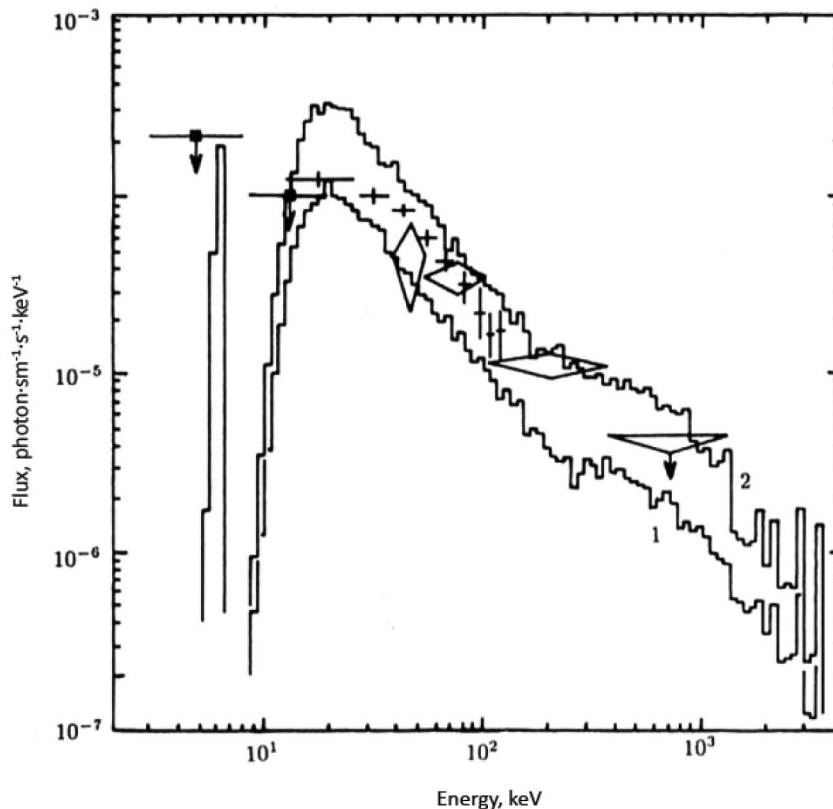
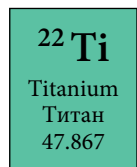


Fig. 3. Spectrum of the Supernova SN1987A observed by the ROENTGEN Observatory (crosses, rhombuses). Histogram shows the results of theoretical predictions [3].

decay of radioactive  $^{56}\text{Co}$  and  $^{57}\text{Co}$  (isotopes providing energy for the remainder of the star in the first three to four years after the explosion) and before the flying away shell fragments start active interaction with the environment.



The result was obtained on the basis of superlong observations of the Large Magellanic Cloud by the INTEGRAL orbital observatory in 2003–2011 with a total exposure of more than six million seconds, which made it possible to register hard X-rays from this residue in the  $^{44}\text{Ti}$  radioactive decay lines at energies of

67.9 and 78.4 keV (Fig. 4, [4]). This was the first direct evidence of titanium production at the time of the explosion of this unique Supernova. The measured radiation fluxes at these energies correspond to the mass of the synthesized  $^{44}\text{Ti}$ , equal to about 0.0002 solar masses, quite sufficient to explain its optical and ultraviolet radiation, observed during the last 20 years. Moreover, titanium  $^{44}\text{Ti}$  decaying with a half-life of 59 years into radioactive

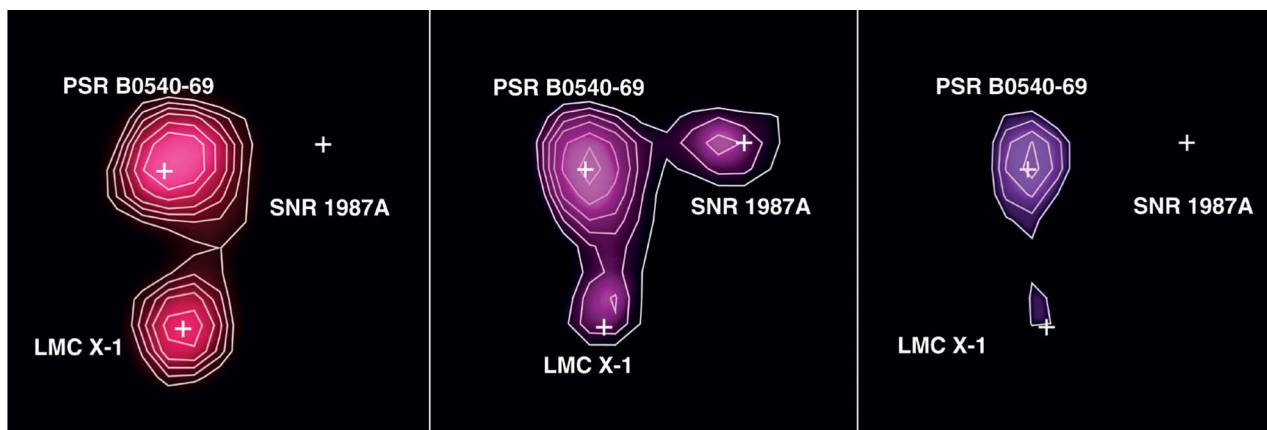
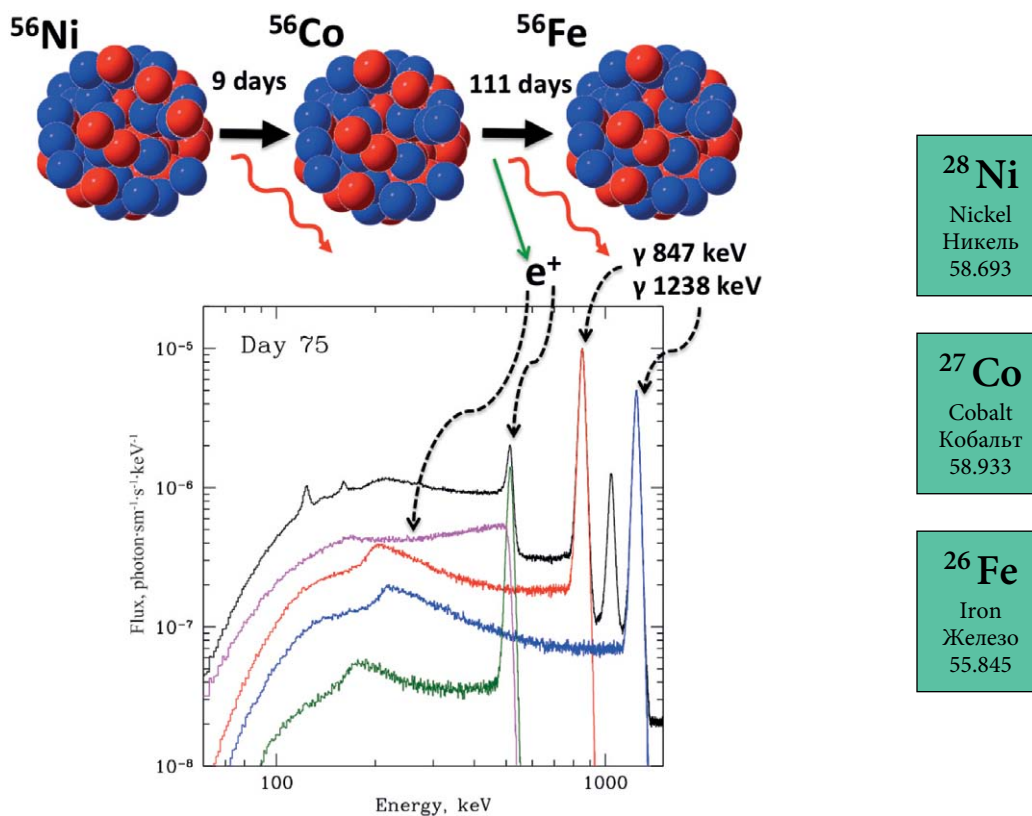


Fig. 4. Images of the sky patch containing the Supernova SN1987A remnant, obtained by the INTEGRAL observatory in different energy ranges. The middle picture corresponds to the energy range of 65–82 keV, which includes both decay lines of radioactive titanium  $^{44}\text{Ti}$  ([4] and ESA site data).



**Fig. 5.** Scheme of the radioactive nickel  $^{56}\text{Ni}$  decay into cobalt  $^{56}\text{Co}$  and further into iron  $^{56}\text{Fe}$ , indicating the energy of the brightest  $\gamma$ -ray lines and characteristic half-lives. (Credit: IKI / E. Churazov, see also [5]).

scandium  $^{44}\text{Sc}$ , and then almost instantaneously into ordinary calcium  $^{44}\text{Ca}$ , will stay active for a long time in this largest for the local universe active dead zone of thermonuclear explosion remnants. It will keep providing powerful radiation in a wide range of electromagnetic spectrum [4].

Supernova SN1987A belonged to the so-called type II supernovae (formed as a result of collapse of a massive star that had highly evolved prior to its collapse). Many heavy elements were formed in its depths as a result of thermonuclear burning reactions. Yet, for type Ia supernovae the situation was not so obvious until the recent time.

As noted above, it is believed that Type Ia supernovae are the result of a thermonuclear explosion of a carbon-oxygen white dwarf, during which a large amount of radioactive nickel  $^{56}\text{Ni}$  is synthesized. After the explosion, the same decay chain occurs as described above for the collapse of a massive star: radioactive nickel turns into cobalt  $^{56}\text{Co}$ , which then disinte-

grates into iron, during which numerous  $\gamma$ -photons are born. They interact with the expanding supernova envelope, heat it and provide powerful optical glow of the envelope. The diagram of the nickel decomposition into cobalt and further into iron, with indications of energy of the brightest  $\gamma$ -lines and the characteristic half-lives is shown in Fig. 5.

It is the brightness and predictable behavior of the optical light curves that awarded Type Ia supernovae with the name of “standard candles”, which are used to calculate distances between objects in the Universe.

Yet, with the hundreds of such supernovae already discovered in different galaxies, their  $\gamma$ -radiation has never been registered. For the while being, researchers are left to deal only with optical radiation – which is the result of processing  $\gamma$ -rays from the outer layers of scattering shell. For the entire space age, that is more than half a century, not a single explosion of type Ia supernova occurred in any of the galaxies nearest to us. And finally, this happens in January 2014, in the form of Supernova SN2014J in Galaxy M82.

It was close enough (11 mln light years) for orbital observatory INTEGRAL to be able to directly detect radiation in the two brightest  $\gamma$ -lines and fully confirm the theoretical concept of type Ia supernovae as giant thermonuclear explosions.

The significance of this event comes not only from confirmation of theoretical predictions. Despite the

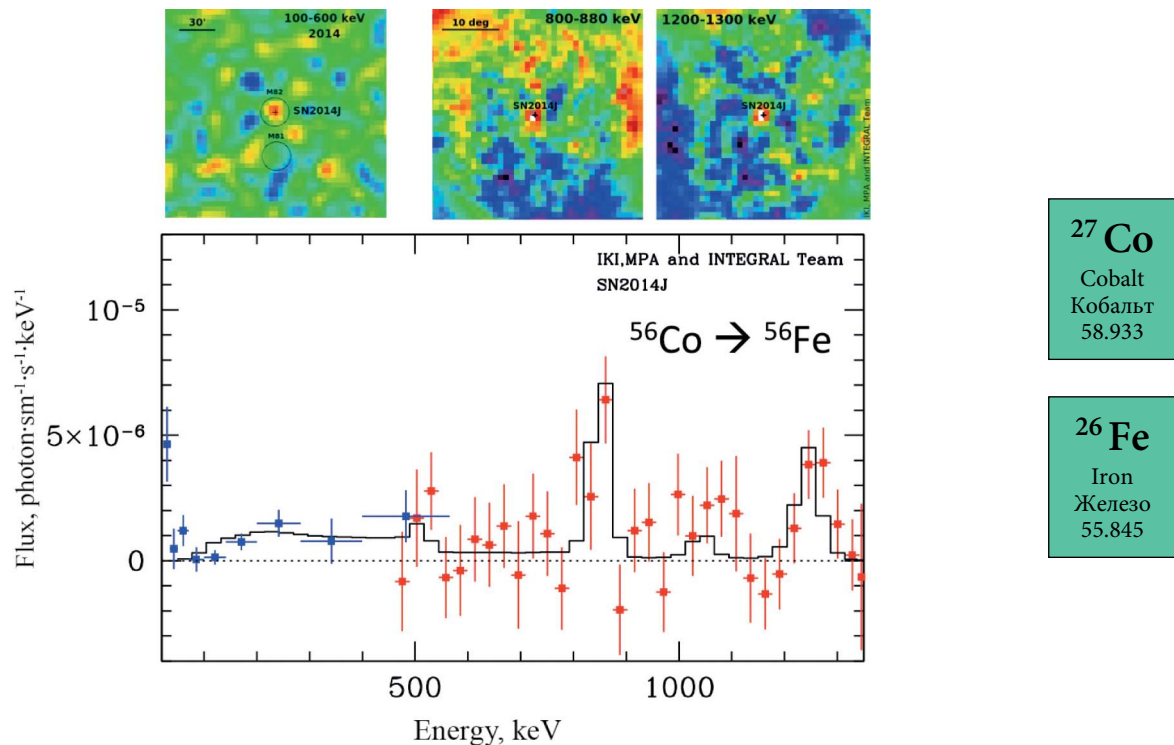


Fig. 6. Observations of SN2014J Supernova obtained by the INTEGRAL observatory. (Credit: IKI / E. Churazov, see also [5]).

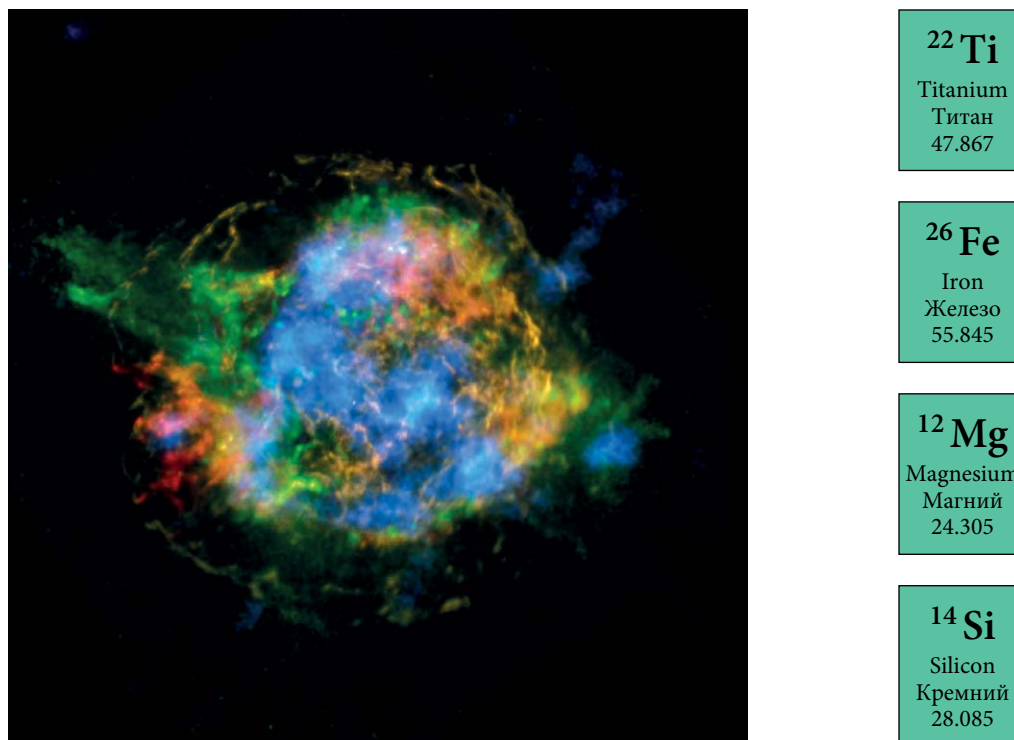
long history of observations and numerical experiments, the detailed physics of type Ia supernova explosions and the evolution of a compact progenitor star before the explosion remains a matter of debate. After the explosion,  $\gamma$ -photons generated by the decay of nickel and cobalt spread through the shell substance and lose their energy as a result of Compton scattering and recoil effect. Nickel  $^{56}\text{Ni}$  decomposes into cobalt  $^{56}\text{Co}$  in just ten days. At this time, the supernova substance is still opaque to  $\gamma$ -quanta, and only the radiation of radioactive nickel located in the outer part of the flying shell, has a chance to go beyond its limits. The subsequent decomposition of cobalt  $^{56}\text{Co}$  into iron  $^{56}\text{Fe}$  takes much longer ( $\sim 111$  days), and by the time the expanding envelope becomes almost transparent, cobalt  $^{56}\text{Co}$  dominates, turning type Ia supernova into a long-lived source of  $\gamma$ -lines of cobalt [5].

The observations carried out by INTEGRAL between the 50<sup>th</sup> and 100<sup>th</sup> days since the explosion was detected, reliably recorded radiation in two of the most powerful  $\gamma$ -decay lines of radioactive cobalt  $^{56}\text{Co}$  at energies 847 and 1237 keV, as well as a continuum of energy of hundreds of keV (Fig. 6). The recorded flux indicates that radioactive nickel in the process of thermonuclear explosion of the star was synthesized in quantity of around 0.6 solar masses. The observed width of the lines indicates that the characteristic velocity of the supernova matter is about 10,000 km/s. All these parameters are in good agreement with the predictions of the simplest scenarios for the evolution of a white dwarf:

explosion occurs as a result of gradual increase in its mass up to the Chandrasekhar limit of 1.4 solar masses [5]. However, the scenario of two merging white dwarfs should neither be left out of consideration.

Modern tools not only allow to register the processes of new elements production during supernova explosions and to determine their abundance, but also to build maps of different elements distribution in the relics of such outbreaks. This allows one to look at a time period of hundreds of years ago, and understand the mechanisms of the explosions and estimate the number of chemical elements produced.

Figure 7 shows the image of the flash remnant of Supernova Cas A, which is essentially an expanding cloud of hot gas formed by the explosion of a massive star that occurred at a distance of about 11,000 light years from Earth. The image is a combination of X-rays taken by the Chandra Observatory in the energy range from 1 to 7 keV, and high-energy X-rays produced as a result of the decay of radioactive titanium  $^{44}\text{Ti}$ , recorded by the NuSTAR Observatory in the energy range from



*Fig. 7. Spatial distribution of different chemical elements in the Cas A Supernova remnant, determined on the base of the Chandra and NuSTAR observatories data. Emission of radioactive titanium  $^{44}\text{Ti}$  is shown in blue, the distribution of the iron is shown in red, green color corresponds to silicon and magnesium. (Courtesy NASA / JPL-Caltech, see also [6]).*

68 to 78 keV [6]. The emission of radioactive titanium is shown in blue (according to estimates it was formed in an amount equal to 0.00012–0.00016 of solar mass), the red color shows the distribution of iron formed, green – silicon and magnesium; yellow color – radiation of a soft x-ray continuum. Observations of the NuSTAR Observatory point to the asymmetry of the explosion and provide new data for further development of the theory of supernova explosions [6].

#### **Neutron star fusions as main sources of elements heavier than iron in the Universe**

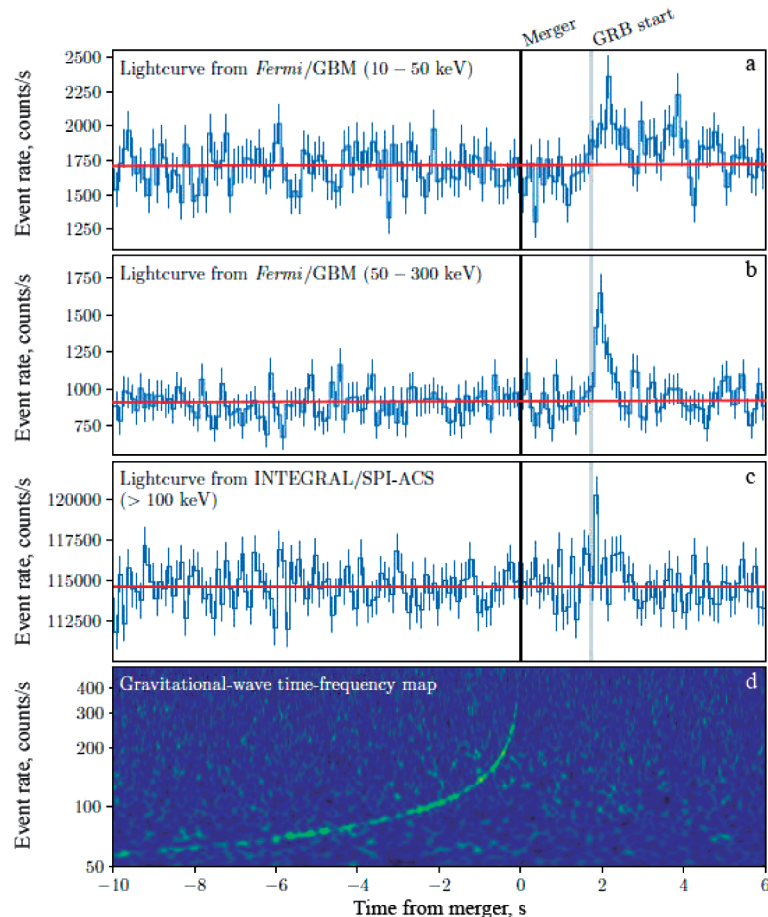
As mentioned earlier, for a long time it was believed that elements heavier than iron are formed only during supernova explosions. However, data from recent years have shown that the observed rate of such outbreaks is not sufficient to explain the observed abundance of heavy elements. Then it was suggested that a significant amount of heavy elements could be born during mergers of neutron stars [7]. Such fusions would have to be accompanied

by the most powerful gamma-ray energy emissions, the so-called short  $\gamma$ -bursts lasting 1–2 seconds.

Neutron stars are in the list of the possible end products of massive stars evolution (Fig. 1), when a supernova does not completely collapse after a flash, and in addition to the matter thrown into space, as discussed above, a compact object remains as the supernova remnant – a black hole or a neutron star.

A neutron star is an extremely compact and dense object: the measured masses for a large number of neutron stars fall within the range of 1–2 masses of the Sun, their radii are only 10–13 km, and density in the center of a neutron star is several times higher than the nuclear density. The exact equation for matter under such extreme conditions is unknown, and it is believed that the neutron star is held back from further collapse by the pressure of degenerate neutron gas. The upper mass limit of a neutron star is estimated at 2–3 times the mass of the Sun, depending on the equation of state. Above this limit, the neutron star collapses into a black hole.

If the system does not collapse during the evolution of a massive binary system and successive outbreaks of supernovae, then two neutron stars might emerge which rotate around each other. In so doing, they will gradually come closer, losing energy in the form of irradiated gravitational waves [8]. Such a system can exist for hundreds of millions of years until the stars come together so close that under the action of gravity and tidal forces



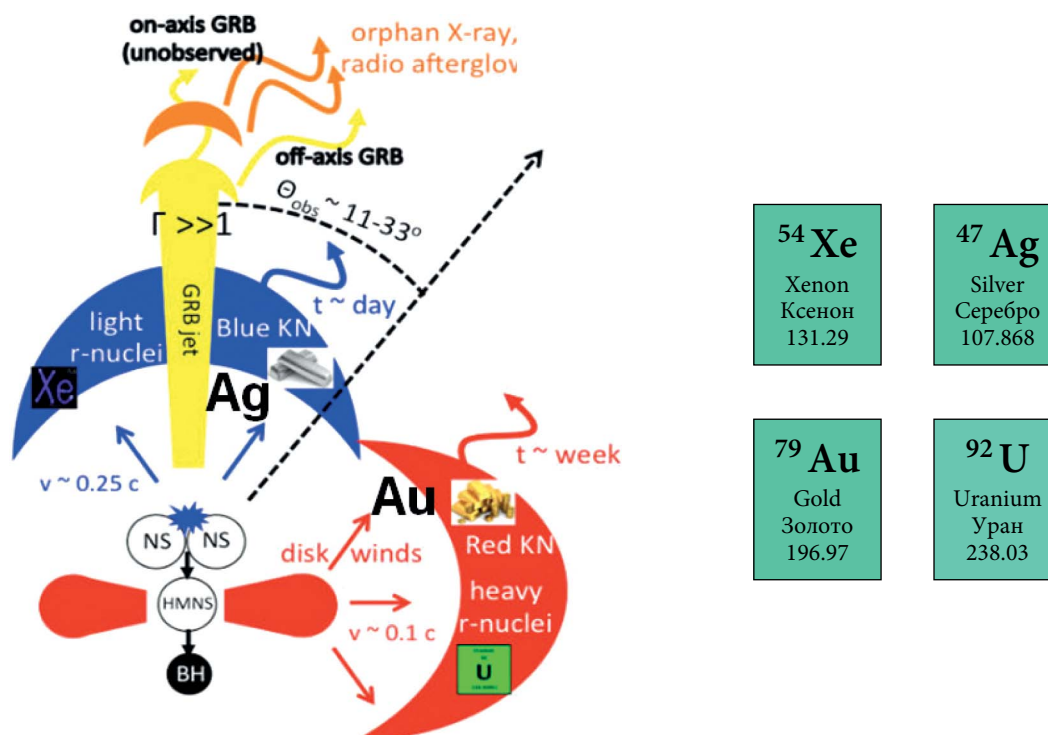
**Fig. 8.** Joint registration of the GW170817 gravitational-wave event and the simultaneous emission of a short  $\gamma$ -ray burst. The plots a and b demonstrate the data of the Fermi observatory, the plot c presents the INTEGRAL observatory data. The gravitational-wave signal obtained by the LIGO observatory is shown on the plot d. The black vertical line is the moment of neutron stars merging; the gray line is the moment of the  $\gamma$ -ray burst [10].

they begin to collapse and the merging process starts, which is accompanied with a flash of gravitational-wave irradiation and a short  $\gamma$ -burst. Proceeding from the expected sensitivity of future instruments and anticipated rarity of neutron star fusions, most scientists believed that such an event could not be registered very soon, and for quite a long time these studies were theoretical.

Everything changed on August 17, 2017, when scientists for the first time could observe the moment of two neutron stars merger. Initially, the gravitational wave signal was registered by the LIGO (USA)/Virgo (Italy) installations, which are three ground-based interferometers for recording such events. In  $\sim 1.7$  seconds after that, the INTEGRAL (ESA) and Fermi (NASA) orbital observatories detected a short  $\gamma$ -burst (Fig. 8, [9, 10]). Almost immediately it became clear that both signals are different manifestations of the same event associated with the collision of two neutron stars. Less than 12 hours after that, optical telescopes discovered a new object on the edge of the NGC4993 galaxy close to us and found that the neutron star fusion event occurred at a distance of about 130 million light years from us. The subsequent afterglow observation campaign from

this source was attended by hundreds of telescopes and thousands of researchers [11], and this was perhaps the most unique of all observation campaigns when research and data processing were carried out literally on the fly with immediate information from colleagues.

Theoretical calculations and computer simulations showed that during such a merger, a minor part of the neutron star matter would be thrown into the surrounding space. The models predicted that due to enormous concentration of neutrons, heavy elements will be synthesized in this cloud of ejected matter, and radioactive glow will be 10 million times brighter than the Sun. This phenomenon was called “kilonova” (derived from “supernova”). The observations had thoroughly confirmed this hypothesis, which allowed one to correctly interpret the data and



**Fig. 9.** A schematic representation of the process of neutron stars merging with the subsequent formation of two ejecta of matter in the form of red and blue kilonova. According to modern concepts, the formation of heavy elements (up to gold and uranium) occurs in these ejecta as a result of neutron capture processes [12].

determine the presence of heavy elements in the fragments of the merger. For example, observations made by the largest world observatories, such as the Gemini (USA), the European Very Large Telescope (VLT) and the Hubble Space Telescope (HST) showed the presence of newly synthesized material, including gold and platinum, as well as radioactive elements such as uranium, thereby giving an answer to the riddle of many decades: in what way about half of all elements heavier than iron are produced in space (Fig. 9).

In April 2019, the LIGO/Virgo observatories began a new cycle of searching and observing gravitational-wave events associated with the mergers of black holes and neutron stars. Space observatories and many ground-based telescopes read from the data stream of the LIGO/Virgo almost in online mode, in order to immediately search for an electromagnetic signal, identify a possible object and continue to study the processes of elements formation in the Universe.

The review has also benefited from materials and illustrations from web-sites of NASA, ESA, LIGO/Virgo, Caltech, Russian Space Research Institute (IKI RAS).

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# Synthesis and Study of the New Superheavy Elements of D.I. Mendeleev Periodic Table of the Elements

*Yuri Ts. Oganessian*

In the sixties of the XX century, the possibility of existence of the region of increased stability of superheavy nuclei in the vicinity of  $Z \approx 114$  and  $N \approx 184$  was proved. For the first time a successful synthesis of superheavy elements was carried out in the Flerov Laboratory of Nuclear Reactions of the Joint Institute for Nuclear Research (JINR). Superheavy elements of D.I. Mendeleev Periodic Table of the Elements with atomic numbers 114–118 were synthesized in the fusion reactions of the nuclei of the transuranic elements with calcium-48 nuclei. The article deals with the choice of reactions for the synthesis of new elements, methods of studying their nuclear-physical and chemical properties. The experimental complex “Factory of superheavy elements” created in JINR and prospects of further research development are described.

**Keywords:** D.I. Mendeleev Periodic Table of the Elements, superheavy elements, heavy ion accelerators, separators of nuclear reaction products.

Since the discovery of the first trans-uranium element – neptunium (Np) – in 1940, and over the next 60 years of the twentieth century, 20 new chemical elements have been synthesized. Two of them, elements with ordinal numbers 102 and 105, were first obtained at Joint Institute for Nuclear Research (JINR), and the physicists of Dubna made a decisive contribution to the discovery of elements with numbers 103, 104, and 108 [1].

Thanks to the data accumulated and the new ideas about the properties of the heaviest nuclides, JINR scientists in 1966 laid grounds for suggesting the existence of an area of increased stability of super-heavy nuclei in the region of charge number  $Z \approx 114$  and the number of neutrons  $N \approx 184$  [2].

The problem of the existence of super-heavy elements (SHE) certainly belongs to the most fundamental problems of natural science and affects a wide range of scientific fields. First of all, these are problems of nuclear physics: the issue of stability limits for nuclear matter. Another set of problems is associated with the properties

of super-heavy atoms – the manifestation of relativistic effects in the chemical properties of elements.

The JINR’s Laboratory of Nuclear Reactions was the first to carry out successful synthesis of super-heavy elements. Fusion reactions of nuclei of artificial elements heavier than uranium with the nuclei of calcium isotope with an atomic mass of 48 were performed to synthesize five new super-heavy elements of Mendeleev’s Periodic Table with serial numbers from 114 to 118.

114 Fl Flerovium Флеровий	115 Mc Moscovium Московский	116 Lv Livermorium Ливерморий	117 Ts Tennessee Теннесси	118 Og Oganesson Оганесон
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The International Union of Pure and Applied Chemistry (IUPAC) has officially approved the names and symbols for new elements [3, 4]: Flerovium (Fl) for the 114<sup>th</sup> element; Moscovium (Mc) for the 115<sup>th</sup> element; Livermorium (Lv) for the 116<sup>th</sup> element; Tennessine (Ts) for the 117<sup>th</sup> element; and Oganesson (Og) for the 118<sup>th</sup> element.

## The foundations of the Universe

The Periodic Table of Dmitry Mendeleev (1869), which revealed a pattern in the chemical behavior of the 63 elements known by that time, showed that an atom (an element) is not indivisible, since it also has an internal structure underlying this pattern. Indeed,



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28 years later, J.J. Thomson discovered smallest negatively charged particles – electrons in atom (1897). Another 14 years later, Ernst Rutherford proposed his famous planetary model of atom (1911) in the form of a dense nucleus carrying almost all the mass and the entire positive charge of an atom, and electrons moving around the nucleus at a great distance. In the first theoretical model (G.A. Gamov, 1928), the atomic nucleus was considered as a spherical uniformly charged drop of special matter resembling a liquid. The model was very productive. Based on it, Gamov himself constructed the theory of  $\alpha$ -decay (1928); the author of the well-known semi-empirical mass formula K.F. von Weizsäcker calculated the binding energy of protons and neutrons in nuclei (1936); N. Bohr and J.A. Wheeler [5] developed the liquid-drop model of nuclear fission (1939).

### Structure and stability of the heaviest nuclei

According to the theory proposed by N. Bohr and J.A. Wheeler, a heavy nucleus is prevented from disintegrating into fragments thanks to a potential barrier. The height of the fission barrier for the  $^{238}\text{U}$  nucleus is 6 MeV. The partial period of spontaneous fission for this nucleus is  $T_{\text{SF}}=10^{16}$  years (G.N. Flerov and K.A. Petrzhak, 1940 [6]). For nuclei heavier than uranium, an increase in the nuclear charge leads to a decrease in the fission barrier and to a significant decrease in the  $T_{\text{SF}}$ . With the disappearance of the barrier ( $B_f=0$ ), the nucleus will be divided into two fragments in the shortest time  $T_{\text{SF}}=10^{-19}$  s. In the liquid drop model, this limit occurs early for nuclei with  $Z \geq 100$ . However, the threshold of existence for elements (atoms) occurs somewhat earlier, because at a  $T_{\text{SF}}$  of  $\leq 10^{-14}$  s, the nucleus decays sooner than orbital electrons appear around it.

However, not all the data obtained from the studies of this process in subsequent years could be described by the liquid drop fission model. The discovery of spontaneously dividing isomers (1962) [7] in 33 isotopes from U to Cf directly contradicted with the liquid drop model. The isomerism of nuclear forms, the presence of two (sometimes three) states in nuclei, from which spontaneous fission occurs, are incompatible with the idea of nucleus as structureless and amorphous matter. A more adequate theory was created in the following years by effort of many world theorists.

One of the fundamental consequences of the new theory was the prediction of hypothetical super-heavy elements. On the way to division of a heavy nucleus, the motion of its nucleons is associated with the collective degrees of freedom of the entire system. This connection is most clearly manifested in the fission of the heaviest nuclei, which can exist only due to a special

internal structure – the so-called shell closure effect, which manifests itself at certain numbers of protons and neutrons: 2, 8, 20, 28, 50, 82 and 126. From this point, the synthesis and study of decay properties of super-heavy nuclei provide a direct test of the basic statements of the microscopic theory of the nucleus.

**$^{82}\text{Pb}$**

Lead  
Свинец  
207.2

The existence of the “second hundred’s” nuclei is expected where new closed shells will arise. In the region of trans-actinides (elements with  $Z > 103$ ), according to the predictions of the macro-micro model of the nucleus, such shells were expected for deformed nuclei with the number of protons  $Z=108$  and the number of neutrons  $N=162$  [8]. A yet stronger effect was predicted for heavier (super-heavy) spherical nuclei, with  $Z=114$  and  $N=184$  [9], similar in shape and internal structure to the “twice magic” nucleus  $^{208}\text{Pb}$  ( $Z=82$ ,  $N=126$ ). Further away from the magic numbers, the effect of shell closing quickly diminishes, which leads to a sharp drop in the stability of the nuclei. Therefore, the areas of existence of super-heavy elements have the form of “islands” with steep slopes, immersed in a deep “sea of instability”, where elements cannot exist in the absence of the closure effect of nuclear shells.

### Search for hypothetical super-heavy elements

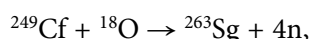
After the first impressive publications about the estimated half-lives of nuclear heavyweights located near the top of the “island”, which at times are comparable with the age of the Solar System, researchers started storming this island in search of hypothetical SHE. The laboratories of Berkeley and Dubna were carrying out difficult but at the time seemingly encouraging experiments on the synthesis of just one element, the  $105^{\text{th}}$ . Not surprisingly, the synthesis of the  $114^{\text{th}}$  element seemed then almost unrealizable.

Each laboratory was tasked with finding a way to synthesize and de-

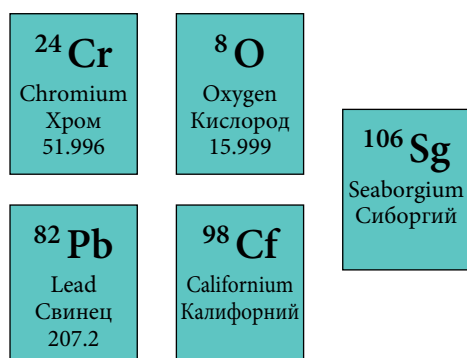
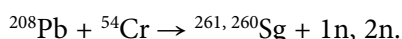
tect super-heavy elements. SHE were searched for in nature: in terrestrial and lunar samples, in cosmic rays and in meteorites. Many attempts have been made to artificially synthesize them using high-flux nuclear reactors, even nuclear explosions, as well as powerful heavy-ion accelerators. Unique facilities and techniques were created with record sensitivity for separating and registering the rarest events of formation and disintegration of super-heavy nuclides. Regretfully, all extensive efforts undertaken over a period of 15 years had failed to find the SHE [10]. This gave rise to some pessimism; in articles and speeches one could often come across the conclusion that the beautiful theoretical hypothesis about SHE might have a right to life, but it is almost impossible to prove it.

### An important off-topic

In 1974, two laboratories with a time-lap of several months obtained the first results on the synthesis of a new, 106<sup>th</sup> element (Sg) in different types of fusion reactions: in Berkeley (USA), it was the reaction [11]:



And in Dubna (USSR), it was a different reaction:



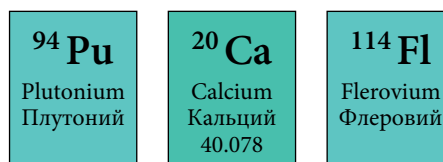
The cross sections for the formation of Sg isotopes in these reactions are approximately the same. But in the way they were obtained there was a significant difference. In fusion with the “magic” nucleus <sup>208</sup>Pb, the excitation energy of the compound nucleus

<sup>262</sup>Sg\* at the Coulomb barrier is about three times less than in Cf + O reaction. Reaction with lead (Pb) is a kind of “cold” fusion, which allows for the compound-nucleus surviving, when cooled by neutron emission. In cold fusion reactions with targets of <sup>208</sup>Pb or <sup>209</sup>Bi, one can increase the mass and the charge of the bombarding ion, always getting a slightly heated compound-nucleus. This became the scenario for the events of the next 38 years. The main activities on synthesis of elements heavier than Sg (Z=106–112) were carried out in 1981–1996 in GSI (Institute of Heavy Ions, Darmstadt, Germany) with the participation of physicists and chemists from Europe and the countries of other continents [13]. Finally, much later, with the new century in full swing, and having shown a certain courage and patience over 10 years of work, the researchers of RIKEN (Tokyo, Japan) in the reaction of <sup>209</sup>Bi + <sup>70</sup>Zn synthesized three atoms of an element with 113 protons [14].

The fact of existing nuclei with Z=106–112, and the character of their consecutive α-decays were quantitatively very close to the calculations based on the macroscopic model of the nucleus. Therefore, the predictions about the existence of a vast “island” of heavier (say, super-heavy) and more stable nuclei, arising due to the closure effect of the spherical shells of Z=114 and N=184, began to look more convincing. Still, all the difficulties of obtaining and studying them were associated with the reactions of SHE synthesis, since none of the real combinations of “bombarding particle – target” could create such a massive nucleus containing more than 60% of neutrons.

### Synthesis Reactions

The only possibility remaining in such a situation was to increase the number of neutrons in the fusing nuclei. For the synthesis of the 114<sup>th</sup> element, a hot fusion reaction was chosen:



where the target nucleus is the long-lived <sup>244</sup>Pu isotope (T<sub>1/2</sub> = 8 · 10<sup>7</sup> years), and the bombarding nucleus is a stable, but rare and very expensive <sup>48</sup>Ca isotope [15].

The <sup>292</sup>Fl\* compound-nucleus, containing 114 protons and 178 neutrons, is still 6 neutrons away from the <sup>292</sup>Fl “doubly magic” nucleus (Z=114, N=184). But for this case, the theory predicted a noticeable increase in the fission barrier of a super-heavy compound nucleus, which should have significantly improved its survival rate in the cooling process. The expectations came true:

the cross section for the formation of  $^{288}\text{Fl}$  in the reaction of  $^{244}\text{Pu} + ^{48}\text{Ca}$  was about 500 times higher than that for the formation of the lighter nucleus  $^{278}\text{Nh}$  ( $Z=113$ ) obtained in the cold fusion reaction of  $^{209}\text{Bi} + ^{70}\text{Zn}$ .

### Experimental technique

The experiments were performed on the U-400 cyclotron (Fig. 1) output beams of accelerated ions at the Laboratory of Nuclear Reactions, JINR.

Cyclotron U-400 was launched in 1980 and has been repeatedly upgraded ever since. The upgrades were aimed at increasing the intensity and the quality of the beams and at expanding the spectrum of accelerated ions.

A cyclotron can be used both as a post-accelerator for producing ion beams of radioactive isotopes, and as an independent unit.

The focus was on ensuring the smooth and stable operation of all systems in long-term experiments. The average cyclotron operation time was more than 6000 hours per year. Approximately  $2/3$  of this time was spent to carry out experiments on the synthesis of super-heavy elements using a  $^{48}\text{Ca}$  beam with energy of 230–280 MeV. When operating the accelerator in this mode, the efficiency of use of the working substance – the rare isotope of  $^{48}\text{Ca}$  – is a critical issue.

This U-400 cyclotron was equipped with ECR-4M – a specialized source of electron cyclotron resonance

ions, designed to produce intense beams of medium-mass ions.

Through optimizing the operating modes of the source, the beam transport channels and the acceleration modes, it was possible to provide a flux of  $^{48}\text{Ca}$  at the target up to  $10^{13} \text{ s}^{-1}$  with a calcium flow rate of 0.4 mg/hour.

To register rare events of formation and disintegration of super-heavy nuclei, a high-speed electromagnetic separator GNS-1 was built [16], shown in Fig. 2.

The separator was designed and tuned to isolate the products of complete fusion reactions. Such nuclei are the heaviest and they are formed as a result of complete impulse transfer of the accelerated ion to the compound-nucleus of the total mass.

The recoil nuclei emitted from the target fall into the low-pressure hydrogen medium (about 1 mmHg) where they acquire different ionic charges depending on the velocity, which makes them different in magnetic rigidity. Selection of recoil atoms according to their energy is carried out in a mag-

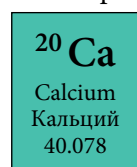


Fig. 1. Heavy ion accelerator U-400 of Flerov Laboratory of Nuclear Reactions JINR.

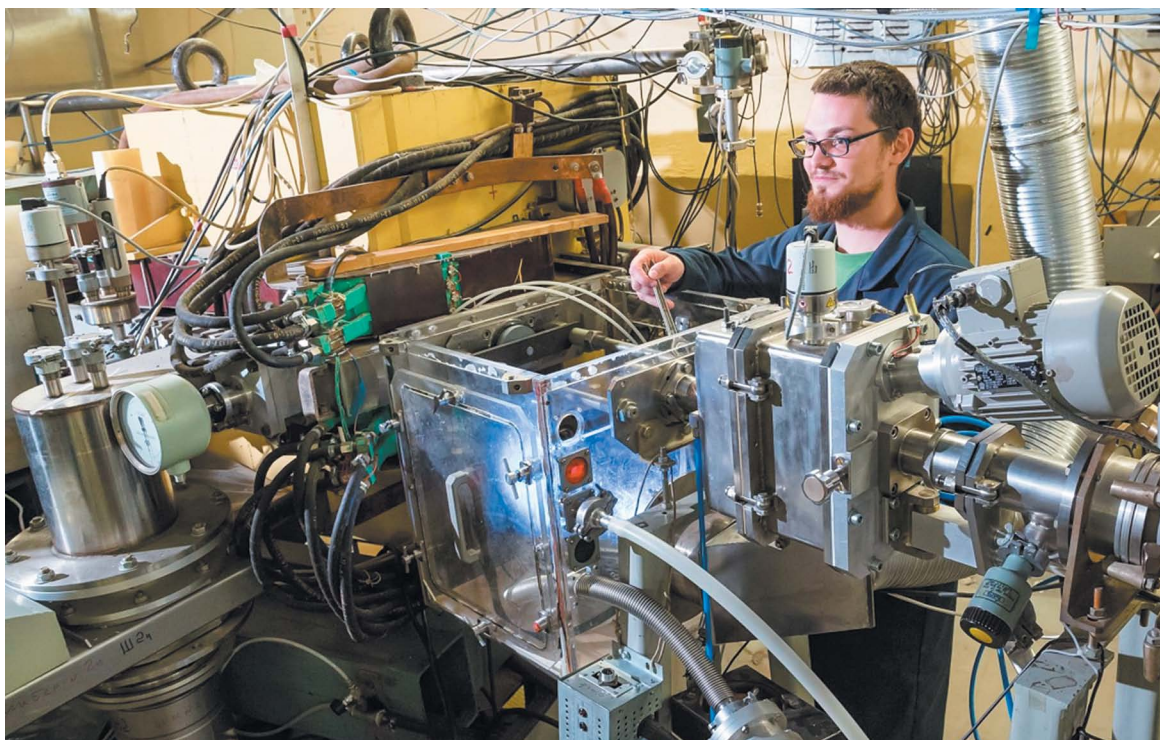


Fig. 2. Gas-filled separator GFS-1.

netic field. Products with maximum magnetic rigidity are collected on the focal plane of the separator, located at a distance of 4 m from the target. A super-heavy atom whizzes over this distance in 1  $\mu$ s.

The detector assembly is located in the focal plane of the separator. The recoil nuclei after passing the time-of-flight spectrometer (TOFMS) are stopped in a position-sensitive front-end detector. The front detector detects the energy and time of arrival of the recoil nucleus, the coordinates of its implantation on the detector surface, as well as the decay products of the implanted nucleus ( $\alpha$ -particles, or fission fragments). Such a registration system allows for verifying the genetic linkage of the nucleus coming from the target with its decay products. The scenario and characteristics of the decay for the entire radioactive family are determined by the radioactive properties of the daughters, granddaughters, great-granddaughters and other nuclei.

### Experimental results

The results of the very first experiments obtained in 2000 in the reactions of  $^{244}\text{Pu} + ^{48}\text{Ca}$  and  $^{248}\text{Cm} + ^{48}\text{Ca}$ ,

as well as the decay scenarios and the properties of nuclei in the chains of successive  $\alpha$ -decays were in good agreement with the above-mentioned calculations made with the use of the macroscopic model. Compared to the heaviest isotopes of the 110<sup>th</sup> and 112<sup>th</sup> elements obtained in cold fusion reactions, the isotopes of these elements, obtained in reactions with  $^{48}\text{Ca}$ , have additional eight neutrons. As a result, their half-lives were increased by about  $10^5$  times! This suggests that the neutron-rich isotopes of these elements have already entered the effective area of the neutron shell  $N=184$ . Note that the heaviest isotopes of the 114<sup>th</sup> and 116<sup>th</sup> elements are still nine and seven neutrons away, respectively, from shell  $N=184$ .

Further events developed fairly quickly [17]. With available and relatively long-lived isotopes Ra, U, Pu, Cm, and Cf as targets in nuclear reactions, it was possible to synthesize from  $^{48}\text{Ca}$  various isotopes of Z-even elements from 108<sup>th</sup> to 118<sup>th</sup>. Virtually all synthesized nuclei undergo one or several  $\alpha$ -decays, which end in spontaneous fission. The energies of  $\alpha$ -transitions for nuclides originating from the maternal nuclei with an even number of protons are consistent with the predictions of various models within 5–7%.

In the decay of the “twice magic” nucleus  $^{270}\text{Hs}$  ( $Z=108$ ,  $N=162$ ), spontaneous fission was not observed ( $T_{\text{SF}} \geq 10$  s). However, with an increase in the number of neutrons in the region of  $N > 162$ , the partial period of spontaneous fission rapidly decreases. It should be noted that isotopes of other elements with

**108 Hs**  
Hassium  
Хассий

Z=110, 112, and 114 in the region of N=169–170 undergo spontaneous fission with a half-life of several milliseconds. This kind of “pit” is located between the closed neutron shells of N=162 and N=184, where the effect of shell closure is minimal.

For N>171, the partial period of  $T_{SF}$  again rapidly increases along with increase in the number of neutrons – the effect of the neutron shell N=184 gains power. Nuclei with  $N \geq 172$  mainly undergo  $\alpha$ -decay. Such a dependence of  $T^{SF}$  on N is a clear demonstration that the stability of super-heavy nuclei against spontaneous fission is entirely determined by the effect of nuclear shells.

The above picture of formation and decay of super-heavy nuclei was added with twenty nine Z-odd isotopes obtained in the reactions of  $^{237}\text{Np}$ ,  $^{243}\text{Am}$  and  $^{249}\text{Bk}$  with the  $^{48}\text{Ca}$  isotope. Due to strong boundary conditions for spontaneous fission of nuclei with an odd number of protons (and neutrons), the chains of consecutive  $\alpha$ -transitions in the nuclei of the 113<sup>th</sup>, 115<sup>th</sup>, and 117<sup>th</sup> elements stretch up to the isotopes of the 105<sup>th</sup> element (Db). In long decay chains, one can observe changes in the stabilizing effect of spherical shell N=184 in super-heavy Mc/Ts nuclei, as well as its diminishing in daughter nuclei and a new gain in the 4–5<sup>th</sup> generations, with approaching the deformed shell N=162 in the final nuclei of  $^{268}\text{Db}$  and  $^{270}\text{Db}$ . For the latter, spontaneous fission is observed with half-lives from 0.2 to 30 hours. That spontaneous fission is very likely to be associated with even-even nuclei  $^{268}\text{Rf}$  (N=164) and  $^{270}\text{Rf}$  (N=166) – the products of electronic

capture of Db isotopes. While Rf nuclei are deformed on their way to the point of rupture, the effect of neutron shell N=82 in fission fragments should lead to almost strictly symmetric fission with reaction energy  $Q_F \sim 280$  MeV.

### Super heavy elements on nuclides map

The synthesizing of new elements in cold and hot fusion reactions with  $^{48}\text{Ca}$  nuclei has significantly enriched the “northeastern” region of the nuclides map (Fig. 3).

This oval zone contains the 57 most neutron-enriched nuclides with Z=104–118, synthesized in reactions under the action of  $^{48}\text{Ca}$ . The heaviest nucleus ever obtained in a laboratory up to date, has a mass of 294. We observed it in the form of two isobars: in reactions with a target of  $^{249}\text{Cf}$ , as an even-even nucleus with Z=118, N=176, going through  $\alpha$ -decay with  $T_{1/2} \approx 0.5$  ms, and further with a target of  $^{249}\text{Bk}$  – as an odd-odd nucleus with Z=117, N=177 and  $T_{1/2} \approx 50$  ms.

The main conclusion that follows from the experimental studies of the past 40 years, is that moving from the last stable elements Pb/Bi to the re-

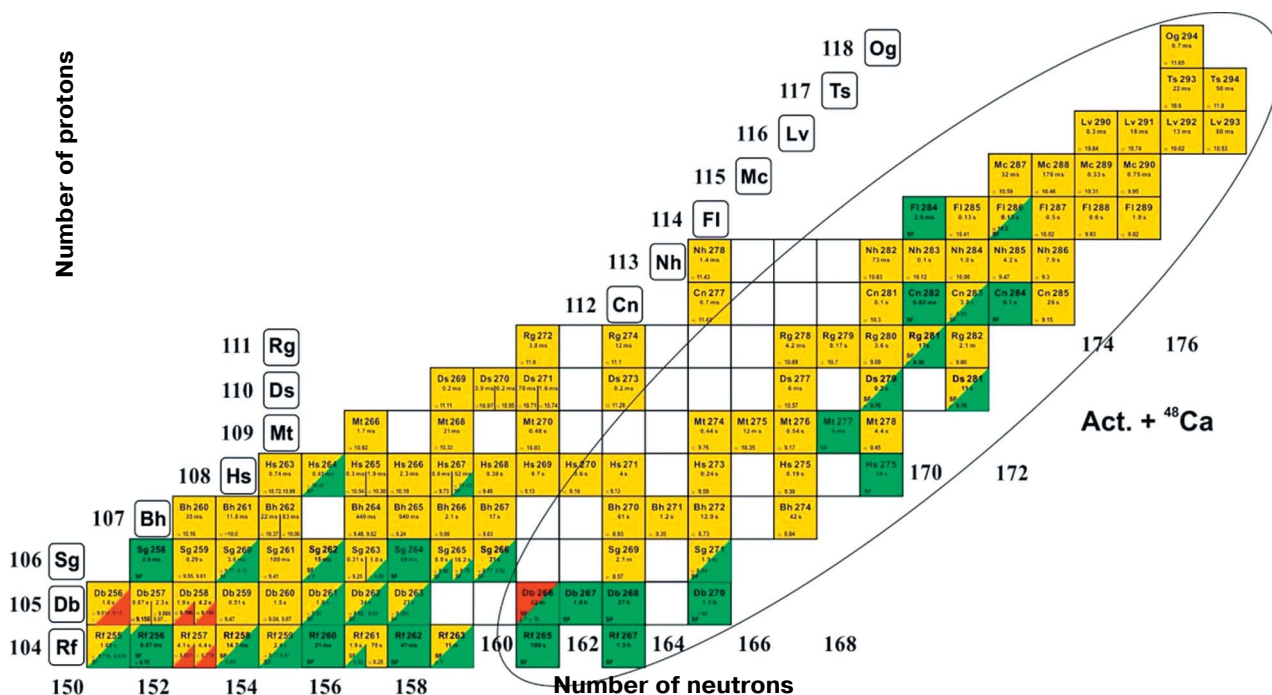


Fig. 3. Map of the heaviest isotopes; nuclides synthesized in reactions with  $^{48}\text{Ca}$ , are shown inside the oval. Yellow-shaded isotopes are experiencing  $\alpha$ -decay, green – spontaneous fission, red –  $\beta^+$ -decay.

gion of heavier nuclides, we observe an amazing vitality of atomic nuclei. Due to the closure of the internal (shell) structure of nuclear substance, the energy of the ground state of a heavy nucleus decreases and a fission barrier arises, which makes it possible for super-heavy elements to exist. *The fundamental predictions of probable super-heavy elements deduced from the microscopic theory of the nucleus have been verified experimentally.*

### Naming of new elements

The priorities in the discovery of new elements with atomic numbers 113–118 were established by the Joint Working Group of Experts, created by a joint decision of the International Union of Pure and Applied Chemistry (IUPAC) and the International Union of Pure and Applied Physics (IUPAP).

**113 Nh**

Nihonium  
Нихоний

The researchers from the RIKEN Research Center (Nishina Center, Japan) who discovered the element with atomic number 113, proposed to name it Nihonium, with symbol Nh. This name is derived from Nihonium (Nihon is one of the names of Japan, which is translated as “The Land of the Rising Sun”).

**114 Fl**

Flerovium  
Флеровий

The long-time partners from the Joint Institute for Nuclear Research (Dubna, Russia) and Lawrence Livermore National Laboratory (USA), who discovered elements No 114 and No 116, suggested for them respectively the name Flerovium with symbol Fl, and the name Livermorium with symbol Lv.

**116 Lv**

Livermorium  
Ливерморий

Flerovium was named in honor of the Laboratory of Nuclear Reactions named after G.N. Flerov – a pioneer in heavy ion physics and the founder of the laboratory, known for its achievements in the synthesis of new elements.

The name Livermorium marks the significant contribution by the scientists from the Lawrence National Livermore Laboratory to joint experi-

mental works conducted in Dubna on the synthesis of new elements, including element 116.

**115 Mc**

Moscovium  
Московский

Researchers from the Joint Institute for Nuclear Research (Dubna, Russia), Lawrence Livermore National Laboratory (USA), Oak Ridge National Laboratory (Tennessee, USA) and Vanderbilt University, by right of discoverers suggested the name Moscovium, with symbol Mc, for the element with atomic number 115. The element with atomic number 117 was named Tennesine, with symbol Ts. These names follow the historical tradition of naming new chemical elements in honor of geographic regions.

Moscovium glorifies the ancient Russian land of Moscovia – the nowadays location of the Joint Institute for Nuclear Research.

**117 Ts**

Tennesine  
Теннесси

Tennesine was named to emphasize the contribution to discovery of super-heavy elements by scientists from Oak Ridge National Laboratory, Vanderbilt University and the University of Tennessee, Knoxville (USA).

**118 Og**

Oganesson  
Оганесон

The element with atomic number 118 got its name Oganesson and symbol Og in honor of the author of this article. Author is deeply thankful to his colleagues for the high honor and recognition of his contribution to the synthesis and research of new elements.

At the same time, discovery of super-heavy elements raises many more questions. Can there be elements heavier than the synthesized SHEs, new nuclear shells and more distant “islands”? Do SHE really form in the Universe, in various astrophysical scenarios of nucleosynthesis? Where are SHE located on the Periodic Table, do they resemble their lighter homologues? And more questions are yet to face us in the future.

### New settlers in the Table of Elements

Fig. 4 presents the Periodic Table of Elements in the version of 2016. According to the calculations performed in nonrelativistic approximation, the Periodic law works for all elements from  $Z=1$  to  $Z=172$ . However, as we move into the region of heavier elements, the velocity of internal electrons increases with increasing nuclear charge, approaching the speed of light. According to the theory of relativity, this leads to an increase in the total electron energy (mass growth effect), resulting from which the radii of the inner shells of heavy atoms are expected to be diminished.

“Relativistic compression” should lead to a change in quantum characteristics and the binding energy of external electrons responsible for chemical behavior of the element. Therefore, moving along the seventh row of the Table from elements with  $Z=104$  to elements with  $Z=118$ , we should see the influence of the “relativistic





Direct synthesis of elements with  $Z > 118$  in fusion reactions is associated with the transition to bombarding nuclei heavier than Ca, since the capabilities of a nuclear reactor in producing target material are limited to the production of Cf isotopes [23]. A number of attempts made in various laboratories and aimed at the synthesis of the 119<sup>th</sup> and 120<sup>th</sup> elements have not lead to positive results. The cross section boundaries in genesis of the nuclei with  $Z=120$  in  $^{248}\text{Cm} + ^{54}\text{Cr}$  reaction and the nuclei with  $Z=119$  in  $^{249}\text{Bk} + ^{50}\text{Ti}$  reaction turned out to be at least 10–20 times narrower than those of the 114–115 elements isotopes production in the  $^{48}\text{Ca}$  experiments.

It is only possible to advance in another direction – to the desired area of more neutron-enriched isotopes of the already known SHEs and get closer to the  $N=184$  shell with the help of radioactive ions, more neutron-rich than  $^{48}\text{Ca}$ . Unfortunately, the intensities of radioactive nuclei beams even on the newly-designed super-power accelerators (such as the FRIB facility, generating ion beams of radioactive isotopes, built at the University of Michigan, which will have a beam power of 400 kW) are extremely low for conducting such experiments.

In these circumstances, it seems appropriate to examine in detail the already synthesized nuclei: to measure their masses, shapes and fission barriers; to find excited states, etc. The separate events of formation and decay of super-heavy nuclides, which have been recorded so far in experiment with a regularity of 1 per day to 1 per month (which is considered a great achievement of the last years) are far from sufficient for these purposes.

Note that the current situation in some aspects repeats the early works on super-heavy elements conducted 20 years ago, when a new approach to the synthesis of SHE in  $\text{Act.} + ^{48}\text{Ca}$  reactions was found, which made it possible to achieve the goal and lead to a significant breakthrough in experimental techniques. In recent years, experimental activity has somewhat decreased and new results almost do not appear, since the focus has shifted to creating new accelerators and more advanced experimental facilities.

We came to an idea that based on the accumulated knowledge, it is possible to increase the productivity of the known methods of SHE isotopes synthesis by almost 100 times. To implement this idea, it was decided to build a specialized experimental complex – “SHE Factory” – which may allow for the next breakthrough into the world of heaviest nuclei and elements.

### Factory of super-heavy elements

The ideas to be embodied in the SHE Factory are associated with the simultaneous development of the future experimental base in several areas at the same time [21, 24]. These areas include:



Fig. 5. The building of the experimental complex “Factory of superheavy elements” (SHE-factory).

- Creation of a new powerful accelerator of stable and long-lived radioactive isotopes;
- Construction of a new experimental building and infrastructure to home the accelerator and the new channels of beam transport in several experimental halls with a total area of 1000 m<sup>2</sup>, equipped with monitoring and protection systems for Class 2 works with radioactive materials;
- Creation of new separation channels and designing new detection modules for studying nuclear, atomic and chemical properties of new elements;
- Production of new target materials and development of technologies for making targets with high thermal and radiation resistance;
- Creating a basis for research in related fields of science and technology.

As of the current moment (spring 2019), the building has been completed, a specialized heavy-duty accelerator of heavy ions (DC-280) has been put into operation, and a gas-filled separator (GNS-2) has been installed. Fig. 5 shows the SHE Factory's building.

### DCT-280 cyclotron for the SHE Factory

A cyclotron was chosen to serve the accelerator function within the Super-Heavy Elements Factory. The principal requirements for the accelerator are given in Table 1.

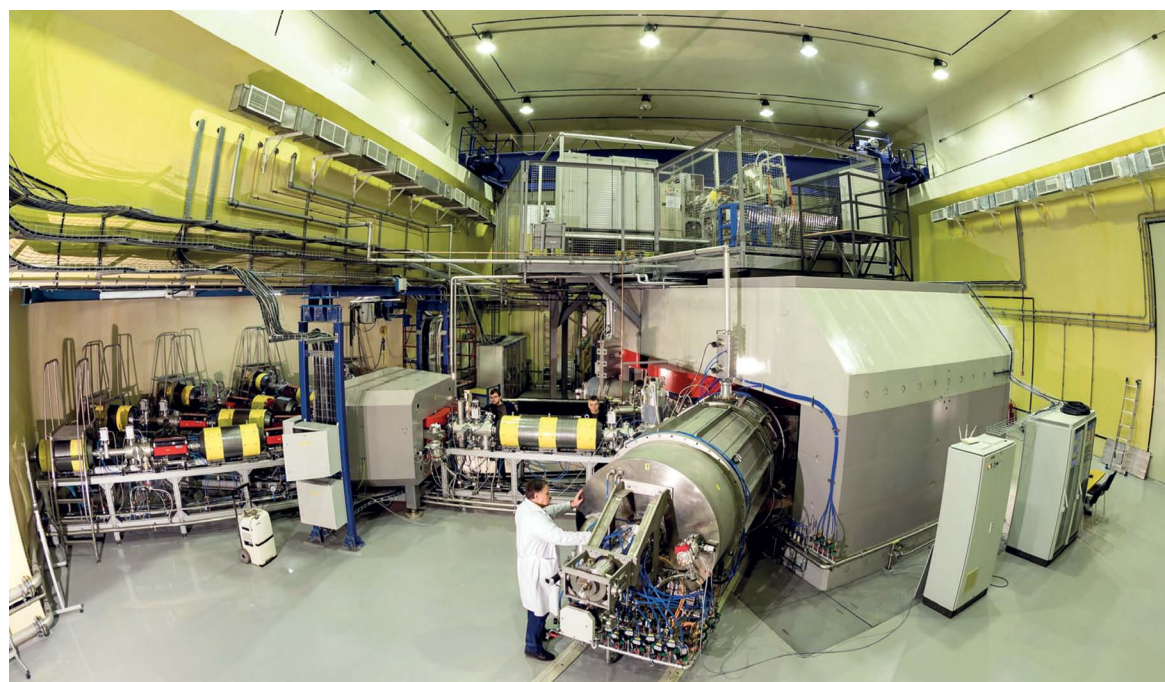
The main parameters of the DC-280 cyclotron were determined in accordance with the accelerator specifications ("280" means the maximum energy to which protons can be accelerated) [25].

Fig. 6 shows a view of DC-280 in the SHE Factory hall.

The DC-280 electromagnet with a pole diameter of 4 m has a weight of about 1000 tons and is intended to create a magnetic field in the range of 0.6–1.3 T. Above the magnet and on top of the high-voltage injection platforms the ECR sources of ions are located.

**Table 1.** Heavy ions accelerator parameter requirements

Heavy ions accelerator parameters	Value range
Ion energies, MeV/nucleon	4–8
Masses of ions, Da	10–238
Beam intensity (up to mass number A=50), s <sup>-1</sup>	10 <sup>14</sup>
Accelerated beam emittance, mm·mrad	<30π
Beam transmission efficiency ion source – target, %	>50



**Fig. 6.** Cyclotron DC-280 in the hall of the SHE-factory.

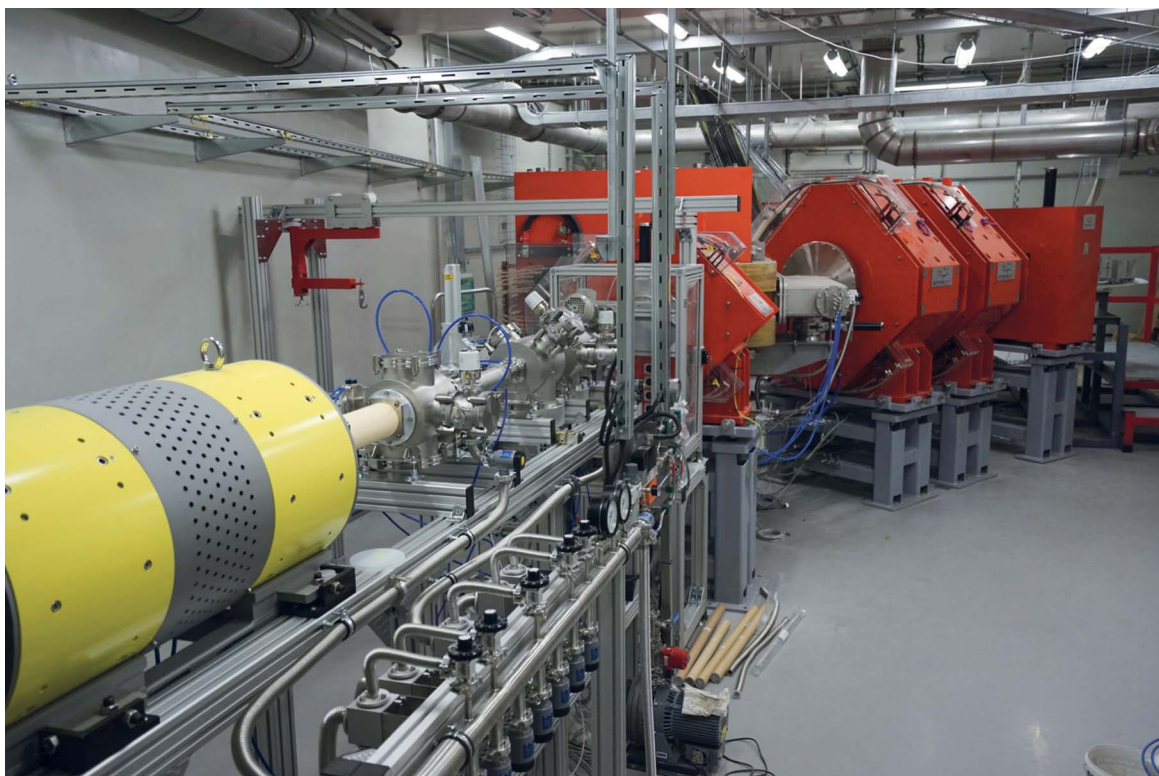


Fig. 7. Gas-filled separator GFS-2 in the experimental hall.

An additional “flat-top” system is used in the cyclotron to flattop the waveform of the accelerating voltage and to get a substantial increase in the efficiency of acceleration.

Extraction of accelerated ions from the accelerator is carried out by electrostatic method. Further on, with the aid of a distribution magnet, ion beams can be fed in one of the five directions towards the booths of the experimental stations.

In January 2019, the first beam of accelerated krypton ions with a charge of +14 was generated in DC-280. This ion was chosen for the test runs, since it does not lead to high activation of the cyclotron elements. The intensity of the beam extracted in front of the distribution magnet reached  $10^{13} \text{ s}^{-1}$ , and the throughput of the beam from the ion source exceeded 30%.

### Gas-filled separator GNS-2

For the study of heavy and super-heavy nuclei formed in the complete fusion reactions of the incident ion with the target nucleus, the most critical requirements are their separation from the bombarding particles of the

beam (as well as from the products of side reactions that are 10–15 orders of magnitude higher in intensity) and efficient transportation to detecting devices.

Judging from the many years of operating experience of the GNS-1 separator and based on the comparison of vacuum separators (such as SHIP speed filter [26] or VASILISA electrostatic separator [27]) against gas-filled separators used in SHE synthesis and study of their properties, the gas-filled units should be preferred.

Gas-filled separator GNS-2 was designed for the SHE Factory [28]. Compared to the previous version, the new separator has a more advanced ion-optical scheme, and its parameters have been optimized for the synthesis of SHE in complete fusion reactions. Fig. 7 shows a view of GNS-2 in the experimental hall of the Factory.

At present (spring 2019), the assembly and installation works on the separator have been completed and commissioning works have started. According to calculations, the new separator should provide two times higher transmission of SHE to the detectors as well as higher suppression of background products.

### First experiments on the Factory

Testing of the accelerator, the diagnostic systems, beam transport and radiation environment, the separator, the detectors and the data collection and processing systems should be completed by the autumn of 2019. After this, experiments on synthesis and study of the properties of SHE will be launched at the Factory.

The first steps will include studying the formation and properties of known isotherms of flerovium in  $^{48}\text{Ca} + ^{242}\text{Pu}$  reaction and Moscovium isotopes in  $^{48}\text{Ca} + ^{243}\text{Am}$  reaction. The cross sections in the formation of these isotopes are approximately 10 pb, which should make it possible to see 10 or more events per day.

These experiments are aimed not only at testing the entire experimental complex, but also at obtaining new information about the properties of isotopes, for example, the presence of isomeric states or a detailed study of the excitation function with evaporation of various numbers of neutrons.

And, finally, in the next step, experiments will be started on the synthesis of elements 119 and 120 in reactions  $^{50}\text{Ti} + ^{249}\text{Bk}$  and  $^{50}\text{Ti} + ^{249-251}\text{Cf}$ .

In previous attempts to synthesize these elements, the reached probability limit of their formation was less than one event per month. With the same assumptions about the cross sections of reactions in the new experimental complex, we can expect more than one event of a new element formation per week. It is obvious that experiments on the synthesis of elements 119 and 120 will take long – possibly years of work.

## Conclusion

The SHE Factory has no analogue in the world practice. It is created with a perspective of 20–25 years, and should be in demand as an experimental complex, providing leadership in the science of heavy and super-heavy elements.

On a final note, the author of this article and his fellow workers express their deep gratitude to Russian Foundation for Basic Research both for financial support and for the continued interest in the problem of super-heavy elements and useful discussions when reviewing the results.

Author takes this opportunity to congratulate all of his colleagues working in the field of synthesis and study of super-heavy elements, as well as all people interested in this problem, on the International Year of the Periodic Table of Elements.

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# Mendeleev's Periodic Table and Marine Biomolecules

Valentin A. Stonik, Tatyana N. Makarieva

The mini-review highlights the involvement of some elements of Mendeleev Periodic Table into marine biogenic compounds and these elements participation in the marine organisms' metabolism. Some metals accumulation by marine invertebrates and the metal complexation by highly structurally diverse secondary metabolites are discussed. In addition, examples of the covalent bonds formation in marine bioorganic molecules with a number of non-metals are considered.

**Keywords:** marine organisms, marine metabolites, metals, non-metals, complexones, elemento-organic biomolecules.

Many elements of the Periodic Table play an important role in living systems. Marine organisms (of which most taxonomic groups appeared on our planet hundreds of millions of years ago) use metal ions in various biochemical processes. It is also likely that they use some of the compounds formed during chemical interactions with each other. They can include into their biomolecules other elements, especially halogens and sulfur, attaching them by covalent bonds to carbon or oxygen atoms and thereby enhancing the biological activity and solubility of their metabolites in water.

It is well known that ions of sodium, potassium, magnesium and calcium regulate the osmotic balance of cells and are involved in the formation of important polysaccharides and proteins in all living organisms. On the other hand, the ions of transition metals, including rare ones, are necessary for the functioning of metal enzymes and various cofactors [1]. Not only marine biopolymers, but also low-molecular secondary marine metabolites selectively bind various elements. In many cases the mechanisms of using such compounds in accumulating the elements are not completely clear, and only assumptions can be made based on the characteristics of their structure [2]. In general, marine biomolecules include at least 40 elements of the Periodic Table. On the list there are not only well represented in many metabolites of terrestrial origin sodium, potassium, calcium, magnesium, iron and zinc, but also manganese, vanadium, copper, nickel, cobalt, molybdenum, tin, lead, chromium, titanium, cadmium, niobium, uranium, zirconium, ruthenium. Besides hydrogen, oxygen, nitrogen and phosphorus, non-metals are also represented by fluorine, chlorine, bromine, iodine, selenium, sulfur and arsenic.

## Binding of metal ions to biopolymers of marine organisms

Many organisms of marine biota, especially marine invertebrates, often have significantly richer content of metal ions compared against their environment. For example, almost a hundred years ago high concentrations of vanadium were detected in ascidia [2, 3]. In some of them, its content was ten or more million times higher than in seawater. A high concentration of vanadium was noted in the blood cells of these animals. It was assumed that the function of chelating agents that bind vanadium is performed by their unusual low-molecular metabolites, such as tunic-chromium-1, but later it was found that tunic-chromium is not present in blood cells. Later vanabin peptides with molecular masses of about 10.5 kDa and nine disulfide bonds were found, and these compounds are contained in ascidian blood cells – vanadocytes. Vanadium ions, whose content in sea water in the form of  $V^{5+}$  is approximately 35 nM/l, penetrate into vanadocytes with the help of transport protein, and then are reduced by nicotinamide adenine dinphosphate (NADP) to  $V^{4+}$  and bind to vanabin 2. Vanabin 2 is able to attach 24 vanadium ions per one molecule due to the formation of coordination



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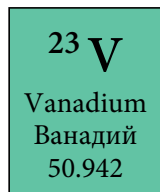
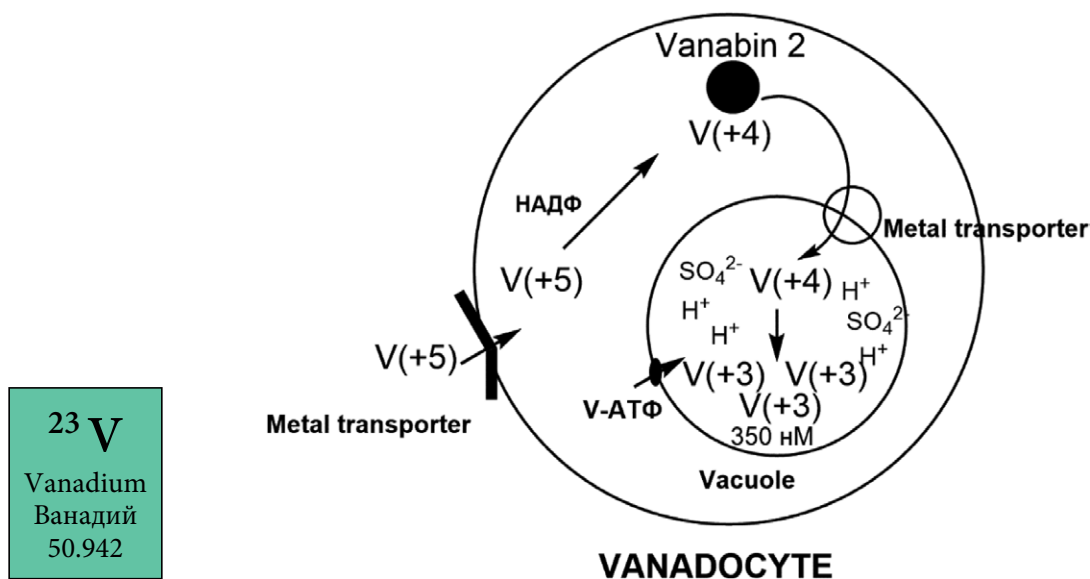


Fig. 1. Scheme of accumulation and reduction of vanadium ions in ascidian vanadocytes.

bonds with the nitrogen atoms of the amino groups of the lysine, arginine and histidine amino acid residues of this protein. Other vanabins can chelate V<sup>5+</sup> and facilitate its reduction by NADPH. Then vanabin 2 transports V<sup>4+</sup> to the vacuole of the vanadocyte, playing the role of a cytoplasmic transporter. Another transport protein brings vanadium ions into the vacuole, where it is reduced to V<sup>3+</sup> state. In the vacuoles of vanadocytes, an extremely low pH value (about 1.9) is maintained due to the formation of significant amounts of sulfuric acid in them. Thus, V<sup>3+</sup> ions are located in these cells along with protons and sulfate anions (Fig. 1). The content of vanadium in the vacuoles of vanadocytes reaches 350 mM [4]. Although it was assumed that vanadocytes need vanadium to regulate oxygen metabolism in these invertebrate organisms and to protect usually immobile ascidians from fouling [5, 6], the accumulation of vanadium by vanadocytes is still a largely mysterious phenomenon [4] when it comes to understanding its functionality.

Different types of ascidians collected at the Great Barrier Reef accumulate tin, manganese, titanium, chromium, iron, niobium, tantalum, and the highest accumulation factors were noted for iron ( $1.6 \cdot 10^7$ ) and manganese

( $2.2 \cdot 10^6$ ). Other metals, such as cadmium and uranium, were also found in ascidians, but their accumulation factors were identified as significantly lower. Some sponges, such as *Crambe crambe*, accumulate lead, copper, cadmium, zinc, and other metals [2]. A number of metals are accumulated in marine macro- and microalgae, bacteria and fungi. Accumulation of metal ions is required since they participate in the most important biochemical transformations catalyzed by enzymes (metalloproteins), while the content of many ions in seawater is very low. There is a significant difference between the environmental concentrations of transition metals for marine and terrestrial organisms. For example, the content of iron in soil and seawater varies dramatically. Many metals, primarily iron, vanadium and molybdenum, play an important role in the productivity of marine communities. At least  $\frac{1}{3}$  of all proteins, including the key enzymes of photosynthesis, respiration and nitrogen fixation, as well as various proteases and anhydrase, belong to metalloproteins. Such enzymes have metal binding sites, and many of their coenzymes are also capable of attaching metal ions. A number of enzymes of marine organisms have no homology with the corresponding biocatalysts from terrestrial organisms. They may contain other ions necessary for their catalytic activity. For example, anhydrases from diatom microalgae have cobalt or cadmium instead of zinc in the active site, while vanadium-dependent enzymes catalyze an oxidative halogenation reaction in marine organisms, which in terrestrial organisms is catalyzed by Fe(III) heme enzymes [7, 8].

Hemocyanins – blue respiratory pigments of marine invertebrates (mollusks, arthropods and horseshoe crabs), capable of attaching oxygen, like hemoglobin, contain copper ions associated with protein in their

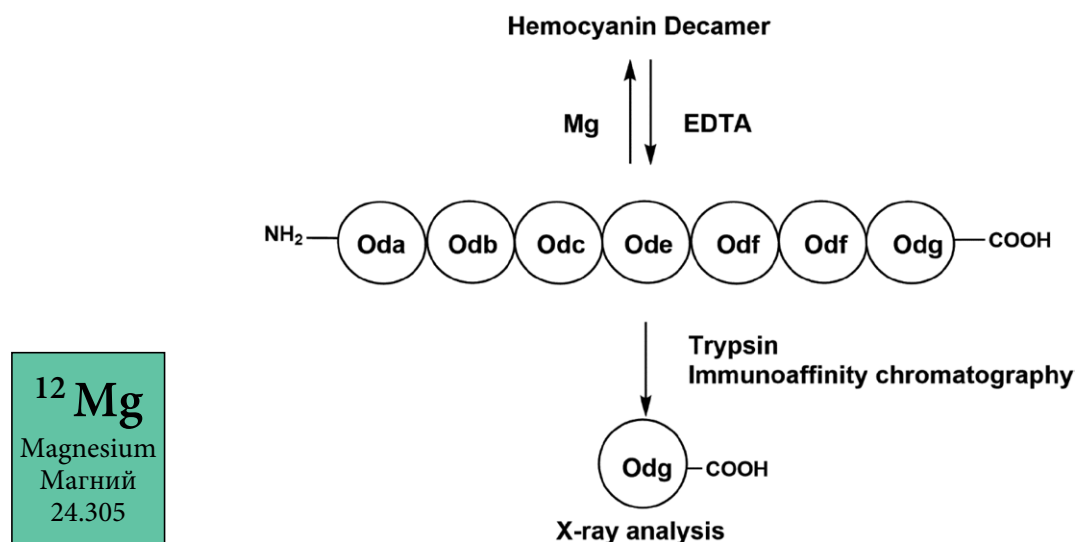


Fig. 2. Scheme of structural study of octopus hemocyanin.

active centers. These oxygen-transporting proteins have extremely high molecular weights (up to 9 mln Da) and many oxygen-binding sites with two copper ions in each of them. Copper ions are linked by coordination bonds with his-tag protein residues, and when oxygen is added (in the form of a peroxide ion) to hemocyanin, Cu(I) ions are oxidized to Cu(II), and the colorless deoxygenated protein becomes blue. The name “hemocyanin” by itself does not come from the word “hem”, since hemocyanins do not contain a heme prosthetic group, but from the Greek “hemociano” – blue blood. Octopus hemocyanins are complexes of 10 proteins that are linked to each other by magnesium ions. In the absence of magnesium ions, these decamers dissociate and give out protein molecules with seven oxygen-binding sites *a–g* (Fig. 2), in Latin letters designated as *Oda–Odg*, which is derived from *Octopus dioxygen*. As a result of proteolysis, the *Odg* subunit, located at the C-terminus of the protein molecule, was separated from other parts of the protein molecule and purified by immuno-affinity chromatography. Features of its structure were studied using X-ray analysis. It has a molecular mass of 47 kDa and consists of two domains, one of which, built of  $\alpha$ -helices, resembles some proteins in its topology. Six histidine residues in this domain bind copper ions [9]. Interestingly, the blue blood of some other marine invertebrates, for example, deep-sea holothurians, does not contain copper, but vanadium.

#### Low-molecular-weight marine metabolites capable of binding metals

The lack of iron in the marine environment is well known in living organisms.  $\text{Fe}^{3+}$  ions in neutral aqueous solutions, including biological fluids, due to the poor solubility of their salts are present in very low concen-

trations ( $10^{-18}$  M), while the growth of bacteria and other microorganisms requires micromolar concentrations of  $\text{Fe}^{3+}$ . Iron deficiency is, for example, a limiting factor for the development of microalgae. Natural iron complexones are mainly of peptide nature, the so-called siderophores often found in bacteria. For example, the marine bacteria *Alteromonas luteoviolaceae* living in oligotrophic and coastal waters produce siderophores of alterobactins A and B (1, 2) [10, 11], which contain the binding sites of the  $\text{Fe}^{3+}$  ion characteristic of siderophores of some terrestrial bacteria, such as fragments of hydroxy acids or aromatic nuclei with two or three hydroxyl groups. Bacteria in both marine and terrestrial environments, in order to survive, synthesize various metabolites attaching iron, and the siderophores of bacteria more effectively bind  $\text{Fe}^{3+}$  ions than the siderophores of fungi. The resulting complexes interact with the receptors of microorganisms and get inside their cells, releasing the necessary iron. Macro-organisms, both of plants and animals, usually can grow in the presence of lower concentrations of iron. In addition, they receive the necessary  $\text{Fe}^{3+}$  ions from symbiotic bacteria.

In some cases, non-peptide complexones binding the ions of  $\text{Fe(III)}$  or  $\text{Fe(II)}$  were also isolated from ma-



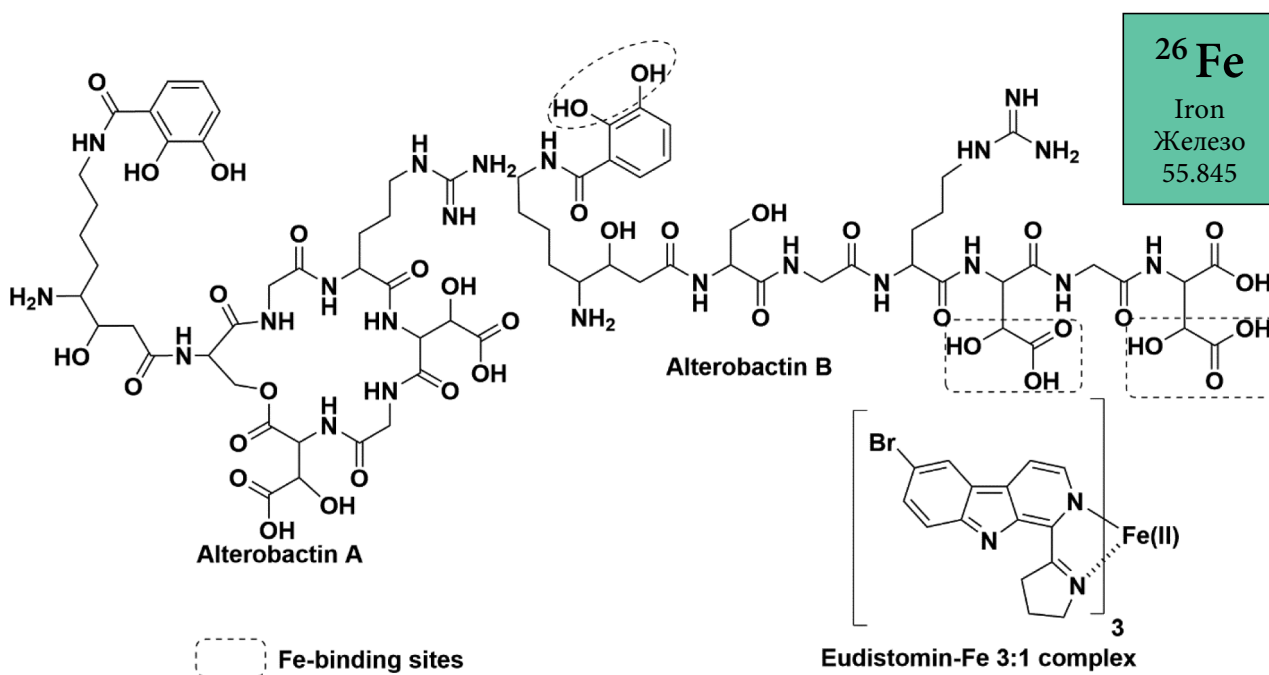


Fig. 3. Iron-binding marine secondary metabolites.

rine invertebrates. Despite the fact that such complexes are very labile and easily decompose when isolated under molecular or reverse phase chromatography, a complex of three molecules of eudistomine and Fe(II) [12] (Fig. 3)

was detected in lipophilic extracts of the ascidian *Eudistoma gilboviride* using gel filtration and subsequent mass spectrometry with inductively coupled plasma.

In a number of other cases, complex compounds with other metal ions have been successfully isolated or identified in some other marine invertebrates and

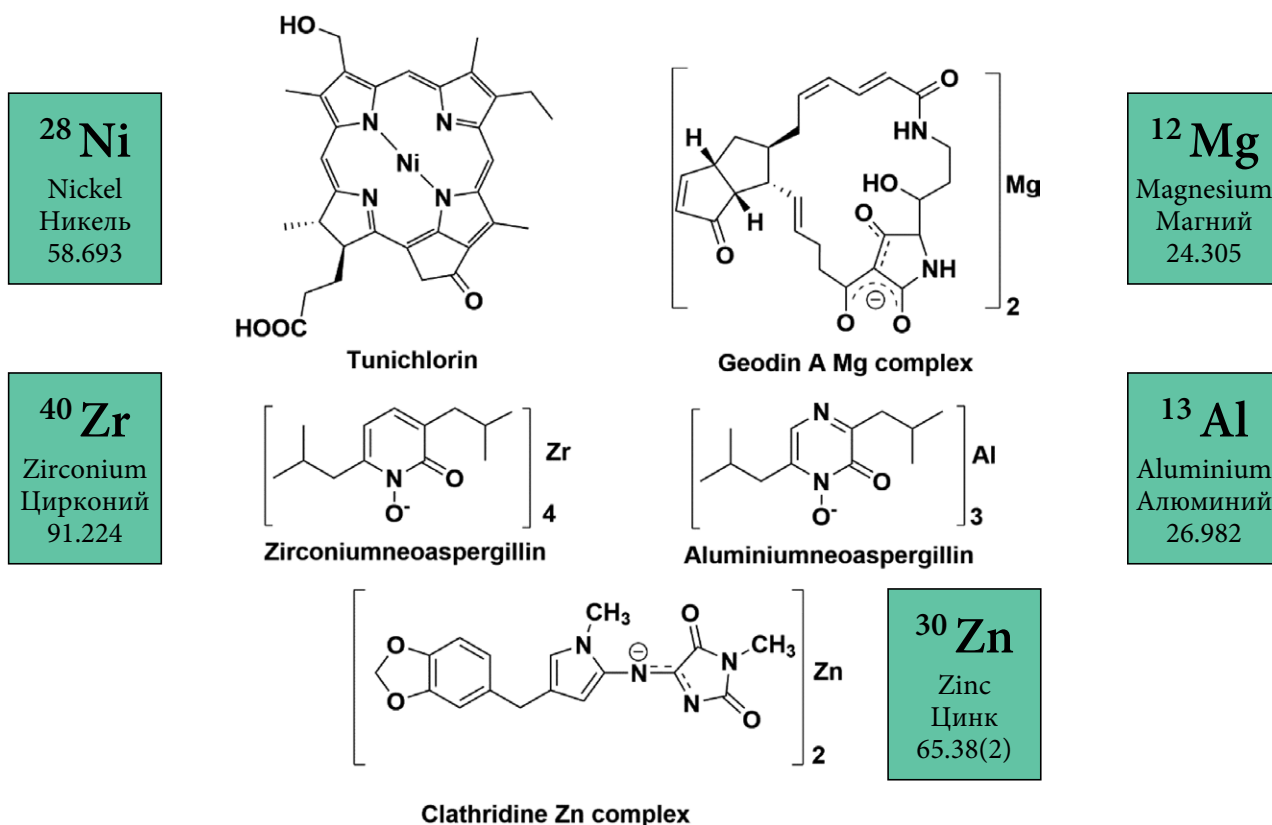


Fig. 4. Some examples of metals complexes isolated from marine organisms.

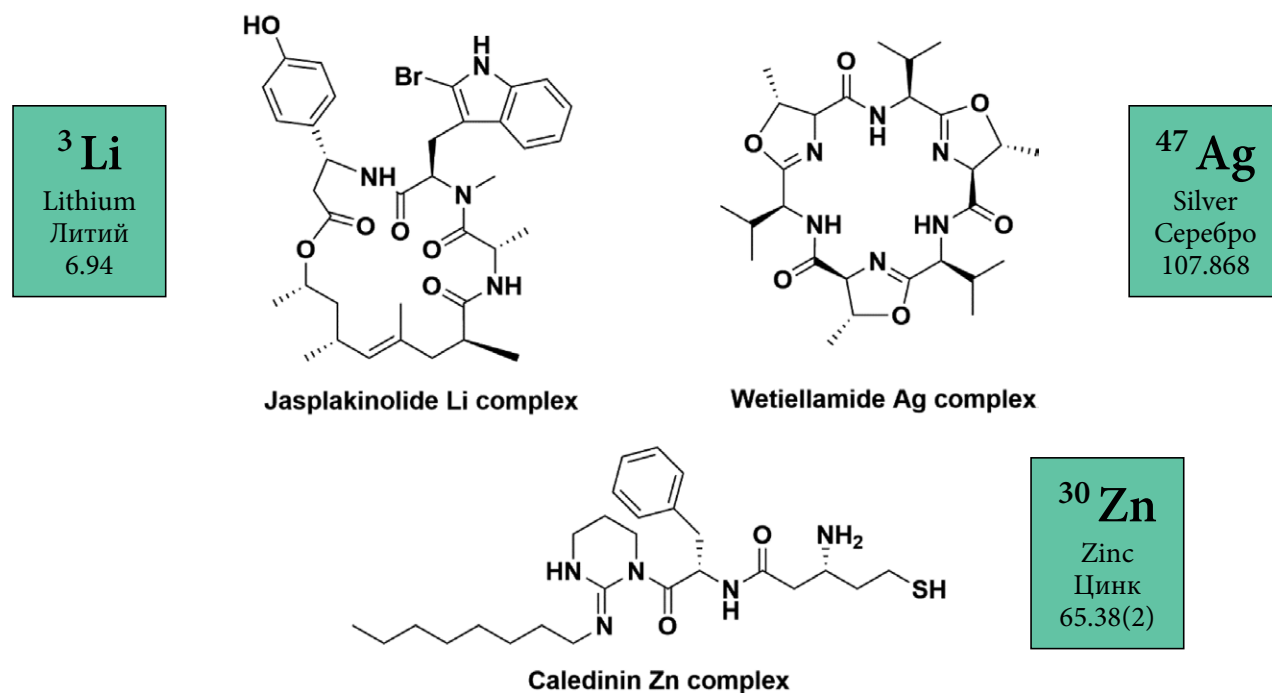


Fig. 5. Some marine metabolites for which the ability to form complexes with metals has been shown experimentally.

microorganisms. Among complexons contained in invertebrate organisms, there are many macrocyclic and heterocyclic compounds (Fig. 4). Thus, tetrapyrrole nickel-containing blue-green pigment of tunichlorin was found in the ascidian *Trididemnum solidum* [13]. Macrocyclic polyketide geodin A from the Australian sponge of the genus *Geodia*, collected on the Great Barrier Reef, is the magnesium salt and has a strong nematocidal effect [14]. Zinc complexes have been isolated from calcium sponge extracts, for example, the clathridine-zinc complex from the Mediterranean sponge *Clathrina clatrus* [15]. The marine fungus isolated from the gorgonian coral *Melitodes squamata* and identified as *Aspergillus sp.* contained several new mycotoxins, including aluminum and zirconium salts of aspergillid acid derivatives [16] (Fig. 4).

However, the isolation of such compounds due to their low stability is still rare, although many metabolites are known to have structural features indicating that they could create such complexes or salts. Among them, there are potential ionophores – macrocyclic compounds, including cyclic peptides, various heterocyclic acids, alcohols, thiols, etc. Therefore, over the past many years, attempts have been made to study the complexation of such marine metabolites with various salts in vitro, or other elements produced by these metabolites (invertebrates, algae, microorganisms). A classic example of such studies was the study of an unusual peptide – caledinin from the New Caledonian ascidian *Didemnum rodriguesix* [17]. To confirm the hypothesis that this compound may be involved in the accumulation of zinc and copper by ascidia, titra-

tion of the caledinin solution with zinc chloride was performed and the changes in the NMR spectra, taking place at the same time, were studied. As a result, it was proven that caledinin forms a complex with zinc ions in the following ratio: two molecules of caledinin per one  $\text{Zn}^{2+}$  ion. Similar experiments showed that jasplakinolide from sea sponges *Jaspis johnstoni* is able to bind lithium ions [18], while westiellamide from blue-green algae *Westiellopsis prolifica* binds silver ions [19] (Fig. 5). Similarly, the ability of other marine metabolites to bind various metals, including copper, iron, zinc, ruthenium, etc., was determined. In so doing, various physical-chemical methods were used, including mass spectrometry [2].

#### Marine natural compounds containing halogens and sulfur

Halogenated metabolites are very widely represented in marine bacteria, plants and animals. Inorganic components of the marine environment often take part in biochemical processes in marine organisms. Sea water is known to contain a huge amount of various salts in solution, therefore it contains metal cations and anions, including

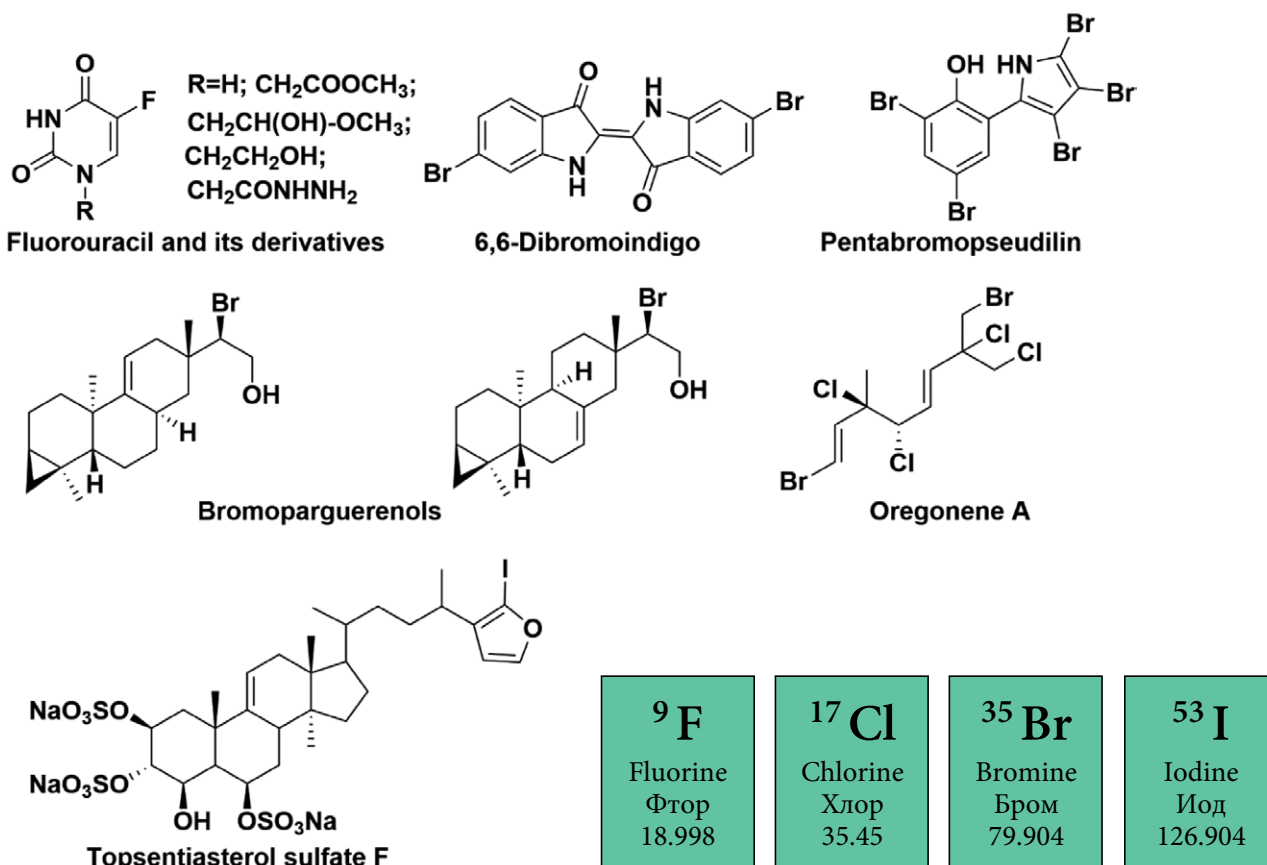
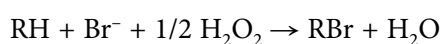


Fig. 6. Some examples of halogenated marine metabolites.

19,000 mg/l of  $\text{Cl}^-$ , 65 mg/l of  $\text{Br}^-$ , 0.06 mg/l of  $\text{I}$  and  $\text{IO}_3^-$ , many sulfate and nitrate anions. All halogens were found in marine secondary metabolites, including fluorine, which is rare in natural compounds. For example, fluorouracil and its derivatives earlier synthesized and used in oncology were then isolated from the *Phakellia fusca* sponge [20] (Fig. 6).

It is a curious fact that not chlorine is found more often in marine natural compounds, though it is the most common halogen in the marine environment, but less common bromine. The latter is obviously related to the biological properties of brominated metabolites. Brominated metabolites (rich sources of such compounds are red algae, mollusks and sponges that feed on them) often show a deterrent effect and deter predators. Vanadium-containing enzymes of bromine peroxidase catalyze the synthesized reaction; it proceeds according to the equation:



These enzymes are widely distributed in algae, up to 70% of which have bromperoxidase activity, which explains the high content of various brominated compounds in them, including terpenoids, alkaloids, polyphenols and other metabolites. Bromination plays a role in the coloring of algae. Bromperoxidases are also found in gastropods of the genus *Murex*, which biosynthesize the purple pigment used in the ancient times to stain royal robes. Its main component is 6,6'-dibromoindigo. Some marine bacteria contain significant amounts of halogenated metabolites, for example pentabrominepseudodilin, which has strong antimicrobial effect, including that against methicillin-resistant strains of pathogenic bacteria [21]. In the red algae of the genus *Laurencia* the diversity of halogenated metabolites is particularly high. For example, unusual diterpenoids – brominated pargueran derivatives [22], were isolated from the Far Eastern *Laurencia nipponica*.

In some marine natural compounds, several halogen atoms are present, and the total halogen content can reach 80% of the molecular weight of these metabolites. Thus, oregonene A from the red alga *Plocamium oregonum* contains six halogen atoms (four chlorine and two bromine atoms) [23].

Iodinated compounds are rarely found, especially for such groups of metabolites as steroids. At the same time, iodine is present along with three sulfate

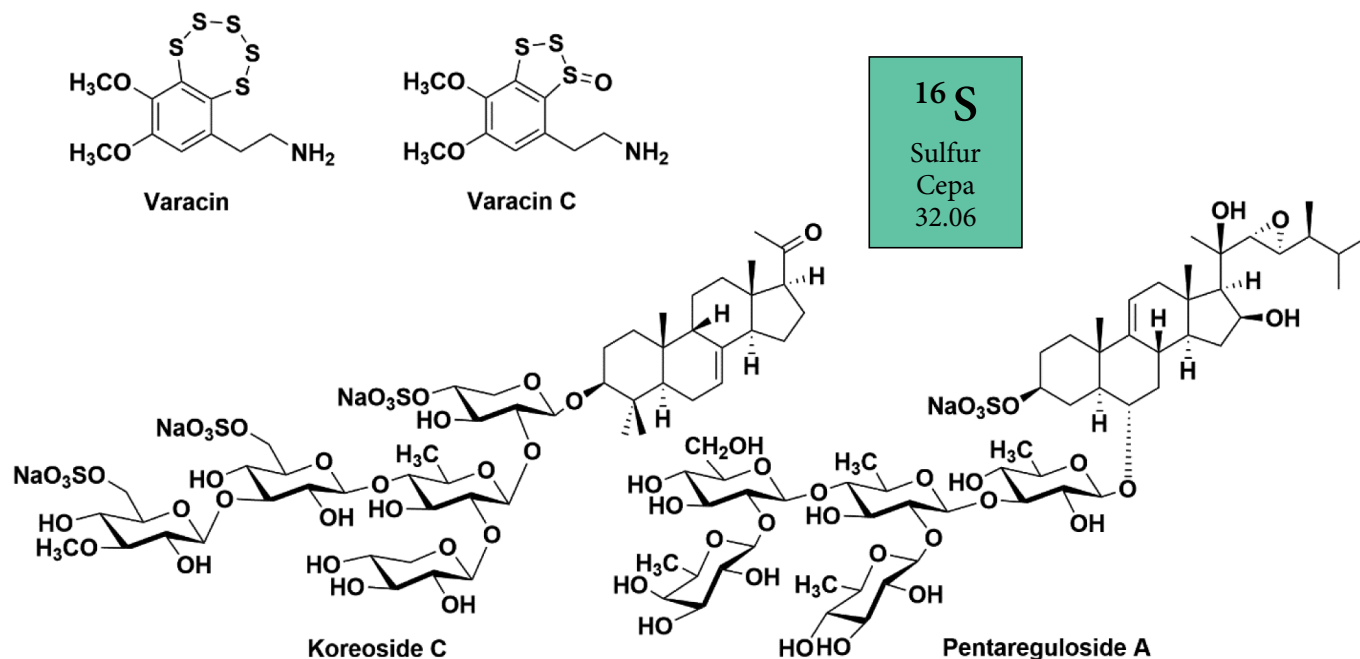


Fig. 7. Some examples of sulfur-containing marine metabolites.

groups [24] in the topsentiasterin sulfate F, which we found in the sponge *Topsentia sp.*

Sulfur-containing metabolites are also widely distributed in marine invertebrate organisms, and they can contain either sulphate groups or polysulfide fragments having from three to five sulfur atoms. Varacin with a pentasulfide fragment in one of its cycles has a strong antimicrobial effect, while trisulfide varacin C very similar to it in structure, and also isolated from ascidian *Polycitor sp.*, is highly toxic to tumor cells [25]. Compounds containing three sulfate groups, for example coreoside C from *Cucumaria koraiensis*, are often found in triterpene glycosides from holothurians [26]. Sulfated steroid and triterpene glycosides are particularly characteristic of echinoderms. For example, steroid glycosides named asterosaponins are almost

always present in sea stars, like pentareguloside A that we found in the star of *Pentaceraster regulus* (Fig. 7) [27]. Asterosaponins are toxic to predatory fish. Algae contain significant amounts of various sulfated polysaccharides.

### Selenium-containing marine metabolites

Selenium is an essential element for the human body. Its food sources are meat, eggs and other products and, not least, fish and other varieties of seafood [28]. Selenium in the composition of selenocysteine amino acid residues is included in a number of

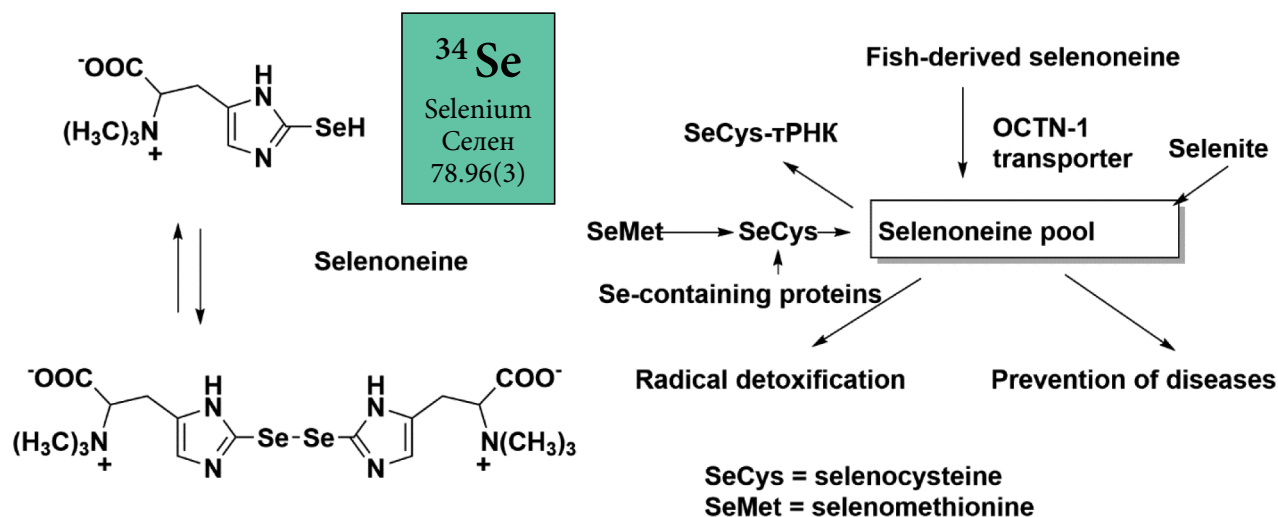
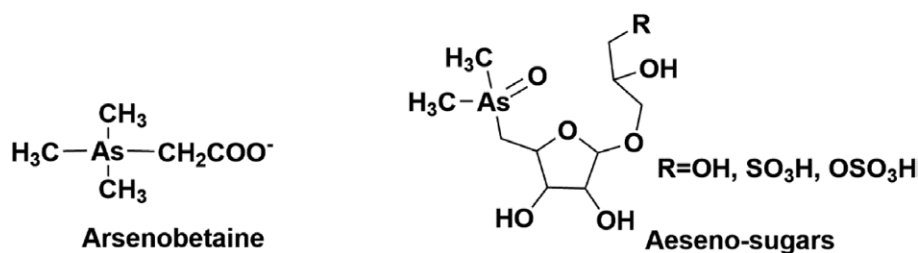


Fig. 8. Selenoneine, its transformations and biological roles.



**33 As**  
Arsenic  
Мышьяк  
74.922

Fig. 9. Arsenic-containing marine metabolites.

important enzymes, for example glutathione peroxidase and thioredoxin reductase. Antioxidant activity of selenium plays an important protective role, defending a person against almost 50 diseases, including colorectal cancer, immunodeficiencies, cardiovascular diseases associated with selenium deficiency.

A new Se-containing metabolite, selenoneine, was isolated as the main form of organic selenium from tuna meat and blood. It contains a selenium atom bound to an imidazole ring. This compound has strong antioxidant activity and, joining the heme proteins to hemoglobin and myoglobin, protects them from oxidation, reduces the formation of free radicals, and slows down chronic diseases and aging [28]. The structure, transformations and the role of selenoneine are shown in Fig. 8.

### Arsenic metabolites

The arsenic content in seawater is 0.003 mg/l, and it is well known to be accumulated in phytoplankton. Through food chains it enters many marine organisms, including those edible to humans. One of the most common marine metabolites containing arsenic – arsenobetaine – was

first found in lobster, and its structure was determined by X-ray structural analysis. Unlike other arsenic derivatives, it turned out to be of low toxicity. Arsenic has also been found in lipid fractions, mainly from algae. The so-called arsenosugars (Fig. 9) were first found in the brown alga *Ecklonia radiata*, and then in a number of other marine organisms [29]. The DNA of the bacterial strain GFAJ-1 was also reported to have arsenic atoms instead of phosphorus, but further studies did not confirm this observation. It is believed that very small doses of natural compounds can be beneficial for an organism, and arsenic itself can be attributed to ultramicroelements.

### Conclusion

Almost half of all stable (non-radioactive) elements of the Periodic Table are able to bind with one or other marine natural compounds. The diversity of such complex compounds in comparison with substances of terrestrial biogenic origin, as well as the diversity of other marine metabolites, is obviously due to the fact that much more representatives of large taxa (types) of animals, plants and microorganisms live in the marine environment. It means that taxonomic diversity of marine organisms is much wider than that of terrestrial organisms. The history of study of marine natural compounds is significantly shorter than that of terrestrial, which is especially true for plant metabolites. Therefore, there is no doubt that numerous new natural complexones and organoelement compounds with unexpected and useful properties will be further found in marine organisms.

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# Analytical Chemistry of the 21<sup>st</sup> Century: New Face of the Science

*Yuri A. Zolotov*

The paper constitutes a review of the analytical chemistry general state, changes in its development trends, as well as substantial rise of both its tasks volume and complexity and its potential. The place that the analytical chemistry takes among other sciences is briefly considered, and its instrumentation improvement is noted. Author focuses on the Russian scientists' advances in this sphere, particularly those whose investigation were supported by the Russian Foundation for Basic Research. Examples of the new analytical methods creation, the original analytical approaches development and the important applied tasks solution in spheres of medicine, environmental protection and the food and medicines quality and safety control are given. Author attempts to forecast the analytical chemistry development prospects for the next 10–15 years.

**Keywords:** analytical chemistry, chemical analysis, methods of analysis, prospects of analytical chemistry development.

## General review of analytical chemistry

A few decades ago, the focus of researchers working in the field of analytical chemistry began to shift from detection and quantification of chemical elements to separation, identification and quantification of organic substances, including those of biological origin – to which most of scientific publications are currently dedicated. This shift is accompanied by intensive development of appropriate methods and tools of analysis – chromatographic, molecular spectroscopic, mass spectrometric, biochemical (such as immunochemical analysis) and others. In 1950–1980s, the training courses in analytical chemistry were devoted mainly to chemical elements, but today this field looks very different. The teaching of analytical chemistry and the training of highly qualified analysts are being adjusted accordingly.

Still, there are extensive and important areas for which elemental analysis remains (and will remain) the main type of chemical analysis. Among the industrial fields these are metallurgy,

mechanical engineering, electronics, the building materials industry; while for agriculture elemental analysis is utterly important in crop farming (for analysis of soil for nitrogen, phosphorus and potassium). The same can be said about prospecting, exploration and primary processing of mineral raw materials. Accordingly, methods and means of elemental analysis are developing, first of all: spectrometric, including X-ray spectral; atomic emission; atomic absorption; as well as elemental mass spectrometry, not to mention the well-established spectrophotometric or electrochemical, which now play a lesser role.

Hardly less important than changes in the toolkit and the priority methods of analysis is the development of new common approaches to analysis, even its new paradigms. In our opinion that would include: analysis without a stationary laboratory but on the site where the analyzed object is located; analysis without any destruction of the analyzed object; analysis at a distance from the object, without direct contact with it; the so-called speciation analysis, that is, identifying the physical and chemical forms in which the component of interest is present in the object (in the simplest case it means finding out the level of oxidation of the element and determining its content for each level); local or distributive analysis, that is finding out the “geography” of a component, meaning its distribution through the mass or along the surface of the sample; continuous



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analysis in a stream of liquid or gas; automation of mass analysis of similar samples.

An example of a change in the analysis paradigm is “analysis without analysis” – identifying an object with the help of an “electronic nose” or an “electronic tongue” through the use of a set of non-selective sensors whose signals are mathematically processed with chemometric techniques. One may add in parentheses that the concept of identification has a wider scope: it applies to both the component and the object as a whole, like in recognizing which type of mineral water we have in hand at the moment.

These manifestations of progress make you think about the methodology, or if you like – about the philosophy of analytical chemistry. Such aspects are not of much interest in the consumer chemical analysis, but are essential for a professional researcher. Mind that when speaking about the times of 50–70 years ago, the key word in the name of our science was definitely the word “chemistry”, while today the emphasis is sometimes placed on “analysis”. Analytical chemistry by no means abandons chemistry in total, since it deals with chemical species - atoms, ions, molecules, phases; they are precisely what it must detect and determine the content of. A departure from chemistry is observed in something else - namely in the methods and means of analysis, and this departure is natural, not only justified but absolutely required. Such withdrawal should not be viewed as the dictates of the times, in fact, analytical chemistry has always proceeded from the “end justifies the means” principle. The first physical method of analysis was applied by Archimedes, who analyzed the golden crown of King Hieron II, determining the specific gravities of pure gold and the crown. Spectral analysis – the usual physical method of analytical chemistry – has been around for a century and a half. X-ray fluorescence and instrumental radioactivity determination methods or a method based on a change in thermal conductivity (catarometer as a chromatographic detector) are all purely physical methods, and each of them is in service with modern analytical chemistry. As, by the way, are many biochemical methods (and even some purely biological). The end justifies the means.

At the same time, the methods of analysis, whatever they are based on, are embedded in the rigid system formed by analytical chemistry, where everything is regulated by the innate laws of this science. This system includes: identification and elimination of interfering influences; rules of graduating (calibrating); assessment of the range of contents, where the certain method works, and the objects to the analysis of which it is applicable; assessment of results reproducibility; evaluation of conformance with sample preparation methods; reasonable «manufacturability» of analysis tools; life-time of the

tools; technological efficiency of the analysis procedure, etc.

Over time, the definition of analytical chemistry has changed. This is how Professor Yury Klyachko described analytical chemistry in 1949 [1]: “Analysis of the chemical composition of a substance, with whatever method of measurement it is carried out, can always be attributed to the field of analytical chemistry, *if special chemical reactions are involved in the process.*” In the period of 40 to 50 years later, the same researcher proposes a new definition [2]: “Analytical chemistry is the science studying the principles and technology of qualitative and quantitative analysis of the chemical composition and chemical structure of substances and materials.” You can see that there is no longer such tight binding to chemistry. Analytical chemistry is a science that creates and develops common methodology, principles, methods and means for determining the chemical composition and chemical structure of a substance, as well as developing methods for analyzing various objects (a slightly modified definition from this was previously published in the book [3]).

Interestingly enough – in order not to be so tightly bonded to chemistry alone, analytical chemistry today often appears under other names: *Analytical Sciences, Analytik (German), Analytiks.*

The fundamental aspect (or one of the fundamental aspects) of analytical chemistry is in the field of searching for phenomena, patterns, properties from which you can “squeeze” a new technique, a new method of analysis, to get an opportunity for improving the characteristics of the already known methods, and so on.

### **The main directions of development and some achievements of Russian analytical chemistry**

The successes of analytical chemistry are enormous, its contribution to the progress of many sciences is very significant (the human genome was decoded thanks to the use of mass



spectrometry and partially of capillary electrophoresis), let alone the decisions in control of technological processes or environmental objects; quality control and safety of many products ranging from heat-resistant steel to aspirin; detection of toxic substances or explosives. A number of analysis methods have been awarded with the Nobel Prize:

- Mass spectrometry, isotope analysis, F. Aston, 1922;
- Micromethods of elemental analysis of organic substances, F. Pregl, 1923;
- Isotope methods, radioactivity analysis, D. Hevesy, 1943;
- Electrophoretic and adsorption analysis of proteins, A. Tiselius, 1948;
- Distribution chromatography, A. Martin and R. Sinj, 1952;
- Polarography, J. Heyrovsky, 1959;
- Radioimmune analysis, R. Yalow, 1977;
- New variants of mass spectrometric analysis, K. Tanaka and J. Fenn, 2002.

Many unique studies have been performed in our country that contributed to global analytical chemistry; the most significant achievements

are described in the recently published monograph “The Russian Contribution to Analytical Chemistry” [4, 5] (Fig. 1).

Very high significance should be attached to new methods and means of highly sensitive remote detection of explosives. Regarding this, at the Institute of Petroleum Geology and Geophysics of the Siberian Branch of the Russian Academy of Sciences (Novosibirsk), the limit of detection of TNT vapors ( $10^{-15}$  g/cm<sup>3</sup>) has been reached, which is two orders of magnitude lower than that of the world-famous tools (V.M. Gruzov *et al.*). At V.V. Zuev Institute of Atmospheric Optics of RAS a lidar method has been developed for detecting microparticles of explosives at rather long distances. In 2019, this work was awarded with the Russian Federation President Prize for Young Scientists.

Of great interest are the results of research with the earlier mentioned systems “electronic tongue” and “electronic nose.” Such systems allow for identification of liquid and gaseous substances, for example, types of tea or coffee after brewing; assessing the suitability of food products by the gas phase above them; and so on. Similar works are on the go in St. Petersburg (the school of Professor Yury Vlasov), in Bashkiria State University (V.N. Maistrenko) and Saratov State University (E.G. Kulagina), in Voronezh State University of Engineering Technologies (T.A. Kuchmenko) (Fig. 2).

In the Samara State Aerospace University named after S.P. Korolev the team of I.A. Platonov *et al.* has developed an unusual gas chromatograph with its very compact size among its other advantages (Fig. 3).

A new version of mass spectrometry analysis (SALDI) has been developed by a group that includes researchers from the Vernadsky Institute of Geochemistry and Analytical Chemistry (A.A. Grechnikov) and from the Prokhorov Institute of General Physics. In general, Russia and the USSR have contributed significantly to mass spectrometric methods of analysis: a mass reflectron by B.A. Mamyrin; orthogonal introduction of sample by A.F. Dodonova; the ERIAD

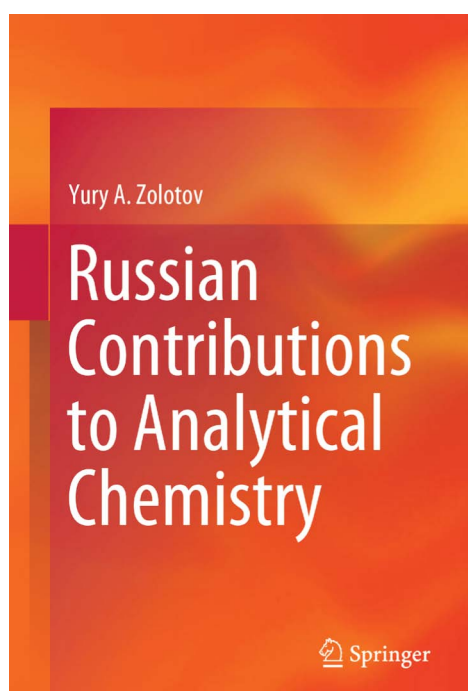


Fig. 1. Cover of the book on main achievements of Russian analysts.

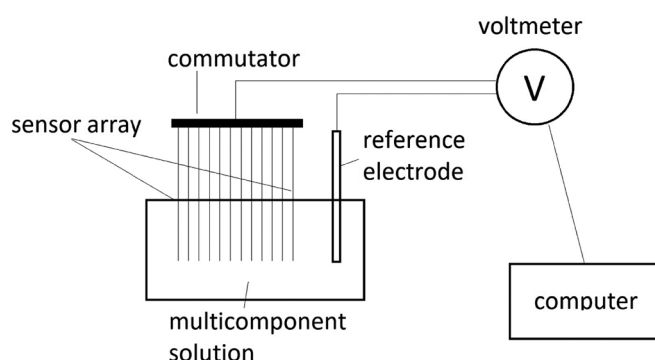


Fig. 2. Scheme of “electronic tongue” based on potentiometric sensors.

method by L.N. Gall (electro-spraying for ionization); photochemical ionization at atmospheric pressure by I.A. Revelsky and others. These, of course, are not recent works, but high-level researches are carried out nowadays too. In addition to the mentioned works on the SALDI method, this includes the creation of “elemental ERIAD” at the Institute for Analytical Instrumentation of the Russian Academy of Sciences (L.N. Gall at al.), achieving very high resolutions using ion cyclotron resonance (E.N. Nikolaev), interesting applications of molecular and elemental mass spectrometry to solving biological, ecological and geological problems (A.T. Lebedev, M.A. Bolshov, V.K. Karandashev at al.). A full scale research area has formed itself, which in our country (in 2007) was given the name of “nanoanalytics”. This direction is not really about analysis of nanoscale objects, but more about the use of nanoparticles and nanotechnologies for the analysis of ordinary objects. For instance, a surface plasmon resonance band is used to determine bioactive organic compounds via spectrophotometric method (S.G. Dmitrienko and V.V. Apyari, Moscow State University); nano-micelles are used in different applications (S.N. Shtykov, Saratov University; A.V. Pirogov, Moscow State University, etc.); new sorbents are created in the form of stationary phases containing gold nanoparticles for high performance liquid chromatography (O.A. Shpigun at al., Moscow State University).

It is often desirable, at least at the first stage of analysis, to avoid identifying each component from a series of more or less the same type of components (different phenols or polyaromatic compounds in waters, various heavy metals), but to evaluate them in total. This is referred to as “determining of integral indicators”. The methods of this analysis type is successfully developed by V.I. Vershinin at Omsk State University as well as by some other groups. If the overall test shows a negative result, there is no need for component-based analysis.

A prominent place in front-line research belongs to development of chemical sensors, and especially biosensors. In this field research is carried out at Kazan (Privolzhsky) Federal University (G.K. Budnikov, G.A. Evtyugin, E.P. Medyantsev at al.), at Moscow University (A.A. Karyakin) and in several other organizations. The results are presented in a large number of publications in high-rated journals, and a monograph written by G.A. Evtyugin [6]. A monograph on ion-selective electrodes (which in fact are chemical sensors) was published by K.N. Michelson of St. Petersburg University [7].

To say more on the notable books, but in different topics: B.L. Milman wrote a monograph on identifica-

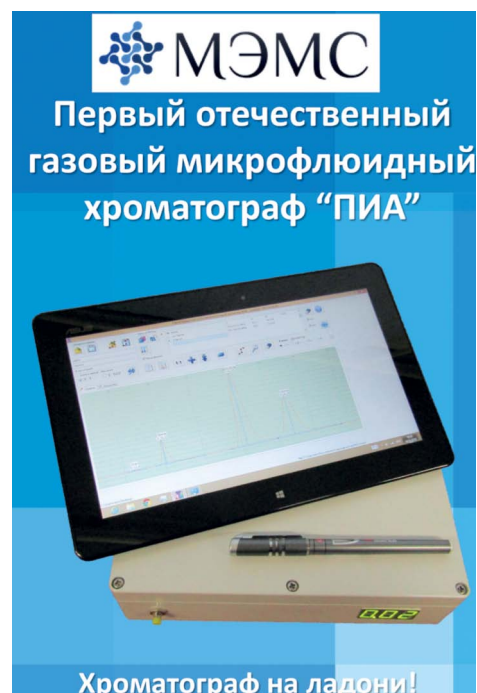


Fig. 3. Portable microfluidic gas chromatograph (leaflet).

tion of chemical compounds [8], and A.T. Lebedev published his monograph on mass spectrometry in organic chemistry [9].

#### **Exemplary results achieved with support from the Russian Foundation for Basic Research**

Now I would like to dwell on some very vivid examples of promising work carried out under projects supported by the Russian Foundation for Basic Research (RFBR).

A lot of research has been carried out recently to create new methods for detecting and determining biologically active substances for: 1) the diseases diagnosing (Fig. 4); 2) assessing quality and safety of food; 3) assessing safety of environmental objects, 4) evaluating authenticity and the quality of pharmaceuticals.

The methods of non-invasive diagnostics of the human body condition by the smell of a bioassay are successfully developed by Tatyana Kuchmenko at earlier mentioned Voronezh State University of Engineering Technologies. Kuchmenko, Professor of the Russian Academy of Science, is in charge of the Department of Physical

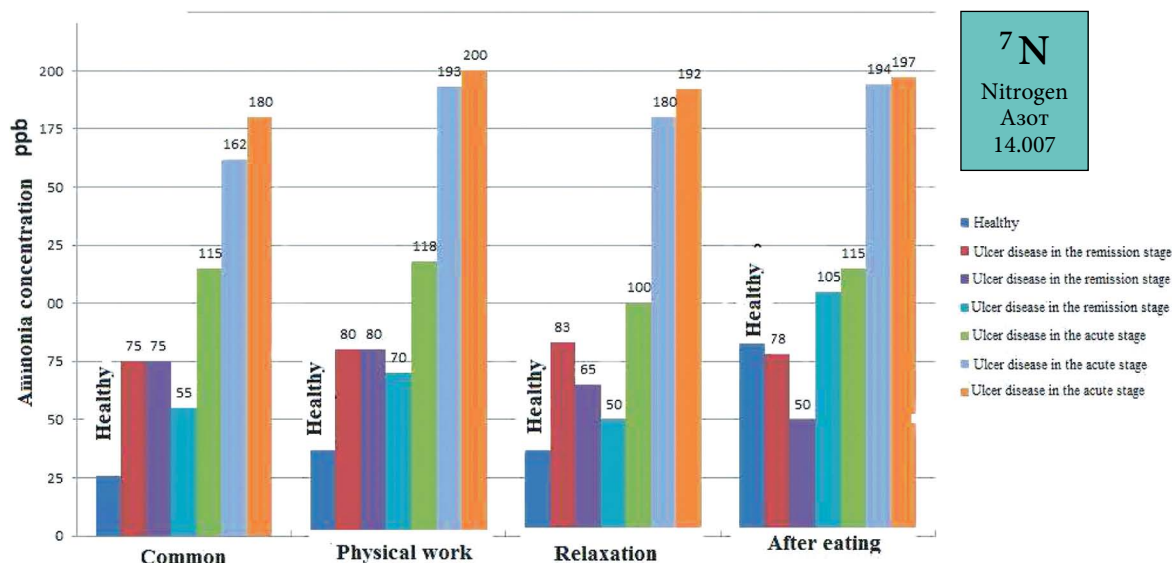


Fig. 4. Ammonia content in the air exhaled by an individual in a range of situations. Diode-laser spectroscopy was used in the experiments (the work was presented by the Prokhorov Institute of General Physics staff).

and Analytical Chemistry at her university, she is a member of the Bureau of the RAS's Scientific Council on Analytical Chemistry. Irina Goryacheva at the Department of General and Inorganic Chemistry, Saratov State University, creates nanosensors based on luminescent quantum dots for diagnostics of lung cancer; the technology also provides for detecting the circulation of miRNAs. While working in front-line topical research, Irina Goryacheva regularly wins RFBR grants. Part of her works, by the way, belongs to the area of nanoanalytics, which was discussed above.

Among exemplary projects aimed at analyzing environmental objects there are projects lead by Tatyana Rusanova (Head of Analytical Chemistry and Chemical Ecology Department, Saratov University). Her team works on the development of biosensor systems based on nanoscale materials; the systems allow detection of toxic substances in water. Peter Fedotov from the Vernadsky Institute of Geochemistry and Analytical Chemistry is thoroughly engaged in the study of nano- and microparticles of soil, dust and ash. He learned to fractionate them, which is important, for example, when assessing the mobility of elemental forms in the environment. To determine biologically important

compounds, Gennady Evtyugin, Head of Analytical Chemistry Department, Kazan (Privolzhsky) Federal University, is developing new chemoresistor structures under an RFBR supported project.

#### “Geography” of science. Conferences

There are several centers in this country where analytical chemistry is developing successfully; many of their employees receive grants from RFBR. There are academic institutions, that include: Vernadsky Institute of Geochemistry and Analytical Chemistry; Kurnakov Institute of General and Inorganic Chemistry; Nametkin Institute of Petrochemical Synthesis; Devyatkh Institute of High-Purity Chemistry; Nikolaev Institute of Inorganic Chemistry; Institute of Microelectronics Technology and High Purity Materials; Institute of Analytical Instrumentation. The state universities include those of Moscow, St. Petersburg, Saratov, Kuban, Voronezh, Omsk, Nizhny Novgorod and Irkutsk; Kazan (Privolzhsky) Federal University, Lipetsk State Technical University, Voronezh State University of Engineering Technologies and others. Among the sectoral research institutes there are: Fedorovsky Institute of Mineral Raw Materials, Mendeleev All-Russian Institute for Metrology, etc.

Russian Foundation for Basic Research regularly supports organizing and carrying out of all-Russian and regional congresses and conferences on analytical chemistry, as well as school conferences for the young. These activities are aimed at the developing of national analytical chemistry and allow us to compare the levels, scale and progress of native research against the achievements of our foreign colleagues. Most often, the RAS Scientific Council on Analytical Chemistry plays the part of organizer of these events.

### Prospects of development in analytical chemistry

The following areas may be outlined for the development of analytical chemistry as a science during the next 10–15 years:

1. Search and study of new properties of substances as well as phenomena and patterns which can be laid in the basis for fundamentally new methods and means of chemical analysis, including multicomponent and highly selective analysis. This search is associated with the expansion of sciences and technologies that may contribute to the field; in addition to chemistry and physics, this list already includes mathematics, biochemistry, a number of technical and technological developments.

2. Intensive development and use of means and approaches to extra-lab (“field”) analysis. In particular this can be done through the development of effective, but easy-to-use means of operational analysis of biomedical objects, determination of food components content, rapid detection of explosives and drugs, etc.

3. Miniaturization of analysis, including, on the one hand, making of compact universal analytical instruments, that could be based, for example, on microfluidic systems. On the other hand, that would include making simpler analyzers; miniaturization can also be achieved through reducing the mass and volume of samples.

4. Development of speciation analysis, that is, methods and means of recognizing and quantifying various chemical and physical forms of components of interest (oxidation state of elements, different chemical compounds of an element, its enantiomers; dissolved, colloidal or sorbed forms, etc.)

5. Development of direct (non-destructive) analysis of solids, mainly in the way of using physical phenomena.

6. Further development of methods and means of local and remote analysis.

7. Development of methods for substances identifying based on evaluation of generalized indicators using mathematical/chemometric devices of pattern recognition (instead of the traditional component-based analysis).

8. Creation and widespread use of continuously operating chemical sensors, such as sensors for assessing the composition of air in industrial and residential premises.

9. Automation of mass analysis, especially on the basis of extensive computerization. Constituent to this process are further automation of measuring devices and sample preparation systems.

10. Expansion and strengthening of the already established segment of analytical chemistry, called nano-analytics, introduction of already developed nano-analytical methods into practice.

11. Development of chemical analysis metrology and other fields relevant to it (development of absolute determination methods, improvement of calibration systems and methods for processing analysis results, etc.).

12. Further development and improvement of spectroscopic, mass-spectrometric, chromatographic, electrochemical, biochemical, thermal and other methods of analysis. Integration of methods and creation of appropriate devices (combined, hybrid methods) will play an increasingly important role.

13. Development of methods and means of sample preparation – for decomposition of samples, separation of mixtures, isolation and concentration of the target components.

14. Creating new methods for analyzing the most important objects and developing analytical chemistry of key analytes. At that, the most important objects would include biomedical materials, foodstuffs, pharmaceuticals; while the list of key analytes predominantly incorporates components of biological fluids and tissues, pesticides, poisonous substances and explosives, dissolved oxygen, etc. In the area of the “classical” objects analyzing (mineral raw materials, metals, oil, etc.) the methods of research will expand towards speciation and non-destructive analysis, automation and so on.

15. When solving practical problems, for example, analyzing environmental objects, the wider use of multistage analysis with screening and rejecting faulty samples at the early stages seems to be the most reasonable approach.

16. In order to advance successfully in these and other areas, laboratories should be provided with efficient analytical equipment. For learning to work with complex and expensive devices, it is advisable to create a system of computer simulators.

To summarize on the above, Author would state that the Russian analytical chemistry is developing suc-

cessfully in general, with many of the results taking a worthy place in world science. The support from federal sci-

entific and technical programs or scientific foundations, primarily RFBR, turns out to be very helpful for the field and its workers.

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