ISSN 2518-718X (Print)
ISSN 2663-4872 (Online)

№ 3(95)/2019

ХИМИЯ сериясы
Серия ХИМИЯ
CHEMISTRY Series

ҚАРАҒАНДЫ УНИВЕРСИТЕТІНІҢ ХАБАРШЫСЫ

ВЕСТНИК КАРАГАНДИНСКОГО УНИВЕРСИТЕТА

BULLETIN OF THE KARAGANDA UNIVERSITY

ISSN 2518-718X (Print)
ISSN 2663-4872 (Online)
Индексі 74617
Индекс 74617

ҚАРАҒАНДЫ УНИВЕРСИТЕТІНІҢ ХАБАРШЫСЫ

ВЕСТНИК КАРАГАНДИНСКОГО УНИВЕРСИТЕТА

BULLETIN OF THE KARAGANDA UNIVERSITY

ХИМИЯ сериясы

Серия ХИМИЯ

CHEMISTRY Series

№ 3(95)/2019

Шілде–тамыз–қыркүйек
30 қыркүйек 2019 ж.
Июль–август–сентябрь
30 сентября 2019 г.
July–August–September
September, 30, 2019

1996 жылдан бастап шығады
Издается с 1996 года
Founded in 1996

Жылына 4 рет шығады
Выходит 4 раза в год
Published 4 times a year

Қарағанды, 2019
Караганда, 2019
Karaganda, 2019

Редакцияның мекенжайы: 100024, Қазақстан, Қарағанды қ., Университет к-сі, 28
Тел.: (7212) 77-03-69 (ішкі 1026); факс: (7212) 77-03-84.
E-mail: vestnick_kargu@ksu.kz; ipustolaikina@gmail.com (*жауапты хатшы*)
Сайты: http://chemistry-vestnik.ksu.kz

Редакторлары

Ж.Т. Нурмуханова, И.Н. Муртазина

Компьютерде беттеген

В.В. Бутяйкин

Қарағанды университетінің хабаршысы. Химия сериясы.
ISSN 2518-718X (Print). ISSN 2663-4872 (Online).

Меншік иесі: «Академик Е.А. Бөкетов атындағы Қарағанды мемлекеттік университеті» РММ.

Қазақстан Республикасының Мәдениет және ақпарат министрлігімен тіркелген. 23.10.2012 ж. № 13110–Ж тіркеу куәлігі.

Басуға 28.09.2019 ж. қол қойылды. Пішімі 60×84 1/8. Қағазы офсеттік. Көлемі 20,0 б.т. Таралымы 300 дана. Бағасы келісім бойынша. Тапсырыс № 110.

Е.А. Бөкетов атындағы ҚарМУ баспасының баспаханасында басылып шықты.
100012, Қазақстан, Қарағанды қ., Гоголь к-сі, 38. Тел. 51-38-20. E-mail: izd_kargu@mail.ru

Адрес редакции: 100024, Казахстан, г. Караганда, ул. Университетская, 28
Тел.: (7212) 77-03-69 (внутр. 1026); факс: (7212) 77-03-84.
E-mail: vestnick_kargu@ksu.kz; ipustolaikina@gmail.com (*отв. секретарь*)
Сайт: http://chemistry-vestnik.ksu.kz

Редакторы

Ж.Т. Нурмуханова, И.Н. Муртазина

Компьютерная верстка

В.В. Бутяйкин

Вестник Карагандинского университета. Серия Химия.

ISSN 2518-718X (Print). ISSN 2663-4872 (Online).

Собственник: РГП «Карагандинский государственный университет имени академика Е.А. Букетова».

Зарегистрирован Министерством культуры и информации Республики Казахстан. Регистрационное свидетельство № 13110–Ж от 23.10.2012 г.

Подписано в печать 28.09.2019 г. Формат 60×84 1/8. Бумага офсетная. Объем 20,0 п.л. Тираж 300 экз. Цена договорная. Заказ № 110.

Отпечатано в типографии издательства КарГУ им. Е.А. Букетова.
100012, Казахстан, г. Караганда, ул. Гоголя, 38, тел.: (7212) 51-38-20. E-mail: izd_kargu@mail.ru

Main Editor
Doctor of chemical sciences, Professor, Corresponding member of NAS RK
Ye.M. Tazhbayev

Responsible secretary **G.Yu. Amanbayeva**, Doctor of phylol. sciences, Professor

Postal address: 28, University Str., Karaganda, 100024, Kazakhstan
Tel.: (7212) 77-03-69 (add. 1026); fax: (7212) 77-03-84.
E-mail: vestnick_kargu@ksu.kz; ipustolaikina@gmail.com (*secretary*)
Web-site: http://chemistry-vestnik.ksu.kz

Editors
Zh.T. Nurmukhanova, I.N. Murtazina

Computer layout
V.V. Butyaikin

Bulletin of the Karaganda University. Chemistry series.

ISSN 2518-718X (Print). ISSN 2663-4872 (Online).

Proprietary: RSE «Academician Ye.A. Buketov Karaganda State University».

Registered by the Ministry of Culture and Information of the Republic of Kazakhstan. Registration certificate No. 13110–Zh from 23.10.2012.

Signed in print 28.09.2019. Format 60×84 1/8. Offset paper. Volume 20,0 p.sh. Circulation 300 copies. Price upon request. Order № 110.
Printed in the Ye.A. Buketov Karaganda State University Publishing house.
38, Gogol Str., Karaganda, 100012, Kazakhstan. Tel.: (7212) 51-38-20. E-mail: izd_kargu@mail.ru

МАЗМҰНЫ

ОРГАНИКАЛЫҚ ХИМИЯ

ФИЗИКАЛЫҚ ЖӘНЕ АНАЛИТИКАЛЫҚ ХИМИЯ

БЕЙОРГАНИКАЛЫҚ ХИМИЯ

ХИМИЯЛЫҚ ТЕХНОЛОГИЯ

ХИМИЯНЫ ОҚЫТУ ӘДІСТЕМЕСІ

ҒЫЛЫМИ ЗЕРТТЕУДІ ШОЛУ

СОДЕРЖАНИЕ

ОРГАНИЧЕСКАЯ ХИМИЯ

ФИЗИЧЕСКАЯ И АНАЛИТИЧЕСКАЯ ХИМИЯ

НЕОРГАНИЧЕСКАЯ ХИМИЯ

ХИМИЧЕСКАЯ ТЕХНОЛОГИЯ

МЕТОДИКА ОБУЧЕНИЯ ХИМИИ

ОБЗОР НАУЧНЫХ ИССЛЕДОВАНИЙ

CONTENTS

ORGANIC CHEMISTRY

PHYSICAL AND ANALYTICAL CHEMISTRY

INORGANIC CHEMISTRY

CHEMICAL TECHNOLOGY

METHODS OF TEACHING CHEMISTRY

REVIEW OF RESEARCH

ОРГАНИКАЛЫҚ ХИМИЯ
ОРГАНИЧЕСКАЯ ХИМИЯ
ORGANIC CHEMISTRY

DOI 10.31489/2019Ch3/8-13

UDC 544.42+519.242.7

M.B. Akhtayeva, G.Ye. Azimbayeva

Kazakh State Women's Teacher Training University, Almaty, Kazakhstan
(E-mail: aktaeva.marzhan@mail.ru)

Research of amino acid content of *Cichorium intybus* L. and *Urtica dioica* L. by means of gas-liquid chromatography

Content of amino acids in *Cichorium intybus* L. and *Urtica dioica* L. has been presented. Researches were carried out by means of gas-liquid chromotography. 20 amino acids were revealed in *C. intybus* L. and *U. dioica* L., (mg/100 g), glutamate: $32 < 2568$; aspartate: $916 < 1820$; alanine: $23 < 1235$; proline: $38 < 962$; glycine: $21 < 425$; leucine: $29 < 42$; isoleucine: $24 < 626$ and arginine: $36 < 58$. Leaves of *U. dioica* L. and stems of *C. intybus*L. contain more glycine than stems of *U. dioica* L. In *C. intybus* L. flowers contain more amino acids than leaves and stems. In *U. dioica* L. leaves contain more amino acids than flowers and stems. In leaves of *U. dioica* L. valine volume was 1.5 times higher than in *C. Intybus* L. Amino acids' content in stems of *C. intybus* L. and *U. dioica* L. were almost identical. Leucine content in leaves and stems was in 1.5–2 times higher in *C. intybus* L. than in *U. dioica* L. The lowest cysteine volume was in leaves and stems of *C. intybus* L. Methionine volume was higher in *U. dioica* L.

Keywords: Cichorium intybus L., *Urtica dioica* L, gas-liquid chromatograph, amino acids, flowers, stems, leaves, BAS.

Introduction

Biologically active substances (BAS) are able to restore pathologically changed organism functions of animals and humans, at the same time they are an admissible source of medicine revealed in various ways. Amino acids are known to be the most important components of biologically active substances. Kazakhstan is rich with both cultivated and important and useful medicinal plants. Area of using the medicines obtained from such plants extends from year to year due to their effectiveness. Identification of plant composition increases quality of selection of raw material for its use in pharmacology. Amino acids hold a specific place in the physiological processes taking place in a human body. At unbalanced nutrition or in case of disease to support the normal level of amino acids the medicines obtained from such medicinal plants are applied. *Cichorium intybus* L. and *Urtica dioica* L. belonging to the *Asteraceae* family are unique among such plants. Researches proved *Cichorium intybus* L. and *Urtica dioica* L. to be the sources of biologically active substances [1].

Totally the genus Urtica includes 50 species, among them one can find only three species in Kazakhstan; and the genus Cichorium includes more than 1000 species, in Kazakhstan one can find only one of them. The most widespread species from these two genera are *Urtica dioica* L. and *Cichorium intybus* L. They are spread across all Kazakhstan and do not choose the soil [2].

Nowadays one of the most used in agriculture, medicine, pharmaceutics, dietology and food industry and effective sources of raw materials are *Cichorium intybus* L. and *Urtica dioica* L. Their various pharmacological, biological and physiological properties are being comprehensively investigated. Nevertheless, studying the amount of biologically active substances and properties in plants with undetermined complete compound, namely in *Cichorium intybus* L. and *Urtica dioica* L., remains very relevant [3, 4] for today.

As it is noticed above amino acids are an important component of biologically active substances [1–3].

Since the molecules of protein compounds which are so important for existence consist of residues of amino acids, their value is great. In the nature there are more than 150 types of amino acids. About 20 of them are monomers of block groups performing very important functions in the structure of protein molecules.

Amino acids are known to take part in the processes of metabolism of an organism. As people and all animals cannot produce amino acids therefore they may get them from the food in ready form. Nowadays the method of biotechnological synthesis is applied (chemistry and microbiology) for producing the amino acids. After that amino acids are added to food of people and animals. Also amino acids are the industrial polyamides which are the products which are always used in production of paints and drugs [2–4].

Under the influence of arginine, one of the major amino acids in a protein molecule functioning in the thyroid gland, which is responsible for exchange of calcium in an organism, improves. Arginine slows down growth of tumors including malignant. It is also applied for increase of functions of purification and excretion of waste of nitric exchange in kidneys [3, 5].

Amino acids, necessary for human, enter our bodies together with food. Valine, leucine, isoleucine, methionine, threonine, phenylalanine, lysine, arginine, histidine and tryptophane are the most necessary among them. Availability of these amino acids as a part of our food increases nutritional value of any product. It is known that about twenty amino acids take part in protein biosynthesis [4–7].

Amino acids hold a specific place in a human body. For example, glutamine was one of the first the synthesized amino acids. The Japanese scientist Kinosita in nature found a special bacterium *Micrococcus glutamicus* and extracted from it this acid. This bacterium can be used for obtaining glutamic acid from nearly 50 % of glucose added to the medium. Nowadays about one hundred thousands of tons of this acid per a year are manufactured in Japan and the USA at special plants. Glyutamic acid in food industry is added to products, improving their quality. In medicine glutamic acid is applied in treatment of diseases of a nervous system.

One of the important amino acids in a molecule of protein is the lysine. 2.1 kg of synthesized lysine being added will cause animals' weight increase for 13.6 % in average, and costs for protein will decrease by 20–25 %. This amino acid is considered to be the most valuable and necessary additive in nutrition ration [5].

Applying lysine in bread baking increases its nutrition value. The lysine in a large amount is also produced by *Enterobacter aerogenes*, *Proteus spp.*, *Bacillus subtilis* and *Torula utilis*.

Under the ultraviolet influence *Micrococcus glutamicus* can synthesize lysine. Nowadays lysine production by using this bacterium is promoted to the industrial level. As the result about ten thousand tons of lysine per a year is produced in Japan, the USA and in other countries [3]. There are two leading companies in the world market of L-lysine production such as the Japanese Ajinomoto Co and the American Archer Daniels & Midlands (ADM), which control 33 % of the world production. Other large players in the market are Degussa-Huels (Germany), BASF (Germany), Kyowa Hokko (Japan) and Cheil Jedang Corporation (South Korea) [8].

In our research it was revealed that such plants as *Cichorium intybus* L. and *Urtica dioica* L., in turn, are the sources of amino acids. In this connection the aim of our research is to determine the volume of amino acids in *Cichorium intybus* L. and *Urtica dioica* L. The amount of amino acids in the samples of *Cichorium intybus* L. and *Urtica dioica* L. was determined by means of gas-liquid chromotography using the device Carlo-Erba-4200 (Italy-USA).

Experimental

Samples of *Cichorium intybus* L. and *Urtica dioica* L. collected in September-October 2016–2017 in the Medeo mountains of Almaty area were the objects of our research.

1 g of raw material was hydrolyzed at 105 ºC within 24 hours in 6N HCl. The obtained hydrolyzate was evaporated in a drying rotor by 3 times, before drying at a temperature of 40–50 ºC and atmospheric pressure in 1 atmosphere. The residue formed was dissolved in 5 ml of sulfosalicylic acid. In 5 minutes the centrifuged liquid of ionomixed pitch was passed through a pipe by means of a mesh of Dauks 50, N-8, 200–400 with velocity of 1 drop per a second. After that pitch was rinsed in 1–2 ml of water and 2 ml of 0.5N acetic acid; then pitch was rinsed with water till obtaining the neutral medium. For an elution of amino acids a sample was passed through a pipe of 3 ml of 6N NH_4OH with velocity of 2 drops per a second. Eluate was gathered together with water into a flask with a round bottom. After that the substance from a flask was evaporated in a rotor-evaporator under the pressure of 1 atmosphere at 45–50 ºC, till drying. Into the same flask there was added 1 drop of freshly prepared solution of 1.5 % $SnCl_2$, 2,2-dimetoxypropane, HCl and 1–2 ml of dense propanol; then it was heated at 110 ºC temperature. This temperature was maintained during 20 minutes, and then the eluate was again evaporated in a rotor-evaporator.

At the following stage 1 ml of freshly prepared acetylated reagent was added to a flask, heated during 1.5–2 minutes at temperature of 60 ºC. This reagent was evaporated till drying, then a sample was again evaporated in a rotor evaporator; 2 ml of ethyl acetate and 1 ml of saturated NaCl solution were poured into the flask. The flask was mixed slowly, at this moment the 2 layers were formed; for gas chromatographic analysis the top layer was taken. Experiment was carried out by the method of gas chromatographic analysis using «Carlo-Erba-4200» device (Italy-USA) [9–11]. The data obtained during the research are presented in Table 1.

Table 1

The volume of amino acids in the samples of *Cichorium intybus* L. and *Urtica dioica* L., mg/100 g

Amino acids	*Cichorium intybus* L. leaves	*Cichorium intybus* L. stem	*Cichorium intybus* L. flower	*Urtica dioica* L. leaves	*Urtica dioica* L. stem	*Urtica dioica* L. root
Threonine* (Thr)	198	182	220	750	384	19
Serine (Ser)	248	234	266	206	68	30
Glycine (Gly)	265	225	300	425	228	21
Alanine (Ala)	714	610	915	1235	754	23
Valine* (Val)	224	202	235	558	325	24
Methionine(Met)	83	73	98	82	30	-
Isoleucine* (Ile)	368	352	372	626	406	24
Leucine* (Leu)	342	315	364	317	214	29
Aspartate (Asp)	1208	1118	1278	1820	916	–
Glutamat (Glu)	2456	2340	2568	348	194	32
Cystine (Cys)	36	26	42	4	2	–
Lysine* (Lys)	224	196	260	342	156	25
Arginine(Arg)	328	305	355	585	478	36
Ornithine(Orn)	2	1	3	376	190	14
Tyrosine (Tyr)	284	270	303	4	2	–
Phenylalanine* (Phe)	255	248	271	2996	2486	–
Tryptophane (Trp)	65	55	88	156	78	–
Proline (Pro)	452	435	476	962	722	38
Histidine (His)	209	192	228	492	322	–
Oxyproline (Oxn)	2	1	3	524	318	32

Note. * — non mixed amino acids.

Results and Discussion

The composition of *Cichorium intybus* L. and *Urtica dioica* L. was revealed to be rich with amino acids. 20 types of amino acids were found in *Cichorium intybus* L. and *Urtica dioica* L. Among them (mg/100 g) glutamate: 32 < 2568, aspartate 916 < 1820, alanine: 23 < 1235, proline: 38 < 962, glycine: 21 < 425, leucine: 29 < 425, isoleucine: 24 < 626 and arginine: 36 < 58. According to results of our research, in comparison with *Cichorium intybus* L. leaves of *Urtica dioica* L. contain more glycine; and in turn stems of *Cichorium intybus* L. contain more glycine than stems of *Urtica dioica* L.

In *Cichorium intybus* L. flowers contain more amino acids than leaves and stems. In *Urtica dioica* L. leaves contain much more amino acids than flowers and stems, twice. In leaves of *Urtica dioica* L. valine amino acid volume was 1.5 times higher than in *Cichorium intybus* L. Content of amino acids in stalks of plants of *Cichorium intybus* L. and *Urtica dioica* L. were almost identical. In leaves and stem of *Cichorium intybus* L. leucine content in 1.5–2 times more than in *Urtica dioica* L. The volume of cysteine was least of all in leaves and a stalk of Cichorium intybus L. Methionine volume in *Urtica dioica* L. was higher than in *Cichorium intybus* L.

Results of our research have something in common with literary sources about structure of the herbs, which underwent an experiment, namely they are rich source of such amino acids as glutamate, aspartate, alanine, proline, arginine, leucine, serine, isoleucine, tyrosine, lysine and glycine [12, 13]. The plants studied by us are widely used in traditional medicine at treatment of many diseases; also they have homeopathic properties. They have property to keep amino acids in the normal state. Also they can be applied not only in the medical purposes, but also as technical raw materials [14].

Amino acids are considered to be a unit of structural proteins. Also proteins participate in such phenomena as digestion, irritation, division, reproduction, the movement; and they are a source of life of live organisms. Protein acts as antibodies protecting a human body from microbes and pathogenic agents [13, 15]. In recent years great attention is paid to production of amino acids necessary for protein synthesis. Before they were made by hydrolysis from valuable raw materials with a large amount of protein, and it demanded big expenses. For the last ten years the new microbiological method of obtaining amino acids has been developed [14].

Conclusions

For the first time the volume of amino acids in *Cichorium intybus* L. and *Urtica dioica* L. growing in the Medeo Mountains in Kazakhstan was revealed. In total 20 amino acids were revealed, among them the most amount was found in flowers of *Cichorium intybus* L. and in leaves of *Urtica dioica* L.

References

1 Серебрянская Т.С. Сравнительный анализ свободных аминокислот сбора лекарственных растений и его полиэкстракта сухого, обладающих нейропротекторным действием / Т.С. Серебрянская, Г.Г. Николаева, М.Ю. Тулонов, С.М. Гуляев // Вестн. Бурят. ун-та. — 2010. — № 12. — С. 88–91.

2 Коломиец Н.Э. Стандартизация листьев крапивы двудомной / Н.Э. Коломиец. Г.И. Калинкина, Н.Н. Сапронова // Фармация. — 2011. — № 6. — С. 22–24.

3 Шкроботько П.Ю. Аминокислотный состав подземных органов валерианы Фории и валерианы бузинолистной / П.Ю. Шкроботько // Фармация. — 2009. — № 7. — С. 19–23.

4 Курбанбаева Н.М. Титриметрическое идентифицирование биологических активных веществ растений *Urtica dioica* L. / Н.М. Курбанбаева, Г.Е. Азимбаева // Формирование инновационной среды в молодежных объединениях вузов: Материалы междунар. науч.-практ. конф., посвящ. дню рожд. Д.И. Менделеева (16 марта 2017 года). — Алматы: Полиграфия ОНОН, 2017. — С. 66–67.

5 Олешко Г.И. Разработка унифицированной методики количественного определения суммы свободных аминокислот в лекарственном растительном сырье и экстракционных препаратах / Г.И. Олешко, Т.И. Ярыгина, Е.В. Зорина, М.Д. Решетникова // Фармация. — 2011. — Т. 60, № 3. — С. 14–17.

6 Уәлиханова Г.Ж. Өсімдік биотехнологиясы: 2-ші толықт. бас. / Г.Ж. Уәлиханова. — Алматы: Дәуір, 2009. — 336 б.

7 Мамонов Л.К. Введение в фитохимические исследования и выявление биологической активности веществ растений / Л.К. Мамонов, Р.А. Музычкин. — Алматы: Школа XXI века, 2008, — 216 с.

8 Сайт исследовательской компании «Abercade» [Электронный ресурс]. — Режим доступа: http://www.abercade.ru/research/analysis/25.html.

9 Вехов В.Н. Практикум по анатомии и морфологии высших растений / В.Н. Вехов, Л.И. Лотова, В.Р. Филин. — М.: Университетская книга, 1980. — 196 с.

10 Химия и применение природных и синтетических биологически активных соединений. — СПб.: Комплекс, 2004.

11 Мартынов А.М. Полифенольные соединения и аминокислоты надземной части Violauniflora (*Violaceae*) / А.М. Мартынов, А.М. Собенин // Растительные ресурсы. — 2011. — Т. 47, Вып. 2. — С. 118–122.

12 Дроздова И.Л. Изучение аминокислотного состава травы короставника полевого / И.Л. Дроздова // Традиционная медицина. — 2012. — № 29. — С. 49–51.

13 Дроздова И.Л. Аминокислотный состав травы икотника серого / И.Л. Дроздова, Т.И. Лупилина // Вестн. ВГУ. Сер. химия, биология, фармация. — 2015. — № 1. — С. 125–127.

14 Баева В.М. Изучение аминокислотного состава порошка и настоя травы манжетки / В.М. Баева // Традиционная медицина. — 2007. — № 1. — С. 53–55.

15 Скрябина Е.А. Аминокислоты растений рода *Melampyrum* L. / Е.А. Скрябина // Медицинский альманах. — 2012. — № 5. — С. 206–208.

М.Б. Ахтаева, Г.Е. Азимбаева

***Cichorium intybus* L. және *Urtica dioica* L. өсімдіктерінің құрамындағы аминқышқылдарының мөлшерін газсұйықтық хроматография әдісімен зерттеу**

Мақалада *Cichorium intybus* L. және *Urtica dioica* L. өсімдіктерінің құрамындағы аминқышқылдарының мөлшерін анықтау нәтижелері көрсетілген. Зерттеу жұмысы газсұйықтық хроматография әдісімен «Carlo-Erba-4200» (Италия–США) газсұйықтық хроматографында жүргізілді. Зерттеу нәтижесі бойынша *Cichorium intybus* L. және *Urtica dioica* L. өсімдіктерінде 20 аминқышқылдары табылды (мг/100 г), олардың мөлшері: глютамат: 32 < 2568; аспаратат: 916 < 1820; аланин: 23 < 1235; пролин: 38 < 962; глицин: 21 < 425; лейцин: 29 < 42; изолейцин: 24 < 626 және аргинин: 36 < 58 аралығында.

U. dioica L. жапырағында және *C. intybus* L. сабағында глициннің мөлшері көп, *U. dioica* L. сабағына қарағанда *C. intybus* L. гүлінде аминқышқылдарының мөлшері жоғары, жапырағы мен сабағына қарағанда. *U. dioica* L., жапырағында сабағы мен тамырына қарағанда, аминқышқылдарының мөлшері көп. *U. dioica* L. жапырағында валиннің мөлшері 1,5 есе жоғары, *C. intybus* L. қарағанда, *C. intybus* L. және *U. dioica* L. өсімдіктерінің сабағында аминқышқылдарының мөлшері шамалас мәнге ие. *C. intybus*. жапырағы мен сабағында, *U. dioica* L. өсімдігіне қарағанда, лейциннің мөлшері 1,5–2 есе жоғары. Ал цистеиннің мөлшері *C. intybus* L. жапырағы мен сабағында ең аз мөлшерді көрсетті. Сондай-ақ метиониннің мөлшері, *C. intybus* L. қарағанда, *U. dioica* L. жоғары мөлшерде табылды.

Кілт сөздер: Cichorium intybus L., *Urtica dioica* L, газсұйықтық хроматография, аминқышқылдары, гүлі, сабағы, жапырағы, ББЗ.

М.Б. Ахтаева, Г.Е. Азимбаева

Исследование объема аминокислот в составе *Cichorium intybus* L. и *Urtica dioica* L. с помощью газожидкостной хроматографии

В статье представлены результаты определения объема аминокислот у *Cichorium intybus* L. и *Urtica dioica* L. Исследования проводились методом газожидкостной хроматографии на приборе «Carlo-Erba-4200» (Италия–США). 20 аминокислот были обнаружены у *C. Intybus* L. и *U. Dioica* L. (мг/100 г), глютамат: 32 < 2568; аспартат: 916 < 1820; аланин: 23 < 1235; пролин: 38 < 962; глицин: 21 < 425; лейцин: 29 < 42; изолейцин: 24 < 626 и аргинин: 36 < 58. Листья *U. dioica* L. и стебли *C. intybus* L. содержат больше глицина, чем стебли *U. dioica* L. У *C. intybus* L. цветки содержат больше аминокислот, чем листья и стебли. В листьях *U. dioica* L. содержится больше аминокислот, чем в цветах и стеблях. В листьях *U. dioica* L. объем валина был в 1,5 раза выше, чем в *C. intybus* L. Содержание аминокислот в стеблях *C. intybus* L. и *U. dioica* L. было практически одинаковым. Листья и стебли *C. intybus*. L. содержат в 1,5–2 раза больше лейцина, чем в *U. dioica* L. Объем цистеина был меньше всего в листьях и стеблях *C. intybus* L. Объем метионина в *U. dioica* L. был выше чем, у *C. intybus* L.

Ключевые слова: Cichorium intybus L., Urtica dioica L., газожидкостная хроматография, аминокислоты, цветы, стебли, листья, БАВ.

References

1 Serebryanskaya, T.S., Nikolaeva, G.G., Tulonov, M.Yu., & Gulyaev, S.M. (2010). Sravnitelnyi analiz svobodnykh aminokislot sbora lekarstvennykh rastenii i eho poliekstrakta sukhoho, obladaiushchikh neiroprotektornym deistviem [The comparative analysis of free amino acids of herbs collection and its poly extract having neuroprotective action]. *Vestnik Buriatskoho universiteta — Bulletin of Buryat University*, *12*, 88–91 [in Russian].

2 Kolomiets, N.E., Kalinkina, G.I., & Sapronova, N.N. (2011). Standartizatsia listiev krapivy dvudomnoi [Standardization of *Urtica dioica*]. *Farmatsiia — Pharmacy*, *6*, 22–24 [in Russian].

3 Shkrobotko, P.Yu. (2009). Aminokislotnyi sostav podzemnykh orhanov valeriany Forii i valeriany buzinolistnoi [Amino acid composition of underground organs of Valerian Foria and Valerian elderberry]. *Farmatsiia — Pharmacy*, *7*, 19–23 [in Russian].

4 Kurbanbayeva, N.M., & Azimbayeva, G.E. (2017). Titrimetricheskoe identifitsirovanie biolohicheski aktivnykh veshchestv rastenii *Urtica dioica* L. [Titrimetric identification of biological active substances of plants *Urtica dioica* L.]. Proceedings from Formation of innovative environment in youth associations of Universities, dedicated to the birthday of D. Mendeleev: *Mezhdunarodnaia nauchno-prakticheskaia konferentsiia (16 marta 2017 hoda) — International Scientific and Practical Conference.* (pp. 66–67). Almaty: ONON polihrafiia [in Russian].

5 Oleshko, G.I., Yarygina, T.I., Zorina, E.V., & Reshetnikova, M.D. (2011). Razrabotka unifitsirovannoi metodiki kolichestvennoho opredeleniia summy svobodnykh aminokislot v lekarstvennom rastitelnom syrie ekstraktsionnykh preparatakh [Development of the unified technique of quantitative determination of the sum of free amino acids in medicinal vegetable raw materials and extraction preparations]. *Farmatsiia — Pharmacy*, *60, 3*, 14–17 [in Russian].

6 Ualikhanova, G.J. (2009). *Osimdik biotehnolohiiasy [Plant biotechnology].* Almaty: Dauir [in Kazakh].

7 Mamonov, L.K., & Muzychkina, R.A. (2008). *Vvedenie v fitokhimicheskie issledovanie i vyiavleniia biolohicheskoi aktivnosti veshchestv rastenii [Introduction to phytochemical studies and identification of biological activity of plant substances].* Almaty: Shkola XXI veka [in Russian].

8 Sait issledovatelskoi kompanii «Abercade» [Site of «Abercade»]. *abercade.ru* Retrieved from http://www.abercade.ru/research/analysis/25.html.

9 Vehov, V.N., Lotova, L.I., & Filin, V.R. (1980*). Praktikum po anatomii i morfolohii vysshikh rastenii [Workshop on anatomy and morphology of higher plants].* Moscow: Universitetskaia kniha [in Russian].

10 (2004). *Khimiia i primeneniie prirodnykh i sinteticheskikh biolohicheski aktivnykh soedinenii [Chemistry and the use of natural and synthetic biologically active compounds].* Sankt Petersburg: Kompleks [in Russian].

11 Martynov, A.M., & Sobenin, A.M. (2011). Polifenolnye soedineniia i aminokisloty nadzemnoi chasti *Viola uniflora* (*Violaceae*) [Polyphenolic compounds and amino acids of the overhead part of *Viola uniflora* (*Violaceae*)]. *Rastitelnye resursy — Plant resources*, *47, 2*, 118–122 [in Russian].

12 Drozdova, I.L. (2012). Izuchenie aminokislotnoho sostava travy korostavnika polevoho [The study of amino acid composition of grass korostovychi field]. *Traditsionnaia meditsina — Traditional medicine*, *29*, 49–51 [in Russian].

13 Drozdova, I.L., & Lupilina, T.I. (2015). Aminikislotnyi sostav travy ikotnika seroho [Amino acid composition of hiccup gray grass]. *Vestnik VGU, Seriia khimiia, biolohiia, farmatsiia — Bulletin of ESU. Series Chemistry, Biology, Pharmacy*, *1*, 125–127 [in Russian].

14 Baeva, V.M. Izuchenie aminokislotnoho sostava poroshka i nastoia travy manzhetki [Study of amino acid composition of the powder and infusion of grass cuff]. *Traditsionnaia meditsina — Traditional medicine*, *1*, 53–55 [in Russian].

15 Skryabina, E.A. (2012). Aminokisloty rastenii roda *Melampyrum L.* [Amino acids of plants of the genus *Melampyrum L.*]. *Meditsinskii almanakh — Medical almanac*, *5*, 206–208 [in Russian].

DOI 10.31489/2019Ch3/14-20

UDC 544.23

A.Kh. Zhakina[1], Ye.P. Vassilets[1], O.V. Arnt[1], A.N. Akzholtay[1],
A.M. Gazaliyev[1], Z.M. Muldakhmetov[1], S.O. Kenzhetayeva[2]

[1]Institute of Organic Synthesis and Coal Chemistry of the Republic of Kazakhstan, Karaganda, Kazakhstan;
[2]Ye.A. Buketov Karaganda State University, Kazakhstan
(E-mail: alzhakina@mail.ru)

Synthesis of a composite material based on coal mining waste using wave chemistry methods

Studies for developing composite materials based on coal waste in combination with coal and polymer raw materials under the influence of ultrasound have been carried out within the framework of creating effective and environmentally friendly technologies for the deep processing of coal waste and the production of new valuable import-substituting chemical products for various purposes. Burned rocks (BR) are used as a filler in the composite material that is a product of oxidative self-firing of waste rock extracted along with coal to the surface. Sodium humate (HNa) obtained by alkaline extraction from oxidized coals from the Shubarkol deposit was used as a modifier. A polymer was introduced into the matrix to increase the chemical resistance and increase the life cycle of the composite material. Polystyrene was used as a polymer in the matrix of the composite material. The choice of polystyrene is due to its widespread application in construction, medicine, and food industry as well as its ease of processing. It is distinguished by high rigidity, hardness and excellent transparency values. Composite material was obtained by the traditional method of impregnation using ultrasonic exposure. By varying the composition of the matrix and the filler, a composite material was obtained properties of which were quantitatively and qualitatively different from the properties of each of its components. The X-ray phase composition of new composite materials was studied on a DRON-2.0 diffractometer using Co(Kα) radiation. Microscopic analysis was performed using a scanning electron microscope to study the surface morphology of the synthesized composite. The resulting composite can be used as a building material.

Keywords: burnt rock, sodium humate, ultrasound, polymerization, reaction initiator, styrene, polystyrene, composite material.

Introduction

Questions on the creation of efficient and environmentally friendly technologies for the deep processing of coal waste and the production of new, valuable import-substituting multi-purpose chemical products that are globally competitive are promising and relevant. Burnt rocks that are products of oxidative self-firing of waste rock extracted along with coal to the surface should be considered as an important object of study. Every year in Kazakhstan, about 40 million cubic meters of burnt rock are produced with the underground mining of coal deposits, which are stored in dumps of various shapes and sizes, occupying a large area of land, polluting the air basin and adversely affecting the environment.

Burned rock of coal deposits, resulting from natural self-firing, should be attributed to promising minerals that can be used as raw materials for processing into various products. The disposal of such wastes and the development of methods for obtaining industrially important products on their basis are of current importance for the Republic of Kazakhstan.

The scope and properties of burned rocks are determined by the conditions of formation, namely the composition of the mineral part and the firing temperature. The importance of burnt rocks as a raw material for processing into various products of construction and filtration purposes is confirmed by significant foreign experience [1–5]. Burnt rocks can be used in the production of binding materials in addition to the construction industry [6, 7]. High adsorption activity and adhesion with organic binders allow their use in asphalt and polymer compositions. Burned rock has a ceramic nature and can also be used in the production of heat-resistant concretes and porous aggregates. Some burnt rocks have a lower average density, which allows their use as aggregates for light mortars and concretes [8, 9].

Currently, there is a considerable interest in research related to the development of new methods for producing composite materials based on coal mining waste and polymer raw materials using ultrasonic exposure and the study of their properties.

The combination of coal waste with polymers leads to the creation of new composite materials those properties are quantitatively and qualitatively different from the properties of each of its components. By varying the composition of the matrix and filler, one can get a wide range of materials with the desired set of properties. Therefore, many composite materials are superior to traditional materials in their mechanical properties. It should be noted that very little attention has been paid to the development of composite materials based on burnt rocks with synthetic polymers. One of the most important problems arising from the creation of such composites is associated with the need for a uniform distribution of the polymer matrix. Improvement of the technology of synthesis of composite materials allows the use of ultrasound (US).

The method for producing new multi-purpose composite materials based on coal mining waste and polymer raw materials using ultrasonic activation has been developed in order to improve chemical resistance, reduce porosity, increase density, water resistance, as well as to improve the strength and deformative indicators. In this regard, it is advisable to develop composite materials based on burnt rocks in combination with coal and polymer raw materials under the influence of ultrasound. Such work with such objects has not been described yet in the literature.

Experimental

Polystyrene (PS) was used as a polymer to create a composite material. Pure styrene $C_6H_5CH=CH_2$ was used to obtain polystyrene, which is a colorless transparent liquid, with boiling point 145.2 ºC and refractive index $n^{20}{}_4=1.5468$. The polymerization of styrene was carried out by a block method in the absence of a solvent, where only monomer and initiator were present in the reaction medium. The initiator used was benzoyl peroxide, the content of which ranged from 0.1 % by weight of styrene. The polymerization process was carried out at a temperature of 80 ºC for 1 hour. There was formed yellowish mass, soluble in benzene, insoluble in water and ethanol. The polymer yield was 48.02 %.

Burned rocks (BR) were used as filler in composite materials that is a product of oxidative self-firing of waste rocks extracted along with coal to the surface modified by the modifier.

Sodium humate obtained by the method of alkaline extraction from oxidized coal from the Shubarkol deposit was used as a modifier. Characteristics of HNa are as follows: ∑COOH + OH — 4.5 mEq/g, ∑COOH — 3.0–3.5 mEq/g, A — 13–15 %, W^a — 10–12 %, nitrogen content — less than 1 % [10].

The ultrasound unit IL-100-6/2 with a maximum power of 1200 W and a cylindrical waveguide was used as an ultrasound source. The device was equipped with an ultrasonic IL-10 generator with a magnetostrictive transducer with an operating frequency of 22 kHz.

Composite material composition polystyrene-burnt rock-sodium humate (PS+BR+HNa, 2:1:1) was synthesized as follows. The objects of study were obtained by the traditional method of impregnation of filler (burnt rock) with a modifier solution (sodium humate) of a given concentration under the influence of ultrasonic treatment for 10 minutes (ultrasound frequency 22 kHz). Next, the mixture was left for impregnation for 24 hours. The composite was dried in a stream of air at 80 ºC for 4 hours after impregnation. The resulting composite material composition (BR+HNa, 1: 1) was further impregnated with hot styrene at a ratio: polystyrene – burnt rock – sodium humate (PS+BR+HNa) that was equal to 2:1:1.

The surface modification of the burned rock was carried out by the methods of impregnation with modifier water solutions at a ratio of BR+HNa (Solid:Liquid = 2:1, 1:1 and 1:2) at 25 ºC, holding suspensions for 1 day, and also under ultrasound conditions radiation, ultrasonic processing time was 0–15 minutes. The control of reactions of modification of the burning rock was carried out by the methods of IR-spectroscopy.

X-ray phase analysis was used to identify mineralogical composition of burnt rock. Phase composition of composites was studied using diffractometer DRON-2.0 with Co(Kα)-radiation $\lambda = 1{,}7902$ Å in interval 10º–90º (2θ), velocity of counter rotation was 2 grad/min, $I = 10$ mA, $U = 30$ kV.

Scanning electron microscope MIRA-3 by TESCAN was used for microscopic analysis to study morphology of the composite synthesized.

Results and Discussion

Burnt rocks from the dumps of the mine named after Gorbachev, Karaganda region were used in the work. The burned rocks extracted from the mine's waste heaps are a brick-red fissured, comminuted stones, and washed away with plenty of water to eliminate carbonaceous and other inorganic impurities. The physicochemical characteristics of the burnt rock are presented in Table 1.

Table 1

Burned rock parameters

Sample	Density, kg/m^3	Bulk specific weight, kg/m^3	Porosity, %	Water absorption, %	Mechanical strength, %	
					Grindability	Abrasion
Burnt rocks	2.66	1000	15	5.2	3.7	0.4

Burnt rock used has the following chemical composition, namely silicon (59 %), aluminum (25 %), iron (4–5 %), potassium, calcium, magnesium up to 2 %, sodium, titanium, and phosphorus up to 1 %. The composition of burned rocks includes valuable natural cement that is the result of burning of limestone and clay in the process of burning coal.

Modification was carried out using sodium humate based on oxidized coals from the Shubarkol deposit in order to improve the technical parameters and reduce the porosity of the burned rock. The effectiveness of sodium humate as chemical and structural modifiers for the filler is due to the peculiarities of its molecular structure, polyfunctionality, the ability to various chemical reactions, as well as donor-acceptor and hydrophobic interactions. The method is based on the immobilization of humate in the porous structure of the burnt rock using ultrasonic dispersion.

The optimal ratio of the initial components is the 1:1 ratio and the optimal ultrasound treatment time is 10 minutes. Ultrasonic processing allows achieving a uniform distribution of sodium humate over the entire volume of the rock. The results of silicate analysis of the impregnation of the burnt rock with sodium humate solution of a given concentration under the influence of ultrasonic treatment for 10 minutes showed that ultrasound promoted the change in the content of silicon and aluminum oxides in composites. Thus, under the influence of US in composites, the content of silicon oxides was significantly reduced (58 %) and the content of aluminum oxides (28 %) increased, which significantly reduced the silicate module in comparison with the module of the initial burnt rock. Upon obtaining the composite BR+HNa removal of oxides of iron, titanium, phosphorus and calcium in the filtrate was observed. The content of exchangeable sodium increased significantly. At the same time, the composites were enriched with calcium and magnesium ions, iron and potassium ions went to the filtrate.

The main disadvantage of composite material (BR+HNa) is its poor chemical resistance when operating in real conditions, when the material is influenced by many factors, namely temperature, aggressive environment, mechanical loads, etc. One way to increase the life cycle of composites is to impregnate the surface of a material with polymers and epoxy resins.

We used polystyrene as a polymer in the composite material. The choice of polystyrene is due to its widespread use in construction, medicine, food industry, electrical engineering as well as its ease of processing. Being a rather fragile material, it is distinguished by high rigidity, hardness and excellent transparency values. The main features of polystyrene include lightness, good mechanical properties and low cost compared with other polymers. Polystyrene is relatively low heat resistant, but very water resistant and frost resistant and has exceptional electrical insulating properties. It has the greatest application in the electrical industry. Recently its use has been expanding for the manufacture of building products and materials, in particular in the manufacture of concrete products with improved quality indicators, the so-called polymer concrete.

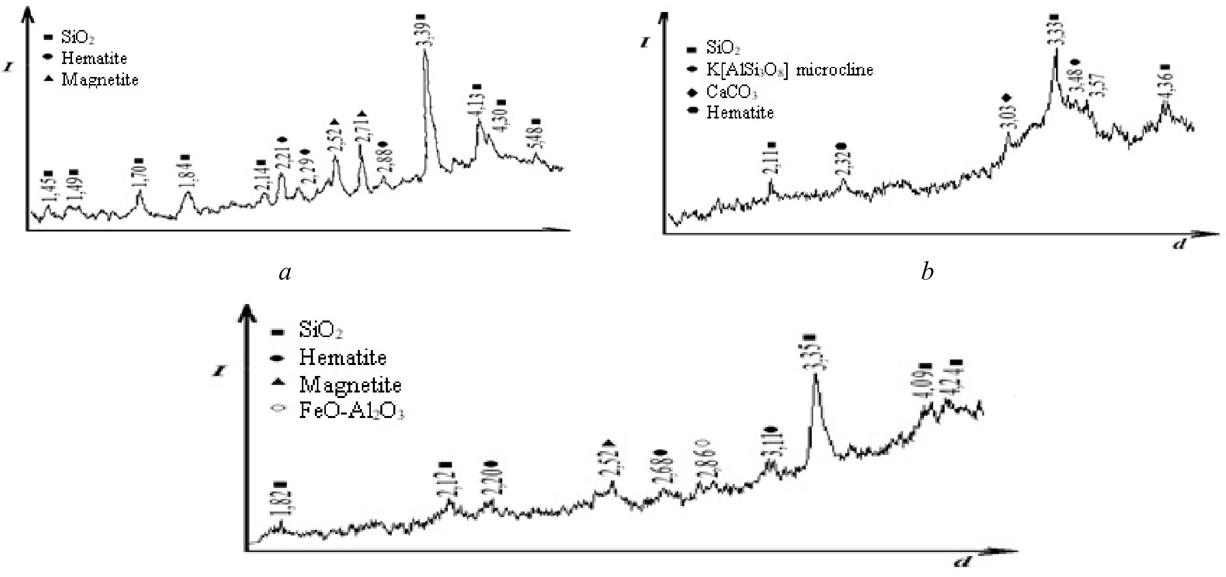
Composite material of polystyrene-burnt sodium-humate rock was obtained by the traditional impregnation method of a modified modifier (sodium humate) of a given concentration under the influence of ultrasound of the filler (burnt rock) with a hot polystyrene solution at a ratio: polystyrene-burnt sodium-humate rock (PS+BR+HNa) that was equal to 2:1:1 and 3:2:1. When cooled, the composite mass hardens. The results of the study are shown in Table 2.

Table 2

Effect of various factors on the yields of composites (PS+BR+HNa)

Composite	Ratio (L:S:S)	US, min	Yield, %
PS+BR+HNa	2:1:1	0	87.40
		10	80.48
	3:2:1	0	79.58
		10	72.20

Among composites PS+BR+HNa = 2:1:1 and PS+BR+HNa = 3:2:1 the composition of PS+BR+HNa = = 2:1:1 (US) is the most promising. Ultrasonic pre-treatment of burnt rock with sodium humate provides a tighter binding between the components. The low content of sodium humate (1/4 of the mass in comparison with the composition of PS+BR+HNa = 3:2:1, where the content of sodium humate is 1/6 of the mass) reduces the chemical resistance of the composite.



a *b*

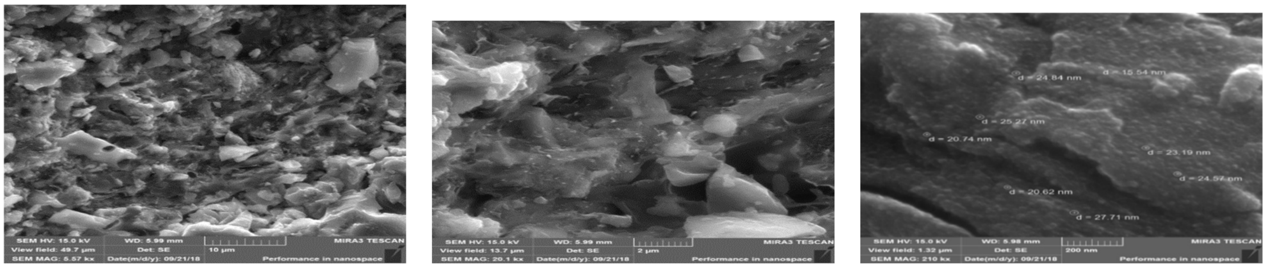
c

a — the original burning rock; *b* — the composite BR+HNa=1:1 (US=10 min);
c — the composite PS+BR+HNa=2:1:1 (US=10 min)

Figure 1. Radiograph

The inorganic part of burned rocks was represented by feldspar minerals, quartz magnetite and hematite according to X-ray phase analysis (XRA). The main component is α-SiO_2 quartz. The heights are indexed in the interplanar spacing for composite PS+HNa (US), namely $d = 2.11$ Å, $d = 2.32$ Å (hematite), $d = 3.03$ Å (calcite), $d = 3.33$ Å, $d = 3.48$ Å (microcline), $d = 3.57$ Å, $d = 4.36$ Å. The main component is α-quartz SiO_2 with $d = 2.11$ Å, $d = 3.33$ Å, $d = 4.36$ Å. The heights are indexed in the interplanar spacing for composite PS+BR+HNa (US), namely $d = 1.82$ Å, $d = 2.12$ Å, $d = 2.20$ Å, $d = 2.52$ Å, $d = 2.86$ Å, $d = 3.11$ Å, $d = 3.35$ Å, $d = 4.09$ Å, $d = 4.24$ Å. The main component is α-quartz SiO_2 with $d = 1.82$ Å, $d = 2.12$ Å, $d = 3.35$ Å, $d = 4.09$ Å, $d = 4.24$ Å. α-Fe_3O_4 is converted into γ-Fe_2O_3 in the range of 2.52 Å, γ-Fe_2O_3 — $d = 2.20$ Å, $d = 2.68$ Å, $d = 3.11$ Å and $FeO{\cdot}Al_2O_3$ (microcline) with $d = 2.86$ Å.

The results of the study of the synthesized composite (PS+BR+HNa=2:1:1) surface morphology are shown in Figure 2.



a — ×5,570 *b* — ×20,100 *c* — ×210,000

Figure 2. Microphotographs of composite PS+BR+HNa = 2:1:1 (US = 10 min)

Pictures of the PS+BR+HNa composite produced by US (Fig. 2) show a rough surface, which consists of two distinct structures, namely darker substrates and lighter inhomogeneous grains that are 10–11 microns in size. Lighter grains rise and have an irregular structure. Troughs and elevations are distinguishable in both structures. An increase of 24,200 times (Fig. 2*b*) shows a part of a dark substrate, which looks like consisting of smoother and more uniform growths with rounded edges, and grainy-like rounded protrusions that are 1–2 μm in size are also distinguishable on them. A further increase (Fig. 2*c*) gives a flat and homogeneous, although not devoid of roughness, surface. The grain is almost completely absent; there are extremely small protrusions, the dimensions of which are much less than a micron, which testifies to the positive influence of the US on the distribution in the composite of components.

Conclusions

Thus, a new composite material was developed using the methods of ultrasonic exposure. By varying the composition of the matrix and filler, the mechanical strength of the composite has been increased. Microscopic analysis was performed using a scanning electron microscope MIRA-3 to study the surface morphology of the composite synthesized. The results of the mapping of the elemental composition of the obtained composites fully confirm their composition. The phase composition of new composite materials was studied on a DRON-2.0 diffractometer using Co(Kα) radiation. The resulting composite can be used as a building material.

The work was done with the financial support of the Ministry of Education and Science of the Republic of Kazakhstan on the target program No. BR05236438 «Development of the scientific foundations of high-tech and resource-saving technologies for producing multifunctional materials based on natural, synthetic raw materials and coal processing waste».

References

1 Баженов Ю.М. Бетонополимеры / Ю.М. Баженов. — М.: Стройиздат, 1983. — 472 с.

2 Гамалий Е.А. Горелые породы как активная минеральная добавка в бетон / Е.А. Гамалий // Вестн. ЮУрГУ. Сер. Строительство и архитектура. — 2008. — № 25. — С. 22–27.

3 Гамалий Е.А. Применение отходов угледобычи в производстве эффективных стеновых материалов / Е.А. Гамалий, Б.В. Боченин // Архитектура и строительство. — 2009. — № 5. — С. 570–574.

4 Куликов В.А. Использование горелых пород в производстве кирпича полусухого прессования / В.А. Куликов, В.З. Абдрахимов, И.В. Ковков // Башкир. хим. журн. — 2010. — № 4. — С. 82–84.

5 Рыбьев И.А. Строительное материаловедение: учеб. пос. / И.А. Рыбьев. — М.: Высш. шк., 2003. — 701 с.

6 Кербер М.Л. Полимерные композиционные материалы. Структура. Свойства. Технологии: учеб. пос. / М.Л. Кербер, В.М. Виноградов, Г.С. Головкин, Ю.А. Горбаткина, В.Н. Крыжановский, В.И. Халиулин, В.А. Бупаков. — СПб.: Профессия, 2008. — 560 с.

7 Чернышов Е.М. Строительно-технологическая утилизация техногенных отходов как комплексная системная эколого-экономическая проблема развития территорий и градостроительства / Е.М. Чернышов, Н.Д. Потамошнева, Н.Д. Монастырев, В.П. Ярцев // Вопросы современной науки и практики. Университет им. В.И. Вернадского. — 2016. — № 4(62). — С. 67–86.

8 Панова В.Ф. Отходы углеобогащения как сырье для получения строительных материалов / В.Ф. Панова, С.А. Панов // Вестн. Сиб. гос. ун-та. — 2015. — № 2(12). — С. 71–75.

9 Патент 2376269 Россия. Способ пропитки полимерными материалами глазурованного бетонного строительного изделия / Федосов С.В., Акулова М.В., Щепочкина Ю.А., Кошелев Е.В. // Опубл. 20.12.2009.

10 Жакина А.Х. Гуминоминеральные сорбенты на основе отходов угледобычи / А.Х. Жакина, Е.П. Василец, А.К. Амирханова, О.В. Арнт, А.Р. Рапиков, З.М. Мулдахметов. — Караганда: Глассир, 2017. — 104 с.

А.Х. Жакина, Е.П. Василец, О.В. Арнт, А.Н. Акжолтай,
А.М. Газалиев, З.М. Мулдахметов, С.О. Кенжетаева

Толқынды химия әдістерін пайдалану арқылы көмір өндіру қалдықтарының негізінде композициялық материалды синтездеу

Көмір өндіру қалдықтарын терең өңдеу және көп мақсатта қолдануға арналған жаңа құнды импорталмастыратын химиялық өнімдерді өндіру бойынша тиімді және экологиялық қауіпсіз технологияларды құру аясында ультрадыбыстың әсерімен көмір және полимер шикізатымен бірге тіркестікте көмір өндіру қалдықтары негізінде композиттік материалдарды әзірлеу бойынша зерттеулер жүргізілді. Композиттік материал құрамында толтырғыш ретінде модификатормен модификацияланған, көмірмен бірге жер бетіне шығарылатын, бос жыныстарды тотықтырғыш өздігінен күйдіру өнімі — жанғыш жыныс қолданылған. Модификатор ретінде Шұбаркөл кен орнының тотыққан көмірінен сілтілі экстракция әдісімен бөлінген натрий гуматы қолданылды. Химиялық төзімділікті жоғарылату және композиттік материалдың өмірлік циклін арттыру үшін матрица құрамына полимер енгізілген. Полимер ретінде композиттік материал матрицасында полистирол қолданылды. Полистиролды таңдау оны өңдеу қарапайымдылығының арқасында құрылыста, медицинада, тамақ өнеркәсібінде кеңінен қолдануға негізделген. Ол жоғары қаттылығы, беріктігі және мөлдірліктің тамаша көрсеткіштерімен ерекшеленді. Композитті материал ультрадыбыстық әсерді пайдалана отырып, дәстүрлі сіңдіру әдісімен алынған. Матрица мен толтырғыштың құрамын түрлендіре отырып, қасиеттері оның әрбір құрамдас қасиеттерінен сандық және сапалық жағынан ерекшеленетін композитті материал алынды. Жаңа композиттік материалдардың рентгенофаздық құрамы ДРОН-2,0 дифрактометрінде Co(Kα)-сәулеленуді пайдалана отырып, зерттелді. Синтезделген композит бетінің морфологиясын зерттеу үшін растрлық электрондық микроскопты қолдану арқылы микроскопиялық талдау жүргізілді. Алынған композитті құрылыс материалы ретінде пайдалануға болады.

Кілт сөздер: жанғыш жыныс, натрий гуматы, ультрадыбыс, полимеризациялау, реакция инициаторы, стирол, полистирол, композитті материал.

А.Х. Жакина, Е.П. Василец, О.В. Арнт, А.Н. Акжолтай,
А.М. Газалиев, З.М. Мулдахметов, С.О. Кенжетаева

Синтез композиционного материала на основе отходов угледобычи с использованием методов волновой химии

В рамках создания эффективных и экологически безопасных технологий по глубокой переработке отходов угледобычи и производству новой ценной импортозамещающей химической продукции многоцелевого назначения проведены исследования по разработке композитных материалов на основе отходов угледобычи, в сочетании с угольным и полимерным сырьем под воздействием ультразвука. В качестве наполнителя в составе композитного материала использована горелая порода — продукт окислительного самообжига пустых пород, извлекаемых вместе с углем на поверхность, модифицированная модификатором. В качестве модификатора использован гумат натрия, выделенный методом щелочной экстракции из окисленных углей Шубаркольского месторождения. Для повышения химической стойкости и увеличения жизненного цикла композитного материала в состав матрицы введен полимер. В качестве полимера в матрице композитного материала использован полистирол. Выбор полистирола обусловлен его широким применением в строительстве, медицине, пищевой промышленности благодаря простоте переработки. Его отличают высокая жесткость, твердость и отличные показатели прозрачности. Композитный материал получен традиционным методом пропитки с использованием ультразвукового воздействия. Варьируя состав матрицы и наполнителя, получен композитный материал, свойства которого количественно и качественно отличаются от свойств каждого из его составляющих. Рентгенофазовый состав новых композитных материалов изучен на дифрактометре ДРОН-2,0 с использованием Co(Kα)-излучения. Для изучения морфологии поверхности синтезированного композита проведен микроскопический анализ с использованием растрового электронного микроскопа. Полученный композит может быть использован в качестве строительного материала.

Ключевые слова: горелая порода, гумат натрия, ультразвук, полимеризация, инициатор реакции, стирол, полистирол, композитный материал.

References

1 Bazhenov, Y.M. (1983). *Betonopolimery [Concrete polymers]*. Moscow: Stroiizdat [in Russian].

2 Gamalii, E.A. (2008). Horelyie porody kak aktivnaia mineralnaia dobavka v beton [Burned rocks as an active mineral additive in concrete]. *Vestnik YuUrGU. Ser. Stroitelstvo i arkhitektura — Bulletin of SUSU. Ser. Construction and architecture, 25,* 22–27 [in Russian].

3 Gamalii, E.A., & Bochenin, B.V. (2009). Primenenie otkhodov uhledobychi v proizvodstve effektivnykh stenovykh materialov [Use of coal waste in the production of efficient wall materials]. *Arkhitektura i stroitelstvo — Architechture and construction, 5,* 570–574 [in Russian].

4 Kulikov, V.A., Abdrahimov, V.Z., & Kovkov, I.V. (2010). Ispolzovanie horelykh porod v proizvodstve kirpicha polusukhoho pressovaniia [The use of burnt rock in production of semi-dry pressing bricks]. *Bashkirskii khimicheskii zhurnal — Bashkir Chemical Journal, 4,* 82–84 [in Russian].

5 Rybev, I.A. (2003). *Stroitelnoie materialovedenie [Construction materials]*. Moscow: Vysshaia shkola [in Russian].

6 Kerber, M.L., Vinogradov, V.M., Golovkin, G.S., Gorbatkina, Yu.A., Kryzhanovskii, V.N., & Khaliulin, V.I., et al. (2008). *Polymernye kompozitsionnye materialy. Struktura. Svoistva. Tekhnolohii [Polymer composite materials. Structure. Properties. Technology]*. Saint Petersburg: Professiia [in Russian].

7 Chernyshov, E.M., Potamoshneva, N.D., Monastyrev, N.D., & Yartsev, V.P. (2016). Stroitelno-tekhnolohicheskaia utilizatsiia tekhnohennykh otkhodov kak kompleksnaia sistemnaia ekoloho-ekonomicheskaia problema razvitiia territorii i hradostroitelstva

[Construction and technological utilization of industrial wastes as a comprehensive system of environmental and economic problems of the development of territories and urban planning]. *Voprosy sovremennoi nauki i praktiki. — Questions of modern science and practice, 4*(62), 67–86 [in Russian].

8 Panova, V.F., & Panov, S.A. (2015). Otkhody uhleobohashcheniia kak syrie dlia polucheniia stroitelnykh materialov [Coal preparation waste as a raw material for the production of building materials]. *Vestnik Sibirskoho hosudarstvennoho universiteta — Bulletin of the Siberian State University, 2*(12), 71–75 [in Russian].

9 Fedosov, S.V., Akulova, M.V., Shchepochkina, Y.A., & Koshelev, E.V. (2009). Sposob propitki polimernymi materialami hlazurovannoho betonnoho pokrytiia [Method for impregnating polymeric materials with glazed concrete pavement]. *Patent 2376269. Russia.* Publ. 20.12.2009 [in Russian].

10 Zhakina, A.Kh., Vassilets, E.P., Amirkhanova, A.K., Arnt, O.V., Rapikov, A.R., & Muldakhmetov, Z.M. (2017). *Huminomineralnye sorbenty na osnove otkhodov uhledobychi [Humic mineral sorbents based on coal waste]*. Karaganda: Glassir [in Russian].

DOI 10.31489/2019Ch3/21-27

UDC 616–018:616:379–008.64

G.G. Meyramov[1], A.Zh. Shaybek[1], K.-D. Kohnert[2], G.T. Kartbayeva[1],
A.P. Andreeva[1], O.-N. Dupont[1]

[1]Ye.A. Buketov Karaganda State University, Kazakhstan;
[2]Institute of Diabetes «Gerhardt Katch», Karlsburg, Germany
(E-mail: meyramow@mail.ru)

Prevention of developing experimental diabetes by reduced form of glutathione

Toxic properties of diabetogenic derivatives of 8-hydroxyquinoline (OX) and diphenylthiocarbazone (DC) on the insulin producing cells of the pancreas and the protective effect of glutathione on its toxic action have been investigated. The mechanism of action of OX derivatives is determined by their ability to form chelate salts of 1:1 composition with zinc-ions containing in B-cells via sulfur and nitrogen atoms at positions 8 and 1 and via the oxygen atoms in positions 8 and 2. Diphenylthiocarbazone forms chelates salts with zinc of 2:1 composition, where zinc is coupled to two molecules of dithizone via sulfur and nitrogen atoms. It is shown that the reduced form of glutathione (GR), containing SH-radical in the structure, has the preventing effect only, unlike the oxidized glutathione (GO) that doesn't contain the SH-radical. It is found that administration of GR to animals in the dose of 1000 mg/kg completely protects B-cells from destruction that is determined by formation of the zinc-GR complex that is not toxic for B-cells. It has been supposed that there are 2 possible types of complex of zinc with RFG: 1) that atom of zinc is fixed between atom of sulfur of the SH-radical and oxygen or nitrogen atom; 2) atom of zinc is fixed between two atoms of sulfur of two SH-radicals of two molecules of RFG that protect B-cells from formation of toxic complexes zinc-DC or zinc-OX.

Keywords: B-cells, reduced form of glutathione, oxidized form of glutathione, insulin, zinc, experimental diabetes.

Introduction

Diphenylthiocarbazon (DZ) and some diabetogenic derivatives of 8-hydroxyquinoline (OX) induce formation of toxic chelate complexes such as «Zn-DC» and «Zn-OX» in cytoplasm of B-cells that result in selective destruction of B-cells within 15–30 min and accompanied by developing of 1st type diabetes in animals [1]. Later it was reported the preventive injection of some amino acids such as cystein and reduced form of glutatione (GR) that contain sulfhydril groups (SH) in the structure of a molecule accompanied by protection of B-cells from destruction caused by DZ and OX that resulted in prevention of developing diabetes in majority of animals [2–5]. High durability of the Zn^{+2}-DC complex of the 2:1 composition (Fig. 2) is determined by space elongation of the DZ molecule and disposition of two phenolic rings on the ends of a molecule that does not prevent the atoms of sulfur and nitrogen located in the center of a molecule to approach zinc atom. Besides, zinc atom is located between atoms of nitrogen and sulfur, regarding to which affinity of zinc is very high and exceeds affinity to oxygen [6]. It was supposed that protective activity of cystein and histidine could be determined by the presence of sulfhydryl groups in a molecule because formation of chelate complexes with DZ and OX was processed by connection of Zn atoms with atom of S, H, O or N [6]. The purpose of investigation is to study the possible preventive effect of aminoacid GR on the model of isolated pancreatic islets.

Experimental Methods

Animals. 16 Rabbits, weight 2400–2850 g.

Group 1. Injection of DC, 48.6–51.2 mg/kg.

Group 2. Injection of RFG, 970–1010 mg/kg and 10 min later of DZ, 49.8–50.6 mg/kg; 4 animals from groups 1 and 2 were killed in 10 min after injection of DZ (1a; 2a) and 4 animals — in 9 days after injection (1b; 2b).

Group 3. Injection of GO, which doesn't contain SH groups in a molecule, 965 mg/kg. Animals were killed 15 min later. Staining zinc in frozen sections of pancreas was determined by 8-para(toluenesulphonylamino)quinoline (TSQ).

Group 4. Injection of GR, 1030 mg/kg. Animals were killed 15 min later. Staining zinc in frozen sections of pancreas was determined by TSQ.

Frosen sections of pancreas of animals 1a and 1b groups were investigated using dark microscopy. Blood glucose level was measured in animals of 1b, 2a and 2b groups before injection of DC and 1, 3, 6 and 9 days after injection. Aldehyde-fuchsine method [7–9] was used for analysis state of histostructure of pancreas tissue and dithizon method with formation of red granules of Zn^{+2}-DC complex that is visible using dark microscopy. Maximum of absorbance of Zn^{+2}-DC complex on spectrum of absorbance correspond for 530 nm [3]. TSQ, a high specific fluorescent reagent, was used for staining Zn-ions in B-cells. TSQ forms fluorescent green complexes with Zn^{+2}-ions that are visible using fluorescent microscopy [10–12].

Results

Group 1a. Administration of DZ accompanied by formation of a large amount of red granules of Zn^{+2}-DC complex in cytoplasm of B-cells (Fig. 1). Maximal concentration of granules located on the pole of B-cells contacted blood capillaries that correspond to concentration of deposited insulin.

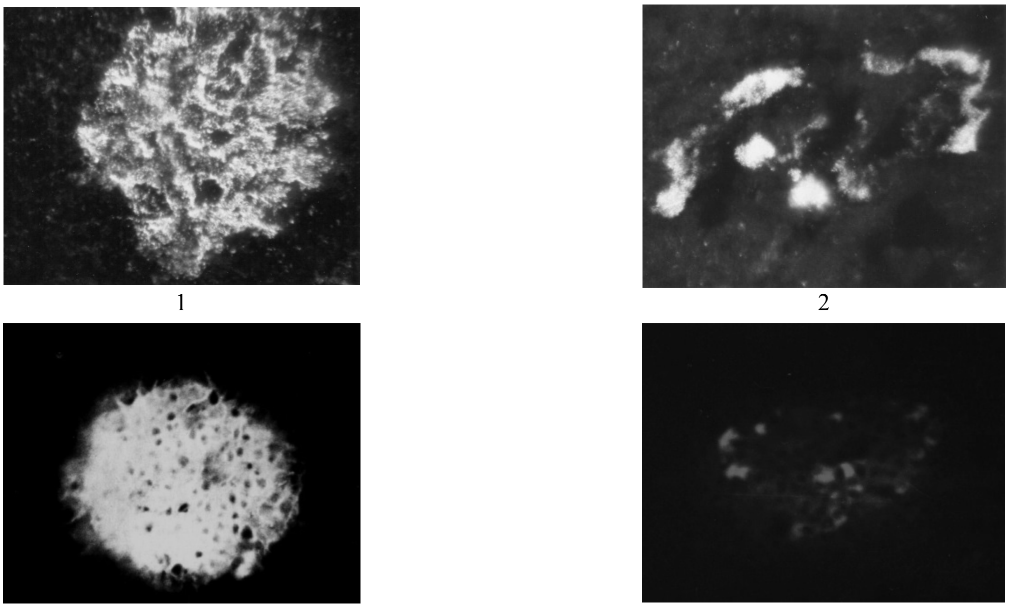
Group 1b. Experimental diabetes. Blood glucose concentration increased from 5.2 ± 0.3 mM to 12.6 mM at 6th day and 16.4 ± 1.7 mM at 9th day (Table). Histology: necrosis and destruction of 70–90 % of B-cells marked decreasing of insulin and zinc content in B-cells.

Group 2a. Preliminary injection of RFG resulted in almost complete prevention of formation of «Zn–DZ» complex in B-cells (Fig. 2).

Group 2b. Administration of RFG before dithizon accompanied by prevention of diabetes development in 3 animals from 4. In one rabbit (N3) blood glucose level increase till 9th day until 7.3. Histologic analysis showed decreasing of insulin content in cells without marked histological changes.

Group 3. Injection of GR: positive reaction for Zinc in B-cells with TSQ (Fig. 1.3) determined by absence of ability of OFG to bind zinc in B-cells; injection of DZ resulted in formation of complex zinc-DC in B-cells and development of diabetes.

Group 4. Injection of GR: negative reaction for Zinc in B-cells as result of binding by GR (Fig. 1.4)



1 — Pancreatic islet of intact rabbit. DZ, 46.8 mg/kg. Large amount of red granules of complex Zn-DZ in B-cells; Dark microscopy; ×280.

2 — Pancreatic islet. reduced Glutathione 1012 mg/kg + DZ Dithizon, 50.1 mg/kg. Almost complete absence of complex Zn-DZ in B-cells; Dark microscopy; ×280.

3 — Pancreatic islet. GO, 1015 mg/kg. Positive fluorescent reaction for Zn-ions in B-cells; ×140.

4 — Pancreatic islet. GR, 965 mg/kg. Negative fluorescent reaction for Zn-ions in B-cells; ×140.

Figure 1. Influence of RFG and OFG on amount of free zinc-ions in pancreatic B-cells

Table

Blood glucose concentration after injection of Dithizon, reduced Glutathion (GR) + DZ and oxidized Glutation (GO)+DZ

Animals	Dose of GR and GO, mg/kg	Dose of DZ, mg/kg	Blood glucose concentration (mM)	
			before	9st day
DZ	–	47.5–52.0	5.34±0.32*	19.8 ±1.72*
GR+DZ	1005–1018	49.3–51.9	5.30±0.55	5.81±0.40
GO+DZ	955–1015	46.8–50.2	5.48±0.56*	17.25±2.60*

Note. * — $p \le 0.005$.

Discussion

Results obtained showed that administration of RFG resulted in binding almost all amount of Zn-ions in B-cells reversibly as least for 24 hours. Injection of DC after RFG was not accompanied by forming chelate complexes Zn-DC in B-cells that resulted in prevention of damage and death of majority of B-cells and prevention of developing diabetes in 3 animals from 4. It is known that aminoacids cystein and L-hystidine possess the same property and their injection protects B-cells from destruction caused by DC and developing diabetes in animals [6, 13]. Howerer, administration of OFG that doesn't contain SH-radicals in the structure doesn't protect B-cells from formation of Zn-DC complex and from destruction and developing diabetes [13]. Binding of Zn-ions of B-cells by glutathione was apparently confirmed by existence of negative reaction for Zn during 24 hours. After that the complex gradually dissociated up and 48–72 hours later DC was able to form toxic complex in B-cells that accompanied by developing experimental diabetes in animals.

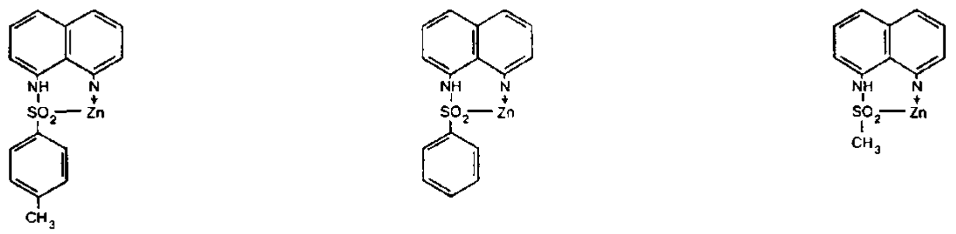
It is known that in the process of formation of the Zn^{+2}-complex with DC or OX zinc atom is fixed between S or O atoms in position 8, and N or O atoms — in positions 1 or 2 (Fig. 2) [14]. OX contains active OH^- radical in the 8 position of quinoline ring or other radicals that contain S, N or O atoms (Fig. 2).

A. Albert [14] showed that 8-hydroxyquinoline, which is usually non-toxic one, is very toxic for cells in the presence of metals, especially in the presence of Zn-ions. It was showed that the possibility was determined by ability of OX to form the chelate metal-complexes, which are toxic for B-cells [14] as complexes formed in B-cells by other chelate active substances such as DC. Studying toxicity of OX for B-cells K. Okamoto [1] reported that injection of it to animals was accompanied by destruction of pancreatic B-cells and developing experimental diabetes. Later it was showed that injection of 18 derivatives of OX was accompanied by destruction of B-cells within 15–30 min that resulted in developing heavy diabetes in animals. It was noted that all those chemicals had OH^- group or any other radical containing S atom or O or N atoms in position 8 of quinoline ring. It was showed that OX possessed high affinity for zinc and formed chelate salts with zinc via radical in position 8 (Fig. 2).

Six isomers of OX that do not contain active groups in position 8 are not able to form chelate complexes with Zn-ions and do not induce experimental diabetes. Experimental diabetes is induced by derivatives such as 8-para-(toluenesulphinylamino)quinoline (8PTSQ), 8-para-(benzenesulphonylamino) quinoline (8PBSQ), 8-para-(methanesulphonylamino)quinoline (8PMSQ), 5-para-(acetaminophenylazo)-8-oxyquinoline (5A8OX), 8-hydroxyquinaldin, 5-amino-8-hydroxyquinoline and others (Fig. 2). It was demonstrated that injection of those derivatives resulted in selective necrosis of B-cells. Injection of those chemicals in doses of 30–100 mg/kg resulted in developing heavy diabetes with marked degenerative changes in islets within a few days [1, 3, 4, 11].

It is known that the most stable complexes are formed when atom of Zn is fixed between S and O atoms in position 8 and between N and O atoms in position 1 or 2. It was showed that only derivatives of 8-hydroxyquinoline, which contained the hydroxyl or another radical with S, N or O atoms in position 8 of quinoline ring, possessed diabetogenic properties [14]. It is known that extraction of these radicals from position 8 is accompanied by complete disappearing of diabetogenic properties of chelators [15]. Formation of chelates by O and N atoms of chelator usually results in forming pentagonal or hexagonal rings [1, 14] (Fig. 2). Pentagonal rings are more stable. Quadrangular complexes with S atom are the most stable ones. It is known that OX derivatives, which form quadragonal complexes with atom of S, are often stable ones. Unshared pair of electrons is displaced from N donor-atom in position 1 to Zn atom.

On the basis of data obtained by A. Albert it is supposed that toxic effect of OX was determined by its ability to bind and eliminate metal ions from B-cells. But later this hypothesis was not confirmed. It was showed that the prolonged elimination of Zn-ions from B-cells did not affect on the state of histostructure and function of B-cells. Finally, S. Rubbo and A. Albert established that toxic effect of OX was determined by its ability to form toxic complexes with metals in cells [16] that many times was confirmed later. It was showed that presence of chelate in cytoplasm of B-cells for a short time was accompanied by alteration of cells. In experiments with azaoxyquinoline (azaoxyn) it was demonstrated that the most toxic were chelates of 1:1 composition with logarifm of stability constant that was equal to 7.6 and higher, up to 9.4. Meanwhile, toxicity of chelates of other isomers of azaoxyn with stability constant 5.8–6.7 was clearly less [5, 14]. It was showed that very toxic chelates of derivatives of 8-hydroxyquinoline with Zn-ions had higher logarithm of stability constant 8.5. G. Weitzel and coll. showed that 1:1 complex contained 1 molecule of 8-hydroxyquinoline and 1 atom of Zn ion was the most toxic for cells [17].



8-para-(toluenesulphonylamino)-quinoline, 30–50 mg/kg

8-para-(benzenesulphonylamino)-quinoline, 30–100 mg/kg

8-para-(methanesulphonylamino)-quinoline, 40–81 mg/kg

Figure 2. Complex salts of diabetogenic zinc-binding chelate active chemicals with Zn-ions and its diabetogenic doses

Stability of 2:1 complexes depends not only on affinity of chelator for metal but on two other properties of chelator and metal: 1) presence of additional radicals in para-positions of chelator molecule, especially in zones contacted with part of a molecule reacting with metal ions with formation of the steric effect. As a result, two molecules of chelator are not able to approach to put an atom of metal in a stable ring; 2) diameter of atom; if a metal atom has a small diameter, ring may be not formed. Zn atom has radius 0.74 nm and it is between berillium (0.31 nm) and rubidium (1.49 nm). A high stability of Zn-DC complex is determined by elongated form of the DC molecule and by location of two phenol rings on two ends of a molecule. That is why N and S atoms are easy to approach to Zn atom. Moreover, Zn atom is fixed between N and S atoms. Meanwhile, it is known that affinity of Zn for N and S atoms is higher comparatively with affinity of Zn for O. In addition, complex formed by two molecule of DZ each of two has a great number of double bonds [1, 5, 14].

Stability of 1:1 complexes formed by derivatives of 8-hydroxyquinoline is determined by a great number of double bonds in a molecule of chelator as well as by forming of quadragonal ring. Derivatives of 8-arenesulphonylaminoquinoline form chelate-complex via S atom. Higher stability of the complex Zn-xanthurenic acid is determined by fixation of the Zn atom between two O atoms.

Isomers of 8-hydroxyqunolines, which do not contain such radicals or atoms in this position (8), or if these radicals are extracted from a molecule, are not capable for forming complex salts with zinc and do not possess diabetogenic properties completely. It is necessary to return the active radicals in position 8 to restore diabetogenic activity of substance [15]. Formation of the chelate complex by O and N atoms is accompanied by forming pentagonal or hexagonal rings [14].

SH groups contain sulfur atom. Meanwhile, as it is described above, it is known that sulfur atom participates in formation of the chelate complexes with Zn as well as N, O and C atoms. It is known that in process of formation of the Zn^{+2}-complexes with DC and OX zinc atom is fixed between S or O atoms in position 8, and N or O atoms — in positions 1 or 2 (Fig. 2) [14].

On the basis of the results obtained we suppose that negative fluorescent reaction for Zn in B-cells after administration of reduced form of glutathione was determined by binding of Zn-ions via atom of sulfur of the SH-group and by disposition of zinc atom between atom of sulfur and, probably, atom of oxygen (Fig. 3) or nitrogen or, more probably, is fixed between two atoms of sulfur from the two molecules of reduced glutathione [18].

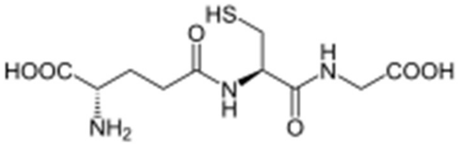


Figure 3. Reduced Glutathione

Conclusions

Reduced form of glutathione, which contains sulfhydryl radical in the structure in the dose of 1000 mg/kg, prevents formation of zinc complexes with diabetogenic zinc-binding chelators in B-cells, protecting B-cells from destruction as well as preventing from development of diabetes in animals. Oxidized form of glutathione, which doesn't contain sulfhydryl radical in the structure in the dose of 1000 mg/kg does not protect B-cells from formation of complexes with DC and does not protect B-cells from destruction and from developing diabetes in animals.

Administration of reduced form of glutathione to animals resulted in blocking of Zn-ions in B-cells that protects from interaction of metal with DC. We suppose that preventive effect after administration of reduced form of glutathione was determined by binding Zn-ions via atom of sulfur of the sulfhydryl radical and followed by disposition of zinc atom between atom of sulfur and atom of oxygen or nitrogen.

References

1 Okamoto K. Experimental production of diabetes / K. Okamoto // Diabetes mellitus: Theory and Practice. — N.Y.: McGraw-Hill Book company, 1970. — P. 230–255.

2 Kawanishi H. Secretion of B-granules in islets of Langerhans in association with intracellular reactive zinc after administration of Dithizone in rabbits / H. Kawanishi // Endocrinol. Jap. — 1966. — Vol. 13, No. 4. — P. 384–408.

3 Лазарис Я.А. К механизму повреждения панкреатических островков при дитизоновом диабете / Я.А. Лазарис, Г.Г. Мейрамов // Бюл. эксп. биологии и медицины. — 1974. — № 3. — С. 19–22.

4 Мейрамов Г.Г. Ультраструктура панкреатических В-клеток при дитизоновом диабете и его предупреждении диэтилдитиокарбаматом натрия / Г.Г. Мейрамов, Н.И. Труханов // Проблемы эндокринологии. — 1975. — Т. 21, № 6. — С. 92–95.

5 Мейрамова А.Г. Диабетогенные цинксвязывающие В-цитотоксические соединения / А.Г. Мейрамова // Проблемы эндокринологии. — 2003. — Т. 49, № 2. — С. 8–16.

6 Meyramov G.G. Cystein protect pancreatic B-cells of destruction caused by Zn^{+2}-chelators / G.G. Meyramov, A.G. Meyramova // DIABETES, the Journal of American Diabetes Association. — 2003. — Vol. 51, No. 6. — P. 552.

7 Kvistberg D. Staining of insulin with aldehyde fucshin / D. Kvistberg, G. Lester, A. Lasarov // Journal of Histochemistry & Cytochemistry. — 1966. — Vol. 14. — P. 609–611.

8 Ortman R. Concerning the staining properties of aldehyde basic fuchsin / R. Ortman, W. Forbes, A. Balasubramanian // Journal of Histochememistry. — 1966. — Vol. 14. — P. 104–111.

9 Orci G. Some aspects of the morphology of insulin secreting cells / G. Orci // Acta Histochemica. — 1976. — No.1. — P. 147–158.

10 Божевольнов Е.А. 8-пара(толуолсульфониламино)хинолин — люминесцентный реактив для выявления цинка и кадмия / Е.А. Божевольнов, Г.В. Серебрякова // Химические реактивы и препараты. — М., 1961. — С. 36–42.

11 Красавин И.А. Гистохимические реакции на цинк в островках Лангерганса и диабетогенная активность используемых для этих целей веществ / И.А. Красавин, З.Е. Бавельский, Я.А. Лазарис., В.М. Дзиомко // Проблемы эндокринологии. — М., 1969. — Т. 15, № 3. — С. 103–105.

12 Meyramov G.G. Histochemical and immunocytochemical investigation of endocrine tissue of pancreas after damage caused by B-cytotoxic chemicals and its prevention by L-hystidine / G.G. Meyramov // Bulletin of the Karaganda University. Ser. Biology, Medicine, Geography. — 2017. — Vol. 85, No. 1. — P. 60–71.

13 Meyramov G.G. Prevention of Diabetes Induced by Chelators by L-Hystidine / G.G. Meyramov, A.G. Meyramova // DIABETES, the Journal of American Diabetes Association. — 2004. — Vol. 52, No. 6. — P. 583.

14 Альберт А. Избирательная токсичность / А. Альберт. — М.: Мир, 1971. — 294 с.

15 Kotake Y. Inhibitory action of the real sulfate of xanturenic acid and kynurenic acid with regard to its diabetogenic property / Y. Kotake, T. Kato // Proc. Jap. Acad. — 1956. — Vol. 32. — P. 361–363.

16 Rubbo S. Studies of diabetogenic action of 8-oxyquinolin / S. Rubbo, A. Albert // Brit. J. Exp. Pathol. — 1950. — Vol. 31. — P. 425–428.

17 Weitzel G. Zinkbindungsvermogen und Blutzuckerwirkung von Xanthurensaure, Kynurenin und Tryptophan / G. Weitzel, E. Buddecke, F.-J. Strecker // Hoppe-Seyler's Z. Physiol. — 1954. — Vol. 298. — P. 169–184.

18 Rubino F.M. Toxicity of Glutathione-Binding Metals: A Review of Targets and Mechanisms / F.M. Rubino // Toxics. — 2015. — Vol. 3, No. 1. — P. 20–62.

Г.Г. Мейрамов, А.Ж. Шайбек, К.-Д. Конерт,
Г.Т. Картбаева, А.П. Андреева, О.Н. Дюпонт

Эксперименттi диабеттiң дамуын глютатион аминқышқылы көмегiмен алдын алу

Авторлар оксихинолиннiң және дифенилтиокарбазонның диабетогендi туындыларының зақымдаушы қасиеттерiнiң ұйқы безiнiң инсулин өндiрушi жасушаларына және глютатион аминқышқылдарының олардың уытты әсерiн алдын алуға қатысты әсерiн зерттеген. Оксихинолин (OX) туындыларының әсер ету механизмiнде олардың құрамында мырыш бар жасушаларда, онымен бiрге iшкi кешендiк тұздар құрамы 1:1, 8 және 1-қалыптардағы күкiрт және азот атомдары арқылы және 8 және 2-қалыптардағы оттегi атомдары арқылы қалыптастыру қабiлетi бар. Дифенилтиокарбазон (DC) құрамында 2:1 мырыш бар хелат түзедi, мұнда мырыш дитизонның екi атомымен күкiрт және азот атомдары арқылы қосылады. Глютатионның тотыққан формасынан айырмашылығы, алдын алу әсерiне құрылымында SH-радикалы бар глютатионның тотықсызданған формасы ие екендiгi көрсетiлген. Жануарларға тотықсыздандырылған глютатионды 1000 мг/кг дозада бiрреттi енгiзу B-жасушаларының бұзылуына және жануарларда диабеттiң дамуына әкелетiн уытты кешендердi қалыптастырумен B-жасушалардың мырышты байланыстыруға толық кедергi келтiретiнi анықталды. Тотықсызданған глютатионның аралшықтардағы мырышпен өзара әрекеттесуiнiң химизмiн зерттеу, оны енгiзу жасушаларда мырышты толық бұғатталуымен қатар жүретiнiн көрсеттi, зерттеу нәтижесiнде ол жоғары арнайы гистохимиялық әдiстердiң көмегiмен гистохимиялық жолмен айқындалмайды. Авторлар тотықсызданған глютатионның алдын алу қабiлетi оның аралшықтардағы мырышты байланыстыру қабiлетiне байланысты деп санайды: 1) мырыш атомы бұл ретте SH-радикал күкiрт атомы мен оттегi немесе азот атомы арасында тiркеледi, бiр жағынан, күкiрт атомы және оттегi атомы, екiншi жағынан, 2) азот арқылы аралшық мырышты байланыстыратын OX немесе DC туындысы енгiзiлген жағдайларда да глютатион молекуласында бар деп пайымдайды.

Кiлт сөздер: B-жасушалары, глютатионның қысқартылған түрi, глютатионның тотығу формасы, инсулин, мырыш, тәжiрибелiк диапазон.

Г.Г. Мейрамов, А.Ж. Шайбек, К.-Д. Конерт,
Г.Т. Картбаева, А.П. Андреева, О.Н. Дюпонт

О предотвращении развития экспериментального диабета с помощью аминокислоты глютатиона

Были исследованы повреждающие свойства диабетогенных производных оксихинолина (OX) и дифенилтиокарбазона (DC) на инсулинпродуцирующие клетки поджелудочной железы и предупреждающее влияние аминокислоты глютатиона в отношении их токсического действия. Механизм действия производных OX имеет способность формировать в клетках, содержащих цинк, внутрикомплексные соли с ним состава 1:1 через атомы серы и азота в положениях 8 и 1 и через атомы кислорода в положениях 8 и 2. Дифенилтиокарбазон формирует хелаты с цинком состава 2:1, где цинк соединяется с двумя атомами дитизона через атомы серы и азота. Показано, что предотвращающим действием обладает восстановленная форма глютатиона, содержащая в своей структуре SH-радикал, в отличие от окисленной формы глютатиона, не содержащей его и не обладающей предотвращающим эффектом. Установлено, что однократное введение восстановленного глютатиона животным в дозе около 1000 мг/кг полностью препятствует связыванию цинка B-клеток с формированием токсических комплексов, вызывающих разрушение B-клеток в результате последующего введения OX и DC и развитие диабета у животных. Исследование химизма взаимодействия восстановленного глютатиона с островковым цинком показало, что введение его сопровождается полным связыванием цинка в B-клетках, в результате чего он не выявляется гистохимически с помощью высокоспецифичных гистохимических методов. Предупреждающая способность восстановленного глютатиона обусловлена его способностью связывать островковый цинк двумя путями: 1) атом цинка при этом может фиксироваться между атомом серы SH-радикала и атомом кислорода или азота, содержащимися в молекуле глютатиона, как и в случаях введения производных OX или дифенилтиокарбазона, связывающих островковый цинк через атом серы, с одной стороны, и атомом кислорода, либо азота, с другой стороны; 2) атом цинка может фиксироваться между двумя атомами серы от двух SH-групп, входящих в состав двух молекул восстановленного глютатиона.

Ключевые слова: B-клетки, восстановленная форма глютатиона, окисленная форма глютатиона, инсулин, цинк, экспериментальный диабет.

References

1 Okamoto, K. (1970). Experimental production of diabetes. *Diabetes mellitus: Theory and Practice*, N.Y.: McGraw-Hill Book company.

2 Kawanishi, H. (1966). Secretion of B-granules in islets of Langerhans in association with intracellular reactive zinc after administration of Dithizone in rabbits, *Endocrinol. Jap, 13(4)*, 384–408.

3 Lazaris, Ya.A., & Meyramov, G.G. (1974). K mekhanizmu povrezhdeniia pankreaticheskikh ostrovkov pri ditizonovom diabete [On the mechanisms of destruction of pancreatic islets in diabetes caused by Dithizon]. *Bulleten Experimentalnoi Biolohii i Meditsiny — Bulletin of Experimental Biology and Medicine, 3*, 19–22 [in Russian].

4 Meyramov, G.G., & Trukhanov, N.I. (1975). Ultrastructura pankreaticheskikh B-kletok pri ditizonovom diabete i eho preduprezhdenii dietildithiokarbamatom natriia [Ultrastructure of pancreatic B-cells in diabetes caused by dithizone and its prevention by diethyldithiocarbamic acid]. *Problemy Endokrinolohii — Problems of Endocrinology, 21, 6*, 92–95 [in Russian].

5 Meyramova, A.G. (2003). Diabetohennyie tsink-sviazyvaiushchiie B-tsitotoksicheskiie soedineniia [Diabetogenic zinc-binding B-cytotoxic chemicals]. *Problemy Endokrinolohii — Problems of Endocrinology, 2*, 8–16 [in Russian].

6 Meyramov, G.G., & Meyramova, A.G. (2003). Cystein protect pancreatic B-cells of destruction caused by Zn^{+2}-chelators. *DIABETES. The Journal of American Diabetes Association*, *51, 6,* 552.

7 Kvistberg, D., Lester, G., & Lasarov, A. (1966). Staining of insulin with aldehyde fuchsin. *Journal of Histochemistry & Cytochemistry, 14*, 609–611.

8 Ortman, R., Forbes, W., & Balasubramanian, A. (1966). Concerning the staining properties of aldehyde basic fuchsin. *Journal of Histochememistry, 14*, 104–111.

9 Orci, G. (1976). Some aspects of the morphology of insulin secreting cells. *Acta Histochemica, 1*, 147–158.

10 Bozhevolnov, E.A., & Serebryakova, G.V. (1961). 8-p-(toluolsulfonilamino)khinolin — liuministsentnyi reaktiv dlia vyiavleniia tsinka i kadmiia [8-p-(toluenesulfonylamino)quinoline — luminescent reagent for detecting zinc and cadmium]. *Khimicheskiie reaktivy i preparaty — Chemical reagents and preparations*, 36–42 [in Russian].

11 Krasavin, I.A., Bavelsky, S.E., Lazaris, Y.A., & Dziomko, V.M. (1969). Histokhimicheskie reaktsii na tsink v ostrovkakh Lanherhansa i diabetohennaia aktivnost ispolzuiemykh dlia etoi tseli veshchestv [Histochemical reaction for zinc in islets of Langerhans and diabetogenic activity of reagents]. *Problemi Endokrinolohii — Problems of Endocrinology, 3*, 103–105 [in Russian].

12 Meyramov, G.G. (2017). Histochemical and immunocytochemical investigation of endocrine tissue of pancreas after damage caused by B-cytotoxic chemicals and its prevention by L-hystidine. *Bulletin of the Karaganda University. Biology. Medicine. Geography series, 85(1)*, 60–71.

13 Meyramov, G.G., & Meyramova, A.G. (2004). Prevention of diabetes induced by chelators by L-hystidine. *DIABETES. The Journal of American Diabetes Association, 52(6)*, 583.

14 Albert, A. (1971). *Izbiratelnaia toksichnost [Selective Toxicity]*. Moscow: Mir [in Russian].

15 Kotake, Y., & Kato, T. (1956). Inhibitory action of etheral sulfate of xanturenic acid and kynurenic acid with regard to its diabetogenic property. *Proc. Jap. Acad., 32*, 361–363.

16 Rubbo, S., & Albert, A. (1950). Studies of diabetogenic action of 8-oxyquinoline. *Brit. J. Exp. Pathol., 31*, 425–428.

17 Weitzel, G., Buddecke, E., & Strecker, F.-J. et al. (1954). Zinkbindungsvermogen und blutzuckerwirkung von xanthurensaure, kynurenin und tryptophan. *Hoppe-Seyler's Z. Physiol., 298*, 169–184.

18 Rubino, F.M. (2015). Toxicity of Glutathione-Binding Metals: A Review of Targets and Mechanisms. *Toxics, 3(1)*, 20–62.

DOI 10.31489/2019Ch3/28-36

UDC 577.127:547.973

M.K. Ibrayev[1], S.B. Akhmetova[2], A.T. Takibayeva[1],
M.B. Issabayeva[1], A.O. Nurkenov[1], O.T. Seilkhanov[3]

[1]Karaganda State Technical University, Kazakhstan;
[2]Karaganda Medical University, Kazakhstan;
[3]Sh. Ualikhanov Kokshetau State University, Kazakhstan
(E-mail: mkibr@mail.ru)

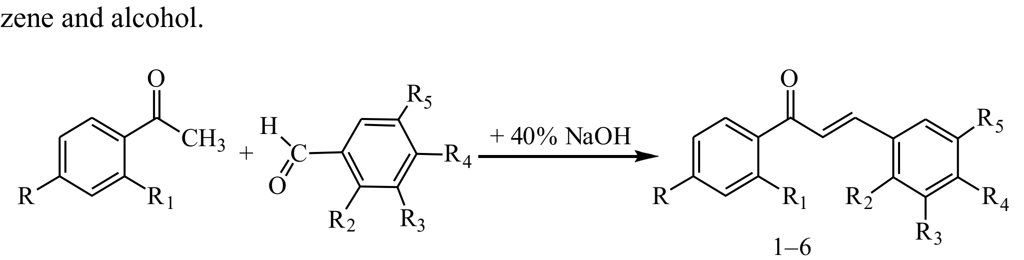
Synthesis, structure and antimicrobial activity of substituted chalcones and their derivatives

In the paper the interaction reactions of the hydroxyl substituted acetophenones with the substituted aromatic aldehydes in the presence of aqueous alcoholic solution of alkali (Claisen-Schmidt condensation), which is as aldol condensation were given. This reaction has a big duration and comes to the end within 62–85 h. The final product contains double bonds in α,β-position to carbonyl group. Further functionalization of the chalcones obtained was performed by their correlation with hydrazine hydrate. It was found that boiling of chalcones with hydrazine hydrate in ethanol led to an intramolecular cyclocondensation of an intermediate hydrazone to form some pyrazole derivatives. Structures of the synthesized compounds were studied with ^{1}H and ^{13}C-NMR spectroscopy, and data on two-dimensional (^{1}H-^{1}H) COSY and (^{1}H-^{13}C) HMQC spectra. Values of the chemical shifts, multiplicity and integral intensity of signals in one-dimensional ^{1}H and ^{13}C NMR spectra were determined. Homo- and heteronuclear interactions confirming structure of the compounds studied were determined with (^{1}H-^{1}H) COSY and (^{1}H-^{13}C) HMQC spectra. Data on the antimicrobial activity of the synthesized chalcones, pyrazolines and flavonones were showed. It was found that all studied substances practically showed a weak antibacterial activity. Exception is S. aureus culture, which possess the moderate actions for compounds of (E)-1.3-bis (2-hydroxyphenyl)-prop-2-en-1-one, (E)-1-(2-hydroxyphenyl)-3-(4-hydroxyphenyl)-prop-2-en-1-one,(E)-3-(ethoxy-4-hydroxyphenyl)-1-(2-hydroxyphenyl)prop-2-en-1-one and 2-(2-hydroxyphenyl)flavone.

Keywords: substituted aromatic aldehyde, chalcone, pyrazoline, flavonone, cytokine, NF-κB transcription factor.

Chalcones are of a considerable interest caused with their easy synthesis, high pharmacological activity and possibility of application as synthon in synthesis of many biologically active heterocyclic compounds, in particular, pyrazolines and flavones. Compounds with chalcone fragment have the high antitumoral, antibacterial, antifungal, antivirus, antimalarial, anti-hyperglycemic, anti-inflammatory and immunomodulatory activities, and demonstrate the chemoprotective and antioxidant properties [1–11]. In addition some chalcone derivatives have an ability to strengthen capillaries [5]. The traditional methods of obtaining chalcones provide the using as catalysts of such strong bases as hydroxides of alkaline and alkaline-earth metals [12]. In this connection the synthesis of new chalcones and nitrogen-containing heterocyclic compounds on their basis is represented an important object.

This paper studied the interaction reactions of the hydroxyl substituted of acetophenones with the substituted aromatic aldehydes in the presence of aqueous alcoholic solution of alkali (Claisen-Schmidt condensation) which was as aldol condensation. The reaction mixture was mixed with a magnetic stirrer at room temperature; reaction has a big duration and comes to the end within 62–85 h. The final product contains double bonds in α,β-position to carbonyl group. The chalcones obtained (1–6) are yellow or orange powders, dissoluble in benzene and alcohol.

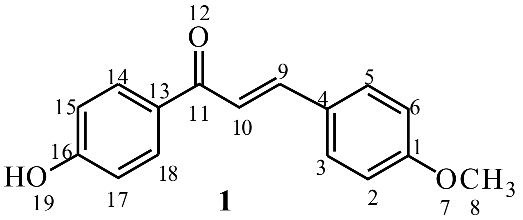


1–6

R = HO; R_1 = H; R_4 = CH_3O; R_2 = R_3 = R_5 = H (1).
R = H; R_1 = HO; R_2 = HO; R_3 = R_4 = R_5 = H (2).
R = HO; R_1 = HO; R_4 = CH_3O; R_2 = R_3 = R_5 = H (3).
R = H; R_1 = HO; R_2 = R_3 = R_5 = H; R_4 = HO (4).
R = H; R_1 = HO; R_2 = R_5 = H; R_3 = C_2H_5O; R_4 =HO (5).
R = Br; R_1 = H; R_2 = HO; R_3 = R_4 = H; R_5 = Br (6).

The structure of the chalcones synthesized (1–6) was proved with IR- and ^{1}H, ^{13}C NMR spectroscopy.

IR spectrum of chalcones (1–6) demonstrates intense absorption bands at 1595–1582 cm^{-1} that correspond to vibrations of C=C bond attached to a carbonyl group.



1

^{1}H NMR spectrum of compound 1 in deuterated DMSO shows the high intense singlet signal with a chemical shift (3.76 ppm) and intensity of 3H belonging to protons of OCH_3^8 methoxy-group. Equivalent protons of methoxy-phenyl fragment of $H^{2.6}$ and $H^{3.5}$ were resonated with doublet signals at 6.95 (2H, ^{3}J 8.5 Hz) and 7.77 ppm (2H, ^{3}J 8.6 Hz), respectively. Protons at double bond of H^{9} and H^{10} give doublet signals at 7.74 and 7.62 ppm with intensity of 1H with splitting of ^{3}J 17.1 and 15.3 Hz, respectively. The equivalent CH-protons of group of other aromatic system were shown with doublet signals with intensity of 2H at 6.86 ($H^{15.17}$, ^{3}J 9.2 Hz) and 8.03 ppm ($H^{14.18}$, ^{3}J 8.5 Hz). A broadened singlet signal at 10.39 ppm demonstrated the phenolic hydroxyl in compound.

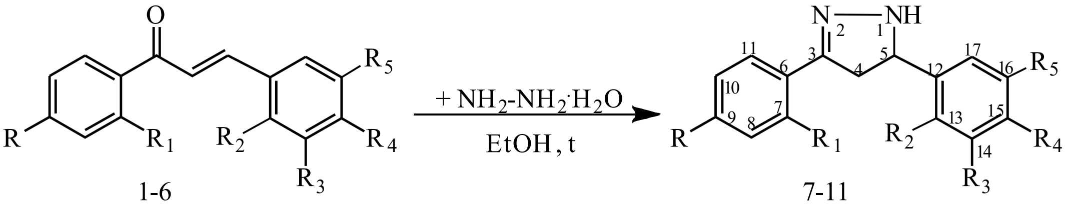
^{13}C NMR spectrum of the studied compound 1 shows a signal of methoxy group at 55.83 ppm. Carbon atoms of the aromatic systems give signals at 114.87 ($C^{2.6}$), 115.88 ($C^{15.17}$), 131.05 ($C^{3.5}$) and 131.57 ppm ($C^{14.18}$). Signals with the chemical shifts of 161.62 (C^{1}), 128.04 (C^{4}), 129.84 (C^{13}), and 162.61 (C^{16}) ppm correspond to quarternary carbon atoms. Signals at 120.08 and 143.21 ppm include the carbon atoms connected by a multiple bond of C^{9} and C^{10} respectively. A weak-field signal at 187.57 ppm corresponds to C^{11} atom of carbonyl group.

The structure of compound (1) was confirmed by two-dimensional NMR, ^{1}H-^{1}H COSY and ^{1}H-^{13}C HMQC spectroscopy for definition of the spin-spin coupling of homo-and heteronuclear nature.

^{1}H-^{1}H COSY spectra of compound 1 demonstrate the spin-spin correlations through three bonds of protons of aromatic systems and olefinic protons of H^{9} and H^{10}. Simple correlations of protons with carbon atoms were determined by ^{1}H-^{13}C HMQC spectroscopy.

Reaction of cyclocondensation of hydrazines with α,β-unsaturated ketones is an important synthetic way to 1.2 azoles. Some pyrazole derivatives show properties of analgetics and inhibitors of thrombocyte aggregation [13], possess the strong antibacterial [14] and anesthetized [15] actions.

In order to determine functions of the chalcones (1–6) obtained their correlation with hydrazine hydrate was studied. It was found that boiling of chalcones with hydrazine hydrate in ethanol led to an intramolecular cyclocondensation of an intermediate hydrazone to formation of pyrazole derivatives (7–11).

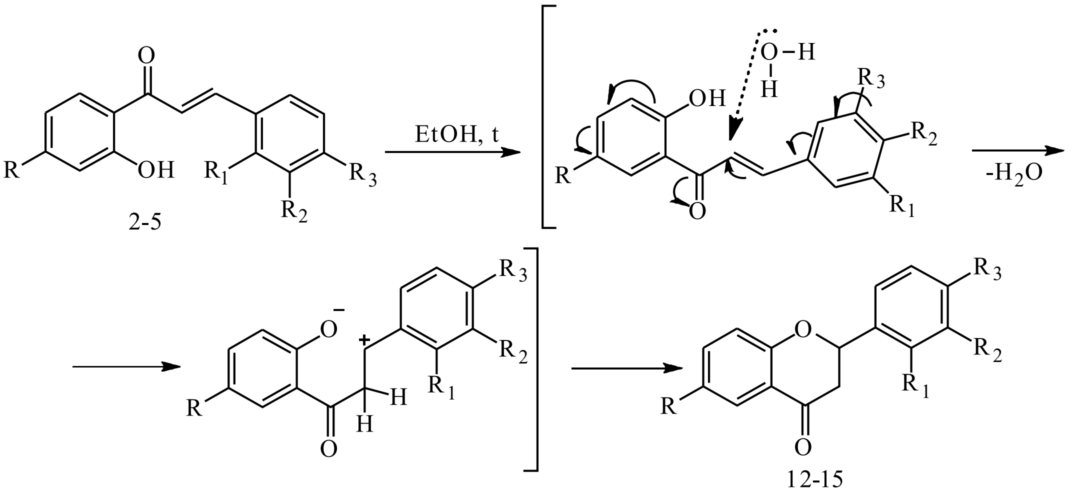


$R = HO$; $R_1 = H$; $R_4 = CH_3O$; $R_2 = R_3 = R_5 = H$ (7).
$R = H$; $R_1 = HO$; $R_2 = HO$; $R_3 = R_4 = R_5 = H$ (8).
$R = HO$; $R_1 = HO$; $R_4 = CH_3O$; $R_2 = R_3 = R_5 = H$ (9).
$R = H$; $R_1 = HO$; $R_2 = R_3 = R_5 = H$; $R_4 = HO$ (10).
$R = H$; $R_1 = HO$; $R_2 = R_5 = H$; $R_3 = C_2H_5O$; $R_4 = HO$ (11).

The structure of compounds (7–11) was confirmed by IR and NMR spectroscopy. Thus, IR spectra of pyrazolines (7–11) demonstrate a strip of average intensity of C=N group of pyrazoline core at 1601–1605 cm^{-1}.

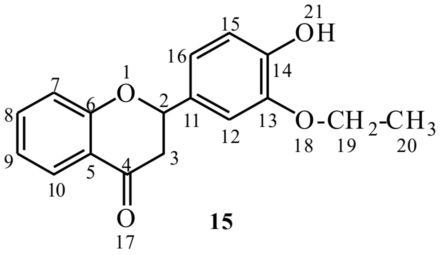
^{1}H NMR spectrum of 4-(5-(4-methoxyphenyl)-4,5-dihydro-1*H*-pyrazole-3-il)phenol (**7**) established that four groups of signals in the low field corresponded to protons of 4-hydroxy- and 4-methoxyphenyl fragments. Two doublets at 7.40 and 7.23 ppm correspond to *ortho*- and *meta*-protons of 4- hydroxyphenyl fragment and two doublets at 6.84 and 6.72 ppm — *ortho*- and *meta*-protons of a 4-methoxyphenyl fragment. Protons of methoxy-group correspond to an intense singlet at 3.67 ppm. The following group of signals representing a triplet at 4.63–4.68 ppm is relevant to a methine proton (CH_{pyr}) of pyrazoline fragment. Methylene protons of this fragment resonate at 2.65–2.72 ppm as two doublets. A weak signal at 9.67 ppm belongs to NH proton of a pyrazoline fragment.

Combination of the structural features of these compounds in one molecule to obtain highly effective biologically active substances is of interest in view of generality of some biogenesis processes of chalcones and flavonoids in a vegetable organism [16, 17]. In connection with this, flavonones (12–15) were obtained from synthesized 2-hydroxyl-containing chalcones under ethanol and catalytic amounts of triethylamine. Long boiling in 95 % ethanol leads to isomerization of chalcones (2–5) into flavonones (12–15). It is demonstrated that isomerization process of chalcones into flavonones in alcohol is catalyzed by water molecules.



R = H; R$_1$ = HO; R$_2$ = R$_3$ = H (12).
R = HO; R$_1$ = R$_2$ = H; R$_3$ = CH$_3$O (13).
R = R$_1$ = R$_2$ = H; R$_3$ = HO (14).
R = H; R$_1$ = H; R$_2$ = C$_2$H$_5$O; R$_3$ = HO (15).

The structure of flavonones (12–15) was proved by IR- and ^{1}H, ^{13}C NMR spectroscopy. Thus, a triplet signal with a center of 1.29 ppm and multiplet at 3.98–4.03 ppm belong to protons of ethoxy-group at C^{20} and C^{19} in ^{1}H NMR spectrum of flavonone 15. Protons of methylene- and CH-groups of the system of condensed cores are shown in a spectrum area: H^2 at 5.47, H^3 — 2.69–3.31, H^7 — 7.06, H^8 — 7.55, H^9 — 7.76 and H^{10} — 7.04 ppm. Resonating at 6.77–6.90 ppm is characteristic for CH-groups of a phenyl radical. A weak pole at 9.00 ppm demonstrates a signal H^{21} of hydroxyl group.



15

Interpretation of DEPT spectra permitted to correlate eight signals of carbon spectrum with methine groups; two signals with methylene groups and one signal with methyl group. The detailed analysis of ^{13}C NMR of compound (15) showed that a signal at 15:29 ppm corresponded to CH_3-group at C^{20} atom. CH_2-groups appear at 44.03 (C^3) and 64.55 (C^{19}) ppm. Eight signals of CH-groups resonate at 79.57 (C^2), 113.10 (C^{12}), 115.86 (C^{15}), 118.57 (C^7), 120.20 (C^{16}), 121.81 (C^9), 128.81 (C^{10}) and 136.71 (C^8) ppm. An additional point is that ^{13}C NMR spectrum shows signals at 121.15, 130.18, 147.20, 147.77 and 161.76 ppm, which belong to C^5, C^{11}, C^{14}, C^{13} and C^6 atoms, respectively. A low field signal at 192.47 ppm belongs to a carbonyl C^4 atom.

Three chalcones (2, 4, 5), two pyrazolines (8, 9) and two flavones (12, 14) were investigated to estimate their antimicrobical activity for the medicinal and sensitive museum strains of bacteria and fungi.

A microbiological laboratory to test the antibacterial and antifungal activities on the basis of Department of Microbiology at Karaganda Medical University studied the synthesized compounds on antimicrobical activity of some drugs such as (E)-1,3-bis(2- hydroxyphenyl)-prop-2-en-1-one (2), (E)-1-(2-hydroxyphenyl)-3-(4-hydroxy-phenyl)-prop-2-en-1-one (4), (E)-3-(ethoxy-4-hydroxyphenyl)-1-(2-hydroxyphenyl)prop-2-en-

1-one (5), 2,2-(4,5-dihydro-1H-pyrazole-3,5-diil)phenol (8), 4-(5-(4-methoxyphenyl)-4,5-dihydro-1H-pyrazole-3-il)benzol-1,3-diol (9), 2-(2-hydroxyphenyl)flavone-4-one (12), 2-(4-hydroxyphenyl)flavone-4-one (14).

Concentrations of the tested drugs were made for an antibacterial activity, namely 1 μg and antifungal — 1 μg. Concentration of reference substances made 1 mg. The antimicrobical activity of samples was estimated on diameter of zones of a growth inhibition of test strains (mm). Diameters of zones less than 10 mm and the continuous growth in dish were estimated as lack of an antimicrobical activity, and 10–15 mm — weak activity, 15–20 mm — moderate activity and over 20 mm — an expressed antimicrobical activity. Each sample was tested in three parallel studies.

The statistical processing was performed by methods of the parametrical statistics with calculation of the average arithmetic and standard errors.

Dilution was made at 1 mg of substance per 1 ml of solvent. Bacteria sensitivity to these substances was determined by a diffusive method with disks. Bacteria such as *S. aureus, Bacillus subtilis, E. Coli, Ps. Aerugiosa* and *Candida albicans* were used. Antibiotic benzylpenicillin sodium salt, gentamicin and cephalosporin antibiotic of the third generation — ceftriaxone were chosen with an antibacterial activity, and an antifungal activity — nystatin.

Results of the revealed growth inhibition on some media are shown in Table.

Table

Antimicrobical and antifungal activities of samples.
Diameters of growth inhibition of test-strains. Solvent is 96 % ethanol

No.	Studied substances	*S. aureus*	*B. subtilis* 6633	*E. coli*	*Ps. aerugiosa* ATCC 9027	*C. alblcans*
1	(E)-1,3-bis(2- hydroxyphenyl)-prop-2-en-1-one (2)	20±1.0	18±1.0	10±1.0	10±1.0	11±1.0
2	(E)-1-(2-hydroxyphenyl)-3-(4-hydroxy-phenyl)-prop-2-en-1-one (4)	19±1.0	11±1.0	11±1.0	10±1.0	10±1.0
3	(E)-3-(ethoxy-4-hydroxyphenyl)-1-(2-hydroxyphenyl)prop-2-en-1-one (5)	18±1.0	14±1.0	12±1.0	11±1.0	11±1.0
4	2,2-(4,5-dihydro-1H-pyrazole-3,5-diil)phenol (8)	14±1.0	13±1.0	13±1.0	11±1.0	12±1.0
5	4-[5-(4-methoxyphenyl)-4,5-dihydro-1H-pyrazole-3-il]benzol-1,3-diol (9)	14±1.0	11±1.0	10±1.0	10±1.0	15±1.0
6	2-(2-hydroxyphenyl)flavone-4-one (12)	18±1.0	11±1.0	10±1.0	10±1.0	11±1.0
7	2-(4-hydroxyphenyl)flavone-4-one (14)	14±1.0	13± 1.0	13±1.0	11±1.0	12±1.0
8	96 % Ethanol	9±1.0	9±1.0	9±1.0	9±1.0	9±1.0
9	Benzylpenicillin sodium salt	15±1.0	–	16±1.0	12±1.0	–
10	Gentamicin	22±1.0	30±1.0	31±1.0	30±1.0	–
11	Ceftriaxone	30±1.0	30±1.0	29±1.0	22±1.0	–
12	Nystatin	–	–	–	–	25±1.0

These cultures were seeded with a lawn method on the following media, namely egg yolk high salt agar, Endo agar, nutrient agar and Sabouraud's medium. Then Petri dishes were incubated for a day at 37 ºC, for fungi at 28 ºC.

Thus, as a result of this research there was established that practically all studied substances showed a weak antibacterial activity. Exception is *S. aureus* culture for compounds of (E)-1.3-bis (2-hydroxyphenyl)-prop-2-en-1-one (**2**), (E)-1-(2-hydroxyphenyl)-3-(4-hydroxyphenyl)-prop-2-en-1-one (**4**), (E)-3-(ethoxy-4-hydroxyphenyl)-1-(2-hydroxyphenyl)prop-2-en-1-one (**5**) and 2-(2-hydroxyphenyl)flavone (**12**) which possess the moderate actions.

Experimental

^{1}H and ^{13}C NMR spectra of compounds 1–15 were recorded on JNN-ECA Jeol 400 spectrometer (frequency 399.78 and 100.53 MHz, respectively) in DMSO-d$_6$ a solvent. The chemical shifts were measured concerning signals of residual protons or carbon atoms of DMSO-d$_6$. The control of the reaction and purity of the compounds obtained was performed by Thin Layer Chromatography method on Silufol UV-254 plates in isopropyl alcohol-benzene-ammonia system (10:5:2). Plates were processed with iodine vapour.

General procedure of the receiving of chalcones (1–6)

The substituted acetophenone (0.013 mol) solution and aromatic aldehyde (0.013 mol) in ethanol (20 ml) were dropped to 20 ml of sodium hydroxide solution (40 %) at stirring and a room temperature. In process of aldehyde addition the reactionary mixture had yellow colour. The reactionary mixture was kept at room temperature for 62–95 h. Then the reactionary mixture was acidified with the diluted hydrochloric acid to neutral medium and kept for night in refrigerator (at temperature –15 ºC). The dropped out light brown powder was filtered, dried and recrystallized from benzene.

(E)-1-(4-Hydroxyphenyl)-3-(4-methoxyphenyl)prop-2-en-1-one (1). Product yield of 1 is 36 %, m.p. is 186–187 ºC. ^{1}H NMR spectrum, δ, ppm: 3.76 s (3H, H^{8}), 6.86 d (2H, H^{15,17}, ^{3}J 9.2 Hz), 6.95 d (2H, H^{2,6}, ^{3}J 8.5 Hz), 7.62 d (1H, H^{10}, ^{3}J 15.3 Hz), 7.74 d (1H, H^{9}, ^{3}J 17.1 Hz), 7.77 d (2H, H^{3,5}, ^{3}J 8.6 Hz), 8.03 d (2H, H^{14,18}, ^{3}J 8.5 Hz), 10.39 br. s (1H, OH). ^{13}C NMR spectrum, δ, ppm: 55.83 (C^{8}), 114.87 (C^{2,6}), 115.88 (C^{15,17}), 120.08 (C^{9}), 128,04 (C^{4}), 129.84 (C^{13}), 131.05 (C^{3,5}), 131.57 (C^{14,18}), 143.21(C^{10}), 161.62 (C^{1}), 162.61 (C^{16}) and 187.57 (C^{11}).

(E)-1,3-bis(2-hydroxyphenyl)-prop-2-en-1-one (2). Product yield of 2 is 84 %, m.p. is 154–155 ºC. ^{1}H NMR spectrum, δ, ppm: 6.85 t (H, H^{14}, ^{3}J 8.7 Hz), 6.90–6.98 m (3H, H^{4,6,10}), 7.26 t (1H, H^{15}, ^{3}J 8.2 Hz), 7.51 t (1H, H^{5}, ^{3}J 7.8 Hz), 7.81 d (1H, H^{17}, ^{3}J 9.6 Hz), 7.89 d (1H, H^{16}, ^{3}J 15.6 Hz), 8.07–8.13 m (2H, H^{3,10}). ^{13}C NMR spectrum, δ, ppm: 116.75 (C^{14}), 118.04 (C^{10}), 119.87 (C^{6}), 121.03 (C^{4}), 121.11 (C^{16}), 121.45 (C^{2}), 121.83 (C^{12}), 129.55 (C^{17}), 131.08 (C^{3}), 132.80 (C^{15}), 136.64 (C^{5}), 140.95 (C^{11}), 158.10 (C^{13}), 194.44 (C^{8}).

(E)-1-(2,4-Dihydroxyphenyl)-3-(4-methoxyphenyl)-prop-2-en-1-one (3). Product yield of 3 is 23.4 %, m.p. is 175–176 ºC. ^{1}H NMR spectrum, δ, ppm: 3.78 s (3H, H^{20}), 6.08 d (1H, H^{6}, ^{4}J 2.3 Hz), 6.26 dd (1H, H$^{4}_{аром}$, ^{3}J 2.1, 8.9 Hz), 6.97 d (2H, H^{15,17}, ^{3}J 8.7 Hz), 7.69–7.77 m (2H, H^{11,12}), 7.79 d (2H, H^{14,18}, ^{3}J 8.7 Hz), 8.01 d (1H, H^{3}, ^{3}J 9.2 Hz). ^{13}C NMR spectrum, δ, ppm: 55.88 (C^{20}), 110.54 (C^{6}), 111.51 (C^{4}), 114.91 (C^{2}), 114.92 (C^{15,17}), 119.52 (C^{11}), 128.06 (C^{13}), 131.21 (C^{14,18}), 133.08 (C^{12}), 142.94 (C^{3}), 161.73 (C^{16}), 166.92 (C^{1}), 167.30 (C^{5}), 190.52 (C^{8}).

(*E)-1-(2- hydroxyphenyl)-3-(4-hydroxyphenyl)-prop-2-en-1-one* (4). Product yield of 4 is 37 %, m.p. is 155–156 ºC. ^{1}H NMR spectrum, δ, ppm: 6.82 d (2H, H^{13,17}, ^{3}J 8.7 Hz), 6.94 m (1H, H^{4}), 6.96 d (1H, H^{11}, ^{3}J 11.9 Hz), 7.49 m (1H, H^{3}), 7.69–7.75 m (2H, H^{5,6}), 7.72 d (2H, H^{14,16}, ^{3}J 8.7 Hz), 8.5 d (1H, H^{10}, ^{3}J 7.8 Hz). ^{13}C NMR spectrum, δ, ppm: 116.37 (C^{13}), 116.67 (C^{17}), 118.39 (C^{11}), 119.60 (C^{4}), 121.20 (C^{2}), 126.17 (C^{12}), 131.05 (C^{10}), 131.87 (C^{14}), 131.94 (C^{16}), 136.53 (C^{3}), 146.10 (C^{5,6}), 161.12 (C^{15}), 162.51 (C^{1}), 194.13 (C^{8}).

(E)-3-(ethoxy-4-hydroxyphenyl)-1-(2-hydroxyphenyl)-prop-2-en-1-one (5). Product yield of 5 is 72 %, m.p. is 151–152 ºC. ^{1}H NMR spectrum, δ, ppm: 1.33 t (3H, H^{9,} ^{3}J 6.9 Hz), 4.11 k (2H, H^{8}, ^{3}J 6.9 Hz), 6.83 d (1H, H^{17}, ^{3}J 8.2 Hz), 6.93 t (1H, H^{3}, ^{3}J 8.2 Hz), 6.97 d (1H, H^{12}, ^{3}J 7.8 Hz), 7.27 dd (1H, H^{18}, ^{3}J 8.2, 1.8 Hz), 7.50 m (2H, H^{4,6}), 7.75 m (2H, H^{19,20}), 8.19 d (1H, H^{11}, ^{3}J 7.8 Hz). ^{13}C NMR spectrum, δ, ppm: 15.26 (C^{9}), 64.82 (C^{8}), 114.11 (C^{4}), 116.39 (C^{17}), 118.06 (C^{11}), 118.45 (C ^{3}), 119.36 (C^{20}), 121.14 (C^{15}), 125.35 (C^{18}), 126.16 (C^{5}), 131.28 (C^{12}), 136.67 (C^{6}), 146.59 (C^{19}), 147.77 (C^{1}), 153.13 (C^{2}), 162.59 (C^{16}), 194.17 (C^{13}).

(E)-1-(4-bromphenyl)-3-(5-brom-2-hydroxyphenyl)-prop-2-en-1-one (6). Product yield of 6 is 35 %, m.p. is 184–185 ºC. ^{1}H NMR spectrum, δ, ppm: 6.84 d (1H, H^{3}, ^{3}J 9.2 Hz), 7.37 dd (1H, H^{2}, ^{3}J 8.7, 2.3 Hz), 7.73 d (2H, H^{15,17}, ^{3}J 7.4 Hz), 7.86–7.96 m (2H, H^{6,10}), 8.05 d (2H, H^{14,18}, ^{3}J 8.3 Hz), 8.11 d (1H, H^{9}, ^{3}J 2.3 Hz). ^{13}C NMR spectrum, δ, ppm: 111.40 (C^{1}), 118.85 (C^{3}), 121.99 (C^{10}), 124.05 (C^{5}), 127.85 (C^{16}), 130.85 (C^{6}), 132.35 (C^{15,17}), 134.97 (C^{2}), 137.07 (C^{13}), 138.47 (C^{9}), 178.78 (C^{11}).

General procedure of the receiving of substituted pyrazolines (7–11)

0.02 mol of hydrazine hydrate was added to substituted chalcone (0.002 mol) in 10 ml of ethanol. Mixture was heated at temperature 70–80 ºC for 4 h, then cooled and diluted in 50 ml of water. A dropped out residue was filtered, washed with water and recrystallized from ethanol.

4-[5-[5-(4-Methoxyphenyl)-4,5-dihydro-1H-pyrazole-3-yl]]phenol (7). Product yield of **7** is 53 %, m.p. is 119–120 ºC. ^{1}H NMR spectrum, δ, ppm: 2.68 dd (1H, H^{4ax}, ^{2}J 16.3 Hz, ^{3}J 11.0 Hz), 3.27 dd (1H, H^{4eq}, ^{2}J 16.5 Hz, ^{3}J 10.5 Hz), 3.67 s (1H, H^{20}), 4.68 t (1H, H^{5}, ^{3}J 10.1 Hz), 6.72 d (2H, H^{8,10}, ^{3}J 8.7 Hz), 6.84 d (2H, H^{14,16}, ^{3}J 8.7 Hz), 7.21 d (2H, H^{13,17}, ^{3}J 8.7 Hz), 7.40 d (2H, H^{7,11}, ^{3}J 8.2 Hz), 9.67 br. s (1H, OH). ^{13}C NMR spectrum, δ, ppm: 41.42 (C^{4}), 55.55 (C^{5}), 63.51 (C^{20}), 114.22 (C^{14,16}), 115.84 (C^{8,10}), 124.92 (C^{6}), 127.52 (C^{13,17}), 128.28 (C^{7,11}), 135.51 (C^{12}), 149.71 (C^{3}), 158.16 (C^{15}), 158.86 (C^{9}).

2,2'-(4,5-dihydro-1H-pyrazole-3,5-diil)phenol (8). Product yield of 8 is 72 %, m.p. is 124–125 ºC. ^{1}H NMR spectrum, δ, ppm: 2.88 dd (1H, CH^{4ax}, ^{2}J 16.5 Hz, ^{3}J 10.1 Hz), 3.53 dd (1H, CH^{4eq}, ^{2}J 16.7 Hz, ^{3}J 10.7 Hz), 5.00 t (1H, CH^{5}, ^{3}J 10.5 Hz), 6.72–6.87 m (4H, CH$^{8,10,14,16}_{аром}$), 7.03–7.07 m (1H, CH$^{11}_{аром}$), 7.15–

7.18 m (1H, CH^{17}_{apom}), 7.25 t (2H, $CH^{9,15}_{apom}$, ^3J 7.8 Hz), 7.50 br. s (1H, NH). NMR ^{13}C spectrum, δ, ppm: 40.01 (C^4), 57.67 (C^5), 115.63 (C^8), 115.91 (C^{14}), 116.41 (C^{10}), 117.45 (C^{16}), 119.50 ($C^{6,12}$), 127.38 (C^{17}), 128.06 (C^{15}), 128.54 (C^9), 130.00 (C^{11}), 153.46 (C^3), 155.33 (C^{13}), 157.28 (C^7).

4-[5-(4-methoxyphenyl)-4,5-dihydro-1H-pyrazole-3-il]benzol-1,3-diol (9). Product yield of 9 is 37 %, m.p. is 149–150ºC. ^1H NMR spectrum, δ, ppm: 2.84 dd (1H, H^{4ax}, ^2J 11.0 Hz, ^3J 11.0 Hz), 3.43 dd (1H, H^{4eq}, ^2J 5.3 Hz, ^3J 10.5 Hz), 3.70 s (3H, H^{21}),4.68 t (1H, H^5, ^3J 10.5 Hz), 6.27 m (2H, $H^{8,10}$), 6.87 d (2H, $H^{14,16}$, ^3J 8.7 Hz), 7.05 d (1H, H^{11}, ^3J 8.7 Hz), 7.27 d (2H, $H^{13,17}$, ^3J 8.7 Hz), 11.22 br. s (1H, NH). ^{13}C NMR spectrum, δ, ppm: 41.59 (C^4), 55.62 (CH_3), 61.86 (C^5), 102.92 (C^8), 107.50 (C^{10}), 109.44 (C^6), 114.35 ($C^{14,16}$), 128.39 ($C^{13,17}$), 129.40 (C^{11}), 134.76 (C^{12}), 153.87 (C^3), 159.09 (C^9), 159.74 (C^{15}), 162.10 (C^7).

2-[5-[5-(4-Hydroxyphenyl)-4,5-dihydro-1H-pyrazole-5-yl]phenol (10). Product yield of 10 is 89 %, m.p. is 110–111 ºC. ^1H NMR spectrum, δ, ppm: 2.89 dd (1H, H^{4ax}, ^2J 15.8 Hz, ^3J 10.8 Hz), 3.47 dd (1H, H^{4eq}, ^2J 16.5 Hz, ^3J 11.0 Hz), 4.69 t (1H, H^5, ^3J 9.8 Hz), 6.70 d (2H, $H^{14,16}$, ^3J 7.3 Hz), 6.81–6.87 m (2H, $H^{8,10}$), 7.13–7.19 m (3H, $H^{9,13,17}$), 7.24 d (2H, H^{11}, ^3J 7.3 Hz), 7.68 br. s (1H, NH), 9.35 s (1H, OH^{19}), 11.16 s (1H, OH^{18}). ^{13}C NMR spectrum, δ, ppm: 41.24 (C^4), 62.36 (C^5), 115.68 ($C^{14,16}$), 116.23 (C^8), 117.35 (C^6), 119.65 (C^{10}), 128.25 (C^{11}), 128.37 ($C^{13,17}$), 130.17 (C^9), 132.79 (C^{12}), 153.06 (C^3), 157.22 (C^{15}), 157.26 (C^7).

2-Etoxy-4-[3-(2-hydroxyphenyl)-4,5-dihydro-1H-pyrazole-5-yl]phenol (11). Product yield of 11 is 93 %, m.p. is 89–90 ºC. ^1H NMR spectrum, δ, ppm: 1.27 t (3H, H^{21}, ^3J 7.3 Hz), 2.92 dd (1H, H^{4ax}, ^2J 16.5 Hz, ^3J 11.0 Hz), 3.49 dd (1H, H^{4eq}, ^2J 16.8 Hz, ^3J 11.0 Hz), 3.96 q (2H, H^{20}, ^3J 6.7 Hz), 4.69 t (1H, H^5, ^3J 11.0 Hz), 6.69–6.74 m (2H, $H^{10,14}$), 6.82–6.92 m (3H, $H^{8,13,17}$), 7.16 d (1H, H^{11}, ^3J 7.3 Hz), 7.25 t (1H, H^9, ^3J 7.3 Hz), 7.71 s (1H, NH), 8.87 br. s (1H, OH^{19}), 11.16 s (1H, OH^{18}). ^{13}C NMR spectrum, δ, ppm: 15.32 (C^{21}), 41.31 (C^4), 62.65 (C^5), 64.37 (C^{20}), 112.75 (C^{17}), 115.88 (C^{10}), 116.23 (C^8), 117.37 (C^6), 119.65 (C^{13}), 119.69 (C^{14}), 128.26 (C^9), 130.18 (C^{11}), 133.29 (C^{12}), 146.68 (C^{15}), 147.17 (C^{16}), 153.16 (C^3), 157.26 (C^7).

General procedure of the receiving of flavanones (12–15)

The reactionary mixture from 0.001 mol of substituted chalcone and catalytic amount of triethylamine in 15 ml of ethanol (95 %) was heated with backflow condenser for 8 h. The dropped out residue was filtered. It was dried at room temperature.

2-(2-hydroxyphenyl)flavone-4-one (12). Product yield of 12 is 94 %, m.p. is 147–148 ºC. ^1H NMR spectrum, δ, ppm: 2.76 dd (1H, H^{3ax}, ^2J 16.7 Hz, ^3J 2.7 Hz), 3.14 dd (1H, H^{3eq}, ^2J 17.0, Hz, ^3J 13.3 Hz), 5.75 dd (1H, H^2, ^3J 13.3, 2.8 Hz), 6.77–6.83 m (3H, $H^{13,14,15}$), 7.05 d (1H, H^{16}, ^3J 7.8 Hz), 6.86 d (1H, H^7, ^3J 8.2 Hz), 7.13 t (1H, H^{10}, ^3J 8.2 Hz), 7.49 t (1H, H^8, ^3J 7.8 Hz), 7.54 t (1H, H^9, ^3J 6.9 Hz), 8.09 s (1H, OH). ^{13}C NMR spectrum, δ, ppm: 43.02 (C^3), 74.85 (C^2), 116.31(C^{13}), 118.27 (C^5), 118.71 (C^7), 119.78 (C^{15}), 121.64 (C^8), 122.07 (C^9), 125.58 (C^{16}), 126.89 (C^{10}), 127.34 (C^{14}), 130.04 (C^{11}), 136.79 (C^{12}), 154.84 (C^6), 162.03 (C^4).

7-Hydroxy-2-(4-methoxyphenyl)flavone-4-on (13). Product yield of 13 is 76 %, m.p. is 146–147 ºC. ^1H NMR spectrum, δ, ppm: 2.59 dd (1H, H^{3ax}, ^2J 16.9 Hz, ^3J 2.8 Hz), 3.08 dd (1H, H^{3eq}, ^2J 16.7 Hz, ^3J 16.1 Hz), 3.71 s (3H, H^{20}), 5.45 dd (1H, H^2, ^3J 12.8, 2.3 Hz), 6.29 s (1H, H^7), 6.46 d (1H, H^9, ^3J 8.0 Hz), 6.97 d (2H, $H^{13,15}$, ^3J 8.2 Hz), 7.39 d (2H, $H^{12,16}$, ^3J 8.7 Hz), 8.14 d (1H, H^{10}, ^3J 8.7 Hz), 10.62 br. s. (1H, OH^{18}). ^{13}C NMR spectrum, δ, ppm: 43.67 (C^3), 55.65 (C^{20}), 79.25 (C^2), 103.09 (C^7), 111.08 (C^9), 114.33 ($C^{13,15}$), 114.94 (C^5), 128.74 ($C^{12,16}$), 131.54 (C^{10}), 133.51 (C^{11}), 159.85 (C^{14}), 165.16 (C^6), 166.34 (C^8), 190.59 (C^4).

2-(4-hydroxyphenyl)flavone-4-one (14). Product yield of 14 is 95 %, m.p. is 184–185 ºC. ^1H NMR spectrum, δ, ppm: 2.73 dd (1H, H^{3ax}, ^2J 16.9 Hz, ^3J 3.2 Hz), 3.18 dd (1H, H^{3eq}, ^2J 16.5, Hz, ^3J 12.8 Hz), 5.48 dd (1H, H^2, ^3J 12.8, 2.8 Hz), 6.77 d (2H, $H^{13,15}$, ^3J 8.2 Hz), 7.30 d (2H, $H^{12,16}$, ^3J 8.3 Hz), 7.00–7.05 m (2H, $H^{7,9}$), 7.52 t (1H, H^8, ^3J 8.2 Hz, 7.75 d (1H, H^{10}, ^3J 7.9 Hz), 9.48 br. s (1H, OH^{18}). ^{13}C NMR spectrum, δ, ppm: 43.94 (C^3), 79.40 (C^2), 115.82 (C^{13}), 115.92 (C^{15}), 118.76 ($C^{7,9}$), 121.19(C^5), 128.54 (C^{12}), 128.91 (C^{16}), 129.69 (C^{11}), 136.80 (C^8), 158.19 (C^{14}), 161.77 (C^6), 192.40 (C^4).

2-(3-etoxy-4-hydroxyphenyl)flavone-4-one (15). Product yield of 15 is 96 %, m.p. is 127–128 ºC. ^1H NMR spectrum, δ, ppm: 1.29 t (3H, H^{20}, ^3J 6.9 Hz), 2.71 dd (1H, H^{3ax}, ^2J 17.0 Hz, ^3J 2.7 Hz), 3.26 dd (1H, H^{3eq}, ^2J 17.0 Hz, ^3J 13.3 Hz), 4.00 k (2H, H^{19}, ^3J 6.9 Hz), 5.47 dd (1H, CH_2, ^3J 12.8, 2.8 Hz), 6.78 d (1H, H^{16}, ^3J 8.2 Hz), 6.89 d (1H, H^{12}, ^3J 8.2 Hz), 7.02–7.06 m (3H, $H^{7,10,15}$), 7.53 t (1H, H^8, ^3J 8,2 Hz), 7.76 t (1H, H^9, ^3J 7.8 Hz), 9.00 s (1H, OH). NMR spectrum ^{13}C, δ, ppm: 15.29 (C^{20}), 44.03 (C^3), 64.55 (C^{19}), 79.57 (C^2), 113.10 (C^{12}), 115.86 (C^{15}), 118.57 (C^7), 120.20 (C^{16}), 121.15 (C^5), 121.81 (H^9), 126.81 (C^{10}), 130.18 (C^{11}), 136.71 ($C^8{}_a$), 147.20 (C^{14}), 147.77 (C^{13}), 161.76 (C^6), 192.47 (C^4).

The study was performed with support of the Ministry of Education and Science of the Republic of Kazakhstan (project number AP05133157).

References

1 Miranda C.L. Antioxidant and prooxidant action of prenylated and nonprenylated chalcones and flavanones in vitro / C.L. Miranda, G.L.M. Aponso, J.F. Stevens, M.L. Deinzer, D.R. Buhler // J. Agric. Food Chem. — 2000. — No. 48. — P. 3876–3884.

2 Sivakumar P.M. Synthesis, antioxidant evaluation and quantitative structure activity relationship studies of chalcones / P.M. Sivakumar, P.K. Prabhakar, M. Doble // Med. Chem. Res. — 2011. — Vol. 20, No. 4. — P. 482–492.

3 Tiwari K.N. In vitro inhibitory properties of ferrocene substituted chalcones and aurones on bacterial and human cell cultures / K.N. Tiwari, J.P. Monserrat, A. Arnaud Hequet, C. Ganem-Elbaz, T. Cresteil, G. Jaouen, A. Vessières, E.A. Hillard, C. Jolivalt // Dalton Trans. — 2012. — Vol. 41. — P. 6451–6457.

4 Dao T.T. Chalcones as novel influenza A (H1N1) neuraminidase inhibitors from Glycyrrhiza inflate / T.T. Dao, P.H. Nguyen, H.S. Lee, E. Kim, J. Park, S. Lim, W.K. Oh // Bioorg. Med. Chem. Lett. — 2011. — Vol. 21, No. 1. — P. 294–298.

5 Hsieh H.K. Synthesis and anti-inflammatory effect of chalcones / H.K. Hsieh, L.T. Tsao, J.P. Wang // J. Pharm. Pharmacol. — 2000. — Vol. 52, No. 2. — P. 163–171.

6 Awasthi S.K. Potent antimalarial activity of newly synthesized substituted chalcone analogs in vitro / S.K. Awasthi, N. Mishra, B. Kumar, M. Sharma, A. Bhattacharya, L.C. Mishra, V.K. Bhasin // Med. Chem. Res. — 2009. — Vol. 18, No. 6. — P. 407–420.

7 Achanta G. A boronic chalcone derivative exhibits potent anticancer activity through inhibition of the proteasome / G. Achanta, A. Modzelewska, L. Feng, S.R. Khan, P.A. Huang // Mol. Pharmacol. — 2006. — Vol. 70. — P. 426–433.

8 Barford L. Chalcones from Chinese liquorice inhibit proliferation of T cells and production of cytokines / L. Barford, K. Kemp, M. Hansen, A. Kharazmi // Int. Immunopharmacol. — 2002. — Vol. 2. — P. 545–550.

9 Satyanarayama M. Synthesis and antihyperglycemic activity of chalcone based aryloxypropanolamines / M. Satyanarayama, P. Tiwari, K. Tripathi, A.K. Srivastava, R. Pratap // Bioorg. Med. Chem. — 2004. — Vol. 12, No. 5. — P. 883–889.

10 Hamdi N. A rapid access to new coumarinyl chalcone and substituted chromeno[4,3-c]pyrazol-4(1H)-ones and their antibacterial and DPPH radical scavenging activities / N. Hamdi, C. Fischmeister, M.C. Puerta, P. Valerga // Med. Chem. Res. — 2011. — Vol. 20, No. 4. — P. 522–530.

11 Lahtchev K.L. Antifungal activity of chalcones: A mechanistic study using various yeast strains / K.L. Lahtchev, D.I. Batovska, S.P. Parushev, V.M. Ubiyvovk, A.A. Sibirny // Eur. J. Med. Chem. — 2008. — Vol. 43, No. 10. — P. 2220–2228.

12 Daskiewicz J.B. Organolithium mediated synthesis of prenylchalcones as potential inhibitors of chemoresistance / J.B. Daskiewicz, G. Comte, D. Barron, A. Di Pietro, F. Thomasson // Tetrahedron Lett. — 1999. — Vol. 40, Issue 39. — P. 7095–7098.

13 Takagi K. Synthesis and reactions of some chromones / K. Takagi, M. Tanaka, Y. Murakami, H. Morita, T. Aotsuka // Eur. J. Med. Chem. Chim. Ther. — 1986. — Vol. 21. — P. 65–69.

14 Ankhiwala M.D. Preparation and antibacterial activity of 1-Phenyl-3-(2″-hydroxy-3″-bromo-4″-n-butoxy-5″-nitrophen-1″-yl)-5-substituted-phenyl-2-pyrazolines and 3-(2″-hydroxy-3″-bromo-4″-n-butoxy-5″-nitrophen-1″-yl)-5-substituted-phenyl-2-isoxazolines / M.D. Ankhiwala, H.B. Naik // Chem. Abstr. — 1991. — Vol. 4. — P. 816.

15 Kaname T. Synthesis and analgesic activity of 4-amino-1,2-dihydro-5-(2-hydroxyphenyl)-3H-pyrazol-3-ones and 5-amino-6-(2-hydroxyphenyl)pyrimidin-4(3H)-ones / T. Kaname, T. Masaaki, M. Hikari, O. Kuniyoshi, I. Katsuyuki, N. Naoki, O. Masayuki // Eur. J. Med. Chem. — 1987. — Vol. 22. — P. 239–244.

16 Литвиненко В.И. Природные флавоноиды / В.И. Литвиненко. — Харьков: ГНЦЛС, 1995. — 56 с.

17 Aitmambetov A., Kubzheterova A. An Improved Method for the Synthesis of Flavanones // Russian Journal of Bioorganic Chemistry. — 2002. — Vol. 28. — P. 165–166

М.К. Ибраев, С.Б. Ахметова, А.Т. Такибаева,
М.Б. Исабаева, А.О. Нуркенов, О.Т. Сейлханов

Ауыстырылған халкондардың және олардың туындыларының синтезі, құрылымы және микробқа қарсы белсенділігі

Мақалада гидроксилді орынбасылған ацетофенондармен ароматты орынбасылған альдегидтердің әрекеттесу реакцияларын, альдольді конденсацияда байқалатын сілтілі сулы-спиртті ерітіндінің (Кляйзен-Шмидт конденсациясы) қатысуымен зерттелді. Бұл реакцияның жүру ұзақтығы көп және аяқталу уақыты 62–85 сағ аралығын құрайды. Соңғы өнімнің құрылысында α,β-жағдайдағы карбонильді топтың қос байланысы бар. Алынған халкондардың функционализациялануы олардың гидразингидратпен әрекеттесуі жолы арқылы жүзеге асырылды. Этанолда халкондар гидразингидратпен қайнатылған кезде аралық гидразон, молекулаішілік циклоконденсацияға ұшырап, пиразол туындылары түзілді. Синтезделген қосылыстардың құрылысы ^{1}H-, ^{13}C-ЯМР-спектроскопия және екі шекті (^{1}H-^{1}H) COSY және (^{1}H-^{13}C) HMQC-спектрлері бойынша дәлелденді. Бірөлшемді ЯМР ^{1}H және ^{13}C спектрлерінде сигналдардың химиялық ығысуының, еселігінің және интегралдық қарқындылығының мәндері анықталды. Зерттелген қосылыстардың құрылымын дәлелдейтін гомо- және гетероядролық өзара әрекеттесулер (^{1}H-^{1}H) COSY және (^{1}H-^{13}C) HMQC спектрлері бойынша анықталды. Синтезделген халкондардың, пиразолиндер мен флавонондардың микробқа қарсы белсенділіктерінің мәліметтері келтірілген. Барлық зерттелген қосылыстар бактерияға қарсы әлсіз белсенділікті көрсетті. Қалыпты айқын әсерге ие (Е)-1,3-бис(2-гидроксифенил)-проп-2-ен-1-он, (Е)-1-(2-гидроксифенил)-3-(4-гидрокси-фенил)-проп-2-ен-1-он, (E)-3-(этокси-4-гидроксифенил)-1-(2-гидроксифенил)проп-2-ен-1-он, 2-(2-гидроксифенил)флавон қосылыстары үшін *S. aureus* ашытқы зеңдерінің дақылы.

Кілт сөздер: орынбасқан ароматикалық альдегид, халкон, пиразолин, флавонон, цитокин, NF-κB транскрипциондық факторы.

М.К. Ибраев, С.Б. Ахметова, А.Т. Такибаева,
М.Б. Исабаева, А.О. Нуркенов, О.Т. Сейлханов

Синтез, структура и антимикробная активность замещенных халконов и их производных

В статье приведены реакции взаимодействия гидроксилзамещенных ацетофенонов с замещенными ароматическими альдегидами в присутствии водно-спиртового раствора щелочи (конденсация Кляйзена-Шмидта), которая представляет собой альдольную конденсацию. Эта реакция имеет большую продолжительность и заканчивается в течение 62–85 ч. Конечный продукт содержит двойные связи в α,β-положении к карбонильной группе. Дальнейшую функционализацию полученных халконов осуществляли путем их взаимодействия с гидразингидратом. Было обнаружено, что кипячение халконов с гидразингидратом в этаноле приводит к внутримолекулярной циклоконденсации промежуточного гидразона с образованием производных пиразола. Структуры синтезированных соединений изучали с помощью ^{1}H и ^{13}C-ЯМР-спектроскопии и данных по двумерным (^{1}H-^{1}H) COSY и (^{1}H-^{13}C) HMQC-спектрам. Определены значения химических сдвигов, кратности и интегральной интенсивности сигналов в одномерных спектрах ЯМР ^{1}H и ^{13}C. Гомо- и гетероядерные взаимодействия, подтверждающие структуру изученных соединений, определяли по спектрам (^{1}H-^{1}H) COSY и (^{1}H-^{13}C) HMQC. Приведены данные по антимикробной активности синтезированных халконов, пиразолинов и флавононов. Установлено, что практически все исследованные вещества показывают слабую антибактериальную активность. Исключение составляет культура дрожжевых грибков *S. aureus* для соединений (E)-1,3-бис(2-гидроксифенил)-проп-2-ен-1-он, (E)-1-(2-гидроксифенил)-3-(4-гидрокси-фенил)-проп-2-ен-1-он, (E)-3-(этокси-4-гидроксифенил)-1-(2-гидроксифенил)проп-2-ен-1-он, 2-(2-гидроксифенил)флавон, которые обладают умеренно выраженным действием.

Ключевые слова: замещенный ароматический альдегид, халкон, пиразолин, флавонон, цитокин, транскрипционный фактор NF-κB.

References

1 Miranda, C.L., Aponso, G.L.M., Stevens, J.F., Deinzer, M.L., & Buhler, D.R. (2000). Antioxidant and prooxidant action of prenylated and nonprenylated chalcones and flavanones in vitro. *J. Agric. Food Chem., 48,* 3876–3884. DOI 10.1016/S0040–4039(99)01461–6.

2 Sivakumar, P.M., Prabhakar, P.K., & Doble, M. (2011). Synthesis, antioxidant evaluation and quantitative structure activity relationship studies of chalcones. *Med. Chem. Res., 20*, 482–492. DOI 10.1007/s00044–010–9342–1.

3 Tiwari, K.N., Monserrat, J.P., Arnaud Hequet, A., Ganem-Elbaz, C., Cresteil, T., Jaouen, G., Vessières, A., Hillard, E.A., & Jolivalt, C. (2012). In vitro inhibitory properties of ferrocene substituted chalcones and aurones on bacterial and human cell cultures. *Dalton Trans., 41,* 6451–6457. DOI 10.1039/C2DT12180H.

4 Dao, T.T., Nguyen, P.H., Lee, H.S., Kim, E., Park, J., Lim, S., & Oh, W.K. (2011). Chalcones as novel influenza A (H1N1) neuraminidase inhibitors from Glycyrrhiza inflate. *Bioorg. Med. Chem. Lett., 21*, 294–298. DOI 10.1016/j.bmcl.2010.11.016.

5 Hsieh, H.K., Tsao, L.T., & Wang, J.P. (2000). Synthesis and anti-inflammatory effect of chalcones *J. Pharm. Pharmacol., 52,* 163–171. DOI 10.1211/0022357001773814.

6 Awasthi, S.K., Mishra, N., Kumar, B., Sharma, M., Bhattacharya, A., Mishra, L.C., & Bhasin, V.K. (2009). Potent antimalarial activity of newly synthesized substituted chalcone analogs in vitro. *Med. Chem. Res., 18,* 407–420. DOI 10.1007/ s00044-008-9137-9.

7 Achanta, G., Modzelewska, A., Feng, L., Khan, S.R., & Huang, P.A. (2006). A boronic chalcone derivative exhibits potent anticancer activity through inhibition of the proteasome. *Mol. Pharmacol., 70,* 426–433. DOI 10.1124/mol.105.021311.

8 Barford, L., Kemp, K., Hansen, M., & Kharazmi, A. (2002). Chalcones from Chinese liquorice inhibit proliferation of T cells and production of cytokines. *Int. Immunopharmacol., 2,* 545–550. DOI 10.1016/ S1567–5769(01)00202–8.

9 Satyanarayama, M., Tiwari, P., Tripathi, K., Srivastava, A.K., & Pratap, R. (2004). Synthesis and antihyperglycemic activity of chalcone based aryloxypropanolamines. *Bioorg. Med. Chem., 12,* 883–889. DOI 10.1016/j.bmc.2003.12.026.

10 Hamdi, N., Fischmeister, C., Puerta, M.C., & Valerga, P. (2011). A rapid access to new coumarinyl chalcone and substituted chromeno[4,3-c]pyrazol-4(1H)-ones and their antibacterial and DPPH radical scavenging activities. *Med. Chem. Res., 20,* 522–530. DOI 10.1007/s00044–010–9326–1.

11 Lahtchev, K.L., Batovska, D.I., Parushev, S.P., Ubiyvovk, V.M., & Sibirny, A.A. (2008). Antifungal activity of chalcones: A mechanistic study using various yeast strains. *Eur. J. Med. Chem., 43,* P. 2220–2228. DOI 10.1016/ j.ejmech.2007.12.027.

12 Daskiewicz, J.B., Comte, G., Barron, D., Di Pietro, A., & Thomasson, F. (2008). Organolithium mediated synthesis of prenylchalcones as potential inhibitors of chemoresistance. *Tetrahedron Lett., 40*, 7095–7098. DOI 10.1016/S0040–4039(99)01461–6.

13 Takagi, K., Tanaka, M., Murakami, Y., Morita, H., & Aotsuka, T. (1986). Synthesis and reactions of some chromones. *Eur. J. Med. Chem. Chim. Ther., 21,* 65–69.

14 Ankhiwala, M.D., & Naik, H.B. (1991). Preparation and antibacterial activity of 1-phenyl-3-(2″-hydroxy-3″-bromo-4″-n-butoxy-5″-nitrophen-1″-yl)-5-substituted-phenyl-2-pyrazolines and 3-(2″-hydroxy-3″-bromo-4″-n-butoxy-5″-nitrophen-1″-yl)-5-substituted-phenyl-2-isoxazolines. *Chem. Abstr., 4*, 816. DOI: 10.1002/chin.199049179

15 Kaname, T., Masaaki, T., Hikari, M., Kuniyoshi, O., Katsuyuki, I., Naoki, N., & Masayuki, O. (1987). Synthesis and analgesic activity of 4-amino-1,2-dihydro-5-(2-hydroxyphenyl)-3H-pyrazol-3-ones and 5-amino-6-(2-hydroxyphenyl)pyrimidin-4(3H)-ones. *Eur. J. Med. Chem., 22*, 239–244. https://doi.org/10.1016/0223–5234(87)90055–9

16 Litvinenko, V.I. (1995). *Prirodnye flavonoidy [Natural Flavonoids].* Kharkov: GNCLS [in Russian].

17 Aitmambetov, A., & Kubzheterova, A. (2002). An Improved Method for the Synthesis of Flavanones. *Russian Journal of Bioorganic Chemistry, 28*, 165–166.

DOI 10.31489/2019Ch3/37-44

UDC 547.7/.8:547.796.1

S.D. Fazylov[1], O.A. Nurkenov[1], T.M. Seilkhanov[2], G.Zh. Karipova[1],
K. Van Hecke[3], Ye.M. Suleimen[4], A.M. Gazaliyev[1]

[1]Institute of Organic Synthesis and Coal Chemistry of Republic of Kazakhstan, Karaganda, Kazakhstan;
[2]S. Ualikhanov Kokshetau State Technical University, Kazakhstan;
[3]Ghent University, Belgium;
[4]Institute of Applied Chemistry, L.N. Gumilyov Eurasian National University, Nur-Sultan, Kazakhstan
(E-mail: iosu8990l@mail.ru)

Synthesis of hydrazone derivatives of isonicotinic acid under microwave activation conditions

In the article the results of studying the reaction of the interaction of isonicotinic acid hydrazide with various derivatives of aromatic aldehydes under conditions of microwave activation in an alcohol medium were described. The results of studying the dependences of the hydrazone yield on the duration of the activation time at various microwave irradiation powers in comparison with the classical method have been presented. It was found that the main factors affecting the nature of the synthesis and the yields of the target products were the power and time of microwave activation, as well as the structural features of the reactants. For all studied reactions, the optimal conditions for obtaining the target product have been shown. As a result of a comparative analysis of the results obtained for the synthesis of new isonicotinic hydrazones, it was determined that the use of microwave irradiation contributed to an increase in the yield of the product and a decrease in the reaction time by 3-4 times than according to traditional technology. The authenticity of each product is unambiguously proved by comparing the melting point, as well as by analyzing the physico-chemical characteristics with previously synthesized hydrazone derivatives of isonicotinic acid obtained by classical synthesis methods. The structure of all synthesized compounds was studied by ^{1}H and ^{13}C NMR spectroscopy, as well as data from two-dimensional COSY (^{1}H-^{1}H) spectra and HMQC (^{1}H-^{13}C). The developed microwave method for the synthesis of hydrazone derivatives of isonicotinic acid complies with the principles of the concept of «Green Chemistry».

Keywords: hydrazide of isonicotinic acid, hydrazone, aromatic aldehydes, microwave activation.

Introduction

According to the World Health Organization (WHO), tuberculosis remains one of the most common and dangerous diseases. Currently, every third inhabitant of the earth is infected with it, i.e. over 2 billion people. Every year, 8 million people fall ill with active tuberculosis, two million die. More than 90 % of the disease is registered in developing countries. At the same time, 75 % of the working-age population is among the patients. Thus, the prevention and treatment of tuberculosis is an important political, economic, social task of any state [1, 2].

Over the past 50 years, research on the synthesis of new anti-TB drugs based on carboxylic acid hydrazides has been carried out in the world. A review of literature data on available anti-tuberculosis drugs shows that the majority of anti-tuberculosis drugs used in medical practice contain a hydrazide fragment in their structure [2–5].

Despite the large number of publications on the synthesis of various hydrazide derivatives, their properties and structure, they are currently promising for further study and improvement [2–6]. In this series of compounds, various derivatives of isonicotinic acid hydrazide (INH), exhibiting a wide spectrum of biological activity, are of particular interest. To date, many different derivatives have been synthesized on the basis of INH with various variations of anti-tuberculosis activity. For example, the tuberculosis drug ftivazide developed in 1951 in the Soviet Union has been widely used in clinical practice to date [6–8]. However, the problem of drug resistance of many pathogenic bacteria and viruses to medicines used for treatment requires constant search and expansion of the arsenal of new highly effective and low-toxic drugs. In recent years, interest in hydrazones has increased again, which is associated with the discovery of high anticancer activity and other types of activities in a number of derivatives of hydrazine compounds [9–11].

Currently, the search strategy for chemical compounds with anti-tuberculosis activity is carried out in several directions. These are chemical modification of known anti-tuberculosis drugs, optimization of pharmacokinetics by obtaining polymeric forms of anti-tuberculosis drugs, developing new composition of dosage forms and synthesizing new classes of organic compounds with anti-tuberculosis properties [11–13].

For a number of years, the Institute of Organic Synthesis and Coal Chemistry of the Republic of Kazakhstan has been carrying out research on the search for new bioactive compounds based on isonicotinic acid hydrazide and optimal methods for their preparation. One-step methods of obtaining known anti-TB drugs, namely 4-pyridinecarboxylic acid hydrazide («isoniazid»), 4-pyridinecarboxylic acid [(4-hydroxy-3-methoxyphenyl)methylene]hydrazide («ftivazide») and other drugs with high yields have been implemented. Syntheses were carried out using microwave activation technology [14]. Microwave (MW) activation of organic reactions is one of the new directions in chemical synthesis [15–18]. Chemical transformations occur with the use of microwave radiation with the participation of solid dielectrics and liquids. The developed methods are consistent with the principles of the concept of «Green Chemistry» [19].

In continuation of the studies [20, 21] we present the results of studying the effect of microwave exposure on the synthesis of certain hydrazone derivatives of isonicotinic acid in the article.

Experimental

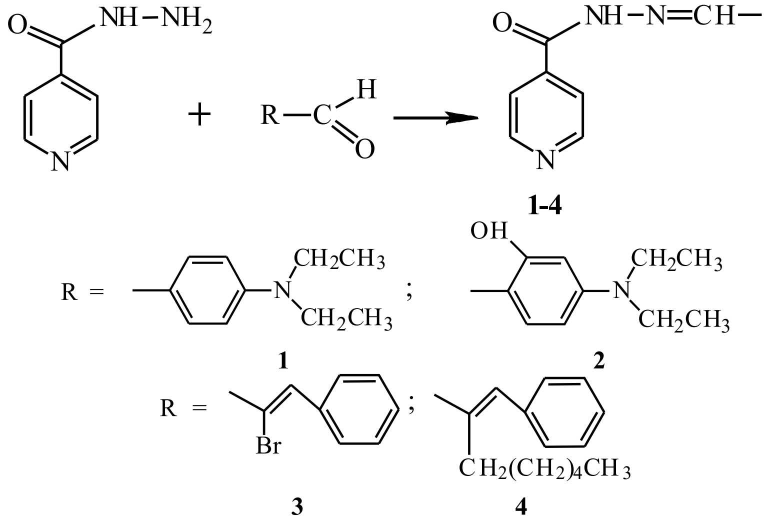
The ^1H and ^{13}C NMR spectra of compounds (1–4) were recorded in DMSO-d_6 using a JNN-ECA 400 spectrometer (400 and 100 MHz on ^1H and ^{13}C nuclei) from Jeol, Japan. The survey was carried out at room temperature using a DMSO solvent. Chemical shifts are measured relative to signals of residual protons or carbon atoms of a deuterated solvent.

Syntheses of the new isonicotinic acid hydrazones under classical conditions were carried out at a 1:1 ratio of initial reactants in an alcohol medium and the reaction time was from 2 to 6 hours with heating (65–75 °C) in a flask with reflux condenser. Similar reactions in the microwave field were carried out in the reactor for microwave synthesis Monowave 300 manufactured by «Anton Paar» with a maximum radiation power of 350 W and a frequency of 2455 MHz.

Synthesis products were isolated and purified by standard, well-known methods. The authenticity of the product is unambiguously proved by comparing the melting point, analyzing the ^1H and ^{13}C NMR spectra with previously synthesized compounds under the conditions of the classical method. Purity was monitored by thin layer chromatography.

Results and Discussion

In this paper, we studied the possibility of optimizing the synthesis of a number of new hydrazone derivatives of isonicotinic acid under microwave (MW) activation conditions in comparison with the classical method. To this end, we conducted a series of experiments to determine the optimal conditions for the synthesis of compounds (1–4). In order to establish the optimal condition, an alcoholic solution of INH and the corresponding aldehyde was placed in a 1:1 ratio in a glass container. The reaction mixture was irradiated with microwaves of 75, 150 and 350 watts. The conditions of the microwave synthesis reaction were selected by varying the time and radiation power.



Comparative results of the optimal conditions for the synthesis of the studied hydrazones (1–4) at different irradiation powers are shown in Table 1.

Table 1

Yields of hydrazones (1–4) under conditions of MW activation at different powers (W) and classical heating (CH), the reaction time is 2 hours

Comp. No.	Compound name	Microwave activation			
		MW radiation power, W	MW time, min	yield, %	
				MW	CH
1	N-(4-(diethylamino) benzylidene)-isonicotinohydrazide	75	70	50	85
		150	30	97	
		350	20	85	
2	N-diethylamino-2-hydroxybenzylidene-isonicotinohydrazide	75	90	65	66
		150	60	80	
		350	30	78	
3	N-(2-bromo-3-phenyl) allylidene)-isonicotinohydrazide	75	60	80	70
		150	70	82	
		350	90	74	
4	N '-(2-benzylidenoctylidene)-isonicotinohydrazide	75	70	85	78
		150	40	95	
		350	60	80	

As follows from the analysis of the obtained data, the duration of the synthesis and the yields of these compounds (1–4) depend on the power and time of the microwave heating. During the interaction of 4-diethylaminobenzaldehyde with INH under microwave irradiation, the maximum yield of N-(4-(diethylamino)benzylidene) isocotinohydrazide 1 (97 %) was found to occur at a power of 150 W and an irradiation time of 30 minutes. Under conditions of classical synthesis, the highest yield of product 1 is 85 % with a reaction time of 160 minutes, i.e. the reaction rate in terms of microwave activation is reduced by 5.3 times.

Similar results were obtained for the remaining reactions. The highest yield of the final product under the conditions of microwave activation with an irradiation power of 150 W was for hydrazone 4 (95 %), which can be explained by the structural features of the reactants. Figure 1 shows the dependence of the influence of the duration of activation time on the hydrazone yield at different microwave activation powers in comparison with the classical method.

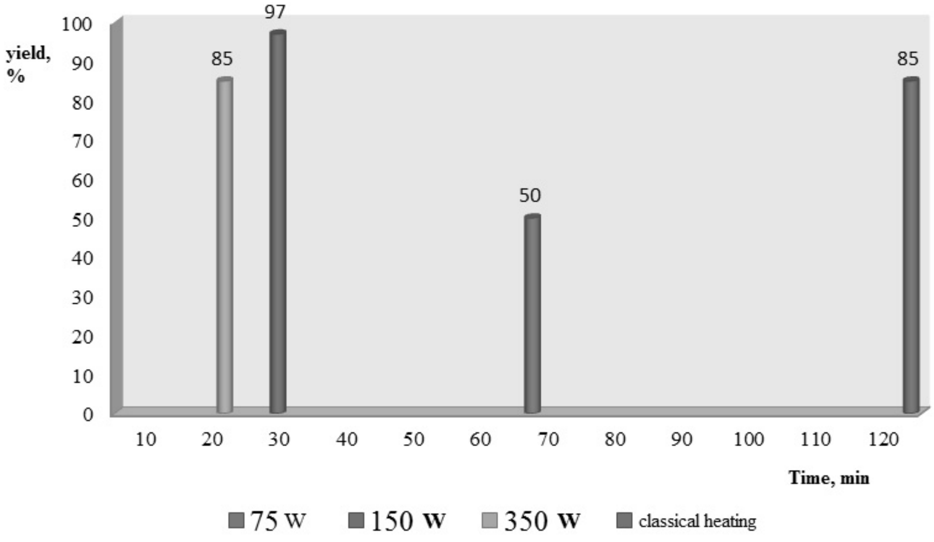


Figure 1. The effect of MW power on the duration of the synthesis and on the yield of N-(4-(diethylamino)benzylidene)isonicotinohydrazide 1

The structure of compounds (1–4) was also confirmed by the methods of two-dimensional NMR spectroscopy COSY (^{1}H-^{1}H) and HMQC (^{1}H-^{13}C), which makes it possible to establish spin-spin interactions of a homo- and heteronuclear nature (Fig. 2, 3). The observed correlations in the molecule are presented in the diagrams. In the spectra of ^{1}H-^{1}H COSY compounds, spin-spin correlations are observed through three bonds of neighboring aliphatic protons in the N-diethyl fragment of $H^{20,22}$-$H^{19,21}$ (1.03; 3.33 and 3.32; 1.05) of the benzylidene core $H^{14,16}$-$H^{13,17}$ (6.65; 7.48 and 7.48; 6.66) and the pyridine ring $H^{3,5}$-$H^{2,6}$ cross-peaks with coordinates at 7.76; 8.72 and 8.71; 7.77 (Fig. 2, 3). The heteronuclear interactions of protons with carbon atoms through one bond were established using ^{1}H-^{13}C HMQC spectroscopy for pairs: $H^{20,22}$-$C^{20,22}$ (1.03; 12.93), $H^{14,16}$-$C^{14,16}$ (6.63; 111.53), $H^{13,17}$-$C^{13,17}$ (7.45, 129.54), $H^{3,5}$-$C^{3,5}$ (7.76; 121.92) and H^{22}-$C^{2,6}$ (8.70; 150.73).

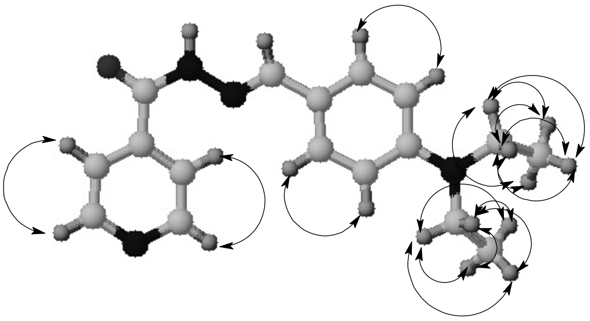


Figure 2. Scheme of correlations of COSY (^{1}H-^{1}H) of compound (1)

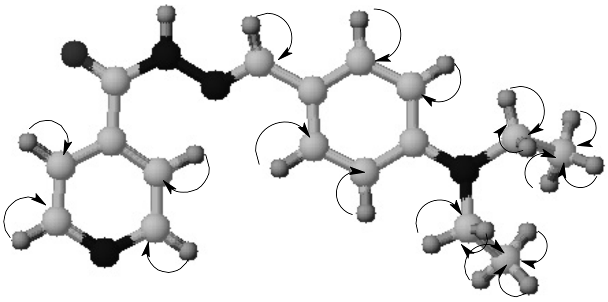


Figure 3. Scheme of correlations of HSCQ (^{1}H-^{13}C) of compound (1)

In order to establish the spatial structure of the molecule N-(4-(diethylamino)benzylidene)isonicotinhydrazide 1, its X-ray diffraction study was carried out. For structure 1, X-ray diffraction data, cell parameters and reflection intensities were obtained at 100 K using an Agilent Supernova, Dual Source, Cu at zero diffractometer equipped with an Atlas CCD detector using α scanning and MoKα (α = 0.71073 Å) radiation. Images were interpreted and integrated using the CrysAlisPro program [22]. The experimental data were processed by the Olex2 program [23], the structure was decoded by direct methods using the ShelXL program, and refined using ShelXS [24, 25] using the least squares method on F^2. Non-hydrogen atoms were anisotropically refined and hydrogen atoms in the upper mode and isotropic temperature factors were fixed at 1.2 times U (eq) of the parent atoms (1.5 times for methyl groups). A general view of the molecule 1 is shown in Figure 4.

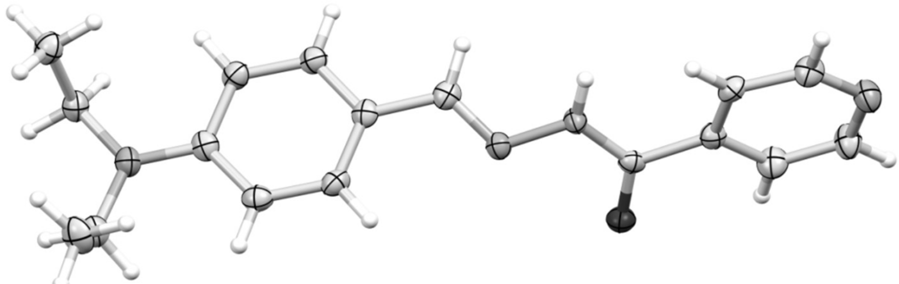


Figure 4. Molecular structure of the compound (1)

From the data obtained it follows that the bond lengths and bond angles in compound (1) are close to normal. The monoclinic crystals, space group Ia (N 9), a = 9.16383 (17), b = 9.45505 (11), c = 18.6806 (2) Å, β = 102.704 (15)°. V = 1578.94 (4) Å^3, Z = 4, T = 100.0 (1) K, ($C_{17}H_{20}N_4O$), M = 296.37 g/mol, d_{comp} = 1.247 g/cm^3, μ = 0,643 mm^{-1}. The scan area is $9.7 \leq 2\theta \leq 150.86$, the number of reflections measured is 30824 (R_{int} = 0.0569, R_{sigma} = 0.0200), 3013 independent reflections with $I \geq 2\sigma(I)$, GooF = 1.053 were used in the calculations. The final divergence factors are R_1 = 0.0446, $_{W}R_2$ = 0.1175 (for reflections with $I \geq 2\sigma(I)$), R_1 = 0.0455, $_{W}R_2$ = 0.1196 (for all reflections). Peaks of residual density: Δρ = 0.21 and –0.31 e/Å^3.

Tables 2 and 3 show the physico-chemical and spectral NMR ^{1}H and ^{13}C data of the synthesized substances (1–4).

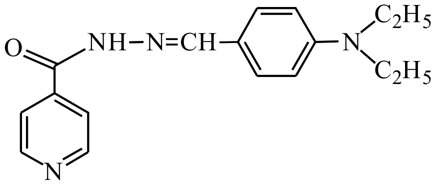
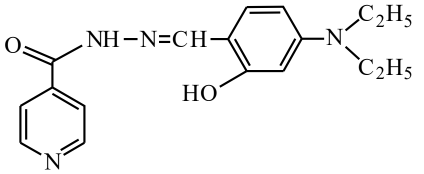
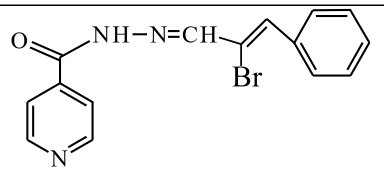
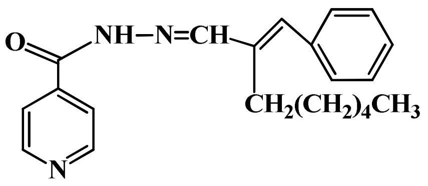
Table 2

Physical and chemical data of the synthesized hydrazones (1–4)

Comp. No.	Compound name	Gross formula	Mol. weight	Yield, %	T. mel., ºC
1	N-(4-(diethylamino) ben-zylidene) isonicotinohydrazide	$C_{17}H_{20}N_4O$	296.37	83.7	192–193
2	N-diethylamino-2-hydroxybenzylidene-isonicotinohydrazide	$C_{17}H_{20}N_4O_2$	312.37	82	224–225
3	N-(2-bromo-3-phenyl) allylidene) isonicotinohydrazide	$C_{15}H_{12}BrN_3O$	330.18	63.04	211–213
4	N '-(2-benzylidenoctylidene) isonicotinohydrazide	$C_{21}H_{25}N_3O$	335.44	98	110–112

Table 3

NMR ^1H and ^{13}C data of the synthesized compounds (1–4)

Compound	^1H and ^{13}C NMR (ppm)
 1	NMR ^1H (DMSO-d_6), δ, m.p.: 1.06 t (6H, 2CH_3), 3.31–3.35 m (4H, 2CH_2), 6.66 d (2H, $CH^{14,16}{}_{Ar}$, ^3J 8.7), 7.48 d (2H, $CH^{13,17}{}_{Ar}$, ^3J 8.7), 7.77 d (2H, $CH^{3,5}$, ^3J 4.6), 8.25 s (1H, N=CH), 8.72 d (2H, $CH^{2,6}$, ^3J 4,6), 11.72 s (1H, NH). NMR ^{13}C (DMSO-d_6), δ, m.p.: 12.96 (2CH_3), 44.26 (2CH_2), 111.56 ($CH^{14,16}{}_{Ar}$), 120.76 ($C^{12}{}_{Ar}$), 122.00 ($CH^{3,5}$), 129.56 ($CH^{13,17}{}_{Ar}$), 141.37 (C_4, N=CH), 149.57 ($CH^{2,6}$), 150.41 ($C^{15}{}_{Ar}$), 161.48 (C=O)
 2	NMR ^1H (DMSO-d_6), δ, m.p. (J, Hz): 1.05 t (6H, 2CH_3-, ^3J 6.9), 3.29–3.35 m (4H, 2CH_2), 6.08 s (1H, CH^{16}), 6.23 d (1H, CH^{14}, ^3J 8.2), 7.19 d (1H, CH^{13}, ^3J 8.7), 7.78 d (2H, $CH^{3,5}$, ^3J 2.7), 8.40 s (1H, N=CH), 8.73 d (2H, $CH^{2,6}$, ^3J 2.7), 11.26 s (OH), 11.99 s (NH). NMR ^{13}C (ДМСО-d_6), δ, m.p.: 13.04 (2CH_3), 44.34 (2CH_2), 97.89 (CH^{16}), 104.27 (CH^{14}), 106.77 (C^{12}), 121.94 ($CH^{3,5}$), 132.15 (CH^{13}), 140.77 (C^4), 150.84 ($CH^{2,6}$), 151.32 (N=CH), 160.32 (C^{17}-OH), 161.10 (C=O).
 3	NMR ^1H (DMSO-d_6), δ, m.p. (J, Hz): 7.38–7.43 m (3H, $CH^{15,17,19}$), 7.67 s (1H, CH^{13}), 7.77 d (2H, $CH^{3,5}$, 3J 1.8), 7.84 d (2H, $CH^{16,18}$, 3J 6.4), 8.34 s (1H, N=CH), 8.75 d (2H, $CH^{2,6}$), 12.19 s (1H, NH). NMR ^{13}C (DMSO-d_6), δ, m.p.: 119.50 (C^{12}), 122.07 ($CH^{3,5}$), 128.99 ($CH^{15,19}$), 130.34 ($CH^{16,18}$), 135.04 (C^{14}), 139.37 (CH^{12}), 140.85 (C^4), 149.53 (N=CH), 150.90 ($CH^{2,6}$), 162.27 (C=O).
 4	NMR ^1H (DMSO-d_6), δ, m.p. (J, Hz): 0.79 t (3H, $CH_3{}^{25}$), 1.05–1.09 m (2H, $CH_2{}^{23}$), 1.21–1.29 m (4H, $CH_2{}^{22}$, $CH_2{}^{24}$), 1.51 m (2H, $CH_2{}^{21}$), 2.56 s (2H, $CH_2{}^{20}$), 6.79 d (1H, CH^{13}), 7.28–7.39 m (4H, $CH^{16,18}$, $CH^{15,19}$), 7.55 d (1H, CH^{11}), 7.76 d (2H, $CH^{3,5}$), 8.13 s (1H, CH^{17}), 8.73 d (2H, $CH^{2,6}$), 11.86 s (1H, NH). NMR ^{13}C (DMSO-d_6), δ, m.p.: 14.46 ($CH_3{}^{25}$), 22.59 ($CH_2{}^{24}$), 26.22 ($CH_2{}^{20}$), 28.53 ($CH_2{}^{21}$), 29.45 ($CH_2{}^{22}$), 31.30 ($CH_2{}^{23}$), 122.04 ($CH^{3,5}$), 128.43 ($CH^{16,18}$), 128.96 ($CH^{15,19}$), 136.58 (C^{14}), 137.15 (CH^{13}), 137.99 (CH^{12}), 141.18 (C^4), 149.83 (N=CH), 150.82 ($CH^{2,6}$), 154.22 (CH^{17}), 161.93 (C=O).

Conclusions

Thus, targeted synthesis of new isonicotinic acid hydrazones on the basis of isonicotinic acid hydrazide, under conditions of convection heating and microwave irradiation was carried out. As a result of a comparative analysis of the data obtained, it was determined that the use of microwave irradiation contributes to an increase in the yield of the product and a decrease in reaction time by a factor of (3–4) than according to traditional technology.

This work was supported by the Science Committee of the Ministry of Education of the Republic of Kazakhstan (Grant N AP05131054).

References

1 O'Brien R.J. The need for new drugs against tuberculosis obstacles, opportunities, and next steps / R.J. O'Brien, P.P. Nunn // Amer. J. Respir. Crit. Care Med. — 2001. — Vol. 163. — P. 1055–1058.

2 Anes E. Selected lipids activate phagosome actin assembly and maturation resulting in killing of pathogenic mycobacteria / E. Anes // Nature Cell Biology. — 2003. — Vol. 5. — P. 793–802.

3 Каюкова Л.А. Основные направления поиска новых противотуберкулезных средств / Л.А. Каюкова, К.Д. Пралиев // Хим. фарм. журн. — 2000. — № 1. — С. 12–19.

4 Тулегенова А.У. Поиск новых противотуберкулезных препаратов — насущное требование современной фтизиатрии / А.У. Тулегенова, Т.А. Муминов, К.Д. Пралиев // Вестн. Каз. гос. мед. ин-та. — 1998. — № 1. — С. 14–22.

5 Bates J.H. Tuberculosis chemotherapy. The need for new antituberculosis drugs is urgent / J.H. Bates // Am. J. resp. a crit. car. med. — 1995. — Vol. 151. — P. 942–943.

6 Машковский М.Д. Лекарства XX века / М.Д. Машковский. — М.: ООО «Новая волна», 1998. — 320 с.

7 Гизатулина Н.Ф. Лечение экспериментального туберкулеза полимерным изониазидом на основе пектина / Н.Ф. Гизатулина, О.Я. Зельман // Здравоохранение Казахстана. — 1992. — № 9. — С. 45–47.

8 Комаров В.М. Синтез R-метансульфонатных производных изониазида / В.М. Комаров, А.А. Цуркан, И.В. Смирнов и др. // Человек и лекарство: материалы III Рос. нац. конгр. (1996 г.). — М., 1996. — С. 28.

9 Шеморова И.В. Синтез новых производных пиразолона и производных никотиновой кислоты. Их влияние на активность цитохрома Р-450 / И.В. Шеморова, Б.Б. Майзель, И.В. Водный // Хим.-фарм. журн. — 2000. — Т. 34, № 10. — С. 17, 18.

10 Хрусталёв Д.П. Синтез гидразида изоникотиновой кислоты в условиях микроволнового облучения / Д.П. Хрусталёв // Современные наукоемкие технологии РАЕ. — 2009. — № 3. — С. 65.

11 Lidstrom P. Microwave assisted organic synthesis / P. Lidstrom, J. Tierney // Org. Process Res. Dev. — 2005. — Vol. 9, No. 5. — P. 697–697. DOI: 10.1021/op050132i.

12 Злотский С.С. Применение микроволнового излучения в реакциях конденсации органических соединений / С.С. Злотский, С.Ю. Шавшукова // Вестн. АН Республики Башкортостан. — 2012. — Т. 17, № 2. — С. 5–8.

13 Фазылов С.Д. Синтез N-замещенных тиоамидов бензойных кислот в условиях микроволновой активации / С.Д. Фазылов, О.А. Нуркенов, Ж.С. Ахметкаримова, Д.Р. Жиенбаева // Журн. общ. хим. — 2012. — Т. 82, Вып. 4. — С. 699, 700.

14 Фазылов С.Д. Синтез 2-анабазинометил-1,3,4-оксадиазола в условиях конвекционного нагрева и микроволнового облучения / С.Д. Фазылов, О.А. Нуркенов, Ж.Б. Сатпаева, Ж.С. Ахметкаримова // Журн. общ. хим. — 2013. — Т. 83, Вып. 7. — С. 1219, 1220.

15 Loupy A. Microwaves in Organic Synthesis / A. Loupy // Org. Proc. Res. Dev. — 2004. — Vol. 8, No. 2. — P. 298, 299. DOI: 10.1021/op034195h.

16 Нуркенов О.А. Синтез и строение новых производных гидразида салициловой кислоты / О.А. Нуркенов, С.Д. Фазылов, Ж.Б. Сатпаева, Т.М. Сейлханов, Г.Ж. Карипова, А.Ж. Исаева // Журн. общ. хим. — 2014. — Т. 84, Вып. 9. — С. 1574–1576.

17 Nurkenov O.A. Synthesis, chemical transformations and antimicrobial activity of some thiosemicarbazides of *o*- and *p*-hydroxybenzoic acid / O.A. Nurkenov, S.D. Fazylov, T.S. Zhivotova, Zh.B. Satpayeva, S.B. Akhmetova et. al. // News of NAS RK. Series of chemistry and technology. — 2015. — No. 1. — C. 9–15.

18 Lukianova T.J. Crystal structure of new organically templated copper sulfate with 2-aminopyridinium / T.J. Lukianova, V. Kinzhybalo, A. Pietraszko // Acta Cryst. E Cryst. Commun. — 2015. — No. 1. — P. 191–192. DOI:10.1107/S2056989015018629.

19 Dolomanov O.V. OLEX2: a complete structure solution, refinement and analysis program / O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann // J. Appl. Cryst. — 2009. — No. 42. — P. 339–341. DOI: 10.1107/S0021889808042726.

20 Sheldrick G.M. A short history of SHELX / G.M. Sheldrick // Acta Cryst. — 2008. — A. 64. — P. 112–123. DOI: 10.1107/S0108767307043930.

21 Sheldrick G.M. Crystal structure refinement with SHELXL / G.M. Sheldrick // Acta Cryst. — 2015. — A. 71. — P. 3–8. DOI: 10.1107/S2053229614024218.

С.Д. Фазылов, О.А. Нүркенов, Т.М. Сейлханов,
Г.Ж. Кәріпова, К. Ван Хекке, Е.М. Сүлеймен, А.М. Ғазалиев

Микротолқынды сәулелендіру жағдайында изоникотин қышқылының гидразонды туындылары синтезі

Мақалада изоникотин қышқылы гидразидінің спирттік ортада микротолқынды активтендіру жағдайында ароматты альдегидтердің түрлі туындыларымен өзара әрекеттесуінің реакциясын зерттеу нәтижелері қарастырылған. Гидразондардың шығымының классикалық әдіспен салыстырғанда микротолқынды сәулеленудің түрлі қуаттары кезінде белсендіру уақытының ұзақтығына байланысты зерттеу нәтижелері келтірілген. Синтездің жүру жағдайына және мақсатты өнімдердің шығымына әсер ететін негізгі факторлары ол микротолқынды белсендірудің қуаты мен уақыты, сондай-ақ реакцияға түсетін заттардың құрылымдық ерекшеліктері болып табылатыны анықталды. Барлық зерттелген реакциялар үшін мақсатты өнімді алудың оңтайлы шарттары көрсетілген. Изоникотин қышқылының жаңа гидразондары синтезінен алынған нәтижелерін салыстырмалы талдау нәтижесінде микротолқынды сәулеленуді пайдалану өнімнің шығымының артуына және реакция уақытының дәстүрлі технологияға қарағанда 3–4 есе төмендеуіне ықпал ететіні анықталды. Әрбір өнімнің түпнұсқалығы балқу температурасын салыстырумен, сондай-ақ классикалық синтез әдістерімен алынған изоникотин қышқылының бұрын синтезделген гидразонды туындыларының физика-химиялық сипаттамаларын талдаумен бірмәнді дәлелденген. Барлық синтезделген қосылыстардың құрылысы ЯМР ^{1}Н- және ^{13}С-спектроскопия әдістерімен, сондай-ақ COSY (^{1}H-^{1}H) және HMQC (^{1}H-^{13}C) екіөлшемді спектрлерінің деректерімен зерттелген. Рентгенқұрылымдық талдау мәліметтерімен N-(4-(диэтиламино)бензилден)изоникотиногидразидтің кристалдық құрылымының негізгі параметрлері белгіленген. Изоникотин қышқылының гидразон туындылары синтезінің әзірленген микротолқынды әдісі «жасыл химия» тұжырымдамасының қағидаттарына сәйкес келеді.

Кілт сөздер: изоникотин қышқылының гидразиді, гидразон, ароматты алдегидтер, микротолқынды сәулелендіру.

С.Д. Фазылов, О.А. Нуркенов, Т.М. Сейлханов,
Г.Ж. Карипова, К. Ван Хекке, Е.М. Сүлеймен, А.М. Газалиев

Синтез гидразоновых производных изоникотиновой кислоты в условиях микроволновой активации

В статье рассмотрены результаты изучения реакции взаимодействия гидразида изоникотиновой кислоты с различными производными ароматических альдегидов в условиях микроволновой активации в спиртовой среде. Приведены результаты изучения зависимостей выхода гидразонов от продолжительности времени активации при различных мощностях микроволнового облучения в сравнении с классическом методом. Установлено, что основными факторами, влияющими на характер протекания синтеза и выходы целевых продуктов, являются мощность и время микроволновой активации, а также структурные особенности реагирующих веществ. Для всех изученных реакций показаны оптимальные условия получения целевого продукта. В результате сравнительного анализа полученных результатов синтеза новых гидразонов изоникотиновой кислоты было определено, что использование микроволнового облучения способствует увеличению выхода продукта и снижению времени реакции в 3–4 раза, чем по традиционной технологии. Подлинность каждого продукта однозначно доказана сопоставлением температуры плавления, а также анализом физико-химических характеристик с ранее синтезированными гидразоновыми производными изоникотиновой кислоты, полученных методами классического синтеза. Строение всех синтезированных соединений исследовано методами ЯМР ^{1}Н- и ^{13}С-спектроскопии, а также данными двумерных спектров COSY (^{1}H-^{1}H) и HMQC (^{1}H-^{13}C). Данными рентгеноструктурного анализа установлены основные параметры кристаллической структуры N-(4-(диэтиламино)бензилиден)изоникотиногидразида. Разработанный микроволновой метод синтеза гидразоновых производных изоникотиновой кислоты соответствует принципам концепции «зеленая химия».

Ключевые слова: гидразид изоникотиновой кислоты, гидразон, ароматические альдегиды, микроволновая активация.

References

1 O'Brien, R.J., Nunn, P.P. (2001). The need for new drugs against tuberculosis obstacles, opportunities, and next steps. *Amer. J. Respir. Crit. Care Med, 163,* 1055–1058.

2 Anes, E. (2003). Selected lipids activate phagosome actin assembly and maturation resulting in killing of pathogenic mycobacteria. *Nature Cell Biology, 5*, 793–802.

3 Kayukova, L.A., & Praliev, K.D. (2000). Osnovnye napravleniia poiska novykh protivotuberkuleznykh sredstv [The main directions of the search for new anti-TB drugs]. *Khimiko-farmatsevticheskii zhurnal — Chemical Pharmaceutical Journal, 1, 12–19* [in Russian].

4 Tulegenova, A.U., Muminov, T.A., & Praliev, K. (1998). Poisk novykh protivotuberkuleznykh preparatov — nasushchnoe trebovanie sovremennoi ftiziatrii [The search for new anti-TB drugs is an urgent requirement of modern phthisiology]. *Vestnik Kazakhskoho hosudarstvennoho medicinskoho instituta — Bulletin of the Kazakh State Medical Institute, 1, 14–22* [in Russian].

5 Bates, J.H. (1995). Tuberculosis chemotherapy. The need for new antituberculosis drugs is urgent. *Am. J. resp. a crit. car. med.*, *151*, 942–943.

6 Mashkovskii, M.D. (1998). *Lekarstva XX veka [Medicines of the XX century].* Moscow: Novaia volna [in Russian].

7 Gizatulina, N.F., & Zelman, O.Y. (1992). Lechenie eksperimentalnoho tuberkuleza polimernym izoniazidom na osnove pektina [Treatment of experimental tuberculosis with pectin-based polymeric isoniazid]. *Zdravookhranenie Kazakhstana — Healthcare of Kazakhstan*, *9*, 45–47 [in Russian].

8 Komarov, V.M., Tsurkan, A.A., & Smirnov, I.V. (1996). Sintez R-metansulfonatnykh proizvodnykh izoniazida [Synthesis of R-Methanesulfonate Isoniazid Derivatives]. Proceedings from Man and Drug: *III Rossiiskii natsionalnyi konhress — III Russian national congress* [in Russian].

9 Shemorova, I.V., Maisel, B.B., & Vodny, I.V. (2000). Sintez novykh proizvodnykh pirazolona i proizvodnykh nikotinovoi kisloty. Ikh vliianiie na aktivnost tsitokhroma R-450 [Synthesis of new pyrazolone derivatives and nicotinic acid derivatives. Their effect on cytochrome P-450 activity]. *Khimiko-farmatsevticheskii zhurnal — Chemical Pharmaceutical Journal, 34*, *10*, 17–18 [in Russian].

10 Khrustalev, D.P. (2009). Sintez hidrazida izonikotinovoi kisloty v usloviiakh mikrovolnovoho obluchenii [Synthesis of isonicotinic acid hydrazide under microwave irradiation] // *Sovremennye naukoemkie tekhnolohii RAE — Modern high technologies of RAE*, *3*, 65 [in Russian].

11 Lidstrom, P., & Tierney, J. (2005). Microwave assisted organic synthesis. *Org. Process Res. Dev., 9, 5*, 697–697. DOI: 10.1021/op050132i.

12 Zlotsky, S.S., & Shavshukova, S.Yu. (2012). Primenenie mikrovolnovoho izlucheniia v reaktsiyakh kondensatsii orhanicheskikh soedinenii [Application of microwave radiation in condensation reactions of organic compounds]. *Vestnik Akademii Nauk Respubliki Bashkortostan — Bulletin of the Academy of Sciences of the Republic of Bashkortostan. 17, 2*, 5–8 [in Russian].

13 Fazylov, S.D., Nurkenov, O.A., Satpayeva, Zh.B., & Akhmetkarimova, Zh.S. (2012). Sintez N-zameshchennykh tioamidov benzoinykh kislot v usloviiakh mikrovolnovoi aktivatsii [Synthesis of N-substituted benzoic acid thioamides under microwave activation conditions]. *Zhurnal obshchei khimii — Journal of General Chemistry, 82, 4,* 699–700 [in Russian].

14 Fazylov, S.D., Nurkenov, O.A., Satpayeva, Zh.B., & Akhmetkarimova, Zh.S. (2013). Sintez 2-anabazinometil-1,3,4-oksadiazola v usloviiakh konvektsionnoho nahreva i mikrovolnovoho obluchenii [Synthesis of 2-anabasinomethyl-1,3,4-oxadiazole under conditions of convection heating and microwave irradiation]. *Zhurnal obshchei khimii — Journal of General Chemistry*, *83, 7,* 1219–1220 [in Russian].

15 Loupy, A. (2004). Microwaves in Organic Synthesis. *Org. Proc. Res. Dev., 8, 2,* 298–298. DOI: 10.1021/op034195h.

16 Nurkenov, O.A., Fazylov, S.D., Satpayeva, Zh.B., Seylkhanov, T.M., Karipova, G.Zh., & Isaeva, A.Zh. (2014). Sintez i stroenie novykh proizvodnykh hidrazida salitsilovoi kisloty [Synthesis and structure of new derivatives of salicylic acid hydrazide]. *Zhurnal obshchei khimii — Journal of General Chemistry*, *84, 9,* 1574–1576 [in Russian].

17 Nurkenov, O.A., Fazylov, S.D., Zhivotova, T.S., Satpayeva, Zh.B., Akhmetova, S.B., Kurmanbayeva, Zh., Karipova, G.K., & Isayeva, A.Zh. (2015). Synthesis, chemical transformations and antimicrobial activity of some thiosemicarbazides of *o*- and *p*-hydroxybenzoic acid. *News of NAS RK. Series of chemistry and technology, 1,* 9–15.

18 Lukianova, T.J., Kinzhybalo, V., & Pietraszko, A. (2015). Crystal structure of new organically templated copper sulfate with 2-aminopyridinium. *Acta Cryst. E Cryst. Commun., 1,* 191–192. DOI: 10.1107/S2056989015018629.

19 Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., Howard, J.A.K., & Puschmann, H. (2009). OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst. 42,* 339–341. DOI: 10.1107/S0021889808042726.

20 Sheldrick, G.M. (2008). A short history of SHELX. *Acta Cryst., A. 64,* 112–122. DOI: 10.1107/S0108767307043930.

21 Sheldrick, G.M. (2015). Crystal structure refinement with SHELXL. *Acta Cryst., 71,* 3–8. DOI: 10.1107/S2053229614024218.

ФИЗИКАЛЫҚ ЖӘНЕ АНАЛИТИКАЛЫҚ ХИМИЯ
ФИЗИЧЕСКАЯ И АНАЛИТИЧЕСКАЯ ХИМИЯ
PHYSICAL AND ANALYTICAL CHEMISTRY

DOI 10.31489/2019Ch3/45-51

UDC544.653.1

P.A. Abdurazova, Sh.T. Koshkarbayeva, M.S. Satayev,
N.O. Dzhakipbekova, Ye.B. Raiymbekov

M. Auezov South Kazakhstan State University, Shymkent, Kazakhstan;
(E-mail: eplusr@bk.ru)

Mechanism of the process of photochemical metallization of dielectric surfaces

The possibility of applying copper-containing films on the surfaces of various samples was investigated in the paper. Flat and smooth copper plates and fabric were used for the study. The sample of dielectric material was immersed in the solution, then they were dried in the sun, and work was done on the deposition of copper on the surface of the sample. The study of the rate of photochemical reduction of copper showed that the process consisted of two stages. In the first 30 minutes of the first stage, by increasing the concentration of Halogens during drying of the coating, a semiconductor layer is formed, and in the second — the direct photochemical reduction of copper, which takes about 30 minutes, but then gradually slows down. At the second stage, the rate of the photochemical reaction is equal to the rate of chemical or galvanic metallization. As a result of the photochemical reaction, when drying the sorption layer under the influence of sunlight, copper semiconductors are formed, which shape metallic coatings on the surface. This, in turn, can be used to make thinner films.

Keywords: mechanism, photochemistry, metallization, dielectric surface, copper, reaction, coating, films.

Introduction

Decomposition of copper halides and their analogs under the influence of light refers to the photochemical method. At the same time, part of the sample exposed to brightened, and particles of copper, gold and silver are formed on the surface.

When processing the surface layer of the material under the influence of solar treatment with CuCl solution, a black layer gradually forms on the surface of the fabric. The reaction is characterized by the following equation:

$$2\mathrm{CuCl} \xrightarrow{h\nu} \mathrm{Cu} + \mathrm{CuCl_2} \qquad (1)$$

When processing the surface of the material is treated with a solution of CuCl, both of these reactions occur on the surface of the fabric and form solid crystals of chlorine copper. Crystals can be rinsed with water, but when added to the water, the black coating of the copper is lost, which indicates the return reaction:

$$\mathrm{Cu} + \mathrm{CuCl_2} \rightarrow 2\mathrm{CuCl} \qquad (2)$$

To obtain high-quality coatings on the surface of dielectric materials and to study their physicomechanical properties, it is necessary to study the mechanism of photochemical reduction of copper coatings and its substrate.

It is known that most unipolar compounds of a copper substrate decompose quickly under the influence of heating or light. It is also known that metal halogenates of a copper substrate are binary semiconductors. Therefore, there is a relationship between semiconductor properties and photosensitivity.

The sensitivity of halides is used to produce metal layers on these surfaces to give them bactericidal properties. Such products may include door handles, fire extinguishers, curtains, pillows, dressings, bactericidal impregnations in household appliances, clothing [1].

Since ancient times, mankind has known about the bactericidal properties of copper and its analogues. In 2008, the status of substances with a bactericidal surface of copper and its several melts was officially given. There is a tendency to use silver, as well as copper, in the production of bactericidal coatings [2, 3].

Thus, the method of laying metal coatings of copper substrate on different surfaces is widely used in different fields of technology. In particular, the use of bactericidal properties of copper and its analogues in medical materials is promising. It is convenient to use copper (II) chloride and gold (III) chloride when removing the light fluidized chloride layer. Therefore, the proposed work provides a mechanism for the transformation of light-sensitive coatings on various materials of these salts [4].

Results and Discussion

Cotton fabric was used in the studies (marking AA010278), which is most widely used for medical purposes [5]. Separate experiments on the photochemical reduction of copper halides were carried out in monovalent copper solutions. Thus, a suspension of 30 g of CuCl in 100 ml of water was prepared to obtain a copper coating on the surface of the fabric material, and then the solution was poured onto the surface of the fabric. Next, the sample is exposed to sunlight. Depending on the drying of the fabric, its surface is covered with a black layer. Covered areas with light-resistant protection remain unchanged in accordance with Figure 1.

Two products obtained by reaction 1 stay on the surface of the fabric as solid crystals of copper di-chloride and nanoparticles of copper. However, the black layer of copper is eliminated by the addition of water, which means a backlash 2.

The correctness of this mechanism is confirmed by experiments on photochemical reactions on the surface of copper samples. In the following experiments, the samples were treated with copper (II) bromide. In this case, the halide compounds react with the copper surface to the following reaction:

$$CuBr_2 + Cu \rightarrow 2CuBr \qquad (3)$$

When the surface is immediately exposed to sunlight after such treatment, its surface layer is colored. In addition, the dark color of the sample depends on its drying. In addition, some areas of the sample were darkened from sunlight when they were exposed to the sun. Figure 2 shows the color change of the copper sample at each stage of the process [6].

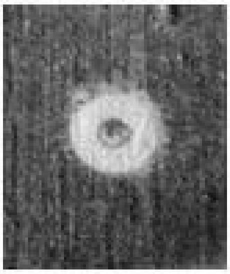
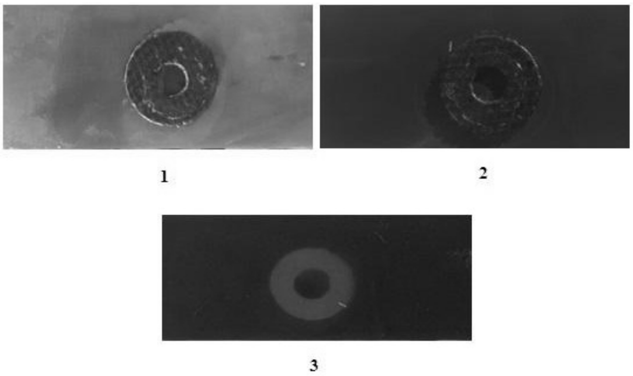


Figure 1. The fabric is treated with an aqueous solution of CuCl and exposed to sunlight



1 — surface layer after treatment in a solution of 30 g/l $CuCl_2$; *2* — sample surface treatment after exposure to sunlight; *3* — surface layer after screening of some parts under the influence of solar treatment

Figure 2. Changing the color of surfaces in samples during exposure to a light-sensitive layer

Consequently, the copper base, which is a reducing agent, contributes to the slowing down of the reaction. Therefore, it is recommended that the sodium hypophosphite solution be added to the solution by coppering dielectric materials.

Methods of copper coating were carried out in fabric samples measuring 2×5 cm to determine the individual technological parameters of the process. The sample is poured with a solution of $CuCl_2 \times 2H_2O$ —

100 g/l. In this connection, the volume of the solution retained by the sample was 0.6 ml. Copper in this solution is about 25×10^{-3} g [7].

The results of the study revealed that the process of photochemical reduction of copper consists of two stages: the formation of a semiconductor layer due to an increase in the concentration of halogen during the drying of the coating occurs in the first 30 minutes of the first stage. Direct photochemical reduction of copper, which takes about 30 minutes, but then gradually slows down in the second stage. Therefore, in the second stage, the rate of the photochemical reaction is equal to the rate of chemical or galvanic metallization.

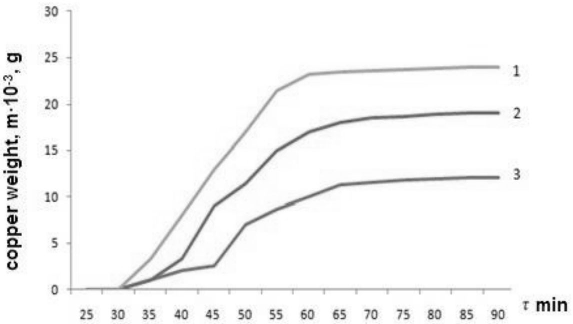
The following empirical relationships were obtained for studying the reaction kinetics mechanism. The influence of the concentration of copper chloride on composite copper and its analogs has been studied. As shown in Table 1, the concentration of copper chloride increases with the weight of the coating, but the thickness of the coating does not affect the absorption rate of copper chloride in accordance with Figures 3–5. Consequently, the reaction rate of copper chloride is 0.

Table 1

Effect of copper chloride concentration on the weight of the film

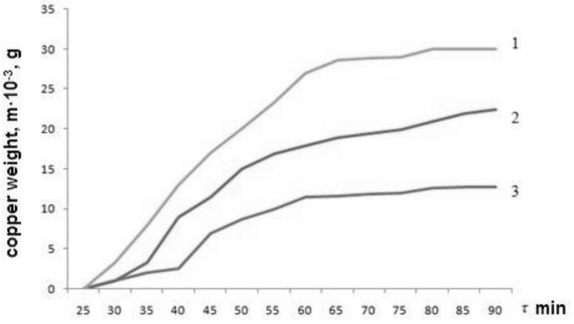
Weight of copper, mg	Time, min	Concentration of copper chloride, g/l							
	0–30 min	0.1	1	10	30	50	70	100	150
		0.024	0.24	2.4	7.2	12	16.8	24	36

The reaction rate of copper chloride at various concentrations (differential method) was studied in accordance with Figures 6–8.



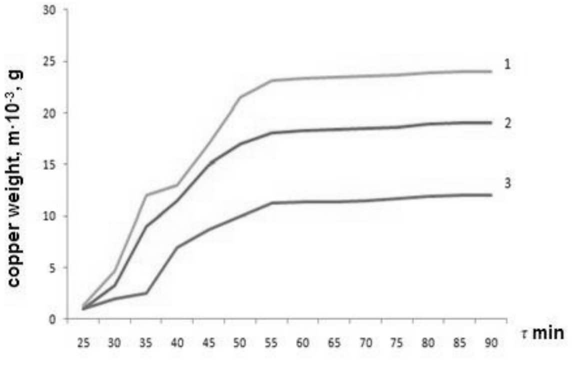
1 — 200 g/l; *2* — 100 g/l; *3* — 50 g/l

Figure 3. The rate of reduction of copper (II) chloride under sunlight at 25 ºC



1 — 200 g/l; *2* — 100 g/l; *3* — 50 g/l

Figure 4. The rate of reduction of copper (II) chloride under sunlight at 35 ºC



1 — 200 g/l; *2* — 100 g/l; *3* — 50 g/l

Figure 5. The rate of reduction of copper (II) chloride under sunlight at 40 ºC

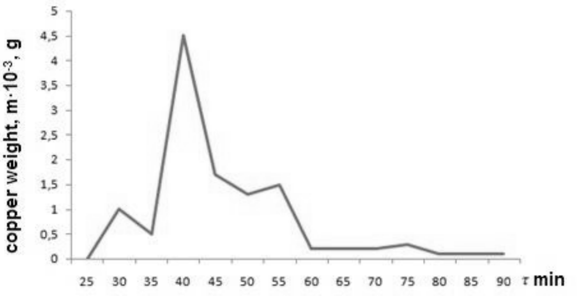


Figure 6. Recovery rate of copper chloride at a concentration of 50 g/l under the influence of sunlight

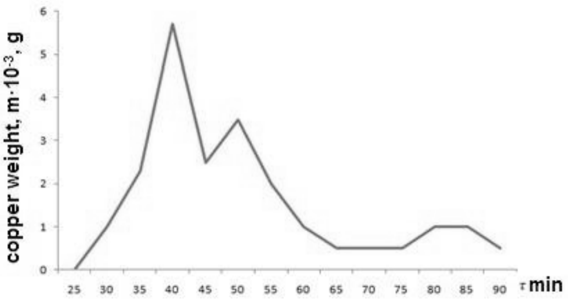


Figure 7. Recovery rate of copper chloride at a concentration of 100 g/l under the influence of sunlight

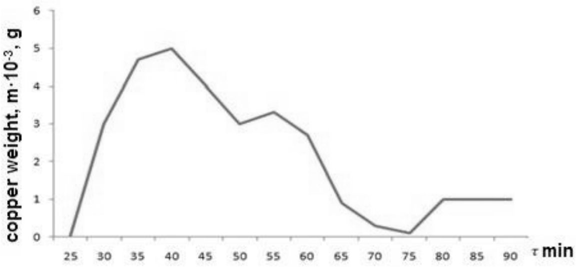


Figure 8. Recovery rate of copper chloride at a concentration of 150 g/l under the influence of sunlight

The reaction rate was studied at different concentrations of copper chloride to determine the order of the reaction.

$$2CuCl_2 + H_2O + NaH_2PO_2 \rightarrow 2CuCl + 2HCl + NaH_2PO_3 \qquad (4)$$

The reaction rate is calculated by the Vant-Hoff method (differential method) using the following formula:

$$n_i = (\lg W_1 - \lg W_2) / (\lg C_{0.1} - \lg C_{0.2}). \qquad (1)$$

Description: W_1, W_2, $C_{0.1}$ and $C_{0.2}$ actual rates of reaction at baseline concentrations; n_i — the concentration is C_0 individually in the component.

The results are shown in Table 2.

Table 2

Effect of copper chloride concentration on the rate and order of the reaction

Concentration of copper chloride, mol/l·10^{-3}	4.5	5.8	5
Actual reaction rate, l/min·10^3	0.112	0.145	0.125
Reaction order	-	0.365	0.365

The reaction rate does not affect the moisture content of the mixture (i.e. H_2O). Let's calculate the true reaction rate:

$$W_1 = {}^{4.5}\!/_{40} = 0.112;$$

$$W_2 = {}^{5.8}\!/_{40} = 0.145;$$

$$W_3 = {}^{5}\!/_{40} = 0.125.$$

$$n_1 = {}^{(\lg W_1 - \lg W_2)}\!\Big/_{(\lg C_{0.1} - \lg W_{0.2})}. \qquad (2)$$

$$n_1 = \frac{0.653 - 0.763}{-1 - (-0.698)} = \frac{-0.110}{-0.301} = 0.365.$$

$$n_2 = {}^{(\lg W_2 - \lg W_3)}\!\Big/_{(\lg C_{0.2} - \lg W_{0.3})}. \qquad (3)$$

$$n_2 = \frac{-0.838 - (-0.903)}{-0.698 - (-0.522)} = \frac{0.064}{0.176} = 0.365.$$

Thus, the kinetic equation for the complete reaction for the formation of composite shells of copper and its analogs is written as follows:

$$V = K \cdot C^{0.366-0.365}. \qquad (4)$$

Description: k — reaction rate constant, min $^{-1}$.

The following formula is used to determine the activation energy:

$$E_{act} = \frac{RT_1T_2\lg\left(\frac{K_{T1}}{K_{T2}}\right)}{T_2 - T_1}. \tag{5}$$

Description: E_{act} — activation energy of the reaction, J/mol.

$$0.1125 = k_1 \cdot 4.5^{0.366};$$

$$k_1 = \frac{0.112}{1.73} = 0.065;$$

$$0.145 = k_2 \cdot 5.8^{0.366};$$

$$k_2 = \frac{0.145}{1.190} = 1.218;$$

$$0.125 = k_3 \cdot 5^{0.366};$$

$$k_3 = \frac{0.125}{1.801} = 0.069.$$

Activation energy:

$$E_{act} = \frac{RT_1T_2\lg\left(\frac{K_{T1}}{K_{T2}}\right)}{T_2 - T_1}. \tag{6}$$

Well, then,

$$E_{act1} = \frac{2.303 \cdot 8.31 \cdot 298 \cdot 308\left(0.064/1.218\right)}{(308 - 298)} = \frac{0.053 \cdot 308 \cdot 298 \cdot 8.31 \cdot 2.303}{10} = 9.437 \cdot 10^3;$$

$$E_{act2} = \frac{2.303 \cdot 8.31 \cdot 298 \cdot 313\left(0.069/1.218\right)}{(313 - 298)} = \frac{0.053 \cdot 308 \cdot 298 \cdot 8.31 \cdot 2.303}{10} = 6.762 \cdot 10^3.$$

The results of the study of the temperature dependence of the reaction rates in time are given in Table 3. Consequently, a low concentration of the coating formation makes it possible to obtain a semigloss coating, which varies from black to gray-black. The coating thickness was about 0.3–0.6 µm, depending on the concentration of copper chloride, the base material and the surface layer. Thus, as a result of photochemical reaction of the sorption layer under the influence of sunlight, copper semiconductors form metal coatings on the surface. This, in turn, can be used to produce thinner coatings.

Table 3

The influence of time and temperature on the reaction rate and its constant

Parameters	Temperature, ºC	Time, min (40 min)
Rate of reaction, sm^3/min	308 298 313	0.112 0.145 0.125
Rate constant, min^{-1}	308 298 313	0.064 0.218 0.069
Activation energy, J/mol		9.437×10^3 6.762×10^3

Conclusions

Mechanisms of photochemical reactions in thin layers of solutions of copper halide are presented. Copper halides and its analogs can participate in the oxidation-reduction reaction under the influence of sunlight. In thin films, monovalent halides are formed first under the action of beams. These are semiconductors, because they are oxidized by the sun's quantum of light, and the positive charge generated at this moment is the «vacancies» of the water molecule or oxidizes the hydroxide layers of material cellulose.

As a result of photochemical reaction in the sorption layer under the influence of sunlight it is proved that semiconductor copper components forming metal coatings on the surface are formed. It is shown that the process of studying the photochemical reduction of copper is two steps.

References

1 Мельников Б. Возобновляемые энергетические ресурсы. Учебные материалы для лиц, принимающих решения в странах Центрально-Азиатского региона / Б. Мельников, Е. Зигангирова, К. Кабутов, В. Кибартас, А. Обозов, С. Турсунов. — Алматы: Кластерное бюро ЮНЕСКО в Казахстане, Кыргызстане, Таджикистане и Узбекистане, 2011. — 25 с.

2 Alan B.G. Silver in healthcare: its antimicrobial efficacy and safety in use / B.G. Alan. — London: Royal Society of Chemistry, 2010. — 274 p.

3 Dykman L.A. Uptake of Engineered Gold Nanoparticles into Mammalian Cells / L.A. Dykman, N.G. Khlebtsov // Chemical Reviews. — 2014. — Vol. 114, No. 2. — P. 1258–1288.

4 Sataev M.S. Photochemical method of applying gold films on the dielectric surfaces / M.S. Sataev, P.A. Abdurazova, Sh.T. Koshkarbaeva, A.B. Tleuova, A.P. Auyezov // Oriental Journal of Chemistry. — 2017. — Vol. 33, No. 2. — P. 835–840.

5 Абдуразова П.А. Механизм фотохимических реакций, протекающих в тонких слоях растворов галогенидов меди и золота / П.А. Абдуразова, Ш.Т. Кошкарбаева, М.С. Сатаев, А.Б. Тлеуова, Ж.С. Уринбаева // Topical Problems of modern science. — 2017. — No. 4. — С. 12–17.

6 Сатаев М.С. Диэлектрлі материалдардың беткі қабатына қапталған металл қабықшалардың қалыңдығын анықтау әдісі / М.С. Сатаев, П.А. Абдуразова, Ш.Т. Кошкарбаева, Е.Б. Райымбеков, У.Б. Назарбек // Қарағанды ун-нің хабаршысы. Химия сер. — 2017. — Т. 86, № 2. — 78–85-б.

7 Абдуразова П.А. Металды және диэлектрлі беттерде күміс қабықшаларын алу / П.А. Абдуразова, Ш.Т. Кошкарбаева, М.С. Сатаев, А.Қыдыралиева // ҚазҰУ хабаршысы. Химия сер. — 2015. — Т. 77, № 1. — 64–71-б.

П.А. Абдуразова, Ш.Т. Қошқарбаева, М.С. Сатаев,
Н.О. Джакипбекова, Е.Б. Райымбеков

Диэлектрлік беттерді фотохимиялық металдау процесінің механизмі

Мақалада мысқұрамдас қаптамаларды әртүрлі үлгілердің бетіне қондыру мүмкіндігі зерттелген. Зерттеу үшін тегіс және жалпақ мыс пластиналар мен мата қолданылды. Диэлектрлі материалдың үлгісі ерітіндіге батырылды, олар күн энергиясымен кептірілді және мыс үлгінің бетіне тұндыру бойынша жұмыс жүргізілді. Мыстың фотохимиялық тотықсыздану жылдамдығын зерттеу процесі екі кезеңнен тұрады. Бірінші кезеңнің алғашқы 30 минуты — бұл қаптаманы кептіру кезінде галогендердің концентрациясын арттыру есебінен жартылайөткізгіш қабаттың қалыптасуы, ал екіншісі — 30 минутқа жуық уақыт алатын мыстың тікелей фотохимиялық тотықсыздануы, бірақ содан кейін біртіндеп баяулайды. Екінші кезеңде фотохимиялық реакция жылдамдығы химиялық немесе гальваникалық метализация жылдамдығына тең. Фотохимиялық реакция нәтижесінде күн сәулесінің әсерінен сорбциялық қабат құрғаған кезде бетінде металл қаптаманы құрайтын мысты жартылайөткізгіштер пайда болады. Бұны, өз кезегінде, жұқа қаптамаларды дайындау үшін пайдалануға болады.

Кілт сөздер: механизм, фотохимия, метализация, диэлектрлік бет, мыс, рекция, қаптама, қабат.

П.А. Абдуразова, Ш.Т. Кошкарбаева, М.С. Сатаев,
Н.О. Джакипбекова, Е.Б. Райымбеков

Механизм процесса фотохимической металлизации диэлектрических поверхностей

В статье исследована возможность нанесения медьсодержащих покрытий на поверхности различных образцов. Для исследования были использованы плоские и гладкие медные пластины и ткань. Образец диэлектрического материала был погружен в раствор, затем они были высушены на солнце, и была проделана работа по осаждению меди на поверхность образца. Изучение скорости фотохимического восстановления меди показывает, что процесс состоит из двух этапов. В первые 30 минут первого этапа за счет увеличения концентрации галогенов при сушке покрытия образуется полупроводниковый слой, а во второй — прямое фотохимическое восстановление меди, которое занимает около 30 минут, но затем постепенно замедляется. На втором этапе скорость фотохимической реакции равна скорости химической или гальванической металлизации. В результате фотохимической реакции при высыхании сорбционного слоя под воздействием солнечных лучей на поверхности образуются медные полупроводники, формирующие металлическую пленку.

Ключевые слова: механизм, фотохимия, металлизация, диэлектрическая поверхность, медь, реакция, покрытие, пленки.

References

1 Melnikov, B., Zigangirova, E., Kabutov, K., Kibartas, V., Obozov, A., & Tursunov, S. (2011). *Vozobnovliaemye enerheticheskie resursy [Renewable energy sources]*. Almaty: UNESCO cluster bureau in Kazakhstan, Kyrgyzstan, Tadzhikistan and Uzbekistan [in Russian].

2 Alan, B.G. (2010). *Silver in healthcare: its antimicrobial efficacy and safety in use*. London: Royal Society of Chemistry.

3 Dykman, L.A., & Khlebtsov, N.G. (2014). uptake of engineered gold nanoparticles into mammalian cells. Chemical reviews, 114(2), 1258–1288.

4 Sataev, M.S., Abdurazova, P.A., Koshkarbaeva, Sh.T., Tleuova, A.B., & Auyesov, A.P. (2017) Photochemical method of applying gold films on the dielectric surfaces. *Oriental Journal of Chemistry, 33(2)*, 835–840.

5 Abdurazova, P.A., Koshkarbaeva, Sh.T., Sataev, M.S., Tleuova, A.B., & Urinbaeva, Zh.S. (2017). Mekhanizm fotokhimicheskikh reaktsii, protekaiushchikh v tonkikh sloiakh rastvorov halohenidov medi i zolota [The mechanism of photochemical reactions occurring in thin layers of copper and gold halide solutions]. *Topical Problems of modern science, 4,* 12–17 [in Russian].

6 Sataev, M.S., Abdurazova, P.A., Koshkarbaeva, Sh.T., Raiymbekov, Y.B., & Nazarbek, U.B. (2017). Dielektrli materialdardyn betki kabatyna kaptalhan metall kabykshalardyn kalyndyhyn anyktau adisi [Method for determining the thickness of metal coating deposited on the surface of dielectric material]. *Qaragandy universitetinin khabarshysy. Khimiia seriyasy — Bulletin of the Karaganda University. Chemistry series, 86(2)*, 78–85 [in Kazakh].

7 Abdurazova, P.A., Sataev, M.S., Koshkarbayeva, Sh.T., & Kydyraliyeva, A. (2015). Metaldy zhane dilektrli betterde kumis kabyk shalaryn alu [Production of silver films on metal and dielectric surfaces]. *Qazaq ulttyq universitetinin khabarshysy. Khimiia seriyasy — Bulletin of the Kazakh National University. Chemistry series, 77(1)*, 64–71 [in Kazakh].

DOI 10.31489/2019Ch3/52-61

UDC 544.723

T.D. Batueva[1], N.B. Kondrashova[1], M.G. Scherban[2]

[1]*Institute of Technical Chemistry of Ural Branch of the RAS, Perm, Russia;*
[2]*Perm State National Research University, Russia*
(E-mail: tdbatueva@mail.ru)

Sorbents based on mesoporous silicas modified with hydrazide functional groups

The silica-based sorbents characterized by MCM-41 pore structure and modified with hydrazide groups were synthesized. The low-temperature nitrogen sorption method, X-ray phase analysis, FT-IR spectroscopy and scanning electron microscopy were used to determine textural-structural properties of the silica sorbents under investigation. The presence of modifier reduces values of specific surface area. The impregnation method enhances adsorption capacity to a larger extent as compared with the direct synthesis method. The sorption of copper (II), nickel (II), and cobalt (II) from aqueous solutions by the obtained reagents was studied. The study of non-ferrous cations' adsorption evinced that, depending on pH value of the medium, both conjoint extraction and separation of cations were possible. The sorbents can be used to quantitatively separate copper (II) ions from nickel (II) ions. The sorption capacity of the reagents as dependent on the method for modification of the silica base and on the monomer concentration was explored under condition of conjoint metal sorption. The effect of temperature on the sorption of metals by the obtained modified silica at different pH values and the method of their interaction with the surface of the MCM were determined.

Keywords: mesoporous silica; modification; hydrazide; sorption; acids Versatic, non-ferrous metals, impregnation method, direct synthesis.

Introduction

Determination of trace amounts of elements by conventional physical and physico-chemical methods is often impossible due to sensitivity and selectivity limitations and rather complicated composition of the solutions analyzed. So, it is very important to develop novel preparation methods of available and inexpensive sorbents for group extraction of metal ions from aqueous solutions of complicated composition. Combined analytical methods, such as determination of the microcomponents after concentrating procedure, seem to be rather promising. Sorption is the most efficient method of concentrating, as the microcomponents from large volumes of solutions can be concentrated using a relatively small amount of sorbent without organic solvents, required for conventional metal extraction processes.

Recently, attention of the researchers has been attracted to application of mesoporous materials, characterized by both regular pore arrangement and high textural parameters. Thus, mesoporous silicas have been widely used as catalyst support materials owing to their unique structure and physicochemical properties [1–8].

Only few papers are devoted to the use of mesoporous structures in extraction and selective sorption processes [9–15]. From a great variety of sorbents suggested for concentrating of elements, the surface-modified ones are known to have the best sorption characteristics. Chemically modified silicas (CMS) belong to this type of sorbents [16–18]. In the modified silicas the favorable properties of the matrix — high specific surface and high mesopore volume — are combined with the presence of functional groups required for isolation of rare-earth and non-ferrous metal acid complexes. As a rule, functionalized organosilanes (with NH_2-, CN-, and other reactive groups in an organic backbone) as well as the salts of transition metals are used for modification of silica surface [19–24]. In this paper, the MCM-41 silica surface was modified with dimethyl hydrazides based on Versatic tert-carboxylic acids $CH_3R_1R_2CCOOH$ where R_1 and R_2 are alkyl radicals and the total length of hydrocarbon chains is 10–19.

The results obtained allow new methods to be suggested for isolation and separation of complexes of non-ferrous and rare metals from wastewater and technological solutions. These methods are based on concentrating of microcomponents from large volumes of solutions using a relatively small amount of a sorbent without organic solvents. Thus, the study of sorption capacity of mesoporous silica structures is undoubtedly urgent.

Present paper is aimed at the study of nickel (II), cobalt (II), and copper (II) sorption onto the surface of modified mesoporous silica sorbents functionalized with hydrazide and amide groups.

Experimental

The silica base of sorbents with ordered structure of mesopores (MCM-41) was obtained by the template synthesis method under hydrothermal conditions at 100 ºC for 2 days [25]. The following compounds were used: tetraethoxysilane (TEOS) as a source of silicon, cetyltrimethylammonium bromide (CTAB) as a structure-forming agent. The synthesis components were taken at the ratio TEOS 1:CTAB 0.2:NH_3 3.5:H_2O 100.

Two methods were used to functionalize the surface of silica specimens: post-synthetic modernization — PM-DMHD and hydrothermal synthesis — HTS-DMHD. Herein, abbreviations DMHD stand for N',N'-dimethylhydrazides. The mentioned compounds are based on the Versatic tert-carboxylic acid fractions with the formula $CH_3R_1R_2CC(O)OH$, where R_1 and R_2 are alkyl radicals with total number of carbon atoms equaling 10.

MCM-41 was modified via the HTS method, the conditions being described above. A functional reagent was introduced into the reaction medium after the formation of a SiO_2 sol during the synthesis of silicon dioxide via CTAB and TEOS interaction. Then hydrothermal treatment of the mixture, followed by separation and drying of the precipitate, was carried out. The template (CTAB) was removed by extraction with ethyl alcohol, acidified with HCl.

The silica framework was functionalized according to the IM method: the MCM-41 sample was placed in a round bottom flask, the calculated amount of DMHD was added and the mixture was refluxed in ethanol medium for 4 hours. Then the reaction mixture was filtered, and the solid residue was dried at 80 ºC to remove the solvent.

Structural pore organization of the silica base was explored by the X-ray phase analysis on the XRD-7000 diffractometer (*Shimadzu*, Japan) using CuK_a-radiation ($\lambda_{av.}$=1.54184 Å) in low-angular 2Θ interval (1.4–10º) with 0.01–0.005º step.

IR Fourier spectrometer, model IFS 66/S (*Bruker*, Germany) was used to explore the structure of modified silica sorbents at 150–4000 cm^{-1}; specimens were 100-fold scanned at room temperature and at 2 cm^{-1} resolution.

Textural parameters of the sorbents (specific surface area, total pore volume, pore diameter, pore size distribution) were determined with use of low-temperature nitrogen sorption at –196 ºC on the ASAP 2020 device (*Micrometrics*, USA) after degassing the material under vacuum at 90 ºC for 3 h.

Structural properties of the copolymers were explored as follows. To adjust the requisite pH value of the 100 ml solution containing only copper (II) ions or conjointly copper (II), nickel (II) and cobalt (II) ions, either hydrochloric acid or ammonium at a respective concentration was added. Next, 0.200 g of modified silica were added to the obtained mix and stirred. 20 Minutes later, residual content of metal ions was determined in the aqueous phase. To this end, the SOLAAR iCE 3500 atomic adsorption spectrometer (*Thermo Fisher Scientific*, USA) was used. The same device was used to determine titers of standard sulfate solutions of copper (II), nickel (II) and cobalt (II).

The values of static metal sorption capacity (E^M), extraction degree (E) and distribution coefficient (D) and separation factor (β) were calculated via the formulas (1–4), with errors not exceeding 5 %.

$$E = (C_0 - C_{eq.})/C_0 \cdot 100\ \%; \tag{1}$$

$$E^M = (C_0 - C_{eq.})V \cdot /\ 1000 \cdot m \cdot M; \tag{2}$$

$$D = (A \cdot 10^3)/C_{Me}; \tag{3}$$

$$\beta = D_{Me1}/D_{Me2}. \tag{4}$$

Herein, C_0 stands for metal concentration in the starting solution, mol/l; C_{eq} — for residual equilibrium concentration of extracted metal in the solution, mol/l; C_{Me} — equilibrium concentration of metal, mg/g; V — volume of the flask, ml; m — weighed portion of sorbent, g; M — molar mass of metal, g/mol; A — equilibrium metal sorption, ml/g.

Thermodynamic characteristics of sorption equilibriums, namely limiting adsorption value (Γ_∞, mol·g^{-1}), and adsorption equilibrium constant (K), were calculated by means of linearization of the Langmuir adsorption isotherm [25]:

$$\Gamma = \Gamma_\infty \cdot K \cdot C/(1+K \cdot C) \tag{5}$$

or rewritten as:

$$C/\Gamma = 1/(K \cdot \Gamma_\infty) + C/\Gamma_\infty \tag{6}$$

Here, Γ stands for adsorption value, mol/g; C — for equilibrium concentration of the substance in the solution, mol/l.

To explore the structure of the surfaces after gravimetrical measurements, the Hitachi S-3400N scanning electron microscope equipped with the energy-dispersive analyzer (*Bruker*, Germany) was used. The surface of the specimens was scanned with x1000 magnification.

Results and Discussion

1. Structure and characteristics of the sorbents

The X-ray phase analysis applied to explore the silica base structure in the low-angle $2\Theta = 1.4^{\circ}–10^{\circ}$ interval has shown evidence of reflexes 100, 110, 200, 210 on the X-ray photograph of silica. These reflexes are characteristic of the steric group *P6mm* and confirm hexagonal pore organization (MCM-41) of the material produced. In addition, the X-ray phase analysis has found out modification of MCM-41 silica by means of hydrazide and amide groups to result in disordering the porous structure.

The results of FTIR-spectroscopic (Table 1) investigations permit the assumption that, during modification of the silica base, the silica matrix and the modifying objects most probably interact. This interaction results, at least, in formation of hydrogen bonds and associates. This phenomenon is evinced by reduced intensity of the band at 3900–2900 cm^{-1}. During hydrothermal synthesis (in the presence of an alkali and quaternary ammonium bases under hydrothermal conditions), amides and hydrazides can, in accord with the Hofmann rearrangement, possibly be cleaved with formation of amines.

Table 1

FT-IR spectroscopy of the modified silica sorbents

Sample	Structural fragments								
	OH, H_2O	NH	C=O	C–N	C=N	C–O	H_{as} Si–O–Si	H_{as} O–Si–O	H_s Si–O–Si
SiO_2 (MCM-41)	3000–4000		1636				1236–1091	969	802
DMHD		3252	1658	1523					
HTS-DMHD	3000–3700		1636		1479		1240–1092	964	800
PM-DMHD	3000–3700	3427	1653	1533	1469	1381	1239–1157–1080	968	805

Investigation in textural characteristics of the MCM-41 silica base has evinced the sorption isotherms of the specimens to be shaped typically of organized mesoporous structures, in accord with the IV type of the IUPAC classification (that is, isotherms with clearly expressed capillary condensation of nitrogen) (Table 2).

Table 2

Textural parameters of the sorbents

Sample	E_a, kJ·mole^{-1}	Textural characteristics		
		Specific surface area, S_{BET} m^2·g^{-1}	Total pore volume, V_{tot} cm^3·g^{-1}	Average pore diameter, D nm
SiO_2 (MCM-41)		952	0.59	2.4
HTS-DMHD	54.6	42	0.07	6.3
PM-DMHD	45.6	239	0.20	3.3

The texture and structure of sorbents was studied by low-temperature nitrogen adsorption method (Table 2). According to the data given in Table 2, the sample is a mesoporous material with a high specific surface area (up to 952 m^2×g^{-1}). The binding energy values obtained using the TGM method (Table 2) prove the grafted groups to be strongly bound to the support surface [26]. The surface area is significantly reduced upon modification procedure. This effect is the most pronounced in case the grafting and synthesis processes are carried out simultaneously. A decrease in the specific surface area and pore volume can result in deterioration of the MSM adsorption characteristics. However, a rather high content of functional groups (13–22 mmol×g^{-1}) and ability of the letter to form six-membered chelate cycles with the complexing ion should be taken into account.

So, these materials can be used as sorbents for concentrating, separation and extraction of nonferrous metals ions from solutions of complicated composition.

The synthesized specimens being planned to be used as sorbents to treat wastewater, adsorption capacity for copper (II), nickel (II) and cobalt (II) ions of the sorbents obtained was explored. Porous structure of a material can appreciably influence the adsorption kinetics. During adsorption, a phenomenon of transferring the substance inside the pores appears. This phenomenon is characteristic of the diffusion mechanism. This stage often determines the time of attaining the adsorption equilibrium. Portions of a metal extracted are dependent on the adsorption conditions — on acidity of the medium and duration of contact between sorbent and solution; therefore, dependence of adsorption on these factors was studied first of all.

The adsorption on the prepared sorbent-support was studied in detail. The optimal contact time of the sorbent-support with a copper-containing solution was shown to be 20 minutes. The adsorption of cobalt and nickel in acidic and neutral media is completed within 60 minutes, and in alkaline medium — within 20 minutes.

The adsorption mechanism in case of the adsorbents with the pore sizes commensurate with the size of the adsorbed molecules is significantly different the one observed on the large-pore adsorbents. No adsorption layers are formed in micro- and mesopores, and adsorption proceeds via a volume-filling mechanism [27].

In wastewater, non-ferrous metal ions are present as mixes; therefore, conjoint adsorption of copper, nickel and cobalt ions was studied. The atomic adsorption spectroscopy applied to control the contents of metal ions in equilibrium solutions during the sorption process had enabled exploring sorption of transition metal ions when conjointly present in solutions and with the regard for mutual influence of ions on the sorption process.

In Table 3 and Figure 1 the data on silica sorbents prepared by the postsynthetic modification (PSM) are shown, the grafting density being different. The molar ratio of the support to the grafted groups varied in the range 1:0 ÷ 1:0.4. The grafting of DMHD groups by the HTS method resulted in a 20-fold reduction of the initial surface area, and these samples were removed from experiment.

Table 3

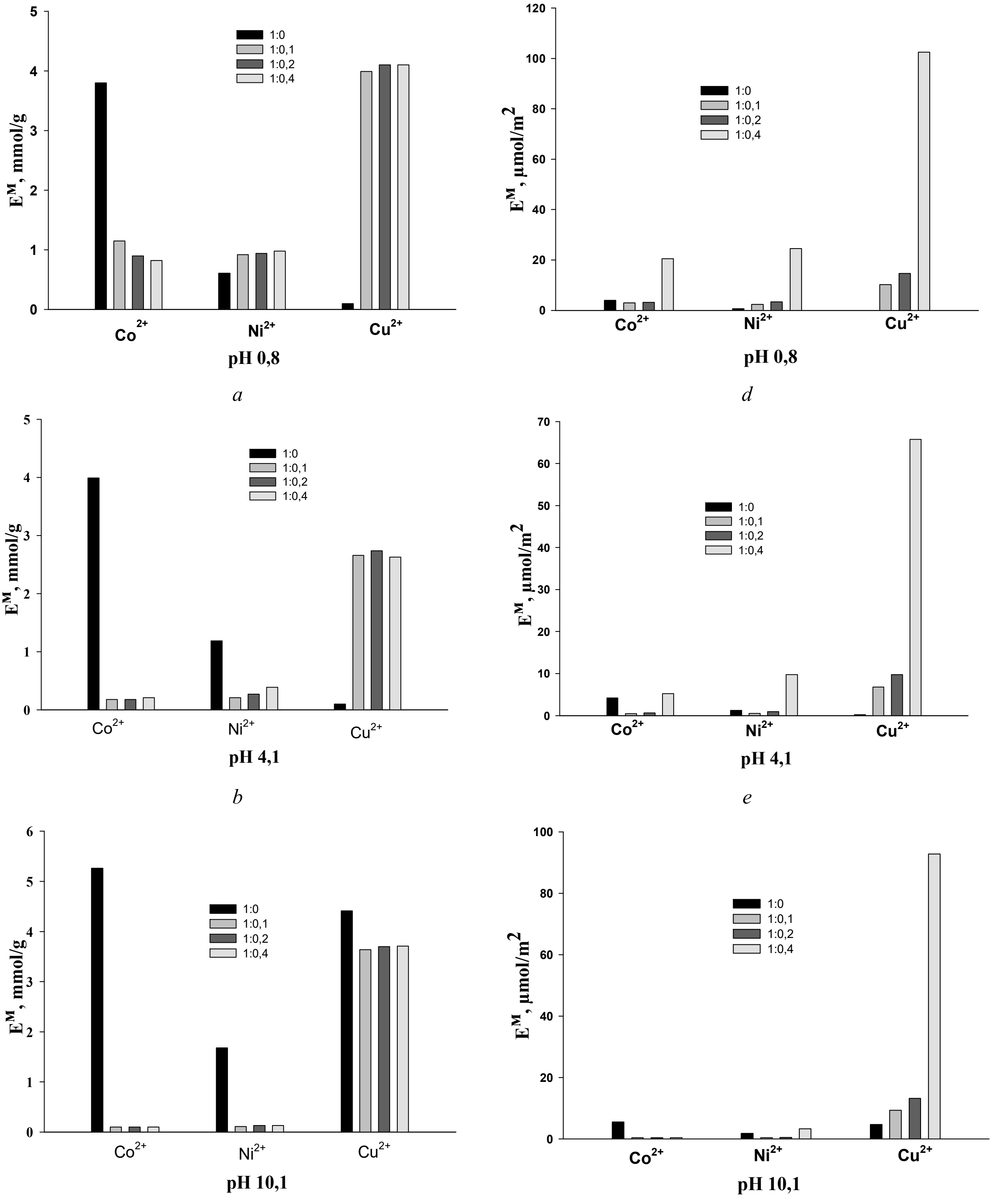
The effect of pH and grafting density on the sorption capacity (E^{M}) of non-ferrous metal ions with silica sorbents obtained by the method of postsynthetic modification

pH	Ratio SiO_2/DMHD	S_{BET}, $м^2·g^{-1}$	E^{M}					
			Co^{2+}		Ni^{2+}		Cu^{2+}	
			$mmol·g^{-1}$	$\mu mol·m^{-2}$	$mmol·g^{-1}$	$\mu mol \times m^{-2}$	$mmol·g^{-1}$	$\mu mol \times m^{-2}$
0.8	1:0.05	950	3.80	4.00	0.61	0.64	0	0.00
	1:0.10	390	1.15	2.95	0.92	2.36	3.99	10.23
	1:0.20	280	0.90	3.21	0.94	3.36	4.10	14.64
	1:0.40	40	0.82	20.50	0.98	24.50	4.10	102.50
4.1	1:0.05	950	3.99	4.20	1.19	1.25	0.00	0.00
	1:0.10	390	0.18	0.46	0.21	0.54	2.66	6.82
	1:0.20	280	0.18	0.64	0.27	0.96	2.74	9.78
	1:0.40	40	0.21	5.25	0.39	9.75	2.63	65.75
10.3	1:0.05	950	5.26	5.53	1.68	1.77	4.41	4.64
	1:0.01	390	0.00	0.00	0.11	0.28	3.64	9.33
	1:0.20	280	0.00	0.00	0.13	0.46	3.70	13.21
	1:0.40	40	0.00	0.00	0.13	3.25	3.71	92.75

A decrease in adsorption parameters observed in some cases (Table 3, Fig. 1 *a–c*) is primarily due to structural changes of the sorbent upon modification. At the same time, the pore size increases significantly. Hence, a pore-size dependent diffusion process is strongly affected by this structural change [27].

Functional groups are reactive enough to bind transition metal ions. So, the adsorption capacity value, or adsorption onto MCM unit surface area, increases proportionally to the grafting density (Fig. 1 *d–f*).

Functionalization of the surface affects the pH range of extraction of metal cations, and separation of metals in the case of joint presence is possible (Table 4).



a *d*

b *e*

c *f*

a, *b*, *c* — E^{M}, mmol·g^{-1}; *d*, *e*, *f* — E^{M}, mcmol·m^{-2}

Figure 1. The effect of pH and density of grafting on the sorption capacity (E^{M}) of non-ferrous metal ions with silica sorbents obtained by the method of postsynthetic modification

Table 4

Effect of pH on the separation of non-ferrous metal cations (joint presence) on the initial MSM-41 and modified IM-DMHD (m_{sorb} = 0.0200 g, V_{flask} = 10 ml, t = 20 min, DMHD/SiO$_2$ = 0.05; 0.1; 0.2

Ions	pH 1.5				pH 5.0				pH 8.7			
	D, µl·m^{-2}		*E*, mmol·m^{-2}		*D*, µl·m^{-2}		*E*, mmol·m^{-2}		*D*, µl·m^{-2}		*E*, mmol·m^{-2}	
	MCM-41	PM-DMHD	MCM-41	PM-DMHD	MCM-41	PM-DMHD	MCM-41	PM-DMHD	MCM-41	PM-DMHD	MCM-41	PM-DMHD
Co	55	130	0.37	0.8	11	109	0.08	0.7	19000	13380	3.9	4.8
Ni	553	610	3.90	5.0	537	369	7.9	5.5	5900	6000	7.4	9.3
β MCM-41	10.1				48818.2				3.2			
β PM-DMHD	4.7				3.4				2.2			
Cu	0	50	0	0.4	28	0	0.23	0	107000	40700	4.5	5.9
Ni	760	930	4.5	5.9	581	750	4.1	5.4	2820	6710	6.5	9.4
β MCM-41	–				20.8				37.9			
β PM-DMHD	20.1				–				6.1			
Cu	0	3420	0	43	0	7940	0	47	134000	5490	4.8	51
Co	107	1040	0.67	7.1	115	190	0.67	2.6	434	2300	1.8	8.9
Ni	577	1400	4.1	3.7	364	780	3.10	5.5	1250	1390	5.7	7.1
β MCM-41	5.4				3.2				Cu^{2+}/Co^{2+} — 308			
									Cu^{2+}/Ni^{2+} — 107			
β MCM-41	Cu^{2+}/Co^{2+} 33				Cu^{2+}/Co^{2+} 42				Cu^{2+}/Co^{2+} 2.4			
	Cu^{2+}/Ni^{2+} 2.4				Cu^{2+}/Ni^{2+} 10				Cu^{2+}/Ni^{2+} 3.9			

As follows from the data obtained, the grafting of hydrazide groups onto silica surface considerably expands the pH range of copper extraction (Tables 3, 4, Fig. 1). The MCM-41 specimen modified with DMHD groups maximally separates copper (II) ions from cobalt (II) and nickel (II) ions in neutral and alkaline media. Ions of the Co(II)–Ni(II) pair can be separated in an alkaline medium. At neutral pH value, ions of the Ni(II)–Cu(II) pair freely separate from one another as the mentioned pair is not adsorbed under these conditions.

The temperature effect on the sorption of metals by the modified silicas was studied at different pH values.

For PM-DGHD samples at low and medium pH values, the sorption capacity was found to be decreased with the temperature rise. This fact indicates physical nature of adsorption.

With high pH values, when non-ferrous metal ions can possibly form complex compounds with DMHD-groups [28, 29], the situation changes. The tangent angle of the ln E vs.1/T (Fig. 2) dependence inverts its sign, i.e. with increasing temperature, adsorption enhances. This becomes possible in case of a chemical reaction on the surface.

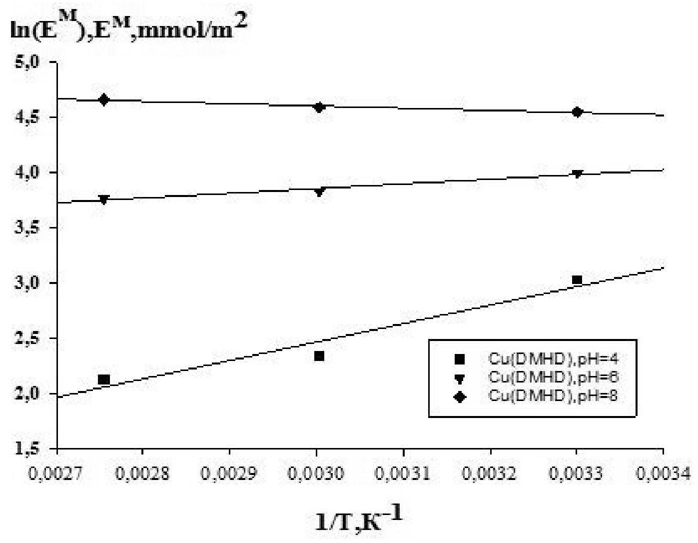
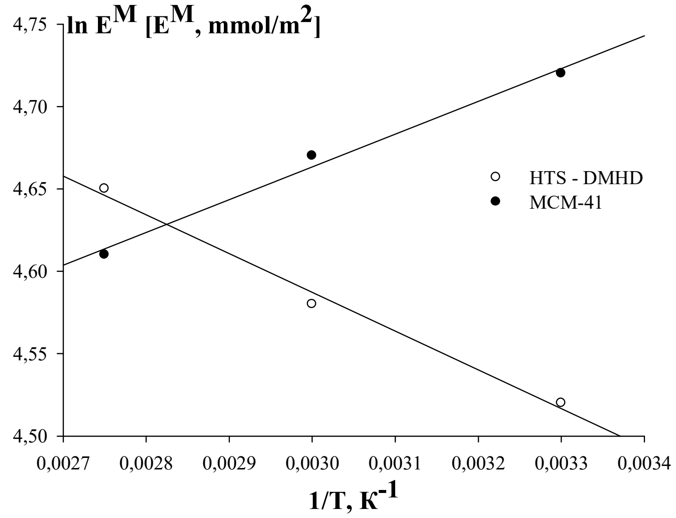


Figure 2. The effect of pH on the temperature dependence of the sorption capacity of the modified silica with respect to Cu^{2+} cations

A similar phenomenon was observed in the case of adsorption of cobalt cations on the surface of the modified silica.

Only physical adsorption onto the initial sorbent surface takes place over the entire pH range studied (Fig. 3).



1 — MCM-41; *2* — HTS-DMHD; m_{sorb} = 0.0200 g; V_{flask} = 10 ml; t = 20 min; pH = 8

Figure 3. Adsorption isotherm of Cu(II) in neutral medium for sorbents:

Chemisorption and covalent bonding with surface functional groups can hinder desorption of metal cations into the solution in further operating cycles of modified sorbents. So, at the next step, the desorption of copper ions from dimethyl hydrazide-functionalized MCM-41 was studied.

Desorption of copper cations from the MSM surface modified by DMHD impregnation was studied at ambient conditions. Copper adsorption was carried out at pH = 8, as at this pH-value copper can be isolated completely. On the contrary, desorption was carried out in an acidic medium, as, according to the data obtained, under these conditions the values of adsorption parameters are significantly lower.

The maximal degree of copper cations' desorption from the surface of sorbents equaled 98 % and was observed at 2M concentration of the acid. In sulfuric acid at 1M concentration, 64 % of copper were desorbed. To reduce concentration of the acid and to increase the degree of copper desorption, the process should be conducted at an elevated temperature. The reason is that physical adsorption largely predominates under these conditions, as is evinced by the adsorption heat values obtained by us.

Conclusions

In this work, structural and adsorptive properties of MCM-41 specimens as influenced upon by (a) modification of their surface with hydrazide groups, and (b) the modification method as well were studied.

Specific surface area of the adsorbent was shown to be significantly reduced after grafting of functional groups. Impregnation method (IM) is more preferable for surface modification than the hydrothermal synthesis (HTS), as in this case surface area reduction is less pronounced and, at the same time, the texture changes are observed. This changes lead to a wider pH-range of extraction and separation of non-ferrous metal cations than the one for the initial MSM.

A comprehensive study to choose the optimal conditions for adsorption and desorption of metal cations (copper (II), nickel (II), cobalt (II)) on the MSM surface modified with chelating functional groups.

The work was performed on the state assignment number AAAA-A18–118032790022–7.

References

1 Doyle A. The evolution of phase during the synthesis of the organically modified catalyst support MCM-48 / A. Doyle, E. Ahmed, B. Hodnett // Catalysis Today. — 2006. — Vol. 116, No. 1. — P. 50–55. DOI: 10.1016/j.cattod.2006.02.083

2 Tsoncheva T. MCM-41 silica modified with copper and iron oxides as catalysts for methanol decomposition / T. Tsoncheva, S. Areva, M. Dimitrov, D. Paneva, I. Mitov, M. Linden, C. Minchev // J. Mol. Catal. — 2006. — Vol. 246, No. 1. — P. 118–127.

3 Liou T-H. A green rout to preparation of MCM-41 silicas with well-ordered mesostructure controlled in acidic and alkaline environments / T-H. Liou // Chemical Engineering Journal. — 2010. — Vol. 171, No. 3. — P. 1458–1468. DOI: 10.1016/j.cej.2011.05.074

4 Das D. Enhanced catalytic activity of Ti, V, Mn-grafted silica spheres towards epoxidation reaction / D. Das, K. Parida // *Reaction Kinetics and Catalysis Letters.* — 2007. — Vol*. 90. — P. 77–84.* DOI: 10.1007/s10562–008–9697–9

5 Lin K. Direct room-temperature synthesis of methyl-functionalized Ti-MCM-41 nanoparticles and their catalytic performance in epoxidation / K. Lin, P. Pescarmona, K. Houthoofd, D. Liang, G. Tendeloo, P. Jacobs // Journal of Catalysis. — 2009. — Vol. 263. — P. 75–82. — DOI: 10.1016/j.jcat.2009.01.013.

6 Elias V. Synthesis of titanium-containing mesoporous silicas as catalysts for cyclohexene epoxidation / V. Elias, M. Crivello, E. Herrero, S. Casuscelli, G. Eimer // Ind. Eng. Chem. Res. — 2009. — Vol. 48. — P. 9076–9082.

7 Eimer G. Synthesis, characterization and selective oxidation properties of Ti-containing mesoporous catalysts / G. Eimer, S. Casuscelli, G. Ghione, M. Crivello, E. Herrero // Applied Catalysis A: General. — 2006. — Vol. 298. — P. 232–242. DOI: 10.1016/j.apcata.2005.10.006.

8 Save M. Atom transfer radical polymerization of styrene and methyl methacrylate from mesoporous ordered silica particles / M. Save, G. Granvorka, J. Bernard, B. Charleux, C. Boissiere, D. Grosso, C. Sanchez // Macromolecular Rapid Communication. — 2006. — Vol. 27. — P. 393–398. DOI: 10.1002/marc.200500798.

9 Козлова С.А. Состояние силанольного покрытия мезоструктурированного силикатного материала MCM-41 в результате постсинтетической активации / В.А. Парфенов, Л.С. Тарасова, С.Д. Кирик // Журн. Сиб. федерал. ун-та. Сер. химия. — 2008. — Т. 1, № 4. — С. 376–388.

10 Фоменко О.Е. Модифицирование силикатных поверхностей путем силилирования их кремнийорганическими соединениями / О.Е. Фоменко, Ф. Рёсснер // Сорбционные и хроматографические процессы. — 2009. — Т. 9, Вып. 5. — С. 633–642.

11 Fryxell G. Environmental applications of nanomaterials synthesis: sorbents and sensors / G. Fryxell, G. Cao // Copyright by Imperial College Press. — 2007. — P. 499–507.

12 Oi H. Application of nanomaterials in electrogenerated chemiluminescens biosensors / H. Oi, Y. Peng, Q. Gao, Cn. Zhang // Sensors. — 2009. — Vol. 9. — P. 674–695. DOI: 10.3390/s90100674.

13 Zhong L. Application of mesoporous silica nanoreservoir in smart drug controlled release systems // L. Zhong, C. Kaiyong, Z. Beilu, D. Lin, L. Aiping, G. Duan // Progress in Chemistry. — 2011. — Vol. 23, No. 11. — P. 2326–2338.

14 Лисичкин Г.В. Химия привитых поверхностных соединений / Г.В. Лисичкин, А.Ю. Фадеев, А.А. Сердан, П.Н. Нестеренко. — М.: Физматлит, 2003. — С. 38–56.

15 Rao V.A. Surface chemical modification of silica aerogels using various alkyl-alkoxy/chloro silanes / V.A. Rao, M.M. Kulkarni, D.P. Amalnerkar, T. Seht // Appl. Surf. Sci. — 2003. — Vol. 203. — P. 262–270.

16 Balakain V.M. New nitrogen phosphorus-containing ampholytes on a polyacrylate matrix and a study of the sorption of copper, zinc, and iron from sulfuric solutions // V.M. Balakain, N.V. Dranitsina, Yu.B. Holmanskaya, A.N. Tesler, A.V. Morozova // Russian Journal of Applied Chemistry. — 1981. — Vol. 54. — P. 781–785.

17 Николаев А.В. Сорбция меди и цветных металлов серой, азотом, серосодержащими сорбентами / А.В. Николаев, А.В. Фокин, С.Ф. Коломиец, И.Н. Грибанова, Н.П. Якунина, Н.Н. Аншиц, Г.В. Виллевальд // Тр. Сиб. отд. АН СССР. Сер. химия. — 1977. — Т. 4. — С. 34–40.

18 Оскотская Е.П. Предварительная групповая концентрация меди, кобальта и никеля с полимерным хелатообразующим сорбентом при анализе природных вод / Е.П. Оскотская, Н.Н. Басаргин, Д.Е. Игнатов, Ю.Г. Росовский // Заводская лаборатория. Диагностика материалов. — 1999. — Т. 65, № 3. — С. 10–14.

19 Zmijewski T. Thermogravimetric study of silica with a chemically modified surface / T. Zmijewski, M. Mioduska, B. Pasewska // J. Thermal. Anal. — 1987. — Vol. 32. — P. 1755–1761.

20 Athens G.L. Functionalization of mesostructured inorganic–organic and porous inorganic materials / G.L. Athens, R.M. Shayib, B.F. Chmelka // Current Opinion in Colloid & Interface Science. — 2009. — Vol. 14. — P. 281–292. DOI: 10.1016/j.cocis.2009.05.012.

21 Truel A. Modification of mesoporous silicas by incorporation of heteroelements in framewotk / A. Truel // Microporous Mesoporous Mater. — 1999. — Vol. 27. — P. 151–169.

22 Macquarrie D.J. Direct preparation of organically modified MCM-type materials. Preparation and characterization of aminopropyl-MCM and 2-cyanoethyl-MCM / D.J. Macquarrie // Chem. Commun. — 1996. — Iss. 16. — P. 1961–1962. DOI: 10.1039/CC9960001961.

23 Zeng W. Organic modified mesoporous MCM-41 through solvotermal process fs drug delivery system / W. Zeng, X-F. Qian, Y-B. Zhang, J. Yin, Z-K. Zhu // Materials Research Bulletin. — 2005. — Vol. 40. — P. 766–772. DOI: 10.1016/j.materresbull.2005.02.011.

24 Badiei A.R. Modification of mesoporous silica by direct template ion exchange using cobalt complexes / A.R. Badiei, L. Bonneviot // Inorg. Chem. — 1998. — Vol. 37. — P. 4142–4145. — DOI: 10.1021/ic971633q.

25 Kondrashova N. Effect of organic-silane additives on textural-structural properties of mesoporous silicate materials / N. Kondrashova, E. Saenko, I. Lebedeva, V. Valtsifer, V. Strelnikov // Microporous and mesoporous materials. — 2012. — Vol. 153. — P. 275–281.

26 Фролов Ю.Г. Курс коллоидной химии. Поверхностные явления и дисперсионные системы / Ю.Г. Фролов. — М.: Альянс, 2004. — 753 с.

27 Тагер А.А. Физико-химия полимеров / А.А. Тагер. — М.: Научный мир, 2007. — 576 с.

28 Radushev A.V. Versatic Functional Tert-Carboxylic Acids as Metal Extractive Agents / A.V. Radushev, T.D. Batueva, A.V. Kataev // Separation science and technology. — 2015. — Vol. 50, No. 4. — P. 512–519.

29 Патент № 2472864 РФ. Способ экстракции ионов меди, никеля и(или) кобальта из слабокислых и аммиачных водных растворов. Опубл. БИ. 2013. № 2. Радушев А.В., Батуева Т.Д.

Т.Д. Батуева, Н.Б. Кондрашова, М.Г. Щербань

Гидразидті функционалды топтармен модификацияланған мезокеуекті кремнеземдер негізіндегі сорбенттер

Кремнезем негізіндегі кеуегі МСМ-41 болатын, Versatic трет-карбон қышқылдары фракциясының негізіндегі гидразидті топтармен модификацияланған сорбенттер синтезделіп алынды. Азоттың төменгі температуралы сорбциясы, рентгенфазалық анализ (РФА), ИҚ-спектроскопиясы және сканерлейтін электрондық микроскопия әдістері арқылы зерттелінетін кремнеземді сорбенттердің текстуралық-құрылымдық қасиеттері анықталды. Адсорбциялық және десорбциялық беттерінің сәйкес келуі сорбент құрылымының реттілігін көрсетеді. Модификатордың болуы меншікті беттік ауданының кемуіне әкеледі. Сулы ерітіндідегі мыс (II), никель (II) және кобальттың (II) сорбциясы зерттелді. Сіңдіру әдісі, тура синтез әдісіне қарағанда, модификацияланған кремнеземнің адсорбциялық қабілеттілігін арттырады, бұл бастапқы МСМ салыстырғанда түсті металдарды бөліп алудың pH диапазонын кеңейтуге мүмкіндік береді. Түсті металдар катиондарының сорбциясын зерттеу ортаның pH көрсеткішіне байланысты катиондарды бірге немесе жекелей бөліп алуға болатынын көрсетті. Сорбенттер мыс (II), никель (II) иондарын мөлшерлік бөліп алуда қолдануға болады. Кремнеземді негіздің модификация әдісі және металдардың бірлескен сорбциясы кезіндегі мономер концентрациясына реагенттердің сорбциялық қабілеттілігінің тәуелділігі зерттелді. pH әртүрлі шамаларындағы және олардың МСМ беттік қабатымен әсерлесуі нәтижесінде модификацияланған кремнезем негізінде алынған металдар сорбциясына температураның әсері анықталды. Сорбенттің беттік қабатындағы мыс катиондарының десорбциясы анықталды.

Кілт сөздер: мезокеуекті кремнезем, модифицикация, гидразид, сорбция, Versatic қышқылдары, түсті металдар, сіңдіру әдісі, тура синтез.

Т.Д. Батуева, Н.Б. Кондрашова, М.Г. Щербань

Сорбенты на основе мезопористых кремнеземов, модифицированных гидразидными функциональными группами

Синтезированы сорбенты на основе кремнезёмов со структурой пор МСМ-41, модифицированные гидразидными группами на основе фракций — трет-карбоновых кислот Versatic. Методами низкотемпературной сорбции азота, рентгенофазового анализа (РФА), ИК-спектроскопией и сканирующей электронной микроскопии определены текстурно-структурные свойства исследуемых кремнеземных сорбентов. Совпадение адсорбционной и десорбционной ветвей свидетельствует о высокой степени упорядоченности структуры сорбента. Наличие модификатора приводит к уменьшению значений удельной площади поверхности. Исследована сорбция меди (II), никеля (II) и кобальта (II) из водных растворов полученными реагентами. Метод пропитки увеличивает адсорбционную способность модифицированного кремнезема в большей степени по сравнению с методом прямого синтеза, что позволяет существенно расширить диапазон pH извлечения и разделения цветных металлов по сравнению с исходным МСМ. Изучение сорбции катионов цветных металлов показало, что, в зависимости от значения pH среды, возможны как совместное извлечение, так и отделение катионов. Сорбенты могут быть использованы для количественного отделения ионов меди (II) от ионов никеля (II). Определена зависимость сорбционной способности реагентов от способа модификации кремнезёмной основы и концентрации мономера при совместной сорбции металлов. Определены влияние температуры на сорбцию металлов полученными модифицированными кремнеземами при разных значениях pH и способ их взаимодействия с поверхностью МСМ. Изучена десорбция катионов меди с поверхности сорбента.

Ключевые слова: мезопористый кремнезем, модифицикация, гидразид, сорбция, кислоты Versatic, цветные металлы, метод пропитки, прямой синтез.

References

1 Doyle, A.M., Ahmed, E., & Hodnett, B.K. (2006). The evolution of phase during the synthesis of the organically modified catalyst support MCM-48. *Catalysis Today, 116(1)*, 50–55.

2 Tsoncheva, T., Areva, S., Dimitrov, M., Paneva, D., Mitov, I., Linden, M., & Minchev, C. (2006). MCM-41 silica modified with copper and iron oxides as catalysts for methanol decomposition. *J. Mol. Catal. A, 246(1)*, 118–127.

3 Liou, T.-H. (2010). A green rout to preparation of MCM-41 silicas with well-ordered mesostructure controlled in acidic and alkaline environments. *Chemical Engineering Journal, 171(3)*, 1458–1468.

4 Das, D.P., & Parida, K.M. (2007). Enhanced catalytic activity of Ti, V, Mn-grafted silica spheres towards epoxidation reaction. *Reaction Kinetics and Catalysis Letters, 90, 77–84.*

5 Lin, K., Pescarmona, P.P., Houthoofd, K., Liang, D., Tendeloo, G.V., & Jacobs, P.A. (2009). Direct room-temperature synthesis of methyl-functionalized Ti-MCM-41 nanoparticles and their catalytic performance in epoxidation. *Journal of Catalysis, 263*, 75–82.

6 Elias, V.R., Crivello, M.E., Herrero, E.R., Casuscelli, S.G., & Eimer, G.A. (2009). Synthesis of titanium-containing mesoporous silicas as catalysts for cyclohexene epoxidation. *Ind. Eng. Chem. Res., 48*, 9076–9082.

7 Eimer, G.A., Casuscelli, S.G., Ghione, G.E., Crivello, M.E., & Herrero, E.R. (2006). Synthesis, characterization and selective oxidation properties of Ti-containing mesoporous catalysts. *Applied Catalysis A: General, 298*, 232–242.

8 Save, M., Granvorka, G., Bernard, J., Charleux, B., Boissiere, C., Grosso, D., & Sanchez, C. (2006). Atom transfer radical polymerization of styrene and methyl methacrylate from mesoporous ordered silica particles. *Macromolecular Rapid Communication*, *27*, 393–398.

9 Kozlova, S.A., Parfenov, V.A., Tarasova, L.S., & Kirik, S.D. (2008). Sostoianie silanolnoho pokrytiia mezostrukturirovannoho silikatnoho materiala MSM-41 v rezultate postsinteticheskoi aktivatsii [State of silanol coating of mesostructured silicate material MCM-41 as a result of postsynthetic activation]. *Zhurnal Sibirskoho federalnoho universiteta — Journal of Siberian Federal University*, *4, 1*, 376–388 [in Russian].

10 Fomenko, O.E., & Ryossner, F. (2009). Modifitsirovanie silikatnykh poverkhnostei putem sililirovaniia ikh kremniiorhanicheskimi soiedineniiami [Modification of silicate surfaces by silylation with their organosilicon compounds]. *Sorbtsionnye i khromatohraficheskie protsessy — Sorption and chromatographic processes*, *9, 5*, 633–642 [in Russian].

11 Fryxell, G.E., & Cao, G. (2007). *Environmental applications of nanomaterials synthesis, sorbents and sensors*. Imperial College Press, 499–507.

12 Oi, H., Peng, Y, Gao, Q., & Zhang, Cn. (2009). Application of nanomaterials in electrogenerated chemiluminescense biosensors. *Sensors*, *9*, 674–695. DOI: 10.3390/s90100674.

13 Zhong, L., Kaiyong, C., Beilu, Z., Lin, D., Aiping, L., & Duan, G. (2011). Application of mesoporous silica nanoreservoir in smart drug controlled release systems. *Progress in Chemistry*, *23*(11), 2326–2338.

14 Lisichkin, G.V., Fadeev, A.Yu., Serdan, A.A., Nesterenko, P.N., Mingalev, R.G., & Furman, L.D. (2003). *Khimiia privitykh poverkhnostnykh soedinenii [Chemistry of Grafted Surface Compounds]*. Moscow: Fizmatlit [in Russian].

15 Rao, V.A., Kulkarni, M.M., Amalnerkar, D.P., & Seht, T. (2003). Surface chemical modification of silica aerogels using various alkyl-alkoxy/chloro silanes. *Appl. Surf. Sci*., *203*, 262–270.

16 Balakain, V.M., Dranitsina, N.V., Holmanskaya, Yu.B., Tesler, A.N., & Morozova, A.V. (1981). New nitrogen phosphorus-containing ampholytes on a polyacrylate matrix and a study of the sorption of copper, zinc, and iron from sulfuric solutions. *Russian Journal of Applied Chemistry*, *54*, 781–785.

17 Nikolaev, A.V., Fokin, A.V., Kolomiec, S.F., Gribanova, I.N. Yakunina, N.P., & Anshic, N.N. et al. (1977). Sorbtsiia medi i tsvetnykh metallov seroi, azotom, serosoderzhashchimi sorbentami [Sorption of copper and non-ferrous metals with sulfur, nitrogen, sulfur-containing sorbents]. *Trudy Sibirskoho otdeleniia Akademii nauk SSSR. Seriia khimiia. — Proceedings of Siberian Branch of Academy of Sciences of USSR. Chemistry Series*, *4*, 34–40 [in Russian].

18 Oskotskaya, E.P., Basargin, N.N., Ignatov, D.E., & Rosovskii, Yu.G. (1999). Predvaritelnaia hruppovaia kontsentratsiia medi, kobalta i nikelia s polimernym khelatoobrazuiushchim sorbentom pri analize prirodnykh vod [Preliminary group concentration of copper, cobalt and nickel with a polymeric chelating sorbent in the analysis of natural waters]. *Zavodskaia laboratoriia. Diahnostika materialov — Factory Laboratory. Material Diagnostics*, *65*, *3*, 10–14 [in Russian].

19 Zmijewski, T., Mioduska, M., Pasewska, B. (1987). Thermogravimetric study of silica with a chemically modified surface, *J. Thermal. Anal. 32*, 1755–1761.

20 Athens, G.L., Shayib, R.M., Chmelka, B.F. (2009). Functionalization of mesostructured inorganic–organic and porous inorganic materials. *Current Opinion in Colloid & Interface Science, 14*, 281–292.

21 Truel, A. (1999). Modification of mesoporous silicas by incorporation of heteroelements in framework. *Microporous Mesoporous Mater*, *27*, 151–169.

22 Macquarrie, D. J. (1996). Direct preparation of organically modified MCM-type materials. Preparation and characterization of aminopropyl-MCM and 2-cyanoethyl-MCM, *Chem. Commun.*, *16*, 1961–1962.

23 Zeng, W., Qian, X-F., Zhang, Y-B., Yin, J., & Zhu, Z-K. (2005). Organic modified mesoporous MCM-41 through solvothermal process fs drug delivery system. *Materials Research Bulletin*, 40, 766–772.

24 Badiei, A.R., & Bonneviot, L. (1998). Modification of mesoporous silica by direct template ion exchange using cobalt complexes. *Inorg Chem.*, *37*, 4142–4145.

25 Kondrashova, N., Saenko, E., Lebedeva, I., Valtsifer, V., & Strelnikov, V. (2012). Effect of organic-silane additives on textural-structural properties of mesoporous silicate materials. *Microporous and mesoporous materials*, *153*, 275–281.

26 Frolov, Yu.G. (2004). *Kurs kolloidnoi khimii. Poverkhnostnye yavleniia i dispersionnye sistemy [Course of colloid chemistry. Superficial phenomena and dispersive systems].* Moscow: Alians [in Russian].

27 Tager, A.A. (2007). *Fiziko-khimiia polimerov [Physical Chemistry of Polymers]*. Moscow: Nauchnyi mir [in Russian].

28 Radushev, A.V., Batueva, T.D. & Kataev, A.V. (2015). Versatic functional tert-carboxylic acids as metal extractive agents, *Separation science and technology*, *50(4)*, 512–519.

29 Radushev, A.V., & Batueva, T.D. (2013). Sposob ekstraktsii ionov medi, nikelia i(ili) kobalta iz slabokislykh i ammiachnykh vodnykh rastvorov [Method for the extraction of copper, nickel and (or) cobalt ions from weakly acidic and ammonia aqueous solutions]. *Patent No. 2472864 RF. Publ. BI, 2* [in Russian].

DOI 10.31489/2019Ch3/62-67

UDC 541.1, 544.2

D.A. Volkov, Y.V. Terenteva, S.A. Beznosyuk

Altai State University, Barnaul, Russia
(E-mail: bsa1953@mail.ru)

Attosecond nanotechnology: quantum dots of nanoelectromechanical systems of $\mathbf{CuIn_xGa_{1-x}S_2}$ compounds

In the paper the thermodynamic stability and variability of the internal energy of continuous substitution solid solutions based on the $CuIn_xGa_{1-x}S_2$ chalcopyrite lattice (CIGS) in a state of the nanoelectromechanical system (NEMS) are studied. These substances are the most effective materials for phototransformation processes. It is known that maximum efficiency reached using a photoconverter based on $CuIn_xGa_{1-x}S_2$ composition amounted up to 21 %, while the same value for photoconverter based on silicon could reach only 15 %, which underlines the relevance of studies of the subject compositions. The equilibrium bond lengths and binding energy values are presented. The change to the internal energy at different temperatures and the change to distribution functions of atoms over radial pairs in a stable system of nanolayers are shown. It was revealed that changing of indium atoms concentration in the system causes non-linear relative changes to the parameters of stable CIGS NEMS nanolayers. It was shown that given behavior is the consequence of a significant difference in both In–S and Ga–S bond lengths and binding energy values in the first coordination area of sulphur.

Keywords: radial pair distribution function, semiconductor, solar cells, nanoelectromechanical system, graphs, Vegard's law.

Introduction

The production and use of semiconductor compounds with specific properties has become associated with the further development of solid-state optoelectronics. In connection with this, at the end of the twentieth century, interest in studying semiconductor materials with a chalcopyrite structure of type $A^1B^3C^6{}_2$ began to gain interest. Beginning in the second half of the twentieth century, after the publication of many publications about the prospects for the development of thin-film photocells based on $A^1B^3C^6{}_2$ structures, the reality of the practical use of these compounds became clear as an effective optical material. They became the subject of close attention of scientists and technologists.

Cu (In, Ga), S_2 (CIGS) and related materials were investigated for thin-film solar cells, since their high absorption coefficient and adjustable band gap can achieve high conversion efficiency. Recently, several groups have reported cell efficacy of over 20 % with alkaline treatment on the surface of CIGS [1–6].

This article describes the study of the stability of nanoelectromechanical systems (NEMS) of CIGS structures conducted using the approximating quasiparticle density functional (calculating the NEMS energy of atomic dimers (Table 1) and the method of steepest descent along the surface of a particle.

The study of the quantum relaxation kinetics of NEMS CIGS was carried out at the temperature of liquid nitrogen (T_1 = 77 K) and normal conditions (T_2 = 293 K). These temperatures are realized by the special method of NEMS kinetics [7].

Table 1

Parameters of dimer bonds

Dimer	Equilibrium bond energy U_0, kJ/mol	Equilibrium bond length R_0, nm	The frequency of zero oscillations ω_0, cm^{-1}
In–S	–293	0.23	359
Cu–S	–193	0.24	268
Ga–S	–243	0.25	349

From the data obtained, it is clear that during the transition, from gallium to indium, the energy and bond length increase, and the frequency of zero-point oscillations decreases.

Computer modelling

For further experiment, we needed to build models of nanolayers CIGS. The parameters of the crystal lattices, $CuInS_2$ and $CuGaS_2$ with the chalcopyrite structure ($a = 5.5170$, $c = 11.0600$) were used for the construction.

Thus, the models of semiconductor nanolayers $CuInS_2$ and $CuGaS_2$, consisting of 6400 atoms of size 20×20×1 e. (221.2 nm × 110.34 nm × 5.170 nm). The image of the structures obtained (with enlarged fragments) is shown in Figure 1. Figure 2 shows the link graph of these structures.

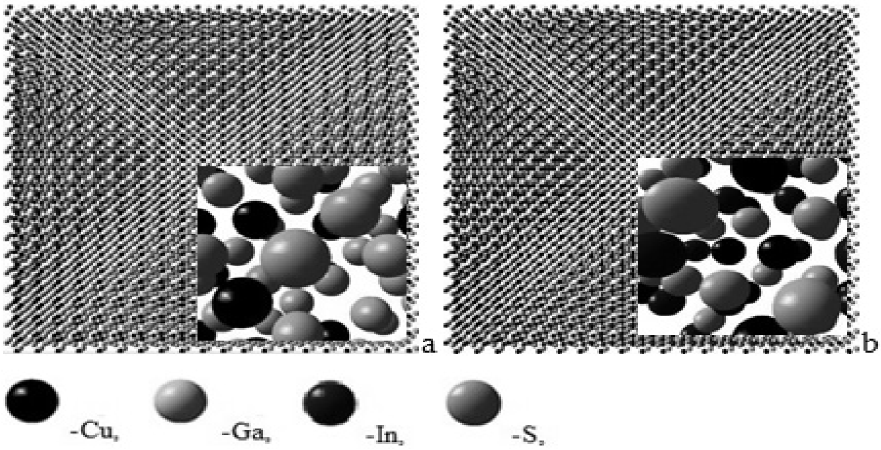


Figure 1. Models of nanolayers with a larger fragment $CuInS_2$ (*a*), $CuGaS_2$ (*b*)

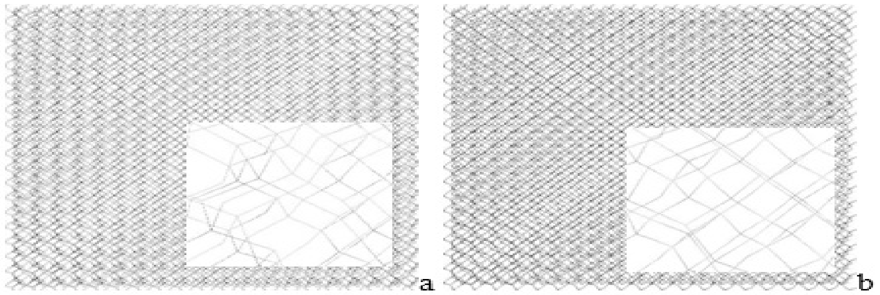


Figure 2. Coupled graphs of nanolayers with an enlarged fragment $CuInS_2$ (*a*), $CuGaS_2$ (*b*)

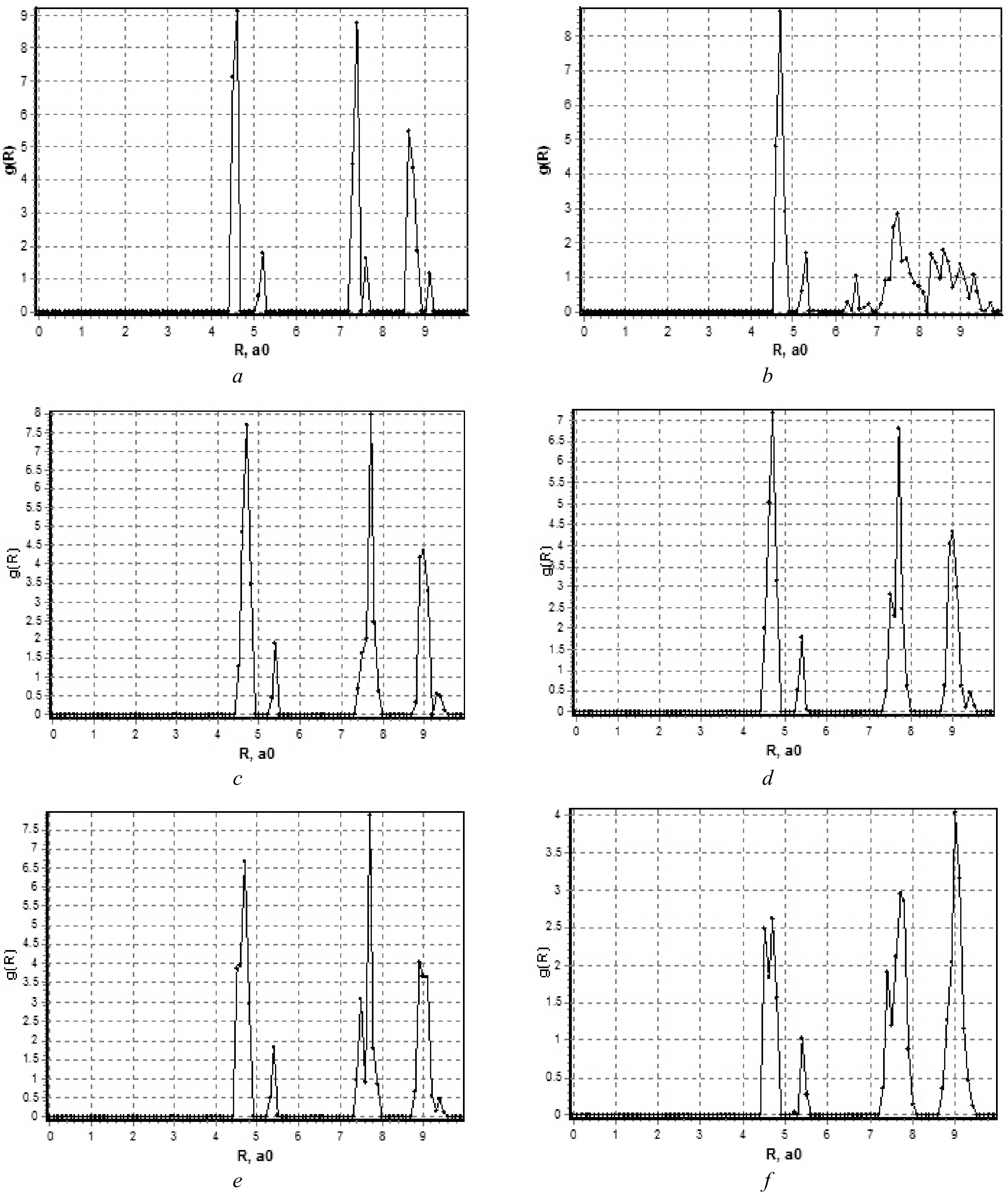
To obtain a complete picture of the correlation of internal energy and changes in the crystal lattice of nanoelectromechanical structures, the use of the «CompNanoTech» [6] software package is required, which uses the parameters of atomic couple bonds obtained by the nonlocal density functional method. This package is used to optimize the geometry of the nanofilm during the pulse action at different temperatures [7].

As a result of a computer experiment at $T_0 = 0$ K, optimized CIGS nanolayer structures ($CuIn_xGa_{1-x}S_2$) were obtained. The values of the energies of nanolayers obtained in the experiment are presented in Table 2 and in Figure 3.

Table 2

The total NEMS bond energies of variable composition $CuIn_xGa_{1-x}S_2$

Nanolayer composition	Nanolayer energy, kJ/mol
$CuGaS_2$	–238
$CuIn_{0,25}Ga_{0,75}S_2$	–246
$CuIn_{0,5}Ga_{0,5}S_2$	–250
$CuIn_{0,75}Ga_{0,25}S_2$	–258
$CuInS_2$	–266



a — $CuGaS_2$ in the initial state; *b* — $CuGaS_2$; *c* — $CuIn_{0.25}Ga_{0.75}S_2$;
d — $CuIn_{0.5}Ga_{0.5}S_2$; *e* — $CuIn_{0.75}Ga_{0.25}S_2$; *f* — $CuInS_2$

Figure 3. Radial pair distribution functions of atoms

Figures show 3 *b–f*, a peak that corresponds to the distribution of copper atoms at distances of 5.2–5.3 *a*0 with an intensity of 2.4, as can be seen from the figures, there is a consistent change in peaks, namely: a decrease in the peak of Ga at distances of 3.7–3.8 *a*0, the peak decreases in values from 2.6 to 0 with increasing In concentration from 0 to 100 %, and, accordingly, the growth of In peak in the range 5.8–6.0 *a*0 from 0 to 2.2 when the concentration of Ga drops to 0 %.

It follows from the analysis that when the In concentration in the system changes over the B^3 sublattice from 0 to 1, a monotonous, quasilinear change in the first coordination sphere occurs, and a decrease in the peaks in the second and third coordination spheres is observed.

Since the NEMS energy of a nanolayer is determined by the radial distribution function of atoms in the system, and the first coordination sphere has the largest contribution to the energy of the nanolayer, a quasilinear dependence of the nanolayer energy on the concentration x occurs (Fig. 4), which shows the Vegard law when the NEMS composition changes.

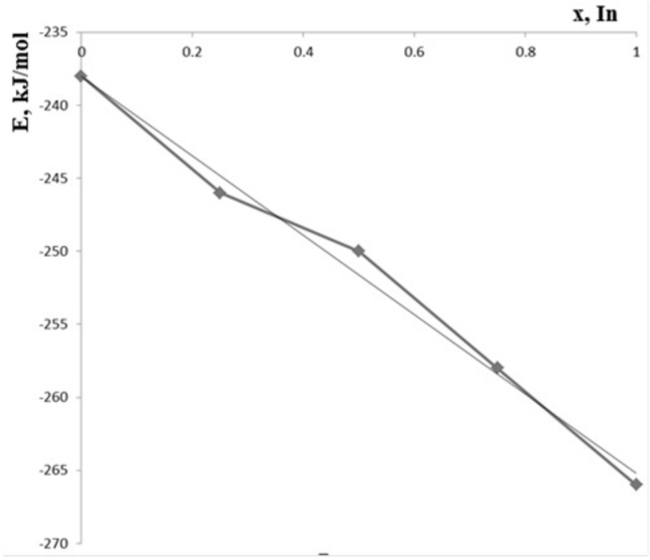


Figure 4. Concentration dependence of the energy of $CuIn_xGa_{1-x}S_2$ semiconductor nanolayers at $T_0 = 0$ K

According to the results of computer simulation using quantum nanokinetics at two temperatures: $T_1 = 77$ K and $T_2 = 298$ K, optimized structures of nanolayers of variable composition $CuIn_xGa_{1-x}S_2$ were obtained, and kinetic curves (Fig. 5) of the system energy change during relaxation were constructed highly nonequilibrium semiconductor NEMSs of nanolayers of variable composition $CuIn_xGa_{1-x}S_2$.

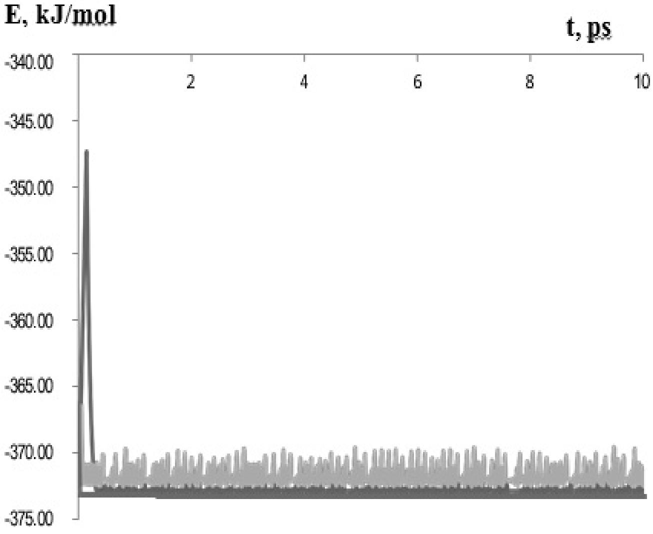


Figure 5. An example of a kinetic curve for the relaxation of $CuGaS_2$ systems

The results of a computer experiment to study the kinetics of relaxation and finite stability of the studied nanolayers, obtained from the kinetic curves constructed for all the $CuIn_xGa_{1-x}S_2$ systems under study in the framework of the electromechanical model, are presented in Table 3.

Table 3

Indicators of femtosecond processing of nanolayers of variable composition $CuIn_xGa_{1-x}S_2$ and at different temperatures

Nanolayer composition	Femtosecond Processing Indicators						
	E_0, kJ/mol	E_{77}, kJ/mol	t_{77}, ps	A_{77}, kJ/mol	E_{298}, kJ/mol	t_{298}, ps	A_{298}, kJ/mol
$CuInS_2$	–416	–415	0.12	0.91	–414	0.09	3.60
$CuIn_{0.75}Ga_{0.25}S_2$	–404	–403	0.77	0.85	–402	0.11	3.333
$CuIn_{0.5}Ga_{0.5}S_2$	–392	–391	0.55	0.84	–390	0.28	3.37
$CuIn_{0.25}Ga_{0.75}S_2$	–386	–385	0.70	0.79	–383	0.20	3.31
$CuGaS_2$	–373	–372	0.44	0.79	–371	0.12	3.22

According to the Table 3 we can draw the following conclusions: for semiconductor nanostructures, femtosecond relaxation from the activated state at $T_0 = 0$ K leads to the state with the greatest stability, with an exact lower energy limit, with low amplitude atomic.

The time interval of the output of an activated nano-layer on a «plateau» depends on temperature, and the evolution of nanolayers in a non-equilibrium state achieves relaxation over different times.

According to the results of computer simulation using the quantum NEMS kinetics at two temperatures $T_1 = 77$ K and $T_2 = 298$ K, radial distribution functions of atoms in the NEMS were constructed for nanolayers of continuous solid solutions of variable composition $CuIn_xGa_{1-x}S_2$.

Conclusions

1. The formation of continuous substitution solid solutions on the B^3 sublattice of compounds of the composition $CuIn_xGa_{1-x}S_2$, as a whole, obeys the Vegard law. Deviations from Vegard's law are due to transformations of the second and third coordination sphere of nanolayers with changes in indium concentration.
2. In $CuIn_xGa_{1-x}S_2$ systems, at indium concentrations $x \leq 0.38$, a stabilizing nonlinear contribution is observed, and for $x > 0.38$, a non-linear, destabilizing positive energy contribution is observed.
3. Under cryogenic ($T = 77$ K) and standard ($T = 298$ K) conditions, the order of the coordination spheres above the first one collapses more with increasing temperature. As the relaxation temperature rises from cryogenic ($T = 77$ K) to standard ($T = 298$ K) conditions, the average energy of NEMS at all concentrations decreases by 1 kJ/mol, and quantum fluctuations increase from 0.64 kJ/mol to 3.06 kJ/mol.

References

1 Chirilă, A., Reinhard, P., Pianezzi, F., Bloesch, P., Uhl, A.R., & Fella, C. et al. (2013). Potassium-induced surface modification of Cu(In, Ga)Se_2 thin films for high-efficiency solar cells. *Nat. Mater., 12*, 1107–1111.

2 Jackson, P., Wuerz, R., Hariskos, D., Lotter, E., Witte, W., & Powalla, M. (2016). Effects of heavy alkali elements in Cu(In, Ga)Se_2 solar cells with efficiencies up to 22.6 %. *Phys. Status Solidi RRL, 10,* 583–586.

3 Reinhard, P., Bissig, B., Pianezzi, F., Avancini, E., Hagendorfer, H., & Keller, D. et al. (2015). Features of KF and NaF postdeposition treatments of Cu(In, Ga)Se_2 absorbers for high efficiency thin film solar cells. *Chem. Mater., 27*, 5755–5764.

4 Shin, Y.M., Lee, C.S., Shin, D.H., Kwon, H.S., Park, B.G., & Ahn, B.T. (2015). Surface modification of CIGS film by annealing and its effect on the band structure and photovoltaic properties of CIGS solar cells. *Curr. Appl. Phys., 15*, 18–24.

5 Kwon, S.H., Park, S.C., Ahn, B.T., Yoon, K.H., Song, J. (1998). Effect of $CuIn_3Se_5$ layer thickness on $CuInSe_2$ thin films and devices. *Sol. Energy*, *64*, 55–60.

6 Beznosyuk, S.A., Zhukovsky, M.S., Vazhenin, S.V., & Lerch, Ya.V. (2009). Computer Nanotechnology («CompNanoTech»). *The Russian Federation Certificate of State Registration of Computer Program. No. 2009613043.*

7 Beznosyuk, S.A., Terenteva, Yu.V., Maslova, O.A., Zhukovsky, M.S., & Volkov, D.A. Attosecond nanotechnology: quantum dots of nanoelectromechanical systems of $CuIn_xGa_{1-x}Se_2$ compounds (2016). *AIP Conf. Proc., 1783*, 020015-1–020015-5. DOI: 10.1063/1.4966308

Д.А. Волков, Ю.В. Терентьева, С.А. Безносюк

Аттосекундты нанотехнологиялар: $CuIn_xGa_{1-x}S_2$ қосылысының наноэлектрмеханикалық жүйелерінің кванттық нүктелері

Мақалада халькопирит $CuIn_xGa_{1-x}S_2$ (CIGS) торы негізіндегі қатты ерітінділердің наноэлектрмеханикалық жүйе (НЭМЖ) күйіндегі термодинамикалық тұрақтылығы мен ішкі энергия өзгерісі зерттелді. Берілген заттар қуаттылығы жоғары фототүрлендіргіш жасауда тиімді болып есептелді. $CuIn_xGa_{1-x}S_2$ құрамды фототүрлендіргіштің максималды тиімділігі 21 % көрсетті, ал кремний негізіндегі ең жақсы фототүрлендіргіштің көрсеткіші 15 % ғана құрайды, бұл берілген құрамдағы зерттеудің өзектілігін көрсетеді. Зерттеу жұмысында ішкі энергия көрсеткіштері, нөлдік тербеліс, жиілік, тепе-теңдік байланыс ұзындықтарының шамалары берілген. Әртүрлі температура кезіндегі ішкі энергия көрсеткіштерінің өзгерісі және наноқабаттардың тұрақты жүйесіндегі радиалды бу бойынша атомтардың таралу функциясының өзгерісі көрсетілген. CIGS НЭМЖ тұрақты наноқабаттары параметрлерінің қатысты өзгерісі жүйедегі индий атомдарының концентрациясына сызықты емес тәуелді екендігі анықталды. Бұндай жағдай In–S және Ga–S НЭМЖ энергиясы мен байланыс ұзындықтары шамаларының айырмашылығынан болатындығы көрсетілді.

Кілт сөздер: таралудың радиалды бу функциясы, жартылайөткізгіш, күн батареялары, наноэлектромеханикалық жүйелер, графалар, Вегард ережесі.

Д.А. Волков, Ю.В. Терентьева, С.А. Безносюк

Аттосекундные нанотехнологии: квантовые точки наноэлектромеханических систем соединений $CuIn_xGa_{1-x}S_2$

В статье изучены термодинамическая стабильность и изменчивость внутренней энергии твердых растворов непрерывного замещения на основе решетки халькопирита $CuIn_xGa_{1-x}S_2$ (CIGS) в состоянии наноэлектромеханической системы (НЭМС). Данные вещества наиболее эффективны для создания фотопреобразователей максимальной мощности. Максимальная эффективность фотопреобразователя на основе состава $CuIn_xGa_{1-x}S_2$ была достигнута до 21 %, в то время как лучший фотопреобразователь на основе кремния мог достигать только 15 %, что подчеркивает актуальность исследования данного состава. В ходе работы представлены значения внутренней энергии, частоты нулевых колебаний и длины равновесной связи. Показаны изменения внутренней энергии при разных температурах и функций распределения атомов по радиальным парам в устойчивой системе нанослоев. Выявлено, что относительное изменение параметров стабильных нанослоев НЭМС CIGS нелинейно зависит от концентрации атомов индия в системе. Показано, что такое поведение является следствием существенного различия в энергии и длине связей НЭМС In–S и Ga–S в первой координационной сфере атомов серы.

Ключевые слова: радиальная парная функция распределения, полупроводник, солнечные батареи, наноэлектромеханическая система, графы, правило Вегарда.

DOI 10.31489/2019Ch3/68-75

UDC 543.552

A.O. Gusar, Ye.V. Dorozhko, K.V. Dyorina, Ye.I. Korotkova

Tomsk Polytechnic University, Russia
(E-mail: anngsa@mail.ru)

Modification of carbon containing electrodes by aryldiazonium iodate salts for electroanalysis

In the work the method of spontaneous chemical modification of a glassy carbon electrode (GCE) with aryl diazonium iodate salts was studied. The adsorption of modifier from the solution was applied for GCE modification. The modification effectiveness assessment was performed for different modifiers under the conditions of modifier concentration varying and the time of electrode keeping in the solution. The cyclic voltammograms of the reversible pair $[Fe(CN)_6]^{3-/4-}$ were recorded in the background KCl 0.5 M electrolyte. Modifier surface layers form spontaneously without the application of potentials. The control of thickness and the conductive characteristics of the modified electrode were performed by the adjusting of concentration and the keeping time of the electrode in modifier solution. It has been established that the oxidation and reduction currents of $[Fe(CN)_6]^{3-/4-}$ are maximum for the 4-carboxybenzodiazonium iodate modifier of GCE with a concentration of 10 $mg \cdot l^{-1}$ when the time of keeping the electrode in its solution is for 5 seconds. The increasing of the reversible pair $[Fe(CN)_6]^{3-/4-}$ current in the indicated conditions after the modification of 4-carboxybenzodiazonium iodate is associated with an increase in the area of the electroactive electrode surface, by almost 2.5 times. The study of the morphology of the electrode surface of the GCE by the method of scanning electrode microscopy confirmed the presence of a polylayer modifier with a carboxy substituent on the surfaces of a glassy carbon electrode. To confirm the presence of organic functional groups of the 4-carboxybenzodiazonium iodate modifier on the surfaces of the GCE, the reflection spectra of the electrode surfaces were obtained by IR spectroscopy. The method of modifying the GCE with iodate salts of aryldiazonium is simple, rapid, has low costs, and can be used to increase the sensitivity of determining a number of analytes in electroanalyses.

Keywords: aromatic diazonium salts, modifiers, glassy carbon electrode, cyclic voltammetry, IR spectroscopy, SEM (scanning electron microscopy), potassium ferrocyanide, spontaneous formation of modifier layer.

Introduction

The search for novel electrode materials and surface modifiers, which provide the necessary level of analytical and metrological characteristics, is on cutting edge of electroanalytical chemistry. One of such materials are the aromatic salts of diazonium (ASD), because as a result, materials with desired properties are formed, which are used in various fields of activity (medicine, analytical chemistry, polymer chemistry, biochemistry, etc.) [1–9].

Therefore, ASD are promising electrode modifiers for electroanalysis [9]. As a result of the modification, new electrode materials are used both for the electrochemical biosensors formation, where the ASD serves as a linker [10], and as organo-modified electrodes for the quantitative determination of biologically active substances in different objects [11, 12].

Currently, there are two fundamental approaches to modifying the ASD electrode surfaces: the adsorption method with the formation of weak physical bonds [13–17] and the method of strong covalent bond formation between the surface and the organic molecule [18–21], which simplifies the control of modification process and provides the higher selectivity of further surface transformations of functional groups [22, 23]. It is known that the implementation of the second modification method is carried out using two approaches: the electrochemical modification [24] and the chemical or spontaneous modification [25].

Electrochemical reduction of ASD [26] is an attractive method that was implemented for carbon electrode materials [27]. However, the issue of controlling the thickness of an organic modifier layer while maintaining the conductive properties is controversial, since in most cases, electrochemical modification results in the rapid formation of ASD multilayer, which reduce the activity of the electrode surface. The electrographing mechanism of diazonium salts is well known and detailed described in the work [28]. The mechanism involves the generation of aryl radicals, followed by the binding of these radicals to the surface via carbon-carbon bonds [29].

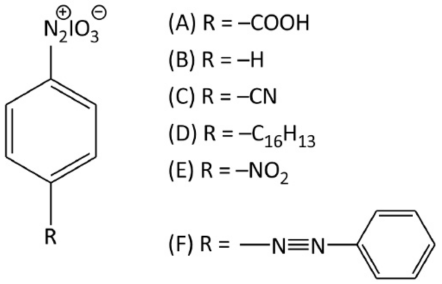
There is a number of works concerned with the spontaneous modification of carbon-containing electrodes. The authors note the simplicity of the spontaneous method of modifying carbon-containing electrodes with obtaining thinner and conductive mono [28] or poly [30] layers of ASD modifiers. Generally, the procedure for modifying the electrodes of an ASD consists of simply immersing the electrode for a certain time in the solutions of the ASD. However, the issue of controlling the thickness of the modifier layer depending on the concentration of the modifier and the time the electrode is kept in the appropriate solution remains controversial.

In the work, the electrochemical properties of GCE when modifying aryldiazonium iodate salts with different functional groups are studied. For the selection of optimal conditions for the spontaneous chemical modification of the GCE, a series of concentrations of 10, 30, 60 $mg \cdot l^{-1}$ and a holding time of 2, 5, 10, 30, 60, 120 seconds were chosen. In order to assess the optimal conditions for modifying the GCE in various modifiers, under conditions of varying their concentration and time of maintaining the GCE, cyclic voltammograms of the reversible pair $[Fe(CN)_6]^{3-/4-}$ were recorded in a background KCl electrolyte of 0.5 M. on the electrically conductive properties of the electrode surface of the GCE. With respect to each modifier, the conditions for spontaneous chemical modification, such as time and concentration, are different. To characterize the surfaces of the electrodes before and after modification, the methods of scanning electron microscopy and IR spectroscopy were used.

Experimental

The following iodate salts of aryldiazonium were chosen as modifiers of the electrode surfaces of the GCE: $[HOOCC_6H_4N_2]IO_3$, $[NCC_6H4N_2]IO_3$, $[O_2NC_6H_4N_2]IO_3$, $[C_6H_5N_2]IO_3$, $[H_{33}C_{16}C_6H_4N_2]IO_3$, $[H_4C_6N_2C_6H_4N_2]IO_3$. Their structures are depicted in Figure 1. All reagents were of analytical grade. The water was obtained by water purification system Milli-Q Direct; water resistivity was 18.2 MΩ cm. Silver chloride electrodes were used as auxiliary electrode and reference electrode.

To select the optimal conditions for the spontaneous modification of GCE with aryldiazonium iodate salts, the concentration of the modifier ($mg \cdot l^{-1}$) and the time of aging of the GCE in the solutions of the corresponding modifiers (sec) were varied. The working concentrations of diazonium salt solutions for modification were 10, 30, 60 $mg \cdot l^{-1}$. The holdup time of GCE in the solutions of the modifiers was 2, 5, 10, 30, 60, 120 seconds. To evaluate the reversibility of electrode processes on the GCE, cyclic voltammograms of hexacyanoferrate salts $[Fe(CN)_6]^{3-/4-}$ of concentration 0.25 M (background 0.5 M KCl) were recorded before and after chemical modification.



A — 4-carboxybenzodiazonium iodate;
B — iodate aryldiazonium;
C — 4-cyanobenzodiazonium iodate;
D — 4-hexadecylbenzodiazonium iodate;
E — 4-nitrobenzodiazonium iodate;
F — 4-(phenyldiazenyl)benzodiazonium iodate

Figure 1. Structural formulas of aryldiazonium salts

A universal electrochemical workstation TA-2 (Tomanalyt, Tomsk, Russian Federation) with a three electrode cell was used. Silver chloride electrodes and glassy carbon electrodes for modification were purchased from LLC Tomanalyt (Tomsk, Russian Federation). Investigations of the cutoffs of the electrode were carried out using a scanning (raster) electron microscope JEOL JSM-7500FA. To confirm the presence of organic functional groups on the glassy carbon electrode surface, IR reflection spectra were obtained. The investigations were carried out using the Cary 660 IR spectrometer (manufactured by Agilent).

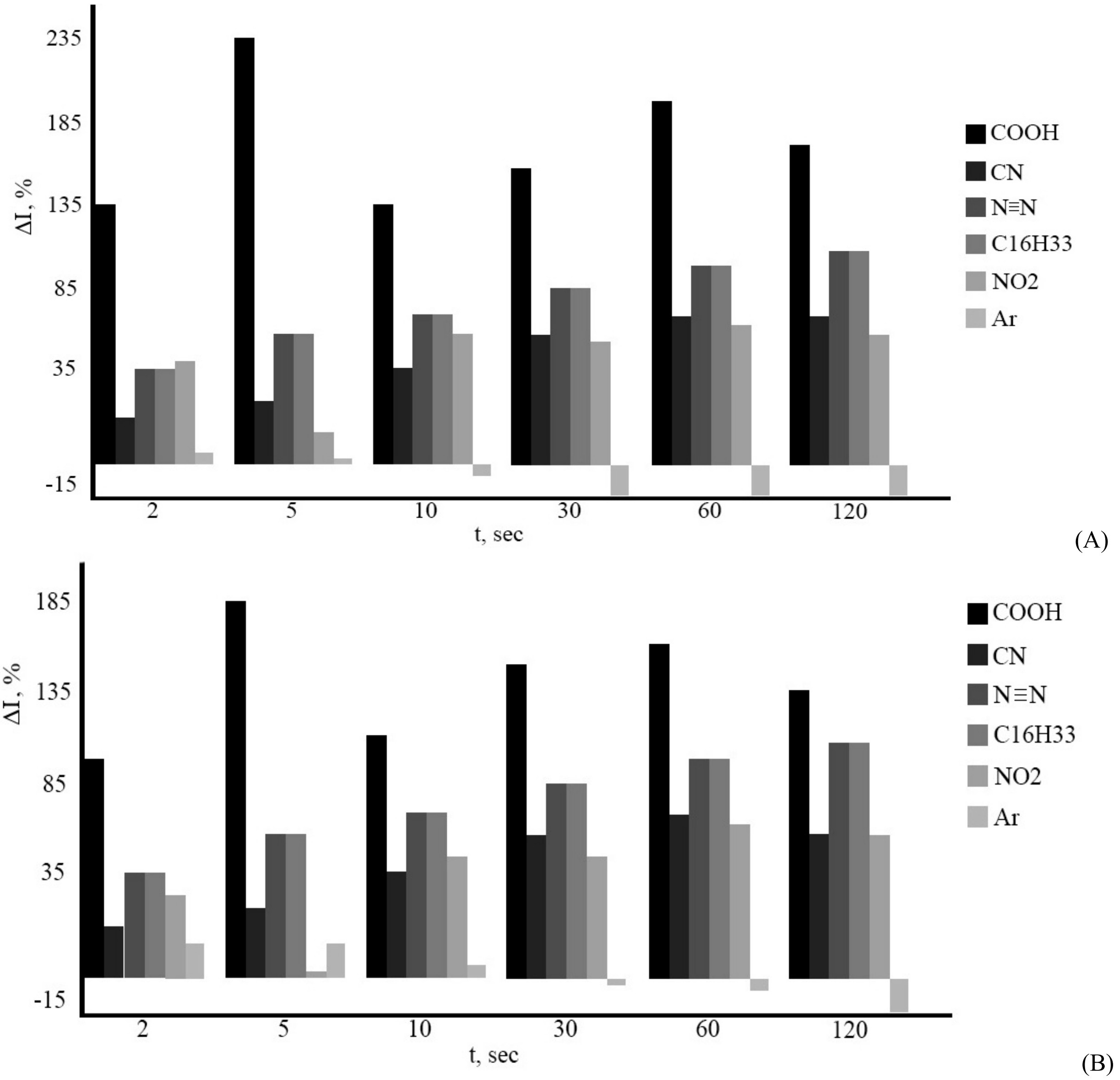
Results and Discussion

To assess the effectiveness of modifying GCE with different modifiers under the conditions of changing the concentration of the modifier and the time of aging of the GCE, the value of ΔI (%) was calculated:

$$\Delta I \frac{(I_1 - I_0)}{I_0} \cdot 100 ,$$

where I_0 is current of $[Fe(CN)_6]^{3-/4-}$ without modifier; I_1 is current of $[Fe(CN)_6]^{3-/4-}$ after aging in the solution of the modifier.

In the course of the study (Fig. 2), it was established that the oxidation and reduction currents of $[Fe(CN)_6]^{3-/4-}$ are maximal for 4-carboxybenzodiazonium iodate of the GCE modifier at the time of holding the electrode in its solution for 5 seconds and the modifier concentration 10 mg·l^{-1} (ΔI = 230 % cathode scan and ΔI = 185 % anode scan).

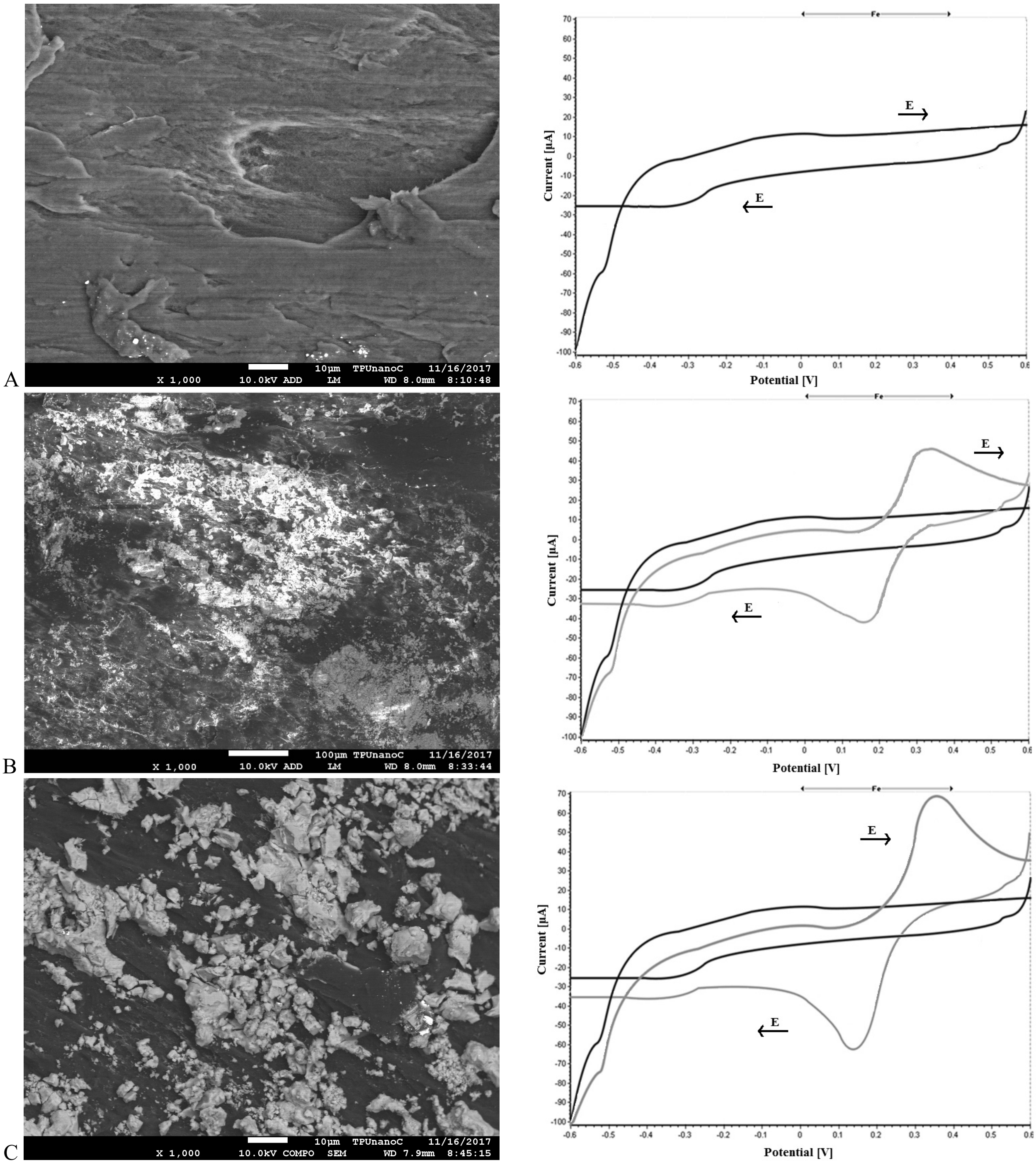


A — cathode currents; *B* — anode currents. The background electrolyte is KCl 0.5 M;
scan rate 80 mV·s^{-1}; concentration 10 mg·l^{-1}

Figure 2. Dependence of the change in the currents of $[Fe(CN)_6]^{3-/4-}$ (ΔI, %) on the time of aging of GCE in the solution of the aryl diazonium iodate salts modifiers

To prove the presence of 4-carboxybenzodiazonium iodate on the surface of the GCE, microscopes of the surfaces of the electrodes were taken before and after the modification by scanning electron microscopy (Fig. 3).

The first sample is the surface of pure GCE, before the reversible $[Fe(CN)_6]^{3-/4-}$ pair is added to the cell. On the sample surface, selective microporosity is observed (Fig. 3A). The pore size does not exceed 10 µm. On the surface there is a slight contamination with an extraneous phase, which has the form of globular particles. Presumably, this phase is a particle of salt, which is part of the background electrolyte. The second sample is the surface of the GCE after introducing a reversible $[Fe(CN)_6]^{3-/4-}$ pair into the cell.



A — GCE without a modifier; *B* — GCE after the addition of the reversible $[Fe(CN)_6]^{3-/4-}$ pair to the cell;
C — GCE after modification of the solution of the 4-carboxybenzodiazonium iodate modifier (10 $mg \cdot l^{-1}$) for 5 sec

Figure 3. Scanning electron microscopy of GCE surfaces and corresponding cyclic voltamograms

On a microscopic photograph, $[Fe(CN)_6]^{3-/4-}$ aggregates are observed on the surface of the electrode, covering the micropores of glassy carbon. Areas with inclusions of a spherical shape are observed (Fig. 3*B*). Presumably, this phase corresponds to iron-containing hexacyanoferrate. The third sample is the surface of the GCE after modification of 4-carboxybenzodiazonium iodate (10 $mg \cdot l^{-1}$ for 5 seconds).

On a microscopic image (Fig. 3*C*), laminated aggregates of irregular shape are observed confirming the flow of adsorption on the surface of the electrode substrate, which proves the fact of the chemical reaction on the GCE surface between the carbon and the diazonium modifier. It is obvious that a covalent modification of the GCE is possible without imposing a potential in a very short period of time. In addition, after the modification, the current-conducting properties of the SEM are increased due to an increase in the currents of the reversible $[Fe(CN)_6]^{3-/4-}$ pair at the potentials of 0.15 V and 0.35 V under the optimum modification conditions.

From the cyclic voltammograms of the reversible pair $[Fe(CN)_6]^{3-/4-}$, the electroactive surface areas of the electrodes were calculated before modification and after according to the Randles-Shevchik equation (Table):

$$Ip = \pm 2.69 \times 10^5 z^{3/2} A D^{1/2} C W^{1/2},$$

Ip — peak current, A; z — the number of electrons ($n = 1$); A — the area of the electroactive surface, cm^2; D — the diffusion coefficient (7.60×10^{-6} cm^2/s); C — concentration $[Fe(CN)_6]^{3-/4-}$ in solution ($1\cdot10^{-3}$M).

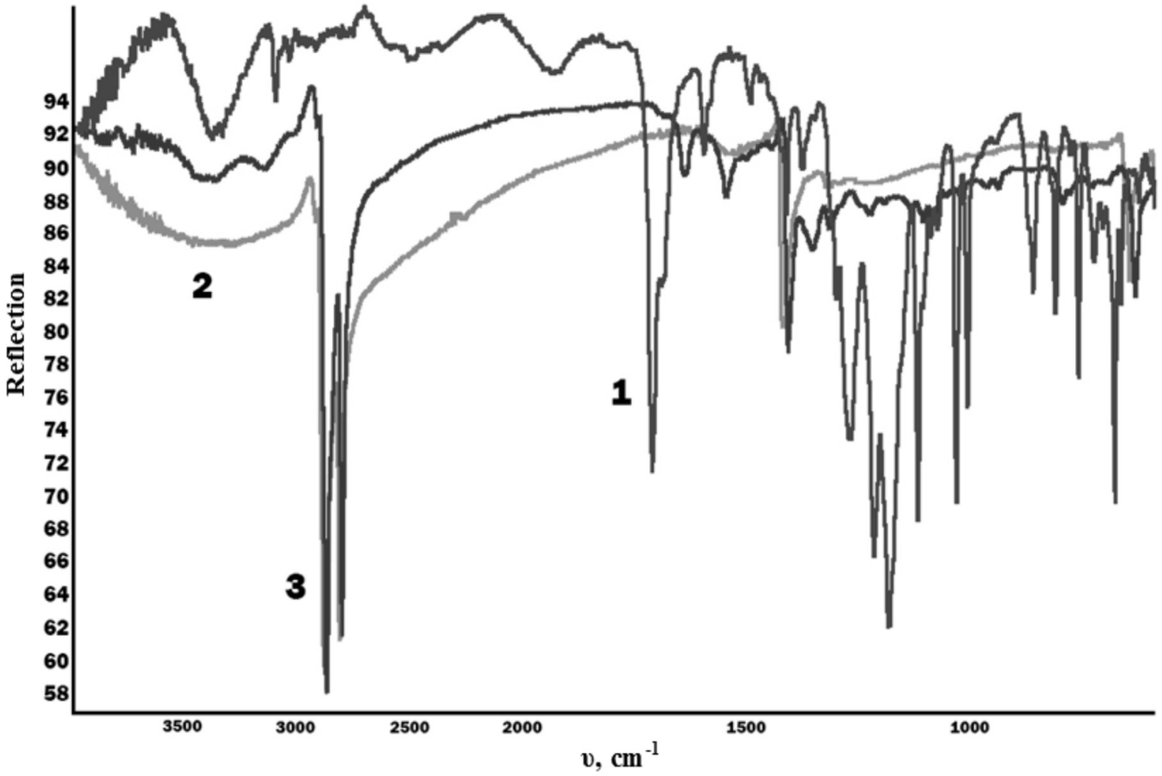
Table

Areas of the electroactive surface of the GCE (cm^2) before modification and after modification

Square electroactive surface of the GCE before modification, cm^2	Square electroactive surface of the GCE after modification, cm^2
0.00452	0.01054

As a result of modifying the GCE using the spontaneous chemical modification method with a carboxy substituent (modifier concentration 10 mg·l^{-1}, aging time 5 seconds), the area of the electroactive surface increases almost 2.5 times, which leads to an increase in the cathodic and anodic currents of the reversible $[Fe(CN)_6]^{3-/4-}$ with respect to the unmodified surface of the GCE.

To further confirm the presence of organic functional groups on the GCE surface, IR reflection spectra (Fig. 4) were obtained: 1) 4-carboxybenzodiazonium iodate modifier with a concentration of 10 mg·l^{-1}; 2) the initial surface of the GCE; 3) the surface of the glassy carbon electrode after modification. The absorption bands at 3659, 1685, 1590, 1710, 878 cm^{-1}, corresponding to the carboxyl group and the phenyl nucleus are observed in the spectrum.



1 — modifier4-carboxybenzodiazonium iodate (c = 10 mg·l^{-1}); *2* — the initial surface of the GCE;
3 — surface of the glassy carbon electrode after modification.

Figure 4. The transmission spectrum of the IR surface of the GCE

If the balance between the concentration of the modifier and the modification time with respect to each modifier is not observed, blocking of the conductive surfaces of the GCE and reduction of the cathodic and anodic currents $[Fe(CN)_6]^{3-/4-}$ is observed.

The phenomena of uncontrolled growth of polylayer modifiers on carbon-containing electrodes, leading to blocking of conductive surfaces after the application of potentials, are described in the literature [28, 29].

Moreover, the mechanism of the formation of different structures of polylayer modifiers is not fully understood. We noted that the growth of modifier polylayers occurs without the application of potentials under conditions of spontaneous adsorption.

Controlling the thickness and, accordingly, the conductive characteristics of the GCE is possible by adjusting the concentration and the holding time of the electrodes with respect to modifiers of different nature, which is confirmed by the data in Figure 2.

For different nature modifiers having a concentration of $10\ mg \cdot l^{-1}$, modification time was: $[HOOCC_6H_4N_2]IO_3$ — 5 seconds, $[NCC_6H_4N_2]IO_3$ — 60 seconds, $[O_2NC_6H_4N_2]IO_3$ — 60 seconds, $[C_6H_5N_2]IO_3$ — 5 seconds, $[H_{33}C_{16}C6H4N2]IO_3$ — 120 seconds, $[H_4C_6\ N_2C_6H_4N_2]IO_3$ — 120 seconds.

Conclusions

Thus, it has been established that $[HOOCC_6H_4N_2]IO_3$ is used as an electrode modifier for the GEC. The optimal modification conditions are a concentration of $10\ mg \cdot l^{-1}$, a holding time of 5 seconds. As a result of the modification of a GCE using the method of spontaneous chemical modification with salts of an ASD with a carboxy substituent, the area of the electroactive surface increases almost 2.5 times. The presence of organic functional groups of the 4-carboxybenzodiazonium iodate modifier on the surfaces of the GCE has been confirmed by SEM IR spectroscopy. Controlling the thickness and, accordingly, the conductive characteristics of the GCE is possible, by adjusting the concentration and the holding time of the electrodes with respect to modifiers of different nature. The method of modifying the GCE with iodate salts of aryldiazonium is simple, rapid, economical, and can be used to increase the sensitivity of the determination of a number of analytes in electroanalysis.

References

1 Otsuka, H., Nagasaki, Y., & Kataoka, K. (2003). PEGylated nanoparticles for biological and pharmaceutical applications. *Adv. Drug Deliv. Rev.*, *55*, 403–419.

2 Sanvicens, N., & Pilar, Marco M. (2008). Multifunctional nanoparticles — properties and prospects for their use in human medicine. *Trends in Biotech.*, *26*, 425–433.

3 Davis, M.E., Chen, Z., & Shin, D.M. (2008). Nanoparticles therapeutics: an emerging treatment modality for cancer. *Nat. Rev.*, *7*, 771–782.

4 Gooding, J.J. (2008). Advances in interfacial design for electrochemical biosensors and sensors: aryl diazonium salts for modifying carbon and metal electrodes. *Electroanalysis*, *20*, 573–582.

5 Pridgen, E.M., Langer, R., & Farokhzad, O.C. (2007). Biodegradable, polymeric nanoparticles delivery systems for cancer therapy. *Nanomedicine, 2*, 669–680.

6 Naka, K., Narita, A., Tanaka, H., Chujo, Y., Morita, M., & Inubushi, T. et.al. (2008). Biomedical applications of imidazolium cation-modified iron oxide nanoparticles. *Polym. Adv. Technol., 19*, 1421–1429.

7 Schrand, A.M., Ciftan Hens, S.A., & Shenderova, O.A. (2009). Nanodiamond particles: properties and perspectives for bioapplications. *Critical reviews in solid state and materials sciences*, *34*, 18–74.

8 Polsky, R., Harper, J.C., Wheller, D.R., Arango, D.C., Brozik, S.M. (2008). Electrically addressable cell immobilization using phenylboronic acid diazonium salt. *Angew. Chem. Int. Ed.*, *47*, 2631–2634.

9 Delamar, M., Hitmi, R., Pinson, J., & Saveant, J.M. (1992). Covalent modification of carbon surfaces by grafting of functionalized aryl radicals produced from electrochemical reduction of diazonium salts. *J. Am. Chem. Soc., 114,* 5883–5884.

10 Md. Mohibul Islam Khan, Mithrabinda K. Poduval, Tae-Hyun Kim, & Kyuwon Kim. (2015). Dually electroactive disulfide-confined aryldiazonium salt used as a linker molecule for preparing immunosensor platforms. *Electroanalysis*, *27*, 1952–1959.

11 Liu, G., & Gooding, J.J. (2006). An interface comprising molecular wires and poly(ethylene glycol) spacer units self-assembled on carbon electrodes for studies of protein electrochemistry. *Langmuir*, *22*, 7421–7430.

12 Nassef, H.M., Civit, L., Fragoso, A., & O'Sullivan, C.K. (2008). Amperometric sensing of ascorbic acid using a disposable screen-printed electrode modified with electrografted o-aminophenol film. *Analyst*, *133*, 1736–1741.

13 Belder, D., & Ludwig, M. (2003). Surface modification in microchip electrophoresis. *Electrophoresis*, *24*, 3595–3506.

14 Huang, H., Pierstoff, E., Osawa, E., & Ho, D. (2007). Active nanodiamond hydrogel for chemotherapeutic delivery. *Nano Lett.*, *7*, 3305–3314.

15 Wan, S., Huang, J., Guo, M., & Zhang, H. (2006). Biocompatible superparamagnetic iron oxide nanoparticle dispersions stabilized with poly(ethylene glycol)-oligo(aspartic acid) hybrids. *Journal of Biomedical Materials Research Part A*, *80*, 946–954.

16 Ackerson, C.J., Sykes, M.T., & Kornberg, R.D. (2010). Defined DNA/nanoparticles conjugates. *PNAS*, *102*, 13383–13385.

17 Lemarchand, C., Gref, R., & Couvreur, P. (2004). Polysaccharide-decorated nanoparticles. *Eur. J. Pharm. Biopharm*., *58*, 327–341.

18 Alexis, F., Basto, P., Levy-Nissenbaum, E., Radovic-Moreno, A.F., Zhang, L., & Pridgen, E. et.al. (2008). HER-2-targeted nanoparticle affibody bioconjugates for cancer therapy. *ChemMedChem*, *3*, 1839–1843.

19 Kato, K., Sato, H., & Iwata, H. (2005). Immobilization of histidine-tagged recombinant proteins onto micropatterned surfaces for cell-based functional assays. *Langmuir*, *21*, 7071–7075.

20 Ma, Y., Yue, B. & Yu, L. (2008). Artificial construction of the magnetically separable nanocatalyst by anchoring nanoparticles on functionalized carbon-encapsulated nickel nanoparticles. *J. Phys. Chem. C*., *112*, 472–475.

21 Hong, S.Y., Tobias, G., Ballesteros, B., El Oualid, F., Errey, J.C., & Doores, K.J. et.al. (2007). Atomic-scale detection of organic molecules coupled to single-walled carbon nanotubes. *J. Am. Chem. Soc.*, *129*, 10966–10967.

22 Herrmann, I.K., Grass, R.N., & Stark, W.J. (2009). High-strength metal nanomagnets for diagnostics and medicine: carbon shells allow long-term stability and reliable linker chemistry. *Nanomedicine, 4*, 787–798.

23 Solanki, A., Kim, J.D., & Lee, K-.B. (2008). Nanotechnology for regenerative medicine: nanomaterials for stem cell imaging. *Nanomedicine, 3*, 567–578.

24 Harnisch, J.A., Gazda, D.B., Anderegg, J.W., & Porter, M.D. (2001). Chemical modification of carbonaceous stationary phases by the reduction of diazonium salts. *Anal. Chem., 73*, 3954–3959.

25 Chamoulaud, Gwenael & Be′langer, Daniel. (2007). Spontaneous derivatization of a copper electrode with in situ generated diazonium cations in aprotic and aqueous. *Media J. Phys. Chem. C., 111*, 7501–7507.

26 Downard, A.J. (2000). Electrochemically assisted covalent modification of carbon electrodes. Electroanalysis, *12*, 1085–1096.

27 Marcoux, P.R., Hapiot, P., Batail, P., & Pinson, J. (2004). Electrochemical functionalization of nanotube films: growth of aryl chains on single-walled carbon nanotubes. *New J. Chem*., *28*, 302–307.

28 Anariba, F., DuVall, S.H., & McCreery, R.L. (2003). Mono- and multilayer formation by diazonium reduction on carbon surfaces monitored with atomic force microscopy «Scratching». *Anal. Chem*, *75*, 3837.

29 Bernard, M.C., Chausse, A., Cabet-Deliry, E., Chehimi, M.M., Pinson, J., Podvorica, F., & Vautrin-Ul, C. (2003). Organic layers bonded to industrial, coinage, and noble metals through electrochemical reduction of aryldiazonium salts. *Chem. Mat., 15*, 3450.

30 Kariuki, J.K., & McDermott, M.T. (1999). Nucleation and growth of functionalized aryl films on graphite electrodes. *Langmuir, 15*, 6534.

А.О. Гусар, Е.В. Дорожко, К.В. Дёрина, Е.И. Короткова

Көміртекқұрамды электродтарды арилдиазонийдің йодты тұздары арқылы электрталдау үшін модификациялау

Мақалада шыныкөміртекті электродты (ШКЭ) арилдиазонийдің йодты тұздарымен химиялық модификациялау әдісі зерттелді. ШКЭ модификациялау сәйкес тұздарының ерітінділерінен адсорбциялау арқылы жүргізілді. ШКЭ модификациялаудың тиімділігін бағалау үшін әртүрлі модификаторлармен олардың концентрациялары және ШКЭ ұстау уақыты өзгеруі жағдайларында, KCl 0.5 M фонды электролитінде $[Fe(CN)_6]^{3-/4-}$ қайтымды жұптың циклді вольтамперограммалары жазылды. Модификаторлардың полиқабаттарының өсуі спонтанды адсорбция жағдайларында потенциалдарының қабаттасуысыз жүреді. ШКЭ қалыңдығын және сәйкесінше тоқ өткізетін сипаттамаларым басқару концентрацияларын реттеу және табиғаты әртүрлі модификаторларға қатысты электродтардың ұсталу уақытын реттеу арқылы мүмкін болады. $[Fe(CN)_6]^{3-/4-}$ тотығу және тотықсыздану тоқтары 4-карбоксибензодиазониум йодаты ШКЭ модификаторы үшін оның концентрациясы 10 мг·л$^{-1}$ және оны ерітіндіде ұстау уақыты 5 с болғанда максималды болатыны анықталды. Қайтымды жұптың $[Fe(CN)_6]^{3-/4-}$ тоқтары артқанда көрсетілген жағдайларда 4-карбоксибензодиазониум йодатының модификациялануынан кейін ұдайы электродтың электрбелсенді бетінің аумағы 2,5 есеге дейін артуымен байланысты. ШКЭ электродты бетінің морфологиясын сканерлейтін спонтанды микроскопия әдісімен зерттеу шыныкөміртектік электрод беттерінде карбоксиорынбасушысы бар модификатордың полиқабаттары бар екенін дәлелдеді. Органикалық функционалды топтарының 4-карбоксибензодиазониум йодат модификаторының құрамында болуын дәлелдеу үшін ШКЭ беттерінде ИҚ-спектроскопия әдісімен электродты беттерінің шағылысу спектрлері жазылды. ШКЭ арилдиазонийдің йодатты тұздарымен модификациялау әдісі қарапайым, үнемді және электрталдауда аналиттер қатарын анықтау сезімталдығын арттыру үшін қолданылуы мүмкін.

Кілт сөздер: диазонийдің ароматты тұздары, модификаторлар, шыныкөміртектік электродтар, циклді вольтамперометрия, ИҚ-спектроскопия, СЭМ (сканерлейтін электронды микроскопия), калийдің гексацианоферраты.

А.О. Гусар, Е.В. Дорожко, К.В. Дёрина, Е.И. Короткова

Модификация углеродсодержащих электродов посредством йодистых солей арилдиазония для электроанализа

В статье изучен способ спонтанной химической модификации стеклоуглеродного электрода (СУЭ) йодатными солями арилдиазония. Модификация СУЭ проводилась адсорбцией из раствора соответствующих солей. Для оценки эффективности модифицирования СУЭ разными модификаторами в условиях изменения их концентрации и времени выдерживания СУЭ были записаны циклические вольтамперограммы обратимой пары $[Fe(CN)_6]^{3-/4-}$ в фоновом электролите KCl 0.5 М. Рост полислоев модификаторов происходит без наложения потенциалов в условиях спонтанной адсорбции. Управление толщиной и соответственно токопроводящими характеристиками СУЭ возможно путем регулирования концентрации и времени выдерживания электродов в отношении разных по природе модификаторов. Установлено, что токи окисления и восстановления $[Fe(CN)_6]^{3-/4-}$ максимальны для модификатора 4-карбоксибензодиазониум йодата СУЭ с концентрацией 10 $\text{мг}\cdot\text{л}^{-1}$при времени выдерживания электрода в его растворе в течение 5 с. Увеличение токов обратимой пары $[Fe(CN)_6]^{3-/4-}$в указанных условиях после модификации 4-карбоксибензодиазониум йодата связано с увеличением площади электроактивной поверхности электрода почти в 2,5 раза. Исследования морфологии электродной поверхности СУЭ методом сканирующей электродной микроскопии подтвердили наличие полислоя модификатора с карбоксизаместителем на поверхностях стеклоуглеродного электрода. Для подтверждения наличия органических функциональных групп модификатора 4-карбоксибензодиазониум йодата на поверхностях СУЭ получены спектры отражения электродных поверхностей методом ИК спектроскопии. Способ модификации СУЭ йодатными солями арилдиазония прост, экономичен и может быть использован для увеличения чувствительности определения ряда аналитов в электроанализе.

Ключевые слова: ароматические соли диазония, модификаторы, стеклоуглеродные электроды, циклическая вольтамперометрия, ИК-спектроскопия, СЭМ (сканирующая электронная микроскопия), гексацианоферрат калия.

DOI 10.31489/2019Ch3/76-82

UDC 546.244: 542.91 + 539.26

K.T. Rustembekov, M.S. Kasymova, Ye.V. Minayeva, D.A. Kaikenov

Ye.A. Buketov Karaganda State University, Kazakhstan
(E-mail: rustembekov_kt@mail.ru)

Synthesis, X-ray and quantum-chemical investigations of double tellurites of holmium

Complex oxide phases, namely new double tellurites of holmium with the composition $HoMe^{II}TeO_{4.5}$ (where Me^{II} — Sr, Ba) were synthesized with the ceramic technology from Ho(II), Te(IV) oxides and carbonates $SrCO_3$, $BaCO_3$ in the range of 800–1200 ºC. For the first time the structure of tellurites was investigated by X-ray phase analysis. X-ray phase analysis was performed on the DRON-2.0 device. The intensity of the diffraction peaks was estimated on a stable scale. Radiographs of the synthesized powders were indicated by the homology method. The type of syngony, unit cell parameters, radiographic and pycnometric tellurite densities were determined. $HoSrTeO_{4.5}$: $a = 14.50$; $b = 14.05$; $c = 9.04$Å; $\rho_{roent.} = 3.73$; $\rho_{pycn.} = 3.59 \pm 0.04$ g/cm^3; $HoBaTeO_{4.5}$: $a = 12.10$; $b = 5.49$; $c = 11.49$Å; $\rho_{roent.} = 4.07$; $\rho_{pycn.} = 3.93 \pm 0.06$ g/cm^3. The correctness of the results of indexing radiographs of tellurites is confirmed by the good agreement between the experimental and calculated values of the reciprocal values of the squares of interplanar distances ($10^4/d^2$) and the consistency of the values of X-ray and pycnometric densities. It has been established that holmium tellurites are synthesized in monoclinic syngony and have a perovskite-like structure. Quantum-chemical calculations of the stable geometry of the synthesized tellurites were carried out using the Gaussian-2009 software package with the help of the UFF molecular method. In this case, equilibrium internuclear distances (long bonds) and bond angles are the parameters. Based on the results of quantum chemical calculations, models of the geometric structure of new holmium tellurites are presented.

Keywords: double holmium tellurites, X-ray phase analysis, syngony, lattice parameters, quantum chemical calculations, structure models.

Introduction

For a long time, the crystal chemistry of the phases of tellurium-containing oxides has been of interest to many scientists. This interest is caused, on the one hand, by the heterogeneity of the compounds based on the stereochemical activity of the lone electron pair of Te^{IV}, on the other hand, on this basis, assumptions related to the use of tellurites as new pyroelectric and nonlinear optical materials are caused.

Both tellurium dioxide (TeO_2) and selenium (SeO_2) dioxide are widely used in the synthesis of many new solid-state materials due to their lower melting point and triple points (733 for TeO_2, 340 for SeO_2), respectively. These available temperatures allowed them to be used for crystal growth [1]. In addition, the excellent reactivity of TeO_2 and SeO_2 allowed them to be used in the formation of many new oxide materials. Variable coordination media of the Te^{4+} and Se^{4+} cations are also of particular interest. In particular, they demonstrate many structural motives, such as the trigonal pyramid and the square pyramid. If various coordination geometries are combined with other multi-faceted fragments, a greater flexibility of the architecture of the structure is possible. Finally, Te^{4+} and Se^{4+} cations, by their nature, have an asymmetric structural geometry related to an unbound electron pair.

Non-centrosymmetric (NCS) materials are of current and technological interest due to their generation of the second harmonic (SHG), piezoelectric, ferroelectric, and pyroelectric properties [2–5]. With oxide materials, structures (NCS) are often observed in materials that contain second-order Jan-Teller distorting cations, octahedral coordinated d^0 transition metal ions (Ti^{4+}, V^{5+}, W^{6+}, etc.) and single pairs of cations (Se^{4+}, Te^{4+}, I^{5+} etc.) [1].

In accordance with these postulates, new double and triple tellurites of a number of *s*-, *d*- and *f*-elements have been synthesized as promising substances with multifunctional properties and their X-ray, thermodynamic and electrophysical properties have been studied at the Department of Inorganic and Technical Chemistry of Buketov Karaganda State University [6–9]. Research in this direction continues.

The aim of this work is the synthesis, X-ray and quantum-chemical studies of new phases of double tellurites of the composition $HoMeIITeO_{4.5}$ (Me^{II} — Sr, Ba).

Experimental

Solid-phase synthesis of compounds was carried out by the method of ceramic technology from holmium (III) oxides of the reagent grade, tellurium (IV) and carbonates of strontium and barium of the analytical grade. Pre-dehydrated at 40 ºC stoichiometric amounts of precursors were thoroughly mixed, ground in an agate mortar. Then, they were annealed in alundum crucibles in the SNOL furnace first at 800 ºC for 20 hours, with periodic grinding in a mortar, then at 1200 ºC for 23 hours, then the mixtures were cooled, mixed, and thoroughly triturated. Low-temperature annealing of the compositions was carried out at a temperature of 400 ºC also for 20 hours.

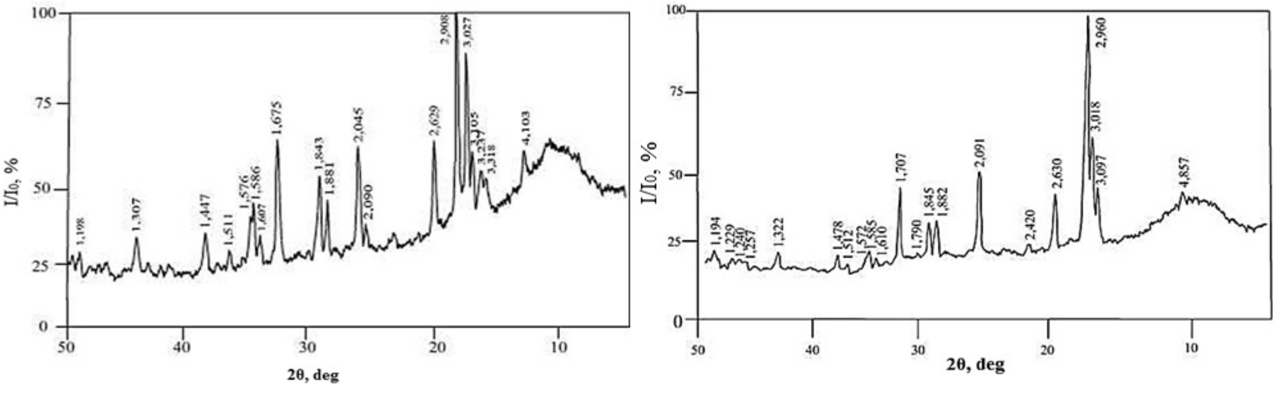
X-ray diffraction investigations of the new phases synthesized were carried out on a DRON-2.0 diffractometer (CuKα-radiation, Ni-filter, $U = 30$ kV, $I = 10$ mA, counter rotation velocity 2 rpm, scale range 1000 imp/s, $\tau = 5$ s, $2\theta = 10$–90º). The intensity of the diffraction peaks was estimated on a 100-point scale. The radiographs of the obtained compounds were indexed by the homology method [10].

The improvement of the computational technologies of modern quantum chemistry led to the creation of powerful commercial software products by individual companies, among which the company Gaussian (USA) founded by John A. Pople stands out. The program «Gaussian-2009» is the latest development from the Gaussian product series. This package of modeling electronic structures is used for developments in the field of chemistry and biochemistry, physics, and other developing fields related to chemical processes [11]. Quantum-chemical calculations of the stable geometry of the synthesized tellurites were carried out using the Gaussian-09 software package with the help of the UFF molecular mechanics method.

Results and Discussion

Each crystalline substance is characterized by its lattice, a certain chemical composition and a certain distribution of atoms in the unit cell of the lattice. The lattice geometry determines the set of interplanar distances (consequently, the Bragg angles θ during diffraction at a given radiation). The individuality and distribution of atoms determines the intensity of the diffracted rays. Qualitative X-ray phase analysis consists in the identification of crystalline phases on the basis of their inherent interplanar spacing $d_{(hkl)}$ values and the corresponding intensities of the $I_{(hkl)}$ lines of the x-ray spectrum.

Figure 1 shows radiographs of the holmium double tellurites synthesized.



a) $HoSrTeO_{4.5}$ *b*) $HoBaTeO_{4.5}$

Figure 1. Radiographs of the holmium double tellurites synthesized

The results of the X-ray indexing of the holmium tellurites synthesized are shown in Table 1.

Table 1

The results of indexing radiographs of holmium double tellurites

I/I_0, %	d, Å	$10^4/d^2_{exp.}$	hkl	$10^4/d^2_{calc.}$
$HoSrTeO_{4.5}$				
11	4.770	439	3 0 0	439
13	4.075	602	1 0 2	602
16	3.924	649	2 3 0	650
23	3.070	1061	4 1 1	1061
56	3.015	1100	1 0 –3	1100
100	2.813	1264	0 5 0	1264
31	2.774	1299	3 2 2	1300
10	2.625	1451	3 4 1	1452
35	2.429	1695	4 2 2	1694
20	2.357	1800	4 2 –3	1801
28	2.266	1947	0 6 1	1946
41	2.227	2016	2 6 0	2016
10	2.081	2309	3 6 –1	2308
21	2.030	2426	1 6 2	2424
17	2.025	2439	5 3 2	2440
7	1.958	2607	0 7 1	2604
14	1.873	2851	2 7 1	2852
14	1.830	2987	7 3 –2	2987
7	1.784	3144	0 0 5	3141
$HoBaTeO_{4.5}$				
6	4.857	424	2 0 1	424
24	3.097	1043	0 1 3	1042
48	3.018	1098	4 0 –1	1097
100	2.960	1141	3 1 1	1142
24	2.630	1446	1 2 –1	1446
5	2.420	1708	5 0 –1	1708
37	2.091	2287	2 1 –5	2287
16	1.882	2823	6 0 1	2824
17	1.845	2938	3 0 –6	2938
4	1.790	3121	5 2 –2	3120
34	1.707	3432	1 3 2	3433
5	1.610	3858	1 3 3	3858
9	1.585	3981	5 1 4	3981
5	1.572	4047	5 1 –6	4046
5	1.478	4578	2 0 7	4577
11	1.322	5722	8 2 –1	5722
11	1.257	6329	8 1 3	6328
4	1.248	6421	3 0 8	6421
5	1.223	6686	8 2 2	6686
5	1.194	7014	3 3 6	7014

Based on the X-ray indexing of the synthesized tellurites, it has been established that they crystallize in a monoclinic syngony (Table 2). The correctness of the results of indexing radiographs of tellurites is confirmed by the good agreement between the experimental and calculated values of the reciprocal values of the squares of interplanar distances ($10^4/d^2$) (Table 1), the consistency of the values of X-ray and pycnometric densities (Table 2). In addition, the type of syngony and the unit cell parameters of the compounds are also presented in Table 2.

Table 2

Syngony type and lattice parameters of HoSrTeO4.5 and HoBaTeO4.5

Compound	Syngony	Lattice parameters, Å			V^0, Å^3	Z	Density, g/cm^3	
		a	b	c			$\rho_{roent.}$	$P_{pycn.}$
$HoSrTeO_{4.5}$	monoclinic	14.50	14.05	9.04	1816.16	10	3.73	3.59±0.04
$HoBaTeO_{4.5}$	monoclinic	12.10	5.49	11.49	747.30	4	4.07	3.93±0.06

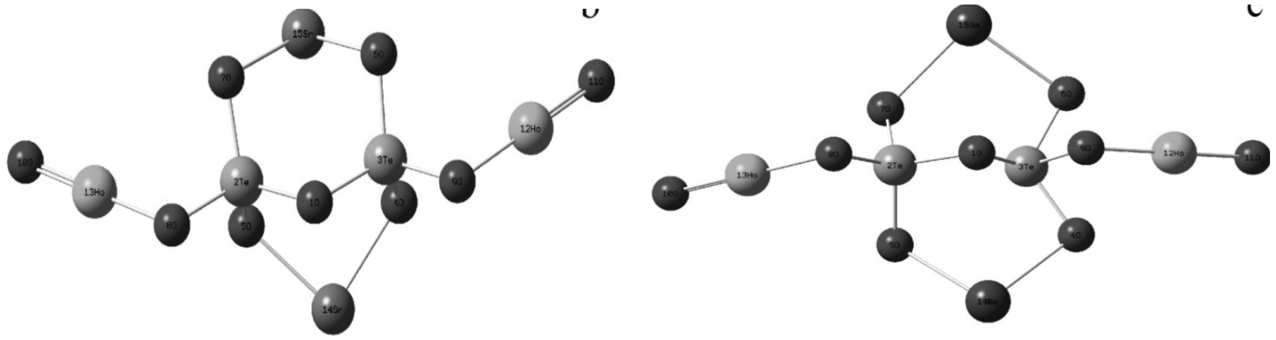
The X-ray data show that the tellurites synthesized crystallize in the distorted perovskite structural type P_m3_m. Therefore, it can be assumed that these compounds can possess valuable electrophysical properties [12]. The results of quantum chemical calculations of the geometry of the structure of holmium double tellurites are presented in Table 3.

Table 3

Basic geometric data of holmium double tellurites according to quantum chemical calculations

Bond	*d*, Å	Bond angle	ω, degree
$HoSrTeO_{4.5}$			
O (1) – Te (2)	2.033	Te (3) – O (1) – Te (2)	108
Te (3) – O (1)	2.033	O (4) – Te (3) – O (1)	112
O (5) – Te (2)	2.025	O (6) – Te (3) – O (1)	112
O (7) – Te (2)	2.024	O (5) – Te (2) – O (1)	112
O (4) – Te (3)	2.025	O (7) – Te (2) – O (1)	112
O (6) – Te (3)	2.024	Sr (15) – O (7) – Te (2)	104
Sr (15) – O (7)	2.533	Sr (14) – O (5) – Te (2)	105
Sr (14) – O (5)	2.533	O (8) – Te (2) – O (1)	107
O (9) – Te (3)	2.024	O (9) – Te (3) – O (1)	107
O (8) – Te (2)	2.024	Ho (12) – O (9) – Te (3)	104
Ho (12) – O (9)	2.211	Ho (13) – O (8) – Te(2)	104
Ho (13) – O (8)	2.211	O (11) – Ho (12) – O (9)	180
O (10) – Ho (13)	1.975	O (10) – Ho (13) – O(8)	180
O (11) – Ho (12)	1.975		
$HoBaTeO_{4.5}$			
O (1) – Te (2)	2.003	Te (3) – O (1) – Te (2)	100
Te (3) – O (1)	2.012	O (4) – Te (3) – O (1)	107
O (5) – Te (2)	2.032	O (6) – Te (3) – O (1)	107
O (7) – Te (2)	2.032	O (5) – Te (2) – O (1)	106
O (4) – Te (3)	2.010	O (7) – Te (2) – O (1)	106
O (6) – Te (3)	2.010	Ba (15) – O (7) – Te (2)	107
Ba (15) – O (7)	2.773	Ba (14) – O (5) – Te (2)	107
Ba (14) – O (5)	2.773	O (8) – Te (2) – O (1)	109
O (9) – Te (3)	2.025	O (9) – Te (3) – O (1)	75
O (8) – Te (2)	2.024	Ho (12) – O (9) – Te (3)	105
Ho (12) – O (9)	2.212	Ho (13) – O (8) – Te(2)	104
Ho (13) – O (8)	2.211	O (11) – Ho (12) – O (9)	180
O (10) – Ho (13)	1.975	O (10) – Ho (13) – O(8)	180
O (11) – Ho (12)	1.975		

Based on the results of quantum chemical calculations, models of the structure of new double tellurites are presented. The spatial geometry of the studied compounds of the tellurium composition $HoMTe_{4.5}$ (M is Sr or Ba) is shown in Figure 2.



a) $HoSrTeO_{4.5}$ *b*) $HoBaTeO_{4.5}$

Figure 2. Models of the geometric structure of the holmium tellurites synthesized

Conclusion

In the work, new double tellurites of holmium-strontium $HoSrTeO4_{.5}$ and holmium-barium HoBaTeO4.5 were synthesized using the ceramic technology method. The X-ray phase analysis method was the first to investigate the crystal characteristics of metal-mixed tellurites and to determine the type of syngony, the unit cell parameters, X-ray and pycnometric densities. It has been established that tellurites crystallize in a monoclinic syngony and have a perovskite-like structure. This suggests that these compounds may have unique electrophysical properties.

Based on quantum chemical calculations, models of the geometrical structure of the synthesized tellurites have been proposed. The X-ray characteristics of the holmium tellurite can be the initial information files of fundamental reference books and data banks and are of interest for chemical informatics.

This work was supported by the Ministry of Education and Science of the Republic of Kazakhstan [grant numbers AP 05132001].

References

1 Lee D.W. New Quaternary Tellurite and Selenite: Synthesis, Structure, and Characterization of Centrosymmetric $InVTe_2O_8$ and Noncentrosymmetric $InVSe_2O_8$ / D.W. Lee, S.-J. Oh, P.S. Halasyamani, K.M. Ok // Inogr. Chem. — 2011. — Vol. 50. — P. 4473–4480.

2 Imaoka M. Glass-formation ranges of ternary systems. 5. Tellurites containing B-groups elements / M. Imaoka, T. Yamazaki // Inst. industr. ski. Tokyo rep. — 1976. — Vol. 26, No. 1. — P. 1–46.

3 Ковалева И.В. Адсорбционные и люминесцентные характеристики РЗЭ активаторов в теллуритном стекле / И.В. Ковалева, В.П. Колобков, А.К. Яхкинд // Физика и химия стекла. — 1975. — Т. 1. — С. 308–313.

4 Reisfeld R. Intensities of electronic transitions and quantum efficioncies of the green luminescence of Er^{3+} in tellurite glasses / R. Reisfeld, Y. Eckstein // Solid State Commun. — 1973. — Vol. 13. — P. 741–744.

5 Weber M.J. Optical properties of Nd^{3+} in tellurite and phosphotellurite glasses / M.J. Weber, J.D. Myers, D.H. Blackburn // J. Appl. Phys. — 1981. — Vol. 52. — P. 2944–2949.

6 Дюсекеева А.Т. Синтез и рентгенография теллуритов некоторых *s*-*d*-элементов / А.Т. Дюсекеева, К.Т. Рустембеков // Вестн. Караганд. ун-та. Сер. Химия. — 2010. — Т. 58, № 2. — С. 37–41.

7 Rustembekov K.T. Tellurites of some *s*–*f* elements: synthesis, X-ray diffraction, and electrophysical properties / K.T. Rustembekov, A.T. Dyusekeeva // Russian Journal of General Chemistry. — 2012. — Vol. 82, No. 8. — P. 1357–1360.

8 Бектурганова А.Ж. Синтез и рентгенографическое исследование новых никелито-теллуритов $La_2MNiTeO_7$ (M — Mg, Ca, Sr, Ba) / А.Ж. Бектурганова, Ж.И. Сагинтаева, К.Т. Рустембеков и др. // Изв. НАН РК. Сер. хим. и технол. — 2017. — Т. 422, № 2. — С. 99–103.

9 Rustembekov K.T. X-ray diffraction and thermodynamic characteristics for tellurite of the composition Li_2CeTeO_5 / K.T. Rustembekov, A.Zh. Bekturganova // Russian Journal of Physical chemistry A. — 2017. — Vol. 91, No. 4. — P. 623–626.

10 Ковба Л.М. Рентгенофазовый анализ / Л.М. Ковба, В.К. Трунов. — М.: Изд-во МГУ, 1976. — 256 с.

11 Цирельсон В.Г. Квантовая химия. Молекулы, молекулярные системы и твердые тела: учеб. пос. для вузов / В.Г. Цирельсон. — М.: БИНОМ. Лаборатория знаний, 2010. — 496 с.

12 Шрайвер Д. Неорганическая химия. — Т. 1 / Д. Шрайвер, П. Эткинс. — М.: Мир, 2004. — С. 83.

К.Т. Рүстембеков, М.С. Қасымова, Е.В. Минаева, Д.А. Қайкенов

Гольмий қос теллуриттерін синтездеу, рентгенографиялық және кванттық-химиялық зерттеу

Керамикалық технология әдісімен 800–1200 °C аралығында Ho(II), Te(IV) оксидтері және $SrCO_3$, $BaCO_3$ карбонаттарынан күрделі оксидтік фазалар — $HoMe^{II}TeO_{4,5}$ (Me^{II} — Sr, Ba) құрамды гольмийдің жаңа қос теллуриттері синтезделді. Алғаш рет теллуриттердің құрылысы рентгендік фазалық талдау әдісімен зерттелді. Рентгенфазалық талдау ДРОН-2,0 аппаратында жүргізілді. Дифракциялық максимумдардың қарқындылығы жүз балдық шкаламен бағаланды. Синтезделген ұнтақтардың рентгенограммаларын индицирлеу гомология әдісімен жүргізілді. Теллуриттердің сингония типі, элементар ұяшық параметрлері, ренгенографиялық және пикнометрлік тығыздықтарының мәндері анықталды: $HoSrTeO_{4,5}$: $a = 14{,}50$; $b = 14{,}05$; $c = 9{,}04$Å; $\rho_{рент,} = 3{,}73$; $\rho_{пикн.} = 3{,}59 \pm 0{,}04$ г/см^3; $HoBaTeO_{4,5}$; $a = 12.10$; $b = 5.49$; $c = 11.49$Å; $\rho_{рент,} = 4.07$; $\rho_{пикн.} = 3.93 \pm 0.06$ г/см^3. Теллуриттердің рентгенограммаларын индицирлеу нәтижелерінің дұрыстығын жазықтықаралық қашықтықтың квадраттарының кері шамасының ($10^4/d^2$) тәжірибелік және теориялық мәндері мен рентгенографиялық және пикнометрлік тығыздықтарының мәндерінің сәйкестігі дәлелденді. Гольмийдің синтезделген қос теллуриттері моноклиндік сингонияда кристалданатыны және перовскит тәрізді құрылысты екендігі анықталды. Синтезделген теллуриттердің тұрақты геометриясын кванттық-химиялық есептеу Gaussian–2009 бағдарламалық пакеті көмегімен, UFF молекулалық механика әдісімен жүргізілді. Бұл жағдайда тепе-теңдік ядроаралық қашықтықтары (байланыс ұзындықтары) және валенттік бұрыштары параметрлері болып табылады. Кванттық-химиялық есептеулердің нәтижесінде гольмийдің жаңа қос теллуриттерінің геометриялық құрылыс модельдері ұсынылды.

Кілт сөздер: гольмий қос теллуриттері, рентгенфазалық талдау, сингония, тор параметрлері, кванттық-химиялық есептеулер, құрылыс модельдері.

К.Т. Рустембеков, М.С. Касымова, Е.В. Минаева, Д.А. Кайкенов

Синтез, рентгенографическое и квантово-химическое исследования двойных теллуритов гольмия

Методом керамической технологии из оксидов Ho(II), Te(IV) и карбонатов $SrCO_3$, $BaCO_3$ в интервале 800–1200 °C синтезированы сложные оксидные фазы — новые двойные теллуриты гольмия состава $HoMe^{II}TeO_{4,5}$ (где Me^{II} – Sr, Ba). Методом рентгенофазового анализа впервые исследованы структуры теллуритов. Рентгенофазовый анализ проведен на установке ДРОН-2,0. Интенсивность дифракционных максимумов оценивали по стабильной шкале. Рентгенограммы синтезированных порошков индицированы методом гомологии. Определены тип сингонии, параметры элементарной ячейки, рентгенографические и пикнометрические плотности теллуритов. $HoSrTeO_{4,5}$: $a = 14{,}50$; $в = 14{,}05$; $c = 9{,}04$Å; $\rho_{рент.} = 3{,}73$; $\rho_{пикн.} = 3{,}59 \pm 0{,}04$ г/см^3; $HoBaTeO_{4,5}$: $a = 12{,}10$; в = 5,49; с = 11,49Å; $\rho_{рент.} = 4{,}07$; $\rho_{пикн.} = 3{,}93 \pm 0{,}06$ г/см^3. Корректность результатов индицирования рентгенограмм теллуритов подтверждается хорошим соответствием экспериментальных и расчетных значений обратных величин квадратов межплоскостных расстояний ($10^4/d^2$) и согласованностью величин рентгеновской и пикнометрической плотностей. Установлено, что синтезированные двойные теллуриты гольмия кристаллизуются в моноклинной сингонии и имеют перовскитоподобную структуру. Квантово-химические расчеты устойчивой геометрии синтезированных теллуритов были проведены с помощью программного пакета Gaussian–2009, методом молекулярной UFF. В данном случае параметрами являются равновесные межъядерные расстояния (длины связей) и валентные углы. На основании результатов квантово-химических расчетов представлены модели геометрического строения новых двойных теллуритов гольмия.

Ключевые слова: двойные теллуриты гольмия, рентгенофазовый анализ, сингония, параметры решетки, квантово-химические расчеты, модели строения.

References

1 Lee, D.W., Oh, S.-J., Halasyamani, P.S., & Ok, K.M. (2011). New quaternary tellurite and selenite: synthesis, structure, and characterization of centrosymmetric $InVTe_2O_8$ and noncentrosymmetric $InVSe_2O_8$. *Inogr. Chem.*, *50*, 4473–4480.

2 Imaoka, M., & Yamazaki, T. (1976). Glass-formation ranges of ternary systems. 5. Tellurites containing B-groups elements. *Inst. industr. ski. Tokyo rep.*, *26*(1), 1–46.

3 Kovaleva, I.V., Kolobkov, V.P., & Yakhkind, A.K. (1975). Adsorbtsionnye i liuministsetnye kharakteristiki RZE aktivatorov v telluritnom stekle [Adsorption and luminescent characteristics of REE activators in tellurite glass]. *Fizika i khimiia stekla — Physics and Chemistry of Glass*, *1*, 308–313 [in Russian].

4 Reisfeld, R., & Eckstein, Y. (1973). Intensities of electronic transitions and quantum efficioncies of the green luminescence of Er^{3+} in tellurite glasses. *Solid State Commun.*, *13*, 741–744.

5 Weber, M.J., Myers, J.D., & Blackburn, D.H. (1981). Optical properties of Nd^{3+} in tellurite and phosphotellurite glasses. *J. Appl. Phys.*, *52*, 2944–2949.

6 Dyusekeyeva, A.T., & Rustembekov, K.T. (2010). Sintez i renthenohrafiia telluritov nekotorykh *s-d*-elementov [Synthesis and radiography of tellurites of some *s-d*-elements]. *Vestnik Karahandinskoho universiteta. Seriia Khimiia — Bulletin of Karaganda University. Chemistry series*, *58, 2*, 37–41 [in Russian].

7 Rustembekov, K.T., & Dyusekeeva, A.T. (2012). Tellurites of some s-f elements: synthesis, X-ray diffraction, and electrophysical properties. *Russian Journal of General Chemistry*, *82*(8), 1357–1360.

8 Bekturganova, A.Zh., Sagintaeva, Zh.I., & Rustembekov, K.T. (2017). Sintez i renthenohraficheskoe issledovanie novykh nikelito-telluritov $La_2MNiTeO_7$ (M — Mg, Ca, Sr, Ba) [Synthesis and X-ray study of new nickelite-tellurites $La_2MNiTeO_7$ (M — Mg, Ca, Sr, Ba]. *Izvestiia NAN RK. Seriia khimii i tekhnolohii. — News of the National Academy of Sciences of Kazakhstan. A series of chemistry and technology*, *422, 2,* 99–103 [in Russian].

9 Rustembekov, K.T., & Bekturganova, A.Zh. (2017). X-ray diffraction and thermodynamic characteristics for tellurite of the composition Li_2CeTeO_5. *Russian Journal of Physical chemistry A*, *91*(*4*), 623–626.

10 Kovba, L.M., & Trunov, V.K. (1976). *Renthenofazovyi analiz [X-ray phase analysis]*. Moscow: Izdatelstvo MGU [in Russian].

11 Tsirelson, V.G. (2010). *Kvantovaia khimiia. Molekuly, molekuliarnye sistemy i tverdye tela [Quantum chemistry. Molecules, molecular systems and solids].* Moscow: BINOM. Laboratoriia znanii [in Russian].

12 Shraiver, D., & Atkins, P. (2004). *Neorhanicheskaia khimiia [Inorganic chemistry]* (Vols. 1–2, Vol. 1). Moscow: Mir [in Russian].

DOI 10.31489/2019Ch3/83-87

UDC 661.522.2

K. Zhumashev[1], A. Narembekova[2], B.B. Katrenov[3]

[1]«Innovatsiya» LLP, Karaganda, Kazakhstan;
[2]Karaganda State Technical University, Kazakhstan;
[3]Zh. Abishev Chemical and metallurgical institute, Karaganda, Kazakhstan
(E-mail: innovaciya_zh@mail.ru)

Determination of the reaction mechanism of the calcium fluoride interaction with ammonium sulphate

Production of ammonium hydrogen fluoride according to the traditional technology using concentrated sulfuric acid is associated with a number of technological difficulties. Considering this, an alternative option for producing ammonium hydrogen fluoride using ammonium sulphate, a by-product of the coke-chemical production has been proposed. Thermodynamic and differential-thermal analyzes of the reaction of the interaction of calcium fluoride with ammonium sulphate were carried out to establish the possibility of using ammonium sulphate as a reagent for the preparation of ammonium fluoride. According to the results of the analysis, the mechanism of the reaction of calcium fluoride with ammonium sulphate was established as the mixture was heated. It is established that there is ammonium sulphate decomposition in the beginning with formation of ammonium hydrosulphate, ammonia, sulfur trioxide and water. Then ammonium hydrosulphate, sulfur trioxide and water interact with calcium fluoride to form ammonium fluoride, fluoric hydrogen and calcium sulphate. Ammonia and fluoric hydrogen then can be also processed on ammonium fluoride. Thus, the possibility of using ammonium sulphate as a reagent for the production of ammonium fluoride from natural calcium fluoride has been established on the basis of the research conducted. The ammonium fluoride then can be processed to ammonium hydrogen fluoride. Thus, the reaction studied can serve as a chemical basis for an alternative technology for the production of ammonium hydrogen fluoride.

Keywords: calcium fluoride, ammonium sulphate, ammonium fluoride, thermal analysis, thermodynamic analysis.

Introduction

Ammonium hydrogen fluoride $NH_4F \cdot HF$ is widely used in heat-and-power engineering, in ferrous and nonferrous metallurgy, in the petroleum industry, as well as in the chemical industry. Ammonium hydrogen fluoride is an expensive imported reagent for enterprises of the Republic of Kazakhstan. Ammonium hydrogen fluoride can be obtained from natural calcium fluoride CaF_2, however, its traditional production technology is based on the reaction of interaction with concentrated sulfuric acid at temperatures above 100 ºC. The implementation of these reactions encounters a number of technological difficulties [1]. Ammonium hydrogen fluoride can also be obtained by dissociating ammonium fluoride NH_4F [2]. Considering this, an alternative method of obtaining $NH_4F \cdot HF$ can be a technology that involves obtaining ammonium fluoride in the first stage, which can then process ammonium hydrogen fluoride.

The main reagents for the production of ammonium fluoride are calcium fluoride and ammonia NH_3. Ammonia is not available in all regions of the Republic of Kazakhstan. In Central Kazakhstan, ammonium sulphate can be a substitute for ammonia, an illiquid by-product of a coke-chemical production containing an ammonium group. With this in mind, it is of interest to determine the possibility of using ammonium sulphate $(NH_4)_2SO_4$ to produce ammonium fluoride [3]. To this end, studies aimed at determining the mechanism of interaction of calcium fluoride CaF_2 with ammonium sulphate $(NH_4)_2SO_4$ have been carried out. The studies included thermodynamic and differential thermal analyzes.

Experimental

Thermodynamic analysis was performed using the HCS-5.1 Chemistry (Outokumpu) software complex [4] and was reduced to calculating the Gibbs energy of chemical reactions, the occurrence of which was the most probable during the interaction of these reagents:

$$CaF_2 + (NH_4)_2SO_4 = CaSO_4 + 2HF\uparrow + 2NH_3\uparrow \quad (1)$$

$$(NH_4)_2SO_4 = NH_4HSO_4 + NH_3\uparrow \quad (2)$$

$$CaF_2 + NH_4HSO_4 = CaSO_4 + NH_4F + HF\uparrow \quad (3)$$

$$(NH_4)_2SO_4 = 2NH_3\uparrow + SO_3\uparrow + H_2O\uparrow \quad (4)$$

$$NH_4HSO_4 = NH_3\uparrow + SO_3\uparrow + H_2O\uparrow \quad (5)$$

$$CaF_2 + H_2O + SO_3 = CaSO_4 + 2HF\uparrow \quad (6)$$

$$NH_3 + HF = NH_4F \quad (7)$$

The results of the thermodynamic analysis of reactions (1)–(7) are presented in Table.

Table

Gibbs energy values for the reaction (1)–(7), kJ (negative values are highlighted in bold)

Temperature, °C	Reaction (1)	Reaction (2)	Reaction (3)	Reaction (4)	Reaction (5)	Reaction (6)	Reaction (7)
0	182.202	100.871	13.475	284.500	183.629	**–102.299**	**–63.893**
100	127.294	97.373	**–8.510**	223.663	126.290	**–96.369**	**–34.468**
200	73.318	93.936	**–29.907**	163.943	70.007	**–90.624**	**–5.327**
300	20.377	90.355	**–52.217**	105.423	15.068	**–85.045**	21.722
400	**–31.436**	86.498	**–74.731**	48.171	**–38.327**	**–79.608**	47.165
500	**–82.035**	82.275	**–96.207**	**–7.749**	**–90.024**	**–74.286**	72.065

From Table 1 it follows that the interaction of calcium fluoride CaF_2 with ammonium hydrogen sulphate NH_4HSO_4 is more probable than with ammonium sulphate $(NH_4)_2SO_4$. The decomposition of ammonium sulphate by reaction (2) with the formation of ammonium hydrosulphate is more probable than the decomposition by reaction (4). Therefore, the interaction of calcium fluoride with ammonium sulphate is probably includes the process of decomposition of the latter with the formation of ammonium hydrosulphate. At temperatures above 300 ºC, ammonium hydrosulphate will begin to decompose according to reaction (5) with the formation of sulfur trioxide SO_3. In return, sulfur trioxide will intensively interact with calcium fluoride, since reaction (6) is exothermic.

Differential-thermal analysis of reactions (1) and (2) was carried out with the Q-1000/D derivatograph of the F. Paulik, J. Paulik and L. Erdey systems of the MOM company in an air atmosphere at a heating rate of 10 ºC/min. The sample weight was 450 mg; calcined alumina served as a reference. Derivatograms (DTA and TG curves) of reaction (1) and decomposition of separately taken ammonium sulphate $(NH_4)_2SO_4$, the results of processing the TG curve with breakdown into three sections are shown in Figures 1 and 2.

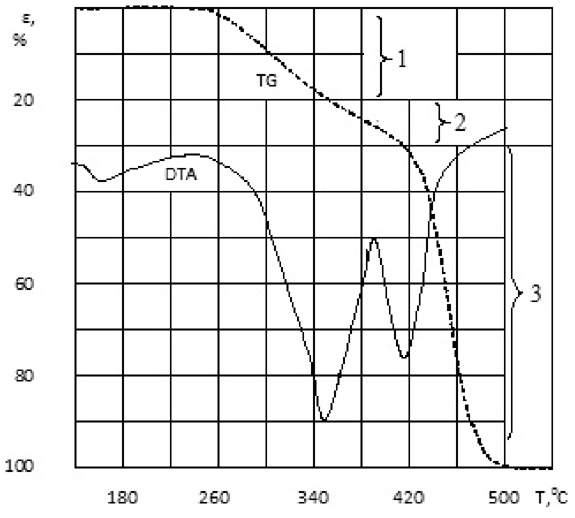


Figure 1. DTA and TG curves of calcium fluoride interaction with ammonium sulphate

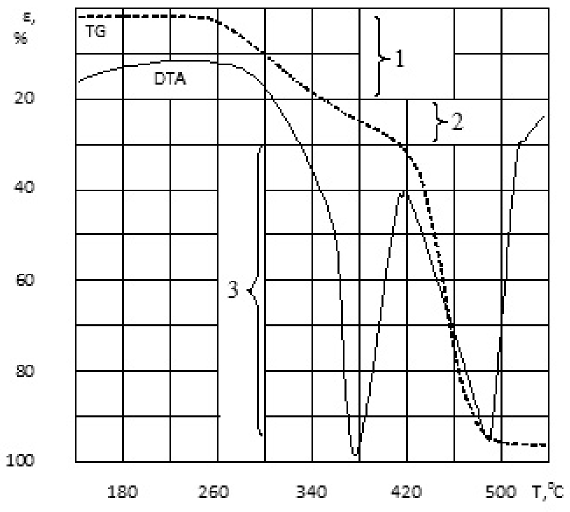


Figure 2. DTA and TG curves of a single ammonium sulphate decomposition

The investigation of the reaction of the interaction of calcium fluoride and ammonium hydrosulphate, DTA reactions (3) and (5) were carried out under the same conditions as for reactions (1) and (2). Derivatograms (DTA and TG curves) of reaction (3) and the decomposition reaction of a single ammonium hydrosulphate NH_4HSO_4, the results of processing the TG curve with breakdown into three (Fig. 3) and two (Fig. 4) sections are shown.

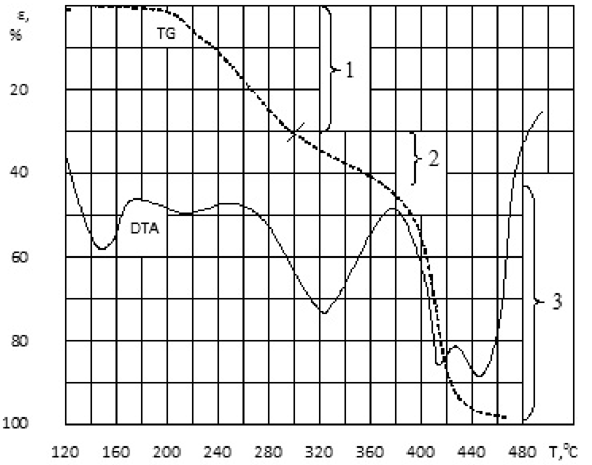


Figure 3. DTA and TG curves of calcium fluoride interaction with ammonium hydrosulphate

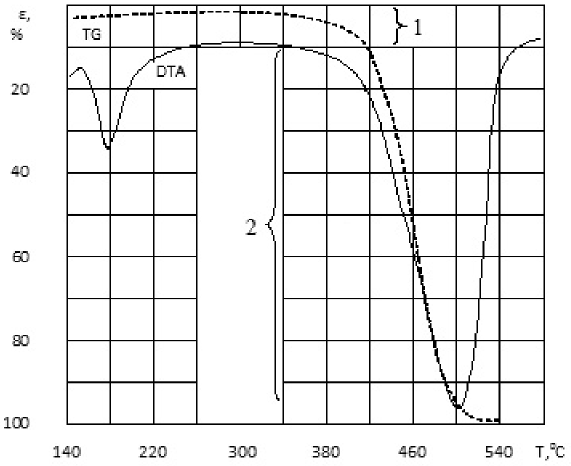


Figure 4. DTA and TG curves of a single ammonium hydrosulphate decomposition

Results and Discussion

Derivatograms presented in Figures 1 and 2 confirm the data of thermodynamic analysis. The decomposition of ammonium sulphate (Fig. 2) proceeds according to reaction (2) with the formation of ammonium hydrosulphate and it begins at 260 ºC (section 1 of the TG curve). The total decomposition of $(NH_4)_2SO_4$ is completed at 380 ºC, which is evidenced by the endothermic effect. At the same time, the process velocity, according to the decrease in the angle of incidence of the TG curve (section 2), slows down in the temperature range 340–420 ºC. This may be due to diffusion difficulty caused by the formation of ammonium hydrosulphate. In this case, reaction (2) is not final, since ammonium hydrosulphate is also decomposed by reaction (5). According to the DTA curve of ammonium sulphate (Fig. 2), the decomposition of ammonium hydrosulphate occurs in the temperature range 420–490 ºC (section 3 of the TG curve).

In the interaction of calcium fluoride with ammonium sulphate, first the decomposition of the latter takes place with the formation of ammonium hydrosulphate, which then reacts with calcium fluoride by reaction (3). This explanation is based on the fact that the character of the DTA and TG curves of decomposition of a single ammonium sulphate (Fig. 2) repeats in form the derivatogram (Fig. 1). The main difference between derivatograms (Fig. 1) and (Fig. 2) is the shift of temperature peaks towards low temperatures on derivatogram (Fig. 1). The shift of the peaks can be explained by the flow of the exothermic process of formation of calcium sulphate by the reaction (6). The heat generated during this process partially compensates for the heat consumption for heating and decomposition of ammonium sulphate. In return, the course of reaction (6) indicates that some part of $(NH_4)_2SO_4$ decomposes according to reaction (4) with the formation of sulfur trioxide SO_3 and water. $(NH_4)_2SO_4$ decomposes by reactions (2) and (4) (section 1 of the TG curve) in the temperature range of 260–350 ºC. Judging by change of slope of the TG curve, there is an interaction of a calcium fluoride with ammonium sulphate decomposition products (NH_4HSO_4, SO_3 and H_2O) in the temperature range of 350–420 ºC (section 2). Judging by the DTA curve, the exothermic process of calcium sulphate formation by the reaction (6) proceeds to a greater degree in the temperature range of 350–390 ºC. The reaction (6) indicates that ammonium hydrosulphate begins to decompose by reaction (5). The reaction of calcium fluoride with ammonium hydrogen sulphate (3) takes place at temperatures of 390–420 ºC. The remaining part of NH_4HSO_4 is decomposed by reaction (5) in the temperature range of 420–500 ºC (section 3). The increase of the DTA curve after 420 ºC is explained by heating the calcium sulphate obtained.

Derivatogram presented in Figures 3 and 4 reflects the processes taking place in reactions (3) and (5). The decomposition of ammonium hydrosulphate (Fig. 4) proceeds according to reaction (5) and begins at 340 ºC (section 1 of the TG curve). The initial endothermic effect at 180 ºC is explained by the melting of NH_4HSO_4 without mass loss. Above 420 ºC, the process is more intense and ends at 500 ºC (section 2), as evidenced by the endothermic effect.

Judging by the DTA and TG curves, the process of calcium fluoride interaction with ammonium hydrosulphate (Fig. 3) is complex and is accompanied by successive processes in the range of 200–450 ºC. Before the interaction, the melting of NH_4HSO_4 takes place first, as evidenced by the presence of an endothermic effect at 150 ºC. The TG curve is straightforward (section 1 of the TG curve) in the temperature range 200–300 ºC, i.e. reaction (3) goes with a constant acceleration factor. The presence of an endothermic effect at 320 ºC indicates the end of this reaction. The angle of incidence of the TG curve decreases in the temperature range of 300–380 ºC, i.e. the velocity of the process slows down, which is probably due to the onset of diffusion hindrance as a result of the formation of a large solid product, calcium sulphate (section 2). The growth of the DTA curve after 320 ºC is explained by heating the calcium sulphate obtained. Unreacted NH_4HSO_4 starts to decompose with the release of sulfur trioxide and water vapor above 380 ºC. The formation of these products contributes to the removal of diffusion difficulties (section 3 on the TG curve), which leads to an increase in the velocity of the process. The dissociation of NH_4HSO_4 proceeds with the absorption of heat, which explains the endothermic effect at 410 ºC. The sulfur trioxide and water react with unreacted calcium fluoride by reaction (6) with the release of heat, which explains the exothermic effect at 430 ºC. The remaining part of NH_4HSO_4 is decomposed by the reaction (5) in the temperature range 430–445 ºC. The growth of the DTA curve after 445 ºC is explained by heating the calcium sulphate obtained.

Conclusion

The results of thermodynamic and differential-thermal analyzes show that as the mixture heats up, the interaction of calcium fluoride with ammonium sulphate proceeds according to the following mechanism:

1) ammonium sulphate decomposes by reaction (2) to form liquid ammonium hydrosulphate, and partially by reaction (4) to form sulfur trioxide and water in the temperature range of 260–350 ºC;

2) calcium fluoride reacts with ammonium hydrosulphate by reaction (3) and with sulfur trioxide and water by reaction (6) with the formation of ammonium fluoride, fluoric hydrogen and calcium sulphate in the temperature range of 350–420 ºC;

3) the remaining part of NH_4HSO_4 is decomposed by reaction (5) with the release of sulfur trioxide and water, which then react with the remaining part of calcium fluoride by reaction (6) above 420 ºC;

4) ammonia and fluoric hydrogen obtained can be also processed into ammonium fluoride by reaction (7).

When the mixture of calcium fluoride and ammonium hydrosulphate is heated, reaction (3) proceeds already in the temperature range of 200–320 ºC. The ammonium fluoride obtained can be used to produce ammonium hydrogen fluoride by decomposing it at a temperature of 138 ºC.

Thus, the possibility of using ammonium sulphate as a reagent for the production of ammonium fluoride from natural calcium fluoride has been established on the basis of the research carried out and the reaction studied (1) can serve as the chemical basis of an alternative technology for the preparation of ammonium hydrogen fluoride.

The work was perfomed out on the basis of «Innovatsiya» LLP within the constraints of current initiative research on the development of alternative technology for the production of ammonium hydrogen fluoride with the involvement of employees of the ChMI named after Zh. Abishev.

References

1 Некрасов Б.В. Общая химия: учеб. / Б.В. Некрасов. — М.: Химия, 1981. — 560 с.

2 Патент 2038299 Россия. Способ получения бифторида аммония / В.П. Харитонов, Л.П. Белова, В.П. Демидов, В.Г. Шумихин, Н.Г. Окатышев, А.С. Захаров. Опубл. 27.06.95.

3 Патент 33055 Казахстан. Способ получения фторида аммония / К.Ж. Жумашев, Б.Ф. Рамазанов, А.К. Нарембекова, Б.Б. Катренов. Опубл. 07.03.2017.

4 Roine A. Outokumpu HSC Chemistry for windows chemical reaction and Equilibrium software with extensive thermochemical data base // Roine A. Pori Outokumpu research OY 2002. Retrieved from www.outotec.com.

К. Жумашев, А. Нарембекова, Б.Б. Катренов

Аммоний сульфаты бар кальций бифторидінің өзара әрекеттесу реакциялар механизмін анықтау

Аммоний бифторидін күкірт қышқылын қолдана отырып, дәстүрлі технологиясымен алу бірқатар технологиялық қиындықтарға алып келеді. Осыны ескере отырып, аммоний сульфатын — кокс-химия өндірісінің жанама өнімі қолдану арқылы аммоний бифторидін алудың балама әдісі ұсынылған. Аммоний фторидін өндіру үшін аммоний сульфатын реагент ретінде қолдану мүмкіндігін анықтау үшін кальций бифторидінің аммоний сульфатымен әрекеттесу реакциясының термодинамикалық және дифференциалды-термиялық талдауы жасалды. Талдаулардың нәтижелері бойынша қоспаны біртіндеп қыздыру кезіндегі кальций бифтордінің аммоний сульфатымен әрекеттесу механизмі анықталды. Аммоний сульфатының әуелі аммоний гидросульфатына, аммиакқа, күкірт триоксидіне және суға ыдырауы анықталған. Сонан соң аммоний гидросульфаты, күкірт триоксиді және су кальций бифторидімен әрекеттесіп, осыдан кейін аммоний фториді, фторлы сутегі, кальций сульфаты деген қосылыстар пайда болады. Аммиак және фторлы сутегі кейін аммоний фторидіне өндіруге болады. Осылайша, өткізген зерттеулерінің негізінде табиғи кальций фторидінен аммоний фторидің өндіру үшін аммоний сульфатын реагент ретінде қолдану мүмкіндігін анықталған. Аммоний фториді кейін аммоний бифторидіне өндіруге болады. Осылайша, зерттелген реакция аммоний бифторидін өндірудің балама технологиясы үшін химиялық негізі бола алады.

Кілт сөздер: кальций бифториды, аммоний сульфаты, аммоний фториді, аммиак, термиялық талдау, термодинамикалық талдау.

К. Жумашев, А. Нарембекова, Б.Б. Катренов

Определение механизма реакции взаимодействия бифторида кальция с сульфатом аммония

Получение бифторида аммония по традиционной технологии с использованием концентрированной серной кислоты сопряжено с рядом технологических затруднений. Учитывая это, предложен альтернативный вариант получения бифторида аммония с использованием сульфата аммония — побочного продукта коксохимического производства. Для установления возможности использования сульфата аммония в качестве реагента для получения фторида аммония были проведены термодинамический и дифференциально-термический анализы реакции взаимодействия бифторида кальция с сульфатом аммония. По результатам проведенных анализов установлен механизм протекания реакции бифторида кальция с сульфатом аммония по мере нагревания смеси. Показано, что вначале происходит разложение сульфата аммония с образованием гидросульфата аммония, аммиака, триоксида серы и воды. Затем гидросульфат аммония, триоксид серы и вода взаимодействуют с бифторидом кальция с образованием фторида аммония, фтороводорода и сульфата кальция. Аммиак и фтороводород затем могут быть также переработаны во фторид аммония. Таким образом, на основании проведенных исследований установлена возможность использования сульфата аммония в качестве реагента для получения фторида аммония из природного фторида кальция. Фторид аммония затем может быть переработан в бифторид аммония. Таким образом, изученная реакция может служить в качестве химической основы альтернативной технологии получения бифторида аммония.

Ключевые слова: бифторид кальция, сульфат аммония, фторид аммония, термический анализ, термодинамический анализ.

References

1 Nekrasov, B.V. (1981). *Uchebnik obshchiei khimii [Book of general chemistry]*. Moscow: Khimiia [in Russian].

2 Kharitonov, V.P., Belova, L.P., Demidov, V.P., Shumikhin, V.G., Okatyshev, N.G., & Zakharov, A.S. (1995). Sposob polucheniia biftorida ammoniia [The producing way of the ammonium bifluoride]. *Patent 2038299 of the Russian Federation*. Publ. 06.27.95 [in Russian].

3 Zhumashev, K.Zh., Ramazanov, B.F., Narembekova, A.K., & Katrenov, B.B. (2017). Metod polucheniia biftorida ammoniia [The producing method of the ammonium bifluoride]. *Patent 33055 of the Republic of Kazakhstan*. Publ. 03.07.17 [in Russian].

4 Roine, A. (2002). Outokumpu HSC Chemistry for windows chemical reaction and equilibrium software with extensive thermochemical data base. *PoriOutokumpu research OY 2002*. Retrieved from www.outotec.com.

DOI 10.31489/2019Ch3/88-95

UDC 662.743

N.I. Kopylov

Institute of Solid State Chemistry and Mechanochemistry of the Siberian Branch of the RAS, Novosibirsk, Russia
(E-mail: kolyubov@narod.ru)

Chemical, phase composition and properties of products of thermal decomposition of coal of Tavantolgoy deposit of Mongolia

The results of investigation of chemical and phase composition of products of thermal decomposition of hard coal of the Tavantolgoy deposit in Mongolia were presented, namely, the solid residue of thermal decomposition of coal, tar fraction, liquid condensate and organic fraction separated from the condensate. Their compositions, temperatures of formation and phase transformations were determined. Relicts of aromatic hydrocarbons, ester groups and phenols were preserved in a small amount in the solid residue. The boiling condensate is an aqueous solution with a small admixture (~1 %) of the organic component that is the extract and traces of the resinous fraction. Condensate extract mainly contains phenol and its derivatives. The resinous fraction contains low-boiling oils and a phase that is thermally similar to asphaltenes, including up to 70 organic substances, with predominance (~40 % relative) of saturated hydrocarbons (cozanes), the presence of various groups of aromatic and polycyclic hydrocarbons, namely benzene derivatives, naphthalenes, phenanthrenes, hopenes, traces of phenols and cholestenes.

Keywords: phase decomposition, solid precipitate, resinous fraction, condensate, sublimates, organic fraction of condensate.

Introduction

The situation concerning the possibility and prospects for the industrial use of coal from the Tavantolgoy deposit in Mongolia that exists until recently was presented in some detail in the study of the phase decomposition of coal from this deposit [1]. It has been noted that the hard coals of Mongolia, in particular the Tavantolgoy deposit, are valuable raw materials for metallurgy, coke chemistry and the chemical industry [2, 3]. The explored reserves of the field, the technical characteristics of these coals, as well as a number of other fields in Central Asia (in particular, Tuva) provide the possibility of their integrated use [4–10].

However, the mined coals of these deposits are mainly used as a fuel for heat and power plants and the private sector due to the remoteness from industrial centers and the lack of necessary transport communications [10–12]. At the same time, dispersed soot and other products of incomplete combustion are formed in the furnaces of CHP plants and domestic furnace units due to the incomplete combustion of coal and the formation of cakes, which leads to the release of environmentally hazardous substances into the environment. The mountainous landscape and continental climate of Central Asia predetermine the formation of stagnant zones, smog in the confined spaces of mountain valleys, which leads to pollution of the atmosphere of urban and other settlements of these regions with products of flue gases with high concentrations of toxic substances, including carcinogens [13].

Despite numerous studies on the modification of materials of this type, the environmental problems of flue gases have not been resolved yet. In this regard, research on the dynamics of decomposition of coals from a number of fields in Tuva and Mongolia during their roasting, for example [1, 14], has been carried out as part of the research program for creating technology for the efficient and environmentally friendly processing of mineral raw materials. In particular, when studying the thermolysis of coal from the Tavantolgoy deposit in Mongolia, the following products were obtained, namely, a solid residue, a resinous fraction (coal tar), a condensate of boiling liquid fraction and an organic extract of this fraction [1]. This article is devoted to the results of further studies of the chemical, phase composition and properties of the products formed during the thermolysis of coal from this field.

Experimental

The composition of thermolysis products was studied by instrumental analysis methods. The structural characteristics of the solid products of thermolysis were determined by IR spectroscopy. Reference manual was used when interpreting the spectrograms obtained [15]. Liquid sublimate condensate and the resinous fraction were investigated by thermal analysis (DTGA) using an MOM-1000 model derivatograph (Paulik, Paulik-Erdey, Hungary). Samples of the organic component of the liquid sublimate condensate were analyzed by gas chromatography-mass spectrometry. The preparation consisted in threefold extraction of organic components with methylene chloride (CH_2Cl_2). The compounds were identified by comparing with known substances from the library of mass spectra of the BIST 08 Library. Chromato-mass spectrometric studies (CMS) of the resins formed during thermolysis were performed using a system that included a gas chromatograph equipped with an interface with a highly efficient mass-selective detector. Mass chromatograms were obtained by total ion current (TIC). Compounds were identified using a computer search in the National Institute of Standards NIST-05 library, according to literature data and by reconstructing structures according to the nature of ion fragmentation during electron impact [16, 17].

Figure 1 shows the obtained IR spectra of the average sample of coal (curve 1) and the solid product of its thermolysis (curve 2) in order to assess the result of thermolysis.

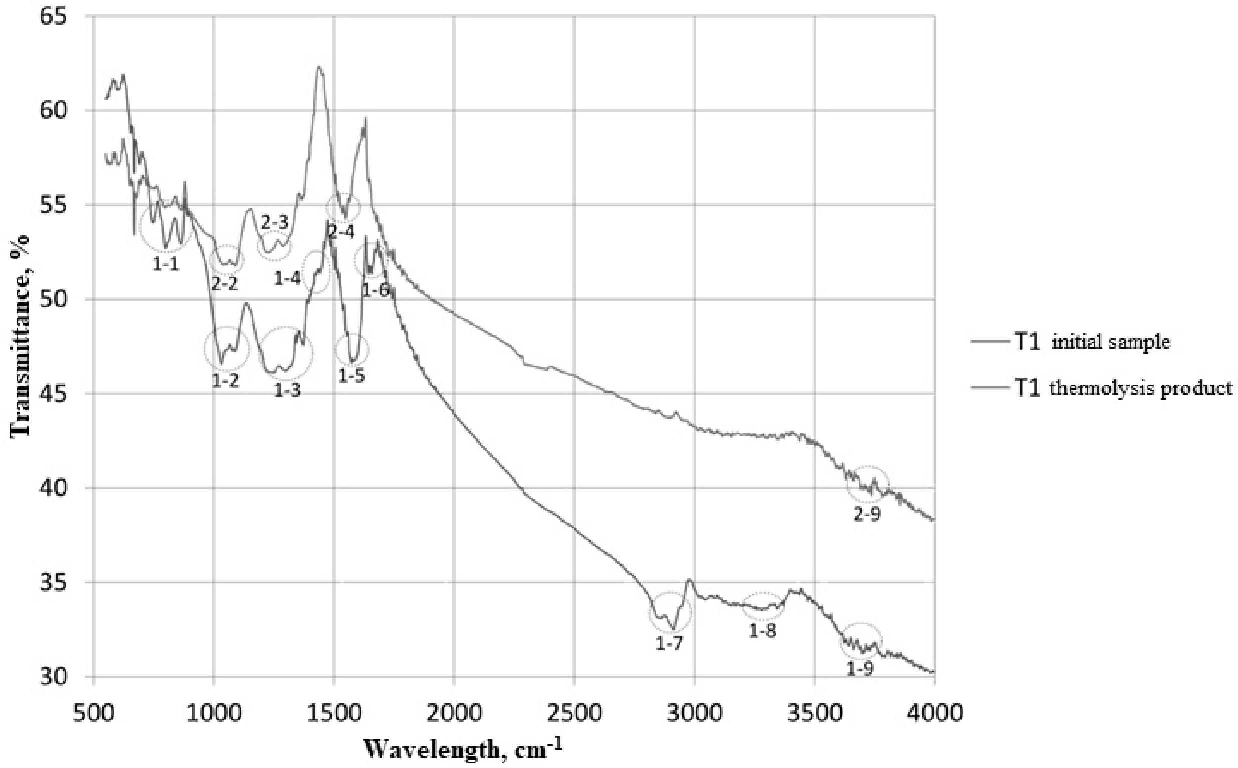
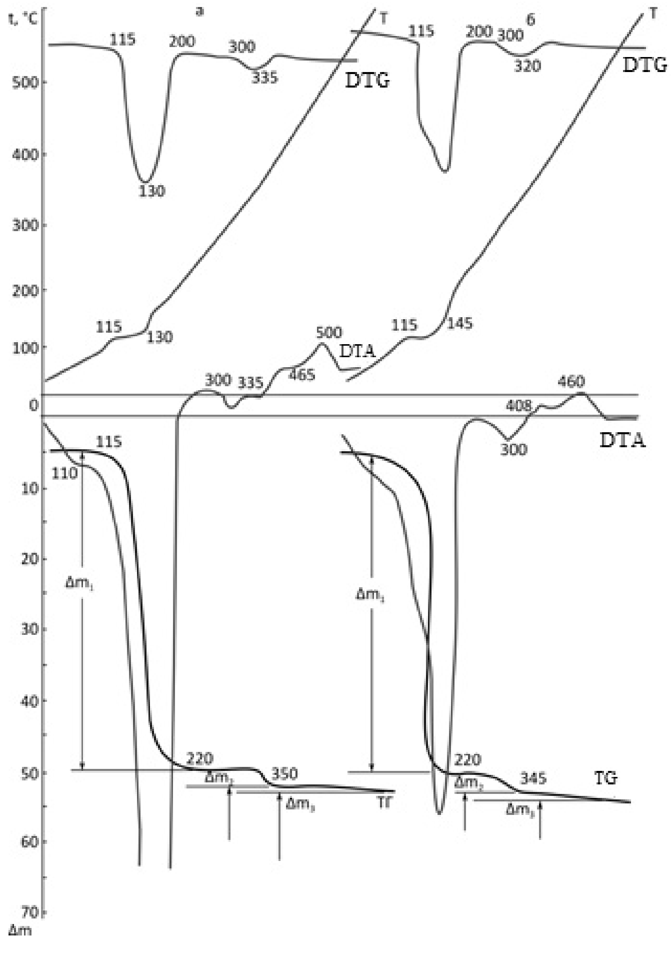


Figure 1. IR spectrograms of the average initial sample of Tavantolgoy coal (*1*) and its thermolysis product (*2*)

The infrared spectrum of the original coal sample (curve 1) shows absorption bands (peak 1) corresponding to the stretching vibrations of C–O–C and bending vibrations of CH, as well as the absorption bands (peaks 2 and 4) related to the vibrations of ether groups. Peak 3 corresponds to C–O vibrations of phenolic groups; C=O vibrations of quinolide groups are peak 5, and peak 6 is due to vibrations of intensive absorption of carbonyl groups. Peak 7 refers to vibrations of CH-aliphatic groups, OH-phenolic groups and carboxylic acids, and peak 8 refers to weak vibrations of OH-phenols and carboxylic acids associated with the presence of a hydrogen bond. Peak 9 is due to vibrations of peripheral phenolic groups.

The IR spectra of solid thermolysis product (curve 2, Fig. 1) are significantly different from the IR spectrum of the starting material. Weak (relic) absorption bands of ether, phenol, and quinol groups are noted. There are no bands related to the vibrations of the CH-aliphatic, OH-phenolic groups and carboxylic acids.

Thermal analysis of sublimates of liquid condensate samples. DTGA samples of liquid condensate from sublimates obtained during thermolysis of an average sample of a batch and a sample prepared from a lumpy, heterogeneous in size starting material (~30 mm diagonally) turned out to be identical (Fig. 2).



a — medium sample; *b* — lump material

Figure 2. DTGA samples of condensate extract sublimates thermolysis

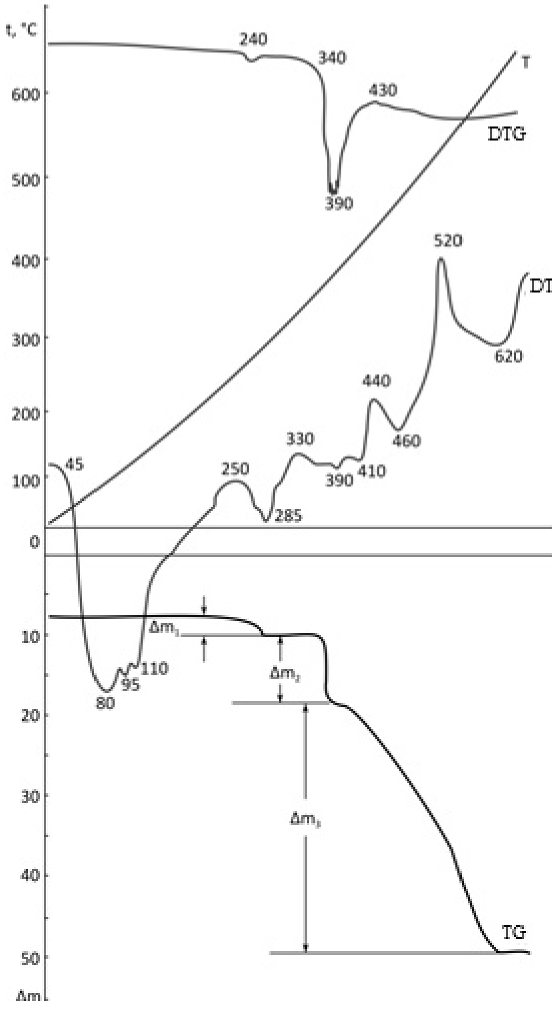


Figure 3. DTGA of tar fraction of coal

There is a deep endothermic effect of evaporation of an aqueous solution at 115–130 ºC and with further heating a number of minor endo-effects are fixed at 300–340, ~ 400.460–500 ºC. This is due to the fact that a small amount of the resinous fraction is formed during thermolysis of samples of this coal, in addition to liquid sublimates. And, apparently, all thermal effects and changes in the mass of the material observed at temperatures above 300 ºC are due to the presence of an admixture of the resinous component in the condensate mechanically trapped or partially dissolved in the condensate. Accompanied thermal effects, the mass loss of samples of liquid condensate of this type of coal occur sequentially in three stages, namely it is 92 % at 115–130 ºC, 5.6 % at 300–350 ºC and then (up to 600 ºC) it has the monotonous nature of the decline and it is about 2 %.

Thermal analysis of the coal tar fraction. The results of DTGA of the coal tar fraction are presented in Figure 3. The course of the thermogram curves shows that a series of combined softening processes (≥45 ºC) and sequential melting of the resin components (80–95–110 ºC) occur in the temperature range of 45–110 ºC, while the mass of the material remains unchanged. At 230–240 ºC, the beginning of the boiling of the liquid is noted, which is fully completed at 285–300 ºC, and a dry porous product is formed at 310–320 ºC. Starting at temperatures of 330–350 ºC, dry decomposition of the sample material is observed. By the heating temperature of 600 ºC, the sample mass is reduced to 0.5 % of the initial sample, and the entire sample is completely sublimated upon subsequent short exposure (5–10 min). From this it follows that the resin material is represented by low-boiling (about 230–250 ºC) mineral oils and a phase that is thermally close to asphaltenes, with solid phase decomposition at 330 to 340 ºC, into components, with higher temperatures (up to 600–650 ºC) dry sublimation.

The material composition of the extract sublimates liquid condensate. The analysis showed that the condensate extract of thermolysis of lump material contained phenol (45.70 %) and its derivatives (in total, by weight, equal to 50.44 %.), as well as impurities, namely cyclopentanone, cyclohexanone, diethyl phthalate, dimethyl derivative cyclopentene and 2-methylquinoline. In total, the mass of phenol and its derivatives was 96.14 % of the total mass of the extract.

The content of phenol is somewhat lower (37.54 %) than in the extract of the lump sample in the liquid extract of sublimation of the initial average sample of this coal, but the content of the derivatives of phenol is approximately the same. The total content of phenols is slightly less and equals to 92.02 %. The content of diethyl phthalate in the material is comparable to that in the lump sample extract. Also there is a small content of cyclohexane in the sample. Unlike lump sample extract, this extract contains a whole group of quinoline derivatives (total of 7.04 %). Thus, the main components of the condensate extract from sublimates of coal from the Tavantolgoy deposit, as well as from brown coal from the Baganur coal [18], are phenol and its derivatives. The extracts of brown and black coal differ in the content of the fractions — small in the mass of components.

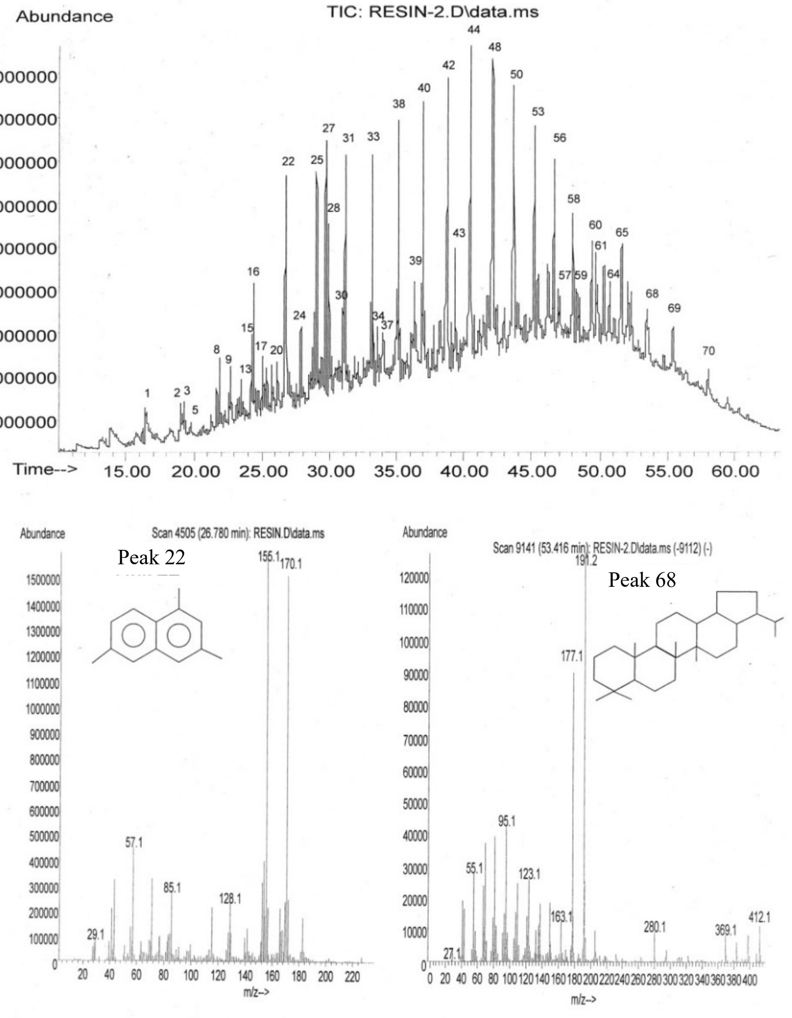


Figure 4. Chromato-mass spectrogram of the resinous coal fraction

The material composition of the resinous fraction of coal. The data obtained by chromatography-mass spectroscopy of the resinous fraction of Tavantolgoy coal (Fig. 4) show a complex composition.

This product consisting of 69 individual compounds belonging to different classes and groups of organic compounds are:

– aromatic hydrocarbons (0.765 % phenols; 15.842 % benzene group);

– polynuclear aromatic hydrocarbons (19.96 % naphthalenes; 11.61 % phenanthrenes);

– polynuclear hydrocarbons (10.50 % hopene-hopane; 0.97 % sterile steroids);

– saturated hydrocarbons (40.32 % cozanes).

Results and Discussion

As a result of thermolysis, Tavantolgoy coal decomposes into solid residue, the resinous fraction (coal tar) and sublimates including the gaseous component and liquid boiling condensate. The process of thermal decomposition of coal from the Tavantolgoy deposit can be represented by the following scheme (Fig. 5).

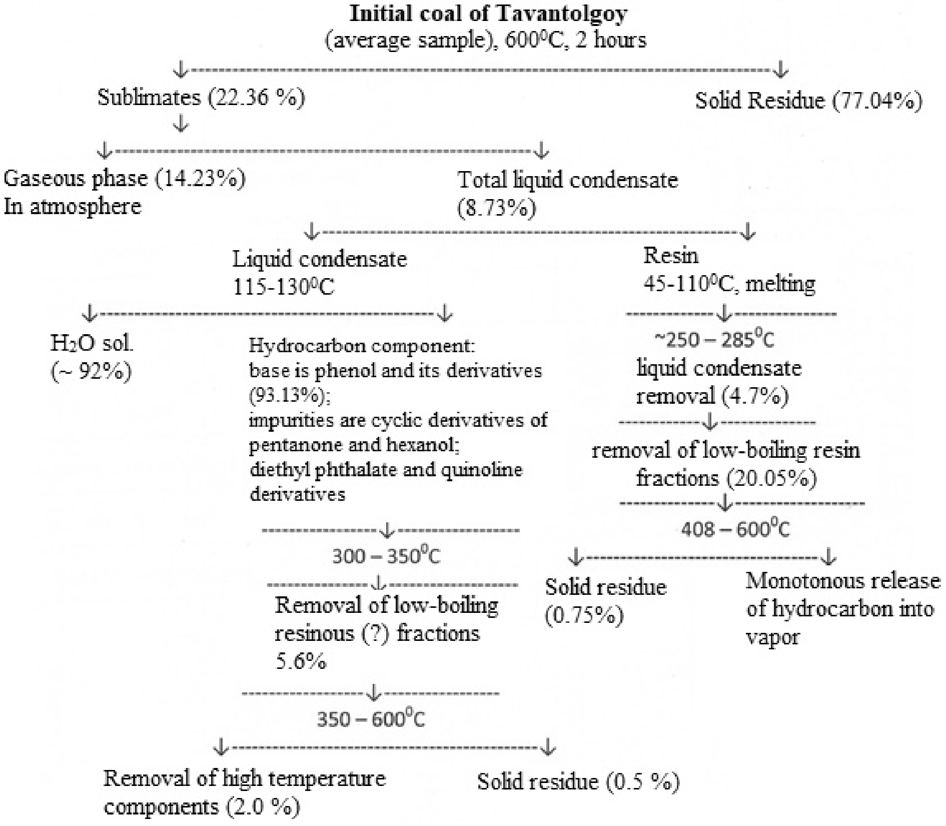


Figure 5. Diagram of the sequence of decomposition of coal during its thermolysis

The hydrocarbon components of the original coal are preserved in small amounts, namely, aromatic hydrocarbons, ether groups, and phenols. Low-boiling condensate, which is an aqueous solution, contains insignificant amounts of the organic component, the extract (up to ~ 1 %), and an impurity of the resinous fraction. This is confirmed by the data of DTGA condensate, where thermal effects in the temperature range of 115–130 ºC indicate boiling of the aqueous solution, and above 300 ºC, the removal of resinous impurities. Sublimate condensate extract mainly contains phenol and its derivatives. Samples obtained from lumpy or averaged material differ somewhat in the ratio of the contents of phenol and its derivatives, as well as in the presence of impurities in them, in particular quinoline and its derivatives.

The resinous fraction obtained during thermolysis (coal tar) contains low-boiling (at 230–250 ºC) mineral oils; a phase similar in properties to asphaltenes, subjected to solid phase decomposition at 330–340 ºC, and components with higher temperatures (up to ≥ 600 ºC) of dry sublimation. It has a complex organo-mineral composition of 69 compounds, mainly saturated hydrocarbons — cozanes (~ 40 %) and compounds of various groups of aromatic and polycyclic hydrocarbons, namely benzene derivatives (~ 16 %), naphthalenes (~ 20 %), phenanthrenes (~ 11 %), hopene (~ 10 %). There are impurities of phenols and cholestenes (<1 % each).

The results of the work confirm the conclusions made on the basis of the results of previous studies on the effect of the aggregate state of coal samples on the material and the effect on it during the storage of the environment on the magnitude of the coal gas during thermolysis and on the impurity composition of the sublimate condensate extract.

The author expresses deep gratitude to chief researcher V.A. Kashirtsev and senior researcher V.M. Melenevsky (INGG SB RAS); senior researcher I.Yu. Prosanov (IHTTM SB RAS); senior researcher Yu.V. Patrushev (Insitute of Catalysis SB RAS) for help in carrying out and discussing the results of research.

References

1 Копылов Н.И. Фазовое разложение каменных углей Тавантолгойского месторождения Монголии при их обжиге / Н.И. Копылов // Вестн. Караганд. ун-та. Сер. Химия. — 2019. — Т. 93, № 1. — С. 78–84.

2 Горная энциклопедия: в 5-ти т. — Т. 5 / под ред. Е.А. Козловского. — М.: Сов. энцикл., 1991. — С. 227.

3 Краткая химическая энциклопедия: в 5-ти т. — Т. 2, 5 / под ред. И.Л. Кнунянца. — М.: Сов. энцикл., 1963, 1967. — С. 330, 326.

4 Семёнов П.П. Тувинские угли как база коксохимической промышленности Востока / П.П. Семёнов // Кокс и химия. — 1958. — № 6. — С. 10, 11.

5 Соднам Н.И. Характеристика каменного угля Каа-Хемского месторождения / Н.И. Соднам, М.Л. Щипко, Б.Н. Кузнецов // Химия твёрдого топлива. — 1987. — № 6. — С. 12–14.

6 Фаткулин И.Я. Использование углей Улуг-Хемского бассейна как возможность улучшения сырьевой базы коксования / И.Я. Фаткулин, М.И. Стуков, Л.Г. Ольшанский, Б.П. Киселёв // Кокс и химия. — 1987. — № 7. — С. 4–6.

7 Лосев А.П. Угольные бассейны и месторождения Тувинской АССР / А.П. Лосев. — М.: Недра, 1964. — 98 с.

8 Фаткулин И.Я. Подготовка резервной базы коксующихся углей Российской Федерации: состояние и перспективы / И.Я. Фаткулин, Л.Г. Ольшанский, Е.В. Пантелеев, Б.П. Киселёв // Кокс и химия. — 1994. — № 7. — С. 2–5.

9 Лебедев В.И. Минерально-сырьевой потенциал Республики Тыва: возможности его использования в 1999–2001 гг. и перспектива дальнейшего освоения / В.И. Лебедев, К.С. Кужигет. — Кызыл: ТувИКОПР СО РАН, 1998. — С. 22–24.

10 Геология Монгольской Народной Республики / под ред. Н.А. Миронова, Р.А. Хасина, Ч. Хурц. — М.: Недра, 1973; 1977. — Т. I. —564 с.; Т. II. — 675 с.; Т. III. — 703 с.

11 Семёнова С.А. Влияние окислительного модифицирования на химический состав и свойства угля месторождения Хушуут (Монголия) / С.А. Семёнова, Н.И. Фёдорова, Д.П. Иванова, А.Н. Заостровский, З.Р. Исмагилов // Химия в интересах устойчивого развития. — 2012. — Т. 20, № 5. — С. 599–605.

12 Erdenetsogt Bat-Orshikh Mongolian coal-bearing basins: Geological settings, coal characteristics, distribution, and resources / Bat-Orshikh Erdenetsogt, Insung Lee, Delegiin Bat-Erdene, Luvsanchultem Jargal // Int. Journal of Coal Geol. — 2009. — Vol. 80, Iss. 2. — P. 87–104.

13 Шабалов В.И. Обобщение результатов геологоразведочных работ по Улуг-Хемскому угольному бассейну по состоянию на 01.01.1993 г. / В.И. Шабалов. — Кызыл: ТТФГИ, 1994.

14 Копылов Н.И. Термическое разложение углей Тувинского месторождения / Н.И. Копылов, Ю.Д. Каминский // Химия в интересах устойчивого развития. — 2013. — Т. 21, Вып. 3. — С. 319.

15 Свердлов Л.М. Колебательные спектры многоатомных молекул / Л.М. Свердлов, М.А. Ковнер, Е.П. Крайнов. — М.: Наука, 1970. — 560 с.

16 Петров А.А. Масс-спектры нефтяных углеводородов. Справочник (атлас) / А.А. Петров, Л.С. Головкина, Г.В. Русанова. — М.: Недра, 1986. — 312 с.

17 Лебедев А.Т. Масс-спектрометрия в органической химии / А.Т. Лебедев. — М.: БИНОМ. Лаборатория знаний, 2003. — 493 с.

18 Копылов Н.И. Термолиз бурого угля Багануурского месторождения (Монголия) / Н.И. Копылов // Вестн. Караганд. ун-та. Сер. Химия. — 2017. — Т. 88, № 4. — С. 80–87.

Н.И. Копылов

Монғолиядағы Таван-Толгой кен орны тас көмірінің термиялық ыдырау өнімдерінің химиялық, фазалық құрамы мен қасиеттері

Мақалада Монғолиядағы Таван-Толгой кен орны тас көмірінің термиялық ыдырау нәтижесінде түзілген өнімдерінің — көмірдің термиялық ыдырау қатты қалдығы, шайырлы фракциясы, сұйық конденсат және конденсаттан бөлінген органикалық фракциясының химиялық, фазалық құрамдарын зерттеу нәтижелері келтірілген. Олардың құрамдары, түзілу және фазалық түрленуінің температуралары анықталды. Қатты қалдықта аздаған мөлшерде ароматты көмірсутектер, эфирлі топтар мен фенолдар қалдықтары қалады. Жеңіл қайнайтын конденсат құрамында органикалық компоненттен (~1 %) тұратын сулы ерітіндіні — экстракт пен шайырлы фракция қалдықтары құрайды. Конденсат экстракты фенол және оның туындыларынан тұрады. Шайырлы фракциясы жеңілқайнайтын майлардан және фазадан тұрады, ол термиялық қасиеттері бойынша асфальтендерге жақын, оның құрамы 70-ке жуық органикалық заттан тұрады, соның ішінде қаныққан көмірсутектер (~40 % жуық), ароматты және көпядролы көмірсутектер: бензол, нафталин, фенантрен, гопен туындылары мен фенол және холестен қалдықтарынан тұратындығы анықталды.

Кілт сөздер: фазалық ыдырау, қатты тұнба, шайырлы фракция, конденсат, возгондар, конденсаттың органикалық фазасы.

Н.И. Копылов

Химический, фазовый состав и свойства продуктов термического разложения каменного угля Таван-Толгойского месторождения Монголии

Приведены результаты исследования химического и фазового состава продуктов термического разложения каменного угля Таван-Толгойского месторождения Монголии: твёрдого остатка термического разложения угля, смолистой фракции, жидкого конденсата и выделенной из конденсата органической фракции. Определены их составы, температуры образования и фазовых преобразований. В твёрдом остатке в небольшом количестве сохраняются реликты ароматических углеводородов, эфирные группы и фенолы. Легкокипящий конденсат представляет водный раствор с небольшой примесью (~1 %) органического компонента — экстракта и следы смолистой фракции. Экстракт конденсата в основном содержит фенол и его производные. Смолистая фракция содержит легкокипящие масла и фазу, по термическим свойствам близкую асфальтенам, включающей до 70 органических веществ, с преобладанием (~40 % отн.) предельных углеводородов, наличия различных групп ароматических и многоядерных углеводородов: производных бензола, нафталинов, фенантренов, гопенов, следы фенолов и холестенов.

Ключевые слова: фазовое разложение, твёрдый осадок, смолистая фракция, конденсат, возгоны, органическая фракция конденсата.

References

1 Kopylov, N.I. (2019). Fazovoe razlozhenie kamennykh uhlei Tavan-Tolhoiskogo mestorozhdeniia Monholii pri ikh obzhihe [Phase decomposition of the coals of the Tavantolgoy deposit in Mongolia during roasting]. *Vestnik Karahandinskoho universiteta. Seriia Khimiia — Bulletin of the Karaganda University. Chemistry series*, *93*(1), 78–84 [in Russian].

2 Kozlovsky, E.A. (Eds.). (1991). *Hornaia entsiklopediia [Mountain Encyclopedia].* (Vols. 1–5; Vol. 5). Moscow: Soviet Entsiklopediia [in Russian].

3 Knunyants, I.L. (Eds.). (1963, 1967). *Kratkaia khimicheskaia entsiklopediia [Brief chemical encyclopedia].* (Vols. 1–5; Vols. 2, 5). Moscow: Soviet Entsiklopediia [in Russian].

4 Semenov, P.P. (1958). Tuvinskiie uhli kak baza koksokhimicheskoi promyshlennosti Vostoka [Tuva coal as a base of the coking industry of the East]. *Koks i khimiia — Coke and Chemistry*, *6*, 10–11 [in Russian].

5 Sodnam, N.I., Shchipko, M.L., & Kuznetsov, B.N. (1987). Kharakteristika kamennoho uhlia Kaa-Khemskoho mestorozhdeniia [Characteristics of the Kaa-Khem coal deposit]. *Khimiia tverdoho topliva. — Chemistry of solid fuels*, *6*, 12–14 [in Russian].

6 Fatkulin, I.Ya., Stukov, M.I., Olshansky, L.G., & Kiselev, B.P. (1987). Ispolzovaniie uhlei Uluh-Khemskoho basseina kak vozmozhnost uluchsheniia syrievoi bazy koksovaniia [Using the Ulug-Khem coal basin as an opportunity to improve the raw material base of coking]. *Koks i khimiia. — Coke and Chemistry*, *7*, 4–6 [in Russian].

7 Losev, A.P. (1964). *Uholnye basseiny i mestorozhdeniia Tuvinskoi ASSR [Coal basins and deposits of Tuva ASSR].* Moscow: Nedra [in Russian].

8 Fatkulin, I.Ya., Olshansky, L.G., Panteleev, E.V., & Kiselev, B.P. (1994). Podhotovka rezervnoi bazy koksuiuschikhsia uhlei Rossiiskoi Federatsii: sostoianiie i perspektivy [Preparation of the reserve base of coking coal of the Russian Federation: status and prospects]. *Koks i khimiia. — Coke and Chemistry*, *7*, 2–5 [in Russian].

9 Lebedev, V.I. & Kuzhiget, K.S. (1998). *Mineralno-syrievoi potentsial Respubliki Tyva: vozmozhnosti eho ispolzovaniia v 1999–2001 hh. i perspektiva dalneisheho osvoieniia [Mineral and Raw Material Potential of Tyva Republic: the possibility of its use in 1999–2001 and the prospect of further development].* Kyzyl: TuvIKOPR SB RAS [in Russian].

10 Mironova, O.N., Hasina, R.A., & Hurz, Ch. (Eds.). (1973, 1977). *Heolohiia Monholskoi Narodnoi Respubliki [Geology of the Mongolian People's Republic].* (Vols. I–III). Moscow: Nedra [in Russian].

11 Semenova, S.A., Fedorova, N.I., Ivanova, D.P., Zaostrovsky, A.N., & Ismagilov, Z.R. (2012). Vliianiie okislitelnoho modifitsirovaniia na khimicheskii sostav i svoistva uhlia mestorozhdeniia Khushuut (Monholiia) [The effect of oxidative modification on the chemical composition and properties of coal from the Khushuut deposit (Mongolia)]. *Khimiia v interesakh ustoichivoho razvitiia — Chemistry in the interests of sustainable development, 20(5)*, 599–605 [in Russian].

12 Bat-Orshikh Erdenetsogt, Insung Lee, Delegiin Bat-Erdene, & Luvsanchultem Jargal (2009). Mongolian coal-bearing basins: Geological settings, coal characteristics, distribution, and resources. *Int. Journal of Coal Geol.*, *80*(2), 87–104.

13 Shabalov, V.I. (1994). Obobshchenie resultatov heolohorazvedochnykh rabot po Uluh-Khemskomu uholnomu basseinu po sostoianiiu na 01.01.1993 h. [Generalization of the results of exploration works on the Ulug-Khem coal basin as of January 1, 1993]. Kyzyl: TTFGI [in Russian].

14 Kopylov, N.I., & Kaminsky, Yu.D. (2013). Termicheskoie razlozheniie uhlei Tuvinskoho mestorozhdeniia [Thermal decomposition of coal from the Tuva deposit]. *Khimiia v interesakh ustoichivoho razvitiia — Chemistry for Sustainable Development*, *21*(3), 319 [in Russian].

15 Sverdlov, L.M., Kovner, M.A., & Krainov, E.P. (1970). *Kolebatelnye spektry mhohoatomnykh molekul [Oscillatory spectra of polyatomic molecules].* Moscow: Nauka [in Russian].

16 Petrov, A.A., Golovkina, L.S., & Rusanova, G.V. (1986). *Mass-spektry neftianykh uhlevodorodov. Spravochnik (atlas). [Mass spectra of petroleum hydrocarbons. Reference (atlas)].* Moscow: Nedra [in Russian].

17 Lebedev, A.T. (2003). *Mass-spektrometriia v orhanicheskoi khimii [Mass spectrometry in organic chemistry].* Moscow: BINOM. Laboratoriia znanii [in Russian].

18 Kopylov, N.I. (2017). Termoliz buroho uhlia Bahanurskoho mestorozhdeniia (Monholiia). Thermolysis of brown coal from the Baganurskoye deposit (Mongolia). *Vestnik Karahandinskoho universiteta. Seriia khimiia — Bulletin of the Karaganda University. Chemistry series*, *88*(4), 80–87.

DOI 10.31489/2019Ch3/96-101

UDC 622.276.58

A.Zh. Naukenova[1], N.D. Sarsenbekov[2], B.Ye. Bekbauov[3]

[1]Al-Farabi Kazakh National University, Almaty, Kazakhstan;
[2]Scientific Research Institute «Caspimunaigas» LLP, Atyrau, Kazakhstan;
[3]K.I. Satpayev Kazakh National Research Technical University, Almaty, Kazakhstan
(E-mail: altynay.naukenova@gmail.com)

A comprehensive review of polymer and alkaline/surfactant/polymer flooding applied and researched in Kazakhstan

Polymer flooding and alkaline/surfactant/polymer flooding have been applied throughout the world for more than 30 years. However, they were not as popular as other types of enhanced oil recovery methods such as thermal methods and gas injection in Kazakhstan. To date, the polymer and alkaline/surfactant/polymer (ASP) flooding processes have been applied successfully in several Kazakhstan oil fields due to technology progress and changes in chemical costs and successful polymer and ASP flooding experiences in the world. This paper shows application of chemical enhanced oil recovery methods in several oil fields in Kazakhstan, where pilot on-site experiments and core flood tests on chemical flooding methods were carried out. The paper describes the latest pilot tests on polymer flooding in oil fields such as Nuraly, Zaburunie and Kalamkas, where polymer flooding alone contributed approximately 150 000 tons of produced crude oil. Several ASP floods also have been tested in local fields. Laboratory researches were carried out in core samples of Eastern Moldabek and Karazhanbas oil fields. Increase in oil recovery up to 80 % have been reported, however pilot tests have not been implemented yet. This paper discusses researches conducted in these fields including field / laboratory results, methods of flooding, polymer types and concentrations used.

Keywords: oil fields, pilot test, polymer flooding, recovery factor, concentration, water cut.

Introduction

The use of chemical flood is not a new technology in enhanced oil and gas recovery methods in local fields. However, recently oil companies in Kazakhstan express their interest in this type of tertiary method again, due to technology progress, changes in chemical costs and successful polymer and ASP flooding in the USA, China and Russia. Several chemical enhanced oil recovery methods such as polymer and ASP flooding are used and are planned to use in Kazakhstan. These methods are based on interfacial tension reduction between oil and water contact, increasing water viscosity as a result improving oil mobility.

Polymer flooding has been applied in Nuraly, Zaburunie and Kalamkas fields. Because of the high water cut in these fields, primary goal of polymer flooding was reduction the amount of water being produced with the oil, while increasing the recovery of the original oil in place. Addition of polymer increases the viscosity of aqueous phase, bringing it closer to that of the heavy oil in place, consequently, decreasing water mobility.

With the polymer flooding ASP flooding is also included to the experiments. Core flood tests on ASP flooding were conducted on core samples of Moldabek and Karazhanbas fields. This type of chemical method integrates the advantages of alkali, surfactant and polymer use. Adding surfactant reduces interfacial tension, injecting alkali results in wettability alteration. Alkali with dilute surfactant solution can change the wettability, the alkali can reduce the surfactant adsorption. Polymer in ASP acts as the mobility control agent. The combination of alkali, surfactant and polymer effects enables ASP process a great potential for enhanced oil recovery. Core flood tests showed optimistic results.

Pilot on-site experiments

Nuraly field

Pilot on-site experiments were carried out on Nuraly field. Polymer flood pilot was started on June 2014. Two injection wells and eight reacted production were used for the polymer application. Location of wells and polymer pilot area are shown in Figure 1.

Field information

The proven oil resource is estimated at 2,712,500 tons, reservoir is located on South Torgai basin, thickness varies in between 3.4 to 24.2 meters. Reservoir is characterized by layered, fissured, heterogeneous sandstone. The reservoir porosity is 22–24.5 % and permeability intervals are in the range of 2 to 2200 md. The field produces light oil (API 40º) with paraffin and asphaltine compounds. Oil production was started in 1996 and water cut before polymer flooding reached 90 % [1].

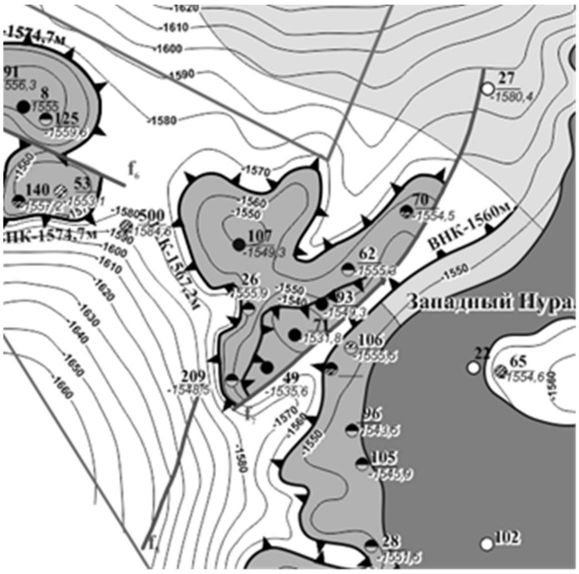


Figure 1. Pilot test area on Nuraly field

Experimental

The Nuraly polymer core flood study was conducted under reservoir conditions with objectives of screening and evaluating suitable polymer and its concentration for the field application. The results of the study showed 10 % increase in oil recovery. After the study it was decided to fill 30 % of pore volume of the reservoir starting from higher concentration slowly lowering it. Therefore, from September until December 2014 the injected polymer concentration was decreased from 6000 ppm to 3000 ppm for well No. 26 and from 4000 ppm to 2000 ppm for well No. 106. Detailed information about results is given in Table 1.

Table 1

Program of the polymer flooding in Nuraly field

Date	Days	Concentration of polymer FP5205VHM (ppm)		Viscosity of polymer, cP		Injection rate, m^3/day		Polymer (tons)	Cumulative polymer (tons)
		Well 26	Well 106	Well 26	Well 106	Well 26	Well 106		
Stages of polymer injection									
23.09–30.11.2014	70	6000	4000	135	53	130	90	84.14	140.80
01.12–09.12.2014	9	5000	3000	89.2	28.4	130	90	8.76	149.56
10.12–14.12.2014	5	4000	2000	50	9.75	130	90	3.72	153.28
15.12–31.12.2014	17	3000	2000	28.4	9.75	130	90	10.44	163.72

For this period of time additional oil recovery was 7005.5 tons. Two wells No. 28 and No. 66 were added to the polymer injection in 2016. Overall, the polymer pilot has been in place for over three years and incremental oil recovery of 92551.4 tons has been obtained on September 2017. Experiment will continue before 30 % of pore volume is filled with polymer.

Zaburunie field

The field is at the final production stage. Therefore, engineers are trying to recover as much as possible of oil original in place (OOIP). Recoverable reserves are estimated at 7065 thousand tons. Before the polymer flooding water cut was 90 %, daily oil production was 5 tons per day [2].

Field information

In this section, we consider only the part of Zaburunie field, where polymer test was applied. Polymer was injected in Neocomian II division, covering 2573 thousand square meters. Reservoir is represented by sandstones, aleuritic and shale deposits with an average net pay 17 meters. The test area has an average porosity of 30 % and permeability reaches maximum value of 2000 md.

Experiment

Pilot on site experiment started on November 22, 2014. The pilot area had 2 injection and 38 reacted production wells. Several polymers were screened on core samples to find the suitable type for reservoir characteristics. In the experiment 4 types of polymer were tested, they are FP 5115 SH (green line), FP 5115 VHM (blue line), FP 5205 SH (red line) and FP 5205 VHM. Relation of viscosity and polymer concentration were found and based on results Flopaam 5205VHM polymer was chosen to the pilot test. Results of the experiment are shown in Figure 2.

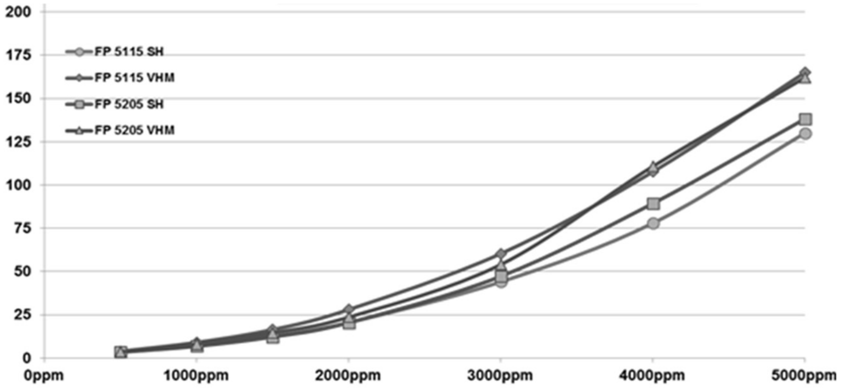


Figure 2. Relation of viscosity and concentration

Different slug process was designed in the following way:

– The concentration of the polymer in the two injection wells increased during the first 15 days from 500 to 1000 ppm in order to track formation response, well reactions for polymer injection, changes in wellhead and bottom hole pressure of injection wells and operation of all units and assemblies.

–As soon as a stable injection volume was established, the injection continued at the required concentration of 2000 ppm.

– Then injection of the polymer at a concentration of 1000 ppm was followed for the next 110 days.

– In the last 50 days of polymer injection, concentration decreased to 500 ppm.

Detailed program of the polymer flooding is shown in Table 2.

Table 2

Program of the polymer flooding in Zaburunie field

Days	Concentration of polymer FP5205VHM (ppm)	Viscosity of polymer	Max injection rate (m^3/day)		Polymer (tons)	Cumulative polymer (tons)
		(cP)	Well 11	Well 55		
1st stage. Pilot on site experiment (6 month)						
5	500	2.5	205	200	1.11	1.11
5	750	4	205	200	1.67	2.78
5	1000	6	205	200	2.23	5.01
169	2000	21	205	200	150.58	155.59
2nd stage. Industrial application (3 years)						
936	2000	21	205	200	833.98	989.57
110	1000	6	205	200	49.01	1038.57
50	500	2.5	205	200	11.14	1049.71

In about a year of the experiment increase in oil production was about 19 086 tons of crude oil and water cut decreased from 87 % to 82 %. Permeability declined to 30 % after the polymer injection. This project is now on industrial application stage. For the period of 2014–2017 an incremental oil recovery is estimated at 89 tons. To the next year of 2018 it is planned to increase the number of injection wells from 2 to 6. Following wells will be added to the polymer flooding area (Fig. 3) No. 14, 48, 42, 34.

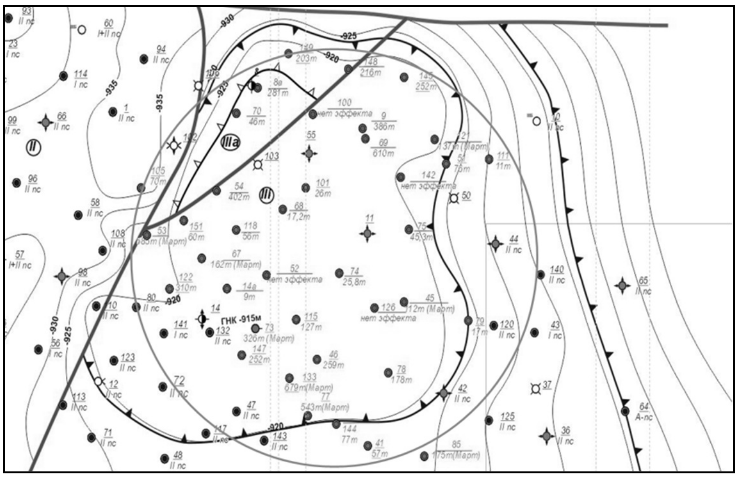


Figure 3. Pilot test area on Zaburunie field

Kalamkas field

The field was discovered in 1976 and the primary production in the field began in 1979. In 2004 oilfield achieved first 100 million tons of crude oil produced [3]. The proven oil resource is estimated at 207883 thousand tons. Field produces a medium viscous oil (API 24º, oil viscosity varies 11.5–21.2 cp) with paraffin and Sulphur compounds [4].

Field information

The field is located on the Buzachi Peninsula in the western part of Kazakhstan.

The reservoir depth is 500–1000 meters, deposit is a complex combined type of massive reservoir with a single hydrodynamic system (reservoirs are combined into one powerful oil and gas reserves). Productive layers are characterized by the terrigenous deposits [5].

Experiment

This field is the pilot test as well. The polymer slug was injected on September 27, 2014. For the polymer program, 2 injection wells (No. 2041, 2049) and 21 reacted production wells were chosen. In about a half of the year increase in oil production was about a thousand ton of crude oil and water cut decreased to 3 %. One more well No. 1580 was added to polymer test in March 2015 and an industrial application is planned before 2020 with 6 % predicted increase in oil recovery. In the history of this oilfield there was a polymer flooding in yearly 1983 and it was a successful project with additional 53920 tons of produced oil [6]. Operating company of the Kalamkas field «Mangystau munaigas» plans to expand polymer flooding to the field «Zhetybai».

Laboratory researches

After these experiments of polymer flooding, chemical enhanced methods are taken into account as alternative production on the latest development stages on the other local fields. For example, several ASP laboratory flood tests were conducted in Eastern Moldabek and Karazhanbas oil fields.

Karazhanbas

Karazhanbas oilfield is located at Buzachi peninsula. It was discovered in 1974 and put into the production in 1980. The reservoir is multi-layered, oil accumulations were discovered in six Lower Cretaceous layers (A1, A2, B, V, G, D) and in two upper Jurassic formations (U-1, U-2). Karazhanbas crude is high viscous oil. It has high-sulfur and resin content.

Experiment

For sand pack filtration experiments, crude oil with 926 kg/m^3 density and 300mPa sec viscosity was used. Models in the experiment were 8.6 cm in length, 4.3 cm in diameter with average permeability 6 Darcy. All filtration experiments were conducted by using «UIK-S(2)» apparatus for cores investigation (Russia). To investigate the oil displacement efficiency by using ASP formula, several experiments with varying concentrations of CROHDA-MAA (0.5 %; 0.25 %; 0.125 %) dissolved in KOH solution were conducted. Results of experiment were optimistic showing decrease in water cut on 50–60 % in all models. Oil displacement coefficient varied from 0.3 to 0.35, maximum was reached by solution with concentration of CROHDA-MAA 0.5 % [7].

Eastern Moldabek

Eastern Moldabek is a part of the Kenbai oil and gas deposits. Production was started in 1999. Ten productive layers which are characterized by Cretaceous and Jurassic layers were included to the production stage. The reservoir is terrigenous, porosity is about 30–34 % and produced oil is highly viscous with sulphur and paraffin compounds [8].

Experiment

For the filtration experiment, 4 core samples of Eastern Moldabek field, crude oil and model of the produced water were used. Core samples had porosity about 22–27 % and different permeability values ranged between 393–2370 md were used. The aim of the experiment was to compare polymer and ASP flooding and determine the effective one for this field. Based on geological characteristics of the field FloPaam 5205 polymer with concentration 2500 ppm was chosen. Experiment was conducted at reservoir conditions, for which the PLS-200 system with 4 coreholders was applied. Results of the experiment showed increase in oil recovery up to 68 % in both cases, in polymer and ASP injections.

The results of filtration experiments in Eastern Moldabek and Karazhanbas fields were successful and for both of these fields they can be considered as enhanced oil recovery method.

Conclusion

Overall, the application of polymer flooding in all three oilfields showed optimistic results on increasing additional oil recovery and decreasing water cut. However, it is too early to make a decision on economic profitability of the projects. Nevertheless, these site experiments help to progress enhanced oil recovery methods and give experience to improve polymer flood technology, including the development of the project, design of polymer type and concentration to better fit reservoir characteristics in order to maximize economic returns.

The authors would like to express their sincere appreciation to management of LLP SRI «CASPIMUNAIGAS» for provided information.

References

1 Абиров Р.Ж. Опытно-промышленное внедрение полимерного заводнения на месторождении Южно-Тургайского бассейна / Р.Ж. Абиров, А.Г. Мухамедова, Б. Панабеккызы, Н.А. Еремин, Ж.Ж. Абиров, А.А. Нестеркин // Нефтепромысловое дело. — 2016. — № 5 — С. 15–19.

2 Муллаев Б. Месторождение Узень. Проблемы и решения. — Т. 2 / Б. Муллаев, А. Абитова, О. Саенко, Б. Туркпенбаева. — Алматы: Нур принт, 2016. — 400 с.

3 Полимерное заводнение в Казахстане [Электронный ресурс]. — Режим доступа https://snf-group.ru/wp-content/uploads/2015/08/Polimernoe-zavodnenie-v-RK.pdf.

4 Официальный сайт комитета геологии и недропользования. Справочник месторождений Казахстана. Нефтегазовые месторождения Казахстана. Каламкас. [Электронный ресурс]. — Режим доступа http://info.geology.gov.kz/ru/informatsiya/spravochnik-mestorozhdenij-kazakhstana/neftegazovye-mestorozhdeniya/item/%D0 %BA%D0 %B0 %D0 %BB%D0 %B0 %D0 %BC%D0 %BA%D0 %B0 %D1 %81.

5 Крымкулов С.Е. Новые данные о строении юрской продуктивной толщи месторождения Каламкас / С.Е. Крымкулов, А.М. Тастыгараев, М.М. Рымбаев, В.П. Токарев, К.В. Виноградова // Геология нефти и газа. — 2003. — № 3. — С. 11.

6 Курбанбаев М.И. Планирование ВГВ на месторождении Каламкас / М.И. Курбанбаев., В.Я. Мирошников., С.И. Толоконский // Нефть. Газ. Новации. — 2010. — № 10. — С. 39–44.

7 Kudaibergenov S. Laboratory study of ASP flooding for viscous oil / S. Kudaibergenov, T.K. Akhmedzhanov, B.Zh. Zhappasbayev, Sh. Gussenov, A.V. Shakhvorostov // International Journal of Chemical Sciences. — 2015. — Vol. 13, No. 4. — P. 2017–2025.

8 Шеркешбаева К. Особенности разработки месторождения Восточный Молдабек / К. Шеркешбаева // Вестн. Национальной инженерной академии РК. — 2008. — № 4. — С. 97–106.

А.Ж. Наукенова, Н.Д. Сарсенбеков, Б.Е. Бекбауов

Қазақстан кен орындарында өткізілген полимерлік және полимер/БАЗ/сілті суландыру бағытындағы зерттеулерге кешенді шолу

Мақалада қазақстандық мұнай кен орындарында қолданылған полимерлік суландыру әдістерін зерттеулері мен оның нәтижелері қарастырылған. Нұралы, Забурунье және Қаламқас кен орындарындағы тәжірибелі-кәсіпшілік сынау сипатталды. Осы кен орындарында тәжірибелік-өнеркәсіптік сынақтар кезеңінде қойнау қабатқа полимерлік әсер етудің есебінен қосымша өндірілген шикі мұнай көлемі шамамен 150000 т құрады. Сондай-ақ авторлар полимердің БАЗ және сілтілермен комбинациядағы ерітінділерімен керндік материалдарды суландыру бойынша зертханалық зерттеулерге тоқталған. Шығыс Молдабек және Қаражанбас кен орындарының керндік үлгілеріне қойнау қабат жағдайында эксперименттер жүргізілді. Сүзгілік зерттеулер нәтижелері оптимистік болып саналады, максималды ығыстыру коэффициенті 80 %-ға дейін артты. Жоғарыда аталған зерттеулер сынақ өткізілген кен орындарының геологиялық қысқаша деректері, полимерлі және аралас суландыру бағдарламасы, пайдаланылған полимер түрі мен концентрациясы көрсетіле отырып берілген және соңғы сынақтардың нәтижелері келтірілген.

Кілт сөздер: мұнай-кен орындары, тәжірибелік-өнеркәсіптік сынақ, полимермен сутоғыту, комбинациялық сутоғыту, итергіштік коэффициенті, кенорнының суланғандық көрсеткіші, концентрация.

А.Ж. Наукенова, Н.Д. Сарсенбеков, Б.Е. Бекбауов

Комплексный обзор исследований на месторождениях Казахстана по полимерному и ПАВ/щелочь/полимерному заводнению

В статье представлены исследования и результаты их полимерных заводнений, применённых на нефтяных месторождениях Казахстана. Описаны опытно-промысловые испытания на месторождениях Нуралы, Забурунье и Каламкас. На данных месторождениях только за счет полимерного воздействия на пласт дополнительно добыто приблизительно 150000 т сырой нефти за период опытно-промышленных испытаний. Также авторами проведены лабораторные исследования по заводнению керновых материалов растворами полимера в комбинации с растворами ПАВ и щелочи. Эксперименты проводились в пластовых условиях, применялись керновые образцы месторождений Восточный Молдабек и Каражанбас. Результаты фильтрационных исследований считаются оптимистичными, максимальный коэффициент вытеснения увеличился до 80 %. Перечисленные выше исследования приведены с указанием кратких геологических данных месторождений, программы полимерного и комбинированного заводнения, концентрации и типа применяемого полимера, а также даны последние результаты испытаний.

Ключевые слова: нефтяные месторождения, опытно-промышленные испытания, полимерное заводнение, комбинированное заводнение, коэффициент вытеснения, обводненность, концентрация.

References

1 Abirov, R.Zh., Muhamedova, A.G., Panabekkyzy, B., Eremin, N.A., Abirov, Zh.Zh., & Nesterkin, A.A. (2016). Opytno-promyshlennoe vnedrenie polimernoho zavodneniia na mestorozhdenii Yuzhno-Turhaiskoho basseina [Experimental and industrial application of a polymer flooding in the South Turgai basin]. *Neftepromyslovoe delo — Petroleum Engineering*, *5*, 15–19 [in Russian].

2 Mullaev, B., Abitova, A., Saenko, O., & Turkpenbaeva, B. (2016). *Mestorozhdeniie Uzen. Problemy i resheniia [Uzen Oilfield. Problems and solutions].* (Vol. 2). Almaty: Nur Print [in Russian].

3 Polimernoe zavodneniie v Kazakhstane [Polymer flooding in Kazakshtan] (2015). *snf-group.ru* Retrieved from https://snf-group.ru/wp-content/uploads/2015/08/Polimernoe-zavodnenie-v-RK.pdf [in Russian].

4 Ofitsialnyi sait Komiteta heolohii i nedropolzovaniia. Spravochnik mestorozhdenii Kazakhstana. Neftehazovye mestorozhdeniia Kazakhstana. Kalamkas [Official web site of Committee of geology subsoil use. Kazakhstan deposits book. Kazakhstan oilfields. Kalamkas]. *info.geology.gov.kz* Retrieved from http://info.geology.gov.kz/ru/informatsiya/spravochnik-mestorozhdenij-kazakhstana/neftegazovye-mestorozhdeniya/item/%D0 %BA%D0 %B0 %D0 %BB%D0 %B0 %D0 %BC%D0 %BA%D0%B0 %D1 %81 [in Russian].

5 Krymkulov, S.E., Tastygaraev, A.M., Rymbaev, M.M., Tokarev, V.P., & Vinogradova, K.V. (2003). Novye dannye o stroenii yurskoi produktivnoi tolshchi mestorozhdeniia Kalamkas [New data on the structure of the Jurassic productive strata of the Kalamkas deposit]. *Heolohiia nefti i haza. — Geology of oil and gas*, *3*, 11 [in Russian].

6 Kurbanbaev, M.I., Miroshnikov, V.Ya., & Tolokonskii, S.I. (2010). Planirovanie VGV na mestorozhdenii Kalamkas [Planning a water-gas injection method in Kalamkas oilfield]. *Neft. Haz. Novatsii. — Oil. Gas. Innovations*, *10*, 39–44 [in Russian].

7 Kudaibergenov, S., Akhmedzhanov, T.K., Zhappasbayev, B. Zh., Gussenov, Sh., & Shakhvorostov, A.V. (2015). Laboratory study of ASP flooding for viscous oil. *International Journal of Chemical Sciences*, *13, 4*, 2017–2025.

8 Sherkeshbayeva, B.K. (2008). Osobennosti razrabotki mestorozhdeniia Vostochnyi Moldabek [Features of the development of Eastern Moldabek deposits]. *Vestnik Natsionalnoi inzhenernoi akademii RK — Bulletin of the National Engineering Academy of RK*, *4*, 97–106 [in Russian].

DOI 10.31489/2019Ch3/102-106

UDC628.16. 066.7

B.B. Orazbayev[1], L.T. Kurmangaziyeva[2], G.K. Shambilova[2], A.A. Muratbekova[3]

[1]L.N. Gumilyov Eurasian National University, Nur-Sultan, Kazakhstan;
[2]Kh. Dosmukhamedov Atyrau State University, Kazakhstan;
[3]Ye.A. Buketov Karaganda State University, Kazakhstan
(E-mail: shambilova_gulba@mail.ru)

The optimization of device parameters for the separation of oily mixtures by sedimentation

Theoretical studies of optimal sizes of sedimentation equipment for water treatment polluted with oil residues and industrial effluents were carried out, and design and operation experience were analyzed. Thus, it was determined that wastewater treatment issues in cities and towns characterized by high productivity were mainly investigated. Oily water formed during the liquidation of emergency oil and petroleum spills is treated at local treatment facilities with low cleaning capacity and specific design and operation features. The effective solution approach to treat oily mixture by sedimentation was proposed. Algorithm was developed to optimize parameters of sedimentation equipment for oily mixture treatment which determines optimal sizes of sedimentation equipment providing the most effective oily mixture treatment at minimum cost of material for equipment fabrication. The proposed algorithm for calculation of sedimentation equipment parameters is based on search and selection of optimal equipment capacity and can be used to calculate rectangular equipment size. Thus, due to the above theoretical studies, a method for calculation of sedimentation equipment optimal size was proposed to be used in optimal equipment design for oil mixture treatment.

Keywords: water treatment, oily mixture, sedimentation, sedimentation equipment, optimization, oily mixture treatment by sedimentation, equipment optimal size.

Introduction

Experience relating to the design and use of sedimentation devices for the separation of water from industrial sources is described in many research works, for example in [1–4]. Most of this experience relates to facilities for the separation of waste water from cities and other populations centres, which are characterized by high productivity.

The separation of water which contains oil, which has resulted in the process of sedimentation accidental spills of oil and oil products, is carried out using local waste water treatment facilities, which have a low through-put, and the design and operation of which have their own peculiarities. For example, treatment facilities may be floating [5] or vehicular platforms.

An approach to the optimization of device parameters for the treatment of oily mixtures by sedimentation has been proposed. The algorithm proposed for the calculation of sedimentation device parameters can be used for the calculation of dimensions of rectangular cross-section devices.

Materials and Methods

The process of separation by sedimentation is based on the separation of the oil and oil product particles from the rest of the water being purificated, under the action of the force of gravity — G_m and the Archimedes force — A. The force resulting from these 2 forces, the force F, which is equal to the vectoral sum of these forces, determines the movement of the impurity particles. In addition to the force F acting on the moving particles, there is also another force, S, water resistance, which is constant for the particles in the process under investigation [6]:

$$S(t) = -k_1 \nu(t),$$

where k_1 is the coefficient of proportionality.

The main parameter describing the process of separation of the particles from the water being purified is the velocity of movement of the foreign particles ν. This velocity can be determined by analysis or experimentation.

The following formulae for determining the velocity of movement of the foreign particles are identified, resulting from analysis of the equations of motion of these particles [3, 6]:

$$m\frac{d\nu}{dt} = -k\nu + \frac{\pi d^3}{6} g\Delta\rho,$$

where m is the mass of the oil product particles; v is their speed; $k = 3\pi d\eta$ is the coefficient of proportionality; η is the medium viscosity (i.e. of water); d is the size of the oil product particles; $\Delta\rho$ is the difference in density between the water and the oil products.

Analysis of the equations of motion shows that, independent of the initial velocity v_0, the movement of the particles very quickly becomes steady with a uniform velocity of v_{pr}:

$$\nu_{pr} = \frac{C}{\alpha} = \frac{g(\Delta\rho)d^2}{18\eta}.$$

Taking into account the direction of flow of the purified water, the velocity $\overline{v}_h$ of the movement of the oil product particles shall equal $\overline{v}_h = \overline{v}_{pr} + \overline{v}_v$, where $\overline{v}_v$ is the velocity of flow of the purified water.

For horizontal single-flow sedimentation devices, in which the flow of purified water moves horizontally, the velocity v_h of movement of the impure oil product particles can be calculated using the formula:

$$\nu_h = \sqrt{\nu_{pr}^2 + \nu_v^2}.$$

For vertical single-flow sedimentation devices, in which the flow is downwards (upwards), the velocity v_h is determined by the formula:

$$\nu_h = v_{pr} - v_v \; (v_h = v_{pr} + v_v).$$

The well-known principles [4, 7] are fundamental to calculations for the sedimentation devices for local water treatment facilities, in connection with which the required volume V of the device is determined by the conditions

$$\Delta t = t_v - t_h \geq 0,$$

where t_v is the time that the water being purified is inside the sedimentation device; t_h is the time that it takes for the oil product particles to rise to the upper part of the sedimentation device, that is to separate from the purified water.

For cylindrical forms of sedimentation devices of a vertical nature with a diameter D and height H

$$t_v = \frac{\pi D^2 H}{4Q}.$$

For horizontal sedimentation devices with a rectangular cross-section

$$t_v = \frac{abh}{Q}.$$

The time of movement of the oil product particles for cylindrical and rectangular cross-section sedimentation devices accordingly equals

$$t_h = \frac{H}{\nu_\eta} \text{ and } t_h = \frac{h}{\nu_h}.$$

Results

As a result of the research which has been carried out, the following sequence of calculations is proposed for the calculation of the dimensions of sedimentation devices, for example for devices having a cylindrical form.

Using the known relationship $t_\theta = t_h$ or $\frac{V}{Q} = \frac{H}{\nu_h}$ it becomes possible to propose a formula for the determination of the volume V of the sedimentation device:

$$V = \frac{QH}{v_h}.$$

The required volume V of various containers can be achieved with various relationships between the dimensions [6, 8]. Taking into account the fact that the existing methods for calculating dimensions of sedimentation devices do not give sufficiently sound recommendations for the determination of their optimal dimensions [4, 9–11], we can use the above mentioned characteristic of geometric shapes to determine the optimal ratio of dimensions for sedimentation devices.

The results of the calculation show that the surface area S of the device for various ratios of dimensions of the device without variation in its volume V will have varying values.

For this calculation, in this paper we are proposing an algorithm consisting of the following basic steps:

1. The diameter of the sedimentation device D is given;
2. Using the formula $H=\frac{4V}{\pi D^2}$ the height H of the sedimentation device is calculated;
3. Using the value of D which is given and the height H of the sedimentation device which is derived in point 2, the surface area S of the device is determined: $S=2\left(\frac{\pi D^2}{4}\right)+\pi DH$;
4. For different diameters D of the sedimentation device, points 2 and 3 are repeated and a range of values for S are calculated for various values of D and H.

Discussion

Figure 1 shows the results of calculations for the surface area S for cylindrical sedimentation devices within the limits of a volume V from 0.25 to 2.0 m^3 [12]. An analysis of the results shows the occurrence of minimal values for surface area S in the size range under consideration. The minimal value of the surface area S corresponds to minimal cost of materials.

However, a more objective indicator of the cost of materials for the production of sedimentation devices is the volume of materials B. Taking into account the thickness of the device walls, and also the presence of rigidity or other such factors in construction, it is possible to calculate the volume B of materials required for various values of D and H.

Results for the calculations of the volume B of materials used in production, taking into account the thickness of the materials and the presence of elements of rigidity are shown in Figure 2. Calculations of the value of B were carried out for devices with a volume V ranging from 1.0; 2.0 and 4.0 m^3. Analysis of the results of the calculations shows the occurrence of minimal values of the volume of material used in production. It is evident that the size of the sedimentation devices which results in a minimal value of B should be used.

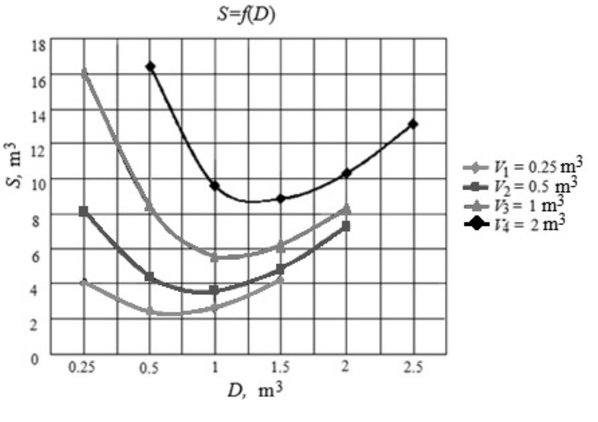


Figure 1. Changes in the surface area of sedimentation devices

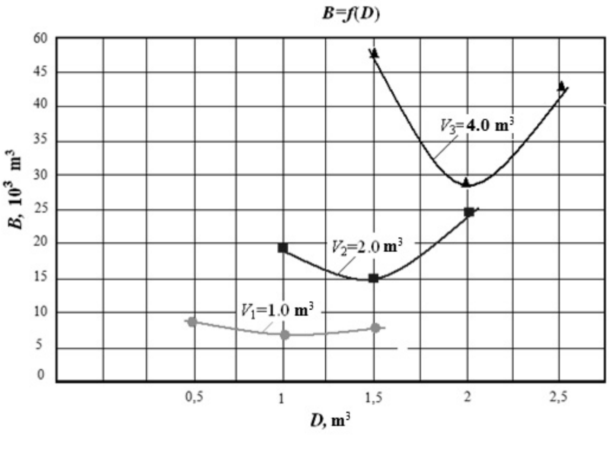


Figure 2. Changes in the volume of materials used in the production of sedimentation devices

The optimal dimensions can be determined as follows: Using the relationship $B=f(D)$, constructed for the required volume V, the value of the diameter D, can be determined for which B will have a minimum value. Using the value for diameter D which has been thus determined and the formula shown above (point 2 of the algorithm) to calculate the height H a new value can be calculated.

Calculations show that the relationship D/H for the range of dimensions under consideration, can have a value from 0.79 to 1.57. For values of $D/H<1$ a horizontal sedimentation device with a cylindrical form is recommended, and for values of $D/H>1$ a cylindrical sedimentation device should be used vertically.

Conclusion

As a result of the theoretical research, which is laid out in this paper, we have been able to propose an algorithm and calculation methods for the computation of optimal dimensions for sedimentation devices, which can then be used in their design.

In this way, according to the research results, this paper has proposed a method for the optimisation of device parameters for sedimentation devices, which allows for the determination of the optimal dimensions of sedimentation devices, ensuring the most effective working regime for the treatment process while minimising expenditure on the materials used to produce the device.

References

1 Жуков А.И. Методы очистки производственных сточных вод / А.И. Жуков, И.Л. Монгайт, И.Д. Родзиллер. — М.: Стройиздат, 1987. — 204 с.

2 Кульский Л.А. Справочник по свойствам, методам анализа и очистке воды / Л.А. Кульский, Н.Т. Гороновский, А.М. Когановский, М.А. Шевченко. — Киев: Наук. думка, 1980. — 126 с.

3 Стахов Е.А. Очистка нефтесодержащих сточных вод / Е.А. Стахов. — Л.: Недра, 1983. — 363 с.

4 Яковлев С.В. Канализация / С.В. Яковлев, Я.А. Карелин, А.И. Жуков. — М.: Стройиздат, 1995. — 632 с.

5 Жигульский В.А. Плавучий комплекс для переработки нефтеводяной смеси / В.А. Жигульский, В.И. Решняк // Судостроение. — 2006. — № 5. — С. 47–48.

6 Зельдович Я.Б. Высшая математика для начинающих физиков и инженеров / Я.Б. Зельдович, И.М. Яглом. — М.: Наука, 1982. — 512 с.

7 Иванов В.М. Экспериментальное исследование поведения частиц жидкого топлива и топливно-водяной эмульсии в окислительной и нейтральной среде / В.М. Иванов, П.И. Нефедов, Б.В. Канторович // Отчеты ИГИ АН СССР, 1960. — 59 с.

8 Решняк В.П. Оптимизация размеров устройств при проектировании природоохранных технических средств: сб. науч. тр. / В.П. Решняк, В.А. Жигульский, Н.Е. Пестерева. — СПб.: СПбГУВК, 2006. — С. 173–178.

9 Яковлев С.В. Очистка производственных сточных вод / С.В. Яковлев. — М.: Стройиздат, 1979. — 35 с.

10 Егорова Е.Н. Методические основы оценки экономического ущерба, возникающего в результате аварийных разливов на морских акваториях / Е.Н. Егорова // Исследование в России. — 2004. — С. 955–971.

11 СНиП 12. 04.03–85 «Проектирование сооружений для очистки сточных вод». — М.: Стройиздат, 1990. — 136 с.

12 Жигульский В.А. Геоэкологические технологии переработки нефтеводяной смеси при ликвидации аварийных разливов: автореф. дис. … канд. техн. наук: спец. 25.00.36 — «Геоэкология» / В.А. Жигульский. — СПб., 2009. — 18 с.

Б.Б. Оразбаев, Л.Т. Курмангазиева, Г.К. Шамбилова, А.А. Муратбекова

Седиментациялау арқылы мұнайсу қоспасын тазалауға арналған құрылғылар көрсеткіштерін оңтайландыру

Мұнай қалдықтары мен өндірістік ағындарымен ластанған сулардың тазалауға арналған седиментациялық құрылғылар өлшемдерінің оңтайлы мәндеріне теориялық зерттеулер жүргізілген. Суды тазалау үшін седиментациялық құрылғаларды жобалау мен пайдалану тәжірибесі талданып, негізінен, үлкен өнімділікпен сипатталатын қалалар мен тұрғын жайлардын ағатын суды тазарту сұрақтары зерттелгені анықталған. Мұнай мен мұнай өнімдерінің апаттық төгілісін жоюда пайда болатын мұнай құрамды суларды тазалау, өздерінің ерекшеліктері бар, өнімі кішігірім локалды тазарту құрылғыларында жүзеге асырылады. Мақалада седиментациялау арқылы мұнайлы су қоспасын тазалау сұрақтарын тиімді шешу тәсілдемесі ұсынылған. Мұнайлы суды тазалайтын седиментациялық құрылғылардың оңтайлы көлемдерін анықтауға мүмкіндік беретін және ондай құрылғыларды дайындауға қажетті минималды материалдар шығынын, тиімді тазалау процесін қамтамасыз ететін седиментациялық құрылғылардың көрсеткіштерін оңтайландыру алгоритмі жасақталып, сипатталған. Седиментациялық құрылғылардың параметрлерін есептеуге, алгоритм құрылғының оңтайлы көлемін іздеуге және таңдап алуға негізделген және тікбұрыш формалы құрылғылар көлемдерін есептеуде қолданылуы мүмкін. Сонымен, теориялық зерттеулер нәтижесінде авторлар мұнайлы су қоспасын тазалау құрылғыларын оңтайлы жобалау кезінде қолдануға болатын, седиментациялық құрылғылар көлемдерінің оңтайлы мәндерін есептеу тәсілін ұсынған.

Кілт сөздер: суды тазалау, мұнайлы су қоспасы, седиментациялау, седиментациялық құрылғы, оңтайландыру, седиментациялау арқылы мұнайлы су қоспасын тазалау, құрылғының оңтайлы өлшемдері.

Б.Б. Оразбаев, Л.Т. Курмангазиева, Г.К. Шамбилова, А.А. Муратбекова

Оптимизация параметров устройств для очистки нефтеводяной смеси седиментацией

Проведены теоретические исследования оптимальных значений размеров седиментационных устройств, предназначенных для очистки воды, загрязненной нефтяными остатками, и промышленных стоков. Проанализирован опыт проектирования и эксплуатации седиментационных устройств для очистки воды, определено, что, в основном исследованы вопросы очистки сточной воды городов и населенных пунктов, которые характеризуются большой производительностью. Очистка нефтесодержащей воды, образующейся при ликвидации аварийных разливов нефти и нефтепродуктов, осуществляется на локальных очистных сооружениях с небольшой производительностью очистки, проектирование и эксплуатация которых имеет свои специфические особенности. В статье предложен подход к эффективному решению вопросов очистки нефтеводяной смеси седиментацией. Разработан и описан алгоритм оптимизации параметров седиментационных устройств для очистки нефтеводяной смеси, который позволяет определить оптимальные размеры седиментационных устройств, обеспечивающих наиболее эффективный режим процесса очистки нефтеводяной смеси при минимальных затратах на материал для изготовления устройств. Предложенный алгоритм расчета параметров седиментационных устройств основан на поиске и подборе оптимального объема устройства и может быть использован для расчета размеров устройств прямоугольной формы. Таким образом, в результате теоретических исследований в настоящей работе предложен метод расчета оптимальных значений размеров седиментационных устройств, который может быть применен при оптимальном проектировании устройств для очистки нефтеводяной смеси.

Ключевые слова: очистка воды, нефтеводяная смесь, седиментация, седиментационное устройство, оптимизация, очистка нефтеводяной смеси седиментацией, оптимальные размеры устройства.

References

1 Zhukov, A.I., Mongait I.L., & Rodziller, I.D. (1977). *Metody ochistki proizvodstvennykh stochnykh vod [Methods of sedimentation of production sewage]*. Moscow: Stroiizdat [in Russian].

2 Kulskiy, L.A., Goronovskiy, N.T., Koganovskiy, A.M., & Shevshenko, M.A. (1980). *Spravochnik po svoistvam, metodam analiza i ochistke vody [Reference guide for the properties analysis methods and treatment of water]*. Kiev: Naukova dumka [in Russian].

3 Stakhov, E.A. (1983). *Ochistka neftesoderzhaschikh stochnykh vod [Treatment of oil containing water sources]*. Leningrad: Nedra [in Russian].

4 Yakovlev, S.V., Kareliv, Y.A., & Zhukov, A.I. (1995). *Kanalizatsiia [Sewage Systems]*. Moscow: Stroiizdat [in Russian].

5 Zhigulskiy, V.S., & Reshnyak, V.I. (2006). Plavuchii complex dlia pererabotki neftevodianoi smesi [Floating complexes for the treatment of oily mixtures]. *Sudostroenie — Shipbuilding, 5*, 47–48 [in Russian].

6 Zeldovich, Ya.B., & Yaglom, I.M. (1982). Vyshaia matematika dlia nachinayushchikh fizikov i inzhenerov [Higher mathematics for elementary physicists and engineers]. Moscow: Nauka [in Russian].

7 Ivanov, V.M., Nefedov, P.I., & Kantorovich, B.V. (1960). Eksperimentalnoe issledovanie povedeniia chastits zhidkoho topliva i toplivno-vodianoi emulsii v okislitelnoi i neitralnoi srede [Experimental research into the behaviour of liquid fuel particles and fuel-water emulsions in acidic and neutral environments]. *Otchety IGI AN SSSR — Reports of IGI of the Academy of Science of the USSR, 59* [in Russian].

8 Reshnyak, V.I., Zhigulskii, V.A., & Pestereva, N.E. (2006). *Optimizatsiia razmerov ustroistv pri proektirovanii prirodookhrannykh tekhnicheskikh sredstv [The optimisation of device dimensions for the design of environmental protection equipment]*. Saint Petersburg: SPBGUVK, 173–178 [in Russian].

9 Yakovlev, S.V. (1979). *Ochistka proizvodstvennykh stochnykh vod [The treatment of industrial water sources]*. Moscow: Stroiizdat [in Russian].

10 Egorova, E.N. (2004). Metodicheskie osnovy otsenki economicheskoho ushcherba, voznikaiuschcheho v rezultate avariinykh razlivov na morskikh akvatoriiakh [A methodological basis for an evaluation of environmental damage, resulting from accidnetal spills into marine basins]. *Issledovanie v Rossii — Research in Russia*, 955–971 [in Russian].

11 *SNiP 12. 04.03–85 Proektirovanie sooruzhenii dlia ochistki stochnykh vod [Construction Norms and Standards 12. 04.03–85 Equipment design for waste water treatment]*. (1990). Moscow: Stroiizdat [in Russian].

12 Zhigulskiy, V.A. (2009). Heoekolohicheskie tehnolohii pererabotki neftevodianoi smesi pri likvidatsii avariynykh razlivov [Geological technology for the treatment of oily mixtures in the clean up of accidental spills]. *Extended abstract of candidate's thesis*. Saint-Petersburg [in Russian].

ХИМИЯНЫ ОҚЫТУ ӘДІСТЕМЕСІ
МЕТОДИКА ОБУЧЕНИЯ ХИМИИ
METHODS OF TEACHING CHEMISTRY

DOI 10.31489/2019Ch3/107-114

UDC 372.854

G.T. Kokibasova[1], A.T. Dyussekeyeva[1], A.Ye. Kaztayeva[2]

[1]Ye.A. Buketov Karaganda State University, Kazakhstan;
[2]Karaganda State Technical University, Kazakhstan
(E-mail: kokibasova@mail.ru)

Methodology and psycho-pedagogical research in realizing profile elective course of Chemistry

The programme of the pre-profile elective course «Chemistry around us, or what you will not learn on the lesson» was designed for 34 hours. When conducting a course at the specialized boarding school «Daryn» among 9th grade students, the following general didactic principles were guided, namely scientific character, accessibility, systematic, voluntary, safety, and visualization. The psychological and pedagogical diagnostics of students for group interaction, the study of personality, the motivation for chemistry teaching process, the study of difficulties and anxiety, as well as age characteristics, were carried out. The determination of the personality result showed a slight increase in the number of ambiverts after the elective course, and the average psychodynamic properties score remained at the same level. Motivation to learn chemistry in the group increased. Testing the control lessons and final testing in chemistry among 9-grade students showed the following results, namely 3 students received «Satisfactory», 5 students obtained «Good», 2 students scored «Excellent». The quality of knowledge was 70 %. On the basis of the obtained data we can draw a conclusion that the course increased knowledge of pupils to studying of a subject.

Keywords: elective course, specialized training, laboratory work, testing, household chemicals, questioning, motivation, students, the programme.

Introduction

The history of the development of specialized training in the Republic of Kazakhstan has for decades. The first stage of the organization of profile education in our country was the Concept for the development of the secondary school of the Republic of Kazakhstan (1996). The second stage of the implementation of the idea of profile education is the realization and introduction of the State Compulsory Standard of Secondary General Education of the Republic of Kazakhstan «Basic Provisions» (SES 2.003–2002) [1].

Subject programmes on the basis of the standard were developed in two areas of study: in natural-mathematical and socially-humanitarian. For the first time domestic specialized textbooks and educational-methodical complexes appeared. They were experimentally tested. And now they are used in 10th grade of secondary schools.

The next stage was the State programme of 12-year education of Kazakhstan 2005–2010. The current stage of the implementation of school education reform in the Republic of Kazakhstan can be called the stage of preparation for the introduction of specialized education. The considerable practical experience was accumulated in organizing teaching on directions and profiles. Thus, in Kazakhstan there are a conceptual and methodological basis for improving the regulatory framework and the scientific and methodological support for the organization of specialized training.

The results of psychological and pedagogical research in the profile chemistry elective course «Chemistry around us, or what you will not learn in class» are presented in this paper. The course programme is designed for 34 hours and is intended for students of the 8–9th grade of the secondary school [2].

Aims and objectives of programme are deepening the basic knowledge of students in chemistry, increasing creative activity and expanding the outlook of students, scientifically substantiate the importance of maintaining a healthy lifestyle through:

- detailed description of substances used by humans (their classification, origin, nomenclature, production, use, properties);
- simulation of the effects of drugs on the human body;
- imparting an applied focus of practical research work to develop students' competent behavior on contact with household chemicals and cosmetics;
- the formation of skills for a healthy lifestyle;
- formation of bright visual images of chemical production.

The content and forms of the elective course should contribute to a deeper and more comprehensive perception of the educational material of the basic course of chemistry.

Lessons in accordance with the programme of the course involve:

- repetition of theoretical issues studied in primary school, their deepening and expansion;
- application of theoretical knowledge in practice;
- familiarity with the main types of chemical production;
- teaching students for independent work using various literature.

Achievements are fixed in the completeness and correctness of the students performing tasks. The requirements for knowledge and achievements of students should not be exaggerated in no case. Excessive requirements generate overload and leads to the extinction of interest. The course should help students to understand their interest level in chemistry and assess their capabilities, fully supported and developed through the accumulation of assessments of individual student achievement.

Experimental

This elective course was introduced in the specialized boarding school «Daryn» in Karaganda city, among 9th grade students, which is confirmed by the introduction act.

We have proposed the following sections of this programme:

I. History of chemistry — 3 hours;
II. Chemistry and production — 4 hours;
III. Ecological chemistry and medicine — 7 hours;
IV. Household chemicals — 4 hours;
V. Food chemistry — 12 hours.

In general, 12 hours were selected for students in grade 9 (16 students).

Preliminary testing was carried out.

Test results were as following: 3 students obtained scores of «Unsatisfactory», 6 students received «Satisfactory», 7 students scored «Good». The quality of knowledge was 44 %. This indicated a lack of information to students in grade 9 on these issues. Students do not know the answers to such questions as:

- What scientist proved the complex composition of air?
- What is another name for acetylsalicylic acid?
- What vitamin deficiency results in form of disease «scurvy»?

After conducting the elective course «Chemistry around us or about what you don't learn in class» at the 12th control lesson we obtained following results: 3 students received «Satisfactory», 5 students obtained «Good», 2 students scored «Excellent». The quality of knowledge was 70 %.

The theoretical part of the pedagogical experiment was held at the «Daryn» school. Laboratory work was carried out at the base of Inorganic and Technical Chemistry Department of the Ye.A. Buketov KarSU. The development of a laboratory work of the elective course is showed below.

Lesson 1. Laboratory work «Chemistry and Washing» — 1 hour [3].

Objective: to explore the properties of detergents, to continue the formation of experimental skills, to develop the ability to analyze the results.

Experience number 1. First, take some chalk or dry egg shells. Then the shell and chalk grind to powder, and then place it in a test tube. Then pour 10 % vinegar there.

What should we watch? The content in the test tube will begin to sizzle and foam. Check what gas is released during the reaction. As soon as the test tube contents begin to hiss and foam strongly, take a match and put it inside the tube. Did the flame go out? It should be so. After all, chalk and egg shell are made up of the same substance — calcium carbonate, which dissolves in vinegar. The carbon dioxide released during this process does not sustain combustion, then match blows out. Write down passed reactions.

Experience number 2. Pour water up to half a clean test tube and add 8–10 drops of soap solution. After closing the neck of the tube with your finger, shake it several times. Foam appeared in the test tube. Then pour 4–6 drops of liquid resulting from the reaction of chalk with vinegar into a test tube with soap suds.

What should we watch? The foam in the test tube will disappear and a white coagulating precipitate will begin to stand out from the soapy water. This is the number one enemy of cleaning and washing.

Conclusion: Calcium compounds are «real thieves of soap». They not only steal soap. The resulting white precipitate is deposited on fibrous tissues and destroys them. It was interesting that experiments showed that after 50 washes in hard water, the strength of linen fabric decreased by 25 %, and cotton by 45 % more than after washing (also 50 times) in soft water. What to do with hard water? After all, it is still necessary to erase! Chemistry comes to the rescue.

Experience number 3. Let's do another experience. Pour water into test tube such that half of test tube is filled with water and add a few drops of the solution, which we got at the beginning of experiment from chalk and vinegar. Add half a teaspoon of soda, close tube and shake it well. After some time, the liquid will become transparent, and small sediment will be visible at the bottom. Carefully pour the transparent liquid into another test tube, add a few drops of soap solution and shake. Foam appears in the tube. This means that the soda has helped: the calcium compounds have disappeared. They were isolated in the form of sediment, which settled on the bottom of the first tube. Hence the conclusion to soften the water should always use soda.

Experience number 4. Add 10 drops of solution of chalk with vinegar to the tube containing water. We will have transparent water which contains many compounds of calcium. Let's take any liquid detergent and we will pour 8 — 10 drops of soap solution in a test tube with hard water.

What must we observe? Having stirred up a test tube, we will see that in it quite good foam turned out after all. The synthetic washing substances are not afraid of hard water. Now we see that chemists do not neglect questions of washing, and combat «thief» of soap.

For production of soap there is a large amount of animal and vegetable fats which should be saved. Now chemists learned to do detergents of oil and coal. They are cheaper than soap and it is more convenient in use. They were convinced what huge role is played by chemistry in washing?

Not always the person resort to washing to put clothes in order. Dresses, suits, trousers, a coat are usually cleaned in the chemical way. However quite often it happens so that on a clean dress accidental pollution — drops of oil or ink, juice, parts of food get. Then it is unlikely it makes sense to give clothes to a dry-cleaner. Most often spots remove in house conditions.

Removal of spots of a grass. In free time you decided to lie down on a grass. At the same time on clothes spots can appear. It is unpleasant, ugly to walk in such clothes. It will be better if you, do not shelve, remove spots especially as it will not take you a lot of time. So, we start removal of spots from a grass on your clothes. At first we will wipe a spot with solution of table salt. For this purpose previously we will prepare it: let's take 2 weight parts of table salt and 10 weight parts of clear water. We remember that fresh grass spots on clothes disappear as well after washing by hot water. If they at the same time do not disappear, use solution of table salt with the subsequent washing by warm water.

Removal of spots from berries. All of us, probably, like to regale in the summer on strawberry, raspberry, currant, etc. But at the same time it is possible that you, having been fond of berries, you will soil the clothes. How to remove spots? For this purpose try the next way: at once fill up a fresh spot with table salt, wash at first with clear water, and then wash off in the usual way.

Removal of spots from fat. Let's put under a spot the soft rag which is easily absorbing liquid. Let's moisten a spot by means of solvent and we will wipe it around or better from edges of a spot to the middle, at first slightly, then stronger. After removal of spots we will wash off these places, then we will wipe with the rag moistened with clear water.

Results of the lesson. Reflection.

Homework. Check out the laboratory work in the form of a report.

In the course of introducing the elective course, psychological and pedagogical diagnostics of students was conducted to study the motivation for the chemistry learning process according to the following psychological developments [4]:

– diagnosis of the structure of educational motivation of the student;

– learning cognitive difficulties;

– degree of interest in chemistry.

Below are the results of each of the ongoing psychological and pedagogical studies of students and a comparative analysis before and after the introduction of the course.

The definition of motives was carried out according to seven parameters: emotional, cognitive, communicative, external, achievements, self-development, the position of the student.

Among these parameters, i.e. types of learning motives 3 dominant motives were identified before and after the introduction of the elective course which are presented in Table 1.

As can be seen from Table 1, the most dominant motive in the group is emotional. The remaining motives prevail in different degrees of significance.

Table 2 presents the dominant motives after the experiment. Here the most dominant motive in the group is now achievements, i.e. motives have changed. The motives of the second and third place also changed.

Table 1

Determination of the dominating motives before the experiment

Group	Studied motive
1st place	Emotional
2nd place	Achievement
3rd place	Informative

Table 2

Determination of the dominant motives after the experiment

Group	Studied motive
1st place	Emotional
2nd place	Achievement
3rd place	Informative

Thus, with the study of the course, the motives of the teachings became more serious. New motives that students are guided by have become more suitable for obtaining high learning outcomes. When comparing the results, it can be seen that the quantitative characteristics of each of the motives in the experimental group before and after the experiment have changed significantly, they have increased.

In the study of cognitive difficulties, the following results were obtained: the question «What in itself does not allow you to study well?» (Before the experiment. Fig. 1). The pupils responded as follows: 30 % of students do not always understand the new material, other 10 % cannot find application of their knowledge in practice, 10 % of students complain of poor memory, 20 % admit that they do not know how to organize their classes, 20 % of students do not have enough time, and 10 % cannot be attentive for a long time during the lesson.

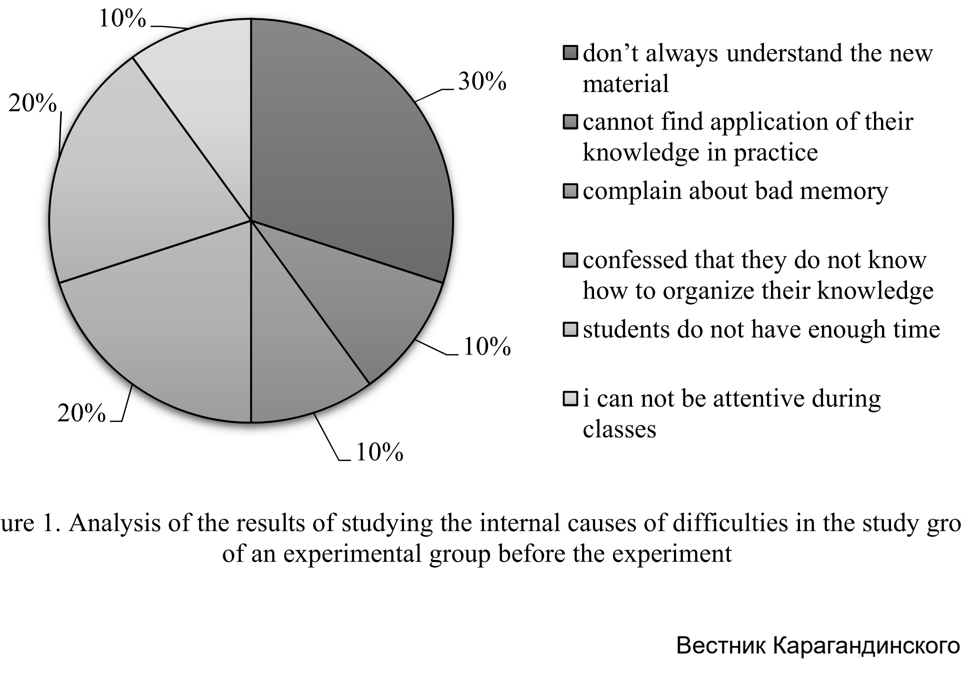


Figure 1. Analysis of the results of studying the internal causes of difficulties in the study group of an experimental group before the experiment

After the experiment (Fig. 2), the question «what doesn't allow you to study well in yourself?» the children answered as follows: 10 % of students do not always understand new material, another 20 % cannot find application of their knowledge in practice, 10 % of students complain about bad memory, 30 % confessed that they did not know how to organize their classes, 20 % of students did not have enough time, and 10 % could not be attentive for a long time during the lesson.

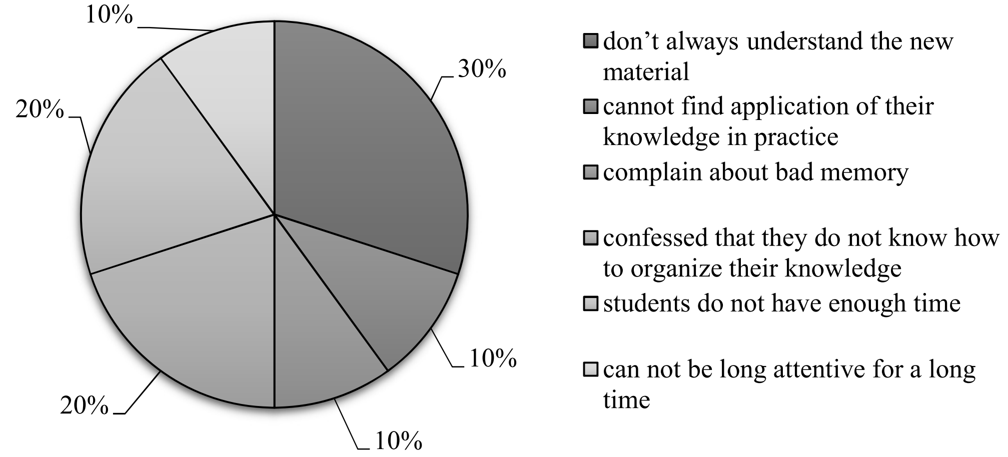


Figure 2. Analysis of the results of studying the internal causes of difficulties in the study group after the experiment

Before the experiment (Fig. 3), to the question «what kind of help do you need first of all?» 10 % of students want to learn how to organize their day correctly, 30 % want to know more about their abilities and capabilities, 20 % want to overcome learning difficulties, 10 % dream of learning some useful practical work, another 20 % want to engage in sections and circles, and 10 % of students need help in studying individual subjects.

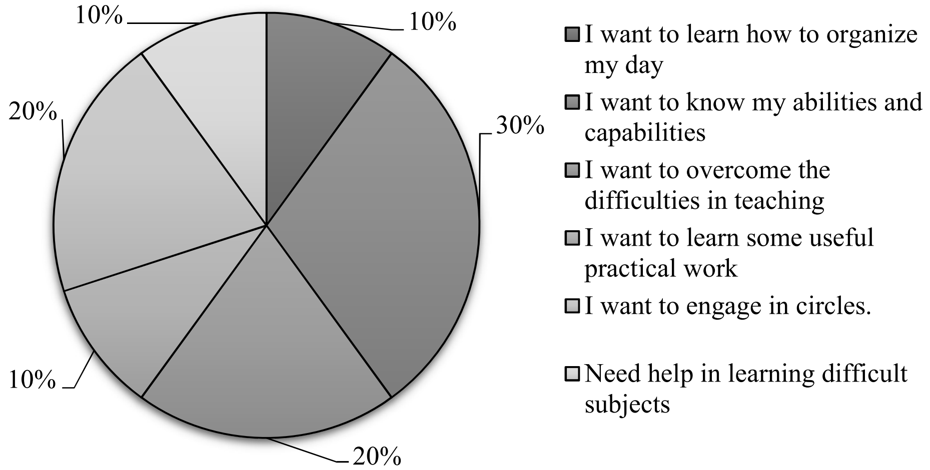


Figure 3. The analysis of results of identification of the necessary help of experimental group before carrying out an experiment for increase in motivation to process of the doctrine

After carrying out an experiment (Fig. 4), on the matter of 20 % of students confessed that they wanted to be learned to be organized correctly during the day, 20 % want to learn more about the abilities and opportunities, 20 % wish to overcome difficulties in the doctrine, 20 % dream to learn some useful practical business, 20 % wish to be engaged in sections and circles.

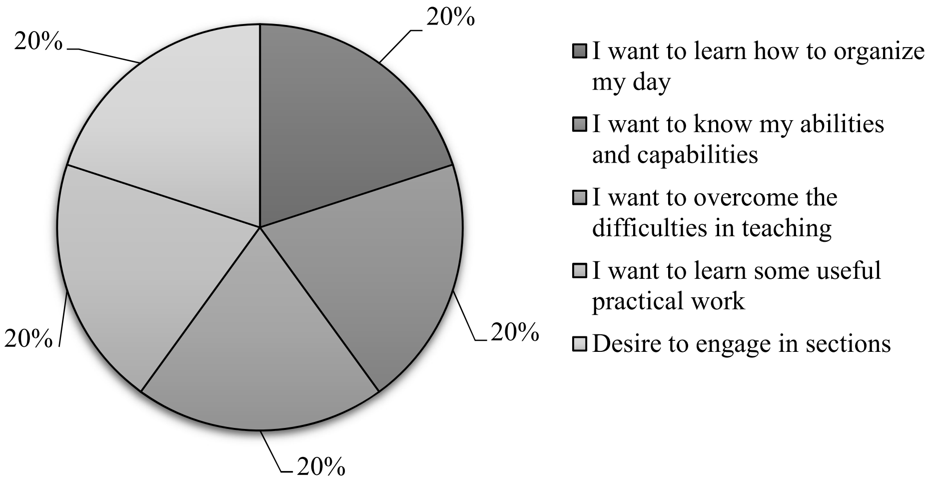


Figure 4. Analysis of the results of identifying the necessary assistance of the experimental group after the experiment to increase the motivation to the process of learning

To determine the degree of interest of students studying chemistry questions were developed:

1. Do you like chemistry?
2. Do you think this is an important science?
3. Would you like to continue to study chemistry?
4. Do you like to solve problems?
5. Do you agree with the statement: «Is everything that surrounds us a chemistry?»
6. Do you consider your chemistry teacher is a strong teacher?
7. Have you ever missed a chemistry lesson without a reason?
8. Do you think chemistry will help you in the future?
9. Do you think your chemistry scores are low?
10. Do you agree with the statement: «Most students do not understand chemistry»?
11. Have you ever written off chemistry tasks?
12. What do you think, additional chemistry lessons will help students to deal with the accumulated questions?
13. Have you ever attended additional chemistry courses?
14. Do you read any literature on chemistry?
15. Did you like the extra chemistry lessons?

Results and Discussion

Based on the data obtained prior to the experiment, the average score of the group is 19 points, which indicates the average degree of interest in chemistry in the group. This is due to the fact that only two students of the 9th grade attended additional courses in chemistry.

After the experiment, the group average score is 24, which indicates a moderately high degree of interest in chemistry for the group. This is due to the fact that during the whole elective course the group worked hard, which contributed to the improvement of interest in this discipline. The main factor is that after the experiment, 8 people answered positively to the question «Did you want to continue studying chemistry», although there were only 3 people before the course.

This indicates that this elective course helped students to establish themselves in a reasonable choice of chemical specialized training; with the role of chemistry in industry, agriculture, medicine, construction, transport, art and other industries and human activities.

References

1 Концепция развития профильного обучения в Республике Казахстан. — Астана, 2010. — 153 с.

2 Кокибасова Г.Т. Разработка программы элективного курса для учащихся профильных классов «Химия вокруг нас, или О чем не узнаете на уроке» / Г.Т. Кокибасова, Т.М. Садыков, О.Г. Федина // Актуальные вопросы современной педагогической науки: материалы X Междунар. науч.-практ. конф. — Чебоксары: НИИ педагогики и психологии, 2014. — С. 36–38.

3 Шкурко Д.И. Забавная химия. Библиотека пионера. Знай и умей / Д.И.Шкурко. — [Электронный ресурс]. — Режим доступа: http://sheba.spb.ru/za/zabavnaia-himia-1976.htm.

4 Бадмаева Н.Ц. Влияние мотивационного фактора на развитие умственных способностей: моногр. / Н.Ц. Бадмаева. — Улан-Удэ, 2004. — 149 с.

Г.Т. Кокибасова, А.Т. Дюсекеева, А.Е. Казтаева

Химияның бейінді элективті курсын жүзеге асырудың әдістемесі мен психологиялық-педагогикалық зерттеулері

«Бізді қоршаған химия, немесе Сабақта үйренбейтін қызықтар» бейіналды элективті курс бағдарламасы 34 сағ құрайды. Элективті курсты өткізу кезінде «Дарын» мамандандырылған мектеп-интернатының 9-сынып оқушылары жалпыдидактикалық қағидаларына бағынды: ғылыми бірізділігі, қолжетімділігі, жүйелігі, өз еріктері бойынша, қауіпсіздігі, көрнекілігі. Оқушылардың топтық оқыту бойынша психологиялық-педагогикалық диагностикасы жүргізілді, тұлғаны зерттеу, химияны оқу кезінде оқушылардың ынтасын арттыру, қиындықтар мен алаңдаушылық деңгейін анықтау және олардың жас ерекшеліктері зерттелді. Тұлғаны анықтауға арналған зерттеу нәтижесі элективті курс өткізілгеннен кейін сыныптағы оқушылардың арасында амбиверттер санының артқанын көрсетті, ал психодинамикалық қасиеттерінің орташа балы өзгеріссіз қалды. Топтың химияны оқуға ынтасы артқаны байқалды. 9-сынып оқушыларының арасында химия пәні бойынша алынған бақылау жұмыстары мен қорытынды тестілеу апробациясы бойынша: 3 оқушы — «қанағаттанарлық», 5 оқушы — «жақсы», 2 оқушы «үздік» нәтиже көрсетті. Білім сапасы — 70 %. Алынған нәтижелер бойынша келесі қорытындыға келуге болады: оқытудың интерактивті әдістерін қолдана отырып, өткізілген «Бізді қоршаған химия, немесе Сабақта үйренбейтін қызықтар» бейіналды элективті курсы оқушылардың пәнді оқуға деген қызығушылығын арттырды, олардың болашақта таңдайтын бағытын таңдауға мүмкіндік тудырды.

Кілт сөздер: элективті курс, бейінді оқыту, зертханалық жұмыс, тестілеу, тұрмыстық химия, сауалнама жүргізу, ынталандыру, оқушылар, бағдарлама.

Г.Т. Кокибасова, А.Т. Дюсекеева, А.Е. Казтаева

Методика и психолого-педагогические исследования при реализации профильного элективного курса химии

Программа предпрофильного элективного курса «Химия вокруг нас, или О чем не узнаешь на уроке» рассчитана на 34 ч. При проведении курса в специализированной школе-интернат «Дарын» среди учащихся 9 классов руководствовались следующими общедидактическими принципами: научность, доступность, систематичность, добровольность, безопасность, наглядность. Проведена психолого-педагогическая диагностика учащихся на групповое взаимодействие, исследование личности, мотивации к процессу обучения химии, изучение затруднений и тревожности, а также их возрастных особенностей. Результат на определение личности показал незначительное увеличение числа амбивертов после проведения элективного курса, а средний бал психодинамических свойств остался на прежнем уровне. Мотивация к обучению химии в группе увеличилась. Апробация результатов контрольных уроков и итогового тестирования по химии среди учеников 9 классов выявила следующее: 3 ученика получили отметку «удовлетворительно», 5 учеников — «хорошо», 2 ученика — «отлично». Качество знаний составило 70 %. На основании полученных данных можно сказать, что проведенный предпрофильный элективный курс «Химия вокруг нас, или О чем не узнаешь на уроке» с использованием интерактивных методов обучения повысил интерес к изучению предмета, перед учащимися появился выбор будущего профиля.

Ключевые слова: элективный курс, профильное обучение, лабораторная работа, тестирование, бытовая химия, анкетирование, мотивация, учащиеся, программа.

References

1 *Kontseptsiia razvitiia profilnoho obucheniia v Respublike Kazakhstan [The concept of development of specialized training in the Republic of Kazakhstan]*. (2010). Astana [in Russian].

2 Kokibasova, G.T., Sadykov, T.M., & Fedina, O.G. (2014). Razrabotka prohrammy elektivnoho kursa dlia uchashchikhsia profilnykh klassov «Khimiia vokruh nas, ili O chem ne uznaete na uroke» [Development of an elective course program for students of specialized classes «Chemistry around us or about what you will not learn in class»]. Proceedings from the Actual problems of modern

pedagogical science: *X Mezhdunarodnaia nauchno-prakticheskaia konferentsiia — X International scientific-practical conference* (pp. 36–38). Cheboksary: Research Institute of Pedagogy and Psychology [in Russian].

3 Shkurko, D.I. (1976). Zabavnaia khimiia. Bibliotechka pionera. Znai i umei [Fun chemistry. Pioneer Library. Know and be able to]. *sheba.spb.ru* Retrieved from: http://sheba.spb.ru/za/zabavnaia-himia-1976.htm [in Russian].

4 Badmaeva, N.Ts. (2004). *Vliianie motivatsionnoho faktora na razvitiie umstvennykh sposobnostei [Influence of the motivational factor on the development of mental abilities]*. Ulan-Ude [in Russian].

ҒЫЛЫМИ ЗЕРТТЕУДІ ШОЛУ
ОБЗОР НАУЧНЫХ ИССЛЕДОВАНИЙ
REVIEW OF RESEARCH

DOI 10.31489/2019Ch3/115-157

UDC 547.875

A.A. Bakibayev[1], K.B. Zhumanov[2], S.Yu. Panshina[1, 3], S.I. Gorbin[3], V.S. Malkov[1],
I.G. Tsoy[2], B.K. Massalimova[2], G.K. Matniyazova[2], E.A. Baybazarova[2]

[1]Tomsk National Research State University, Russia;
[2]M.Kh. Dulati Taraz State University, Kazakhstan;
[3]Tomsk National Research Polytechnic University, Russia
(E-mail: bakibaev@mail.ru)

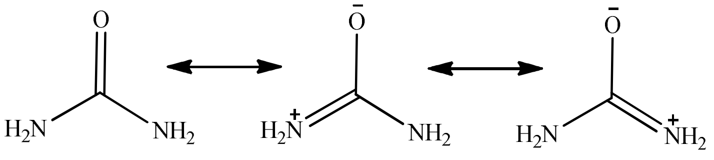
Synthesis methods of phosphorylated carbamide containing acyclic and heterocyclic compounds

In the paper, for the first time, an attempt of systematization of knowledge in the field of reactions of ureas and their heterocyclic derivatives with phosphorus containing reagents has been carried out. In the review due to the significant differences in the substrates and reagents used, methods for producing phosphorylated nitrogen-containing compounds according to their final structure are grouped in three directions of their formation — the synthesis of acyclic, monocyclic and bicyclic ureas. Thus, the methods for the production of acyclic N-phosphorylated ureas by reactions of the corresponding N-phosphoisocyanates with aliphatic and aromatic amines of various structures are considered, and rarely used alternative methods for the synthesis of such compounds are considered. An analysis of the known methods for the synthesis of phosphorylated monocyclic carbamide-containing compounds suggests that: five-membered phosphazacycles, most of them are represented by imidazolidine structures, while tetracyclic phosphazacycles are diazaphosphetidinones, and six-membered phosphazacycles are diazophosphorins and triazaphophorphoryphorphoridine. The synthesized and studied phosphorylated bicyclic bisurea are represented by diphosphadione, diphosphaspirooctanedione, and phosphorylated tetraazabicyclo octionic structures. It was concluded that, on the basis of the systematization of the results of experimental studies on the methods of synthesis of phosphorylated ureas, it can be expected that their development will allow finding ways to obtain new highly effective drugs and synthons of their production.

Keywords: urea, phosphorylation, heterocyclic compounds, N-phosphoisocyanates, imidazolidines, diazaphosphetidinones, diazophosphorins, triazaphosphorinandionones, diphosphadiones, diphosphaspiroctanediones, phosphorylated tetraazibicyclooctandiones, glycoluryl.

Introduction

The chemistry of acyclic and cyclic ureas, primarily due to the availability and polyfunctionality of the latter, has undergone rapid development in various spheres of human activity. Since F. Wöhler discovered the synthesis of urea 1 based on inorganic substances, urea has always been the object of close research attention of both chemists and pharmacological specialists.



1

More than one and a half-century history of urea chemistry was marked by the creation on their basis of many dozens of valuable substances that have been used as effective drugs [1], herbicides [2], fertilizers [3] and other biologically active compounds.

Despite the wide popularity of ureas as objects of the synthetic "simulator", the chemistry of ureas is constantly evolving, and the traditional ways of their use in organic synthesis are constantly being improved.

Synthesis and study of phosphorus-containing compounds based on urea is one of the progressive trends in the development of urea chemistry. The combination of urea fragments and phosphoryl groups in a molecule makes it possible to impart specific useful properties to the target substance, which is the subject of a wide discussion of methods for producing phosphorylated ureas [4, 5].

Some of the acyclic organophosphorus nitrogen-containing compounds are being used as therapeutic drugs, such as zoledronic acid (zoledronate), which has a selective effect on bone tissue and is therefore used in the treatment of osteoporosis [6]. One of the widely used non-selective systemic herbicides is glyphosate (N-(phosphonomethyl)-glycine) [7]. Due to its unique properties, this drug is the first in the world production of herbicides. In addition, glyphosate is used in the production of polymeric materials, especially non-combustible and chemically resistant ion exchange resins, used in the analysis and production of highly pure substances, and other areas of technology.

Monocyclic nitrogen-containing heterocycles containing a urea moiety in the cyclic skeleton are attractive because the latter is often a key multifunctional structural element of these compounds. The presence of N- and O-nucleophilic reaction centers in the urea molecule promotes their cyclization under the action of various phosphorylating agents [8].

Generally the nature and direction of cyclization is influenced, first of all, by the nature of the substituent at the amide nitrogen atom of urea and the conditions of the reaction studied. The direction of the reactions of phosphazacyclization of urea by ethers of chlorine derivatives of phosphoric acids often depends on the coordination number of phosphorus.

The development and improvement of known methods for the synthesis and functionalization of monocyclic nitrogen-containing heterocycles is greatly stimulated by their well-known participation in human activity. For example, among cyclic compounds, based on phosphorylated ureas, polymeric compounds [9] and drugs with high pesticidal, anticholinesterase, antiviral, and antimicrobial activity [10] are found.

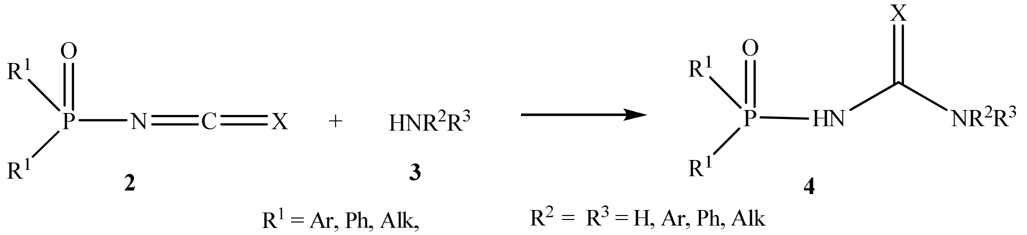
The chemistry of bicyclic bisureas occupies a special place among nitrogen-containing heterocyclic compounds, primarily due to the framework structure and the presence of multifunctional reaction centers. 2,6-diacetyl glycoluryl diphosphonic acid is known among the phosphorylated bicycles, which has been used as an electrode modifier for quantitative determination of cholesterol by voltammetry [11].

Since there is currently no information in the available literature, summarizing synthesis and research methods of chemical properties of phosphorylated urea-containing acyclic and heterocyclic compounds, we have systematized knowledge in this area, which was the basis for writing an independent review article. The review of literature data is systematized according to the methods of synthesis of phosphorylated acyclic, monocyclic and bicyclic carbamide containing compounds.

1 Synthesis methods of phosphorylated acyclic ureas

1.1 Isocyanate method for producing acyclic N-phosphorylated ureas

Among the relatively large number of methods for producing N-phosphorylated ureas, reactions based on the interaction of the corresponding N-phosphoisocyanates with various amines are prevalent. Methods for obtaining phosphorus-containing isocyanates and their chemical properties are discussed in the review [12], where the reactions of the latter with various organic substrates, including amines, are also given. Thus, according to the general scheme 1, the reaction of isocyanates 2 with primary and secondary amines 3 leads to the formation of various 1,3-disubstituted ureas 4:



R^1 = Ar, Ph, Alk,
X = O, S

R^2 = R^3 = H, Ar, Ph, Alk
R^2 = H, R^3 = Ar, Ph, Alk,

Scheme 1

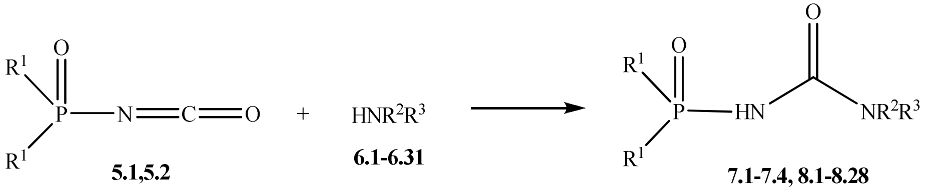
This method is widely used, including for the synthesis of various ureidophosphoric acids [13–21].

It was shown [13] that fluorinated 5.1 phosphoisocyanates in reactions with primary and secondary amines 6.1–6.4 turned out to be convenient reagents for the synthesis of fluorine derivatives of N-alkyl- and N-aryl-substituted phosphorylated urea 7.1–7.4 (Scheme 2).

One of the variants of the synthesis of arylcarbamidophosphoric acids is [14] that isocyanate phosphoric acid chloride **5.2** can easily react with various amines 6.4–6.21. However, the authors emphasize that aromatic amines with electron-withdrawing substituents (such as p-chloro 6.10 and p-bromoaniline 6.11, o- and m-nitroaniline 6.5 and 6.6, etc.) react slower. Even greater difficulties are caused by interactions with secondary arylamines (diphenylamine 6.21), but at the same time, the product yield of 8.1–8.18 are 62–99 % (Scheme 2).

The authors of [15], developing their work [16, 17] aimed at crystal structure, biological activitystudy and some electronic aspects, synthesized the already known series of dichlorophosphoryl derivatives of N-substituted phenylureas 8.1–8.6 and supplemented it with similar interactions of dichlorophosphoisocyanate 5.2 with the corresponding aryl amines 6.22–6.26 with the formation of compounds 8.19–8.23 (Scheme 2). Based on the compounds obtained 8.1–8.6, 8.19–8.23, the authors synthesized a number of biologically active diazaphosphorinanes 45.1–45.11 and diazaphospholanes 46.1–46.11 for further study (Scheme 12).

In order to search for new biologically active compounds, the authors of [18–20] using known methods [14, 21] synthesized a similar series of dichlorophosphoryl derivatives of N-substituted phenylureas 8.7–8.10, 8.24–8.28 using the corresponding amines 6.10–6.13, 6.27–6.31 (Scheme 2) for further condensation of ureas 8.7–8.10, 8.24–8.28 with various substrates (Scheme 3).



5.1,5.2

6.1-6.31

7.1-7.4, 8.1-8.28

5. 1: $R^1 = F$
2: $R^1 = Cl$

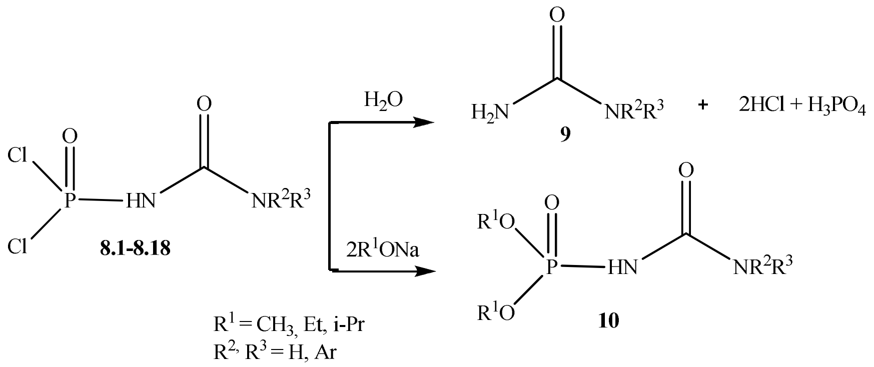
7. 1: $R^1 = F, R^2 = H, R^3 = Ph$
2: $R^1 = F, R^2 = H, R^3 = C_2H_5$
3: $R^1 = F, R^2 = R^3 = C_2H_5$
4: $R^1 = F, R^2 = C_6H_5CH_3,$
$R^3 = CH_3$

6. 1: $R^2 = 4\text{-}CH_3\text{-}C_6H_4, R^3 = CH_3$
2: $R^2 = H, R^3 = C_2H_5$
3: $R^2 = R^3 = C_2H_5$
4: $R^2 = H, R^3 = Ph$
5: $R^2 = H, R_3 = 2\text{-}NO_2\text{-}C_6H_4$
6: $R^2 = H, R^3 = 3\text{-}NO_2\text{-}C_6H_4$
7: $R^2 = H, R^3 = 4\text{-}NO_2\text{-}C_6H_4$
8: $R^2 = H, R^3 = 2\text{-}CH_3\text{-}C_6H_4$
9: $R^2 = H, R^3 = 4\text{-}CH_3\text{-}C_6H_4$
10: $R^2 = H, R^3 = 4\text{-}Cl\text{-}C_6H_4$
11: $R_2 = H, R_3 = 4\text{-}Br\text{-}C_6H_4$
12: $R^2 = H, R^3 = 4\text{-}CH_3O\text{-}C_6H_4$
13: $R^2 = H, R^3 = \alpha\text{-}C_{10}H_7$
14: $R^2 = H, R^3 = 4\text{-}C_2H_5\text{-}C_6H_4$
15: $R^2 = H, R^3 = 4\text{-}i\text{-}C_3H_7\text{-}C_6H_4$
16: $R^2 = H, R^3 = 4\text{-}C_2H_5O\text{-}C_6H_4$
17: $R^2 = H, R^3 = 2\text{-}NO_2\text{-}C_6H_4\text{-}4\text{-}CH_3$
18: $R^2 = H, R^3 = 2,4,6\text{-}Cl\text{-}C_6H_2$
19: $R^2 = H, R^3 = \beta\text{-}C_{10}H_7$
20: $R_2 = C_2H_5, R_3 = C_6H_5$
21: $R_2 = R_3 = Ph$
22: $R^2 = H, R^3 = 4\text{-}CN\text{-}C_6H_4$
23: $R_2 = H, R_3 = 4\text{-}F\text{-}C_6H_4$
24: $R_2 = H, R_3 = 3\text{-}F\text{-}C_6H_4$
25: $R_2 = H, R_3 = 2\text{-}F\text{-}C_6H_4$
26: $R^2 = H, R^3 = 3\text{-}CH_3\text{-}C_6H_4$
27: $R^2 = H, R^3 = 2,4\text{-}(CH_3)_2\text{-}C_6H_4$
28: $R^2 = H, R^3 = 3,4\text{-}(CH_3O)_2\text{-}C_6H_4$
29: $R^2 = H, R^3 = CH_2\text{-}C_6H_4\text{-}Cl\text{-}2$
30: $R^2 = H, R^3 = C_6H_{11}\text{-}c$
31: $R^2 = H, R^3 = C_2H_4O\text{-}c$

8. 1: $R^1 = Cl, R^2 = H, R^3 = Ph$
2: $R^1 = Cl, R^2 = H, R_3 = 2\text{-}NO_2\text{-}C_6H_4$
3: $R^1 = Cl, R^2 = H, R^3 = 3\text{-}NO_2\text{-}C_6H_4$
4: $R^1 = Cl, R^2 = H, R^3 = 4\text{-}NO_2\text{-}C_6H_4$
5: $R^1 = Cl, R^2 = H, R^3 = 2\text{-}CH_3\text{-}C_6H_4$
6: $R^1 = Cl, R^2 = H, R^3 = 4\text{-}CH_3\text{-}C_6H_4$
7: $R^1 = Cl, R^2 = H, R^3 = 4\text{-}Cl\text{-}C_6H_4$
8: $R^1 = Cl, R_2 = H, R_3 = 4\text{-}Br\text{-}C_6H_4$
9: $R^1 = Cl, R^2 = H, R^3 = 4\text{-}CH_3O\text{-}C_6H_4$
10: $R^1 = Cl, R^2 = H, R^3 = \alpha\text{-}C_{10}H_7$
11: $R^1 = Cl, R^2 = H, R^3 = 4\text{-}C_2H_5\text{-}C_6H_4$
12: $R^1 = Cl, R^2 = H, R^3 = 4\text{-}i\text{-}C_3H_7\text{-}C_6H_4$
13: $R^1 = Cl, R^2 = H, R^3 = 4\text{-}C_2H_5O\text{-}C_6H_4$
14: $R^1 = Cl, R^2 = H, R^3 = 2\text{-}NO_2\text{-}C_6H_4\text{-}4\text{-}CH_3$
15: $R^1 = Cl, R^2 = H, R^3 = 2,4,6\text{-}Cl\text{-}C_6H_2$
16: $R^1 = Cl, R^2 = H, R^3 = \beta\text{-}C_{10}H_7$
17: $R^1 = Cl, R_2 = C_2H_5, R_3 = C_6H_5$
18: $R^1 = Cl, R_2 = R_3 = Ph$
19: $R^1 = Cl, R^2 = H, R^3 = 4\text{-}CN\text{-}C_6H_4$
20: $R^1 = Cl, R_2 = H, R_3 = 4\text{-}F\text{-}C_6H_4$
21: $R^1 = Cl, R_2 = H, R_3 = 3\text{-}F\text{-}C_6H_4$
22: $R^1 = Cl, R_2 = H, R_3 = 2\text{-}F\text{-}C_6H_4$
23: $R^1 = Cl, R^2 = H, R^3 = 3\text{-}CH_3\text{-}C_6H_4$
24: $R^1 = Cl, R^2 = H, R^3 = 2,4\text{-}(CH_3)_2\text{-}C_6H_4$
25: $R^1 = Cl, R^2 = H, R^3 = 3,4\text{-}(CH_3O)_2\text{-}C_6H_4$
26: $R^1 = Cl, R^2 = H, R^3 = CH_2\text{-}C_6H_4\text{-}Cl\text{-}2$
27: $R^1 = Cl, R^2 = H, R^3 = C_6H_{11}\text{-}c$
28: $R^1 = Cl, R^2 = H, R^3 = C_2H_4O\text{-}c$

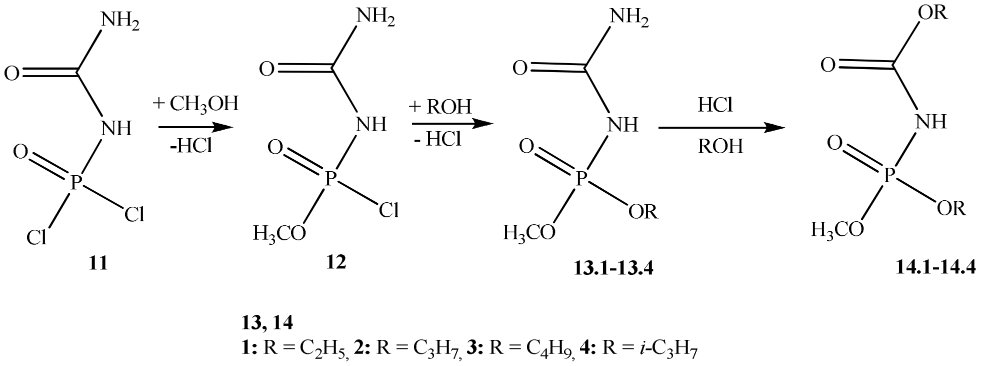
Scheme 2

Arylcarbamidophosphoric acid chlorides 8.1–8.28 [14] are crystalline compounds difficultly soluble in benzene, ether, carbon tetrachloride, chloroform, slowly decompose in air, slowly react with water at room temperature, but when heated, the hydrolysis passes quickly. Water is mainly attached through the P–N bond, since it was found that the main products of hydrolysis are N-aryl urea 9, while the acid chlorides 8.1–8.18 (Scheme 2) give the corresponding esters 10 [14] under the action of alcoholates (Scheme 3).



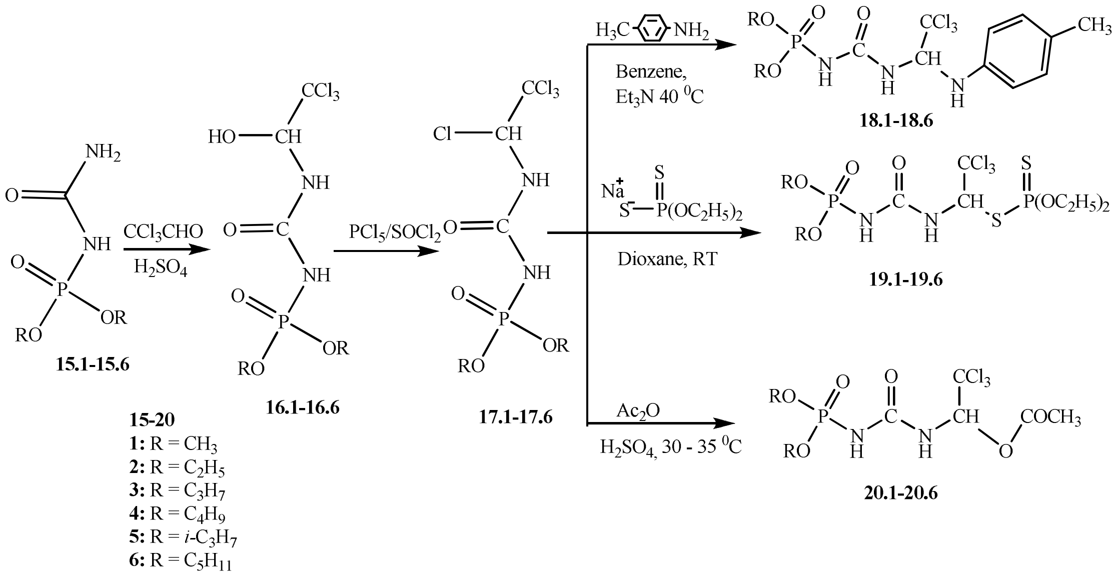
Scheme 3

In a number of subsequent works, this method of synthesis of phosphorylated ureas was further developed [22, 23]. Thus, it was shown [22] that the reaction of ureidophosphoric acid dichloride 11 with alcohols in the presence of hydrogen chloride proceeds in steps, which makes it possible to obtain dialkyl esters of ureidophosphoric acid 13.1–13.4 with different alkoxy substituents at phosphorus atoms. Under the action of methanol on 11, ureidophosphoric acid methyl ester chloride 12 was obtained, which was separated from the reaction mass and further treated with an excess of dry alcohols (ethanol, propanol, butanol, isopropanol) to obtain N-(methoxy alkoxyphosphoryl) ureides 13.1–13.4. When the esters 13.1–13.4 are heated in the presence of alcohol and an excess of HCl, dialkyl esters of urethanphosphonic acid 14.1–14.4 are formed (Scheme 4).



Scheme 4

To study the biologically active properties of organophosphorus compounds, N-alkylphosphoryl urea 15.1–15.6 was condensed with chloral (Scheme 5) [23].

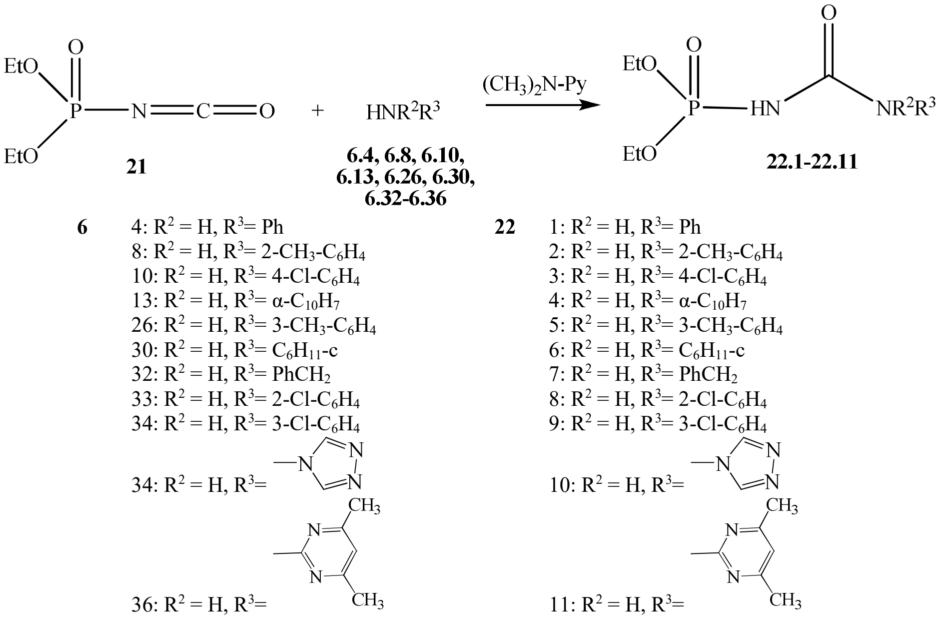


Scheme 5

The hydroxyl group in the resulting products 16.1–16.6 is replaced by chlorine in reactions with chlorinating agents such as PCl_5, $SOCl_2$. In turn, the resulting N-dialkylphosphoryl-N'-1,2,2,2-tetrachloroureas 17.1–17.6 react with amines, alcohols, salts, forming the corresponding substituted urea 18–20 with yields of 43–95 % (Scheme 5).

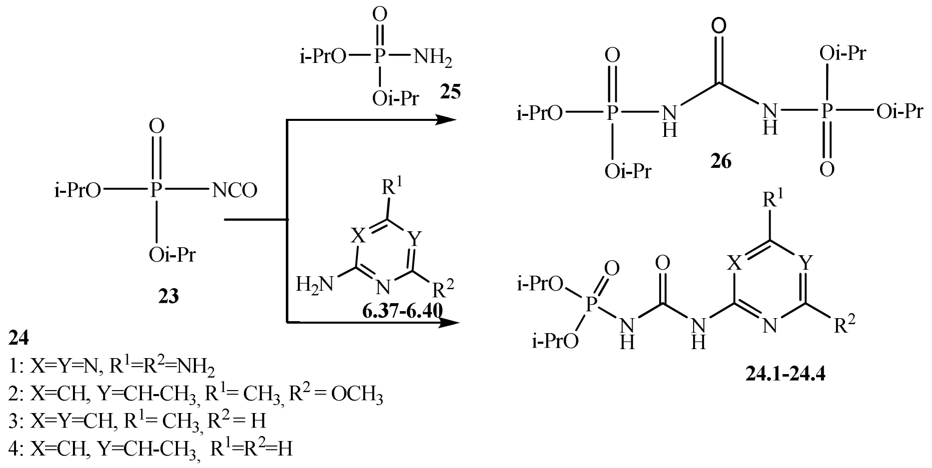
For the substances 18–20 obtained, their antiviral activity was reported in [23].

Esters of ureidophosphoric acid 22.1–22.11 can be obtained according to a scheme similar to the reaction of isocyanates (Scheme 2). For example, in the work [24], phosphoryl isocyanate ethyl ether 21 reacted with aryl and hetarylamines 6.4, 6.8, 6.10, 6.13, 6.26, 6.30, 6.32–6.36 in the presence of catalytic amounts of 4-dimethylaminopyridine (Scheme 6).



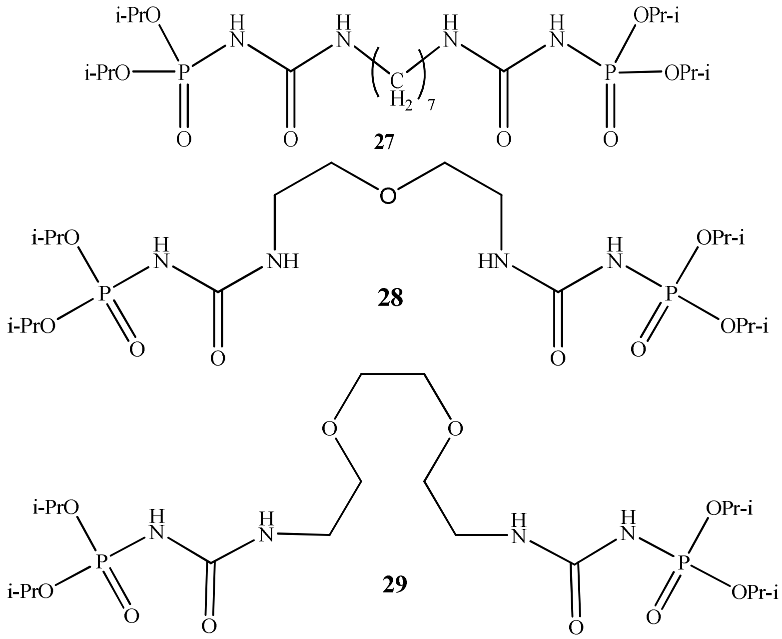
Scheme 6

In order to search for biologically active compounds based on esters of substituted phosphorylated ureas, reactions [25] of diisopropoxyphosphoryl isocyanate 23 with some heterocyclic amines 6.37–6.40 in inert atmosphere with subsequent production of urea derivatives 24.1–24.4 were studied (Scheme 7). The authors also noticed that the interaction of diisopropoxyphosphoryl isocyanate 23 with diisopropoxyphosphorylamide 25 gives rise to diphosphorylated symmetric urea 26.



Scheme 7

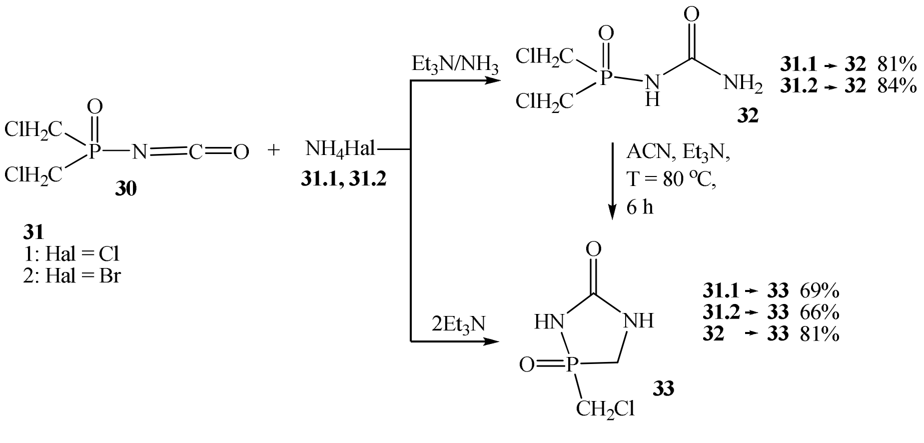
Similarly, N-phosphorylated bromides 27–29 based on reactions of diisopropoxyphosphoryl isocyanate 23 and α, ω-diamines were synthesized in order to study the extractive properties of Eu (III) [26] (Scheme 8).



Scheme 8

Studied podands 27–29 differ in the link between two phosphorylated urea fragments. Bonds with oxygen atoms can form a crown ether cavity, which can compete with the complexing ends of the bidentate parts of the extractant.

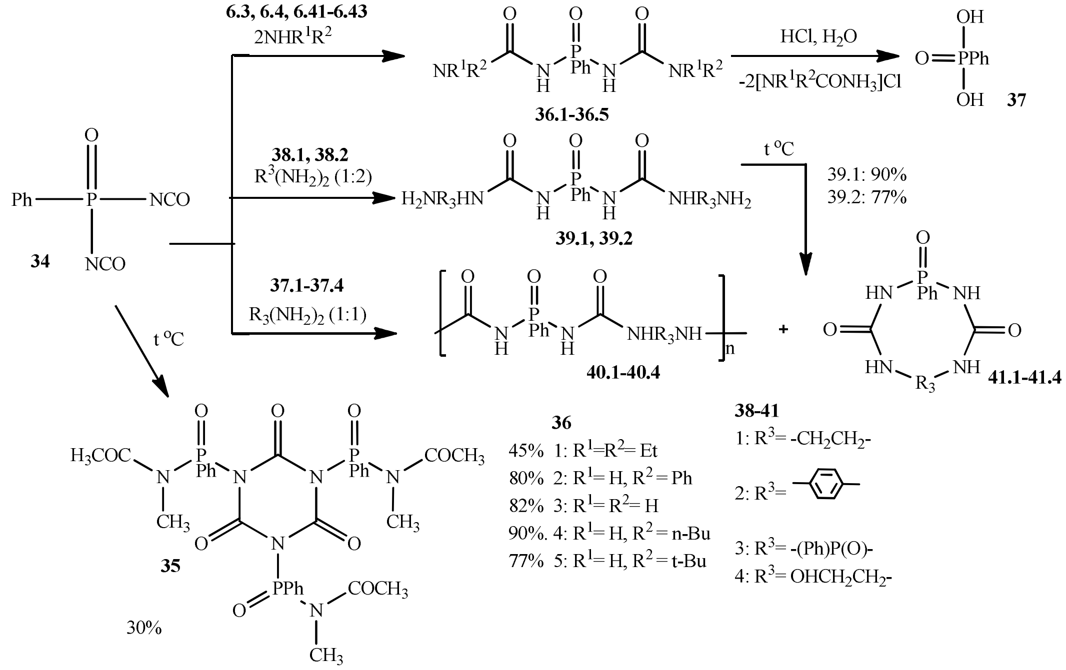
To obtain monosubstituted phosphorylureas, it is also possible to use both ammonia [27] and ammonium halides 31.1, 31.2 (Scheme 9). [28] showed that bis(chloromethyl)phosphine isocyanate 29 reacts with chloride 31.1 or ammonium bromide 31.2 at room temperature in chloroform and an equimolar amount of triethylamine, which leads to the formation of N-[bis(chloromethyl)phosphinoyl] urea 32 with outputs 81 and 84 %, respectively (Scheme 9):



Scheme 9

However, it was found that a double excess of triethylamine and boiling the reaction mass for 12 hours, lead to the formation of phosphazocyclic urea 33 with 69 % yield when using ammonium chloride 31.1 and 66 % when using ammonium bromide 31.2 Heating urea 32 in anhydrous acetonitrile with an equimolar amount of triethylamine during 6 hours at 80 °C also leads to the formation of 33 with a yield of 81 % (Scheme 9).

The works [5, 29] are devoted to the synthesis of di- and tri-ureides of phosphoric acid from the corresponding di- and tri-isocyanate phosphates. So, in work [29], reactions of phenyl diisocyanate phosphate 34 with various amines 6.3, 6.4, 6.41–6.43 in the medium of dry benzene during boiling were investigated. At the same time, the authors said that phenyl diisocyanate phosphate 34, with long-term temperature exposure, is capable of homopolymerization — a light brown glassy homopolymer is formed — isocyanurate 35 with a yield of 30 %, which is unstable in air (Scheme 10).



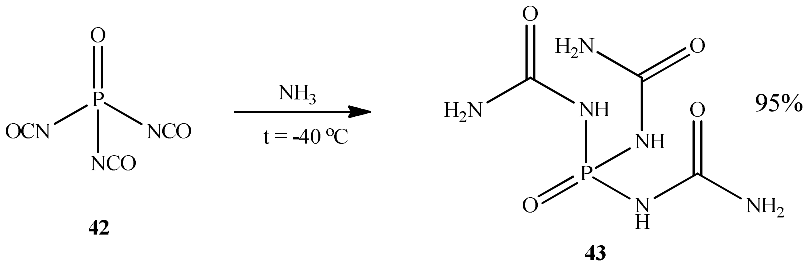
Scheme 10

Diisocyanate of benzenephosphonic acid 34 reacts with monoamines 6.3, 6.4, 6.41–5.43 to form benzenephosphonyl bis(ureas) 36.1–36.5 (Scheme 10). Products 36.1–36.5 are insoluble in benzene, carbon tetrachloride, chloroform, chloro- and fluorocarbons and ether, but they dissolve easily in polar solvents (methanol, nitromethane, acetone). Despite the fact that substances 36.1–36.5 are resistant to water and ammonia, the P–N bond is cleaved during acid hydrolysis to form phenylphosphoric acid 37 (Scheme 10).

In the reaction of phenyl diisocyanate phosphate 34 with diamines 38.1–38.4, polyureas 40.1–40.4 and 41.1–41.4 are formed in equal (1: 1) quantities, while the products of polymeric and cyclic structure are in the same reaction mass (Scheme 10). Polyureas 40.1–40.4 and 41.1–41.4 in organic solvents are insoluble, partially dissolve in dimethylformamide when heated. Also, the substances are not wetted with water and are resistant to diluted acids and alkalis.

Products 39.1, 39.2, obtained in the reaction with diamines 38.1, 38.2 in the ratio 1: 2 with prolonged heating to the melting temperature, are capable of self-condensation (Scheme 10).

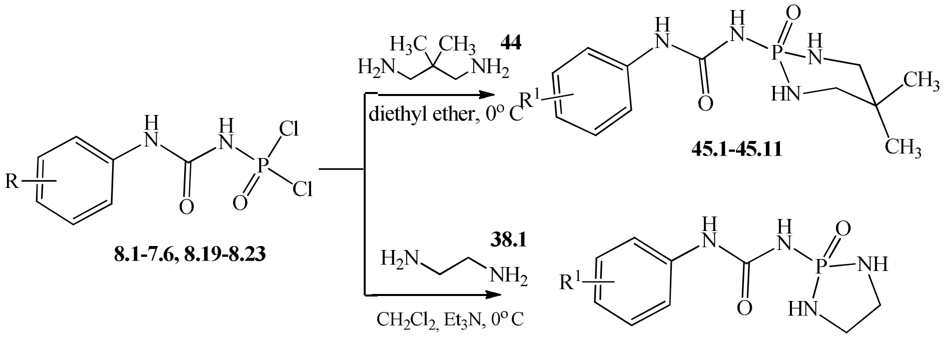
[5] reported on the synthesis of phosphorous triureide 42 by treating phosphorus triisocyanate (V) 42 with an excess of liquid ammonia at –40 °C, and the yield of phosphorous triureide 43 was 95 % (Scheme 11).



Scheme 11

Thus, the resulting aryl carbamidophosphoric acid chlorides 8.1–8.28 using the methods described above [14–17, 21] were involved in various studies with the aim of obtaining a wide range of substances with biological activity.

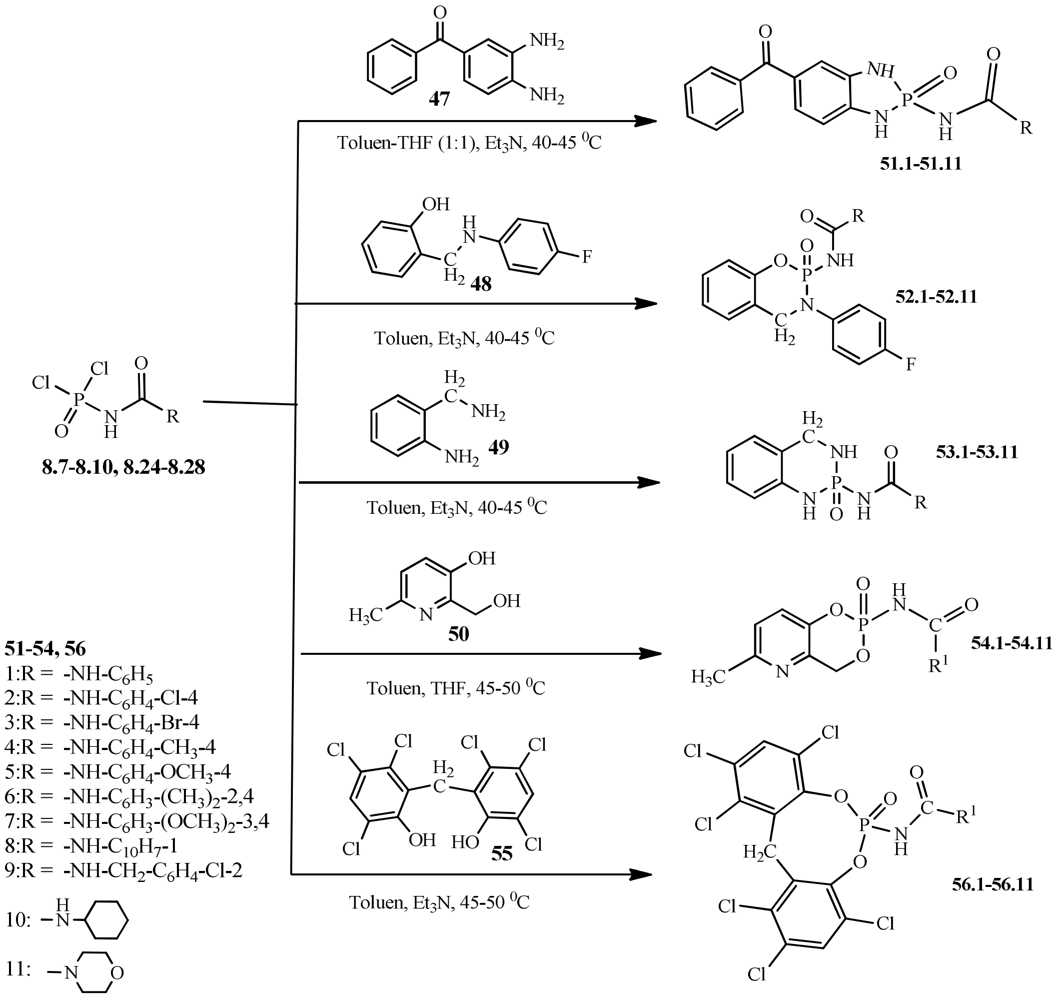
The authors of [15], a series of dichlorophosphoryl derivatives of N-substituted phenylureas 8.1–8.6, 8.19–8.23, was converted to the corresponding diazaphosphorinanes 45.1–45.11 and diazaphospholanes 46.1–46.11 under the action of 2,2-dimethyl-1,3-diaminopropane 44 and ethylenediamine 38.1, respectively (Scheme 12).



45, 46
1: R = H, 2: R = 2-NO$_2$, 3: R = 3-NO$_2$, 4: R = 4-NO$_2$. 5: R = 2-CH$_3$, 6: R = 4-CH$_3$,
7: R = 4-CN, 8: R = 4-F, 9: R = 3-F, 10: R = 2-F, 11: R = 3-CH$_3$

Scheme 12

The synthesized dichlorophosphoryl derivatives of N-substituted phenylureas 8.7–8.10, 8.24–8.28, the authors of [18, 19], using similar methods [14, 21], were involved in condensation reactions with various diamines 47–50 to produce a wide range of compounds 51–54 based on phosphorylated ureas with antimicrobial activity (Scheme 13).



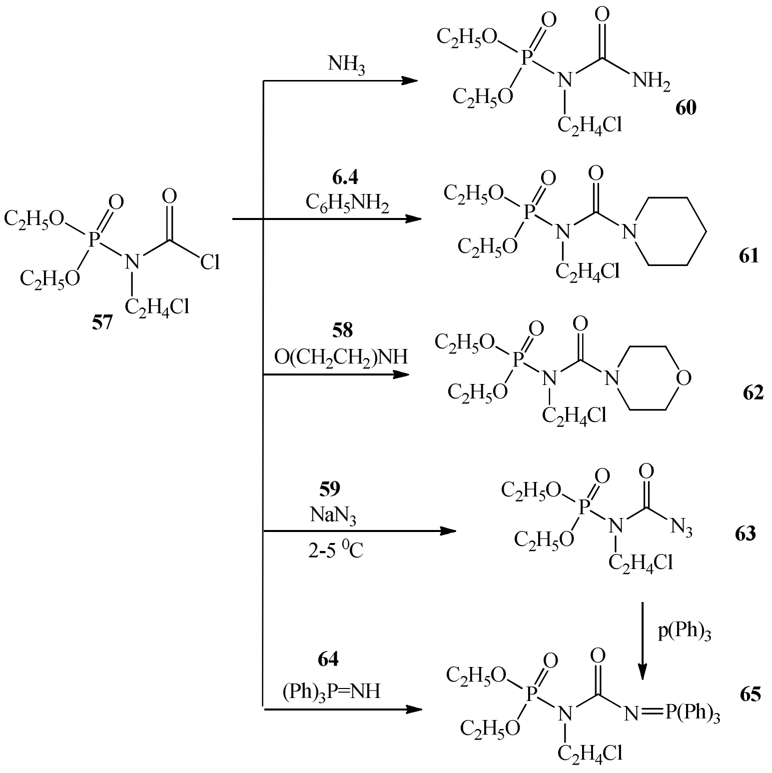
51-54, 56
1:R = -NH-C$_6$H$_5$
2:R = -NH-C$_6$H$_4$-Cl-4
3:R = -NH-C$_6$H$_4$-Br-4
4:R = -NH-C$_6$H$_4$-CH$_3$-4
5:R = -NH-C$_6$H$_4$-OCH$_3$-4
6:R = -NH-C$_6$H$_3$-(CH$_3$)$_2$-2,4
7:R = -NH-C$_6$H$_3$-(OCH$_3$)$_2$-3,4
8:R = -NH-C$_{10}$H$_7$-1
9:R = -NH-CH$_2$-C$_6$H$_4$-Cl-2
10:
11:

Scheme 13

In continuation of these works, later [20], by a similar reaction of condensation a number of biologically active dibenzodioxaphosphociline urea 56.1–56.11 (Scheme 13) were obtained from polychlorinated 2,2-dihydroxydiphenylmethane 55. Reactions given in Scheme 13 were carried out with weak heating in the presence of triethylamine in toluene, or in a mixture of toluene–THF (1:1) with average yields (47–71 %) for 51–54, 56.

1.2 Other methods for producing acyclic N-phosphorylated ureas

Along with isocyanates, N-dialkylphosphono-N-(2-chloroethyl)carbamic acid chloride 57 can be used as a starting phosphorylating reagent 57. The authors of [30] obtained a series of urea derivatives 60–63 by reacting N-diethylphosphono-N-(2-chloroethyl)carbamic acid 57 with ammonia, aniline 6.4, morpholine 58, and sodium azide 59 (Scheme 14):

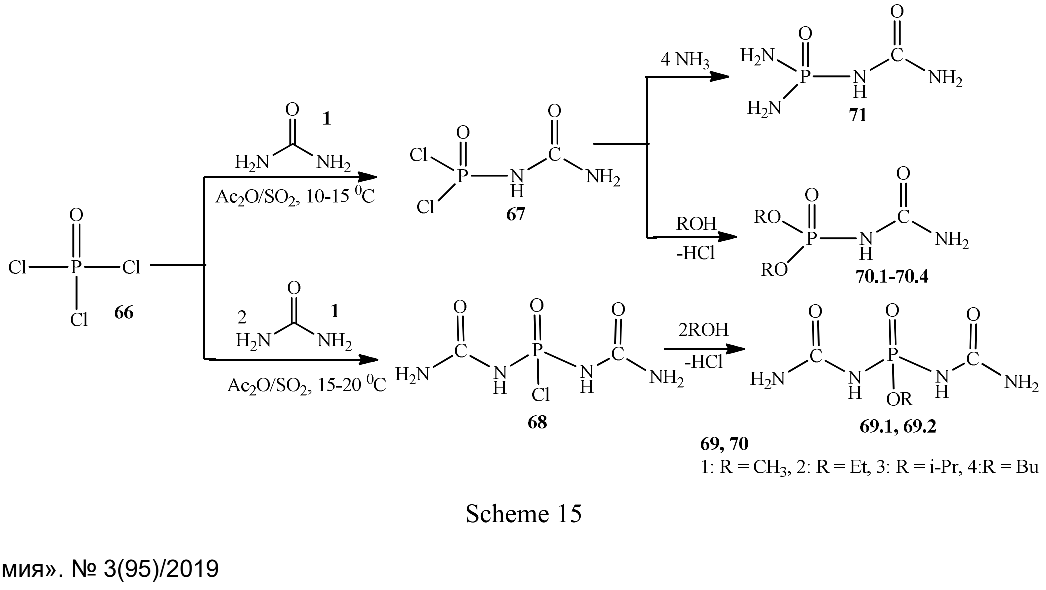


Scheme 14

N-diethylphosphono-N-(2-chloroethyl)carbamic acid chloride 57 reacts with sodium azide 59 at 2–5 °C [30]. The phosphoazide 63 obtained in this way, like acyl azides, reacts with triphenylphosphine to form N-diethylphosphono-N-(2-chloroethyl)amidetriphenylphosphazo-carbonic acid 65, which is also obtained by reacting the acid chloride 57 with triphenylphosphoimine 64 (Scheme 14).

In the patent literature [31, 32] there are reports of the synthesis of phosphorus-substituted ureas 60–65 exhibiting nematocidal activity.

A convenient method of direct phosphorylation of urea1 was proposed [5], based on the reaction of urea 1 with phosphorus oxychloride in polar solvents, which resulted in dichlorohydrophosphoric acid 67 and diureid phosphoric acid 68 (Scheme 15).



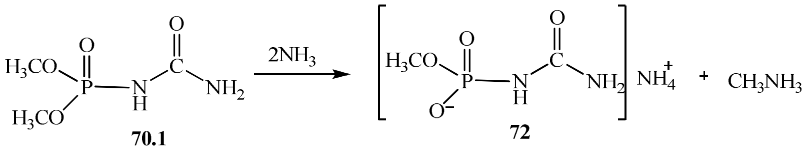
Scheme 15

It is concluded that the conditions of the process have a significant influence on the reaction. When using acetic anhydride as a solvent, the yield of 67 and 68 acids was 30 and 56 %, respectively. Replacing the solvent with liquid sulfur dioxide reduces the yield 67 significantly (30 %) (Scheme 15).

A similar method was used in [33] to obtain phosphorylated alkylureas, where the authors used a number of solvents. However, the highest yield was achieved at a molar ratio of alkyl urea: phosphorus oxychloride 66 as 4:1 in liquid sulfur dioxide.

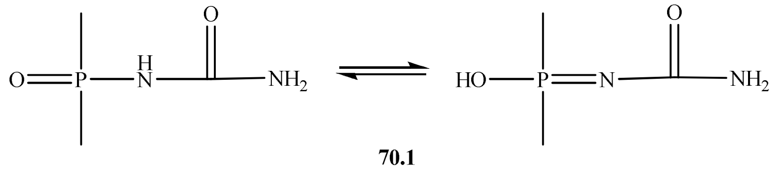
Compounds 67 and 68 obtained were used for further reactions with alcohols to produce the corresponding esters. Reactions of ureidophosphoric acid dichloride 67 with monofunctional alcohols led to the preparation of dimethyl 70.1, diethyl 70.2, diisopropyl 70.3 and dibutyl esters of ureidophosphoric acid 70.4. It has been shown that ureidophosphoric acid dichloride 68 produced the corresponding esters 69.1, 69.2 with methanol and ethanol (Scheme 15).

It is also shown [5] that ureidophosphoric acid dichloride 67 reacts with liquid ammonia at –70 °C with the release of white colored substance (Scheme 15). Dimethyl ester of ureidophosphoric acid 70.1, when dissolved in liquid ammonia, gives the ammonium salt of methoxouridophosphoric acid 72 (Scheme 16).



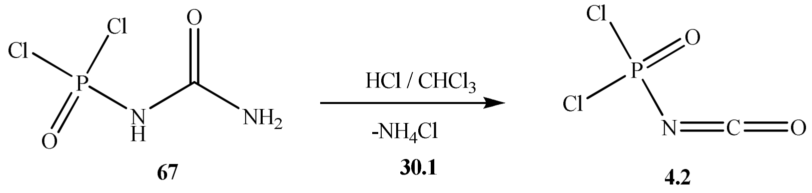
Scheme 16

Dimethyl ester of ureidophosphoric acid and phosphoroxytriureide are weak acids, prone to tautomerism, neutralization of which causes an increase in the P–N bond order (Scheme 17) [5].



Scheme 17

[34] reported that dichlorophosphorylurea 67 is almost quantitatively hydrolyzed to dichloroisocyanate phosphate 4.2 and ammonium chloride 30.1 in boiling chloroform by passing HCl (Scheme 18). This reaction takes place regardless of the nature of the substituents at the phosphorus atom (alkyl, aryl-amino) in the case of both phosphates and thiophosphates.

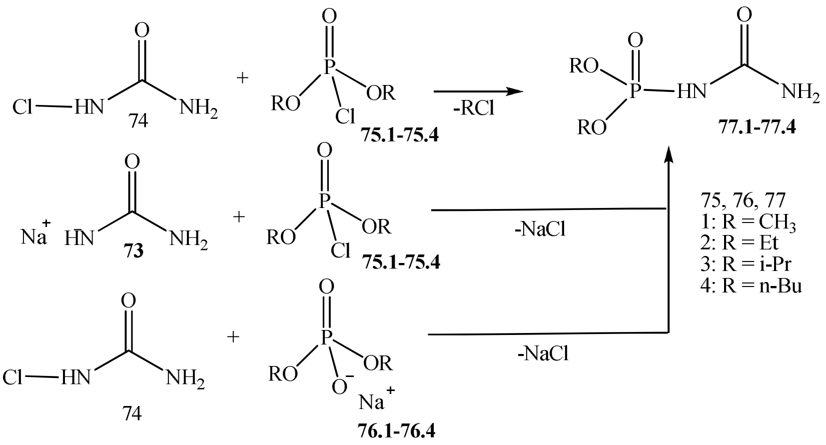


Scheme 18

It is believed [34] that the rate of isocyanate formation is consistent with differences in the electron density on the phosphorus atom, and with increasing electron density, the reaction rate increases (Scheme 18). Another way to synthesize N-phosphorylated urea is to use both the sodium salt of urea 73 and chlorine-substituted urea 74 in reactions with phosphorylating agents.

N-Chlorourea 74 and tertiary alkylphosphites 75 (methyl 75.1, ethyl 75.2, isopropyl 75.3 and n-butyl 75.4 derivatives) give ureidophosphoric esters and the corresponding alkyl halide (Scheme 19). The reaction proceeds instantly at temperatures as low as –40 °C. Substances 77.1–77.4 are resistant to acid and alkaline hydrolysis [35].

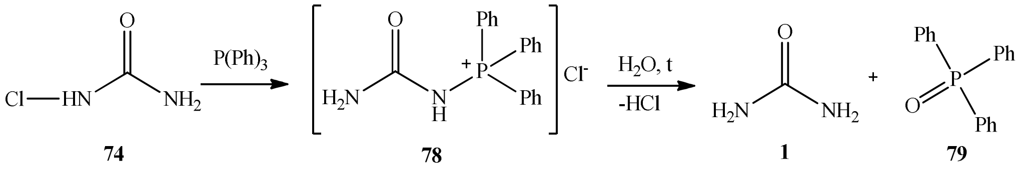
The reaction products 77.1–77.4 were confirmed by counter syntheses of N-chlorourea 74 with sodium salts of dialkyl phosphites 76.1–76.4, sodium salts of urea 73 with dialkyl chlorophosphates 75.1–75.4 (Scheme 19).



Scheme 19

In the method proposed, the reactions are carried out in an aprotic polar solvent, while the yields of the substances 77.1–77.4 obtained are 42–50 % [35].

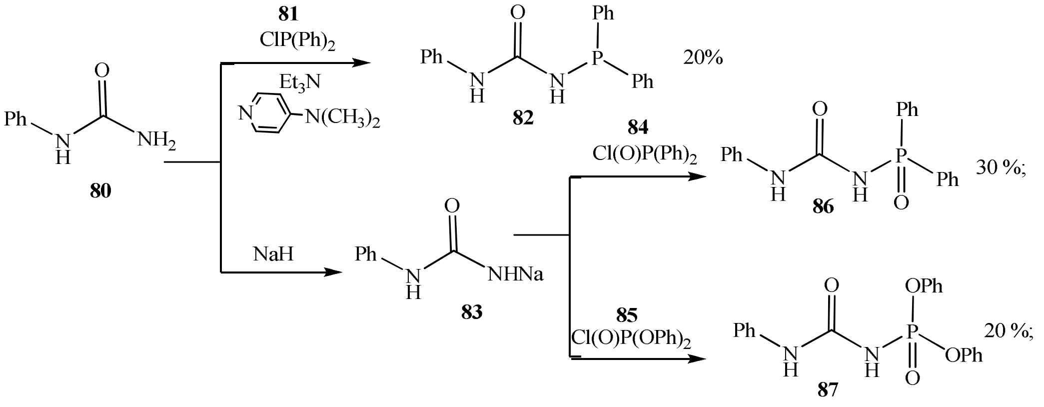
The use of triphenylphosphine as a phosphorylating component in the reaction with N-chlorourea 74, which reacts in the same way as tertiary phosphites, leads to the formation of quasiphosphonium salt 78, hydrolysis of which in warm water leads to the formation of HCl, urea 65 and triphenylphosphine oxide 79 [35] (Scheme 20).



Scheme 20

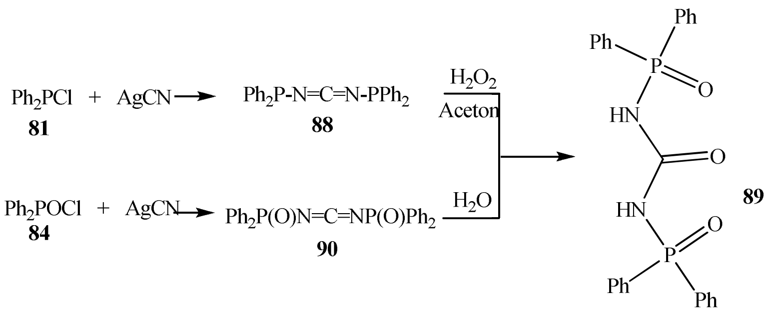
Chlorodiphenylphosphine 81 is condensed with N-phenylurea 80 in the presence of an excess of triethylamine and a catalytic amount of 4-(dimethylamino)pyridines to produce 1-(diphenylphosphinyl)-3-phenylurea 82 [36] (Scheme 21).

Also, phosphorylated ureas 86, 87 were obtained with low yields by the reaction of sodium salt of N-phenylurea 83 and phosphorus diphenyloxochloride 84 or phosphorus diphenoxyoxochloride 85, respectively [36] (Scheme 21).



Scheme 21

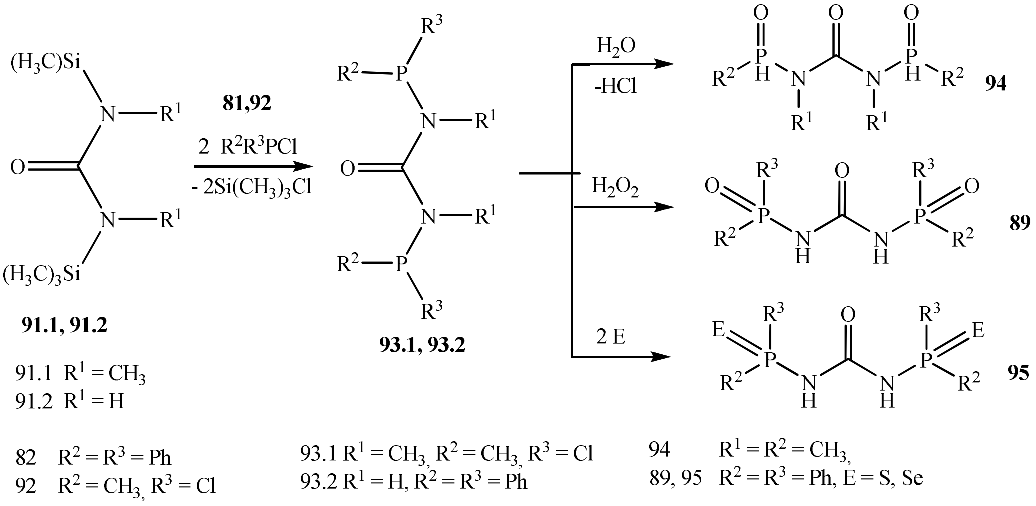
1,3-Bis(diphenylphosphoryl)urea 89 was obtained [37] by treating 1,3-bis(diphenylphosphino)carbodiimide 88, previously synthesized by the reaction of diphenylchlorophosphine 81 and AgCN, with hydrogen peroxide. The water treatment of 1,3-bis(diphenylphosphono)carbodiimide 90, obtained by the reaction of phosphorus diphenyloxochloride 84 with AgCN, leads to the same urea 89 (Scheme 22).



Scheme 22

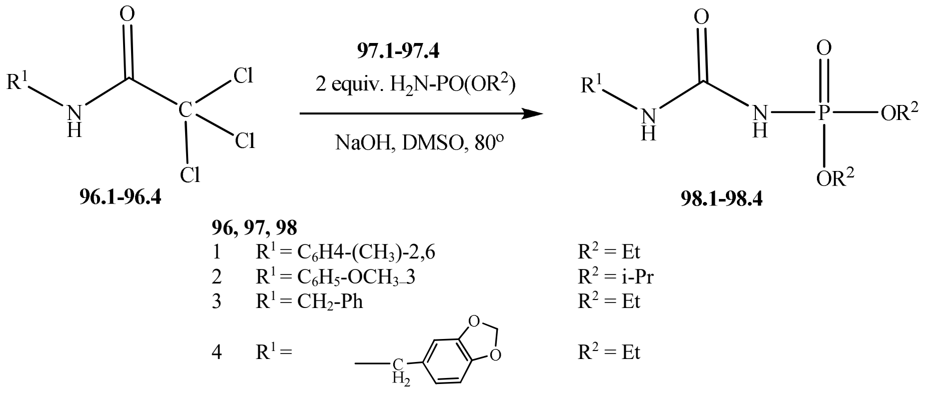
The authors of [38, 39] synthesized phosphorylated N,N'-dialkylureas 89, 94, 95 using their N,N-trimethylsilylated derivatives 91.1, 91.2 as substrates. Thus, [38] reported N,N'-bis(chloro(methyl)phosphino)-N,N'-dimethylurea 93.1 synthesis from N,N'-dimethyl-bis(trimethylsilyl)urea 91.1 and dichloromethylphosphane 92. Urea 93.1 is prone to hydrolysis with the cleavage of the chlorine atom with obtaining N,N'-dimethyl-N,N'-bis(methylhydrophosphoryl)urea 94 (Scheme 23).

In [39], it was shown that bisphosphorylated urea 93.2 is formed as a result of the reaction of diphenylchlorophosphine 81 with 1,3-bis (trimethylsilyl) urea 91.2 at 70–80 ºC. Its oxidation with hydrogen peroxide leads to the formation of urea 89, and the use of oxidizing agents (S, Se) leads to compounds of type 95 (Scheme 23).



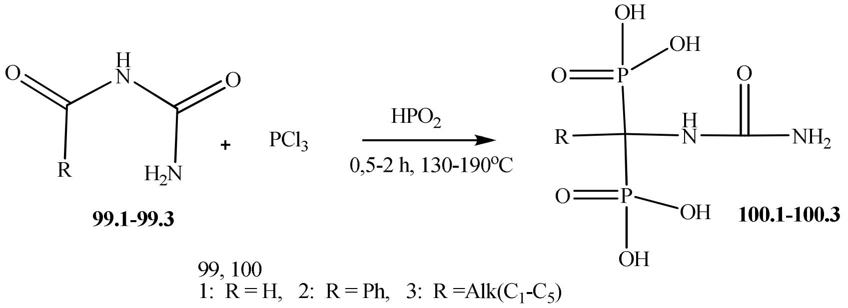
Scheme 23

The authors of [40] synthesized a series of N-phosphorylureas 98.1–98.4 by the reaction of phosphorylamides 97.1–97.4 with N-substituted trichloroacetamides 96.1–96.4 (Scheme 24).



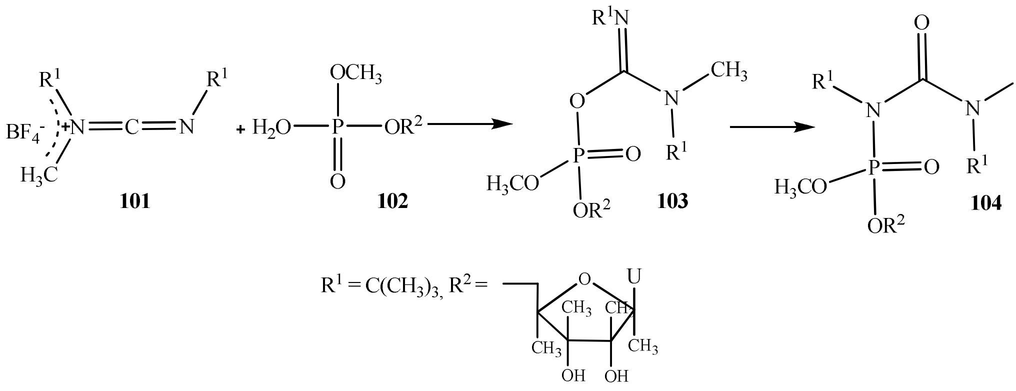
Scheme 24

The method of obtaining ureidoxyalkyl-1,1-diphosphonic acids 100.1–100.3 is described in the patent [41], which is based on the interactions formyl- 99.1, acetophenyl- 99.2, acylureas 99.3 with a mixture of phosphorous acid and PCl_3 (Scheme 25).



Scheme 25

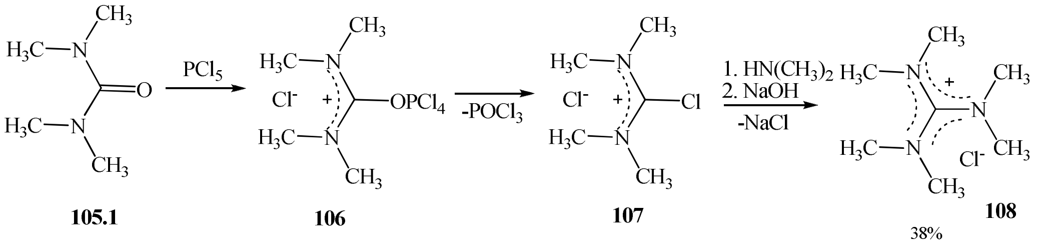
Studies [42] have shown that tetrafluoroborate-N-methyl-N,N'-di-tert-butylcarbodiimidium 101, in reaction with methyridin-5-phosphate 102, is converted to phosphorylated urea 104 through the O→N migration of the phosphate link in the intermediate compound 103 (Scheme 26).



Scheme 26

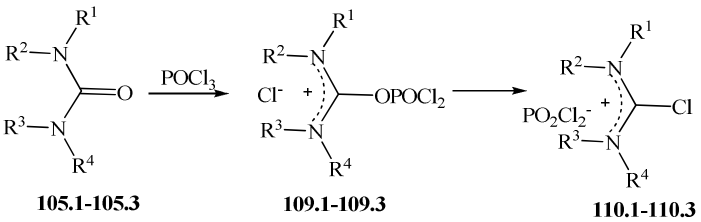
Urea's tendency to salification is interestingly used in the study of their reactions with phosphorus chlorides. Thus, during the study of the reaction of tetra-substituted ureas with various reagents, their transformations were studied, including under the action of phosphorus chlorides [43]. It was found that N,N,N',N'-tetraalkylureas 105.1–105.3 form adducts with $POCl_3$ and PCl_5.

In the reaction of phosphorus pentachloride (PCl_5) with tetramethylurea 105.1, adduct 106 is mainly formed, which turns into 107 only with increasing temperature with elimination of $POCl_3$. After alkaline treatment of 107, the reaction product is a black oil, which contains about 38 % guanidinium salt 108 (Scheme 27).



Scheme 27

It was shown that N,N,N',N'-tetraalkylureas 105.1–105.3 form adducts with $POCl_3$, which are equilibrium mixtures of imine salts 109 and 110 (Scheme 28).

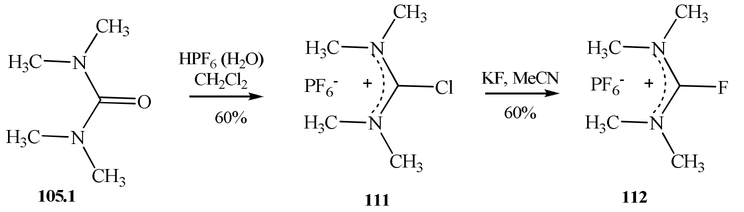


105, 109, 110
1: $R^1 = R^2 = R^3 = R^4 = CH_3$, 2: $R^1 = R^2 = R^3 = CH_3$ $R^4 = Ph$, 3: $R^1 = R^2 = R^3 = CH_3$ $R^4 = C_6H_5\text{-}OCH_3\text{-}4$;

Scheme 28

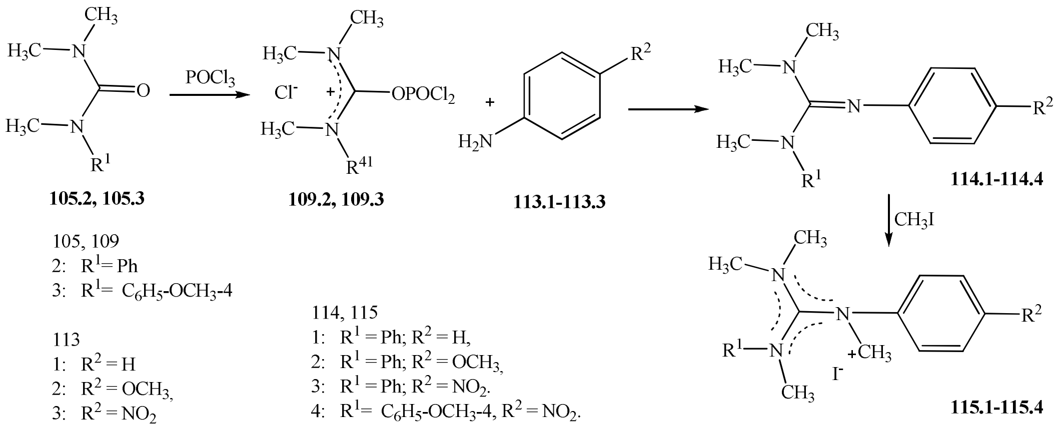
The equilibrium between urea 105.1 and $POCl_3$ in the adduct 109.1 is slow, while the equilibrium 109.1–110.1 is established quickly. The reactivity of acidic amides and ureas with respect to $POCl_3$ is in the following order: N,N-dimethylformamide > N,N-dimethylacetamide > N,N,N',N'-tetramethylurea > N,N,N',N'-tetrabutylurea [43].

The detection of adducts 109, 110 also indicates that 105.1 and HPF_6 leads to the formation of chloroformamidium hexafluorophosphate 111, which can be converted to fluoroformamidium hexafluorophosphate 112 under the action of potassium fluoride (Scheme 29).



Scheme 29

The interaction of $POCl_3$ with ureas 105.2, 105.3 in benzene (as shown earlier in scheme 28) gives equilibrium salts 109.2, 109.3. When exposed to aniline 113.1–113.3 on these salts 109.2, 109.3 and with further water-alkali treatment, you can get a mixture, consisting of urea 105.2, 105.3, guanidine 114.1–114.4 and aniline 113.1–113.3. Anilines 113.1–113.3 of the mixture can be washed out, but ureas 105.2, 105.3 and guanidines 114.1–114.4 are difficult to separate. However, pure guanidinium iodides 115.1–115.4 can be quantitatively isolated if methyl iodide is acted on (Scheme 30).



105, 109
2: $R^1 = Ph$
3: $R^1 = C_6H_5\text{-}OCH_3\text{-}4$

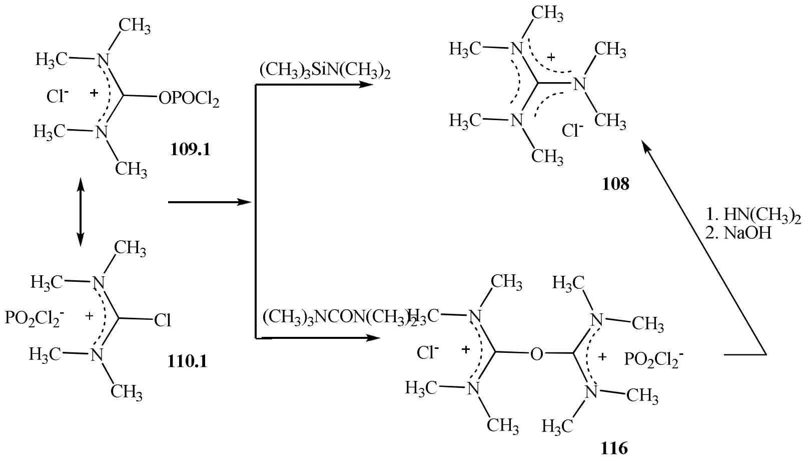
113
1: $R^2 = H$
2: $R^2 = OCH_3$,
3: $R^2 = NO_2$

114, 115
1: $R^1 = Ph$; $R^2 = H$,
2: $R^1 = Ph$; $R^2 = OCH_3$,
3: $R^1 = Ph$; $R^2 = NO_2$.
4: $R^1 = C_6H_5\text{-}OCH_3\text{-}4$, $R^2 = NO_2$.

Scheme 30

The authors, in their preliminary experiments, concluded that the yield of the guanidine salt 108 depends on the reaction conditions, in particular, on the molar ratio of the adducts. The guanidinium salt 108 can be obtained with a large yield by adding an excess of urea 105.1 to the iminium salts 109, 110. This may indicate the presence of other two-cationic equilibrium salts 116 in the system (Scheme 31).

The proposed ways of converting tetrasubstituted ureas with phosphorus chlorides open wide possibilities for the functionalization of the synthesized salts into new nitrogen-containing acyclic and heterocyclic compounds.



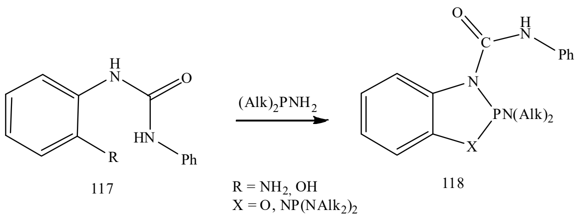
Scheme 31

Summing up this section of the review, we note that the main method for producing acyclic N-phosphorylated ureas is based on reactions that correspond to N-phosphoisocyanates with amines of various structures. Alternative methods for the synthesis of acyclic phosphazamide are represented by individual reactions, and these data are not systemic.

2 Synthesis methods of phosphorylated monocyclic ureas

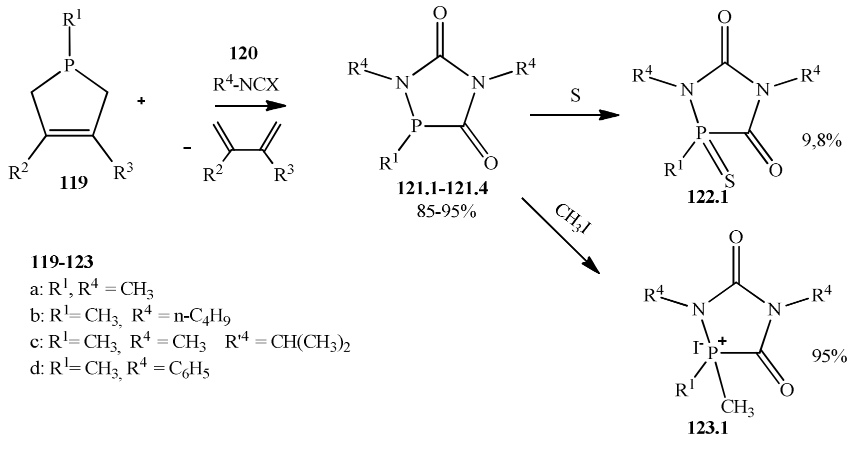
2.1 Preparation and properties of five-membered phosphorylated carbamide-containing cycles

By condensation of o-amino or o-hydroxy-substituted diphenylureas 117 with tris (dialkylamino) phosphine, the corresponding substituted 1,3,2 oxaza- and diazabenzophospholenes 118 were obtained (Scheme 32) [44].



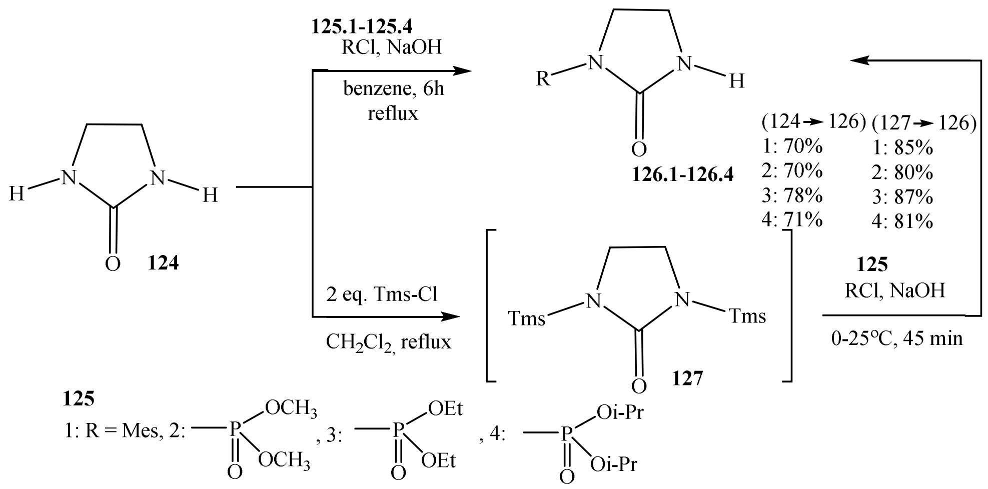
Scheme 32

A method was patented for producing 1,4,2-substituted diazaphospholidine-3,5-dione of 121.1–121.4 by the reaction of the corresponding isocyanates 120 with 1-methyl-2,5-dihydro-1H-phospholates 119 [45]. In particular, the work provides examples of the preparation of methyl- 121.1, butyl- 121.2, isopropyl- 121.3, phenyl- 121.4 derivatives of diazaphospholidine-3,5-dione, and also their modification with the production of sulfides 122 and salts 123 (Scheme 33).



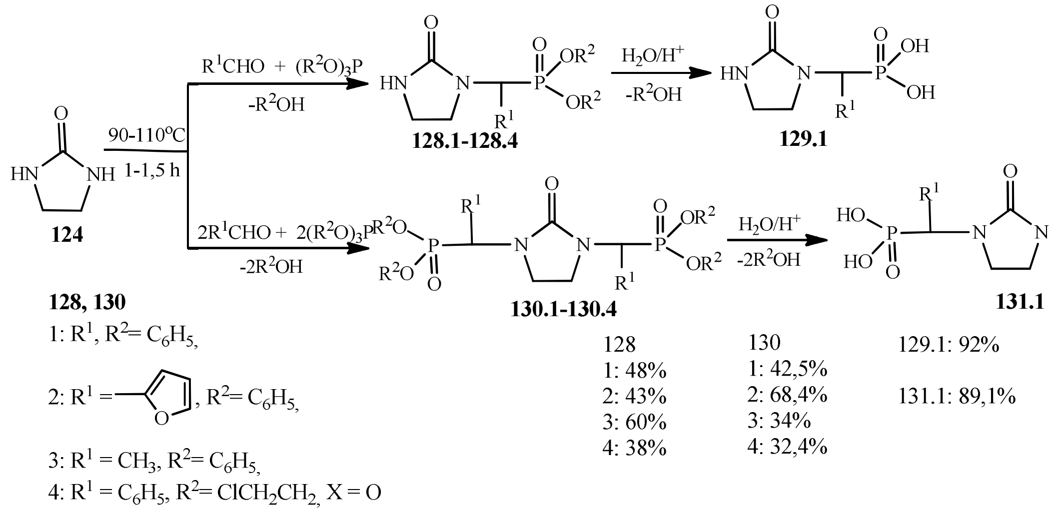
Scheme 33

It was shown that 2-imidazolidinone 124 in a strongly alkaline medium in reactions with phosphorus oxochloride esters 125.1–125.4 undergoes conversion to N-phosphorus substituted 2-imidazolidinones 126.1–126.4 with yields of 70–78 % [46]. The authors also developed an alternative pathway to compounds 126.1–126.4 with higher yields (80–87 %) via intermediate product 127 of N,N-trimethylsilylation of 2-imidazolidinone (Scheme 34).



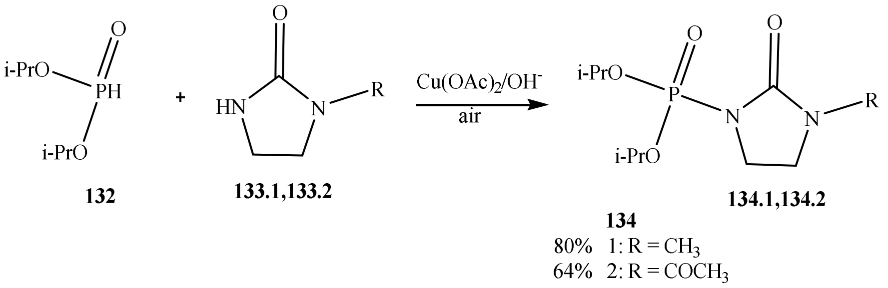
Scheme 34

It was established that the direction of the 3-component reaction of imidazolidinone 124 with aldehydes and trialkyl(aryl phosphites depends on the molar amount of the aldehyde. Thus, when using one equivalent of aldehyde and trialkyl(aryl)phosphite, 128.1–128.4 are formed, and two equivalents of aldehyde and trialkyl(aryl)phosphite in the reaction with 124 two nitrogen atoms are replaced to form 130.1–130.4. The resulting phosphoesters 128.1–128.4, 130.1–130.4 readily hydrolyze to the corresponding acids 129.1, 131.1 (Scheme 35) [47].



Scheme 35

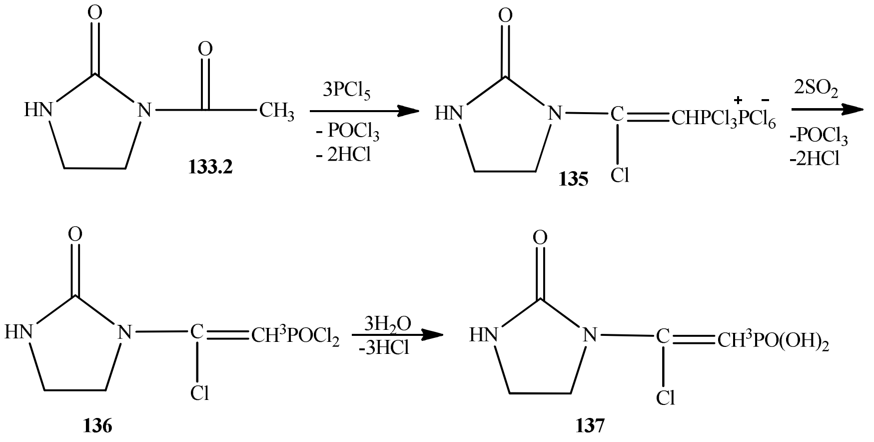
Relatively new method for the phosphorylation of organic compounds — metal complex catalysis — has been developed. As shown by the authors [48], the introduction of copper (II) acetate and the corresponding base can contribute to the occurrence of oxidative crosslinking of H-phosphonates 132 and cycloamides 133.1, 133.2 in the presence of air as the final oxidant (Scheme 36).



Scheme 36

The range of change in the amount of substrate was broad with respect to dialkyl-H-phosphonates, giving the corresponding binding products P–N 134.1, 134.2 with moderate and high yields. Among the copper catalysts studied by the authors, Cu(OAc)2 showed the highest activity and selectivity.

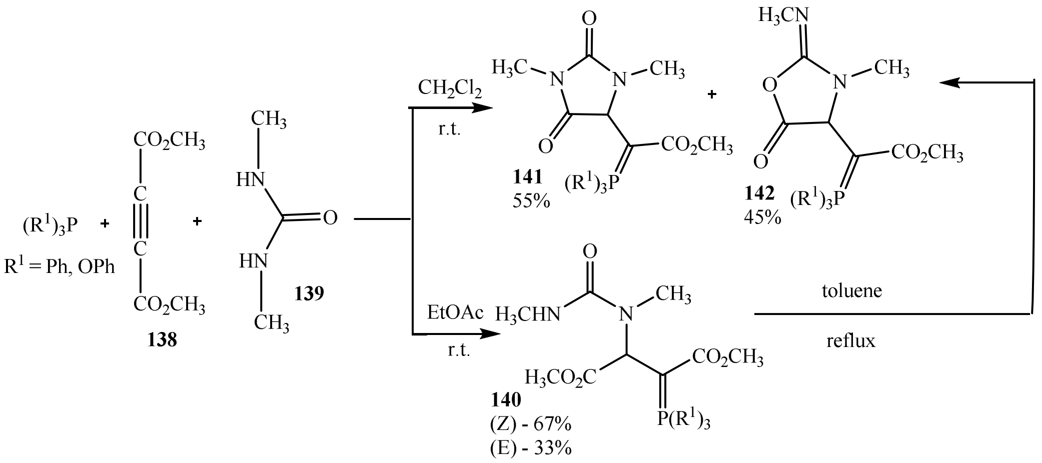
[49] studied the effect of phosphorus pentachloride on N-acetyl-N,N'-ethylene urea 133.2, which leads to the formation of 2-(2-oxo-1-imidazolidinyl)-2-chloro-ethenyltrichlorophosphonium hexachlorophosphate 135 (Scheme 37).



Scheme 37

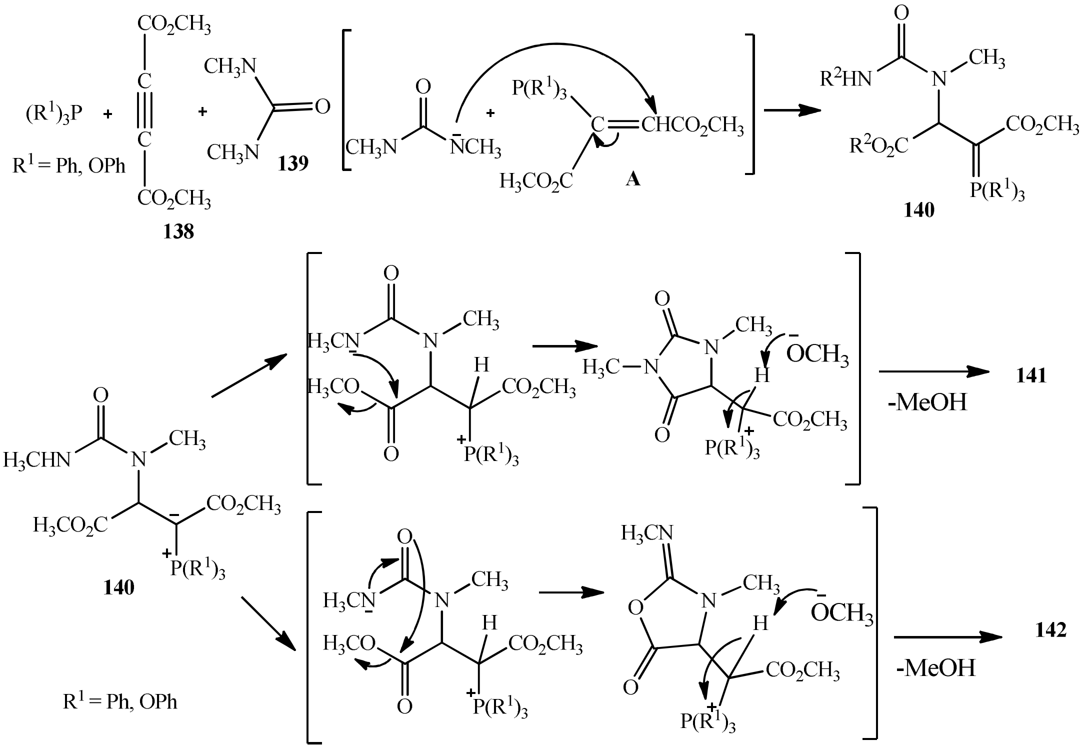
Compound 135, when treated with sulfur dioxide, is converted to 2-(2-oxo-1-imidazolidinyl)-2-chloro-ethenylphosphonic acid dichloride 136, upon hydrolysis of which 2-oxo-2- (2-oxo-1-imidazolidinyl) ethyl phosphonic acid 137 is formed (Scheme 37).

Multicomponent reactions proved to be very effective in assembling diversified molecules and searching for new ways to obtain heterocycles and organophosphorus compounds. It was reported about the reaction of compounds with the presence of three-coordinated phosphorus $(PhO)_3P$ and/or Ph_3P with dimethylacetylenedicarboxylate 138 in the presence of N,N'-dimethylurea 139 to obtain β-amidophosphonates 141, phosphonates 142, and stable phosphorus ylides 140 (Scheme 38) [50].



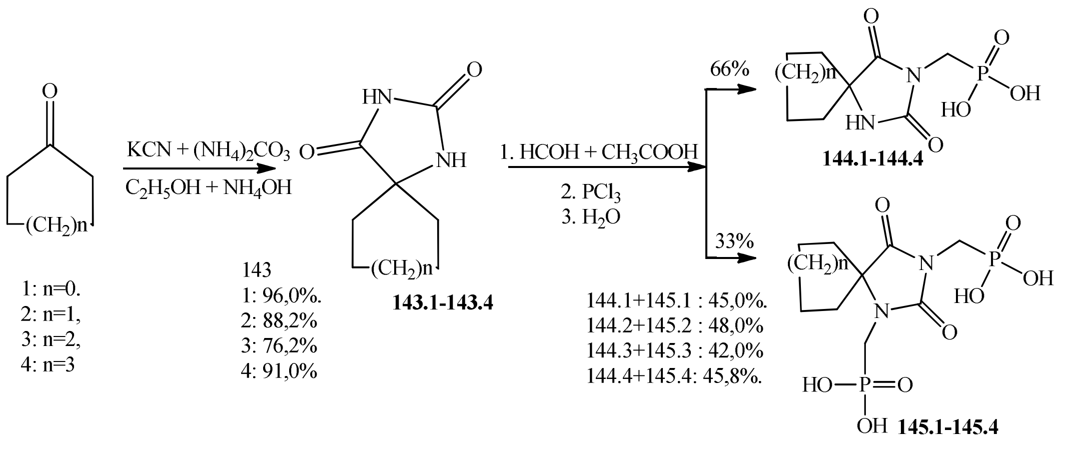
Scheme 38

This reaction (Scheme 38) was carried out in the presence of triphenylphosphine in dry dichloroethane CH_2Cl_2 as a solvent at room temperature. As a result of the reaction, hydantoin 141 and oxazolidine 142 were obtained, containing stable phosphorus ylides with good yields. Usually, the solubility of phosphorus ylides in ethyl acetate is less than in methylene chloride, therefore, the authors suggest using ethyl acetate to limit the reaction and isolate the intermediate acyclic products 140. The stepwise mechanism shown in scheme 39 is provided by a nucleophilic attack of the olefinic carbon atom of intermediate phosphoalkene by the urea anion with the formation of ureidoylide 140, the fate of which, depending on the chemistry of the process, ends with the formation of phosphorane cycles of hydantoin 141 or oxazalidinone type 142 [50].



Scheme 39

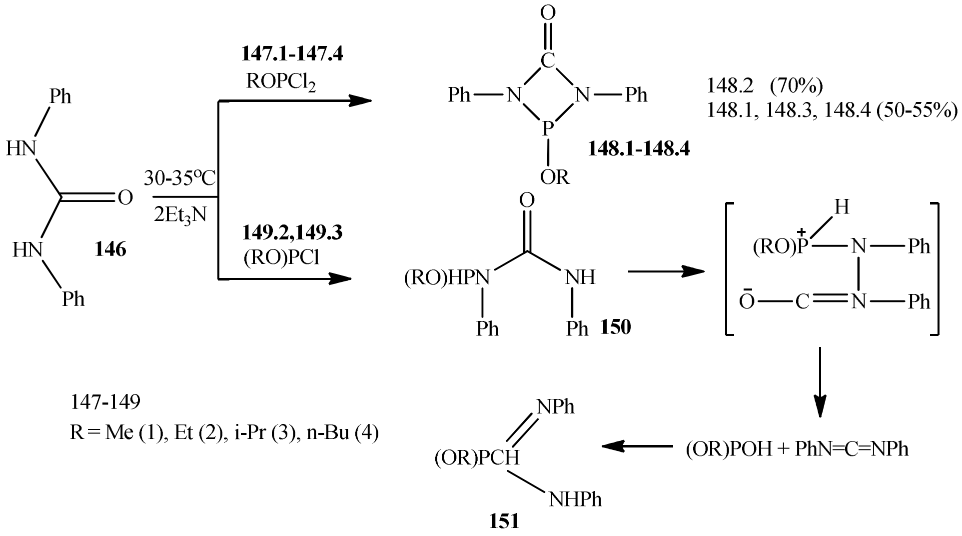
Hydantoins 143.1–143.4, previously synthesized by the Bucherer reaction [51] in the condensation reaction with formaldehyde, give regioisomers 144 and 145 in a ratio of 66 % : 33 %, respectively (Scheme 40) [10].



Scheme 40

2.2 Preparation and properties of tetracyclic phosphorylated urea derivatives

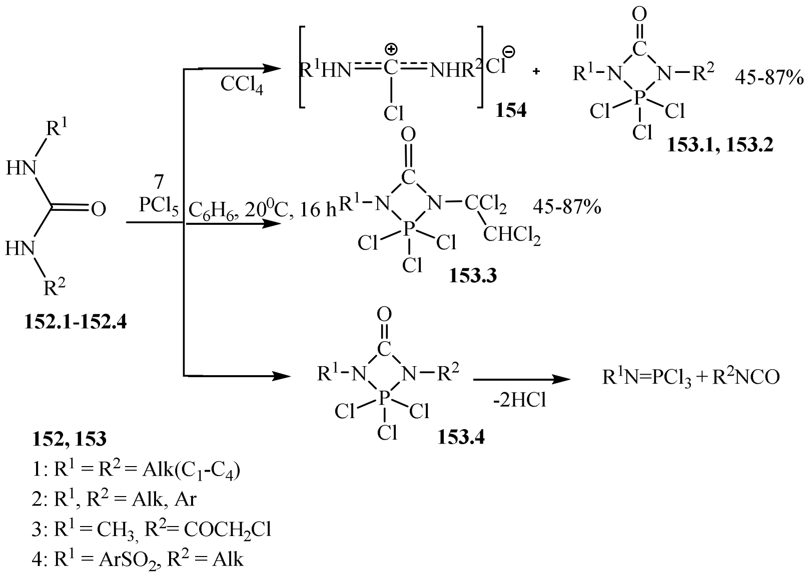
It has been established that the direction of urea phosphorylation reactions by ethers of chlorine derivatives of phosphoric acids depends on the coordination number of phosphorus: in the case of using a three-coordinated phosphorus atom, phosphorylation takes place [52]. For example, when using monoalkoxyphosphoric acid dichlorides 147.1–147.4, successful phosphazacyclization was achieved through the intermediate phosphorylation of diphenylurea 146, where the products are 1,3-diaza-2-phosphetidin-4-ones 148.1–148.4 (Scheme 41) [53].



Scheme 41

Unlike dichlorides 147.1–147.4, dialkoxyphosphoric acid monochlorides 148.1–148.2 react with diphenylurea 146 in the presence of the HCl acceptor with the initial formation of phosphorylated urea 150, which is unstable and prone to rearrangement (accelerated upon heating) into phosphorylated amidine 151 (Scheme 41). However, when using derivatives of a tetracoordinated phosphorus atom, the reaction can proceed in a different direction through the process of dehydrating diphenylurea 146 [52, 53].

Reactions of phosphorus pentachloride with 1,3-disubstituted ureas 152.1–152.2 containing primary alkyl substituents occur predominantly through the nitrogen atoms to form a four-membered cyclic structure 153.1 (Scheme 42) [54]. While ureas containing secondary alkyl groups form only minor amounts of compound 153.1, the predominant product is chloroformamidinium chloride 154 (Scheme 42) [54, 55].



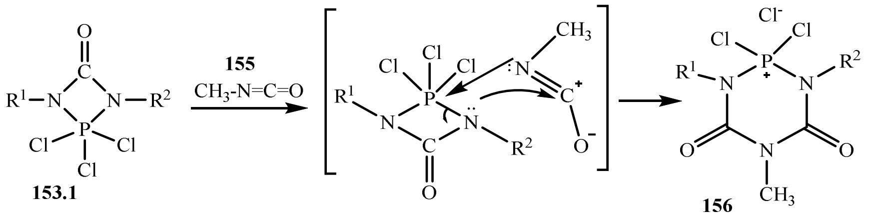
Scheme 42

Similarly, N,N'-Dialkyl(alkylaryl)urea 152.2 with phosphorus pentachloride in equimolar amounts give derivatives of trichloro-1,3,2-diazaphosphetidin-4-one 153.2 [56], although it was reported that when using an excess of PCl_5, the carbonyl group was chlorinated [56].

When N-methyl-N'-chloroacetylurea 152.3 interacts with phosphorus pentachloride, a substituted 1,2,3-diazaosphetidin-4-one 153.3 is formed [57, 58] (Scheme 42).

The effect of the structure of substituents on the nitrogen atom in urea was manifested when an attempt was made to phosphorylate 1-arylsulfonyl-3-alkyl urea 152.4. It was shown that the cyclic compound 153.4 obtained turned out to be extremely unstable (Scheme 42) [54].

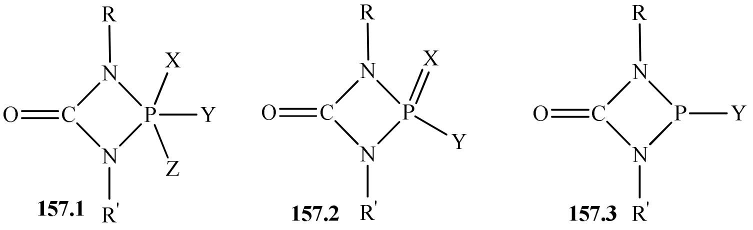
[55] reported that if methyl isocyanate 155 acts on the obtained phosphocycle 153.1, then the cycle is expanded to a 6-membered one, and the final product is isolated as a salt 156 (Scheme 43).



153. 1: $R^1 = R^2 = Alk(C_1\text{-}C_4)$

Scheme 43

Based on previously developed convenient methods for producing diaza-2-phosphetidin-4-ones of type 153 (Scheme 42), namely, with methyl substituents (R = R '= Me) [57], aryl substituents (R, R' = Ar) [58], [59] diaza-2-phosphetidin-4-ones 157.1–157.3 were synthesized in a similar way (scheme 44) [60, 61]. The dynamic behavior of the phosphorus atom was studied by low-temperature NMR spectroscopy.

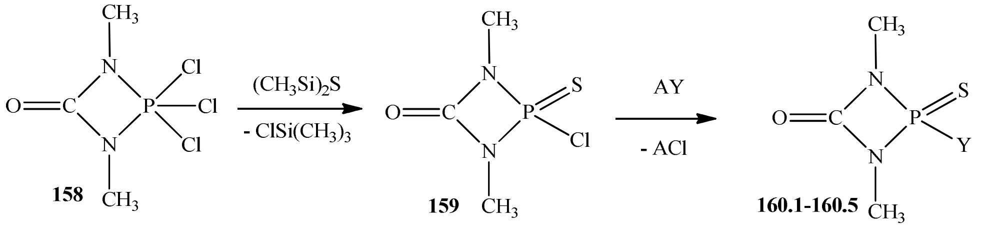


R, R' =Alk, Ar
X = O, S
Y = NR''_2, OR'', SR''
Z = Cl

Scheme 44

By transformation with the corresponding nucleophilic reagents of phosphazacycles 153, diazaphosphetidinones of type 157 (R, R' = C) with substituents (Y = N) C_2 [62], NEt_2 [63, 64], OC [65], and CCl_3 were obtained [66].

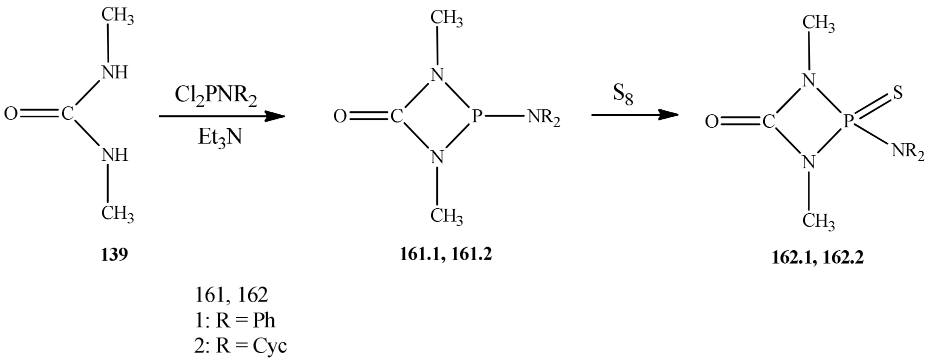
On the basis of the already studied methods for obtaining diaza-2-phosphetidin-4-ones 157.1–157.3 (Scheme 44), [67] suggested ways of converting 158 to the corresponding 2-thioderivatives 159, 160 (Scheme 45), 162 (Scheme 46). The authors report that the thio-derivatives of diazaphosphetidinone 159 can be obtained by direct oxidation of compound 158 (Scheme 45). A suitable method for the preparation of compounds 160.1–160.5 is the reaction with trimethylsilyl derivatives (AY), since the direct use of secondary amines leads to ring opening. The amino groups NR_2 (R = Me, Et, $(CH_2)_4$, OCH_3 and SCH_3) of trimethylsilyl derivatives (AY) in the reaction with 159 replace the chlorine atom, which leads to the formation of thiophosphoric acid amides 160.1–160.5 (Scheme 45).



A = H, $Si(CH_3)_3$
Y = $N(CH_3)_2$ (1), $N(Et)_2$ (2), $N(CH_2)_4$ (3), OCH_3 (4), SCH_3 (5)

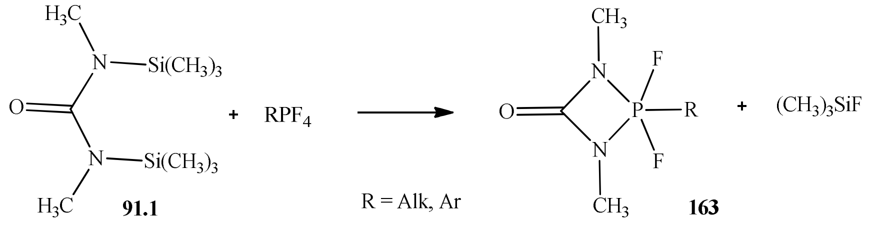
Scheme 45

However, for the synthesis of compounds 162.1, 162.2 with cyclic amine residues (NPh_2 and $N(cycl)_2$) by reacting N,N'-dimethylurea139 with the corresponding dichlorophosphorusigamide, compounds 161.1, 161.2 were obtained first, and then the phosphorus atom was oxidized with sulfur (Scheme 46).



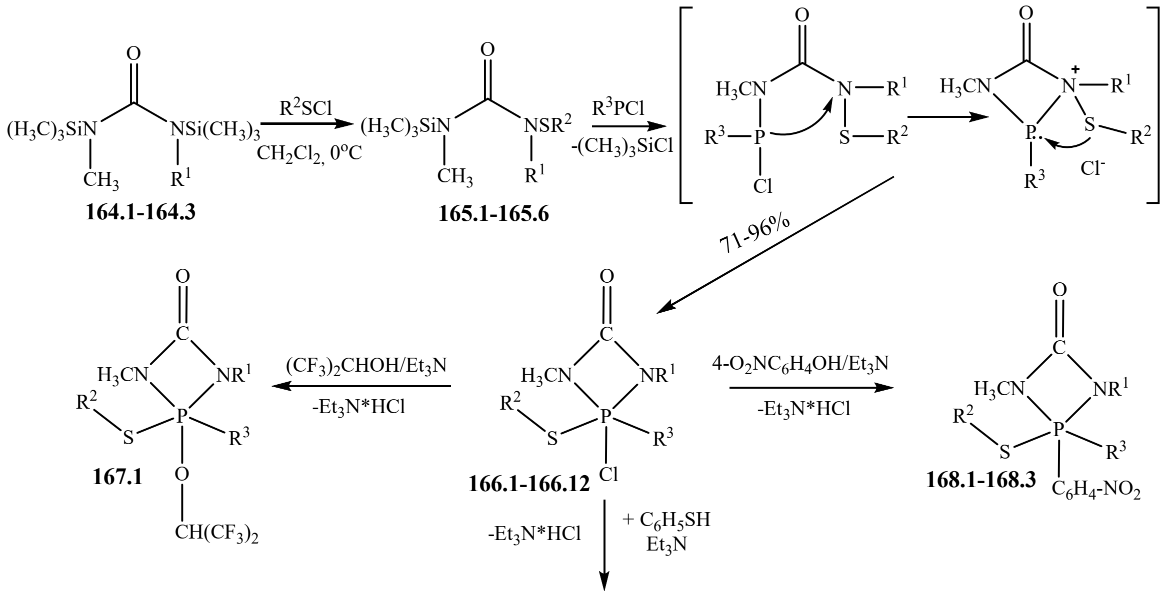
Scheme 46

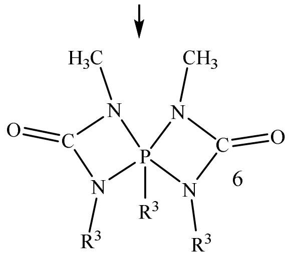
In addition, the reaction properties of 158 with respect to iso- and isothiocyanates MeNCO, PhNCO, and MeNCS were studied in [55, 68, 69]. Under the action of alkyl- or aryl-fluorophosphanes on symmetric trimethylsilyl urea derivatives 91.1, cyclization occurs with the splitting of the Si–N bond and fluorophosphadiazetinones 163 are formed (Scheme 47) [70].



Scheme 47

1-Methylsilyl-3-alkyl(aryl)sulfonyl urea 165.1–165.6, obtained from trimethylsilyl derivatives of carbamide 164.1–164.6 in reaction with aryl dichlorophosphines, cyclized smoothly to chlorophosphetidinone 166.1–166.12, which can be converted into trifluoromethyloloxy derivatives 167.1, P-aryl substituted or are subject to bicyclization to compound 169.1 [71] (Scheme 48):





169.1

64	1: R^1 = Ph, 2: R^1 = 4-$O_2NC_6H_4$, 3: R^1 = 4-$CH_3C_6H_4$,	
165	1: R^1 = Ph, R^2 = CH_3; 2: R^1 = Ph, R^2 = Ph; 3: R^1 = 4-$O_2NC_6H_4$, R^2 = CH_3; 4: R^1 = 4-$O_2NC_6H_4$, R^2 = Ph; 5: R^1 = 4-$CH_3C_6H_4$, R^2 = CH_3; 6: R^1 = 4-$CH_3C_6H_4$, R^2 = Ph;	
167	1: R^1 = CH_3, R^2 = Ph, R^3 = Ph;	68 %
168	1: R^1 = CH_3, R^2 = Ph, R^3 = Ph;	77 %
	2: R^1 = CH_3, R^2 = 4-$CH_3C_6H_4$, R^3 = t-Bu;	83 %
	3: R^1 = CH_3, R^2 = 4-$CH_3C_6H_4$, R^3 = Ph;	75 %
169	1: R^3 = CH_3;	23 %

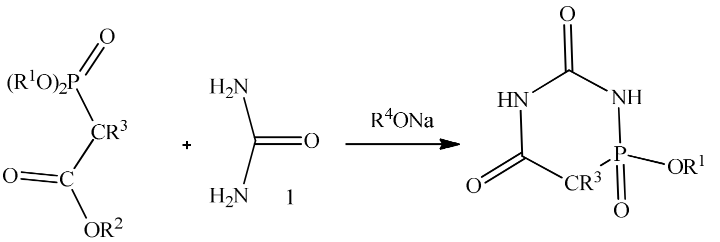
166	1: R^1 = Ph, R^2 = CH_3, R^3 = Ph;	87 %
	2: R^1 = Ph, R^2 = Ph, R^3 = Ph;	92 %
	3: R^1 = Ph, R^2 = CH_3, R^3 = CH_3;	87 %
	4: R^1 = Ph, R^2 = Ph, R^3 = CH_3;	90 %
	5: R^1 = 4-$CH_3C_6H_4$, R^2 = CH_3, R^3 = CH_3;	94 %
	6: R^1 = 4-$CH_3C_6H_4$, R^2 = Ph, R^3 = CH_3;	85 %
	7: R^1 = 4-$CH_3C_6H_4$, R^2 = CH_3, R^3 = CH_2Cl;	90 %
	8: R^1 = 4-$CH_3C_6H_4$, R^2 = CH_3, R^3 = t-Bu;	71 %
	9: R^1 = 4-$O_2NC_6H_4$, R^2 = CH_3, R^3 = Ph;	91 %
	10: R^1 = 4-$O_2NC_6H_4$, R^2 = Ph, R^3 = Ph;	96 %
	11: R^1 = 4-$CH_3C_6H_4$, R^2 = CH_3, R^3 = Ph;	
	12: R^1 = 4-$CH_3C_6H_4$, R^2 = Ph, R^3 = Ph;	

Scheme 48

Thus, in this work, it is shown that the resulting phosphazacycles 167–169 are the products of nucleophilic substitution reactions of the chlorine atom in chlorophosphetidinone 166 (Scheme 48).

2.3 Preparation and properties of six-membered cycles of phosphorus derivatives of ureas

When urea 1 itself is condensed with phosphonoacetic acid esters 170.1–170.2 in the presence of sodium alcoholate, cyclic phosphoric analogues of barbituric acid 171.1–171.2 are formed (Scheme 49) [72, 73].



170.1-170.2

171.1-171.2

170,171

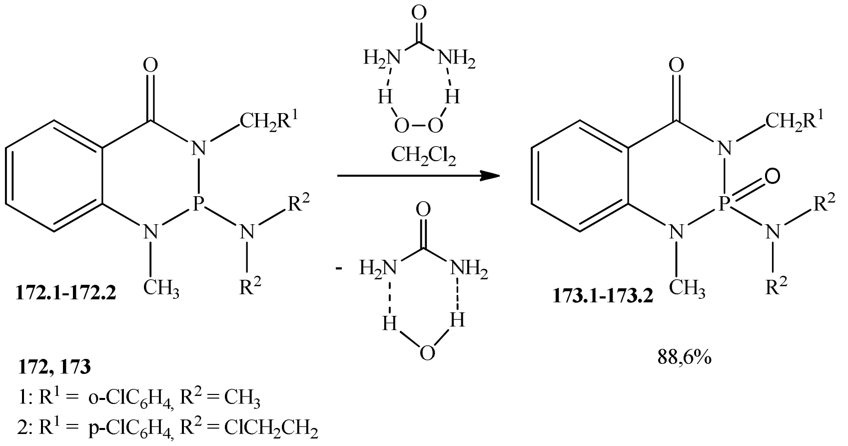
1: R^3= H_2, R^1, R^2, R^4 = Alk

2: R^3 = C_3H_5 - cycl, R^1, R^2, R^4 = Alk

Scheme 49

An increase in the length of the alkyl radical in phosphonic acid with an excess of sodium alkoxide can lead to spiro derivatives of barbituric acid, as it was demonstrated [73] by the example of the preparation of spirocyclopropane diazaphosphorinone 171.2 (Scheme 49).

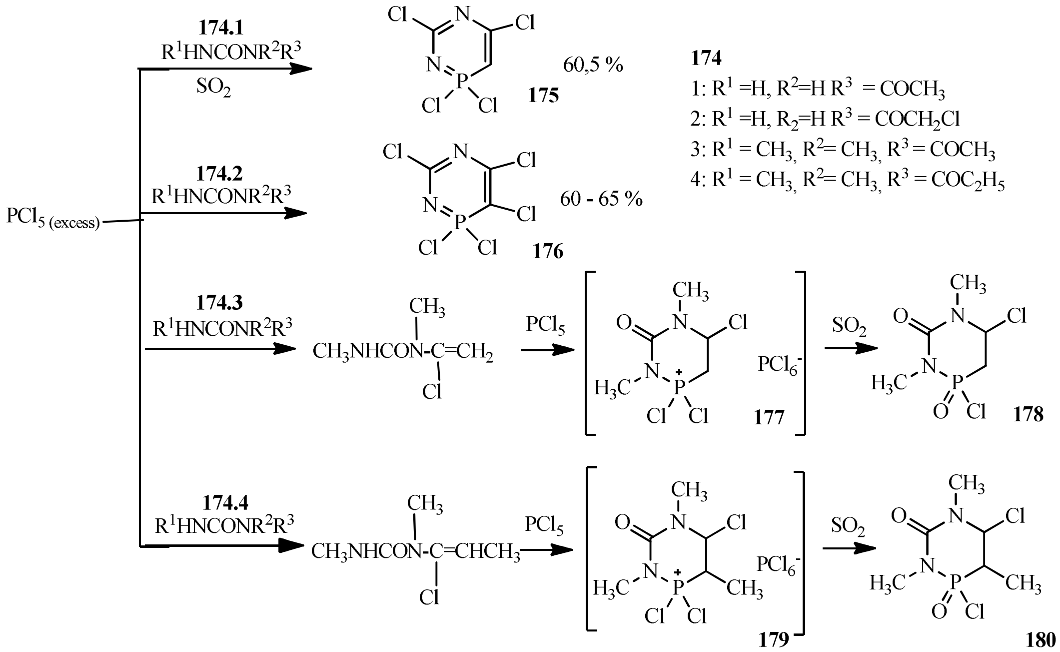
It is curious that diazaphosphorinones 172.1–172.2 under the action of the H2O2: urea 1 complex with good yields are oxidized to phosphodiazacycles 173.1–173.2 (Scheme 50) [74], which is convenient for the conversion of aminophosphites172 into the corresponding phosphates 173.



172, 173
1: R^1 = o-ClC_6H_4, $R^2 = CH_3$
2: R^1 = p-ClC_6H_4, $R^2 = ClCH_2CH_2$

Scheme 50

In a series of papers [8, 75–78], the processes of formation of various phosphase heterocycles based on the interaction of N-substituted acylureas 174.1–174.4 with an excess of PCl_5 were studied (Scheme 51).



174
1: R^1 =H, R^2=H R^3 = $COCH_3$
2: R^1 =H, R_2=H R^3 = $COCH_2Cl$
3: $R^1 = CH_3$, $R^2 = CH_3$, $R^3 = COCH_3$
4: $R^1 = CH_3$, $R^2 = CH_3$, $R^3 = COC_2H_5$

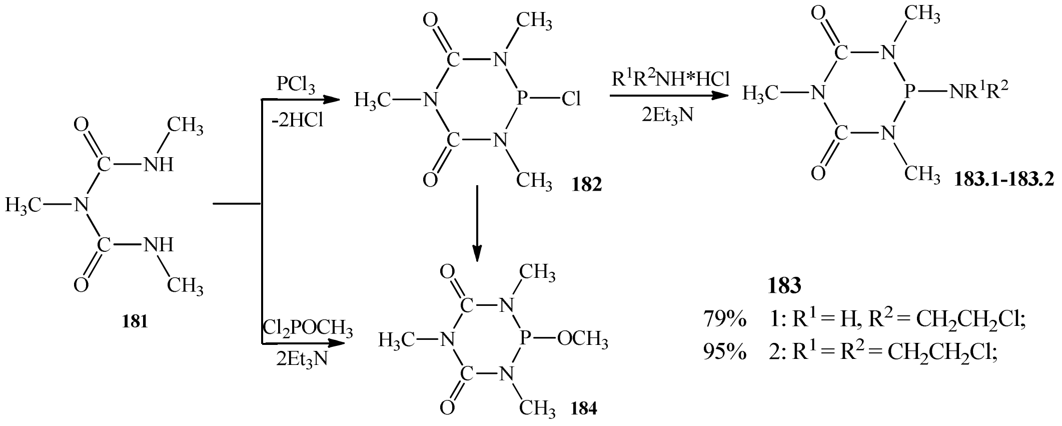
Scheme 51

It has been proved [75–77] that the cyclization of N-acetylurea 174.1 under the action of a fivefold excess of PCl_5 occurs with the participation of the acetyl group and the amino group to form trichlorophosphate heterocycle 175 (Scheme 51).

Chloroacetylurea 174.2 when heated with phosphorus pentachloride forms diazophosphorin 176, which differs from compound 175 in that in this case one more proton is replaced by a chlorine atom [78] (Scheme 51).

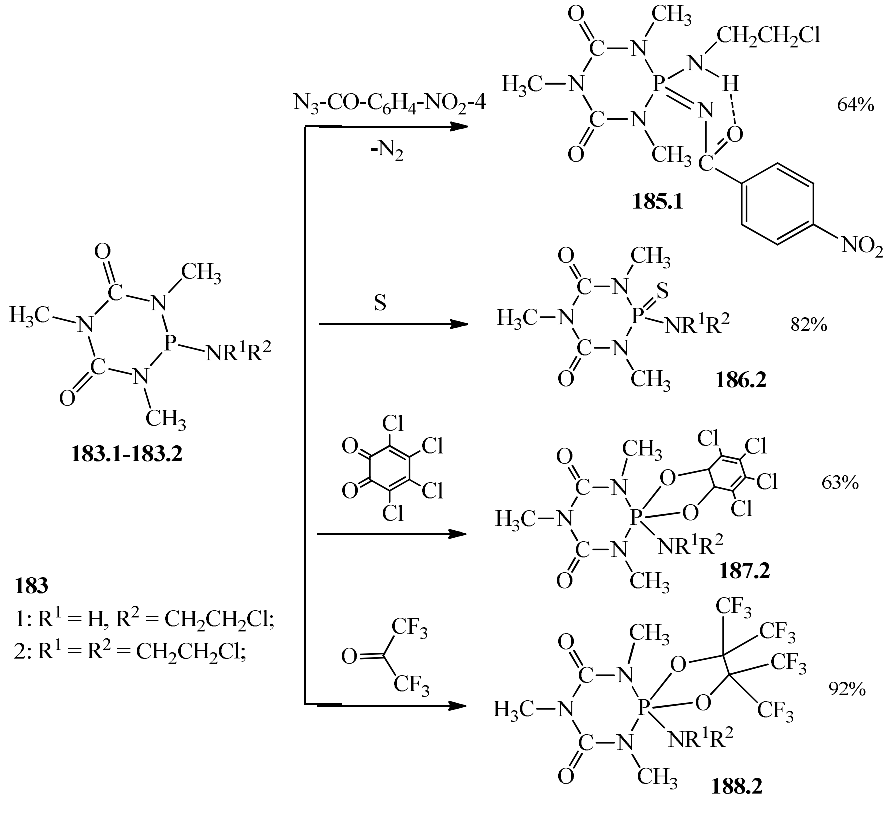
When N,N'-dimethylacetylureas 174.3–174.4 interact with phosphorus chloride in a 1:5 ratio, diazaphosphorionic salts 177, 179 are formed, which are in situ transformed into diazaphosphorins 178 and 180, respectively [8] when treated with SO_2 (Scheme 51).

A method for the synthesis of 1,3,5-triaza-2-phosphorinanediones 182, 183.1–183.2 was developed [79]. containing the carbamide moiety in the cycle, by reacting PCl_3/Cl_2POCH_3 and 1,3,5-trimethylburet 181 (Scheme 52), the methoxy derivative 184 is obtained from the chlorine derivative 1,3,5-triaza-2-phosphorinanedione 182 [80].



Scheme 52

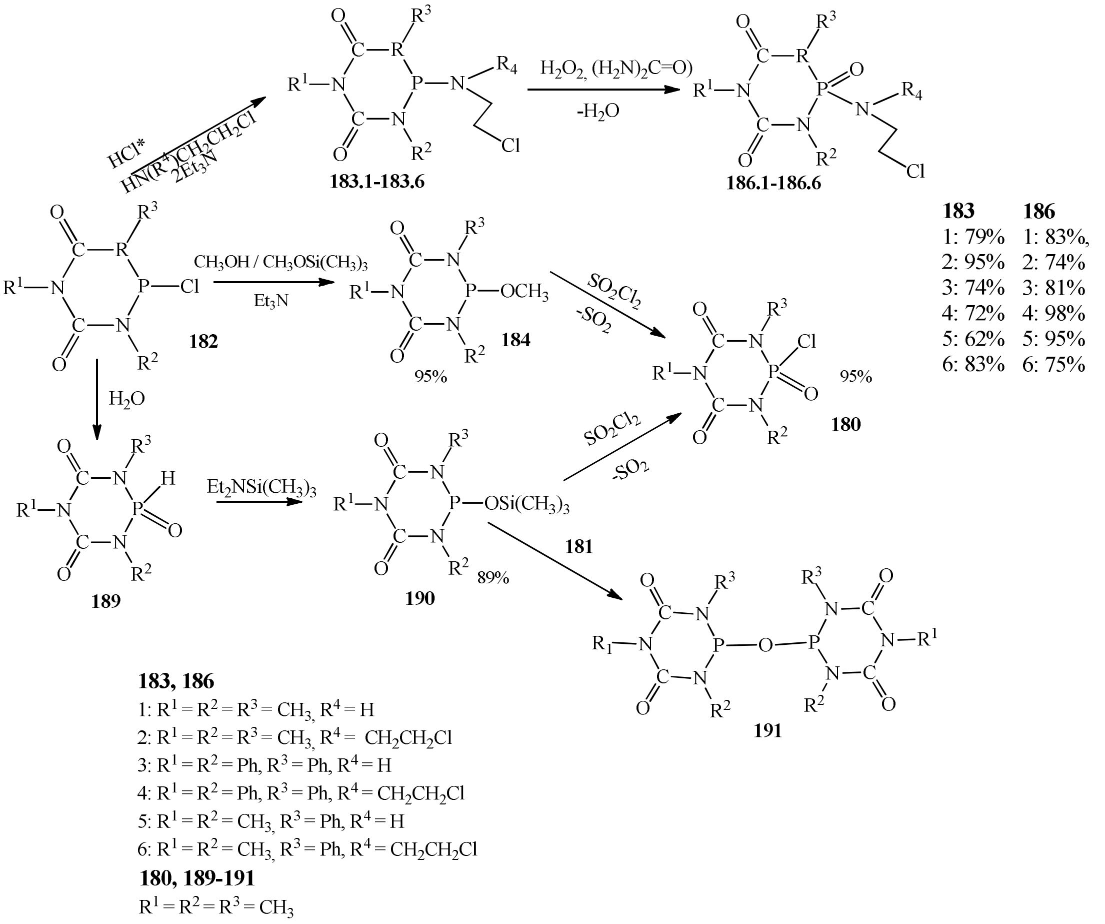
In the same work [79], the authors studied some of the chemical properties of 183.1–183.2, where, in diagram 53, the following processes were demonstrated for 183.1–183.2: oxidative ammonolysis (compound 185.1, sulphidation (compound 186.2), oxycyclization (compounds 187.2 and 188.2).



Scheme 53

In subsequent reports [80–82] the authors involved the synthesized 1,3,5-triaza-2-phosphorinanediones 182–184 in a wide range of chemical transformations 180, 186–201 (Schemes 54–57).

Scheme 54 reflects the reactions of 1,3,5-triaza-2-phosphorinanediones 182–184 [80]: oxidation (compounds 186.1–186.6), hydrolysis (compound 189), oxidative chlorination (compound 181), which proceeds through an intermediate salt formation 192 [55] (Scheme 55), silylation (compound 190) and esterification (Compound 191) (Scheme 54).

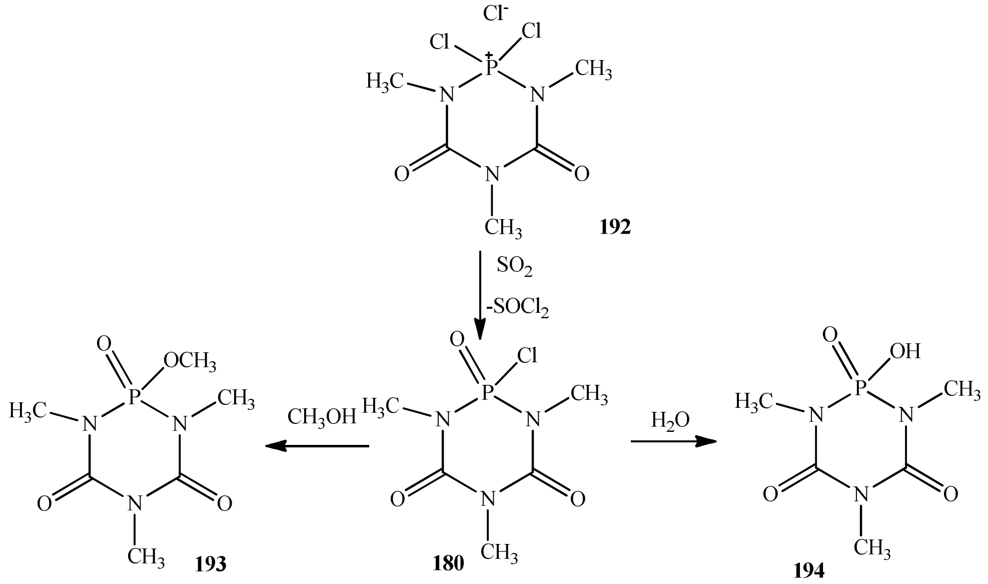


183	186
1: 79%	1: 83%,
2: 95%	2: 74%
3: 74%	3: 81%
4: 72%	4: 98%
5: 62%	5: 95%
6: 83%	6: 75%

183, 186
1: $R^1 = R^2 = R^3 = CH_3$, $R^4 = H$
2: $R^1 = R^2 = R^3 = CH_3$, $R^4 = CH_2CH_2Cl$
3: $R^1 = R^2 = Ph$, $R^3 = Ph$, $R^4 = H$
4: $R^1 = R^2 = Ph$, $R^3 = Ph$, $R^4 = CH_2CH_2Cl$
5: $R^1 = R^2 = CH_3$, $R^3 = Ph$, $R^4 = H$
6: $R^1 = R^2 = CH_3$, $R^3 = Ph$, $R^4 = CH_2CH_2Cl$
180, 189-191
$R^1 = R^2 = R^3 = CH_3$

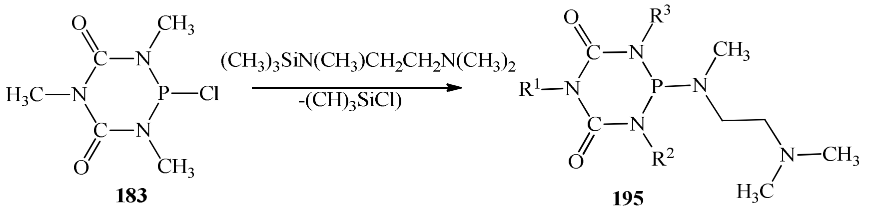
Scheme 54

When exposed to SO_2 gas on a 6-membered cycle 192, the latter is able to take a more stable form 180, capable in further interactions to easily exchange the chlorine atom for the OH and OCH_3-group under the action of water or methanol to produce products 193, 194 (Scheme 55) [55].



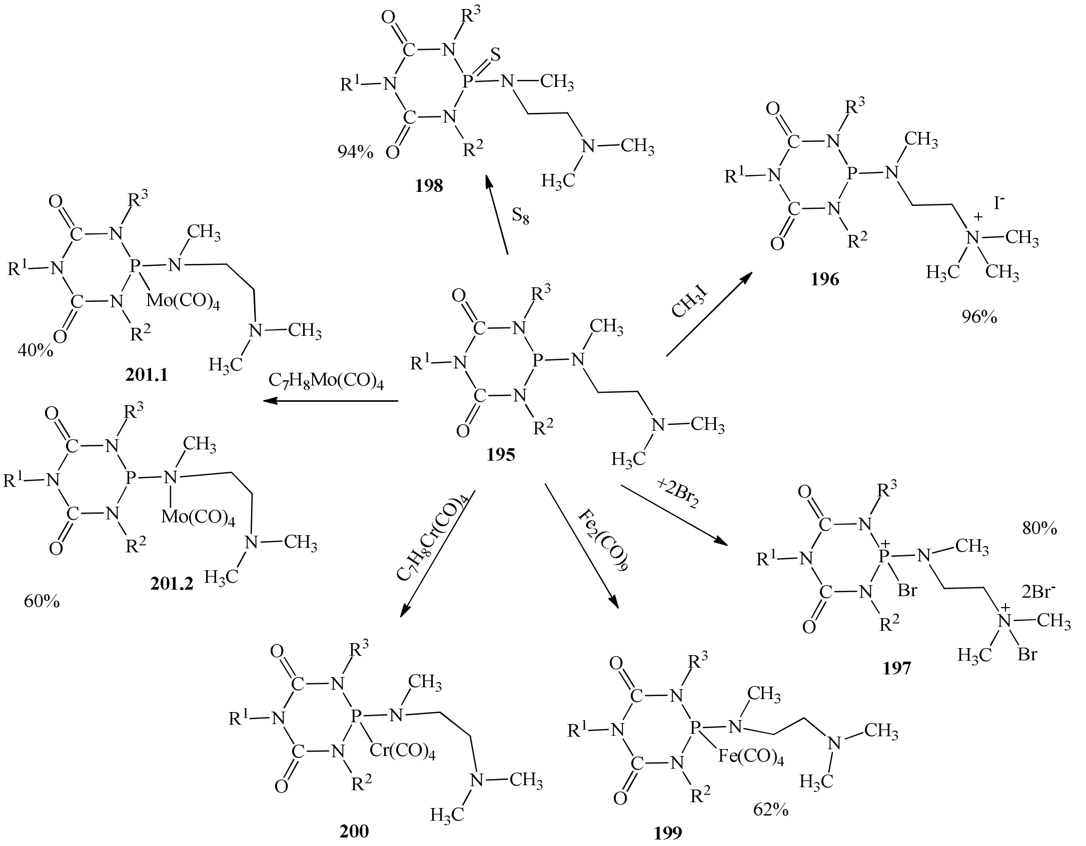
Scheme 55

Scheme 56 shows the process of exchanging the chlorine atom of the cyclic compound 182 for an amino group with the production of the diamine derivative 1,3,5-triaza-2-phosphorinane-dione 195 [82].



Scheme 56

Scheme 57 shows various variants of modification of compound 195, carried out in [82] and leading to the formation of the corresponding salts 196, 197, sulfide 198, and complex compounds 199–201.



Scheme 57

The demonstrated path of transformation of the phosphazacycle 195 using simple and accessible reagents serves as an illustrative example of the possibility of synthesizing a variety of phosphazaheterocycles that have a wide potential for their practical application.

Thus, an analysis of the available literature data on the methods of synthesis and properties of phosphorylated monocyclic carbamide-containing compounds suggests that the five-membered cycles in the vast majority are represented by imidazolidine structures 124, 126, 128–131, 134–137, 141, 144, 145, containing phosphorylated groups in the side chain, with the exception of individual imidazolidines containing a phosphorus atom in the cycle (diazabenzophospheneum 118 and diazaphospholidinedione 212.1.1–121.4).

The formation of tetracyclic phosphorylated ureas by corresponding reactions leads only to diazaphosphetidinones with the three-coordinated phosphorus atom 148, 161, and with the five-coordinated phosphorus atom in the cycle as well 153, 158–160, 162, 163, 166–168.

The formation of six-membered phosphorylated urea-containing azacycles is mainly come down to diazophosphorins 175, 176, 178, 180 and triazaphosphorinanionones 182–201, although there are some cases of synthesis of phosphoric analogues of barbituric acid 171.1–171.2.

A curious observation is the ability of transformation of four-membered diazaphosphetidinones into six-membered triazaphosphorinanionones (Scheme 43).

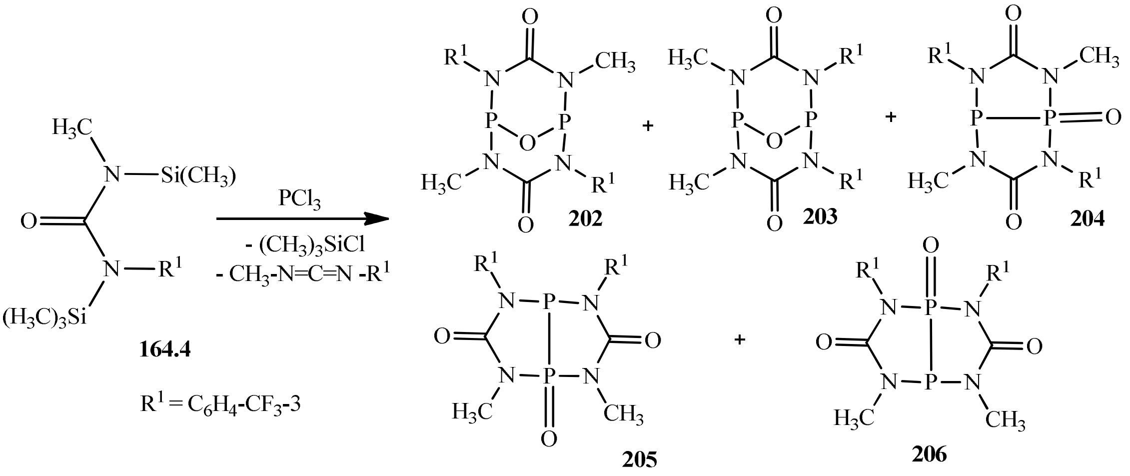
3 Synthesis methods of phosphorylated bicyclic bisureas

3.1 Bicyclic bisureas with diphosphate[3,3,0]-3,7-dione structure

An analysis of the literature data showed that 1,3-bis(trimethylsilyl)urea and its derivatives (91, 164) were often used to construct heterocyclic compounds. The attractiveness of the latter is determined by the fact that they turned out to be very convenient synthons for building a number of phosphorus-containing bicyclic bromides 202–209, 212, 213 (Schemes 58–60).

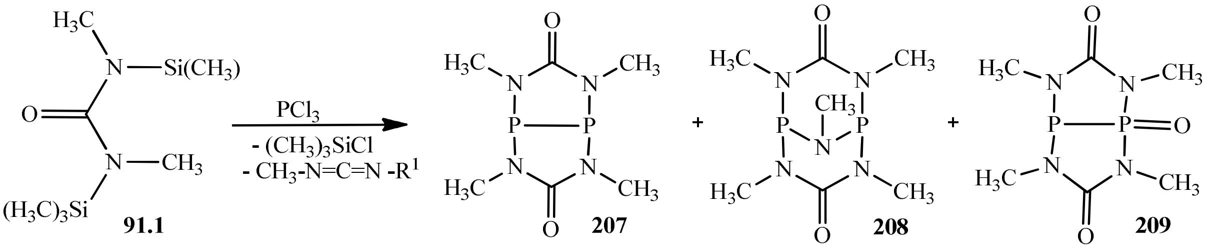
Thus, bis(trimethylsilyl)urea 164.4 was used by the authors [83] in reactions with PCl$_3$, where the product was cyclo[3,3,1]nonane-3,7-dione 202 (41 %). At the same time, carbodiimide 3-CF$_3$C$_6$H$_4$–N=C=N–CH$_3$ was released as a by-product in the reactions (Scheme 58).

In other studies, the authors of [84], by varying the conditions of the process of phosphorylation reaction 164.4 with PCl$_3$, found that in a similar reaction 164.4 with PCl$_3$ individual substance 202 was not formed, but a series of bicyclic diuretic [3,3,0]-3,7-dione structures 202–206 with nodal P–P bond (Scheme 58).



Scheme 58

In extension of their research, the authors [84] studied the reaction of 1,3-dimethyl-1,3-(trimethylsilyl)urea 91.1 with PCl$_3$, where it was also noted that in addition to the target product 207, compounds 208, 209 are obtained as well (Scheme 59).



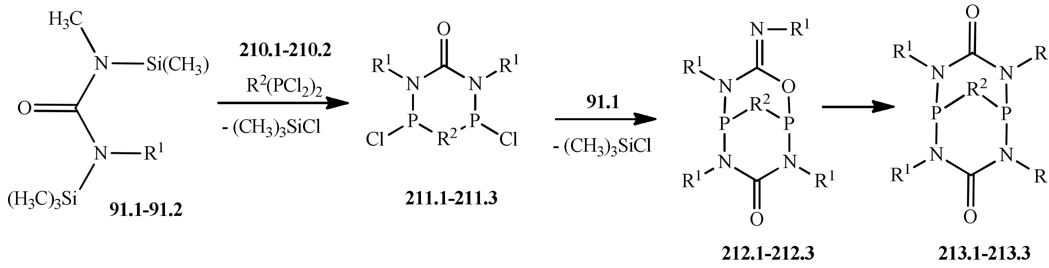
Scheme 59

It was found [85] that the reaction of methylsilyl urea 91.1 with methylenediphosphodichloride 210.1 in an inert atmosphere is completed by bicyclization to diphosphate[3.3.1]nonan-3,7-dione 213.1 and 213.2, respectively, while the reaction of urea 91.2 with dichloromethylene di-phosphodichloride 210.2 proceeds with the formation of dichloro-derivative diphosphate[3.3.1]nonan-3,7-dione 213.3 (Scheme 60).

It is postulated that these reactions proceed through intermediate monocycles 211.1 and intermediates 212.1, which regroup to thermodynamically more stable products 213.1 [86] (Scheme 60).

Dichloro derivative diphosphate[3.3.1]nonan-3,7-dione 213.3 reacts nucleophilic substitution with triisopropylphosphine, which, as expected, led to C-phosphine substituted ylide 214, (Scheme 61). Bicyclic ylide 214 was detected by deciphering ^{31}P NMR spectra, but was not isolated due to low stability [86].

The properties of bicyclic bisureas 205, 207, and 209 were studied in [84, 86–88].

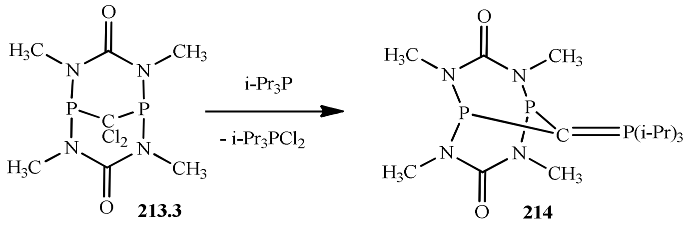


91 1: $R^1 = CH_3$, 2: $R^1 = H$

210 1: $R^2 = CH_2$, 2: $R^2 = CCl_2$

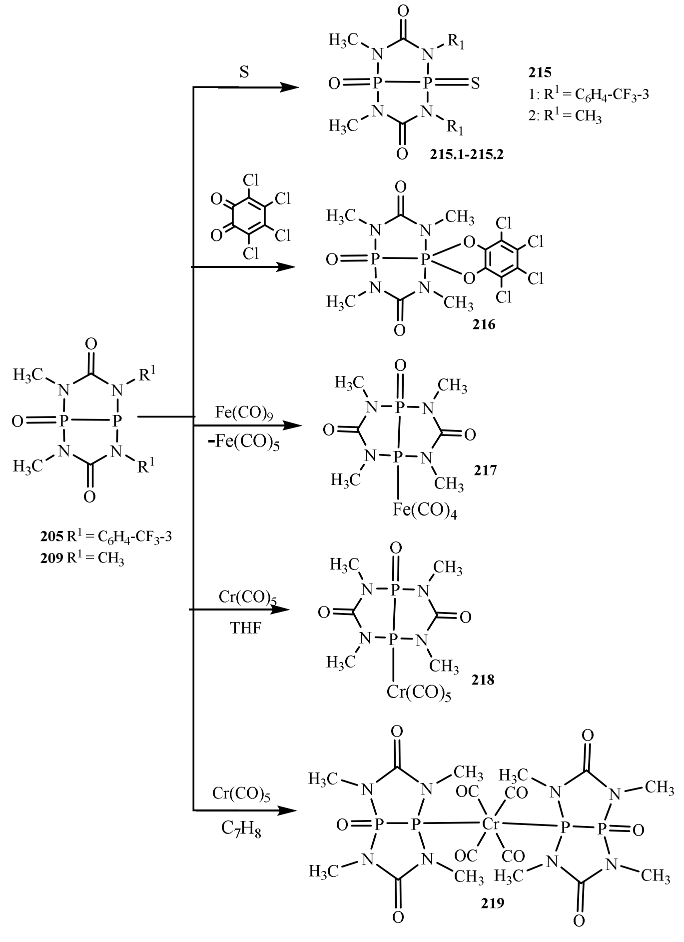
211, 212, 213 1: $R^1 = H$, $R^2 = CH_2$
2: $R^1 = CH_3$, $R^2 = CH_2$
3: $R^1 = CH_3$, $R^2 = CCl_2$

Scheme 60



Scheme 61

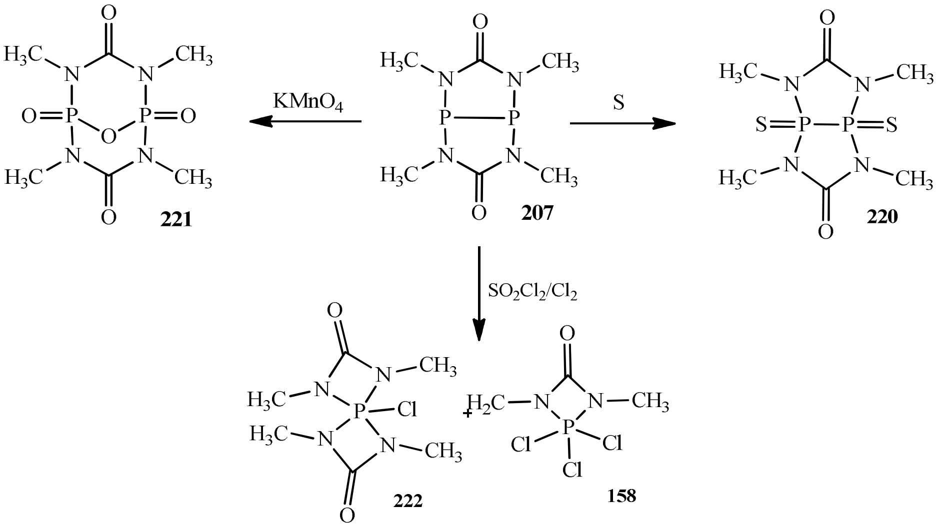
Compounds 205, 207, and 209, when interacting with elemental sulfur, tend to form a P=S bond in bicycles 215.1–215.2, 220 (Scheme 62, 63) [87]. It was also found that compound 209, in turn, readily reacts with hexachlorobenzene to form a modified cycle 216, which is a colorless solid, melts at 204–206 °C, is sensitive to hydrolysis and is easily soluble in CH_2Cl_2 and toluene (Scheme 62) [88].



Scheme 62

In the course of further study of the properties of phosphazabicycle 209, complexes 217–219 with $Fe_2(CO)_9$ and $Cr(CO)_5$ were isolated and studied. Complexes 217, 218 are obtained in a molar ratio of 1:1. Complex 219 is obtained in the reaction with a ratio of 2:1 phosphorus derivative 209 (o) $Cr(CO)_4C_7H_8$, respectively.

During the oxidation of a phosphazabicycle 207 by potassium permanganate, the phosphorus in the P–P node of the bicycle is oxidized to the pentavalent state with the formation of a P–O–P bridge in compound 221 (Scheme 63) [87]. Further study of the properties of the phosphazabicycle 207 showed that the treatment of the latter with 207 molecular chlorine or SO_2Cl_2 leads to the formation of a mixture of phosphetidinone 158 and a spirocycle 222 with a P–Cl bond (Scheme 63) [84].

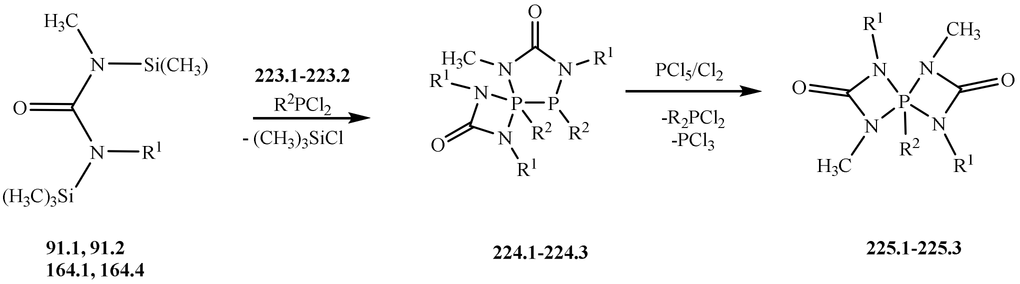


Scheme 63

To identify specific interactions of the phosphazabicycle 207, the ability of complex 207 to complexation with $Cr(CO)_5$ was shown in [84]. Thus, in the works [84, 86–88], bicyclic di-phosphate[3,3,0]-3,7-dione structure 202–209, 212–222 synthesized on the basis of bis(trimethylsilyl)urea 91, 164 were obtained and studied.

3.2 Bicyclic bisureas with difosfaspiro[3,4]octane-2,7-dione structure

[89] reported that the participation of 2 molecules of 1,3-bis(trimethylsilyl)urea 91.1, 91.2, 164.1, 164.7 in reactions with two molecules of dichloro(aryl)phosphanes 223.1–223.2 leads to bicyclization to tetraazadifosfaspiro[3, 4]octane-2,7-dyons 224.1–224.3 with a fairly good yield (87 %) (Scheme 64).



91
1: $R^1 = CH_3$,
2: $R^1 = H$
164
1: $R^1 = C_6H_5$,
4: $R^1 = C_6H_4\text{-}CF_3\text{-}3$,

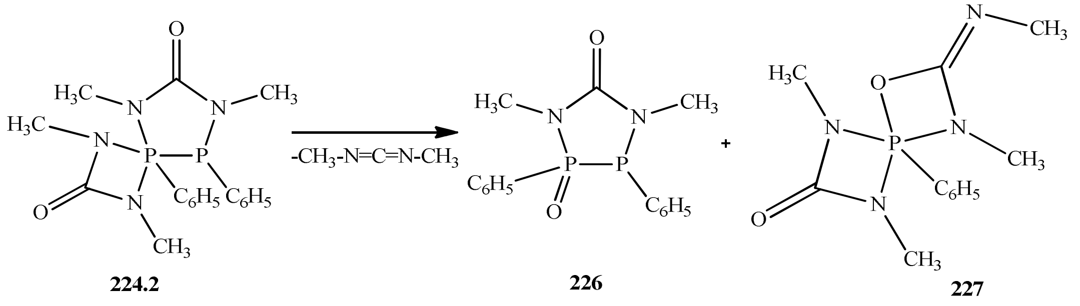
223
1: $R^2 = C_6F_5$
2: $R^2 = C_6H_5$

224, 225
1: $R^1 = C_6H_4\text{-}CF_3\text{-}3$, $R^2 = C_6F_5$
2: $R^1 = CH_3$, $R^2 = C_6H_5$
3: $R^1 = C_6H_5$, $R^2 = C_6H_5$

Scheme 64

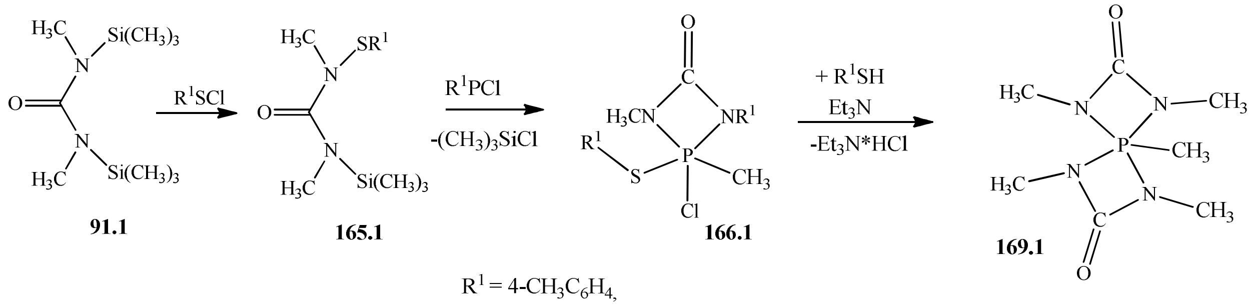
Further, when studying individual chemical properties of 224.1–224.3, it was established [83] that when exposed to molecular chlorine or PCl_5, [3,4]-octane cycles 224.1–224.3 are converted into [3,3]-heptane cycles 225.1–225.3 (Scheme 64).

In the process of studying the properties of spirobicyclic compounds, compound 224.2 was pyrolyzed, which contributed to the narrowing of its cycle to diazaphospholidin-5-one-2-oxide 227, through the formation of an intermediate monocycle 226. In this case, the corresponding carbodiimide is eliminated (Scheme 65) [87].



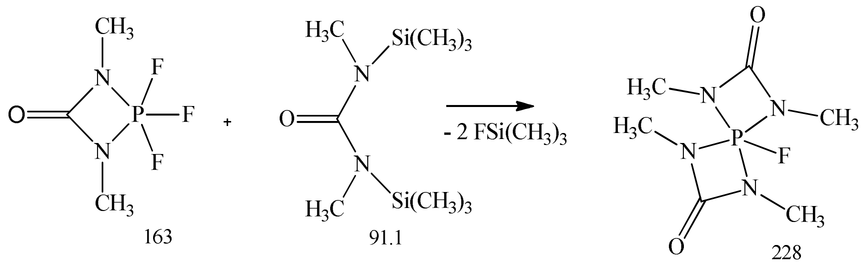
Scheme 65

1-Methylsilyl-3-alkyl(aryl)sulfonyl urea 165.1, previously prepared from trimethylsilylcarbamide derivative 91.1 in reaction with aryl dichlorophosphines, is cyclized to form a bicycle 169.1 through the formation of chlorophosphetidinone 166.1 (Scheme 66) [72].



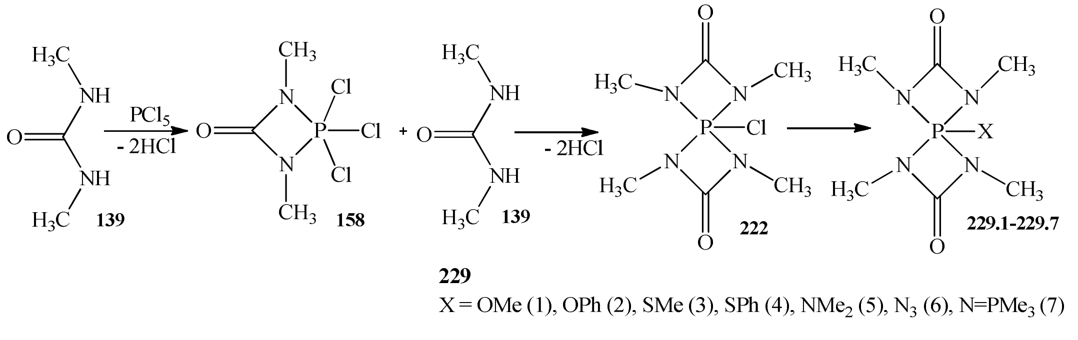
Scheme 66

Phosphaspiro[3.3]heptane-2,6-dione 228 with P-F bond was synthesized and studied with a yield of 59 % in [90] by the reaction of 91.1 with 2,2,2-trifluorodiazaphosphetidinone 163 (Scheme 67).



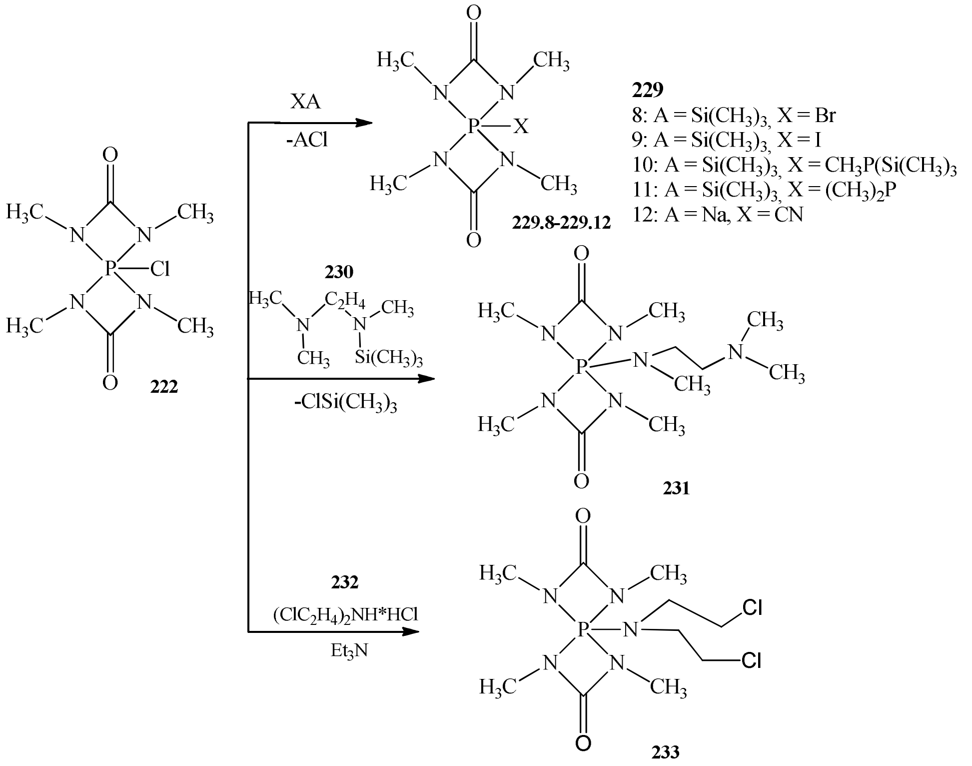
Scheme 67

Chlorophosphaspiro[3.3]heptane-2,6-dione 222 with a P–Cl bond is obtained by the interaction of symmetric dimethyl urea 139 with PCl_5 through intermediate 2,2,2-trichlorodiazaphosphetidinone 158 (Scheme 68) [90].



Scheme 68

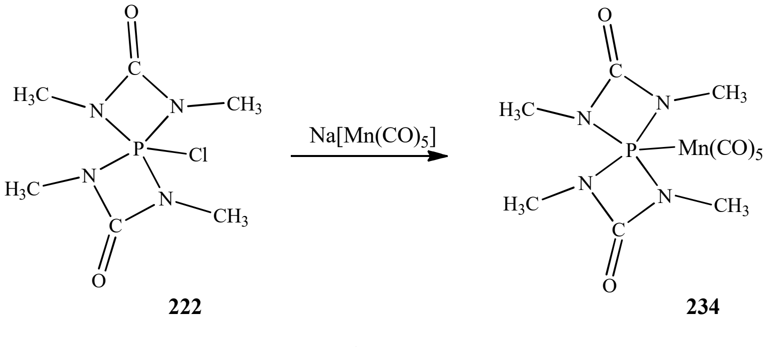
In chlorophosphaspiro[3.3]heptane-2,6-dione 222, the chlorine atom without any difficulties is subject to functionalization by various reagents with preservation of the bicyclic structure 229.1–229.12, [90, 91] (Schemes 68, 69). Similar substitution reactions were considered in [92, 93].



Scheme 69

The condensation processes of 4-chloro-1,3,5,7-tetramethyl-1,3,5,7-tetraaza-4-phosphaspiro[3.3]heptane-2,6-dione 222 with trimethyl-(trimethylsilyl)ethane-1,2-diamine 230 and bis-2-chloroethylamine 232, during which bicyclic bisureas with P–N bond 231 and 233 were obtained, respectively [92, 93].

The ability to complexation 222 was considered in [94], where it was found that the chlorine atom in an inert medium is replaced by pentacarbonylmanganese 234 (Scheme 70).

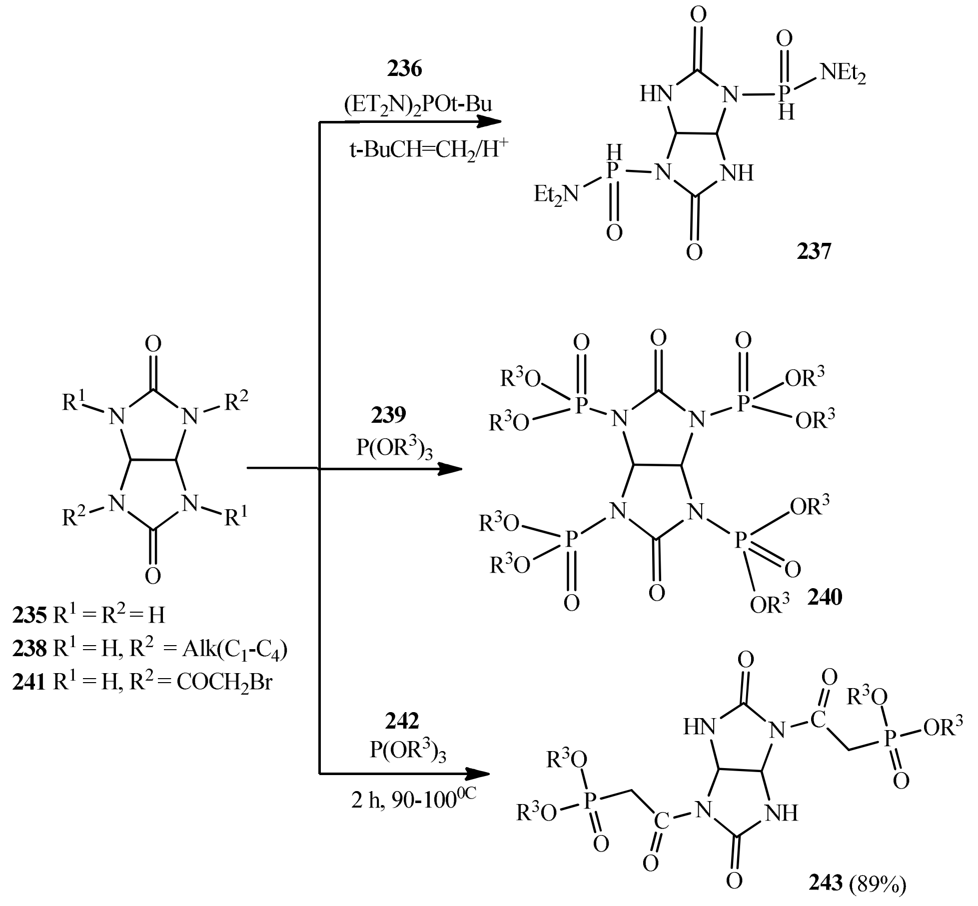


Scheme 70

3.3 Phosphorylated tetraazabicyclo[3.3.0.]octane-3,7-diones

The analysis of the available literature data has shown that the range of information on phosphorylation reactions of 2,4,6,8-tetraazabicyclo[3.3.0.]octane-3,7-dione (glycoluril) 235 has been expanding. Glycoluril 235 is product of bicyclization of urea and is its derivative, but, unlike urea, glycoluril 235 is multifunctional. Glycoluril 235 has four donor groups (–NH) and two acceptor (C=O) groups. According to chemical properties, glycoluril is a typical N-nucleophile and is easily able to enter phosphorylation reactions.

The authors [95] investigated the reaction of transamidation using glycoluril 235 and tetraethyl diamido-tert-butyl phosphite 236, which led to the formation of glycoluryl substituted diethylamido-tert-butylphosphite 237 (Scheme 71). The reaction was carried out by heating the mass of glycoluril 235 and tetraethyldiamido-tert-butylphosphite 236 in a 1:2 ratio in ethyl acetate. This ratio allows two t-butylphosphite 236 molecules to be coordinated to two amino groups (positions 2, 6). At the same time, the valence of the phosphorus atom is preserved, which causes considerable interest in this product for further research.



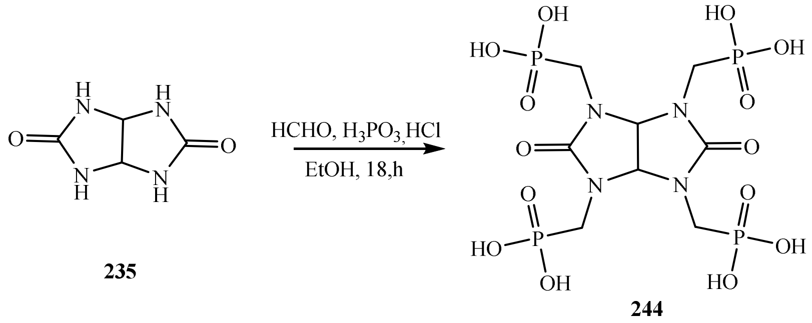
Scheme 71

In a series of Chinese patents [96–98] flame retardant substances N-phosphorylated derivatives of glycoluril 240 and methods for their preparation based on N-alkyl derivatives of glycoluril 238 (Scheme 71) were developed. These compounds are excellent nitrogen-phosphorus synergistic flame retardants.

The high nucleophilicity of the phosphorus atom is ensured by the presence of a lone electron pair on the phosphorus atom, as well as by the donor effect of alkyl groups, which facilitate the second stage of the Arbuzov's reaction — dealkylation.

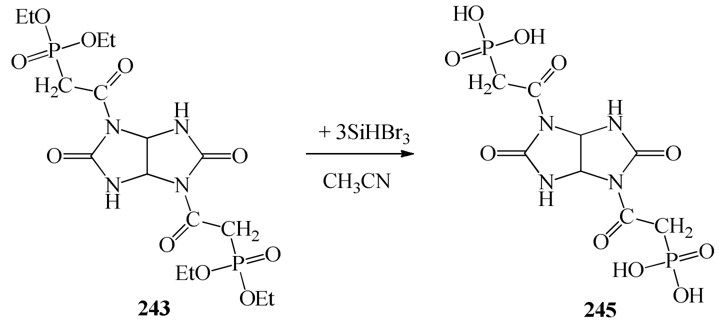
The authors [99] obtained 2,6-di(1-diethylphosphonoacetyl)2,4,6,8-tetraazobicyclo[3.3.0]octane-3,7-dione 243 by phosphorylation of 2,6-di(1-bromoacetyl)-2,4,6,8-tetraazobicyclo[3.3.0]octane-3,7-dione 241 with an equimolar amount of triethyl phosphite 242. Phosphonic acids have significant biological activity compared to their esters, which causes some interest in such structures.

The authors [100] used glycoluryl tetrakis(methylene phosphoric acid) 244 as an effective catalyst for the synthesis of pyrazole-5,10-dione derivatives. The main advantages of using this catalyst are high yields, quick reaction and the possibility of multiple use of the catalyst. Substance 244 is synthesized by single-stage N-transalkylation of glycoluril 235 with p-formaldehyde and phosphorous acid in boiling ethyl alcohol under reflux (Scheme 72).



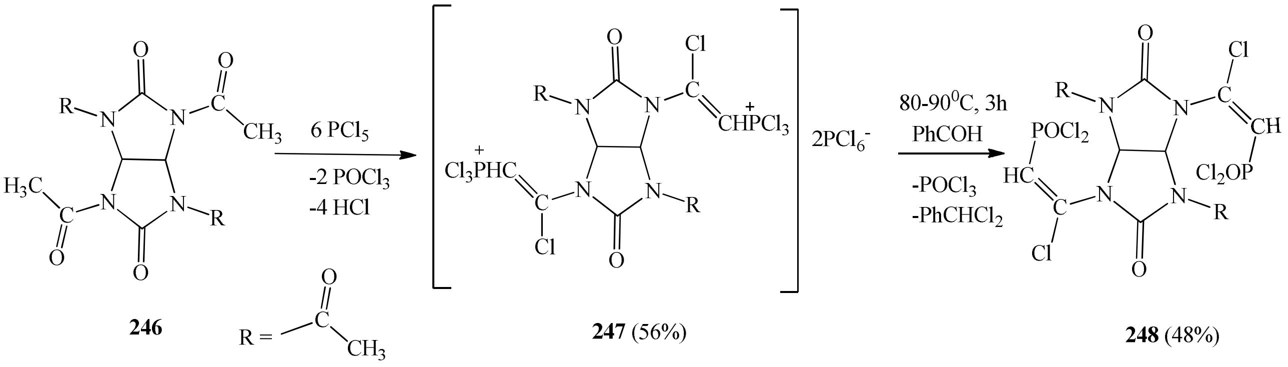
Scheme 72

Authors [99] carried out acid hydrolysis of diphosphonate 243 with tribromosilane in acetonitrile, leading to the corresponding diphosphonic acid 245 (Scheme 73).



Scheme 73

Diphosphone complex of teraacetylglycoluril – 2,6-di-(4,8-diacetyl-2,4,6,8-tetraazabicyclo[3.3.0]octane-3,7-dione)2,6-di-(6,8-dione)-2,6-di-(chloro-ethenyltri-chlorophosphonium) 247 was obtained in [101]. It 247 is a white crystalline, unstable in air compound obtained by the phosphorylation of 2,4,6,8-tetraacetyl-2,4,6,8-tetraazabicyclo[3,3,0]octane-3,7-dione 246 with phosphorus pentachloride (Scheme 74).

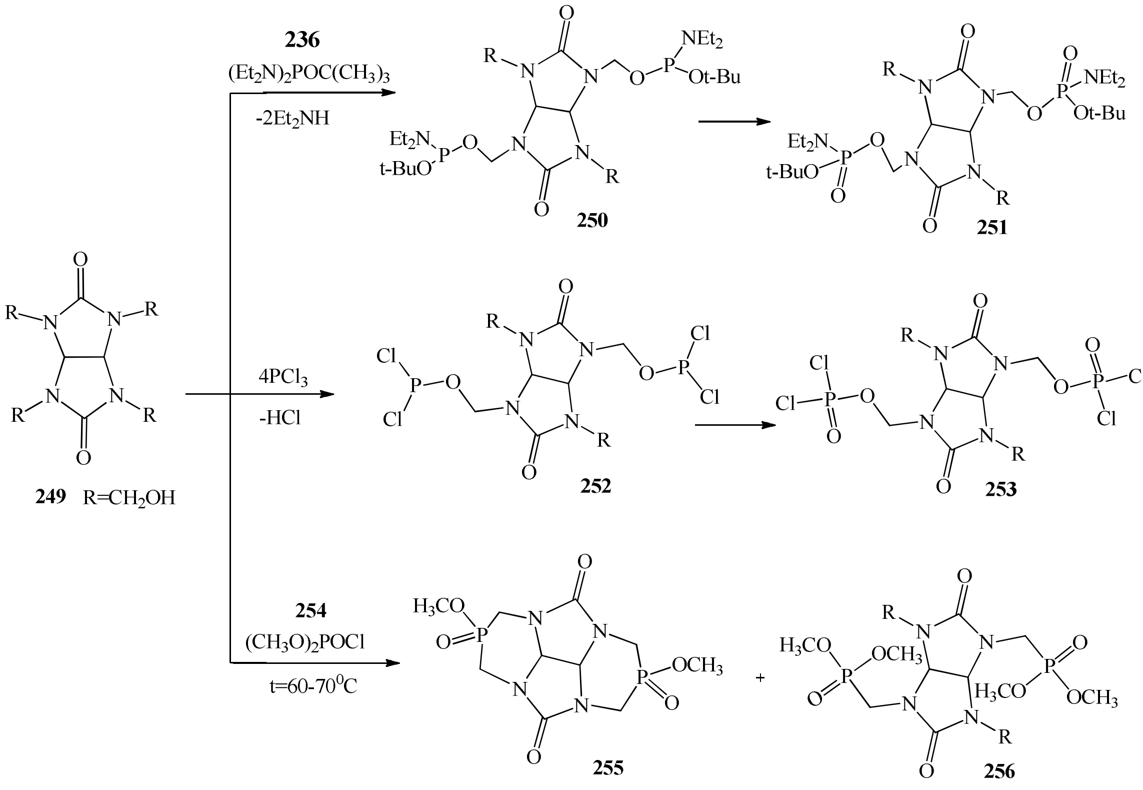


Scheme 74

The reaction takes place when heated under argon in trichloromethane in the ratio of 1 mol 2,4,6,8-tetraacetyl-2,4,6,8-tetraazabicyclo[3.3.0]octane-3,7-dione 246 to 6 mol phosphorus pentachloride.

The reaction proceeds through the stage of addition of phosphorus pentachloride at the oxygen atom of the acetyl group to form complex 247, which is further decomposed by benzaldehyde to produce 248 (Scheme 74).

The phosphorylation reaction of tetra-N-methylolglycoluryltetraethyldiamido-tert-butylphosphite 236 [95] was carried out in ethyl acetate with simultaneous distillation of diethylamine. As a result, the oily product 2,6-di- (N-diethylamidomethylolphosphato)-2,4,6,8-tetraazobicyclo[3.3.0.]octane-3,7-dione 25 was isolated through the formation of intermediate product 252 (Scheme 75).



Scheme 75

When studying the reactivity of tetra-N-methylol glycoluril 249 in phosphorylation reactions, its interaction with phosphorus trichloride was carried out [95] (Scheme 75). Phosphorylation was carried out under fairly mild conditions in hexane when heated. The isolated yellow crystalline substance of 2,6-di-(N-methyl chlorophosphato)-4,8-chloromethyl-2,4,6,8-tetraazobicyclo[3.3.0.]octane-3,7-dione 253 was the product of oxidation of phosphoric fragments in compound 252 to the pentavalent state (Scheme 75).

It is known [102] that among the compounds of trivalent phosphorus, phosphorous ester amides are fairly easily exchanging the amide group under the action of alcohols, amines and phenols. This method is very convenient for obtaining amidophosphites that are difficult to access in the direct synthesis.

Reaction 249 in absolute benzene with two equivalents of dimethoxychlorophosphate 254 and pyridine as an acceptor of hydrogen chloride leads to the formation of a mixture of products 255 and 256 (Scheme 75). The reaction proceeds with a strong heat release, requiring significant cooling. The structures of the synthesized compounds 255 and 256 were proved using the data of IR, NMR spectra [95].

Summarizing the available literature data on the methods of synthesis and properties of phosphorylated bicyclic bisureas, it should be noted that the latter are represented by diphosphadionic 202–209, 212–221, diphosphaspirooctandionic 169, 222, 224, 225, 227–229, 231, 233,234 and phosphorylated tetraazabicyclooctandione structures 237, 240, 243–245, 247, 248, 250–253, 255, 256. Structural differences of the above phosphorylated compounds lie in the fact that diphosphadiones 202–209, 212–221 have a nodular bridge link that can contain three and/or pentavalent phosphorus.

Diphospaspiroooctanediones 169, 222, 224, 225, 227–229, 231, 233, 234 contain a central (nodal) pentavalent phosphorus atom that conjugates two cycles. Phosphorylated tetraazabicyclooctandiones 237, 240, 243–245, 247, 248, 250–253, 255, 256 are principally distinguished by the fact that they do not contain an endocyclic phosphorus atom. A special case is represented by bicyclic bisureas of the glycoluril series, which have phosphorylated substituents only in side chains, which makes them attractive for further transformations.

This work systemizes knowledge of reactions of ureas and their derivatives with phosphorus containing reagents by compiling overview information. Since there is currently no information available in literature summarizing the methods of synthesis and studies of phosphorus derivatives of carbamide containing compounds, this work can serve as a tool for a better understanding of the tendency of the development of synthetic works in the field of obtaining of in the field of phosphaze compounds.

References

1 Машковский М.Д. Лекарственные средства: пос. для врачей / М.Д. Машковский. — М.: Новая волна, 2012. — 1216 с.

2 Захаренко В.А. Гербициды / В.А. Захаренко. — М.: Агропромиздат, 1990. — 240 с.

3 Вагапова Л.И. Новые солевые структуры на основе аминометилированных каликс[4]резорцинов и (1-гидроксиэтан-1,1-диил)бисфосфоновой кислоты / Л.И. Вагапова, З.А. Насирова, Е.А. Бурилова, В.В. Зобов, А.Р. Бурилов, Р.Р. Амиров, М.А. Пудовик // Журн. орг. хим. — 2017. — Т. 53, № 2. — С. 310–312.

4 Пудовик М.А. Фосфорилирование этилуретана, мочевины, ацетамида бис(хлорметил)хлорфосфинатом в присутствии поташа / М.А. Пудовик, Л.К. Кибардина, Г.М. Саакян, Н.А. Хайлова, А.А. Шаймарданова, Н.Е. Крепышева, А.Н. Пудовик // Журн. общ. хим. — 2002. — Т. 72, № 7. — С. 1157–1159.

5 Markalous F. Über Phosphorsäureureide / F. Markalous, Z. Jerman, J. Beránek, M. Černík, J. Toužín // Collection of Czechoslovak Chemical Communications. — 1972. — Vol. 37, No. 3. — P. 725–734.

6 Nakamura T. Efficacy and safety of once-yearly zoledronic acid in Japanese patients with primary osteoporosis: two-year results from a randomized placebo-controlled double-blind study (ZOledroNate treatment in Efficacy to osteoporosis; ZONE study) // T. Nakamura, M. Fukunaga, T. Nakano et al. // Osteoporos International. — 2016. — Vol. 28, No. 1. — P. 389–398.

7 Martini C.N. Glyphosate-based herbicides with different adjuvants are more potent inhibitors of 3T3-L1 fibroblast proliferation and differentiation to adipocytes than glyphosate alone / C.N. Martini, M. Gabrielli, M.M. Codesido, M.C. del Vila // Comparative Clinical Pathology. — 2016. — Vol. 25, No. 3. — P. 607–613.

8 Дмитриченко М.Ю. Фосфорсодержащие енмочевины I. Фосфорилирование N-ацил-N,N'-диметилмочевин пятихлористым фосфором / М.Ю. Дмитриченко, В.Г. Розинов, В.И. Донских, Г.В. Ратовский, Л.М. Сергиенко, Г.В. Долгушин, Р.В. Валеев // Журн. общ. хим. — 1988. — Т. 58, № 10. — С. 2252–2261.

9 Naz Guven Urea dimethacrylates functionalized with bisphosphonate/bisphosphonic acid for improved dental materials / Naz Guven, M. Akyol, E. Demir, F. Duman et al. // Journal of Polymer Science Part A: Polymer Chemistry. — 2017. — Vol. 55, No. 19. — P. 3195–3204.

10 Naydenova E.D. Synthesis and Characterization of Novel Cycloalkanespiro-5-Hydantoin Phosphonic Acids / E.D. Naydenova, P.T. Todorov, K.D. Troev // Phosphorus, Sulfur, and Silicon and the Related Elements. — 2010. — Vol. 185, No. 7. — P. 1315–1320.

11 Воронова О.А. Вольтамперометрический способ определения общего холестерина в биологических объектах / О.А. Воронова, К.В. Дёрина, Е.В. Дорожко, Е.И. Короткова. пат. РФ 2629836, 2016.

12 Derkatsch G.I. Phosphorus Isocyanates / G.I. Derkatsch // Angewandte Chemie International Edition in English. — 1969. — Vol. 8, No. 6. — P. 421–428.

13 Kuhn S.J. Organophosphorus compounds: X. Phosphorisocyanatidic difluoride and chloride fluoride. Preparation of alkyl carbamatophosphorodifluoridates and ureidophosphorodifluoridates / S.J. Kuhn, G.A. Olah // Canadian Journal of Chemistry. — 1962. — Vol. 40, No. 10. — P. 1951–1954.

14 Кирсанов А.В. Хлорангидриды и эфиры арилкарбамидофосфорных кислот / А.В. Кирсанов, А.С. Левченко // Журн. общ. хим. — 1956. — Т. 26, № 8. — С. 2285–2289.

15 Dorosti N. Synthesis, crystal structure, biological evaluation, electronic aspects of hydrogen bonds, and QSAR studies of some new N-(substituted phenylurea)diazaphosphore derivatives as anticancer agents / N. Dorosti, B. Delfan, K. Gholivand, A.A.E. Valmoozi // Medicinal Chemistry Research. — 2016. — Vol. 25, No. 4. — P. 769–789.

16 Gholivand K. Synthesis, spectroscopic characterization, crystal structures, theoretical studies, and antibacterial evaluation of two novel N-phosphinyl ureas / K. Gholivand, N. Dorosti // Monatshefte Für Chemie — Chemical Monthly. — 2011. — Vol. 142, No. 2. — P. 183–192.

17 Gholivand K. N-phosphinyl ureas: Synthesis, characterization, X-ray structure, and in vitro evaluation of antitumor activity / K. Gholivand, N. Dorosti, F. Ghaziany, M. Mirshahi, S. Sarikhani // Heteroatom Chemistry. — 2011. — Vol. 23, No. 1. — P. 74–83.

18 Vasu Govardhana Reddy P. Synthesis and Antimicrobial Activity of N-(substituted)-N′-(2,3-dihydro-2-oxido-5-benzoyl-1H-1,3,2-benzodiazaphosphol-2-yl)ureas / P. Vasu Govardhana Reddy, C. Suresh Reddy, R. Naga // Chemical & pharmaceutical bulletin. — 2003. — Vol. 51, No. 7. — P. 860–863.

19 Vasu Govardhana Reddy P. Synthesis and antimicrobial activity of N-substituted N′-[6-methyl-2-oxido-1,3,2-dioxaphosphinino(5,4,-b)pyridine-2-yl]ureas / P. Vasu Govardhana Reddy, C. Suresh Reddy // Venugopal heteroatom chemistry. — 2003. — Vol. 14, No. 6. — P. 509–512.

20 Haranath P. Synthesis and antimicrobial activity of N-(substituted)-N-[1,2,4,8,10,11-hexachloro-6-oxido-12H-dibenzo(d,g)(1,3,2)-dioxaphosphocin-6-yl]ureas / P. Haranath, U. Anasuyamma, P. Vasu Govardhana Reddy, C. Suresh Reddy // Journal of Heterocyclic Chemistry. — 2004. — Vol. 41, No. 6. — P. 1001–1004.

21 Rao L.N. Synthesis and antimicrobial activity of N-(substitutedphenyl)-N'-[1,2,3,4-tetrahydro-2-oxido-1,3,2-benzodiazaphosphorine-2-yl]ureas / L.N. Rao, C.D. Reddy, B.S. Reddy // Indian Journal of Chemistry — Section B. — 2001. — Vol. 40, No. 9. — P. 817–821.

22 Антохина Л.А. О некоторых превращениях дихлорангидрида уреидофосфорной кислоты / Л.А. Антохина, З.Я. Латыпов, К.В. Никоноров // Журн. общ. хим. — 1983. — Т. 53, № 6. — С. 1258–1260.

23 Никоноров К.В. Фосфорорганические производные хлоральмочевины / К.В. Никоноров, Э.А. Гурылев, Л.А. Антохина, З.Я. Латыпов // Журн. общ. хим. — 1978. — Т. 49, № 3. — С. 541–545.

24 Moll R. Organische Phosphor verbindungen. XVI. Zur Chemie des Isocyanatophosphorsäurediethylesters / R. Moll, R. Jentzsch, G.W. Fischer // Journal Für Praktische Chemie. — 1990. — Vol. 332, No. 4. — P. 439–443.

25 Арбузов Б.А. Диизопропоксифосфорилгетерилмочевины / Б.А. Арбузов, Н.Р. Федотова, Н.Н. Зобова // Журн. общ. хим. — 1990. — Т. 60, № 5. — С. 1002–1004.

26 Selucký P. Synergistic extraction of Eu(III) with N-phosphorylated bis-ureas and chlorinated cobalt bis(dicarbollide)ion / P. Selucký, M. Bubeníková, J. Rais, B. Grüner, V.V. Brusko // Radiochimica Acta. — 2013. — Vol. 101, No. 1. — P. 27–32.

27 Чмутова Г.А. Теоретическое исследование направлений внутримолекулярной циклизации фосфорилированных мочевин и тиомочевин / Г.А. Чмутова, В.В. Зверев, М.А. Пудовик, Н.А. Хайлова, А.Н. Пудовик // Журн. общ. хим. — 2003. — Т. 73, № 11. — С. 1793–1798.

28 Багаутдинова Р.Х. Реакция бис(хлорметил)изоцианатофосфината с аммонийгалогенидами / Р.Х. Багаутдинова, М.А. Пудовик // Журн. общ. хим. — 2007. — Т. 77, № 12. — С. 2067–2068.

29 Utvary K. Umsetzungen des Benzolphosphonsäure-diisocyanates / K. Utvary, E. Freundlinger, V. Gutmann // Monatshefte für Chemie. — 1966. — Vol. 97, No. 3. — P. 679–688.

30 Губницкая В.С. Производные этиленамидов диалкилфосфорных кислот / В.С. Губницкая, Н.С. Тищина, А.В. Кирсанов // Журн. общ. хим. — 1973. — Т. 43, № 4. — С. 741–743.

31 Meyer W. S-dialkyl urido thiophosphates / W. Meyer, B. Bohner, D.O. Dawes. US3957924A, 1974.

32 Aller H.E. Nematocidal phosphoramidates / H.E. Aller, E.E. Kilbourn, E.D. Weiler, W.D. Weir. US4259330A, 1976.

33 Schaffrath W. Reaktion von N-Alkylharnstoffen mit Phosphoroxidtrichlorid / W. Schaffrath, J. Tschirpig, S. Uhlmann, H.A. Lehmann // Zeitschrift Für Chemie. — 1978. — Vol. 18, No. 5. — P. 179–180.

34 Flemming R. Ein einfacher Weg der Gewinnung von Phosphorylisocyanaten aus Phosphorylureiden / R. Flemming, H.-A. Lehmann, W. Schütt // Zeitschrift Für Chemie. — 1977. — Vol. 17, No.11. — P. 413–414.

35 Wiesboeck R.A. The Reaction of Chlorourea with Tertiary Phosphite Esters and Triphenylphosphine / R.A. Wiesboeck // The Journal of Organic Chemistry. — 1965. — Vol. 30, No. 9. — P. 3161–3163.

36 Gholivand K. Some new compounds with P(E)NHC(O) (E = lone pair, O, S) linkage: synthesis, spectroscopic, crystal structures, theoretical studies, and antimicrobial evaluation / K. Gholivand, N. Dorosti // Monatshefte Für Chemie. — 2013. — Vol. 144, No. 9. — P. 1417–1425.

37 Weisz A. Symmetrische, phosphorsubstituierte Carbodiimid / A. Weisz, K. Utvary // Monatshefte für Chemie. — 1968. — Vol. 99, No. 6. — P. 2498–2503.

38 Weferling N. N,N-Dimethylharnstoff-verbrückte Diphosphorverbindungen; Struktur eines Spirophosphorans mit λ^5-Phosphor als Brückenglied / N. Weferling, R. Schmutzler, W.S. Sheldrick // Liebigs Annalen Der Chemie. — 1982. — Vol. 1. — P. 167–181.

39 Bhattacharyya P. Diphosphine derivatives of urea and thiourea / P. Bhattacharyya, A.M.Z. Slawin, M.B. Smith, D.J. Williams, J.D. Woollins // Journal of the Chemical Society, Dalton Transactions. — 1996. — Vol. 129, No. 18. — P. 3647–3651.

40 Petrov J. Synthesis of N-phosphorylureas by reaction of phosphorylamides with N-substituted trichloroacetamides / J. Petrov, I. Atanassova, V. Ognyanova // Organic Preparations and Procedures International. — 1994. — Vol. 26, No. 3. — P. 357–360.

41 Klaus Dipl Chem Dr Sommer, G.R. Verfahren zur herstellung von 1-ureido- und carbamoyloxy-alkan-1,1diphosphonsaeuren = Process for the preparation of 1-ureido- and carbamoyloxy-alkane-1,1-diphosphonicacids / G.R. Klaus Dipl Chem Dr Sommer. — 1974. — Pat. DE2446749A1.

42 Schnur R.C. Dehydrations with N-methyl-N,N’-di-tert-butylcarbodiimidium ion / R.C. Schnur, E.E. Van Tamelen // Journal of the American Chemical Society. — 1975. — Vol. 97, No. 2. — P. 464–465.

43 Kantlehner W. Orthoamide und Iminiumsalze, LXXXVIII. Synthese N,N,N′,N′,N″,N″-persubstituierter Guanidiniumsalze aus N,N′-persubstituierten Harnstoff / Säurechlorid-Addukten / R.C. Schnur, E.E. Van Tamelen // Zeitschrift Für Naturforschung B. — 2015. — Vol. 70, No. 1. — P. 9–27.

44 Ma X.-B. New derivatives of 4,5-benzo-1,3,2-oxaza(or diaza)-phospholane from convenient condensation of substituted urea with tris(dialkylamino)phosphine / X.-B. Ma, J.-L. Zhang // Phosphorus, Sulfur, and Silicon and the Related Elements. — 1990. — Vol. 53, No. 1–4. — P. 227–231.

45 Richter F. 1,4,2-diazaphospholidine derivatives / F. Richter. — Pat. US20110207927A1. — 2008.

46 Atanassova T.N.A.P.A. ChemInform Abstract: Synthesis of N-Substituted Derivatives of 2-Imidazolidinone. / T.N.A.P.A. Atanassova // ChemInform. — 1992. — Vol. 23, No. 20. — P. 1.

47 Mikroyannidis J.A. Synthesis of substituted N-[(phosphonyl)methyl]-2-imidazolidinones and N-[(phosphonyl)methyl]-2-pyrrolidinonem // Phosphorus and Sulfur and the Related Elements. — 1982. — Vol. 12, No. 2. — P. 249–258.

48 Jin X. Copper-Catalyzed Oxidative Cross-Coupling of H-Phosphonates and Amides to N-Acylphosphoramidates / X. Jin, K. Yamaguchi, N. Mizuno // Organic Letters. — 2013. — Vol. 15, No. 2. — P. 418–421.

49 Ларина Л.И. Фосфорилирование N-ацетил-N,N-этиленмочевины пентахлоридом фосфора / Л.И. Ларина, М.Ю. Дмитриченко, В.Г. Розинов, А.В. Бенедюк // Журн. общ. хим. — 2005. — Т. 75, № 3. — С. 520, 521.

50 Zabarjad-Shiraz, N., Yavari, I., Biglari, A., Izadiar, S.A., Bijanzadeh H.-R. Three-Component Reaction Between Trivalent Phosphorus, Dimethyl Acetylenedicarboxylate, and Amide Derivatives // Phosphorus, Sulfur, and Silicon and the Related Elements, 2009. — Vol. 184, No. 11. — P. 3023–3037.

51 Bucherer H.T. Über die Bildung substituierter Hydantoine aus Aldehyden und Ketonen. Synthese von Hydantoinen / H.T. Bucherer, V.A. Lieb // Journal für Praktische Chemie. — 1934. — Vol. 141, No. 1–2. — P. 5–43.

52 Алимов П.И. Фосфорилирование формамида / П.И. Алимов, Л.Н. Лебкова // Изв. АН СССР. Отд. хим. наук. — 1964. — Т. 13, № 10. — С. 1709–1713.

53 Никоноров К.В. Реакция фосфорилхлоридов с дифенилмочевиной / К.В. Никоноров, Е.А. Гурилев, Л.А. Антохина, З.Я. Латыпов // Изв. АН СССР. Отд. хим. наук. — 1981. — Т 30, № 12. — С. 2330–2333.

54 Ulrich H. Synthesis of isocyanates and carbodiimides / H. Ulrich, A.A.R. Sayigh // Angewandte Chemie International Edition in English. — 1966. — Vol. 5, No. 8. — P. 704–712.

55 Latscha H.P. Ein neues sechsgliedriges Ringsystem mit Phosphor, Stickstoff und Kohlenstoff als Ringglieder / H.P. Latscha Zeitschrift für anorganische und allgemeine Chemie. — 1966. — Vol. 346, No. 3–4. — P. 166–172.

56 Goehring M.B. Über Phosphorstickstoff-Verbindungen. XXXI. Über neue viergliedrige Ringsysteme mit Stickstoff, Phosphor und Kohlenstoff im Ring / M.B. Goehring, H. Schwind // Zeitschrift für anorganische und allgemeine Chemie. — 1970. — Vol. 327, No. 3. — P. 285–291.

57 Ulrich H. 2-Phospha-1.3-diazetidinone, eine neue Verbindungsklasse / H. Ulrich, A.A.R. Sayigh // Angewandte Chemie. — 1964. — Vol. 76, No. 14. — P. 647.

58 Дмитриченко М.Ю. Синтез 1-метил-2,2,2-трихлор-3-(1,1,2,2-тетрахлорэтил)-1,3-диаза-2-фосфетдинона / М.Ю. Дмитриченко, В.Г. Розинов, В.И. Донских // Журн. общ. хим. — 1989. — Т. 59, № 3. — С. 715, 716.

59 Деркач Г.И. Производные фосфадиазациклобутанона / Г.И. Деркач, А.В. Нарбут // Журн. общ. хим. — 1965. — Т. 35, № 5. — С. 932.

60 Harris R.K. Nuclear Magnetic Resonance Studies of Diazaphosphetidines and Phosphadiazetidinones / R.K. Harris, J.R. Woplin, R.E. Dunmur, M. Murray, R. Schmutzler // Berichte der Bunsengesellschaft für physikalische Chemie. — 1972. — Vol. 76, No. 1. — P. 44–52.

61 Schlak O. Preparative and N.M.R. studies of phosphorus-fluorine compounds undergoing intramolecular exchange. Part 2. Unsymmetrical fluorinated phosphadiazetidinones / O. Schlak, R. Schmutzler, R.K. Harris, E.M. McVicker, M. I.M. Wazeer // Phosphorus and Sulfur and the Related Elements. — 1981. — Vol. 10, No. 1. — P. 87–97.

62 Devillers J., Willson M., Burgada R. // Bull. Soc. Chim. Fr. — 1968. — P. 4670.

63 Fluck E. Über Diazadiphosphetidine, VI. Synthese von Diazaphosphetidinen, Diazadiphosphetidinen und Thiadiazaphosphetidinen / E. Fluck, H. Richte // Chemische Berichte. — 1983. — Vol. 116, No. 2. — P. 610–617.

64 Bermann M. Diazaphosphetidinones with four-co-ordinated phosphorus // M. Bermann, J.R. Van Wazer // Journal of the Chemical Society. Dalton Transactions. — 1973. — No. 8. — P. 813–815.

65 Burgada R. Bull. Soc. Chim. Fr. — 1971. — P. 136.

66 Bettermann G. Dissertation, Technische Universität Braunschweig, 1986.

67 Breker J. Verbindungen mit dem 1,3-Dimethy1-1,3-diaza-2-phosphetidin-4-on-Grundgerüst; Synthese von l,3-Dimethyl-2-thia-l,3-diaza-2 λ^4-phosphetidin-4-on-Derivaten / J. Breker, U. Wermuth, R. Schmutzle // Zeitschrift für Naturforschung B. — 1990. — Vol. 45. — 1398–1406.

68 Hormuth P.B. Über Reaktionen von Phosphorverbindungen mit Isocyanaten. V. Über die Umsetzung der viergliedrigen Ringe $C_3H_6Cl_3N_2OP$, $(C_6H_5Cl_2PNCH_3)_2$ und $((C_6H_5)_2ClPNCH_3)_2$ mit Phenyl-bzw / P.B. Hormuth, H.P. Latscha // Methylisocyanat. Zeitschrift für anorganische und allgemeine Chemie. — 1969. — Vol. 365, No. 1–2. — P. 26–30.

69 Hormuth P.B. Über Reaktionen von Phosphorverbindungen mit Isocynaten. VI. Die Umsetzung von Cyclo-1-trichlorphospha-2,4-azamethyl-3-on mit Methylisothiocyanat / P.B. Hormuth H.P. Latscha Zeitschrift für anorganische und allgemeine Chemie. — 1969. — Vol. 369, No. 1–2. — P. 59–63.

70 Козюков В.П. Кремнийсодержащие мочевины / В.П. Козюков, В.Д. Шелудяков, В.Ф. Миронов // Успехи химии. — 1975. — Т. 44, № 5. — С. 897–934.

71 Pinchuk V.A. Reactions of sulfenamides with compounds of trivalent phosphorus / V.A. Pinchuk, C. Müller, A. Fischer, H. Thönnessen, P.G. Jones, R. Schmutzler, L.N. Markovsky, Y.G. Shermolovich, A.M. Pinchuk // Zeitschrift für anorganische und allgemeine Chemie. — 1995. — Vol. 621, No. 12. — P. 2001–2011.

72 Шабан М.Р. Фосфорпроизводные барбитуровой кислоты / М.Р. Шабан, В.М. Исмаилов, Н.Н. Усубов, А.Н. Гумилев, Ш.С. Насибов // Материалы III Респ. конф. молодых ученых-химиков. — Баку, 1988. — С. 169.

73 Abd-ellah I.M. Studies in cyclodiphosphazanes. Some reactions of hexachlorocyclo-diphosphazanes with urea and thiourea derivatives / I.M. Abd-ellah, E.H.M. Ibrahim, A.N. El-khazandar // Phosphorus and Sulfur and the Related Elements. — 1987. — Vol. 29. — P. 2–4.

74 Melnicky C. Darstellung und charakterisierung von 2-amino- und 2-methoxysubstituierten benzodiazaphosphorinonen mit phosphor in den koordinationszahlen drei, vier und fünf / C. Melnicky, I. Neda, R. Schmutzler // Phosphorus, Sulfur, and Silicon and the Related Elements. — 1995. — Vol. 106, No. 1–4. — P. 65–73.

75 Дмитриченко М.Ю. Фосфорсодержащие азабутадиены и гетероциклы из N-метил-N'-ацетилмочевины / М.Ю. Дмитриченко, В.Г. Розинов, В.И. Донских, Г.В. Ратовский, В.Г. Ефремов, Г.В. Долгушин // Журн. общ. хим. — 1992. — Т. 62, № 2. — С. 306–317.

76 Розинов В.Г. Способ получения 2,2,4,6-тетрахлор-2,2-дигидро-1,5,2 диазафосфорина / В.Г. Розинов, М.Ю. Дмитриченко, В.И. Донских, Г.В. Долгушин, А.В. Калабина // Пат. СССР 1583423. — 1988.

77 Розинов В.Г. 1,3,4-Диазафосфорин из N-ацетилмочевины / В.Г. Розинов, М.Ю. Дмитриченко, В.И. Донских, Г.В. Долгушин, В.П. Фомин // Журн. общ. хим. — 1987. — Т. 57, № 1. — С. 228–229.

78 Дмитриченко М.Ю. 1,5,2-Диазафосфорины II. Синтез и особенности циклизации фосфорсодержащих азабутадиенов на основе ацетил- и хлорацетилмочевин / М.Ю. Дмитриченко, В.Г. Розинов, В.И. Донских, Г.В. Ратовский, В.Г. Ефремов, Г.В. Долгушин, В.Ю. Витовский, С.В. Шилин // Журн. общ. хим. — 1991. — Т. 61, № 3. — С. 643–656.

79 Neda I. Zur Chemie der 4,6-Dioxo-l,3,5,2-triazaphosphinane, Teil III. Darstellung von 4,6-Dioxo-1,3,5,2 λ^3-, 4,6-Dioxo-1,3,5,2 λ^4- und 4,6-Dioxo-1,3,5,2 λ^5-triazaphosphinanen / I. Neda, M. Farkens, A. Fischer, P.G. Jones, R.R. Schmutzle // Zeitschrift für Naturforschung B. — 1993. — Vol. 48b. — S. 443–451.

80 Neda, I. Zur Chemie der l,3,5-Triaza-2-phosphorinan-4,6-dione. Teil VII. Über die Synthese von 2-Methoxy- und 2-Trimethylsiloxy-l,3,5-trimethyl-1,3,5-triaza-2λ^3-phosphorinan-4,6-dion sowie 2-Chlor-l,3,5-trimethyl-1,3,5-triaza-2-oxo-2λ^4-phosphorinan-4,6-dion / I. Neda, M. Farkens, R. Schmutzler // Zeitschrift für Naturforschung B. — 1994. — Vol. 49b. — S. 165–170.

81 Farkens M. Zur Chemie der l,3,5-Triaza-2-phosphorinan-4,6-dione. Teil VIII. Weitere l,3,5-Triaza-2 λ^3- und 1,3,5-Triaza-2 λ^4-phosphorinan-4,6-dione mit (2-Chlorethyl)amino- und Bis(2-chlorethyl)amino-Substituenten / M. Farkens, I. Neda, R. Schmutzler // Zeitschrift für Naturforschung B. — 1994. — Vol. 49b. — S. 445–450.

82 Kaukorat T. Verbindungen mit dem 1,3,5,2-Triazaphosphorinan-Grundgerüst: Synthese und Koordinationschemie neuartiger, N,N,N′-Trimethylethylendiamin-substituierter Verbindungen mit drei-und vierfach koordiniertem Phosphor / T. Kaukorat, I. Neda, A. Fischer, P.G. Jones, R. Schmutzler // Chemische Berichte. — 1993. — Vol. 126, No. 6. — S. 1265–1270.

83 Roesky H.W. Darstellung Reaktionen und Strukturen spirobicyclischer Phosphorane / H.W. Roesky, K. Ambrosius, M. Banek, W.S. Sheldrick // Chemische Berichte. — 1980. — Vol. 113, No. 5. — S. 1847–1854.

84 Roesky H.W. Structural chemistry of 1-oxo-2,8-dimethyl-4,6-bis[3-(trifluoromethyl)phenyl]-2,4,6,8-tetraaza-1.lambda.5–5.lambda.3-diphosphabicyclo[3.3.0]octane-3,7-dione and the synthesis, structure, and reactions of 2,4,6,8-tetramethyl-2,4,6,8-tetraaza-1.lambda.3–5.lambda.3-diphosphabicyclo[3.3.0]octane-3,7-dione. Bicyclic Compounds with Phosphorus-Phosphorus Bond / H.W. Roesky, H. Zamankhan, W.S. Sheldrick, A.H. Cowley, S.K. Mehrotra // Inorganic Chemistry. — 1981. — Vol. 20, No. 9. — P. 2910–2915.

85 Neidlein R. Synthesen und spektroskopische Eigenschaften methano-überbrückter Phosphaheterocyclen. Syntheses and Spectroscopic Properties of Methano-Bridged Phosphaheterocycles / R. Neidlein, H.J. Degener // Archiv Der Pharmazie. — 1984. — Vol. 317, No. 12. — P. 1053–1055.

86 Shevchenko I. Urea-bridged bicyclic bisphosphines containing the grouping $P\text{-}CCl_2\text{-}P$ / I. Shevchenko, A.K. Fischer, P.G. Jones, R. Schmutzler // Zeitschrift Fur Anorganische Und Allgemeine Chemie. — 2002. — Vol. 628, No. 8. — P. 1903–1907.

87 Sheldrick W.S. Uber Reaktionen an Heterocyclen, die eine P–P-Bindung enthalten / W.S. Sheldrick, S. Pohl, H. Zamankhan, M. Banek, D. Amirzadeh-Asl, H.W. Roesky // Chemische Berichte. — 1981. — Vol. 114, No. 6. — P. 2132–2137.

88 Roesky H.W. Darstellung und Reaktionen von bicyclischen Verbindungen mit einer Phosphor-Phosphor-Bindung / H.W. Roesky, D. Amirzadeh-Asl // Zeitschrift für Naturforschung. — 1983. — Vol. 38b. — P. 460–464.

89 Roesky H.W. Darstellung und Struktur eines neuartigen spirobicyclischen Phosphorans mit einer $\lambda^3P\text{-}\lambda^5P$-Bindung / H.W. Roesky, K. Ambrosius, W.S. Sheldrick // Chemische Berichte. — 1979. — Vol. 112, No. 4. — P. 1365–1371.

90 Breker J. Chemie des 4-chlor-1,3,5,7-tetramethyl-1,3,5, 7-tetraaza-4HHDFFHV-phosphaspiro[3.3]heptan-2,6-dions; Kristall- und molekul struktur von halogen(F, Br)- und pseudohalogen(CN)- phosphoranen / J. Breker, P.G. Jones., R. Schmutzler, D. Schomburg // Phosphorus, Sulfur, and Silicon and the Related Elements. — 1991. — Vol. 62, No. 1–4. — P. 139–153.

91 Schomburg D. Chemie des 4-Chlor-1,3,5,7-tetramethyl-1,3,5,7-tetraaza-$4\lambda^5$-phosphaspiro[3.3]heptan-2,6-dions; Kristall- und Molekül struktur eines Chlortetraaza- und zweier Pentaazaphosphorane / D. Schomburg, U. Wermuth, R. Schmutzler // Chemische Berichte. — 1987. — Vol. 120, No. 10. — P. 1713–1718.

92 Neda I. Verbindungen mit dem 1,3,2-benzodiazaphosphorinan-4-on grundgerust: synthese von neuartigen, N,N-dimethylamino- und bis-2-chlorethylamino-substituierten derivaten mit drei-, vier- und funffach koordiniertem phosphor / I. Neda, A. Fischer, P.G. Jones, R. Schmutzler // Phosphorus, Sulfur, and Silicon and the Related Elements. — 1993. — Vol. 78, No. 1–4. — P. 271–278.

93 Neda I. Umsetzungen von 4-chlor-1,3,5,7-tetramethyl-1,3,5,7-tetraaza-$4\lambda^5$-phosphaspiro[3,3]heptan-2,6-dion, bis(trimethylsilyl)-trimethylbiuret und bis(2-chlorethyl)-aminophosphorsauredichlorid mit $Me_2NCH_2CH_2N(Me)SiMe_3$; studium intramolekularer p-n-wechselwirku / I. Neda, T. Kaukorat, R. Schmutzler // Phosphorus, Sulfur, and Silicon and the Related Elements. — 1993. — Vol. 80, No. 1–4. — P. 173–179.

94 Anand B.N. Synthesis and characterization of four-membered, spirobicyclic, transition-metal-substituted phosphoranes / B.N. Anand, R. Bains, K. Usha // J. Chem. Soc. Dalton, Trans. — 1990. — Vol. 7. — P. 2315–2317.

95 Салькеева Л.К. Синтез и исследование полифункциональных производных гликолурила / Л.К. Салькеева, Е.К. Тайшибекова, Е.В. Минаева, Л.М. Сугралина, Б.К. Макин, Т.С. Абайдильдин, А.В. Омашева, Ф.Е. Кумаков // Вестн. Караганд. ун-та. Сер. Химия. — 2016. — Т. 84, № 4. — С. 14–20.

96 Wang Y. Fire retardant 4-(O,O-dimethyl phosphoryl)glycoluril compound and preparation method thereof / Y. Wang, Y. Sheng. — Pat. CN103387590A. — 2013.

97 Wang Y. Fire retardant tetra(O,O-dibutyl-phosphoryl)glycoluril compound and preparation method thereof / Y. Wang, Y. Sheng. — Pat. CN103396450A. — 2013.

98 Wang Y. Flame retardant tetra(O,O-diisopropylphosphoryl)glycoluril compound and preparation method thereof / Y. Wang, Y. Sheng. — Pat. CN103387590A. — 2013.

99 Салькеева Л.К. Новые фосфорилированные производные гликолурила / Л.К. Салькеева, Е.К. Тайшибекова, А.А. Бакибаев, Е.В. Минаева, Б.К. Макин, Л.М. Сугралина, А.К. Салькеева // Журн. общ. хим. — 2017. — Т. 87, № 3. — С. 435–440.

100 Moradi S. Synthesis of a Biological-Based Glycoluril with Phosphorous Acid Tags as a New Nanostructured Catalyst: Application for the Synthesis of Novel Natural Henna-Based Compounds / S. Moradi, M. Zolfigol, M. Zarei, D. Alonso, A. Khoshnood // Chemistry Select. — 2018. — Vol. 3, No. 11. — P. 3042–3047.

101 Тайшибекова Е.К. Фосфорорганические производные на основе аминотиазолов и гликолурила: дис. … д-ра филос. PhD: 6D060600 — Химия / Е.К. Тайшибекова. — Караганда, 2015. — 167 с.

102 Корбридж Д. Фосфор: Основы химии, биохимии, технологии / Пер. с англ. — М.: Мир, 1982. — 680 с.

А.А. Бакибаев, К.Б. Жуманов, С.Ю. Паньшина, С.И. Горбин, С.В. Мальков,
И.Г. Цой, Б.К. Масалимова, Г.К. Матниязова, Э.А. Байбазарова

Фосфорланған карбамидқұрамды ациклді және гетероциклді қосылыстарды синтездеу әдістері

Мақалада алғаш рет мочевина және оның гетероциклді туындыларының фосфорқұрамды реагенттермен реакциясын зерттеудің қазіргі күйін жүйелеуге талпыныс жасалды. Қолданылатын субстраттар мен реагенттердің айтарлықтай айырмашылығына байланысты, шолуда фосфирленген азотқұрамды қосылыстарды алу әдістері оның құрылымына сәйкес түзілуіне қарай үш бағыт бойынша жіктелді: ациклді, моноциклді және бициклді мочевиналардың синтезі. Мысалы, жұмыста N-фосфоизоцианаттардың құрылымы әртүрлі алифатты және ароматты аминдермен реакциясы нәтижесінде N-фосфорленген мочевинаны синтездеп алудың әдістері қарастырылған, осы қосылыстарды алудың балама сирек қолданылатын әдістері келтірілген. Фосфирленген моноциклді карбамидқұрамды қосылыстарың синтездеп алудың белгілі әдістерін талдау нәтижесінде бесмүшелі фосфазациклдер имидазолидинді құрылымы түрінде келтірілген, ал тетрациклді фосфазациклдер диазафосфетидинондар құрылымды, алтымүшелі фосфазациклдер — диазофосфориндер және триазафосфоринандионондар түрінде болатындығы көрсетілген. Синтезделген және зерттелінген фосфорланған бициклді бисмочевиналар дифосфадионды, дифосфаспирооктандионды және фосфорланған тетраазабициклооктандионды құрылымдарда көрсетілген. Фосфорланған мочевина химия мен технологияның көптеген салаларында қолдануда қызығушылық туғызады. Фосфорланған мочевиналарды синтездеп алудың әдістері бойынша зерттеу жұмыстарының нәтижелерін жүйелеу нәтижесінде зерттеуді әрі қарай дамыту жаңа тиімділігі жоғары дәрілік заттарды алудың әдістерін іздестіруге мүмкіндік береді.

Кілт сөздер: мочевина, фосфорлану, гетероциклді қосылыстар, N-фосфоизоцианаттар, имидазолидиндер, диазафосфетидинондер, диазофосфориндер, триазафосфоринандионондар, дифосфадиондар, дифосфаспирооктандиондар, фосфорланған тетраазабициклооктандиондар, гликолурил.

А.А. Бакибаев, К.Б. Жуманов, С.Ю. Паньшина, С.И. Горбин, С.В. Мальков,
И.Г. Цой, Б.К. Масалимова, Г.К. Матниязова, Э.А. Байбазарова

Методы синтеза фосфорилированных карбамидсодержащих ациклических и гетероциклических соединений

В статье впервые предпринята попытка систематизации современного состояния знаний в области исследования реакций мочевин и их гетероциклических производных с фосфорсодержащими реагентами. Ввиду существенных различий используемых субстратов и реагентов, в обзоре методы получения фосфорилированных азотсодержащих соединений согласно их конечной структуре сгруппированы по трем направлениям их образования — синтез ациклических, моноциклических и бициклических мочевин. Так, в работе рассмотрены методы получения ациклических N-фосфорилированных мочевин реакциями соответствующих N-фосфоизоцианатов с алифатическими и ароматическими аминами различного строения, а также приведены редко применяемые альтернатативные методы синтеза такого рода соединений. Анализ известных методов синтеза фосфорилированных моноциклических карбамидсодержащих соединений свидетельствует о том, что пятичленные фосфазациклы в большинстве представлены имидазолидиновыми структурами, тогда как тетрациклические фосфазациклы — диазафосфетидинонами, а шестичленные фосфазациклы — диазофосфоринами и триазафосфоринандиононами. Синтезированные и изученные фосфорилированные бициклические бисмочевины представлены дифосфадионовыми, дифосфаспирооктандионовыми и фосфорилированными тетраазабициклооктандионовыми структурами. Самостоятельный интерес фосфорилированные мочевины представляют для развития перспектив их практического применения в различных областях химии и технологий. Сделан вывод о том, что на основании проведенной систематизации результатов экспериментальных исследований по методам синтеза фосфорилированных мочевин можно ожидать, что их развитие позволит найти пути получения новых высокоэффективных лекарственных средств и синтонов их получения.

Ключевые слова: мочевина, фосфорилирование, гетероциклические соединения, N-фосфоизоцианаты, имидазолидины, диазафосфетидиноны, диазофосфорины, триазафосфоринандиононы, дифосфадионы, дифосфаспирооктандионы, фосфорилированные тетраазабициклооктандионы, гликолурил.

References

1 Mashkovskiy, M.D. (2012). *Lekarstvennye sredstva [Medicinal Products]*. Moscow: Novaia volna [in Russian].

2 Zakharenko, V.A. (1990). *Herbitsidy [Herbicides]*. Moscow: Ahropromizdat [in Russian].

3 Vagarova, L.I., Nasirova, Z.K., Burilova, E.A., Zobov, V.V., Burilov, A.R., & Amirov, R.R. et al. (2017). New salt structures based on aminomethylatedcalix[4]-resorcinarenes and (1-hydroxyethane-1-1-diyl)bisphosphonic acid. *Russian Journal of Organic Chemistry*, *53*(2), 312–314.

4 Pudovik, M.A., Kibardina, L.K., Saakyan, G.M., Khaylova, N.A., Shaymardanova, A.A., & Krepysheva, N.Ye. et al. (2002). Fosforilirovanie etiluretana, mocheviny, atsetamida bis(khlormetil)khlorfosfinatom v prisutstvii potasha [Phosphorylation of ethyluretane, urea, acetamide bis(chloromethyl)chlorophosphinate in the presence of potash]. *Zhurnal obshchei khimii — Journal of General Chemistry, 72*, *7*, 1157–1159 [in Russian].

5 Markalous, F., Jerman, Z., Beránek, J., Černík, M., & Toužín, J. (1972). Über Phosphorsäureureide. *Collection of Czechoslovak Chemical Communications*, *37*(3), 725–734.

6 Nakamura, T., Fukunaga, M., & Nakano, T. et al. (2016). Efficacy and safety of once-yearly zoledronic acid in Japanese patients with primary osteoporosis: two-year results from a randomized placebo-controlled double-blind study (ZOledroNate treatment in Efficacy to osteoporosis; ZONE study). *Osteoporos International, 28*(1), 389–398.

7 Martini, C.N., Gabrielli, M., Codesido, M.M., & del Vila, M.C. (2016). Glyphosate-based herbicides with different adjuvants are more potent inhibitors of 3T3-L1 fibroblast proliferation and differentiation to adipocytes than glyphosate alone. *Comparative Clinical Pathology, 25*(3), 607–613.

8 Dmitrichenko, M.Yu., Rozinov, V.G., Donskikh, V.I., Ratovskiy, G.V., Sergiyenko, L.M., Dolgushin, G.V., & Valeyev, R.V. (1988). Fosforsoderzhashchie yenmocheviny I. Fosforilirovaniie N-atsil-N,N'-dimetilmochevin piatikhloristym fosforom [Phosphorus-containing Urea I. Phosphorylation of N-acyl N,N'-dimethylurea phosphorus pentachloride]. *Zhurnal obshchei khimii — Russian Journal of General Chemistry, 58, 10*, 2252–2261 [in Russian].

9 Naz Guven, M., Akyol, E., & Demir Duman, F. et al. (2017). Urea dimethacrylates functionalized with bisphosphonate/bisphosphonic acid for improved dental materials. *Journal of Polymer Science Part A: Polymer Chemistry, 55*(19), 3195–3204.

10 Naydenova, E.D., Todorov, P.T., & Troev, K.D. (2010). Synthesis and Characterization of Novel Cycloalkanespiro-5-Hydantoin Phosphonic Acids. *Phosphorus, Sulfur, and Silicon and the Related Elements, 185*(7), 1315–1320.

11 Voronova, O.A., Dorina, K.V., Dorozhko, Ye.V. & Korotkova, Ye.I. (2016). Voltamperometricheskii sposob opredeleniia obshcheho kholesterina v biolohicheskikh obiektakh [Voltamperometric method for determining total cholesterol in bioloical objects]. *Pat. RF 2629836* [in Russian].

12 Derkatsch, G.I. (1969). Phosphorus Isocyanates. *Angewandte Chemie International Edition in English, 8*(6), 421–428.

13 Kuhn, S.J., & Olah, G.A. (1962). Organophosphorus compounds: X. Phosphorisocyanatidic difluoride and chloride fluoride. Preparation of alkyl carbamatophosphorodifluoridates and ureidophosphorodifluoridates. *Canadian Journal of Chemistry, 40*(10), 1951–1954.

14 Kirsanov, A.V., & Levchenko, A.S. (1956). Khloranhidridy i efiry arilkarbamidofosfornykh kislot [Chlorides and esters of aryl carbamidophosphoric acids]. *Zhurnal obshchei khimii — Russian Journal of General Chemistry, 26*, 8, 2285–2289 [in Russian].

15 Dorosti, N., Delfan, B., Gholivand, K., & Valmoozi, A.A.E. (2016). Synthesis, crystal structure, biological evaluation, electronic aspects of hydrogen bonds, and QSAR studies of some new N-(substituted phenylurea)diazaphosphore derivatives as anticancer agents. *Medicinal Chemistry Research, 25*(4), 769–789.

16 Gholivand, K., & Dorosti, N. (2011). Synthesis, spectroscopic characterization, crystal structures, theoretical studies, and antibacterial evaluation of two novel N-phosphinyl ureas. *Monatshefte Für Chemie — Chemical Monthly, 142*(2), 183–192.

17 Gholivand, K., Dorosti, N., Ghaziany, F., Mirshahi, M., & Sarikhani, S. (2011). N-phosphinyl ureas: Synthesis, characterization, X-ray structure, and in vitro evaluation of antitumor activity. *Heteroatom Chemistry, 23*(1), 74–83.

18 Vasu Govardhana Reddy, P., Suresh Reddy, C., & Naga, R. (2003). Synthesis and Antimicrobial Activity of N-(Substituted)-N′-(2,3-dihydro-2-oxido-5-benzoyl-1H-1,3,2-benzodiazaphosphol-2-yl)ureas. *Chemical & pharmaceutical bulletin, 51*(7), 860–863.

19 Vasu Govardhana Reddy, P., & Suresh Reddy, C. (2003). Synthesis and antimicrobial activity of N-Substituted N′-[6-methyl-2-oxido-1,3,2-dioxaphosphinino(5,4,-b)pyridine-2-yl]ureas. *Venugopal heteroatom chemistry, 14*(6), 509–512.

20 Haranath, P., Anasuyamma, U., Vasu Govardhana Reddy, P., & Suresh Reddy, C. (2004). Synthesis and antimicrobial activity of N-(substituted)-N-[1,2,4,8,10,11-hexachloro-6-oxido-12H-dibenzo(d, g)(1,3,2)-dioxaphosphocin-6-yl]ureas. *Journal of Heterocyclic Chemistry, 41*(6), 1001–1004.

21 Rao, L.N., Reddy, C.D., & Reddy, B.S. (2001). Synthesis and antimicrobial activity of N-(substitutedphenyl)-N'-[1,2,3,4-tetrahydro-2-oxido-1,3,2-benzodiazaphosphorine-2-yl]ureas. *Indian Journal of Chemistry — Section B, 40*(9), 817–821.

22 Antokhina, L.A., Latypov, Z. Ya., & Nikonorov, K.V. (1983). O nekotorykh prevrashcheniiakh dikhloranhidrida ureidofosfornoi kisloty [On Some Interventions of Ureidophosphoric Acid Dichloride Anhydride]. *Zhurnal obshchei khimii — Russian Journal of General Chemistry, 53*, *6*, 1258–1260 [in Russian].

23 Nikonorov, K.V., Gurylev, E.A., Antokhina, L.A., & Latypov, Z. Ya. (1978). Fosfororhanicheskie proizvodnye khloralmocheviny [Organophosphate derivatives of chloralm urea]. *Zhurnal obshchei khimii — Russian Journal of General Chemistry, 49*, *3*, 541–545 [in Russian].

24 Moll, R., Jentzsch, R., & Fischer, G.W. (1990). Organische Phosphor verbindungen. XVI. Zur Chemie des Isocyanatophosphorsäurediethylesters [For the chemistry of Isocyanatophosphorsurediethylesters]. *Journal Für Praktische Chemie — Journal of Practical Chemistry, 332*, 4, 439–443 [in German].

25 Arbuzov, B.A., Fedotova, N.R., & Zobova, N.N. (1990). Diizopropoksifosforilheterilmocheviny [Diisopropoxyphosphorylheterylurea]. *Zhurnal obshchei khimii — Russian Journal of General Chemistry, 60, 5*, 1002–1004 [in Russian].

26 Selucký, P., Bubeníková, M., Rais, J., Grüner, B., & Brusko, V.V. (2013). Synergistic extraction of Eu(III) with N-phosphorylated bis-ureas and chlorinated cobalt bis(dicarbollide)ion. *Radiochimica Acta, 101(1)*, 27–32.

27 Chmutova, G.A., Zverev, V.V., Pudovik, M.A., Khailova, N.A., & Pudovik, A.N. (2003). Pathways of Intramolecular Cyclization of Phosphorylated Ureas and Thioureas: A Theoretical Study. *Russian Journal of General Chemistry, 73*(11), 1696–1701.

28 Bagautdinova, R.K., & Pudovik, M.A. (2007). Reaction of bis(chloromethyl)phosphinic isocyanate with ammonium halides. *Russian Journal of General Chemistry, 77*(12), 2212–2213.

29 Utvary, K., Freundlinger, E., & Gutmann, V. (1966). Umsetzungen des Benzolphosphonsäure-diisocyanates [Reactions of the benzene phosphonic acid diisocyanate]. *Monatshefte für Chemie, 97*(3), 679–688.

30 Gubnitskaya, V.S., Tishchina, N.S., & Kirsanov, A.V. (1973). Proizvodnye etilenamidov dialkilfosfornykh kislot [Derivatives of ethyleneamides of dialkylphosphoric acids]. *Zhurnal obshchei khimii — Russian Journal of General Chemistry, 43*, *4*, 741–743 [in Russian].

31 Meyer, W., Bohner, B., & Dawes D.O. (1974). S-dialkyl urido thiophosphates, *Pat. US3957924A*.

32 Aller, H.E., Kilbourn, E.E., Weiler, E.D., & Weir, W.D. (1976). Nematocidal phosphoramidates, *Pat. US4259330A*.

33 Schaffrath, W., Tschirpig, J., Uhlmann, S., & Lehmann, H.A. (1978). Reaktion von N-Alkylharnstoffen mit Phosphoroxidtrichlorid [Reaction of N-alkyl ureas with phosphorus oxytrichloride]. *Zeitschrift Für Chemie — Journal of Chemistry. 18*(5), 179–180.

34 Flemming, R., Lehmann, H.-A., & Schütt, W. (1977). Ein einfacher Weg der Gewinnung von Phosphorylisocyanaten aus Phosphorylureiden [A Simple Way to Obtain Phosphoryl Isocyanates from Phosphorylureas]. *Zeitschrift Für Chemie — Journal of Chemistry, 17*(11), 413–414.

35 Wiesboeck, R.A. (1965). The Reaction of Chlorourea with Tertiary Phosphite Esters and Triphenylphosphine. *The Journal of Organic Chemistry. 30*(9), 3161–3163.

36 Gholivand, K., & Dorosti, N. (2013). Some new compounds with P(E)NHC(O) (E = lone pair, O, S) linkage: synthesis, spectroscopic, crystal structures, theoretical studies, and antimicrobial evaluation. *Monatshefte Für Chemie — Chemical Monthly, 144*(9), 1417–1425.

37 Weisz, A., & Utvary, K. (1968). Symmetrische, phosphorsubstituierte Carbodiimid. *Monatshefte für Chemie, 99*(6), 2498–2503.

38 Weferling, N., Schmutzler, R., & Sheldrick, W.S. (1982). N,N-Dimethylharnstoff-verbrückte Diphosphorverbindungen; Struktur eines Spirophosphorans mit λ^5-Phosphor als Brückenglied [N,N-dimethylurea bridged diphosphorus compounds; Structure of a spirophosphoran with λ^5-phosphorus as a bridge member]. *Liebigs Annalen Der Chemie — Liebig's Annals of Chemistry, 1*, 167–181 [in German].

39 Bhattacharyya, P., Slawin, A.M.Z., Smith, M.B., Williams, D.J., & Woollins, J.D. (1996). Diphosphine derivatives of urea and thiourea. *Journal of the Chemical Society, Dalton Transactions, 129*(18), 3647–3651.

40 Petrov, J., Atanassova, I., & Ognyanova, V. (1994). Synthesis of N-phosphorylureas by reaction of phosphorylamides with N-substituted trichloroacetamides. *Organic Preparations and Procedures International, 26*(3), 357–360.

41 Klaus Dipl Chem Dr Sommer, G.R. (1974). Verfahren zur herstellung von 1-ureido- und carbamoyloxy-alkan-1,1diphosphonsaeuren [Process for the preparation of 1-ureido- and carbamoyloxy-alkane-1,1-diphosphonicacids]. *Pat. DE2446749A1*.

42 Schnur, R.C., & Van Tamelen, E.E. (1975). Dehydrations with N-methyl-N,N'-di-tert-butylcarbodiimidium ion. *Journal of the American Chemical Society, 97*(2), 464–465.

43 Kantlehner, W., Kreß, R., Mezger, J., & Ziegler, G. (2015). Orthoamide und Iminiumsalze, LXXXVIII. Synthese N,N,N′,N′,N″,N″-persubstituierter Guanidiniumsalze aus N,N′-persubstituierten Harnstoff / Säurechlorid-Addukten. *Zeitschrift Für Naturforschung B., 70*(1), 9–27.

44 Ma, X.-B., & Zhang, J.-L. (1990). New derivatives of 4,5-benzo-1,3,2-oxaza(or diaza)-phospholane from convenient condensation of substituted urea with tris(dialkylamino)phosphine. *Phosphorus, Sulfur, and Silicon and the Related Elements. 53(1–4)*, 227–231.

45 Richter, F. (2008). 1,4,2-diazaphospholidine derivatives, *Pat. US20110207927A1*.

46 Atanassova, T.N.A.P.A. (1992). ChemInform Abstract: Synthesis of N-Substituted Derivatives of 2-Imidazolidinone. *ChemInform., 23*(20), 1.

47 Mikroyannidis, J.A. (1982). Synthesis of substituted N-[(phosphonyl)methyl]-2-imidazolidinones and N-[(phosphonyl)methyl]-2-pyrrolidinone. *Phosphorus and Sulfur and the Related Elements, 12*(2), 249–258.

48 Jin, X., Yamaguchi, K., & Mizuno, N. (2013). Copper-Catalyzed Oxidative Cross-Coupling of H-Phosphonates and Amides to N-Acylphosphoramidates. *Organic Letters, 15*(2), 418–421.

49 Larina, L.I., Dmitrichenko, M.Y., Rozinov, V.G., & Benedyuk, A.V. (2005). Phosphorylation of N-Acetyl-N, N′-ethyleneurea with Phosphorus Pentachloride. *Russian Journal of General Chemistry, 75*(3), 484–485.

50 Zabarjad-Shiraz, N., Yavari, I., Biglari, A., Izadiar, S.A., & Bijanzadeh H.-R. (2009). Three-Component Reaction Between Trivalent Phosphorus, Dimethyl Acetylenedicarboxylate, and Amide Derivatives. *Phosphorus, Sulfur, and Silicon and the Related Elements, 184*(11), 3023–3037.

51 Bucherer, H.T., Lieb, V.A. (1934). Über die Bildung substituierter Hydantoine aus Aldehyden und Ketonen. Synthese von Hydantoinen [On the formation of substituted hydantoins from aldehydes and ketones. Synthesis of hydantoins]. *Journal für Praktische Chemie — Journal of Practical Chemistry, 141*(1–2), 5–43.

52 Alimov, P.I., & Lebkova, L.N. (1964). Fosforilirovanie formamida [Phosphorylation of formamide]. *Izvestiia Akademii nauk SSSR. Otdelenie khimicheskikh nauk — Bulletin of the Academy of Sciences of the USSR, Division of chemical science, 13*(10), 1709–1713 [in Russian].

53 Nikonorov, K.V., Gurylev, E.A., Antokhina, L.A., & Latypov, Z.Ya. (1981). Reaktsiia fosforilkhloridov s difenilmochevinoi [Reaction of phosphorus acid chlorides with diphenylurea] *Izvestiia Akademii nauk SSSR. Otdelenie khimicheskikh nauk — Bulletin of the Academy of Sciences of the USSR, Division of chemical science, 30*(12), 2330–2333 [in Russian].

54 Ulrich, H., & Sayigh, A.A.R. (1966). Synthesis of isocyanates and carbodiimides. *Angewandte Chemie International Edition in English*, *5*(8), 704–712.

55 Latscha, H.P. (1966). Ein neues sechsgliedriges Ringsystem mit Phosphor, Stickstoff und Kohlenstoff als Ringglieder [A new six-membered ring system with phosphorus, nitrogen and carbon as ring members]. *Zeitschrift für anorganische und allgemeine Chemie — Journal of inorganic and general chemistry, 346*(3–4), 166–172.

56 Goehring, M.B., & Schwind, H. (1970). Über Phosphorstickstoff-Verbindungen. XXXI. Über neue viergliedrige Ringsysteme mit Stickstoff, Phosphor und Kohlenstoff im Ring. *Zeitschrift für anorganische und allgemeine Chemie, 327*(3), 285–291.

57 Ulrich, H., & Sayigh, A.A.R. (1964). 2-Phospha-1.3-diazetidinone, eine neue Verbindungsklasse. *Angewandte Chemie, 76*(14), 647.

58 Dmitrichenko, M.Yu., Rozinov, V.G., & Donskikh, V.I. (1989). Sintez 1-metil-2,2,2-trikhlor-3-(1,1,2,2-tetrakhloretil)-1,3-diaza-2-fosfetdinona [Synthesis of 1-methyl-2,2,2-trichloro-3-(1,1,2,2-tetrachloroethyl)-1,3-diaza-2-phosphetdinone]. *Zhurnal obshchei khimii — Russian Journal of General Chemistry, 59, 3*, 715–716 [in Russian].

59 Derkach, G.I., & Narbut, A.V. (1965). Proizvodnyie fosfadiazatsiklobutanona [Phosphadiazacyclobutanone derivatives]. *Zhurnal obshchey khimii — Russian Journal of General Chemistry*, *35*, *5*, 932 [in Russian].

60 Harris, R.K., Woplin, J.R., Dunmur, R.E., Murray, M., & Schmutzler, R. (1972). Nuclear Magnetic Resonance Studies of Diazaphosphetidines and Phosphadiazetidinones. *Berichte der Bunsengesellschaft für physikalische Chemie, 76*(1), 44–52.

61 Schlak, O., Schmutzler, R., Harris, R.K., McVicker, E.M., & Wazeer, M.I.M. (1981). Preparative and N.M.R. studies of phosphorus-fluorine compounds undergoing intramolecular exchange. Part 2. Unsymmetrical fluorinated phosphadiazetidinones. *Phosphorus and Sulfur and the Related Elements, 10*(1), 87–97.

62 Devillers, J., Willson, M., Burgada, R. (1968). *Bull. Soc. Chim. Fr.,* 4670.

63 Fluck, E., & Richte, H. (1983). Über Diazadiphosphetidine, VI. Synthese von Diazaphosphetidinen, Diazadiphosphetidinen und Thiadiazaphosphetidinen. *Chemische Berichte, 116*(2), 610–617.

64 Bermann, M., & Van Wazer, J.R. (1973). Diazaphosphetidinones with four-co-ordinated phosphorus. *Journal of the Chemical Society, Dalton Transactions, 8*, 813–815.

65 Burgada, R. (1971). *Bull. Soc. Chim. Fr.*, 136.

66 Bettermann, G. (1986). *Dissertation, Technische Universität Braunschweig.*

67 Breker, J., Wermuth, U., & Schmutzle, R. (1990). Verbindungen mit dem 1,3-Dimethy 1–1,3-diaza-2-phosphetidin-4-on-Grundgerüst; Synthese von l,3-Dimethyl-2-thia-l,3-diaza-2 λ^4-phosphetidin-4-on-Derivaten, *Zeitschrift für Naturforschung B., 45,* 1398–1406.

68 Hormuth, P.B., & Latscha, H.P. (1969). Über Reaktionen von Phosphorverbindungen mit Isocyanaten. V. Über die Umsetzung der viergliedrigen Ringe $C_3H_6Cl_3N_2OP$, $(C_6H_5Cl_2PNCH_3)_2$ und $((C_6H_5)_2ClPNCH_3)_2$ mit Phenyl-bzw. *Methylisocyanat. Zeitschrift für anorganische und allgemeine Chemie, 365*(1–2), 26–30.

69 Hormuth, P.B., & Latscha, H.P. (1969). Über Reaktionen von Phosphorverbindungen mit Isocynaten. VI. Die Umsetzung von Cyclo-1-trichlorphospha-2,4-azamethyl-3-on mit Methylisothiocyanat. *Zeitschrift für anorganische und allgemeine Chemie, 369*(1–2), 59–63.

70 Kozyukov, V.P., Sheludyakov, V.D., & Mironov, V.F. (1975). Kremniisoderzhashchie mochevini [Silicon-containing ureas]. *Uspekhi khimii — Advances in Chemistry, 44, 5*, 897–934 [in Russian].

71 Pinchuk, V.A., Müller, C., Fischer, A., Thönnessen, H., Jones, P. G., Schmutzler, R., Markovsky, L. N., Shermolovich, Y.G., & Pinchuk, A.M. (1995). Reactions of Sulfenamides with Compounds of Trivalent Phosphorus. *Zeitschrift für anorganische und allgemeine Chemie — Journal of inorganic and general chemistry, 621*(12), 2001–2011.

72 Shaban M.R., Ismailov V.M., Usubov N.N., Gumilev A.N., & Nasibov Sh.S. Phosphorproizvodnye barbiturovoi kisloty *[Phosphorus derivatives of barbituric acid].* Proceedings from the III Republican conference of young chemists. Baku, 1988, 169 [in Russian].

73 Abd-ellah, I.M., Ibrahim, E.H.M., & El-khazandar, A.N. (1987). Studies in cyclodiphosphazanes. Some reactions of hexachlorocyclo-diphosphazanes with urea and thiourea derivatives. *Phosphorus and Sulfur and the Related Elements, 29*, 2–4.

74 Melnicky, C., Neda, I., & Schmutzler, R. (1995). Darstellung und charakterisierung von 2-amino- und 2-methoxysubstituierten benzodiazaphosphorinonen mit phosphor in den koordinationszahlen drei, vier und fünf. *Phosphorus, Sulfur, and Silicon and the Related Elements, 106*(1–4), 65–73.

75 Dmitrichenko, M.Yu., Rozinov, V.G., Donskikh, V.I., Ratovskiy, G.V., Yefremov, V.G., & Dolgushin, G.V. (1992). Fosforsoderzhashchiie azabutadiieny i heterotstkly iz N-metil-N'-atsetilmocheviny [Phosphorus-containing azabutadienes and N-methyl-N'-acetylurea heterocene]. *Zhurnal obshchei khimii — Russian Journal of General Chemistry, 62, 2*, 306–317 [in Russian].

76 Rozinov, V.G. Dmitrichenko, M.Yu., Donskikh, V.I., Dolgushin, G.V., & Kalabina, A.V. (1988). Sposob polucheniia 2,2,4,6-tetrakhlor-2,2-digidro-1,5,2-diazafosforina [The method of obtaining 2,2,4,6-tetrachloro-2,2-dihydro-1,5,2 diazaphosphorin], *pat. SSSR1583423* [in Russian].

77 Rozinov, V.G. Dmitrichenko, M.Yu., Donskikh, V.I., Dolgushin, G.V., & Fomin, V.P. (1987). 1,3,4-Diazafosforin iz N-atsetilmocheviny [1,3,4-Diazaphosphorin from N-acetylurea*]. Zhurnal obshchei khimii — Russian Journal of General Chemistry, 57, 1*, 228–229 [in Russian].

78 Dmitrichenko, M.Yu., Rozinov, V.G., Donskikh, V.I., Ratovskiy, G. V., Yefremov, V.G., & Dolgushin, G.V. et al. (1991). 1,5,2-diazafosforiny II. Sintez i osobennosti tsiklizatsii fosforsoderzhashchikh azabutadienov na osnove atsetil- i khloratsetilmochevin [1,5,2-diazaphosphorins II. Synthesis and peculiarities of cyclization of phosphorus-containing azabutadienes based on acetyl and chloroacetylureas]. *Zhurnal obshchei khimii — Russian Journal of General Chemistry, 61, 3*, 643–656 [in Russian].

79 Neda, I., Farkens, M., Fischer, A., Jones, P. G., & Schmutzler, R. (1993). Zur Chemie der 4,6-Dioxo-l,3,5,2-triazaphosphinane, Teil III. Darstellung von 4,6-Dioxo-1,3,5,2 λ^3-, 4,6-Dioxo-1,3,5,2 λ^4- und 4,6-Dioxo-1,3,5,2 λ^5-triazaphosphinanen. *Zeitschrift für Naturforschung B, 48b,* 443–451.

80 Neda, I., Farkens, M., & Schmutzler, R. (1994). Zur Chemie der l,3,5-Triaza-2-phosphorinan-4,6-dione. Teil VII. Über die Synthese von 2-Methoxy- und 2-Trimethylsiloxy-l,3,5-trimethyl-1,3,5-triaza-2λ^3-phosphorinan-4,6-dion sowie 2-Chlor-l,3,5-trimethyl-1,3,5-triaza-2-oxo-2λ^4-phosphorinan-4,6-dion. *Zeitschrift für Naturforschung B, 49b,* 165–170.

81 Farkens, M., Neda, I., & Schmutzler, R. (1994). Zur Chemie der l,3,5-Triaza-2-phosphorinan-4,6-dione. Teil VIII. Weitere l,3,5-Triaza-2 λ^3- und 1,3,5-Triaza-2 λ^4-phosphorinan-4,6-dione mit (2-Chlorethyl)amino- und Bis(2-chlorethyl)amino-Substituenten. *Zeitschrift für Naturforschung B, 49b,* 445–450.

82 Kaukorat, T., Neda, I., Fischer, A., Jones, P.G., & Schmutzler, R. (1993). Verbindungen mit dem 1,3,5,2-Triazaphosphorinan-Grundgerüst: Synthese und Koordinationschemie neuartiger, N,N,N'-Trimethylethylendiamin-substituierter Verbindungen mit drei- und vierfach koordiniertem Phosphor. *Chemische Berichte, 126*(6), 1265–1270.

83 Roesky, H.W., Ambrosius, K., Banek, M., & Sheldrick, W.S. (1980). Darstellung Reaktionen und Strukturen spirobicyclischer Phosphorane. *Chemische Berichte, 113*(5), 1847–1854.

84 Roesky, H.W., Zamankhan, H., Sheldrick, W.S., Cowley, A.H., & Mehrotra S.K. (1981). Structural chemistry of 1-oxo-2,8-dimethyl-4,6-bis[3-(trifluoromethyl)phenyl]-2,4,6,8-tetraaza-1.lambda.5–5.lambda.3-diphosphabicyclo[3.3.0]octane-3,7-dione and the synthesis, structure, and reactions of 2,4,6,8-tetramethyl-2,4,6,8-tetraaza-1.lambda.3–5.lambda.3-diphosphabicyclo[3.3.0]octane-3,7-dione. *Bicyclic Compaunds with Phosphorus-Phosphorus Bond. Inorganic Chemistry, 20*(9), 2910–2915.

85 Neidlein, R., & Degener, H.J. (1984). Synthesen und spektroskopische Eigenschaften methano-überbrückter Phosphaheterocyclen. Syntheses and Spectroscopic Properties of Methano-Bridged Phosphaheterocycles. *Archiv Der Pharmazie, 317*(12), 1053–1055.

86 Shevchenko, I., Fischer, A.K., Jones, P.G., & Schmutzler, R. (2002). Urea-bridged Bicyclic Bisphosphines Containing the Grouping P-CCl_2-P. *Zeitschrift Fur Anorganische Und Allgemeine Chemie, 628*(8), 1903–1907.

87 Sheldrick, W.S., Pohl, S., Zamankhan, H., Banek, M., Amirzadeh-Asl, D., & Roesky, H.W. (1981). Uber Reaktionen an Heterocyclen, die eine P–P-Bindung enthalten. *Chemische Berichte, 114*(6), 2132–2137.

88 Roesky, H.W., & Amirzadeh-Asl, D. (1983). Darstellung und Reaktionen von bicyclischen Verbindungen mit einer Phosphor-Phosphor-Bindung. *Zeitschrift für Naturforschung, 38b*, 460–464.

89 Roesky, H.W., Ambrosius, K., & Sheldrick, W.S. (1979). Darstellung und Struktur eines neuartigen spirobicyclischen Phosphorans mit einer λ^3P-λ^5P-Bindung. *Chemische Berichte, 112*(4), 1365–1371.

90 Breker, J., Jones, P.G., Schmutzler, R., & Schomburg, D. (1991). Chemie des 4-chlor-1,3,5,7-tetramethyl- 1,3,5, 7-tetraaza-4HHDFFHV-phosphaspiro[3.3]heptan-2,6-dions; Kristall- und molekul struktur von halogen(F, Br)- und pseudohalogen(CN)- phosphoranen. *Phosphorus, Sulfur, and Silicon and the Related Elements, 62*(1–4), 139–153.

91 Schomburg, D., Wermuth, U., & Schmutzler, R. (1987). Chemie des 4-Chlor-1,3,5,7-tetramethyl-1,3,5,7-tetraaza-4λ^5-phosphaspiro[3.3]heptan-2,6-dions; Kristall- und Molekül struktur eines Chlortetraaza- und zweier Pentaazaphosphorane. *Chemische Berichte, 120*(10), 1713–1718.

92 Neda, I., Fischer, A., Jones, P.G., & Schmutzler, R. (1993). Verbindungen mit dem 1,3,2-benzodiazaphosphorinan-4-on grundgerust: synthese von neuartigen, N,N-dimethylamino- und bis-2-chlorethylamino-substituierten derivaten mit drei-, vier- und funffach koordiniertem phosphor. *Phosphorus, Sulfur, and Silicon and the Related Elements, 78*(1–4), 271–278.

93 Neda, I., Kaukorat, T., & Schmutzler, R. (1993). Umsetzungen von 4-chlor-1,3,5,7-tetramethyl-1,3,5,7-tetraaza-4λ^5-phosphaspiro[3,3]heptan-2,6-dion, bis(trimethylsilyl)-trimethylbiuret und bis(2-chlorethyl)-aminophosphorsauredichlorid mit $Me_2NCH_2CH_2N(Me)SiMe_3$; studium intramolekularer p-n-wechselwirku. *Phosphorus, Sulfur, and Silicon and the Related Elements, 80*(1–4), 173–179.

94 Anand, B.N., Bains, R., & Usha, K. (1990). Synthesis and characterization of four-membered, spirobicyclic, transition-metal-substituted phosphoranes. *J. Chem. Soc. Dalton, Trans., 7,* 2315–2317.

95 Sal'keeva L.K., Taishibekova E.K., Bakibaev A.A., Minaeva E.V., Sugralina L.M., & Makin B.K. et al. (2016). Sintez i issledovaniie polifunktsionalnykh proizvodnykh hlikolurila [Synthesis and study of polyfunctional glycoluril derivatives]. *Vestnik Karahandinskoho universiteta. Seriia khimiia — Bulletin of the Karaganda University. Chemistry series, 84, 4*, 14–20 [in Russian].

96 Wang, Y., & Sheng Y. (2013). Fire retardant 4-(O,O-dimethyl phosphoryl)glycoluril compound and preparation method thereof, *Pat. CN103387590A*.

97 Wang, Y., & Sheng Y. (2013). Fire retardant tetra(O,O-dibutyl-phosphoryl)glycoluril compound and preparation method thereof, *Pat. CN103396450A*.

98 Wang, Y., & Sheng, Y. (2013). Flame retardant tetra(O,O-diisopropylphosphoryl)glycoluril compound and preparation method thereof, *Pat. CN103387590A*.

99 Sal'keeva, L.K., Taishibekova, E.K., Bakibaev, A.A., Minaeva, E.V., Makin, B.K., & Sugralina, L.M.et al. (2017). New Phosphorylated Glycoluril Derivatives. *Russian Journal of General Chemistry, 87*(3), 442–446.

100 Moradi, S., Zolfigol, M., Zarei, M., Alonso, D., & Khoshnood, A. (2018). Synthesis of a Biological-Based Glycoluril with Phosphorous Acid Tags as a New Nanostructured Catalyst: Application for the Synthesis of Novel Natural Henna-Based Compounds. *Chemistry Select, 3*(11), 3042–3047.

101 Taishibekova, Ye.K. (2015). Fosfororhanicheskie proizvodnye na osnove aminotiazolov i hlikolurila [Organophosphate derivatives on the basis of aminothiazole glycoluril]. *PhD Doctor s thesis.* Karaganda [in Russian].

102 Korbridzh, D. (1982). *Fosfor: Osnovy khimii, biokhimii, tekhnolohii [Phosphorus: Fundamentals of Chemistry, Biochemistry, Technology].* (transl.) Moscow: Mir [in Russian].

АВТОРЛАР ТУРАЛЫ МӘЛІМЕТТЕР
СВЕДЕНИЯ ОБ АВТОРАХ
INFORMATION ABOUT AUTHORS

Abdurazova, P.A. — PhD, Department of Chemical technology of inorganic substances, M.O. Auezov South Kazakhstan State University, Shymkent, Kazakhstan.

Akhmetova, S.B. — Candidate of Medical Sciences, Head of Microbiology Department, Karaganda Medical University, Kazakhstan.

Akhtayeva, M.B. — PhD student, Kazakh State Women's Teacher Training University, Almaty, Kazakhstan.

Akzholtay, A.N. — BSc, Engineer of the laboratory of polymer chemistry, Institute of Organic Synthesis and Coal Chemistry of the Republic of Kazakhstan, Karaganda, Kazakhstan.

Andreeva, A.P. — Candidate of Biological Sciences, Ye.A. Buketov Karaganda State University, Kazakhstan.

Arnt, O.V. — MSc, Researcher of the laboratory of polymer chemistry, Institute of Organic Synthesis and Coal Chemistry of the Republic of Kazakhstan, Karaganda, Kazakhstan.

Azimbayeva, G.Ye. — Candidate of Chemical Sciences, Professor, Kazakh State Women's Teacher Training University, Almaty, Kazakhstan.

Bakibayev, A.A. — Doctor of Chemical Sciences, Professor, Tomsk State University, Russia.

Batueva, T.D. — PhD in Chemistry, Senior Researcher of the laboratory of organic complexing reagents, Institute of Technical Chemistry, Ural Branch of the Russian Academy of Sciences, Perm, Russia.

Baybazarova, E.A. — PhD student, Teacher, M.Kh. Dulati Taraz State University, Kazakhstan.

Bekbauov, B.Ye. — PhD, Associate Professor, K.I. Satbayev Kazakh National Research Technical University, Almaty, Kazakhstan.

Beznosyuk, S.A. — Doctor of Physical and Mathematical Sciences, Professor, Head of Physical & Inorganic Department, Altai State University, Barnaul, Russia.

Dorozhko, Ye.V. — Ph.D., Associate Professor of the Department of Chemical Engineering, School of Natural Resources, Tomsk Polytechnic University, Russia.

Dupont, O.N. — Student, Biology Department, Ye.A. Buketov Karaganda State University, Kazakhstan.

Dyorina, K.V. — Assistant of the Department of Chemical Engineering, School of Natural Resources, Tomsk Polytechnic University, Russia.

Dyussekeyeva, A.T. — Candidate of Chemical Sciences, Associate Professor, Department of Inorganic & Technical Chemistry, Ye.A. Buketov Karaganda State University, Kazakhstan.

Dzhakipbekova, N.O. — Doctor of Technical Sciences, Professor, Department of Chemical technology of inorganic substances, M.O. Auezov South Kazakhstan State University, Shymkent, Kazakhstan.

Fazylov, S.D. — Doctor of Chemical Sciences, Professor, Institute of Organic Synthesis and Coal Chemistry of the Republic of Kazakhstan, Karaganda, Kazakhstan.

Gazaliyev, A.M. — Doctor of Chemical Sciences, Professor, Institute of Organic Synthesis and Coal Chemistry of the Republic of Kazakhstan, Karaganda, Kazakhstan.

Gorbin, S.I. — Junior Researcher, National Research Tomsk Polytechnic University, Russia.

Gusar, A.O. — Engineer, Department of Chemical Engineering, School of Natural Resources, Tomsk Polytechnic University, Russia.

Ibrayev, M.K. — Doctor of Chemical Sciences, Professor, Karaganda State Technical University, Kazakhstan.

Issabayeva, M.B. — Candidate of Chemical Sciences, Associate Professor of Chemistry and Chemical Technologies Department, Karaganda State Technical University, Kazakhstan.

Kaikenov, D.A. — Researcher of the laboratory of the engineering profile «Physical and chemical methods of research», Ye.A. Buketov Karaganda State University, Kazakhstan.

Karipova, G.Zh. — MSc, Researcher of the laboratory synthesis of biologically active substances, Institute of Organic Synthesis and Coal Chemistry of the Republic of Kazakhstan, Karaganda, Kazakhstan.

Kartbayeva, G.T. — Candidate of Biological Sciences, Associate Professor, Head of Zoology Department, Ye.A. Buketov Karaganda State University, Kazakhstan.

Kasymova, M.S. — Candidate of Chemical Sciences, Assistant professor of the Department of Physical and Analytical Chemistry, Ye.A. Buketov Karaganda State University, Kazakhstan.

Katrenov, B.B. — Researcher, Zh. Abishev Chemical Metallurgical Institute, Karaganda, Kazakhstan.

Kaztayeva, A.Ye. — Master Student, Karaganda State Technical University, Kazakhstan.

Kenzhetayeva, S.O. — Candidate of Chemical Sciences, Professor, Organic Chemistry and Polymers Department, Ye.A. Buketov Karaganda State University, Kazakhstan.

Kohnert, K.-D. — Doctor of Medical Sciences, Professor, Institute of Diabetes «Gerhardt Katch», Karlsburg, Germany.

Kokibasova, G.T. — Candidate of Chemical Sciences, Associate Professor, Inorganic & Technical Chemistry Department, Ye.A. Buketov Karaganda State University, Kazakhstan.

Kondrashova, N.B. — PhD in Chemistry, Researcher of the laboratory of multiphase dispersed systems, Institute of Technical Chemistry, Ural Branch of the Russian Academy of Sciences, Perm, Russia.

Kopylov, N.I. — Doctor of Technical Sciences, Professor, Institute of Solid State Chemistry and Mechanochemistry of the Siberian Branch of the Russian Academy of Sciences, Novosibirsk, Russia.

Korotkova, Ye.I. — Doctor of Chemical Sciences, Professor, Department of Chemical Engineering, Engineering School of Natural Resources, Tomsk Polytechnic University, Russia.

Koshkarbayeva, Sh.T. — Candidate of Technical Sciences, Associate Professor, Department of Chemical technology of inorganic substances, M.O. Auezov South Kazakhstan State University, Shymkent, Kazakhstan.

Kurmangaziyeva, L.T. — Candidate of Technical Sciences, Associate Professor, Kh. Dosmukhamedov Atyrau State University, Kazakhstan.

Malkov, V.S. — Candidate of Chemical Sciences, Associate Professor, Tomsk National Research State University, Russia.

Massalimova, B.K. — Candidate of Chemical Sciences, Head of Department, M.Kh. Dulati Taraz State University, Kazakhstan.

Matniyazova, G.K. — Doctor PhD, M.Kh. Dulati Taraz State University, Kazakhstan.

Meyramov, G.G. — Doctor of Medical Sciences, Professor, Biology Department, Ye.A. Buketov Karaganda State University, Kazakhstan.

Minayeva, Ye.V. — Candidate of Chemical Sciences, Assistant Professor of the Organic Chemistry and Polymers Department, Ye.A. Buketov Karaganda State University, Kazakhstan.

Muldakhmetov, Z.M. — Academician of the National Academy of Sciences of the Republic of Kazakhstan, Honored Scientist of the Republic of Kazakhstan, Doctor of Chemical Sciences, Professor, Director of the Institute of Organic Synthesis and Coal Chemistry of Republic of Kazakhstan, Karaganda, Kazakhstan.

Muratbekova, A.A. — Candidate of Chemical Sciences, Associate Professor, Ye.A. Buketov Karaganda State University, Kazakhstan.

Narembekova, A. — Candidate of Technical Sciences, Associate Professor, Department of Nanotechnology and Metallurgy, Karaganda State Technical University, Kazakhstan.

Naukenova, A.Zh. — PhD Student, Department of Mechanics, Al-Farabi Kazakh National University, Almaty, Kazakhstan.

Nurkenov, A.O. — Master in Engineering and Technology, Karaganda State Technical University, Kazakhstan.

Nurkenov, O.A. — Doctor of Chemical Sciences, Professor, Head of the laboratory of synthesis of biologically active substances, Institute of Organic Synthesis and Coal Chemistry of the Republic of Kazakhstan, Karaganda, Kazakhstan.

Orazbayev, B.B. — Doctor of Technical Sciences, Professor, Academician of the National Engineering Academy of the Republic of Kazakhstan, L.N. Gumilyov Eurasian National University, Nur-Sultan, Kazakhstan.

Panshina, S.Yu. — Postgraduate student, National Research Tomsk Polytechnic University, Russia.

Raiymbekov, Ye.B. — Master of technical sciences, Department of Chemical technology of inorganic substances, M.O. Auezov South Kazakhstan State University, Shymkent, Kazakhstan.

Rustembekov, K.T. — Corresponding Member of the Kazakhstan National Academy of Natural Sciences (KazNANS), Doctor of Chemical Sciences, Professor of Inorganic and Technical Chemistry, Ye.A. Buketov Karaganda State University, Kazakhstan.

Sarsenbekov, N.D. — Managing director of Scientific Laboratory Research Center, Scientific Research Institute «Caspimunaigas» LLP, Atyrau, Kazakhstan.

Satayev, M.S. — Doctor of Technical Sciences, Professor, Department of Chemical technology of inorganic substances, M.O. Auezov South Kazakhstan State University, Shymkent, Kazakhstan.

Scherban, M.G. — PhD in Chemistry, Assistant Professor, Perm State National Research University, Russia.

Seilkhanov, O.T. — Master physicist, Deputy Head of the laboratory of engineering profile of NMR spectroscopy, Sh. Ualikhanov Kokshetau State University, Kazakhstan.

Seilkhanov, T.M. — Candidate of Chemical Sciences, Full Professor, Head of the laboratory of engineering profile of NMR spectroscopy, Sh. Ualikhanov Kokshetau State University, Kazakhstan.

Shambilova, G.K. — Doctor of Chemical Sciences, Professor, Kh. Dosmukhamedov Atyrau State University, Kazakhstan.

Shaybek, A.Zh. — MSc in Biology, Senior teacher, Biology Department, Ye.A. Buketov Karaganda State University, Kazakhstan.

Suleimen, Ye.M. — Candidate of Chemical Sciences, PhD, Associate Professor, Director of the Institute of Applied Chemistry, L.N. Gumilyov Eurasian National University, Nur-Sultan, Kazakhstan.

Takibayeva, A.T. — Candidate of Chemical Sciences, Acting Head of Department of Chemistry and Chemical Technologies, Karaganda State Technical University, Kazakhstan.

Terenteva, Y.V. — Candidate of Physical and Mathematical Sciences, Senior Lecturer of Physical & Inorganic Department, Altai State University, Barnaul, Russia.

Tsoy, I.G. — Candidate of Chemical Sciences, Associate Professor, M.Kh. Dulati Taraz State University, Kazakhstan.

Van Hecke, K. — Professor at the Department of Inorganic and Physical Chemistry, Ghent University, Belgium.

Vassilets, Ye.P. — Master of education, Researcher of the laboratory of polymer chemistry, Institute of Organic Synthesis and Coal Chemistry of the Republic of Kazakhstan, Karaganda, Kazakhstan.

Volkov, D.A. — Master of Chemical Sciences, Graduate student of Physical & Inorganic Department, Altai State University, Barnaul, Russia.

Zhakina, A.Kh. — Candidate of Chemical Sciences, Assistant professor, Head of the laboratory of polymer chemistry, Institute of Organic Synthesis and Coal Chemistry of the Republic of Kazakhstan, Karaganda, Kazakhstan.

Zhumanov, K.B. — PhD student, M.Kh. Dulati Taraz State University, Kazakhstan.

Zhumashev, K. — Doctor of Chemical Sciences, Director, «Innovatsiya» LLP, Karaganda, Kazakhstan.