

NEWS

OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN

SERIES CHEMISTRY AND TECHNOLOGY

ISSN 2224-5286

<https://doi.org/10.32014/2020.2518-1491.85>

Volume 5, Number 443 (2020), 92 – 98

UDC 54.01: 546.881:541.124.

R.N. Nasirov¹, B.K. Kuspanova², A.S.Kalauova², K.G. Satenov¹

¹Atyrau State University named after H.Dosmuhamedov, Atyrau, Kazakhstan;

²Atyrau Oil and Gas University named after S. Utebayev.

E-mail: rnasirov.48@mail.ru

**BINDING d-ELEMENT OF THE 4TH PERIOD OF V-GROUP
OF THE PERIODIC SYSTEM OF D.I. MENDELEYEV
AND ITS PARAMAGNETIC PROPERTIES**

Abstract. Vanadium is a connecting element between the main subgroup VA and the subgroup VB. In the opinion of B.V. Nekrasov, if we compare the VB group of vanadium elements with the valence states of P and As VA main subgroup, then in the oxidation states of -3, 0, +3 arsenic is an analogue of phosphorus, and in the oxidation state +5, it will not be an analogue of phosphorus. In contrast, in the low oxidation degrees of vanadium, it differs from phosphorus, and in the oxidation state of +5 vanadium is not a complete analogue of phosphorus.

The similarity of the electronic configuration of atoms for vanadium and phosphorus in the +5 oxidation state specifies the similarity of the properties of their chemical compounds.

When comparing vanadium and its compounds with elements of the VA subgroup, we conclude that vanadium is a binding element between the VA subgroup and the VB subgroup and the compounds have similar properties.

As a result of many years of work, it was found that vanadium in the penta- and tetravalent states has paramagnetic properties. In crude oil, it is in a tetravalent state.

In order to improve the standard photocalorimetric method for determining vanadium in oil and petroleum ashes, a more rapid method was proposed for estimating the total concentration of vanadium based on the interaction of V₂O₅ with concentrated hydrochloric acid.

Studies of the EPR spectra of porphyrin complexes with transition metals such as copper were of great importance in the identification of natural porphyrin complexes.

In the course of comparison of experimental works of paramagnetic properties of vanadium and phosphorus with each other, it can be said that their application is of great practical importance in different fields of science.

Summing up the results of studying the reduction of triphenylphosphine with an alkali metal, we proposed a scheme for the splitting of triphenylphosphine, including the formation of radical anions.

Keywords: binding d-element, vanadium, incomplete analogue, electronic structure, paramagnetism.

Vanadium is a connecting element between the main subgroup VA and the subgroup VB. It is the first d-element of the VB subgroup, its analogues are niobium and tantalum. Their electronic structure and valence states are equal. The VB element group resembles the IVB group of elements. In normal conditions, vanadium in the cold dissolves in “aqua regia” and when heated in nitric and concentrated sulfuric acids. Upon fusion with alkalis, anionic oxo complexes are formed. The oxidation degree of niobium and tantalum in the form of a halide is +4 [1-3]. Vanadium in the form of vanadyl - VO²⁺ ion enters into many chemical reactions and is found in complex compounds [4].

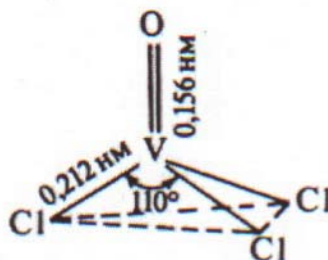
In the opinion of B.V. Nekrasov [5], if we compare the VB group of vanadium elements with the valence states of P and As VA main subgroup, then in the oxidation states of -3, 0, +3 arsenic is an analogue of phosphorus, and in the oxidation state +5, it will not be an analogue of phosphorus. In contrast, in the low oxidation degrees of vanadium, it differs from phosphorus, and in the oxidation state of +5 vanadium is not a complete analogue of phosphorus (Table 1).

The 3d orbital of the phosphorus atom makes phosphorus chemistry deeply different from the nitrogen properties. The similarity of the electronic configuration of atoms for vanadium and phosphorus in the +5 oxidation state specifies the similarity of the properties of their chemical compounds.

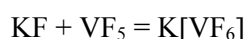
Table 1 - Comparison of the valence states of vanadium, phosphorus, and arsenic

| Valence | Electron arrangement by energy levels in atoms of elements | | |
|---------|--|---------------|------------------|
| | V (VB) | P (VA) | As (VA) |
| -3 | - | 2,8, 8 | 2,8,18, 8 |
| 0 | 2,8,11, 2 | 2,8, 5 | 2,8,18, 5 |
| +3 | 2,8, 10 | 2,8, 2 | 2,8,18, 2 |
| +5 | 2,8, 8 | 2, 8 | 2,8, 18 |

Vanadium (V) oxychloride - a liquid (mp. -77°C , bp. 127°C). VOCl_3 has the form of a distorted tetrahedron with a vanadium atom in the center [2].



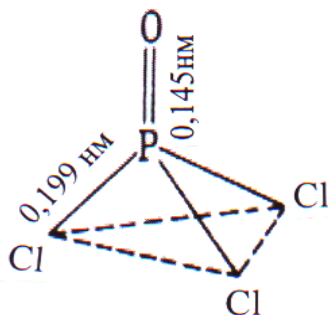
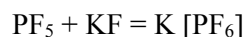
Vanadium (V) halogenide reacts with the main halogenide to form an anionic complex:



Phosphorus oxotrichloride (V) - a liquid (mp 1°C , bp 107°C) formed by heating the mixture of P_2O_5 and PCl_5 :



POCl_3 has the form of the distorted tetrahedron [2] (see Fig.). In non-aqueous solutions, PF_5 interacts with basic fluoride:



The coordination number in the vanadium (V) and phosphorus (V) complex compounds is 6. For the compounds under consideration, in which these elements are in the valence state 5, the chemical properties are similar.

When comparing vanadium and its compounds with elements of the VA subgroup, we conclude that vanadium is a binding element between the VA subgroup and the VB subgroup and the compounds have similar properties.

It is known that vanadium (V) oxide in an acidic environment exhibits oxidizing properties:



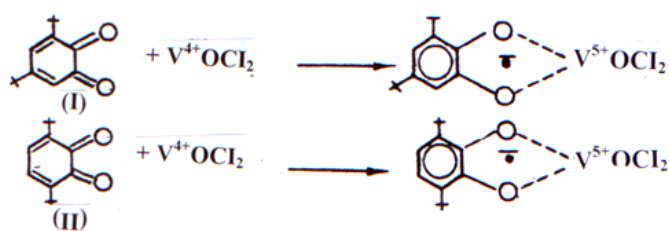
At present, in many research laboratories, the methods of neutron activation analysis (NAA) and X-ray fluorescence analysis (XRF) are used to determine vanadium and other trace elements in oils and petroleum products. The use of neutron activation analysis for these purposes is associated with several known technological difficulties. The main drawback of X-ray fluorescence analysis is the superimposition of the titanium spectral line on the vanadium spectral line in the X-ray fluorescence spectra.

Due to the existing shortcomings of these methods in the geological calculation of vanadium reserves and mass laboratory analyzes, GOST 10364-63 is used to determine the content of vanadium in oils and petroleum products, the essence of which is the photometry of the phosphoric-tungsten-vanadium complex formed after cineration of the test sample of the oil and petroleum product as well as after the processing of the ash by hydrochloric and phosphoric acids and sodium tungstate. However, the photocolometric method does not always have the necessary sensitivity and selectivity. Also, one analysis takes a lot of time, and analytically requires many operations.

To improve the common photocolometric method for determining vanadium in petroleum ashes, a more rapid method is proposed for estimating the total amount of vanadium in petroleum ashes based on the interaction of V_2O_5 with concentrated hydrochloric acid. The vanadium concentration in the studied petroleum ashes of the Caspian Sea region was determined by the anisotropic electron paramagnetic resonance (EPR) spectrum of the resulting vanadyl chloride [6]. The advantages of the EPR method for determining total vanadium in petroleum ash are its performance, selectivity, high accuracy, and reliability compared to traditionally used photocolometric methods.

In this work, we propose the EPR method for estimating the total vanadium concentration in petroleum ashes based on the ability of vanadium d-elements to form stable paramagnetic complexes with sterically hindered quinones [7]. This was facilitated by the forming complexes of o-semiquinones with metal chlorides of group III [8].

In this regard, we attempted to study the interaction of vanadyl chloride with 3,5-di-tert-butylorthobenzoquinone and 3,6-di-tert-butyl-orthobenzoquinone in toluene. This type of redox process reduces to the oxidation of V^{4+} to V^{5+} with the formation of a vanadium-containing complex with a paramagnetic o-benzosemiquinone ligand [7]:



where $\text{---}+ = \text{C}(\text{CH}_3)_3$

The analysis of the vanadium content in oil and petroleum products plays a significant role in oil refining and identifying promising deposits for the extraction of valuable metal.

In the natural porphyrin complexes identification, studies of the EPR spectra of porphyrin complexes with transition metals such as copper were of great importance [9]. If we compare the EPR spectrum of the VO – EP complex (figure 1a) and the Cu^{2+} – EP obtained from it, we receive very interesting data.

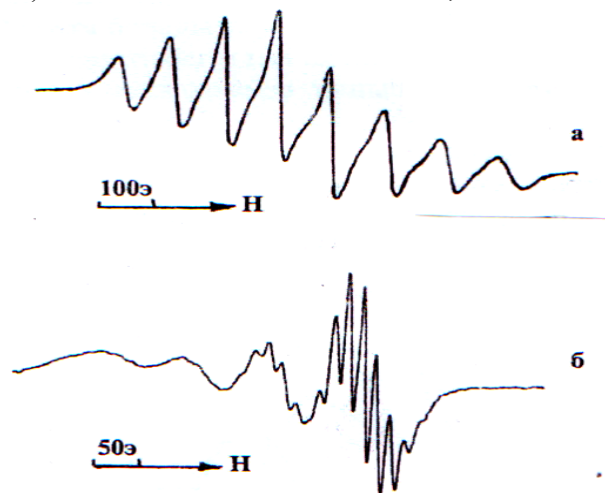


Figure 1 - EPR spectrum of the VO - EP (a) complex from the Karazhanbas oil and obtained Cu^{2+} - EP (b)

Cu^{2+} -EP has a square - planar structure in which a copper ion lies in the plane of four equivalent nitrogen atoms of the porphyrin ligand (Fig. 1b). The isotropic spectrum of this complex, recorded in solution, consists of four hyperfine structure (HFS) lines due to the interaction of an unpaired copper electron with a $^{63,65}\text{Cu}$ nucleus; HFS constant is $a_{\text{Cu}}=102.5$ Gs with $g_{\text{H}30}=2.101$.

An additional hyperfine structure is observed near the band in a strong field due to the interaction of an unpaired electron with ligand nitrogen nuclei. The line intensity of the additional HFS is expressed by the ratio 1:4:10:16:19:16:10:4:1. Nine lines of the hyperfine structure with splitting between the lines $a_{\text{N}}=12.5$ Gs are due to the interaction of the unpaired electron with the magnetic moments of four united nitrogen atoms ($I_{\text{N}}=1$) of the porphyrin macrocycle. Thus, the homologues of all VOP VO^{2+} extracted from oils coordinate with the four nitrogen atoms of the pyrrole nuclei.

Summing up the study of the recovery of triphenylphosphine with an alkali metal, Brit and Kaiser [10] proposed a triphenylphosphine splitting scheme that does not include the formation of an anion radical (AR).

When reducing triphenylphosphine with alkali metals (K and Na) in 1,2-dimethoxyethane (DME) and tetrahydrofuran (THF) at -70 °C with EPR method, we found almost the same EPR spectrum [11] as Ilyasov [12] during electrochemical recovery. In DME, the spectrum is described by the following hyperfine structure constants:

$$a_p = a_H^{\text{para}} = 2.5 \text{ Гс}, a_H^{\text{ortho}} = 1.25 \text{ Гс}$$

The analysis of the spectrum hyperfine structure shows that an unpaired electron is regularly delocalized throughout the molecule. Figure 2 shows the quantum numbers under the spectrum corresponding to the projections of the resultant spin of 3 pairs of protons ($I_{\text{H}}=1/2$) and one phosphorus nucleus ($I_{\text{P}}=1/2$). As follows from the experimental data, the triphenylphosphine reaction network in the interaction with alkali metals should include the stage of single electron transfer from the metal and the formation of the primary triphenylphosphine anion radical

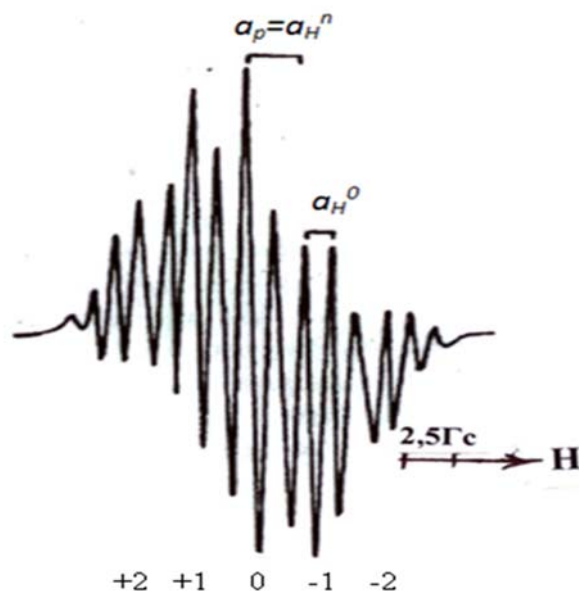
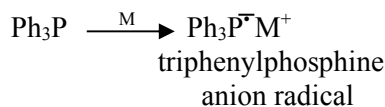


Figure 2 - EPR spectrum of triphenylphosphine-potassium anion radical in DME at -60°C

Therefore, during the organic elements chemistry course [13–15] for students of chemical specialties in universities, it should be noted that upon the preparation of organic alkali metal derivatives from triphenylphosphine, the very first-stage triphenylphosphine anion radical is formed.

In recent years, the intensive development of the homolytic chemistry of phosphorus has aroused interest in the phosphorus centric and, in particular, phosphonyl radicals [16,17].

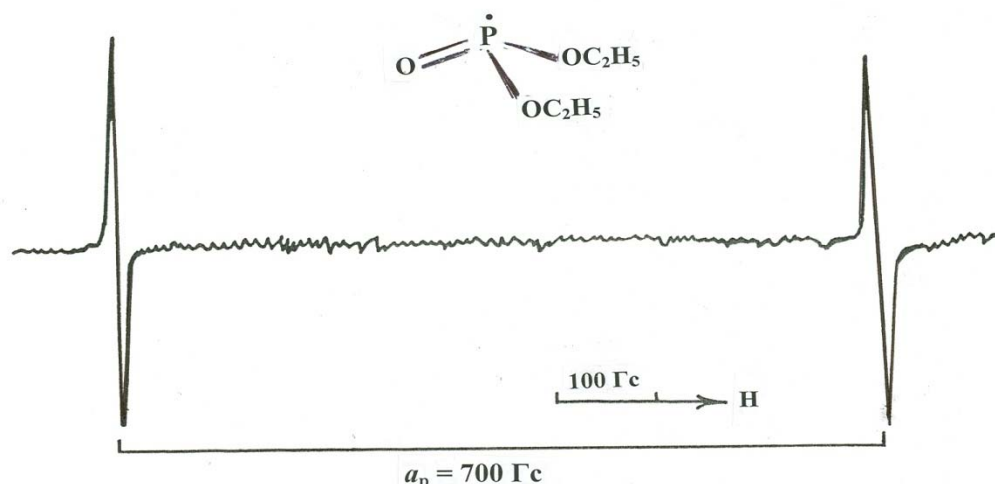
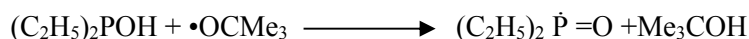


Figure 3 - EPR spectrum of phosphonyl radicals

Phosphonyl radicals (figure 3) are easily formed during the photolysis of the corresponding hydrophosphoryl compounds into di-tert-butyl peroxides.



In this case, the unpaired electron is delocalized mainly in the phosphorus atom. The same spin as the proton, i.e., $\frac{1}{2}$, is possessed by ^{31}P nuclei that are part of various phosphonyl compounds. The hyperfine interaction of the unpaired electron with this magnetic core in radicals leads to doublet splitting in the EPR spectrum as in the case with a proton.

Experimental part. The triphenylphosphine anion radical was received in DME by the common method on metal mirrors of K and Na at $-70^{\circ}C$ in a vacuum. The EPR spectrum was recorded with a Varian E-12 spectrometer.

Using the methods of demetallization and chromatographic separation, etioporphyrin was obtained from vanadyl porphyrin concentrates of the Karazhanbass oil. Bivalent copper complexes were prepared by reacting of the anhydrous salt $CuCl_2$ with etioporphyrin in dry chloroform at room temperature.

Р.Н. Насиров¹, Б.К. Куспанова², А.С. Калауова², К.Г. Сатенов¹

¹Х.Досмухамедов атындағы Атырау мемлекеттік университеті;

²С. Өтебаев атындағы мұнай және газ университеті

Д.И. МЕНДЕЛЕЕВТИҢ ПЕРИОДТЫҚ ЖҮЙЕСІНІҢ 4-ПЕРИОДЫ V ТОБЫНЫҢ БАЙЛАНЫСТЫРУШЫ D-ЭЛЕМЕНТІ ЖӘНЕ ОНЫҢ ПАРАМАГНИТТІК ҚАСИЕТТЕРІ

Аннотация. Ванадий VA негізгі тобы мен VB кіші тобы арасындағы байланыстырушы элемент ретінде әрекет етеді.

Б.В. Некрасовтың ұсынысына сәйкес, егер ванадий элементі VB тобын негізгі топтың P және As VA валентті күйімен салыстырсақ, онда тотығу дәрежесінде -3, 0, +3 күшала фосфордың аналогы болып саналады, ал тотығу дәрежесі +5 болса, күшала фосфордың аналогы болмайды. Керісінше, ванадий тотығуының төменгі дәрежесінде фосфордан ерекшеленеді, ал тотығу дәрежесі + 5 ванадий фосфордың толық емес аналогы болып есептеледі.

Ванадий мен фосфор атомдарының электрондық конфигурациясының тотығу дәрежесі +5 болуы олардың химиялық қосылыстары ұқсастық қасиеттерін тудырады.

Ванадий мен оның қосылыстарын VA негізгі топ элементтерімен салыстыру барысында біз ванадий – VA кіші топшасы мен VB негізгі топшасы арасындағы байланыстырушы элемент, ал қосылыстары ұқсас қасиеттерге ие деген қорытындыға келдік.

Көпжылдық жұмыстың нәтижесінде ванадий бес және төрт валентті күйінде парамагнетизм қасиетінің бар екендігі анықталды. Шикі мұнайда ол төрт валентті күйде болады.

Мұнай және мұнай өнімдері күлдеріндегі ванадийді анықтаудың стандартты фотокалориметрлік әдісін жетілдіру мақсатында жұмыста ванадийдің жалпы мөлшерін бағалау үшін ванадийдің бес валентті оксидін (V_2O_5) концентрлі тұз қышқылымен өзара әрекеттестіруге негізделген неғұрлым жылдам анықтау әдістемесі ұсынылған.

Табиғи текті порфирин кешендерін сәйкестендіруде мыс сияқты өтпелі металдармен порфирин кешендерінің ЭПР спектрлерін зерттеу үлкен маңызға ие болды.

Ванадий мен фосфордың парамагнитті қасиеттерін бір-бірімен салыстыра отырып, оларды ғылымның түрлі салаларында қолдану зор практикалық маңызға ие деп айтуға болады.

Трифенилфосфиннің сілтілі металмен тотықсыздануын зерттеу нәтижесінде анион радикалдар түзетін трифенилфосфиннің ыдырау схемасын ұсындық.

Түйін сөздер: байланыстырушы d-элемент, ванадий, толық емес аналогы, электрондық құрылысы, парамагнетизм.

Р.Н. Насиров¹, Б.К. Куспанова², А.С. Калауова², К.Г. Сатенов¹

¹Атырауский государственный университет им. Х.Досмухамедова;

²Атырауский университет нефти и газа им. С. Утебаева

СВЯЗУЮЩИЙ d-ЭЛЕМЕНТ 4-го ПЕРИОДА V- ГРУППЫ ПЕРИОДИЧЕСКОЙ СИСТЕМЫ Д.И.МЕНДЕЛЕЕВА И ЕГО ПАРАМАГНИТНЫЕ СВОЙСТВА

Аннотация. Ванадий выступает как бы связующим элементом между главной подгруппой VA и подгруппой VB.

Согласно представлениям Б.В.Некрасова, если сопоставить VB группу элементов ванадия с валентными состояниями P и As VA главной подгруппы, то в степенях окисления -3, 0, +3 мышьяк является *аналогом* фосфора, а в степени окисления +5 мышьяк не будет аналогом фосфора. Напротив, в низких степенях окисления ванадий отличается от фосфора, а в степени окисления +5 ванадий является *не полным аналогом* фосфора.

Аналогичность электронной конфигурации атомов для ванадия и фосфора в степени окисления +5 обуславливает сходства свойств их химических соединений.

В ходе сравнения ванадия и его соединений с элементами VA подгруппы мы пришли к выводу, что ванадий- связующий элемент между подгруппой VA и подгруппой VB, а соединения обладают аналогичными свойствами.

В результате многолетней работы было установлено, что ванадий в пяти и четырехвалентном состоянии обладает парамагнетизмом. В сырой нефти он находится в четырехвалентном состоянии.

С целью усовершенствования стандартного фотокалориметрического метода определения ванадия в золах нефтей и нефтепродуктах в работе предложена более экспрессная методика для оценки общего количества ванадия, основанная на взаимодействии V_2O_5 с концентрированной соляной кислотой.

В идентификации порфириновых комплексов природного происхождения большое значение имели исследования спектров ЭПР комплексов порфиринов с такими переходными металлами, как медь.

В ходе сравнения экспериментальных работ парамагнитных свойств ванадия и фосфора друг с другом, можно сказать, что их применение имеет большое практическое значение в разных областях науки.

Подводя итоги изучения восстановления трифенилфосфина щелочным металлом, мы предложили схему расщепления трифенилфосфина, включающую образование анион радикалов.

Ключевые слова: связующий d-элемент, ванадий, неполный аналог, электронная структура, парамагнетизм.

Information about the authors:

Nasirov R., **Doctor of Chemical Sciences, Professor of** Atyrau State University named after H.Dosmuhamedov, <https://orcid.org/0000-0003-4023-7689>; nasirov.48@mail.ru;

Kalauova A.S., **Candidate of Chemical Sciences, Docent of** Atyrau Oil and Gas University named after S. Utebayev, <https://orcid.org/0000-0003-3024-6020>; skalauova@mail.ru;

Kuspanova B., **Candidate of Chemical Sciences, Docent of** Atyrau Oil and Gas University named after S. Utebayev, <https://orcid.org/0000-0002-6209-8352>; kuspanovabagila@mail.ru;

Satenov K.G., **Candidate of Chemical Sciences, Head of the Department of Chemistry and Chemical Technology of** Atyrau State University named after H.Dosmuhamedov, <https://orcid.org/0000-0002-6396-913X>; satenoff@mail.ru;

REFERENCES

- [1] Chang R. General Chemistry.-New York. Higher Education. 2006.734 p.
- [2] Akhmetov N.S. General and inorganic chemistry. M. High school. 2001.743p. (in Russ.).
- [3] Greenwood N., Earnshaw A. Chemistry of elements. Book 1. M.: Binom. Laboratory of Knowledge, 2008. 607 p. (in Russ.).
- [4] Matveeva E.F., Nasirov R.N. Natural complexes. Composition, structure, use. Chemistry at school. No. 9. 2013. p. 7-9. (in Russ.).
- [5] Nekrasov B.V. Fundamentals of General Chemistry. M. Publ. Chemistry. 1969. Volume 3. p. 236. (in Russ.).
- [6] Nasirov R., Nasirov A.R. Investigation of Vanadium in Crude Oils of the Caspian Region by Electronic Paramagnetic Resonance (EPR). Abstract of 48th Rocky mountain conference on analytical chemistry. Breckenridge. Colorado. 2006. P. 65.
- [7] Nasirov R. Free radicals in the interaction of sterically hindered orthoquinones with vanadyl chloride // Reports of NAS RK, 1995. No. 5. p.63-65. (in Russ.).
- [8] Razuvaev G.A., Abakumov G.A., Klimov E.S. Complexes of o-semiquinones with metal chlorides of group III // Reports of USSR Academy of Sciences. 1971. V. 201. Number 3. p.624-627. (in Russ.).
- [9] Nasirov R. Complexes of porphyrins of the Karazhanbass oil with transition metal ions // Chemistry of Natural Compounds. 1990. No. 5. p.621-624. (in Russ.).
- [10] Britt A.D., Kaiser E.T. Phys. Chem. **69**, 2775 (1965).
- [11] Nasirov R., Solodovnikov S.P., Kabachnik M.I. The study of the reduction and cleavage of triphenylphosphine by alkali metals by the EPR method // Bulletin of the USSR Academy of Sciences, Chemical series. 1976.№10. p.2387-89.
- [12] Ilyasov A.V., Kargin Yu.M., Morozova I.D. EPR spectra of organic ion radicals. -M.: Nauka, 1980.-168 p. (in Russ.).
- [13] Kabachnik M.I. Chemistry of organophosphorus compounds. Selected Works: in 3 v. / Inst. Organoelement compounds n/a A.N. Nesmeyanov RAS.- M.: Nauka, 2008. (in Russ.).
- [14] Kaminsky V.A. Organic chemistry. Part 2. M.: Yurayt Publishing House, 2017. - 314 p. (in Russ.).
- [15] Velikorodov A.V. Organic synthesis. -Moscow: Knorus, 2016, 375 p. (in Russ.).
- [16] Nasirov R., Solodovnikov S.P., Tumansky B.L., Bubnov N.N., Kardanov N.A., Petrova R.G., Churkina T.D., Kandror I.I. EPR spectra of phosphonylthio substituted ethyl radicals // News of USSR Academy of Sciences, Ser. Chem., 1984. No. 10. p. 2224-2229. (in Russ.).
- [17] Nasirov R., Tumansky B.L., Malysheva N.A., Kardanov N.A., Godovikov N.N., Bubnov N.N., Prokofiev A.I., Kabanchik M.I., Solodovnikov S.P. Interaction of phosphonyl radicals with spatially-hindered carbonyl compounds // News of USSR Academy of Sciences, Ser. Chem., 1985. No. 2. p. 420-427. (in Russ.).