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# Х А Б А Р Л А Р Ы

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## ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК  
РЕСПУБЛИКИ КАЗАХСТАН

АО «ИНСТИТУТ ТОПЛИВА, КАТАЛИЗА И  
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## NEWS

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OF THE REPUBLIC OF KAZAKHSTAN

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R.N. Nasirov

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rnasirov.48@mail.ru**DETERMINATION OF VANADIUM IN THE PRECASPIAN REGION'S OIL BY THE EPR-SPECTROSCOPY METHOD**

**Abstract.** In the article of 1977, it is considered the preparation of anisotropic EPR spectrum of a vanadyl ion complex consisting of 8 lines of hyperfine structure, as a result of a decrease in the viscosity of Karazhanbas oil. In recent years, lectures on EPR spectroscopy have been given in the subjects of petroleum chemistry and petroleum geology for students of higher educational institutions. The practical side of this lecture should begin with a simple isotropic vanadium spectrum. A method is proposed for determining vanadium and FR in crude oils at a temperature of liquid nitrogen. An important scientific and practical result of the proposed new method for the determination of vanadium in crude oils, in contrast to the method of American authors, is a reduction in nitrogen consumption, and an additional advantage of the method consists in reducing the cost of the process, since the use of an expensive temperature attachment is excluded. The EPR method is also proposed to estimate the total amount of vanadium in oil zones based on the interaction of  $V_2O_5$  with concentrated hydrochloric acid. The standard photocolometric method for the determination of vanadium in oil ash can be replaced by a more rapid and selective EPR technique.

**Keywords:** organic free radicals, vanadyl ion  $VO^{2+}$ , electron paramagnetic resonance, isotropic vanadium spectrum, anisotropic vanadium spectrum.

The first report on the paramagnetism of crude oils was made by N.S. Garifiyanov and B.M. Kozyrev in 1956 [1] who, while studying the oil of the Bavly field in the EPR spectrum, found a single absorption line with a g-factor equal to 2 (Fig. 1). H.K. Gutovsky and co-workers [2] found that most crude oils produce an EPR spectrum, this spectrum consisting of a single line with a g-factor of 2.009, a width of about 4.5 Oe, and hyperfine structure lines.

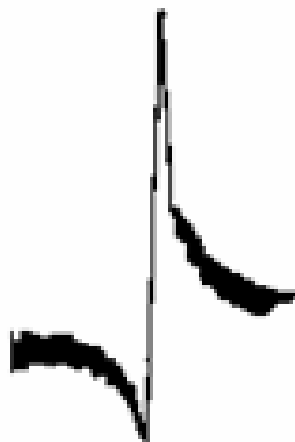


Figure 1-Electronic paramagnetic resonance in oil samples of the Bavly deposit (Tataria).  
A single line is due to the free radical ( $R \cdot$ ) of the asphaltene structure [2]

The latter was attributed to a paramagnetic vanadyl ion, and the singlet was due to free carbon bonds in condensed aromatic structures in colloidal particles of asphaltenes (Fig. 2).

A large number of lines indicates the anisotropic nature of the hyperfine interaction of an unpaired electron with the nuclear magnetic moment of the vanadium (spin of the nucleus -  $I_V=7/2$ ). The anisotropy of hyperfine interaction is caused by the high viscosity of the oil.

R. Nasirov and S.P. Solodovnikov [3,4] found that dissolution of oil in toluene (1:3.55) and heating to 120 °C in a vacuum sealed ampoule result in the complex anisotropic spectrum transforming into a simple isotropic spectrum consisting of 8 hyperfine structure lines (HFS) due to the interaction of an unpaired electron with the nuclear magnetic moment of the vanadium (nuclear spin -  $I_V=7/2$ ), as is seen in Fig. 3. The narrow ( $\Delta H = 7\pm 0.5$  G) intense line at the center of the spectrum belongs to the so-called "free radical" (R•).

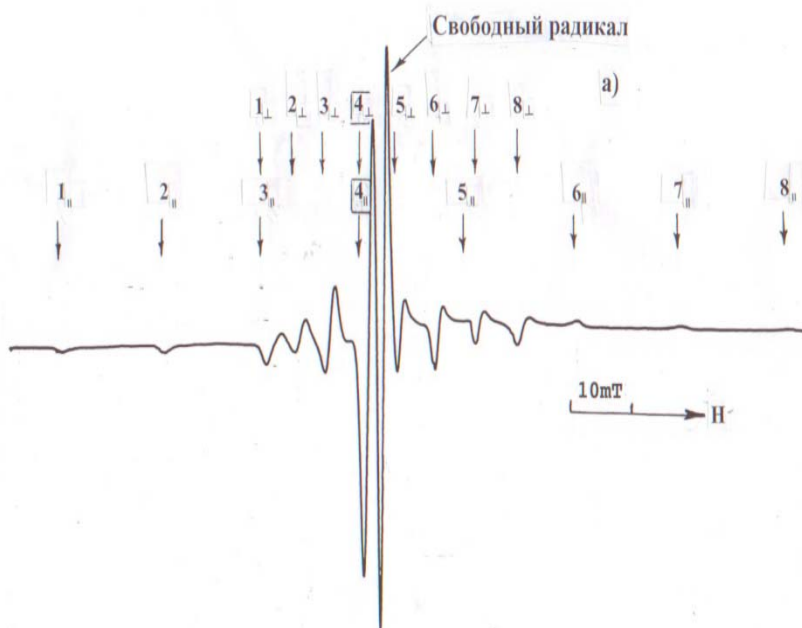


Figure 2- EPR spectrum of the Karazhanbas oil (well No. 851) at room temperature: the hyperfine lines  $I_{||}$ - $8_{||}$  and  $I_{\perp}$ - $8_{\perp}$  belong to the oxo-vanadyl  $VO^{2+}$  cations, and the single line in the high field refers to the free radical

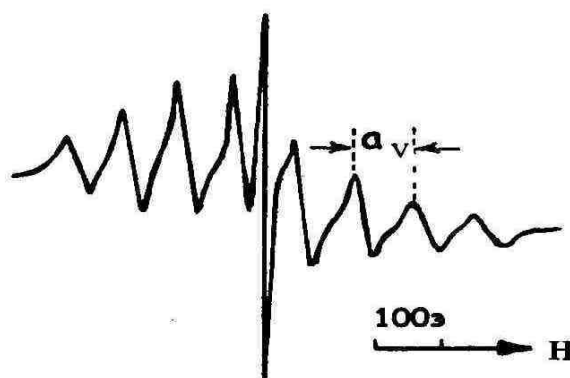


Figure 3-Isotropic EPR spectrum of vanadyl complexes ( $VO^{2+}$ ) of mixtures of the Karazhanbas oil with toluene (1:3.55) at + 120 °C

EPR spectra were recorded on the E-12 spectrometer of the "Varian" company at a frequency of 9000 MHz with a magnetic field strength of 3000 Oe. As a standard, the Urikhtau oil of the Emba region with a vanadium content of 28 g/t was used. For measurements, a double resonator was used, which makes it possible to monitor the recordings of each spectrum with the help of the "Strong pic" reference sample

included in the instrument. The amount of vanadium in the investigated oil samples was determined directly from the EPR spectra with the hyperfine structure of the complexes of tetravalent vanadium (see Fig. 4). The lines of HFS  $1_{\parallel} - 8_{\parallel}$  and  $1_{\perp} - 8_{\perp}$  belong to the oxo-vanadyl  $\text{VO}^{2+}$  cations. Of the two intense central lines, the line in the low field refers to the highest peak of  $4_{\perp}$  HFS  $\text{VO}^{2+}$ , and a single line in the high field - to the "coal" free radical. To determine the  $\text{V}^{4+}$  content, the amplitude of the most intense line of the spectrum, which is adjacent to a single line of the free radical in the region of a weaker magnetic field, was measured.

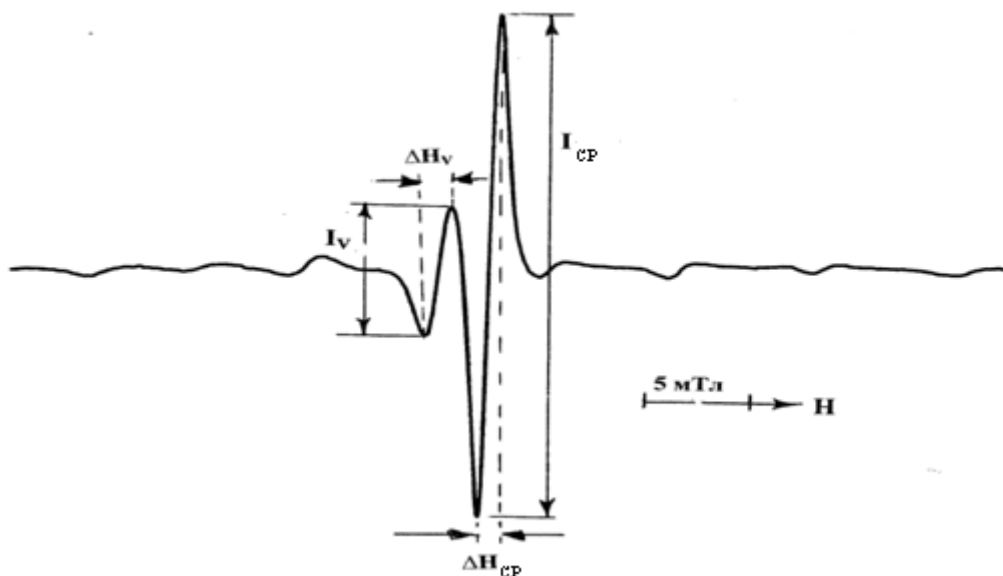


Figure 4-The central parts of the EPR spectrum (at liquid nitrogen temperature) of the oil of the Urikhtau deposit, well # 8:  $I_V$  - the amplitude of the vanadium signal,  $I_{CP}$  - the amplitude of the FR signal

The  $\text{V}^{4+}$  content was determined by comparing the spectral amplitudes of the investigated sample  $I_V$  and the standard  $I_{cr}$  by the formula:  $C_V = I_V I_{3,cr} / I_{cr} I_3$ , where  $I_{3,cr}$  - the amplitude of the reference sample line when recording the standard spectrum;  $I_3$  - the amplitude of the same line when recording the spectrum of the sample. It was assumed that the widths of the spectral lines of the sample and the standard are the same.

On the recommendation of the American authors [5], the EPR spectra of  $\text{V}^{4+}$  are measured at a temperature of  $-90^\circ\text{C}$ , at which the oil hardens, and the amplitude of the measured signal does not depend on the viscosity of the oil. Thermostating of the sample was carried out by blowing it with nitrogen gas, heated to a given temperature.

Of particular interest was the effect on the accuracy of the determination of vanadium in oils extracted from different wells, the use of liquid nitrogen temperature ( $-196^\circ\text{C}$ ), which greatly expands the possibilities of laboratory determination of vanadium and increases the efficiency of the method.

Before using liquid nitrogen as a coolant in the determination of vanadium, it was necessary to investigate the nature of the saturation curves of EPR signals  $\text{V}^{4+}$  depending on the power  $P$  of ultra-high frequency, since such a dependence exists.

Figure 5 shows the saturation curves of the  $\text{V}^{4+}$  EPR signal as a function of the square root of the UHF power taken in a special double resonator at various temperatures.

In the first case, a quartz Dewar vessel (Figure 6) containing an ampoule with oil in liquid nitrogen was located in one resonator, in the second resonator, there was the standard "Strong pitch" of the E-12 spectrometer of the Varian company, used to monitor the UHF power.

In the second case, in the determination of vanadium at  $-90^\circ\text{C}$ , a quartz vacuum-treated tube with the oil sample was used in one resonator through which nitrogen vapors of the corresponding temperature were blown, in the second resonator, there was a standard.

Since, in the absence of saturation, the intensity of the EPR signal is  $I \approx \sqrt{P}$ , the intensity of the standard was a relative measure used as the scale of abscissas in Fig. 5.



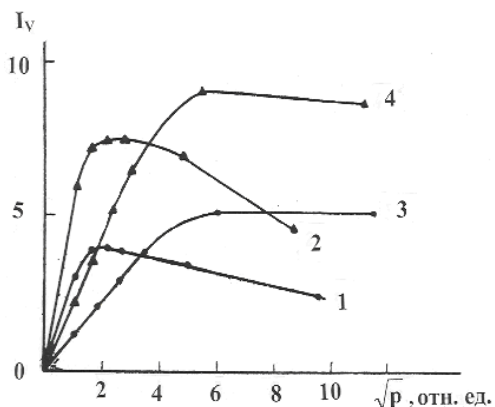


Figure 5 - Dependence of intensity change I EPR  $V^{4+}$  of oil of the South-East Kamyshitovoye field on  $\sqrt{P}$ .  
Well 1: 1 - at -196 °C, 3- at -90 °C; well 16: 2 - at -196 °C, 4 - at -90 °C

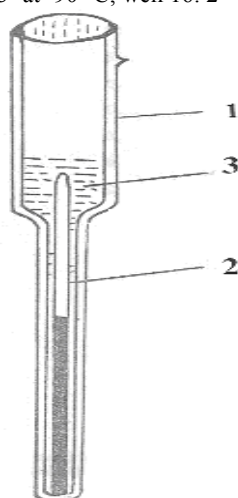


Figure 6-System for measuring EPR spectra of oils at liquid nitrogen temperature:  
1 - Dewar vessel; 2 - ampoule with oil; 3 - liquid nitrogen

Table 1- Results of the  $V^{4+}$  determination in the region of linear dependence  
of I on  $\sqrt{P}$  on the South-East Kamyshitovoye deposit

N of well	$V^{4+}$ , g/t	
	-90°C	-196°C
1	25.0	25.0
2	68.6	40.0
3	10.3	10.6
4	16.8	16.5
5	15.5	15.7
14	36.7	34.7
16	71.0	68.3
19	24.6	24.1
21	11.2	10.5
110	71.1	70.8
111	34.3	35.0
115	14.5	14.1
117	10.9	10.2
123	10.2	10.3
120	11.6	10.6

As can be seen from Figure 5, there is a significant region of linear dependence of I on  $\sqrt{P}$ , in which a correct determination of the  $V^{4+}$  vanadium content is possible at both -90 °C and -196 °C. Regardless of the concentration of vanadium (see wells 1 and 16 in Table 1), the regions of linear dependence for the

same temperature are approximately the same, but differ significantly at different temperatures: at  $-196^{\circ}\text{C}$ , the linear section is about 3 times shorter than at  $-90^{\circ}\text{C}$ .

Table 1 presents a good correspondence of the data, which makes it possible to recommend the use of liquid nitrogen as a coolant in mass laboratory determinations of vanadium.

In order to improve the standard photocolorimetric method for determination of vanadium in oil ash, a more rapid method was proposed for estimating the total amount of vanadium in oil ash, based on the interaction of  $\text{V}_2\text{O}_5$  with concentrated hydrochloric acid according to the following scheme:



Figure 7 shows the anisotropic EPR spectrum of vanadium chloride formed from reactive vanadium oxide. The same spectrum was obtained from the ash of Kalamkas oil, well N 52 (Fig. 7) and other oils. The concentration of vanadium in the studied oil ash (Table 2) of the Caspian region is determined from the anisotropic EPR spectrum of the formed vanadium chloride by the methods of [6-8]. As can be seen from Table. 2, the results of determining the content of vanadium in oil ash by the chemical method and EPR and XRF methods are consistent. The advantage of the EPR method for determining the total vanadium from oil ash is its productivity, selectivity, high accuracy and reliability in comparison with conventionally used photocolorimetric methods.

Table 2-Vanadium content in oils and their ash, %

Oil	Ash output	Vanadium content		Vanadium content per ash
		по РФА	по ЭПР	
Kalamkas, 52	0.087	0.015	0.0148	17.5
Botakhan, 68	0.037	0.0025	0.0022	12.9
Karazhanbas, 851	0.09	0.029	0.026	28.9

The results of these studies on the determination of vanadium in crude oils using EPR-radiospectroscopy were used by geologists and scientists of the All-Russian Petroleum Research Exploration Institute (VNIGRI) as reference samples for calculating the geological reserves of vanadium in the Karazhanbas, North Buzachinsky, Kalamkas and Zhalgiztobe oil fields of the Mangyshlak region (Act on the Use of Materials by R. Nasirov in the works on calculating the reserves of vanadium in the oil deposits of the Mangyshlak region, 24.03.1992, №08-signed by the head of the department of the VNIGRI, doctor of geological and mineralogical sciences, laureate of the State award, V.V. Gribkov) [9].

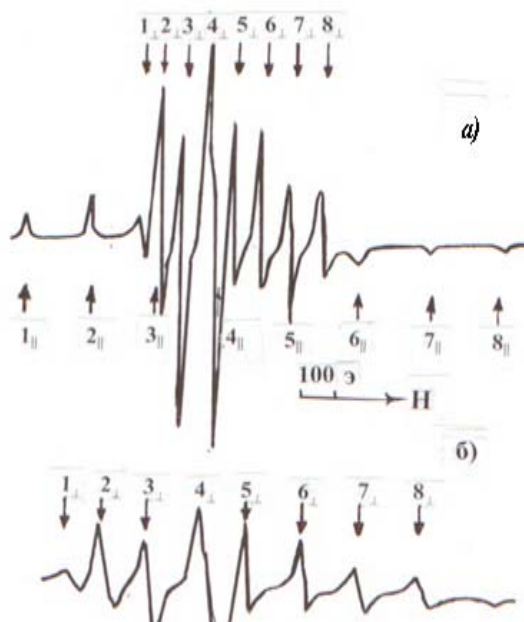


Figure 7- EPR spectra of vanadyl chloride at  $-196^{\circ}\text{C}$ , obtained: a) from  $\text{V}_2\text{O}_5$  b) from the ash of Kalamkas oil, well N 52 (here are recorded the hyperfine lines  $1_{\perp} - 8_{\perp}$  of vanadyl ion)

The developed method "The results of determination of tetravalent vanadium in oils by the EPR spectroscopy" is also recommended for students of higher education institutions studying in the specialties "Geology and geochemistry of oil and gas" [10] and "Oil and gas chemistry" [11]. In these textbooks, EPR spectroscopy is widely used not only in petrochemistry, but also in other geological and geochemical studies, in particular, in the allocation of oil strata on the relationship between the concentration of ions of divalent manganese, vanadium  $V^{4+}$  and FR in rocks

The presence of porphyrins with vanadium in the form of vanadyl ion  $VO^{2+}$  is evidence in favor of the theory of the organic origin of oil (chemofossilia). pigments with a porphyrin structure (plant chlorophyll, animal hemoglobin) are considered as biological precursors of oil porphyrins widely distributed in nature [12]. Allocated from vanadylporphyrin concentrates of Karazhanbas oil, free porphyrins were used by us to obtain complex copper compounds [13]. In order to establish the structure of the oil porphyrins in the EPR spectrum, hyperfine splitting from the interaction of an unpaired electron with copper nuclei and four atoms of  $^{14}N$  pyrolic rings was observed.

### Conclusions.

1. It was found that dissolution of oil in toluene (1:3.55) and heating to 120 °C in a vacuum-sealed ampoule result in the complex anisotropic spectrum transforming into a simple isotropic spectrum consisting of 8 hyperfine structure lines (HFS), caused by the interaction of the unpaired electron with the nuclear magnetic moment of the vanadium (the nuclear spin  $I_v=7/2$ ).

2. For the first time a new method for determination of vanadium and FR in crude oils at liquid nitrogen temperature is proposed. An important scientific and practical result of the new proposed method for the determination of vanadium in crude oils, in contrast to the method of American authors, is a reduction in nitrogen consumption, and an additional advantage of the method is to reduce the cost of the process, since the use of an expensive temperature attachment is excluded.

3. The advantage of the EPR method for determining the total vanadium in oil ash is its productivity, selectivity, high accuracy and reliability in comparison with conventionally used photocolometric methods.

4. The developed method "The results of determination of tetravalent vanadium in oils by the EPR spectroscopy" is also recommended for students of higher educational institutions studying in the specialization of "Geology and geochemistry of oil and gas" and "Oil and gas chemistry".

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### **ЭПР СПЕКТРОСКОПИЯ КӨМЕГІМЕН КАСПИЙ МАҢЫНДАҒЫ МҰНАЙЛАРДАҒЫ ВАНАДИЙДІ АНЫҚТАУ**

**Аннотация.** Мақалада 1977 жылы мұнайдың тұтқырлығын азайту нәтижесінде төрт валентті ванадий ионы комплексінің 8-желіден тұратын тәжірибелік изотропты ЭПР-спектрі алынғаны сөз болады. Соңғы жыдары мұнай химиясы және геологиясы пәндері бойынша студенттерге ЭПР – спектроскопиядан дәрістер оқыла бастады, ал дәрістің практикалық негізі осы жәй изотропты спектрден бастау алынуы керек. Ванадийді және еркін радикалды мұнайларда сұйық азот температурасында анықтау әдісі ұсынылады. Зертхана жағдайында ванадийді жаппай анықтау кезінде ұсынылған әдістің американдық ғалымдардың ұсынысынан өзгешілігі азотты көп шығындамайды, температура қондырғысын қажет етпейтіндігі және экспресті болатындығы. Сол сияқты бұл жұмыста ЭПР әдісі мұнайдың күліндегі жалпы ванадийді анықтауға болатындығы тәжірибе негізінде дәлелденді және қазіргі кезде қолданылып жүрген фотоколориметрлік әдісті толық ығыстырады.

**Түйін сөздер:** органикалық еркін радикалдар, ванадил ионы  $VO^{2+}$ , электрондық парамагниттік резонанс, ванадийдің изотропты спектрі, ванадийдің анизотропты спектрі.

УДК 546.881:553.982:538.113

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### **ОПРЕДЕЛЕНИЕ ВАНАДИЯ В НЕФТЯХ ПРИКАСПИЙСКОГО РЕГИОНА МЕТОДОМ ЭПР-СПЕКТРОСКОПИИ**

**Аннотация.** В статье 1977 года рассматривается получение изотропного спектра ЭПР комплексного иона ванадила, состоящего из 8 линий сверхтонкой структуры, в результате уменьшения вязкости Каражанбасской нефти. В последние годы по предметам: химии нефти и геологии нефти для студентов высших учебных заведений читаются лекции по ЭПР – спектроскопии. Практическая сторона этой лекции должна начинаться с простого изотропного спектра ванадия. В работе предлагается способ определения ванадия и СР в сырых нефтях при температуре жидкого азота. Важным научно-практическим результатом предлагаемого нового способа определения ванадия в сырых нефтях, в отличие от метода американских авторов является снижение расхода азота, а дополнительное преимущество способа заключается в удешевлении процесса, так как исключается применение дорогостоящей температурной приставки при массовых лабораторных определениях ванадия. Так же предлагается метод ЭПР для оценки общего количества ванадия в золах нефти, основанной на взаимодействии  $V_2O_5$  с концентрированной соляной кислотой. Стандартный фотоколориметрический метод определения ванадия в золах нефтей можно заменить более экспрессной и избирательной методикой ЭПР.

**Ключевые слова:** органические свободные радикалы, ион ванадила  $VO^{2+}$ , электронный парамагнитный резонанс, изотропный спектр ванадия, анизотропный спектр ванадия.

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МАЗМҰНЫ

<i>Кантуреева Г.О., Defrancesco E., Алибеков Р.С., Уразбаева К.А., Ефимова И.Е.</i> Қазақстанның дәстүрлі азық-түлік өнімдерді сәйкестендіру жаңа тенденциялары .....	6
<i>Туктин Б.Т., Теңізбаева А.С., Нұрғалиев Н.Н., Шаповалова Л.Б., Яскевич В.И.</i> Модифицирленген Ni(Co)-Mo- Al <sub>2</sub> O <sub>3</sub> катализаторларында тура айдалған бензин фракциясын гидроизомерлеу және гидроөңдеу .....	13
<i>Ахметалимова А.М., Ивасенко С.А., Марченко А.Б., Ишмуратова М.Ю., Полезчак Э., Людвичук А., Посева И.В.</i> Қарағанды өңіріндегі <i>THYMUS EREMITA</i> KLOK. және <i>THYMUS RASITATUS</i> KLOK. өсімдіктерінің химиялық құрамын зерттеу.....	20
<i>Фазылов С.Д., Нұркенов О.А., Журинов М.Ж., Әрінова А.Е., Туктаров А.Р., Исәева А.Ж., Шаихова Б.К.</i> С <sub>60</sub> фуллеренге гидразондардың палладий комплекстерімен катализденетін циклооксидің синтезі .....	26
<i>Опимах Е.В., Левданский А.Э., Голубев В.Г., Корганбаев Б.Н., Сарсенбекулы Д.</i> Ұсақтау барысындағы меншікті энергия шығындарын төмендетудің келешекті бағыттары .....	32
<i>Қапсәмет М.Ж., Тәжібаева С.М., Уракаев Ф.Х., Уралбеков Б.М., Бүркімбаев М.М., Бачилова Н.В.</i> Нанокүкіртті алу және тұрақтандыру .....	41
<i>Байсанов С.О., Толоконникова В.В., Нарикбаева Г.И., Корсукова И.Я., Жучков В.И.</i> Күй диаграммасына талдау жасау негізінде марганецті және хромды феррокорытпаларды балқытуға термодинамикалық бағалау.....	47
<i>Құлекеев Ж.Ә., Нұртаева Г.Қ., Мұстафин Е.С., Айнабаев А.А., Мұстафин Т.Е., Борсынбаев А.С., Жарикесов Ф.А.</i> Теңізге төгілген мұнайды жоюда хердерлерді пайдаланудың мүмкіндіктері .....	58
<i>Туктин Б.Т., Нурғалиев Н.Н., Тенизбаева А.С., Шаповалова Л.Б., Комашко Л.В.</i> Бензиннің әртүрлі фракцияларын модифицирленген алюмокобальтмолибден катализаторларында гидрожақсарту .....	67
<i>Қалдыбекова А.Ж., Амангазиева А.Т., Халменова З.Б., Үмбетова А.К.</i> <i>Harporhyllum</i> A. Juss шөбінен биологиялық белсенді заттардың кешенді бөліну технологиясын дамыту .....	74
<i>Опимах Е.В., Левданский А.Э., Волненко А.А., Жумадуллаев Д.К.</i> Флотациялық процесстерді жүргізу әдістері .....	82
<i>Чиркун Д. И., Левданский А. Э., Волненко А.А., Сарсенбекулы Д.</i> Соккылы-ортдан тепкіш диірмендердегі бөлшектердің динамикасын зерттеу .....	92
<i>Баймұқашева Г.К., Қалауова А.С., Құспанова Б.К., Насиров Р.Н.</i> Үшфенилфосфиннің анион-радикалы.....	102
<i>Баешова А.К., Молайган С., Баешов А.Б.</i> Сутектік энергетиканың қазіргі замандағы жағдайы және сутекті алу әдістері .....	107
<i>Закарина Н.А., Дәлелханұлы О., Жумадуллаев Д.А., Акурпекова А.К., Джумабаева Л.С.</i> Al, AlZr және Ti-мен пилларирленген Na- және Ca-формалы монтмориллонитке енгізілген Pt- және Pd-катализаторларындағы тікелей айдалған бензиннің жеңіл фракциясының изомеризациясы.....	117
<i>Нәсіров Р.Н.</i> ЭПР спектроскопия көмегімен каспий маңындағы мұнайлардағы ванадийді анықтау.....	125
<i>Байжуманова Т.С., Тунгатарова С.А., Xanthopoulou G., Жексенбаева З.Т., Кауменова Г.Н., Еркибаева М.К., Жумабек М., Касымхан К.</i> Метанның олефиндерге дейін каталитикалық конверсиясы.....	132
<i>Калимукашева А.Д., Калиманова Д.Ж., Иманкулова З.А.</i> Формативті бағалау-химия сабақтарында оқыту процесінің ажырамас бөлігі.....	139
<i>Масенова А.Т., Калыкбердиев М.К., Сасс А.С., Кензин Н.Р., Канатбаев Е.Т., Цыганков В.П.</i> Бензин фракцияларындағы хош иісті көмірсутектерді жоғары қысымда отырғызылғын катализаторларды қолдану арқылы сутектендіру.....	146

## СОДЕРЖАНИЕ

<i>Кантуреева Г.О., Defrancesco E., Алибеков Р.С., Уразбаева К.А., Ефимова И.Е.</i> Новые тенденции в идентификации традиционной пищевой продукции Казахстана .....	6
<i>Туктин Б.Т., Тенизбаева А.С., Нурғалиев Н.Н., Шаповалова Л.Б., Яскевич В.И.</i> Исследование гидроочистки и гидроизомеризации прямогонной бензиновой фракции на модифицированных Ni(Co)-Mo- Al <sub>2</sub> O <sub>3</sub> - катализаторах .....	13
<i>Ахметалимова А.М., Ивасенко С.А., Марченко А.Б., Ишмуратова М.Ю., Полезчак Э., Людвичук А., Лосева И.В.</i> Исследование химического состава <i>THYMUS EREMITA KLOK.</i> и <i>THYMUS RASITATUS KLOK.</i> Карагандинского региона .....	20
<i>Фазылов С.Д., Нуркенов О.А., Журинов М.Ж., Аринова А.Е., Туктаров А.Р., Исаева А.Ж., Шахова Б.К.</i> Катализируемое комплексами палладияциклоприсоединение гидразонов к фуллерену C <sub>60</sub> .....	26
<i>Опимах Е.В., Левданский А.Э., Голубев В.Г., Корганбаев Б.Н., Сарсенбекулы Д.</i> Перспективные направления снижения удельных энергозатрат при измельчении .....	32
<i>Кансамет М.Ж., Тажиббаева С.М., Уракаев Ф.Х., Уралбеков Б.М., Буркитбаев М.М., Бачилова Н.В.</i> Получение и стабилизация наносеры .....	41
<i>Байсанов С.О., Толоконникова В.В., Нарикбаева Г.И., Корсукова И.Я., Жучков В.И.</i> Термодинамическая оценка выплавки марганцевых и хромистых ферросплавов на основе анализа их диаграмм состояния .....	47
<i>Кулекеев Ж.А., Нуртаева Г.К., Мустафин Е.С., Айнабаев А.А., Мустафин Т.Е., Борсынбаев А.С., Жарикесов Г.А.</i> Возможности использования хердеров при ликвидации разливов нефти на море .....	58
<i>Туктин Б.Т., Нурғалиев Н.Н., Тенизбаева А.С., Шаповалова Л.Б., Комашко Л.В.</i> Гидрооблагораживание различных бензиновых фракций на модифицированных алюмокобальтмолибденовых катализаторах .....	67
<i>Калдыбекова А.Ж., Амангазиева А.Т., Халменова З.Б., Умбетова А.К.</i> Разработка технологии комплексного выделения биологических активных веществ из растений рода <i>Naplophyllum</i> A. Juss .....	74
<i>Опимах Е.В., Левданский А.Э., Волненко А.А., Жумадуллаев Д.К.</i> Методы проведения флотационных процессов .....	82
<i>Чиркун Д. И., Левданский А. Э., Волненко А.А., Сарсенбекулы Д.</i> Исследование динамики частиц в ударно-центробежных мельницах .....	92
<i>Баймукашева Г.К., Калауова А.С., Куспанова Б.К., Насиров Р.Н.</i> Анион-радикал трифенил-фосфина .....	102
<i>Баешова А.К., Молайган С., Баешов А.Б.</i> Современное состояние водородной энергетики и способы получения водорода .....	107
<i>Закарина Н.А., Дәлелханұлы О., Жумадуллаев Д.А., Акурпекова А.К., Джумабаева Л.С.</i> Изомеризация легкой фракции прямогонного бензина на Pt- и Pd-катализаторах, нанесенных на пилларированный Al, AlZr и Ti монтмориллонит в Na- и Ca-формах .....	117
<i>Насиров Р.Н.</i> Определение ванадия в нефтях прикаспийского региона методом ЭПР-спектроскопии .....	125
<i>Байжуманова Т.С., Тунгатарова С.А., Xanthoroulou G., Жексенбаева З.Т., Кауменова Г.Н., Еркибаева М.К., Жумабек М., Касымхан К.</i> Каталитическая конверсия метана в олефины .....	132
<i>Калимукашева А.Д., Калиманова Д.Ж., Иманкулова З.А.</i> Формативное оценивание - неотъемлемая часть процесса обучения на уроках химии .....	139
<i>Масенова А.Т., Калыкбердиев М.К., Сасс А.С., Кензин Н.Р., Канатбаев Е.Т., Цыганков В.П.</i> Гидрирование ароматических углеводородов в бензиновых фракциях на нанесенных катализаторах под давлением .....	146

CONTENTS

<i>Kantureeva G.O., Defrancesco E., Alibekov R.S., Urazbayeva K.A., Efimova I.E.</i> New trends in the identification of the traditional food products of Kazakhstan .....	6
<i>Tuktin B.T., Tenizbaeva A.S., Nurgaliyev N.N., Shapovalova L.B., Yaskevich V.I.</i> Study of hydro purification and hydroisomerization straight-run gasoline fraction over modified Ni(Co)-Mo- Al <sub>2</sub> O <sub>3</sub> - catalysts .....	13
<i>Akhmetlimova A.M., Ivashenko S.A., Marchenko A.B., Ishmuratova M.Yu., Poleszak E., Ludwiczuk A., Loseva I.V.</i> The study of the chemical composition of <i>THYMUS EREMITA</i> KLOK. and <i>THYMUS RASITATUS</i> KLOK. from the Karaganda region .....	20
<i>Fazylov S.D., Nurkenov O.A., Zhurinov M.Zh., Arinova A.E., Tuktarov A.R., Issayeva A.Zh., Shaihova B.K.</i> Catalyzed by palladium complexes the cycloaddition of hydrazones to fullerene C <sub>60</sub> (in English).....	26
<i>Apimakh Ye.V., Leudanski A.E., Golubev V.G., Korganbayev B.N., Sarsenbekuly D.</i> Promising directions of reducing specific energy costs in grinding (in English).....	32
<i>Kapsamet M.Zh., Tazhibayeva S.M., Urakaev F.Kh., Uralbekov B.M., Burkitbayev M.M., Bachilova N.V.</i> Obtaining and stabilization of nanosulfur .....	41
<i>Baisanov S.O., Tolokonnikova V.V., Narikbayeva G.I., Korsukova I.Ya., Zhuchkov V.I.</i> Thermodynamic assessment of smelting of manganese and chromium ferroalloys based on the analysis of their state diagrams .....	47
<i>Kulekeyev Zh.A., Nurtayeva G.K., Mustafin E.S., Ainabayev A.A., Mustafin T.E., Borsynbayev A.S., Zharikessov G.A.</i> Using herders for oil spill response in the sea .....	58
<i>Tuktin B.T., Nurgaliyev N.N., Tenizbaeva A.S., Shapovalova L.B., Komashko L.V.</i> Hydrotreating of various petrol fractions over modified alumocobaltmolybdenic catalysts .....	67
<i>Kaldybekova A.Zh., Amangazyeva A.T., Halmenova Z.B., Umbetova A.K.</i> Development of technology for the complex isolation of biological active substances from plants of the genus <i>Haplophyllum</i> A. Juss .....	74
<i>Apimakh Ye.V., Leudanski A.E., Volnenko A.A., Zhumadullaev D.K.</i> Methods of carrying out flotation processes .....	82
<i>Chyrkun D.I., Levdanskiy A.E., Volnenko A.A., Sarsenbekuly D.</i> Study of the particle dynamics in impact-centrifugal mills (in English).....	92
<i>Baymukasheva G.K., Kalauova A.S., Kuspanova B., Nasirov R.N.</i> Triphenylphosphine anion radical.....	102
<i>Bayeshova A.K., Molaigan S., Bayeshov A.B.</i> Hydrogen energetics current state and hydrogen production methods.....	107
<i>Zakarina N.A., Dolelkhanyly O., Jumadullaev D.A., Akurpekova A.K., Djumabaeva L.S.</i> Isomerization of light fraction of straight-run gasoline on Pt-and Pd-catalysts supported on pillared by Al, AlZr and Ti montmorillonite in Na-and Ca-forms.....	117
<i>Nasirov R.N.</i> Determination of vanadium in the precaspian region's oil by the EPR-spectroscopy method.....	125
<i>Baizhumanova T.S., Tungatarova S.A., Xanthopoulou G., Zheksenbaeva Z.T., Kaumenova G.N., Erkibaeva M.K., Zhumabek M., Kassymkan K.</i> Catalytic conversion of methane into olefins.....	132
<i>Kalimukasheva A.D., Kalimanova D.Z., Imankulova Z.A.</i> Formative evaluation is an uninterrupted part of the training process on lessons of chemistry.....	139
<i>Massenova A.T., Kalykberdiyev M.K., Sass A.S., Kenzin N.R., Kanatbayev E.T., Tsygankov V.P.</i> Hydrogenation of aromatic hydrocarbons in gasoline fractions over supported catalysts under pressure.....	146

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