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Ünvan: 20 Azadlıq pr., Bakı, AZ1010, Azərbaycan, Tel: +994124986533, E-mail: minira_baku@yahoo.com, mayaabdullayeva@hotmail.com.	

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Contacts	
Address: 20 Azadliq av., Baku, AZ1010, Azerbaijan, Phone: +994124986533, E-mail: minira_baku@yahoo.com, mayaabdullayeva@hotmail.com.	

CONTENT

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SYNTHESIS AND STUDY OF MIXED PROPYLENE GLYCOL DIESTERS OF SYNTHETIC PETROLEUM- AND FATTY ACIDS

N.F. Sadiyeva[0000-0002-1633-6292], *S.A. Iskenderova*[0000-0001-5192-0665],
Y.P. Cherepnova[0000-0001-6590-4797], *G.Q. Nasibova*[0000-0002-1460-3061],
L.M. Afandiyeva[0000-0002-1043-3446], *S.G. Aliyeva*[0000-0002-9169-8875]
Y.H.Mamedaliyev's Institute of Petrochemical Processes of the National Academy of Sciences of Azerbaijan
uta1980@inbox.ru

The article presents a one-stage method for the synthesis of mixed diesters based on propylene glycol, synthetic petroleum- and aliphatic fatty acids (C_6-C_8) using a ZnO catalyst under optimal conditions - temperature -110-120°C, amount of catalyst - 1.3% wt. (by acid), molar ratio of components - acid:alcohol - 2:1.3. The properties of the synthesized mixed diesters were studied and their parameters were determined by analytical and spectral methods. In order to determine the plasticizing properties of the mixed diesters, compositions were prepared under laboratory conditions with the addition 100 m.p. of polyvinyl chloride (PVC) for 30-70 m.p. of synthesized diesters and compared them with an industrial plasticizer - dioctyl phthalate. Also, these diesters have been studied as antioxidants that improve the thermal-oxidative stability of diesel fuel. An analysis of the research results shows that the synthesized mixed diesters can be proposed as effective plasticizers for PVC and new antioxidants for diesel fuels.

***Keywords**: propylene glycol, synthetic petroleum acids, mixed diesters, diesel fuel, antioxidant, polyvinyl chloride, plasticizer*

INTRODUCTION

Despite the significant volume of production of esters of carboxylic acids, the need for them is not fully satisfied, due to the shortage of raw materials and the creation of waste-free technology. Interest in such products is due to the fact that they are good solvents, plasticizers for polymeric materials and antioxidants for diesel fuels. From this point of view, the synthesis of such universal products (having good compatibility with polymers, chemical stability, low volatility, the ability to improve the thermal-oxidative properties of diesel fuels) based on available materials with a high yield is considers relevant and promising.

Considering the urgency of the problem and the prospects of esters, we have synthesized mixed glycol esters based on petroleum acids (PA), which exhibit properties as a solvent, plasticizer and antioxidant. Scientific studies on the preparation of PA esters with the participation of catalysts of various nature are reflected in the literature [1–5]. But, the need for esters of petroleum acids in the capacity of perspective products opens the way to the synthesis of new PA esters, which were obtained in this work.

EXPERIMENTAL PART

For obtain new diesters were used as raw materials synthetic petroleum acids (SPA), aliphatic fatty acids of the series C_6-C_8, propylene glycol (PG) and technical-ZnO as a catalyst. SPA was obtained by liquid-phase oxidation of the diesel fraction of a mixture of Azerbaijani oils in the presence of a catalyst (salt of petroleum acids) in a bubbling reactor at a temperature of 135-140°C (physicochemical parameters: acid number - 220 mg KOH / g, m.v. - 255 g/mol, n_D^{20}-1.4651, ρ_4^{20}-0.9805) [6,7].

The IR-spectrum of the SPA was recorded on an Alpha IR-Fourier spectrometer manufactured by the German company BRUKER (fig.1).

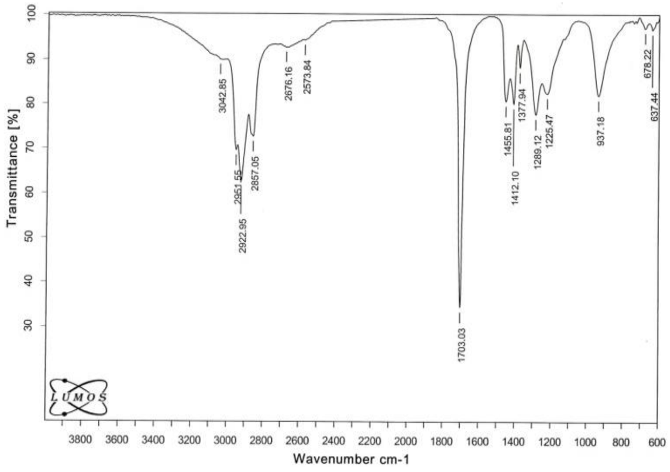
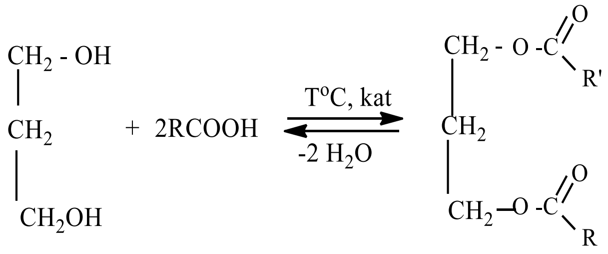


Fig.1. IR- spectrum of SPA.

In the IR- spectrum of the SPA were observed the following absorption bands:

937 sm^{-1}	– deformation vibrations of the O-H bond of the OH group of the acid;
1225, 1289 $sm-^{1}$	– C-O bonds of –COOH acid group;
1703 sm^{-1}	– C=O bonds of –COOH acid group;
1377, 1412, 1455, 2857, 2922, 2951 sm^{-1}	– bending and stretching vibrations of C-H bond of CH_3 and CH_2 groups;
2573, 2676 sm^{-1}	– COOH group of acid.

The preparation of mixed diesters of propylene glycol based on SPA and fatty acids with the participation of a ZnO catalyst was carried out by a one-stage method according to the following scheme:



where: R is the SPA radical, R^1 ÷ C_5H_{11}, C_6H_{13} and C_7H_{15} radicals.

Referring to previous studies [3], the influence of the molar ratio of reaction components, the amount of catalyst and temperature on the course of the reaction was studied and a number of reactions were carried out in order to select the optimal conditions for obtaining high yields of mixed PG diesters (table 1, fig. 2-4).

Table 1

Optimum conditions for the production of propylene glycol mixed diester based on SPA and caproic acid . SPA - 1 mol, $C_5H_{11}COOH$ - 1 mol

Amount of PG, mol	T,°C	Amount of catalyst, % wt.		Diester yield, %	
		ZnO	KU-2	ZnO	KU-2
1,1	80-90	1,1	9	50,2	40,5
1,2	80-90	1,3	10	56,4	42,8
1,3	80-90	1,4	11	70,2	50,3
1,1	110-120	1,3	10	70,1	50,8
1,2	110-120	1,3	11	80,2	69,0
1,2	130-140	1,4	10	89,8	72,0
1,3	110-120	1,3	12	92,8	75,0
1,4	110-120	1,4	13	92,8	75,1

To compare the catalytic properties of ZnO with the activity of other catalysts, we used the heterogeneous catalyst KU-2 (H^+). Due to the fact that KU-2(H+) is an acidic catalyst, the raw diester is subjected to additional processing: washing, neutralization, re-washing from alkali, due to which the process becomes multi-stage with waste production, the yield of diesters is 75% of theory, and with the use of ZnO increases by 20-25% (table 1).

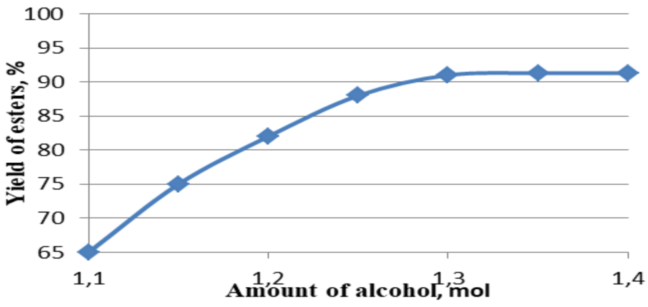


Fig.2. Dependence of the yield of propylene glycol diester based on SPA and caprylic acid from the amount of alcohol.

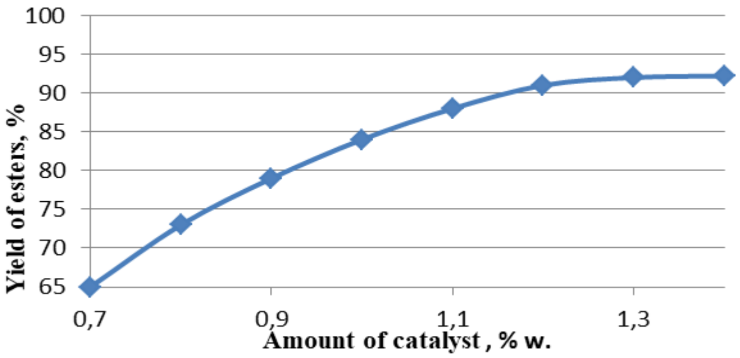


Fig.3. Dependence of the yield of propylene glycol diester based on SPA and caprylic acid from the amount of catalyst.

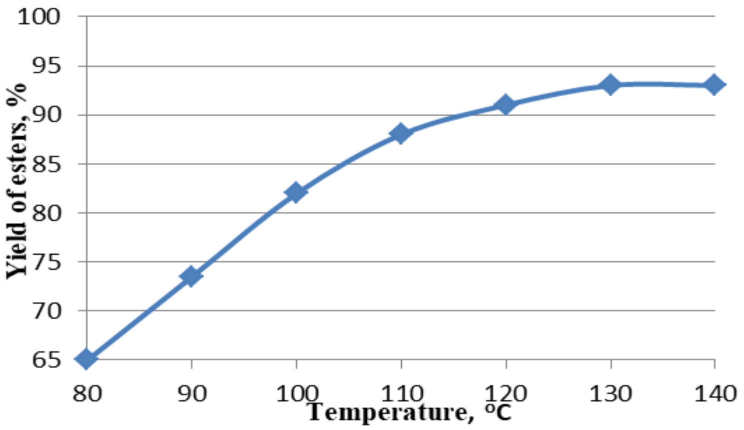


Fig.4. Dependence of the yield of propylene glycol diester based on SPA and caprylic acid from the amount of temperature.

At the optimal conditions (temperature - 110-120°C, amount of catalyst - 1.3%, acid:alcohol ratio - 2:1.3 mol), were synthesized mixed diesters of propylene glycol based on SPA and fatty acids. The following is a synthesis based on enanthic acid:

- 49.4 g (0.65 mol) of propylene glycol, 127.5 g (0.5 mol) of SPA, 65 g (0.5 mol) of enanthic acid, 2.5 g (0.03 mol) of ZnO catalyst, 171 .0 g (1.9 mol) of toluene was loaded into a three-necked flask and the reaction was continued for 3.5-4 hours. At the end of the reaction, the reaction product was filtered on a paper filter, the catalyst was removed, after the solvent was distilled off, the raw diester was subjected to vacuum distillation and the physicochemical parameters were determined (table 3). The material balance of the process of obtaining a mixed propylene glycol diester based on SPA and enanthic acid is compiled and shown in table 2.

In order to update a number of new antioxidants for diesel fuels, when mixed diesters were added to 100 ml of hydrotreated diesel fuel (D/F) at a concentration of 0.004%, studies were carried out and the maximum result was shown by a mixed propylene glycol diester synthesized on the basis of SPA and caprylic acid, where the amount of sediment from 4.6 mg/100 sm3 decreases to 1.2 mg/100 sm^3 [5].

Diesters obtained in the laboratory based on SPA, their high plasticity, as well as an increase in the service life of D/F, open up opportunities for further researches in this direction.

Table 2

Material balance of obtaining a mixed propylene glycol diester based on SPA and enanthic acid

Taken			Received		
Denomination	Amount		Denomination	Amount	
	g	%		g	%
SPA $C_7H_{15}COOH$	127,5 65,0	30,70 15,64	Waters	18,0	4,33
Propylene glycol	49,4	11,90	Propylene glycol	11,0	2,64
ZnO	2,5	0,60	ZnO	2,35	0,57
Toluene	171,0	41,16	Toluene	165,0	39,72
Total	415,4	100	Mixed diester	212,5	51,16
			Remainder	6,55	1,58
			Total	415,4	100

The IR- spectrum of a mixed propylene glycol diester based on SPA and enanthic acid is shown in fig. 5:

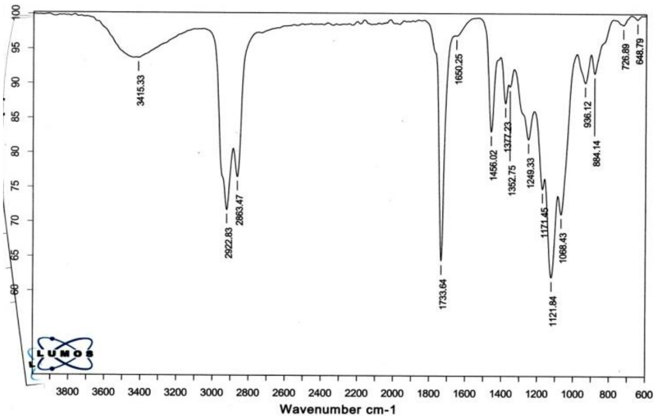


Fig.5. The IR- spectrum of a mixed propylene glycol diester based on SPA and enanthic acid.

In the IR- spectrum of the mixed diester were observed the following absorption bands:

3415 sm^{-1}	– stretching vibrations of the O-H bond of the COH group;
1121, 1171 $sm\text{-}^{1}$	– C-O-C bond of the mixed diester;
1733 sm^{-1}	– C=O bond of the mixed diester;
2863, 2922 sm^{-1}	– bending and stretching vibrations of C-H bond of CH_3 and CH_2 groups.

The physicochemical parameters of mixed propylene glycol diesters based on SPA and fatty acids were determined and are shown in table 3.

Table 3

Physicochemical parameters of mixed propylene glycol diesters based on SPA and fatty acids

R	Boiling temperature, °C, $2,66 \cdot 10^{-4}$ MPa	ρ_4^{20}, g/sm^3	n_D^{20}	A.n., mgKOH/g	S.n., mgKOH/g	Kinematic viscosity, mm^2/s	Volatility, %	Yield, %
C_5H_{11}	195-240	0,9859	1,4583	0,50	275,05	16,02	0,55	92,8
C_6H_{13}	205-255	0,9862	1,4580	0,35	270,15	17,10	0,57	90,85
C_7H_{15}	215-275	0,9867	1,4575	0,72	259,05	18,05	0,62	90,1

Seeing SPA mixed diesters are high-quality and effective plasticizers, the laboratory studied the compatibility of the synthesized diesters, as well as the industrial plasticizer - dioctyl phthalate with polyvinyl chloride (PVC) [2] by preparing compositions with the addition of 100 m.p. PVC, 30-70 m.p. tested diester, 1 m.p. stabilizer (calcium stearate) and these compositions were kept in a thermostat for 3-6 hours depending on the temperature at 65°C, 75°C, 85°C. After that, the compositions were cooled to room temperature, kept under a load of 0.5 kg until the greasy spots on the filter paper disappeared, and the optimal limit of compatibility with PVC was determined (30-40 m.p.).

CONCLUSION

Mixed diesters of propylene glycol based on SPA and fatty acids were synthesized with the participation of ZnO catalysts and it was found, that ZnO is theoretically and practically (intermediate stages shortened) more appropriate in the esterification process. In order to select the optimal synthesis conditions, the influence of various amounts of the catalyst, the molar ratio of the components involved in the reaction, and the temperature regime on the course of the reaction was studied, mixed diesters were synthesized in high yield (92.8%), their physicochemical parameters were determined analytically and spectrally. The compatibility of mixed diesters synthesized on the basis of SPA and fatty acids with PVC was studied, tested as a new component to improve the thermal-oxidative stability of D/F, and recommended as effective plasticizers for polymeric materials and high-quality antioxidants for D/F.

REFERENCES

1. Sadiyeva N.F., İskenderova S.A., Afandiyeva L.M., Babanlı N.N., Nasibova G.G. , Aliyeva S.G., Asadova Sh.N., “Synthesis of mixed diethylene glycol diester based on natural petroleum acid” Azerbaijan Oil Industry Journal. 2020, №4, pp.37-39

2. Sadiyeva N.F., Iskenderova S.A., Afandiyeva L.M., Kuliyeva E.M., Asadova Sh.N. "Obtaining mixed diesters of petroleum acids and their use as plasticizers and antioxidants" Oil refining and petrochemistry. №6, 2020, pp.19-21
3. Sadiyeva N.F., İskenderova S.A., Afandiyeva L.M., Aliyeva S.G., Nasibova G.G., Musayeva A.P., Bagirova M.N. "Synthesis and application of mixed diesters of ethylene glycol based on petroleum acids" Bulletin of the Higher Technical Universities of Azerbaijan.Vol. 07, №3, 2021, pp. 41-49
4. Sadiyeva N.F., İskenderova S.A., Cherepnova Y.P., Bagirova M.N., Bayramova M.N., Jeferova A.A., Gurbanova G.K. Synthesis of mixed diesters of natural petroleum acids and study of their applications II International Scientific Conference "Reconstruction and recovery in post-conflict situations", ISCRRRPCS-2022, Baku. 24.02.2022, pp.175-179
5. Sadiyeva N., Isgenderova S.,Cherepnova Yu.,Afandiyeva L.,Quliyeva E., Mamedov A. Research and application of mixed propylene glycol diesters based on natural petroleum- and fatty acids Polish journal of science. 2022, №47, pp. 13-18
6. Abbasov V.M., Aliyeva L.I., Babanly N.N., Afandiyeva L.M., Nasibova G.Q. The creation of conservation liquids on the bases of synthetic and oxy-petroleum acids salts obtained from catalytic oxidation of Naphthene-paraffin hydrocarbons Processes of petrochemistry and oil-refining (PPOR). 2019, V.20, №1, pp.63-69
7. Abbasov V.M., Afandiyeva L.M., Rustemli G.Y., Nasibova G.G., Ahmedbeyova S.F, Tahirova F.F., İbrahimov H.C. Catalytic effect of γ-Al_2O_3 modified with Cr-, Co-, Mn- salts on the oxidation of naphthene-paraffin hydrocarbons in the liquid phase / The İnternational Scientific Conference "Actual Problems of Modern Chemistry".Baku, 2-4 October 2019, 150 p

СИНТЕЗ И ИССЛЕДОВАНИЕ СМЕШАННЫХ ПРОПИЛЕНГЛИКОЛЕВЫХ ДИЭФИРОВ СИНТЕТИЧЕСКИХ НЕФТЯНЫХ- И ЖИРНЫХ КИСЛОТ

Н.Ф. Садиева, $^{0000-0002-1633-6292}$ *С.А. Искендерова*$^{0000-0001-5192-0665}$, *Ю.П. Черепнова*$^{0000-0001-6590-4797}$, *Г.Г. Насибова*$^{0000-0002-1460-3061}$, *Л.М. Эфендиева*$^{0000-0002-1043-3446}$, *С.Г.Алиева*$^{0000-0002-9169-8875}$
Институт Нефтехимических Процессов им. Ю.Г.Мамедалиева Национальной Академии Наук Азербайджана
uta1980@inbox.ru

В статье приведен одностадийный метод синтеза смешанных диэфиров на основе пропиленгликоля, синтетических нефтяных- и алифатических жирных кислот (C_6*-*C_8*) с использованием катализатора ZnO при оптимальных условиях: температура -110-120°C, количество катализатора - 1,3% мас. (по кислоте), мольное соотношение компонентов - кислота:спирт - 2:1,3. Изучены свойства синтезированных смешанных диэфиров, определены их параметры аналитическим и спектральным методами. С целью изучения пластифицирующих свойств смешанных диэфиров в лабораторных условиях были приготовлены композиции с добавлением 100 м.ч. поливинилхлорида (ПВХ) на 30-70 м.ч. синтезированных диэфиров и их сравнивали с промышленным пластификатором - диоктилфталатом. Также эти диэфиры подверглись исследованию в качестве антиоксидантов, улучшающих термоокислительную стабильность дизельного топлива. Анализ результатов исследований показывает, что синтезированные смешанные диэфиры могут быть предложены в качестве* *эффективных пластификаторов для ПВХ и новых антиоксидантов для дизельных топлив.*

***Ключевые слова**: пропиленгликоль, синтетические нефтяные кислоты, смешанные диэфиры, дизельное топливо, антиоксидант, поливинилхлорид, пластификатор.*

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N.F. Sədiyeva$^{0000-0002-1633-6292}$, S.A. İsgəndərova$^{0000-0001-5192-0665}$,Y.P. Çerepnova$^{0000-0001-6590-4797}$, G.Q. Nəsibova$^{0000-0002-1460-3061}$, L.M. Əfəndiyeva$^{0000-0002-1043-3446}$,*S.Q.Əliyeva*$^{0000-0002-9169-8875}$
Azərbaycan Milli Elmlər Akademiyasının akad. Y.H.Məmmədəliyev adına
Neft-Kimya Prosesləri İnstitutu
uta1980@inbox.ru

Məqalədə ZnO katalizatorunun iştirakı ilə sintetik neft- və (C_6-C_8) alifatik yağ turşuları əsasında propilenqlikolun qarışıq diefirlərinin: temperatur - 110-120°C, katalizatorun miqdarı - 1,3 % kütlə (turşuya görə), komponentlərin molyar nisbəti - turşu:spirt - 2:1,3 optimal şəraitdə birmərhələli üsulla sintezi göstərilmişdir. Sintez olunmuş qarışıq diefirlərin xassələri öyrənilmiş, göstəriciləri analitik və spektral üsullarla təyin edilmişdir. Qarışıq diefirlərin plastifikasiya xassələrinin öyrənilməsi məqsədi ilə laboratoriya şəraitində 100 hissə polivinilxloridə (PVX) 30-70 hissə sintez olunmuş qarışıq diefirləri əlavə etməklə kompozisiyalar hazırlanmış və onlar sənaye plastifikatoru olan dioktilftalatla müqayisə edilmişdir. Həmçinin, bu diefirlər dizel yanacağının termooksidləşmə stabilliyini yaxşılaşdıran antioksidant kimi də tədqiq olunmuşlar. Aparılan tədqiqatların nəticələrinin təhlili göstərir ki, sintez olunmuş diefirlər PVX-ya səmərəli plastifikator və dizel yanacaqlarına keyfiyyətli antioksidant kimi təklif oluna bilər.

***Açar sözlər:** propilenqlikol, sintetik neft turşuları, qarışıq diefirləri, dizel yanacağı, antioksidant, polivinilxlorid, plastifikator.*

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n-HEXANE HYDROISOMERIZATION ON INDUSTRIAL NICKEL-CONTAINING CATALYSTS

*E.T.Zeynalov*0000-0002-5372-8754
Azerbaijan State Oil and Industrial University
elshan.zeynalov@sabah.edu.az

In this work, we studied the process of hydroisomerization of n-hexane on various industrial nickel-containing catalysts. Ni/diatomaceous earth and $NiCr_2O_3$*, which were not previously used in the isomerization process, but were used in various industrial processes, were used as catalysts in this process. For comparative purposes, the studies varied the hydrogen to feed ratio to varying degrees and calculated the conversion and isomer yield on both catalysts, which are key process indicators. On the basis of the studies performed, the optimal mode of the n-hexane hydroisomerization process on the studied catalysts was selected.*

Keywords: *hydroisomerization, n-hexane, nickel-containing catalysts, yield of isomers, conversion.*

INTRODUCTION

One of the main directions of deep oil refining processes is an increase in the amount of isostructured hydrocarbons in crude oil used as a motor fuel. For this, the process of catalytic isomerization of normal paraffinic hydrocarbons is used [1,2].

For isomerization reactions to proceed regularly on metal-containing catalysts, it must be carried out in a hydrogen atmosphere. For various catalysts used in isomerization processes, the kinetic regularities of the isomerization of paraffinic hydrocarbons and inhibition are observed together with an excess of hydrogen. For all catalysts, the dependence of the reaction rate on the partial pressure of hydrogen is extreme after hydrogen has reached a certain concentration on the catalyst surface.

In the current research work, the process of hydroisomerization of n-hexane at different temperatures and H_2: the feedstock was carried out on various nickel-containing industrial catalysts - Ni/diatomaceous earth and $NiCr_2O_3$.

The $NiCr_2O_3$ catalyst is mainly used in the processes of fine purification of hydrogen-containing gas from oxygen, carbon monoxide and carbon dioxide, hydrogenation of aromatic hydrocarbons, conversion of methane to carbon dioxide, dehydrogenation of low-molecular alcohols, oxygen-containing compounds (benzene, phenyl, phenyl, etc.).

The Ni/diatomaceous earth catalyst is used in the petrochemical and chemical industries to hydrogenate a mixture of acetylene compounds to isoprene and 1,3-butadiene, a mixture of carbonyl compounds to butanol, etc. It is also used in the food industry for the hydrogenation of vegetable oils, animal fats and fatty acids.

EXPERIMENTAL PART

Hydroisomerization of n-hexane was studied in a flow reactor in the presence of 5 sm^3 of a catalyst at a temperature of 200-350 ° C, in the ratio $H_2{:}n\text{-}C_6H_{14} = (2 \div 3){:}1$. The catalysts used were Ni/diatomaceous earth and $NiCr_2O_3/C$ catalysts. The hydrogen required for the process is supplied to the system through a generator. The liquid products of the hydroisomerization reaction were analyzed using a CHROM-5 chromatograph equipped with a 1 m glass column filled with a sorbent impregnated with vaseline oil on Inzen brick (INZ-600).

RESULTS AND DISCUSSION

In developed countries, isomerization processes are becoming a key element of the technological schemes of oil refineries, their competitiveness increases in comparison with other processes aimed at obtaining gasoline components.

As a result of the research, the indicators of the hydroisomerization process ((isomer yield and conversion) on both catalysts were calculated. Based on the results obtained, the time schedule of the process of hydroisomerization of n-hexane on Ni/diatomaceous earth (fig. 1) and $NiCr_2O_3/C$ (fig. 2) catalysts is shown.

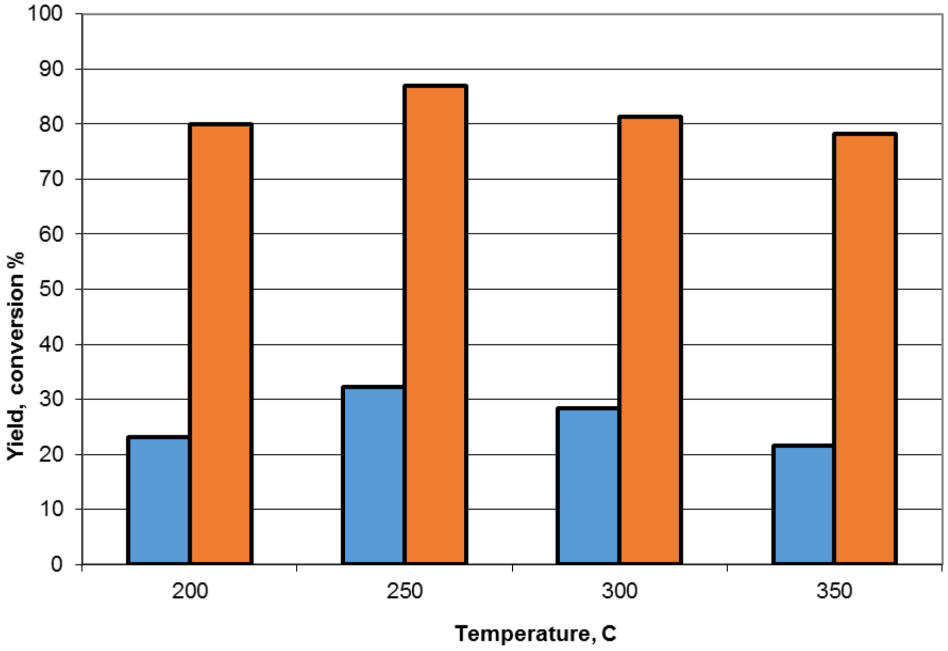

Fig. 1. Temperature dependence of the main parameters of the n-hexane hydroisomerization process on the Ni/diatomaceous earth catalyst:
🟦 - isomer yield; 🟧 - conversion

As can be seen from fig.1, the output of the isomers on the catalyst Ni/diatomaceous earth is reduced, passing through the maximum. Since, the yield of isomers on the same catalyst at a temperature of 200 °C increases from 23.2% (wt.) To a maximum value at a temperature of 250 °C, i.e. 32.3% (mass.). As the process temperature rises, the yield of isomers begins to decrease. As the temperature rises to 300 and 350 °C, the yield of isomers decreases to 28.4% and 21.6%, respectively. At the beginning of the process, the conversion increases from 80% at 200 °C to 87% at 250 °C (maximum) and decreases to 78.2% at 350 °C at the end of the process. Both the maximum yield of isomers and the maximum conversion on this catalyst were obtained at 250 °C.

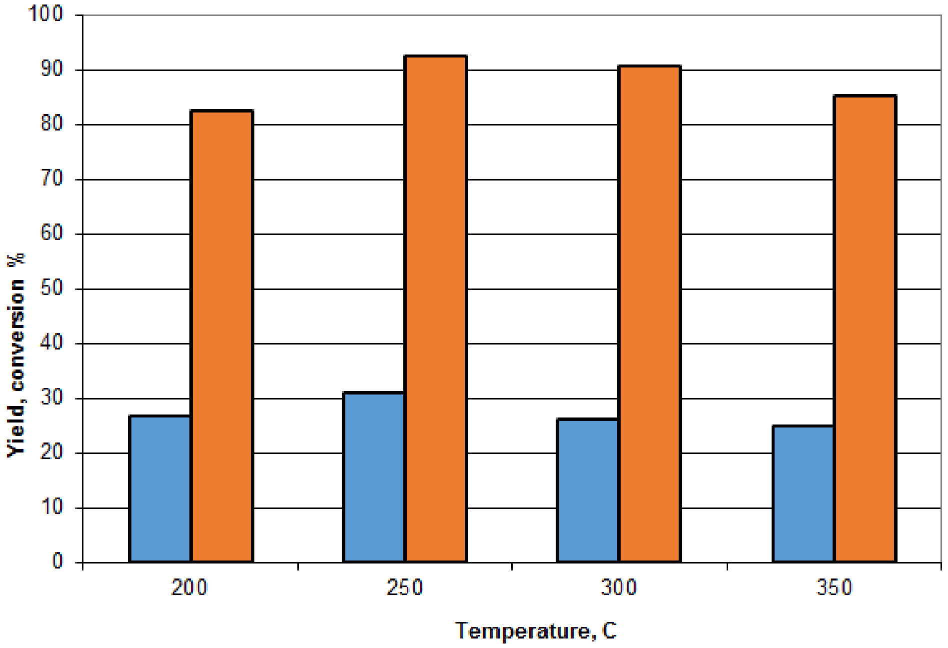

Fig.2. Temperature dependence of the main parameters of the n-hexane hydroisomerization process on the $NiCr_2O_3/C$ catalyst:
🟦 - isomer yield; 🟧 - conversion

As can be seen from fig.2, the same picture is observed for the $NiCr_2O_3/C$ catalyst, but the isomer yield is relatively low and the conversion is higher. As in the previous catalyst sample, the yield of isomers decreases, passing through a maximum, depending on the temperature. And here the maximum yield of isomers (30.8% (wt.)) Is observed at a temperature of 250 ° C. Then, at 350 ° C, it decreases to 24.9% (wt.). As already mentioned, the conversion on this catalyst is higher than on the previous catalyst. The maximum conversion (92.3%) on this catalyst was obtained at T = 250 ° C. Subsequently, with an increase in temperature to 350 ° C, the conversion decreased to 85.0%.

It can be concluded that the yield of isomers on the Ni/diatomaceous earth catalyst is higher than on the $NiCr_2O_3/C$ catalyst. Studies have shown that in the process of n-hexane hydroisomerization, the $NiCr_2O_3/C$ catalyst shows better results at a lower temperature (200°C). The Ni/diatomaceous earth catalyst exhibits isomerization activity at relatively higher temperatures (250-300 °C).

For a continuous isomerization reaction on a metal catalyst, it must be carried out in a hydrogen atmosphere. This is due to the adsorption and dissociation of hydrogen on the metal and the transfer of hydrogen particles from the metal to the support.

For a more accurate determination of the n-hexane hydroisomerization process, a comparative study of nickel-containing catalysts was carried out. For comparison, different ratios of H_2:n-C_6H_{14} (2: 1 and 3: 1) were taken at the same temperature (250 ° C). Both catalysts were tested as described above. The results are presented in the table.

Table 1

Comparative analysis of n-hexane hydroisomerization on nickel-containing catalysts (T = 250 °C)

Indıcators	Catalyst			
	Ni/diatomaceous earth		$NiCr_2O_3/C$	
H_2 : n-C_6H_{14}	2 : 1	3 : 1	2 : 1	3 : 1
Isomer yield,% (mass.)	31.6	22.0	28.7	19.1
Conversion	69.4	80.3	67.2	78.3

As can be seen from the table, when the ratio of hydrogen to feed is 2:1, the yield of isomers on both catalysts is high, and the conversion is low. Conversely, when the hydrogen to feed ratio is increased to 3:1, the isomer yield is low and the conversion is high.

CONCLUSION

Thus, as a result of the hydroisomerization of n-hexane on various industrial nickel-containing catalysts, the following results were obtained:

1. The $NiCr_2O_3/C$ catalyst shows a relatively high activity in the n-hexane isomerization process at relatively low temperatures;
2. In contrast, the Ni / diatomaceous earth catalyst exhibits relatively high isomerization activity at higher temperatures;
3. Studies show that the optimal condition for the process of hydroisomerization of n-hexane is H_2:n-C_6H_{14} = 2: 1 at T = 250 °C. In this case, the yield of isomers and conversion of feedstock for both catalysts can be considered appropriate.

REFERENCES

1. Chica A., Corma A., Miguel P.J. Isomerization of C_5-C_7 n-alkanes on unidirectional large pore zeolites: activity, selectivity and adsorption features Catalysis Today. 2001, pp. 101-110
2. Hou Zh., Han B., Zhang J., Liu Zh, He J., Zhang X, Yang G. n-Pentane isomerization in different phase regions near the critical temperature //J. Supercritical Fluids. 2020, Vol. 25, № 1, pp. 81-90
3. IFP Training. Isomerization of Light Gasoline ENSPM Formation Industry.2008, 298 p
4. Benitez V. M. Silica supported superacid isomerization catalysts V. M. Benitez C.R. Vera C. L. Pieck F. G. Lacamoire J. C. Yori, J. M. Grau, J. M. Parera Catalysis Today. 2015,Vol. 107-108, pp.651–656
5. Loften T. Isomerisation of n-hexane over sulphated zirconia modified by noble metals / T. Loften, E. Blekkan . Applied Catalysis A: General. 2006, Vol.299,№ 1–2, pp. 250–257
6. Chen X R., Du Y. Q., Chen C L., Xu N. P., Moi C. Y. Highly active and stable n-pentane isomerization catalysts without noble metal containing: Al- or Gapromoted tungstated zirconia. Catal. Lett. 2016, № 3-4, pp. 187—193

7. Jordao M.H., Simoes V., Cardoso D. Zeolite supported Pt-Ni catalysts in n-hexane isomerization. Applied Catalysis A: General. 2007, pp. 1-6
8. Brito K.D., Sousa B.V., Rodrigues M.G.F., Alves J.J.N. Kinetic modelling of the isomerization of n-hexane using bifunctional Pt-Ni/Mor catalysts // Brazilian Journal of Petroleum and Gas. 2018, Vol. 2, №1, pp. 1-8

ГИДРОИЗОМЕРИЗАЦИЯ н-ГЕКСАНА НА ПРОМЫШЛЕННЫХ НИКЕЛЬСОДЕРЖАЩИХ КАТАЛИЗАТОРАХ

Э.Т.Зейналов$^{0000-0002-5372-8754}$
Азербайджанский Государственный Университет Нефти и Промышленности
elshan.zeynalov@sabah.edu.az

В данной работе изучен процесс гидроизомеризации н-гексана на различных промышленных никельсодержащих катализаторах. Ni/кизельгур и $NiCr_2O_3$, которые ранее не использовались в процессе изомеризации, но использовались в различных процессах в промышленности, были использованы в качестве катализаторов в этом процессе. В целях сравнительного анализа в исследованиях варьировали соотношение водорода к сырью в различной степени и рассчитывали конверсию и выход изомеров на обоих катализаторах, которые являются ключевыми показателями процесса. На основании проведенных исследований выбран оптимальный режим процесса гидроизомеризации н-гексана на исследуемых катализаторах.

Ключевые слова: *гидроизомеризация, н-гексан, никельсодержащие катализаторы, выход изомеров, конверсия.*

NİKEL TƏRKİBLİ SƏNAYE KATALİZATORLARI ÜZƏRİNDƏ n-HEKSANIN HİDROİZOMERLƏŞMƏSİ

E.T.Zeynalov $^{0000-0002-5372-8754}$
Azərbaycan Dövlət Neft və Sənaye Universiteti
elshan.zeynalov@sabah.edu.az

Mövcud tədqiqat işində müxtəlif nikeltərkibli sənaye katalizatorları üzərində n-heksanın hidroizomerləşmə prosesi tədqiq edilmişdir. Prosesdə katalizator kimi əvvəllər izomerləşmə prosesində işlədilməyən, sənayedə isə müxtəlif proseslərdə tətbiq olunan Ni/kizelqur və $NiCr_2O_3$-dan istifadə olunmuşdur. Müqayisəli təhlil aparmaq məqsədilə tədqiqatlarda hidrogenin xammala olan nisbəti müxtəlif hədlərdə dəyişdirilmiş və hər iki katalizator üzərində prosesin əsas göstəriciləri olan konversiya və izomerlərin çıxımı hesablanmışdır. Aparılmış tədqiqatlar əsasında tədqiq edilmiş katalizatorlar üzərində n-heksanın hidroizomerləşmə prosesi üçün optimal rejim seçilmişdir.

Açar sözlər: *hidroizomerləşmə, n-heksan, nikeltərkibli katalizatorlar, izomerlərin çıxımı, konversiya.*

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SYNTHESIS AND PROPERTIES OF RUTHENIUM CLUSTER COMPLEXES

M.M.Aghahuseynova $^{0000-0003-2471-2136}$*,D.N.Balakishiyeva,*
Azerbaijan State Oil and Industry University
minira_baku@yahoo.com

Methods for the synthesis of ruthenium cluster complexes based on carbonyl and amine-containing organic bifunctional ligands have been developed. The structure of the obtained combinations of clusters were determined on the basis of IR spectroscopy data, thermogravimetry, and elemental analysis. Samples of ligands I and II were obtained by condensation of carboxylic acid chlorides of cyclopentane and cyclohexane with ethylene followed by replacement of the chlorine atom by amine groups. To obtain cluster complexes of ruthenium with the synthesized ligands the ruthenium trichloride salt (RuCl3) was dissolved in water, and the calculated amount of sodium borohydride was added in portions to the resulting solution under vigorous stirring in nitrogen atmosphere. Rapidly emerging black-dispersed nanoparticles of metallic ruthenium did not precipitate. When organic ligands I and II are added, the corresponding cluster compounds III and IV are formed, which gradually over 45 min. precipitated from an aqueous solution. The resulting dark-brown precipitates were washed with distilled water and dried in a nitrogen atmosphere at a temperature of 35-400C. The melting temperatures of the synthesized compounds were determined, the components for cluster III - 206^0C *and cluster IV -* 222^0C *(with decomposition). The IR spectra of cluster compounds show intense absorption bands characterizing the presence of both the ketone carbonyl group and the amine fragment. The absorption bands of ketone groups in cluster compounds are shifted towards higher frequencies compared to the initial ligands. A similar picture is also observed when comparing the IR vibrations of CN bonds in the initial ligands and the corresponding cluster compounds. The results of elemental analysis confirm the structures of cluster compounds and are in complete agreement with the concept that cluster compounds are formed upon the reduction of ruthenium salts with metal hydrides in an aqueous solution. Apparently, in this case, the most stable ruthenium clusters with tetrahedral structure are formed.. Thermogravimetric analysis made it possible to establish the presence of a peak at a temperature of* 318^0C *with a mass number of 744.8 , corresponding to a cluster combination of four ruthenium atoms. At each stage of decomposition, the experimental mass losses are in good agreement with the calculated values.*

Keywords: *synthesis, ruthenium, cluster complexes, amine and caryonyl containing ligands, bifunctional ligands, cyclopentyl amino ketone, cyclohexyl amino ketone.*

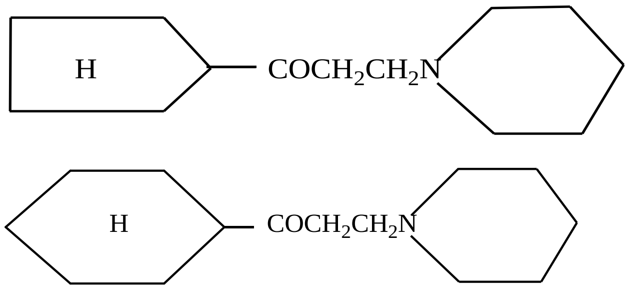
INTRODUCTION

The development of inorganic chemistry in the 20th century was accompanied by remarkable discoveries. Increasingly, complex compounds, the molecules of which contain several metal ions, the so-called polynuclear coordination compounds, where the bond length between metal atoms is noticeably shortened compared to compact metals, began to fall into the field of view of scientists inorganic chemists. In contrast to classical single-center coordination compounds, here the ligands are surrounded by several metal atoms (ions) closely bonded to each other. For the first time such polynuclear complexes were $Ta_6C_{l14}\times7H_2O$,$MoCl_2$ and some of its derivatives. An interesting fact is that as early as 1943, the polynuclear complex compound Rh_4COn was obtained by carbonylation of anhydrous Rh_4Cl_3. In 1963, the structure of rhenium chloride was established, in which the rhenium atoms form a triangle with short Ru-Ru distances of only 2.47 A^0. The discovery of antitumor activity and unique low toxicity and a fairly wide range of biological activity favorably distinguish rhenium complexes from analogs [1–4]. A characteristic feature of compounds containing polyvalent transition metal atoms is the formation of cluster compounds. In recent years, the chemistry of cluster compounds of transition metals, including ruthenium, has been one of the most rapidly developing areas of modern inorganic chemistry [5–13].

Despite the progress achieved in the cluster chemistry of transition metals, halide and chalcogenide-containing complexes have been the most widely studied until recently, while nitrogen-containing complexes have been considered to a lesser extent. While quite extensive material has been accumulated for Mo, W and Ru , there are big problems in the cluster chemistry of ruthenium. In this regard, it was of interest to obtain polynuclear metal complexes of ruthenium with organic bifunctional ligands and to study their structure and properties. This work is devoted to the synthesis of cluster compounds with carbonyl and amine-containing organic bifunctional ligands. The structures of the synthesized cluster compounds were studied by elemental analysis, IR spectroscopy, and thermogravimetric analysis.

EXPERIMENTAL PART

These ligands were synthesized according to the procedure described in [11]. Samples of ligands I and II were obtained, respectively, by condensation of carboxylic acid chlorides cyclopentane- and cyclohexane with ethylene followed by replacement of the chlorine atom by amine groups.



I II

The purity of these ligands was determined by gas-liquid chromatography.

To obtain cluster complexes of rutheium with the above ligands, we have previously prepared an ultra-fine solution of ruthenium in distilled water. For this purpose, 0.775 g (0.001 mol) of ruthenium trichloride was dissolved in 50 ml of distilled water. 0.114 g (0.001 mol) of sodium borohydride was added to the resulting solution with vigorous stirring in portions over 40 seconds under a nitrogen atmosphere. Black-dispersed nano-particles of metallic ruthenium quickly appear, which do not precipitate. After the evolution of gases (H_2 and BH_3) ceased, 0.209 g (0.001 mol) of aminoketone I was added to the reaction mixture with vigorous stirring. After completion of the reaction, stirring was continued for another 28 min. On standing, 0.67

g dark-brown crystals of cluster complex III with m.p. 206^{0}C (decomposition during melting). Found, %: Ru 46.89; From 39.20; H 6.2; N 3, 47 $Ru_4C_{52}H_{92}O_4N_4$. Calculated, %: Ru 47.12; From 39.47; H, 5.82; N 3.54.

A similar procedure was used to obtain cluster compound IV, yield 47%, m.p. 222^{0}C (melts with decomposition).

Found, %: Ru- 45.2; S. 39.9; H 6.23; N 3.53.

Ru4C56 H100 O4 N4. Calculated, %: Ru-45.5; S. 41.06; H 6.11; N 3.42.

Elemental analysis for C, H, N was performed on a Carlo Erba 1106 and Vario EL instrument. IR spectra were recorded on a Bruker IFS-85 Fourier spectrometer (KBr pellets).

Thermogravigrams of cluster compounds III and IV were obtained on a Netzsch STA 449 F3 Yupiter apparatus.

RESULTS AND DISCUSSION

The structures of the obtained compounds III and IV were determined on the basis of IR spectral analysis, thermogravimetry, and elemental analysis. In the IR spectrum of compounds III and IV, intense absorption bands were found at 1718 cm-1 and 1720 cm-1, respectively characterizing the presence of the ketone carbonyl group.

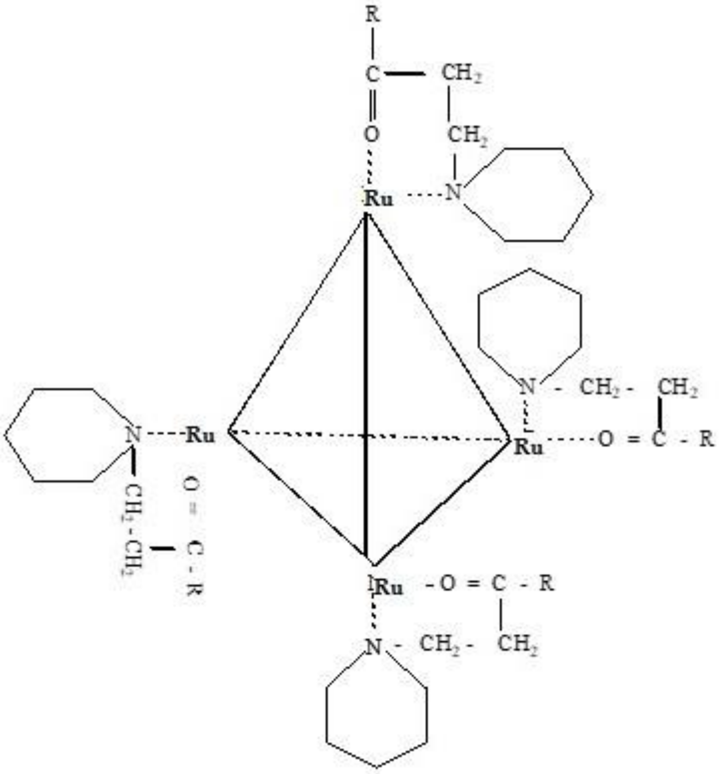
The absorption bands at 2727 cm-1 and 2720 cm-1 correspond to the amine fragment in compound III. The absorption bands at 2613 cm-1 and 2609 cm-1 characterize the presence of an amine group in cluster compound IV.

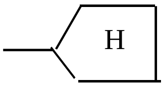
So, if in the initial ligands I and II the absorption bands of the ketone carbonyl group are 1712 cm-1 and 1714 cm-1, then in the composition of cluster substances III and IV the absorption bands of these groups appear at 1718 cm-1 and 1720 cm-1, respectively .

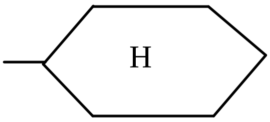
A certain regularity is observed when comparing the IR vibrations of the C–N bonds in the initial ligands I and II and in the corresponding cluster compounds III and IV. So, if in the initial ligands the absorption bands of C – N bonds appear at 2727 cm-1 and 2720 cm-1, then in the corresponding clusters III and IV these vibrations are 2613 cm-1 and 2609 cm-1.

The thermogravimetric analysis of these compounds revealed a "peak" at a temperature of 318^{0}C with a mass number of 744.8 , corresponding to a cluster combination of four ruthenium atoms. It should be noted that the absorption bands of ketone groups in the initial ligands I and II are markedly reduced when these substances are compared in the composition of cluster compounds. It was also established by the thermogravimetric method that compounds III and IV are stable up to temperatures of 187^{0}C and 201^{0}C, respectively; above these temperatures, aminoketones I and II are released, accompanied by endothermic effects in the range of 177^{0}C - 229^{0}C with maxima at 195^{0}C and 209^{0}C, respectively. The experimental and calculated molecular weight loss for clusters III and IV is 20.40% and 21.09%, respectively.

After the complete removal of amino-ketone I at a temperature of 650^{0}C, the mass according to thermogravimetric data of rhenium was 79.2%. The theoretically calculated weight loss is 78.89%. At each stage of decomposition, the experimental mass losses are in good agreement with the calculated values. Cluster compound IV was analyzed by a similar method. The results obtained are in good agreement with the assigned composition.



(III), R = 

(IV) R = 

The results of elemental analysis also confirm the assigned structures of cluster compounds III and IV. Our experimental data are in complete agreement with the concept that the reduction of ruthenium salts with element hydrides in an aqueous solution results in the formation of clusters of ruthenium atoms.

Apparently, the Ru metal cluster, which has a tetrahedral structure, is the most stable among them.

CONCLUSION

1. A method has been developed for the synthesis of ruthenium cluster complexes based on carbonyl and amine-containing organic bifunctional ligands.
2. It has been established that the reduction of a ruthenium salt in an aqueous solution results in the formation of ultrafine nanoparticles of metallic ruthenium, which, upon interaction with β-aminoketones, form cluster complexes.
3. The structure of the resulting clusters was determined based on the data of elemental analysis, IR spectroscopy, and thermogravimetric studies.
4. It was revealed that ruthenium has tetrahedral coordination in the synthesized cluster complexes.

REFERENCES

1. Rosenberg B., Van L., Trosko J.E, Mansour V.H, Platinum compounds: a new class of potent antitumour agents// Nature..1969, Vol.222, № 5191, pp.385-389
2. Ruiz J., cutillas N., Vicente CC, Villa MD, Lypez G., Lorenzo J. and etc., New complexes of platinum(II): antitumar activity and interaction with DNA// Inorg. Chem. 2005, Vol.44, pp.7365-7376
3. Keppler B.K, Voqel E.A.Anti-tumour properties of metal complexes. Handbook of metal-ligand interactions in biological Cuids – bioinorganic medicine .1995 ,Vol 2, Part 3, pp. 1200-1229
4. Shtemenco N.İ., Zabitskaya E.D. Berzenina O.V.,Yeqorova D.E., Shtemenko A.V. Liposomol forms of cluster compounds enhancement of biological activity.Chem.Biodivers.2008, №5, pp.1660-1667
5. Bennett M.A.,Huang T.N.,Matheson T.W.,Smith A.K.Inorganic Synthesis USA. 2007, pp.74-78
6. Mironov Yu.V., Fedorov V.E, Four-atom cluster chalcogenide complexes of rhenium with a cubane nucleus. Synthesis, structures and properties II Izv. Acad. Science, ser. chem. 2002, № 4, pp.529-539
7. Ryabchikov D.I., Lazarev A.I. On the analytical chemistry of rhenium, Zh.analyte Chemistry. 1955, T.10, № 4, pp .228-235
8. Gubin S.P. Chemistry of clusters, M.; Nauka. 1987, 260 p
9. Tarasenko M.C., Ledneva A.Yu., Kuratieva H.B, Naumov D.Yu., Kim S.-D., Fedorov V.E., Naumov N.G., Synthesis and structure of new coordination compounds based on Re6Q8(CN) (Q = S, Se) and (SnMe3)+ Coord. Chemistry. 2007,T. 33, № 12, pp. 892-901
10. Fadeeva N.V. Investigation of the complexation of rhenium (V) with thiourea and its derivatives // Abstract of the thesis. ...cand. chem. Sciences. Leningrad 1973, 15p
11. Hobert S.E, Noll B.C, Rakowski DuBois M. Synthesis of a rhenium(V) polysulfide complex and a study of its reactivity with hydrogen II Organometallics .2001, Vol. 20, №7, pp. 1370-1375
12. Nazarov A, Baquie M, Sliwinska P. Synthesis and characterization of a new class of anti-angiogenic agents based on ruthenium clusters Sci Rep .2013,№3 , pp.1485-1496
13. Naumov N.G, Ledneva A.Y, Kim S.-J., Fedorov V.E, New trans-Re6S8(CN)4L2."-rhenium cluster complexes: syntheses, crystal structure and properties II J. Cluster Sci. 2009,Vol. 20, pp. 225-239
14. Tsukada S.Sagawa T.Gunji T.Carbon monoxide addition to ruthenium-dithiolene complex and polisiloxane hybrid film formation Chem.Asian J.2015 ,pp. 1881-1883

СИНТЕЗ И СВОЙСТВА КЛАСТЕРНЫХ КОМПЛЕКСОВ РУТЕНИЯ

М.М.Агагусейнова [0000-0003-2471-2136], *Д.Н.Балакишиева*
Азербайджанский Государственный Университет Нефти и Промышленности
minira_baku@yahoo.com

Разработаны способы получения кластерных соединений рутения с карбонильными и аминсодержащими лигандами. На основании совокупности физико-химических *исследований – элементного анализа, ИК-спектроскопии и термогравриметрического анализа установлена структура синтезированных соединений и определены температуры плавления кластерных соединений рутения. Выявлены определенные спектральные закономерности, заключающиеся в смещение интенсивных полос поглощения, характеризующих наличие как кетонной группы, так и аминного фрагмента в сторону высоких частот. Подобная картина наблюдается и при сравнении ИК-колебательных полос поглощения C-N связи в исходных лигандах и соответствующих кластерных соединений. Установлено образование устойчивых кластерных комплексов рутения, имеющих тетраэдрическую структуру.*

Ключевые слова: *рутений, кластерные соединения, аминсодержащие лиганды, карбонил содержащие лиганды, наночастицы металлического рутения.*

RUTENİUMUN KLASTER KOMPLEKSLƏRİNİN SİNTEZİ VƏ XASSƏLƏRİ

M.M.Ağahuseynova $^{0000-0003-2471-2136}$, *D.N.Balakişiyeva*
Azərbaycan Dövlət Neft və Sənaye Universiteti
minira_baku@yahoo.com

Amin və karbonil tərkibli liqandlarla ruteniumun klaster birləşmələrinin alınma metodu işlənib hazırlanmışdır. Bir sıra fiziki-kimyəvi metodlarla - İQ-spektroskopiya, termoqravimetriya və element analizi sintez olunmuş klaster birləşmələrinin quruluşu təyin olunmuşdur. Keton qrupunun və amin fraqmentinin mövcudluğunu xarakterizə edən intensiv udma zolaqlarının yüksək tezliklərə doğru yerdəyişməsindən ibarət müəyyən spektral qanunauyğunluqlar aşkar edilmişdir. Oxşar hal ilkin liqandlarda və müvafiq klaster birləşmələrində C-N rabitəsinin İQ-titrəyişlərinin müqayisəsi zamanı da müşahidə olunur. Ruteniumun tetraedrik quruluşa malik daha möhkəm klaster birləşmələrinin əmələ gəlməsi müəyyən olunmuşdur.

Açar sözlər: *rutenium, klaster birləşmələr, amin tərkibli liqandlar, karbonil tərkibli liqandlar, rutenium metalının nanohissəcikləri.*

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RESULTS OF EXPERIMENTAL-INDUSTRIAL TESTS OF NANODEMULSIFIER "IKHLAS-1" ON THE OBJECTS JSC "OZENMUNAIGAZ" RK

A.A.Gasanov[0000-0002-0149-1943], *T.K.Dashdiyeva*[0000-0001-7962-4323]
Azerbaijan State Oil and Industry University
turanamammadova15@gmail.com

The article presents comparative results of experimental-industrial tests (EIT) of the nanodemulsifier "IKHLAS-1" at the facilities of JSC "Ozenmunaigas" of the Republic of Kazakhstan. As a result of local EIT, for the first time, cost-effective nanoecotechnologies were proposed using the "IKHLAS-1" nanodemulsifier with a polynanostructure to improve water preparation at the PWDU-1 (preliminary water discharge unit), as well as for the processing of historical sediments at the OPPSh (Oil Preparation and Pumping Shop) of "Uzen" oil field central production facility. The quality of commercial oil in all EIT carried out was significantly better compared to the base demulsifier "Randem-2201".

Keywords: *nanodemulsifier "IKHLAS-1" with polynanostructure, "Uzen" oil field, utilization of hard to destroy water-oil emulsions and suspensions, oilfield nanoecotechnologies, primary preparation of oil.*

INTRODUCTION

"Uzen" is one of the large and complex fields of the Republic of Kazakhstan (RK) in terms of technological processes of primary preparation of oil (PPO). The oil of the "Uzen" oil field refers to highly paraffinic oils (up to 25%), and PPO, according to scientists and specialists of the Republic of Kazakhstan, is accompanied by the formation of hard to destroy water-oil emulsions (HDWOE) [1]. Until 2012, the well-known demulsifier Dissolvan-4411 (BASF Chemical Company, Germany or Clariant - Swiss chemical company) was used at "Uzen", which had a number of disadvantages (formation of HBWOE and other wastes) during PPO [2]. Then the demulsifier "Randem-2201" (Nalco Rauan) [3] was used which also has similar disadvantages. Numerous samples of demulsifiers from the world's leading companies were tested at the "Uzen" field. However, positive results were not [1, 4]. As the literature review compiled by us in this area shows, for numerous well-known demulsifiers, oil preparation at highly paraffinic and highly resinous fields is similar to the fields of the RK (for example: 'Uzen', 'Zhetibai', "Tenge Oil & Gas", "Taspolad", "Zhalgiztobe", "Buzachi", "Phystech II", "Ansagan", "Karajanbasmunay", "Arman", "Embamunaigas" JSC "Balgimbayev" ("Zhayikmunaygas" OGPD), "Embamunaigas" JSC "Karsak", "Prorva", etc.) is characteristic not only with some complicated technological parameters of PPO processes (relatively high specific consumption of demulsifiers and oil preparation temperature, a long duration of oil preparation, high oil content in the wastewater composition), which together determine the effectiveness of demulsifiers, as well as with the formation of undesirable petroleum nanocolloids [HDWOE; hard to destroy water-oil suspensions, - HDWOS; viscoelastic systems, - VES based on water-oil emulsions (VESBWOE); gas-saturated hydrates (GSG), curd-like sediments of demulsifiers (CLSD), trap oil, oil sludge, etc. (the terms oil nanocolloids, HDWOS, GSG, CLSD were first introduced by us)], which are potential environmental pollutants [1, 5-7]. Therefore, the development and implementation of special demulsifiers with a polynanostructure for the destruction of water-oil, oil-water emulsions, as well as for inhibiting the formation of the above oil nanocolloids under PPO conditions, is one of the topical issues of oilfield nanotechnology [6, 7]. In this regard, the demulsifiers developed by us with the code names “IKHLAS” were the first samples of such reagents [8].

EXPERIMENTAL PART

As a demulsifier, the “IKHLAS-1” nanodemulsifier with a polynanostructure was used. The purpose of the experimental-industrial tests (EIT) is to identify the effectiveness of the demulsifier "IKHLAS -1" in the preparation of oil at the facilities of JSC "Ozenmunaigas" in comparison with the basic demulsifier "Randem 2201". The facilities of Ozenmunaigas JSC (“OMG”) as part of the OPU (oil preparation unit) and WP (waste pumping) of “OMG” JSC were:

- PWDU-1 (preliminary water discharge unit), which receives oil from OGPD-1, 3 (oil and gas production department) and having its own chemical laboratory;
- PWDU-2, which receives oil from OGPD-2, 4 and having its own chemical laboratory;
- OPPSh (Oil Preparation and Pumping Shop). In the complex of OPPSh works around the clock "Central Laboratory of Physicochemical Analysis of Oil and Water" (CLPhChAO&W).

The main directions for the implementation of EIT have been agreed in the program of EIT of the demulsifier of the "IKHLAS-1" brand at the oil treatment facilities of “OMG” JSC. The experimental part are held by the personnel of the chemical laboratories of the PWDU-1, 2 and the OPPSh in two stages: at the first stage, a preliminary analysis was performed in the laboratories of the PWDU-1, 2 before and after of the water discharge; at the second stage, before the delivery of the commercial product to the "KazTransOil" analyzes in the CLPhChAO&W out for all the necessary parameters. Analyzes for the required parameters were carried out according to the following standards:

- concentration of water in the composition of oil (limit up to 0.5% GOST 31378-2009) in accordance with GOST 2477-2014;
- concentration of chloride salts in the composition of oil (limit up to 100 mg/dm^3 GOST 31378-2009) in accordance with GOST 21534-76;
- concentration of mechanical impurities in the composition of oil (limit up to 0.05% GOST 31378-2009) in accordance with GOST 6370-2018;
- concentration of oil in waste water (limit up to 50 mg/dm^3) in accordance with OST 39–225–88;
- concentration of organochlorine compounds in the composition of oil (limit up to 10 mg/dm^3 or 10 ppm GOST 31378-2009) in accordance with GOST R 52247-2004;

RESULTS AND DISCUSSION

Results of monitoring before EIT of "IKHLAS -1" at oil preparation facilities of JSC "OMG"

Monitoring was carried out in accordance with the EIT program and presented in the form of tables in the common electronic system of "OMG" JSC. According to the average values of the main monitoring values, the following most significant indicators can be distinguished by average values:

- PWDU-1 entrance to OPPSh, water 4%;
- PWDU-2 entrance to OPPSh, water 5.4%;
- VST-4 of OPPSh: 6.82 m, water 0.45%; chloride salts 68.8 mg/l;
- VST-4 of OPPSh: 7.82 m, water 0.34%; chloride salts 55.6 mg/l;
- VST-4 of OPPSh: 8.82 m, water 0.26%; chloride salts 43.6 mg/l;
- VST-4 of OPPSh: 9.82 m, water 0.19%; chloride salts 32.8 mg/l;
- VST-4 of OPPSh: overflow water 0.24%; chloride salts 37.3 mg/l;
- Water cut and chloride salts of commercial oil for the period 01.01.19-07.31.19 are 0.17% and 31.3 mg/l, respectively.
- VST-4 of OPPSh: 8.82 m, iron sulfides up to 3806 mg/l (according to KazNIPI);
- Specific consumption of "Randem 2201" at PWSU-2 190 g/t;
- Specific consumption of "Randem 2201" for PWSU-1 181 g/t
- With the basic technology in the VST-4 of OPPSh, an intermediate layer (HDWOE) is continuously formed, therefore, every day at a level of 5.82 m, a certain layer is cut off as an HDWOE.
- The daily volume of HDWOE, which are formed during the PPO is ~219 t (according to KazNIPI);
- Costs for processing 1m^3 on a tricanter is ~18,000 tenge (~46.4 $) [6];
- The cost of one ton of "Randem-2201" is 1,450,000 tenge (~3740 $) [6];
- The cost of one ton of "IKHLAS -1" is 1,200,000 tenge (~3095 $) [6];
- In commodity tanks, bottom sediments are formed on the basis of HDWOS and HDWOE.

All of the above pre-EIT monitoring indicators were used to compare with the results of the EIT (fig. 1-6 and tables 1, 2) and to draw the main conclusions of the EIT.

Explanation of symbols according to fig.1-6: 1-“Randem-2201”; 2 –“IKHLAS-1; CCh - comparison charts; C_B - concentration of water in oil; Cxc - concentration of chloride salts in oil; C_{FeS} – iron sulfide concentration in oil; $У_p$ – specific consumption of demulsifiers; IPWR - installation preliminary water reset; OPPSh - oil preparation and pumping shop; VST - vertical steel tanks Based on the data in figs. 1-6, table 1 presents generalized comparative data on the main analytical parameters for evaluating the effectiveness of EIT. table 1 conclusions:

As follows from the data in table 1, the “IKHLAS-1” nanodemulsifier prevails over a clear advantage in all comparison options under conditions of a decrease in specific consumption to 129 g/t for PWDU-2 over the last 14 days of pilot testing and a decrease in specific consumption to an average of 170 g/t , and in some period (August 21-August 24) up to 135 g/t at PWDU-1 at pilot testing. Regardless of the levels of reduction in specific consumption, “IKHLAS-1” in the delivery of commercial oil in terms of residual water (3.4 times) and chloride salts (1.9 times) as well as for iron sulfides (200 times) was significantly better compared to “Randem-2201”.

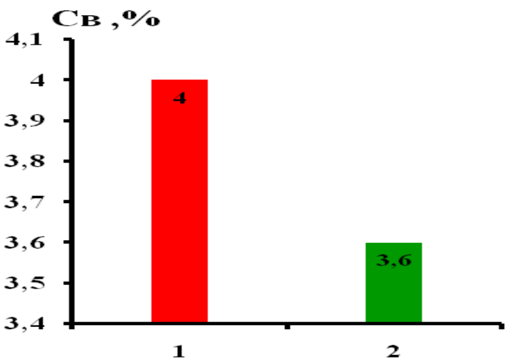

Fig.1. CCh for C_B (input of IPWR-1 at OPPSh).

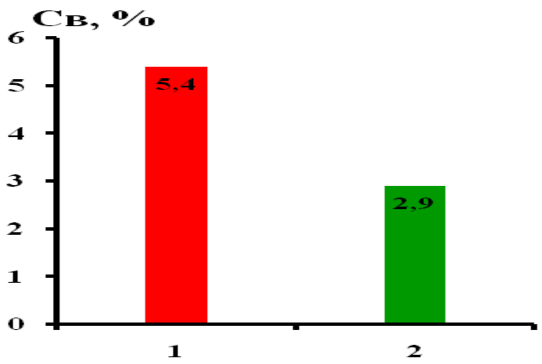

Fig.2. CCh for C_B (input of IPWR-2 at OPPSh).

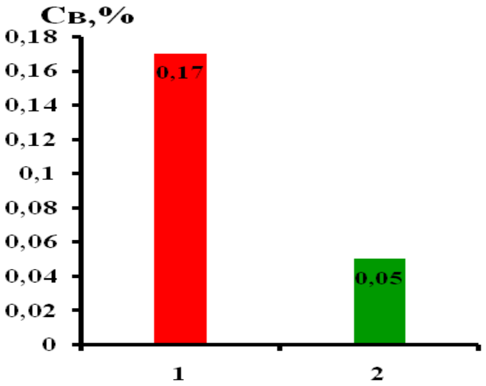

Fig.3. CCh for C_B of commercial oil.

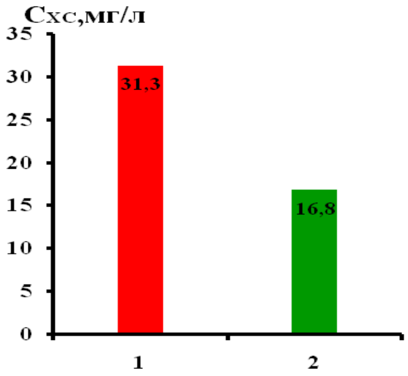

Fig.4. CCh for C_{XC} (mg/l) of commercial oil.

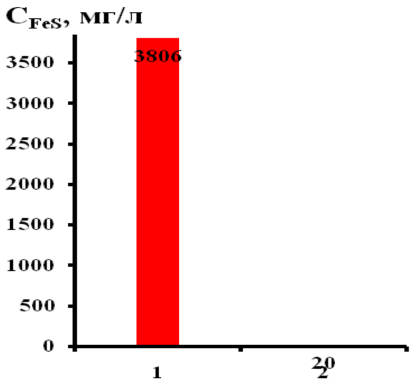

Fig.5. CCh for C_{FeS} (mg/l)at IPWR-2.

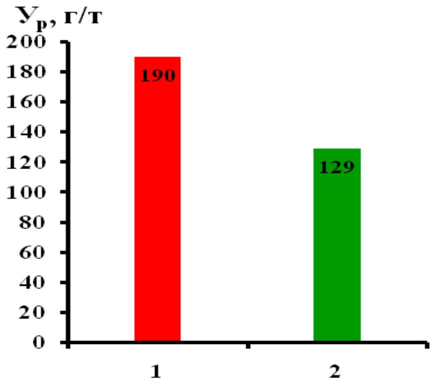

Fig.6. CCh for $У_p$ (g/t) at IPWR-2.

Table 1

Comparative data on the main analytical parameters for evaluating the effectiveness of the EIT (for the period 08.08.2019-02.09.2019) of the “IKHLAS-1”
(total consumption ~65 t)

The main analytical parameters for evaluating the effectiveness of the EIT	“Randem -2201”	“IKHLAS -1”	Efficiency, % (or times)
PWDU-1 entrance to OPPSh: water, %	4	3.6	10%
PWDU-2 entrance to OPPSh: water, %	5.4	2.9	46.3% (1.9 times)
VST-4 of OPPSh: 6.82 m, water, %	0.45	0.34	24.4%
VST-4 of OPPSh: 6.82 m, chloride salts, mg/l	68.8	57.7	16.1%
VST-4 of OPPSh: 7.82 m, water, %	0.34	0.25	26.5%
VST-4 of OPPSh: 7.82 m, chloride salts, mg/l	55.6	45	19.1%
VST-4 of OPPSh: 8.82 m, water, %	0.26	0.20	23.1%
VST-4 of OPPSh: 8.82 m, chloride salts, mg/l	43.6	38	13.2%
VST-4 of OPPSh: 9.82 m, water, %	0.19	0.15	21%
VST-4 of OPPSh: 9.82 m, chloride salts, mg/l	32.8	31	5.5%
VST-4 of OPPSh: overflow, water, %	0.24	0.17	29.2%
VST-4 of OPPSh: overflow, chloride salts, mg/l	37.3	33.7	9.6%
Commersial oil upon delivery to “KazTransOil”: water, %	0.17	0.05	70,6% (3.4 times)
Commersial oil upon delivery to “KazTransOil”:chloride salts, mg/l	31.3	16.8	46,3% (1.9 times)
VST-4 OPPSh 8.82 m: iron sulfides up to mg/l	3806	20	99,5% (200 times)
Specific consumption of demulsifier at PWDU-2, g/t	190	129***	32,1% (1.5 times)
Specific consumption of demulsifier at PWDU-1, g/t	181	170*;135**	6,1%*; 25,4%**

*E=6.1% (at Уp =170 g/t on the PWDU -1 on average for the weight period of the EIT); E**=25.4% (at Уp =135 g/t at PWDU -1 for the period 21.08.19-24.08.19 EIT); ***E=32.1% or in 1.5 (at Уp=129 g/t for PWDU -2 for the period 20.08.19-02.09.19 EIT): E – efficiency of “IKHLAS-1” relative to “Randem-2201”; Уp - specific consumption of demulsifiers.

RESULTS AND DISCUSSION

In the practice of conducting any EIT, it is not excluded that significant side effects are also detected when testing new equipment and technology. In this regard, the issues of improving the water preparation system at PWDU-1, as well as the processing of accumulated historical nanocolloids based on mixture of HDWOE and HDWOS at OPPSh, found their primary solutions during EIT. This deserved attention from the management of “OMG”.

Possible solutions to the problem of water preparation at the PWDU-1

The results of the EIT study established that, along with the above advantages of “IKHLAS-1” in oil and water preparation at PWDU-2; oil preparation at PWDU-1; oil preparation at the OPPSh and during the delivery of commercial oil to “KazTransOil”, more serious problems were also identified in water preparation at the PWDU-1, due to the removal of iron sulfides from oil, as well as from historical sedimennts [1] in equipments, due to the high purification abilities "IKHLAS-1". Nanodemulsifier “IKHLAS-1”, having a complex of properties of intensive demulsification, intensive oil refining, as well as possessing the properties of a sludge deposit destructor based on iron sulfides and mechanical impurities, in settling tanks leads to an intensive removal of iron sulfides into the water phase. Taking into account the above circumstances, together with the specialists of the OPU and WP “OMG” and KazNIPI, it was decided, if possible, to conduct local EIT in order to demulsify the accumulated oil sludge (in the form of a suspension) in the VST-3 (5000m^3) PWDU-1. From August 16 to August 17, 2019, oil sludge was circulated with the addition of IKHLAS-1 demulsifier at a dosage of 250 g/t. After circulation, settling was carried out for 36 hours, and the results of layered analyzes are shown in table 2.

Table 2

Results of layer-by-layer analyzes of oil sludge in VST-3 of PWDU-1before and after circulation (specific consumption “IKHLAS-1” 250 g/t;
consumption “IKHLAS-1” 752 kg)

Before circulation					After circulation								
date	sampling height, m	water, %	chloride salts, mg/l	FeS, mg/l	date	sampling height, m	water, %	FeS, mg/l	date	sampling height, m	water, %	chloride salts, mg/l	FeS, mg/l
15.08.19	12,9	0,1	129	963	19.08.19	12,9	0.48	318	21.08.19	12,9	0,03	59	242
15.08.19	11,9	0,2	198	1020	19.08.19	11,9	0.54	299	21.08.19	11,9	0,03	86	211
15.08.19	10,9	0,2	251	1027	19.08.19	10,9	0.90	296	21.08.19	10,9	0,1	113	161
15.08.19	9,9	0,2	286	1084	19.08.19	9,9	0.60	254	21.08.19	9,9	0,5	96	143
15.08.19	8,9	0,2	397	1540	19.08.19	8,9	0.54	276	21.08.19	8,9	0,8	106	129
15.08.19	7,9	0,2	632	1076	19.08.19	7,9	0.54	258	21.08.19	7,9	0,2	118	138
15.08.19	6,9	0,3	966	1084	19.08.19	6,9	0.30	228	21.08.19	6,9	0,2	133	145
15.08.19	5,9	0,2	1385	1155	19.08.19	5,9	0.36	279	21.08.19	5,9	0,2	148	127
15.08.19	-	-	-	-	19.08.19	-	-	273	21.08.19	5.5	6	152	124
mean			531	1119				276				112	158

Table 2 conclusions:

1. Chloride salts and iron sulfides in oil are reduced by 4.7 and 7 times, respectively;
2 The level of bound water does not exceed the levels of existing standards (no more than 0.5%);
3. Calculations show that the oil yield from the volume of oil sludge is ~86.7%.

Similar EIT were also successful for the VST-4 (5000m^3) of PWDU-1.

THE RESULTS OF THE LOCAL EIT "IKHLAS-1" FOR THE DESTRUCTION OF HISTORICAL SEDIMENTS IN VST-3 OF OPPSh

On August 26, 2019, representatives of KazNIPI and management of “OMG”, after successful local EIT at VST-3, 4 of PWDU-1, decided to go for more global local EIT “IKHLAS-1” to destroy the sediments based of mixture of HDWOE and HDWOS in the VST-3 (20000 m^3) of OPPSh (9150 m^3) without the use of tricanters. Water cut of the treated historical sediments after the local EIT was 0.06%, which is 3 times better than the commercial oil of "Randem-2201". This was a record achievement in the history of oil nanocolloids processing, accumulated at the OPPSh of “OMG” during PPO.

CONCLUSION

The results of the main and sides EIT at the facilities of JSC "Ozenmunaigas" confirmed the high efficiency of the nanodemulsifier "IKHLAS-1" relative to the base demulsifier "Randem-2201" in oil and water preparation at the PWDU-2; oil treatment at PWDU-1; oil preparation at the OPPSh during the delivery of commercial oil to KazTransOil . Based on the results of side EIT, for the first time, cost-effective nano-ecotechnologies were developed using the "IKHLAS-1" nanodemulsifier with a polynanostructure to improve water preparation at the UWV-1, as well as to process historical sediments in the “Uzen” oilfield OPPSh based of mixture of HDWOE and HDWOS to the level of residual water 0.06% in the composition of commercial oil. This Total actual economic efficiency of EIT is 295,162,265 tenge (or $761,395). Nanodemulsifier "IKHLAS-1" was recommended for further EIT and implementation at the facilities of JSC "Ozenmunaigas".

REFERENCES

1. Mullaev B.T,Abitova A.Zh, Saenko O.B [and others]. The Uzen oilfield. Problems and solutions: [in 2 volumes] . - Aktau: Strelbitsky Multimedia Publishing House. 2018, Vol. 1, 424 p
2. Zharmagambetova A.K., Tumabaev N.Zh., Dzhumekeyeva A.I. Demulsification of oil-water emulsions of the Kenlyk and Uzen fields. Izvestiya NAS RK. Series of Chemistry and Technology. - Almaty: NAS RK. 2015, 6 (114), pp. 22-29
3. Saenko O.B., Mullaev B.T., Serkebaeva B.S. An effective way to reduce the content of oil products in waste water during the preparation of oil at the fields // Proceedings of AONIPIneftegaz "Actual issues of the oil and gas industry", Proceedings Issue 3, Aktau.2016, pp. 145-157

4.Studying the conditions for the formation of TRNE and developing recommendations for its destruction / Information report of KazNIPI, Aktau. 2018, 267 p

5.Gasanov A.A., Dashdiyeva T.K., Dashdiyeva R.A. Evaluation of novel nanodemulsifier based on colloidal and non-colloidal surfactants for the removal of hydrocarbons from wastewaters.Journal of water chemistry and technology, - Kiev: 2019, 41 (6), pp. 377-383

6.Dashdiyeva T.K.Nanotechnology in the Oil and Water Preparation Using Nanodemulsifiers// Chennai: International Journal of Innovative Research in Science, Engineering and Technology. 2019, 8 (9), pp. 9477-9487

7.DashdiyevaT.K.Results of laboratory and industrial tests of “IKHLAS-1” nanodemulsifier on “Akkulka” field and the new mechanism of destruction of oil emulsions. Baku: Azerbaijani Chemistry Journal.2020, №3, -pp. 34-45

8. Nugmanov A.K.Demulsifier for the destruction of water-oil and oil-water emulsions, Patent № 30960, Republic of Kazakhstan . Orazbek A.B., Dashdieva T.K. [and others] .2016

РЕЗУЛЬТАТЫ ОПЫТНО-ПРОМЫШЛЕННЫХ ИСПЫТАНИЙ НАНОДЕЭМУЛЬГАТОРА “IKHLAS-1” НА ОБЪЕКТАХ АО «ОЗЕНМУНАЙГАЗ» РК

А.А.Гасанов[0000-0002-0149-1943], *Т.К.Дашдиева*[0000-0001-7962-4323]
Азербайджанский Государственный Университет Нефти и Промышленности
turanamammadova15@gmail.com

В статье изложены сравнительные результаты опытно-промышленных испытаний нанодеэмульгатора “IKHLAS-1” на объектах АО «Озенмунайгаз» РК. Результатами локальных ОПИ, впервые предложены экономически выгодные наноэкотехнологии с помощью нанодеэмульгатора “IKHLAS-1” с полинаноструктурой для улучшения водоподготовки на УПСВ-1 (установка предварительного сброса воды), а также для переработки исторических отложений в ЦППН (цех подготовки и перекачки нефти) месторождения «Узень». Качество товарной нефти во всех проводимых ОПИ было значительно лучше, по сравнению с базовым деэмульгатором “Randem-2201”.

Ключевые слова: *нанодээмульгатор “IKHLAS-1” с полинаноструктурой , месторождение «Узень», утилизация трудно разрушаемых водонефтяных эмульсий и суспензий, нефтепромысловые наноэкотехнологии, первичная подготовка нефти*

QAZAXSTAN RESPUBLİKASININ «OZENMUNAYQAZ» OBYEKTLƏRİNDƏ “İKHLAS-1” NANODEEMULQATURUNUN TƏCRÜBİ-SƏNAYE SINAQ NƏTİCƏLƏRİ

Ə.A.Həsənov[0000-0002-0149-1943], *T.K.Daşdiyeva*[0000-0001-7962-4323]
Azərbaycan Dövlət Neft və Sənaye Universiteti
turanamammadova15@gmail.com

Məqalədə Qazaxstan Respublikasının «Озенмунайгаз» obyektlərində “IKHLAS-1” nanodeemulqaturu ilə həyata keçirilmiş təcrübi-sənaye sınaqlarının (TSS) nəticələri şərh edilmişdir. SİAQ-1-də (suyun ilkin axıdılması qurğusunda) və “Uzen” yatağının NHVS-də *(nrftin hazırlanma və vurma sexi) tarixi çöküntülərin emalı məqsədi ilə polinanoquruluşlu "IKHLAS-1" nanodeemulqaturu ilə aparılan lokal TSS nəticələri əsasında ilk dəfə olaraq, iqtisadi baxımdan əlverişli olan nanoekotexnologiyalar təklif edilmişdir. Bütün TSS-lər zamanı əmtəə neftinin keyfiyyət göstəriciləri "Randem-2201" deemulqaturu ilə müqiyəsədə daha yüksək olmuşdur.*

Açar sözlər: *polinanoquruluşlu "IKHLAS-1" nanodeemulqaturu, "Uzen" yatağı, çətin parçalanan suneft emulsiya və suspenziyalaının utilizasiyası, neft-mədən nanoekotexnologiyaları, neftin ilkin hazırlanması*

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DETERMINATION OF ECOTOXIC SUBSTANCES IN WASTEWATER FORMED IN THE PURIFICATION PROCESS OF PETROLEUM OILS WITH HYDROGEN BY SPECTRAL METHODS

A.M.Huseynli 0000-0002-4265-0445*, G.İ.Bayramov*
Baku State University
atlashuseynli@yahoo.com

The article analyzes the determination of the amount of dissolved ecotoxicants in the sample taken from the industrial wastewater obtained during the process of hydrogen treatment of petroleum oils. During the hydrogenation process, different types of wastes are formed, depending on the nature of each compound contained in petroleum distillates. Every gas, liquid, solid waste formed during the process of hydrogen purification of petroleum distillates by the oil refining industry has a negative impact on the environment in various ways. One of the main directions of our scientific research is the ecological assessment of the environmental impact of wastewater formed in the process of hydrogen treatment of petroleum distillates.Based on the results obtained, the environmental impact of the wastewater was assessed. The amount of volatile ecotoxicants in the wastewater sample was determined by spectral methods and is shown in the table. We used gas chromatography-mass spectrometry method for the polycyclic aromatic hydrocarbons; optical emission spectrometry method for metals; spectrometry method for phenols, dyes and fluorine; nephelometry method for turbidity; the gravimetry method for total suspended particles. Based on the results obtained, it is possible to assess the environmental impact of wastewater generated during the technological process at the hydrogen treatment plant.

Keywords: *petroleum distillates, hydrogen purification, spectral method, ecotoxicants, effluents.*

INTRODUCTION

The hydrogen treatment plant for petroleum distillates and other oil distillates at the Heydar Aliyev Oil Refinery is considered to be more environmentally and economically efficient than the old classical technological plants.As it is known, so far the complete reduction of emissions has not been achieved during the technological processes of oil refining in the developed countries of the world oil industry [1-3].

That is why conducting environmental research in various areas is one of the most important topics in the assessment of environmental impact of each of the many existing technological processes in the oil refining industry, as one of the main environmental safety requirements of the time [4,5].

From this point of view, the main purpose of our research is to program an environmental assessment of the environmental impact of the process of hydrogen purification of petroleum oils at the facility №501 of the Heydar Aliyev Oil Refinery [6]. One of the industrial wastes generated during the technological process of this facility is wastewater.The amounts of ecotoxicant organic and inorganic substances in the water sample taken from the effluent of the plant's industrial wastewater were determined by the mass spectrum method in the laboratory.

For the first time, ecotoxicants in soluble form in industrial wastewater formed when using Autol 8 and Autol 15 oil distillates as raw materials in the hydrogen cleaning process mentioned by us were determined spectrally.

As noted in the technical literature, the process of hydrogen purification of petroleum oils has great economic and environmental advantages.Thus, the process of preparation of petroleum distillates as a commodity has been carried out for many years by acid-base, contact methods.Even in the oil refining industry of Azerbaijan, as in many countries, these classic processes are currently used in small quantities, which in turn creates environmental problems.In the process of refining oil and oil distillates by the above-mentioned classical methods, economically and ecologically effective, high-quality petroleum oils are produced, despite the fact that they create a very dangerous and harmful conditions [7-9].

In this case, fumes of sulfuric acid, sodium hydroxide and other ecotoxicants are go up into the atmosphere, along with harmful hydrocarbons of various compositions. At the same time, acidic waters containing aromatic hydrocarbons and other harmful substances containing polystyrene wastewater are discharged into water bodies without thorough cleaning. It is known that in the oil refining industry, as in other industries, it has not yet been possible to carry out completely waste-free technological processes [11-15].

From this point of view, various types of industrial wastes are formed during the plant of the purification processes with hydrogenation of petroleum oils of Heydar Aliyev Oil Refinery during the for the production of various brands of petroleum oils, as well as light oil distillates as commodities [16].

One of the main directions of our research is the initial assessment of the environmental impact of wastewater generated at the facility.The following analyzes were performed for this purpose.

EXPERIMENTAL PART

Spectral analysis of volatile ecotoxicants in water samples taken from wastewater formed during the hydrogenation of Autol 8 and Autol 15 oil distillates as catalysts as the main raw material was carried out in the above-mentioned facility.Spectral analysis is a method of quantitative and qualitative determination of the composition of a substance.Based on the study of absorption, emission and luminescence spectra.

Spectral analysis is divided into several independent methods.These include infrared and ultraviolet spectroscopy, atomic absorption, luminescence and fluorescence analysis, reflection and Raman spectroscopy, spectrophotometry, X-ray spectroscopy and several other methods.

We use gas chromatography-mass spectrometry method for the analysis of PAH (Polycyclic aromatic hydrocarbons); optical emission spectrometry method for metals; spectrometry method for phenols, dyes and fluorine; nephelometry method for turbidity; gravimetry method for common suspended particles. These methods are shown in the table below (table 1).

The results obtained during laboratory measurements by taking water samples from the general wastewater outlet of the facility in accordance with the known methods are shown below (table 2,3).

Table 1

Methods of studying the composition of industrial wastewater

Assigned indicator	Method	MDL	MU
Blurring	SM 2130	1 NTU	5%
Color	SM 2120C	2.5 color (mg/l Pt)	10%
Common suspended solids	EN 872; SM 2540D	2 mg/l	5%
Fluorides	Spectroquant Fluoride Test 1.14598.0001, 1.14598.0002 (0.1-20 mg/l)	0.1 mg/l F	10%
Phenols (spectrophotometric method)	SM 5530D	0.03 mg/l	10%
Aluminum (Al)	ISO 11885, SM 3120B, EPA 6010D	0.02 mg/l	15%
Cobalt (Co)	ISO 11885, SM 3120B, EPA 6010D	0.008 mg/l	15%
Molybdenum (Mo)	ISO 11885, SM 3120B, EPA 6010D	0.005 mg/l	15%
Nickel (Ni)	ISO 11885, SM 3120B, EPA 6010D	0.008 mg/l	15%

MDL – Minimum setting limit
MU – Possible error in measurement

Table 2

Results of analysis of industrial wastewater

Assigned indicator	Amounts. mg/l
Polycyclic aromatic hydrocarbons (PAH)	
Naphthalene	9.8
Acenaphthylene	0.06
Acenaphthene	0.06
Fluorene	0.17
Phenanthrene	0.27
Anthracene	0.18
Fluoranthene	0.23
Pyrene	0.36
Benzo (a) anthracene	0.34
Chrysene	0.53
Benzo (b + j + k) fluoranthene	0.30
Benzo (a) pyrene	0.18
Indeno (1,2,3-cd) pyrene	0.08
Benzo (ghi) perylene	0.09
Dibenzo (ah) anthracene	0.09
∑ 16 PAH	12.7

As can be seen from the results obtained from the tables, the reasons for the formation of all volatile organic and inorganic substances with all ecotoxicant properties in the water sample taken from the plant of the refinery can be explained as follows:

Table 3

Results of analysis of industrial wastewater

Assigned indicator	Amounts
Blurring, NTU	2.1
Color, mg/l Pt	1882
Total suspended solids, mg/l	6.0
Fluorides, mg/l	6.9
Phenols (spectrophotometric method), mg/l	<0.03
Aluminum (Al), mg/l	<0.02
Cobalt (Co), mg/l	<0.008
Molybdenum (Mo), mg/l	<0.005
Nickel (Ni), mg/l	<0.008

- Chemical transformations of hydrogen gas with Autol 8 and Autol 15 distillates due to the presence of sulfur, nitrogen, oxygen, phosphorus organic compounds, various mixtures of hydrocarbons and metal salts and catalysts, pressure and temperature up to 280-310^{0}C resulting in volatile ecotoxicants.
- Although the individual quantities of the refinery are less than normal, as can be seen from the table, their total amount is very high and toxic.

As can be seen from table 3, the total amount of suspended solids and fluorides is above normal and their harm to human health is known to science.The content of dissolved ecotoxicants in the waste water sample of the plant depends mainly on the amount of sulfur, nitrogen, oxygen, metal, etc. compounds in the raw materials Autol 8 and Autol 15 distillates, as well as petroleum acids. The following are views of chromatograms of spectral analysis:

Thus, in short, the following explanations can be given about the technological process of hydrotreating of petroleum distillates and the reactions that take place during this process.

-The hydrotreating process is carried out in a hydrogen environment with the presence of alumocobaltmolibdenum and alumonicelmolibdenum catalysts at a temperature of 350-430^{0}C, 30-70 atmospheres, 100-600 m^3 of circulating hydrogen gas as raw material and 60-95% hydrogen.

-During this process occur reactions such as hydro-desulfurization, hydrocracking, hydrogenation of unsaturated hydrocarbons, isomerization of paraffin and naphthenic hydrocarbons.

-During the hydrogenation process, different types of wastes are formed, depending on the nature of each compound contained in petroleum distillates.Phenols, ketones, alcohols in the resin formed in the technological process are easily reduced by hydrogen.

-The mixture of these resins is saturated with hydrogen and broken down to form hydrocarbons, hydrogen sulfide, ammonia and the above-mentioned volatile compounds with ecotoxicant properties.Wastewater containing a mixture of dissolved ecotoxicants is separated from the technological process [17-20].

As can be seen from the above-mentioned basic scientific theoretical explanations, during the process of hydrogen purification of petroleum distillates, depending on the composition of these distillates, gaseous substances of different composition, ecotoxic properties have high volatility and dissolve in high concentration in wastewater.

That is why every gas, liquid, solid waste formed during the process of hydrogen purification of petroleum distillates by the oil refining industry has a negative impact on the environment in various ways. One of the main directions of our scientific research is the ecological assessment of the environmental impact of wastewater formed in the process of hydrogen treatment of petroleum distillates.

RESULTS AND DISCUSSION

The following explanations can be given about the results of the research:

- The rate of emission of each of the dissolved ecotoxicants into the atmosphere in the sample of the main industrial wastewater formed in the technological process of hydrogen purification of petroleum distillates was determined by spectral method.
- The reasons for the production of organic and inorganic volatile compounds in the wastewater of the hydrotreating process and our initial classification are given.

Rapid evaporation of volatile ecotoxicants from a sample of industrial wastewater during a study based on information on environmental and sanitary permissible concentration limits in the technological literature, despite their short-term natural dilution in the atmosphere, each of which causes environmental pollution.

As it is known, even in the developed countries of the world, most of the wastewater treatment plants formed in the oil refining industry have an open surface, so volatile compounds of various compositions are released into the atmosphere from these plants.

Therefore, despite the environmental treatment of industrial wastewater generated in the oil industry, the presence of oil-dependent substances, phenol-type compounds in these waters, as well as the release of some of them into the water basins due to the above-mentioned volatile ecotoxicants have a negative environmental impact on flora and fauna.

At the same time, the evaporation of harmful substances from the industrial wastewater becomes a source of environmental pollution of the atmosphere, as well as the lithosphere.Thus, given the extensive information in the technical literature on the effects of each identified ecotoxicant on human health and the ecosphere, the biosphere in general, and their allowable concentrations in the industrial wastewater taken from the hydrogen treatment plant during the study, there is no need additional explanations of the impact of these substances on the environment.

Sampling of each of the gas, liquid and solid wastes formed in each of the processes of hydrogenation of petroleum oils and other petroleum distillates at the facility No.501 of the Heydar Aliyev Oil Refinery is carried out by various flexible, express and spectral methods.The analysis of the components is programmed by us.

Based on the determination of ecotoxicants contained in various types of waste generated in the facility depending on the composition of raw materials of technological processes the assessment of environmental impact can be considered scientifically based.

CONCLUSION

According to the results of the research, it can be noted that the industrial wastewater discharged from the oil refinery's facility №501 has a content that will damage the ecosphere and biosphere.

As a result of our analysis of the composition of these waters, polycyclic aromatic hydrocarbons and other harmful substances in the wastewater, no matter how much the harmful elements in the waste water are cleaned, they remain dissolved in the water and dumped into water bodies.Over many years, these small amounts can cause huge damage. Accumulation of these elements in the bottom sediments damages the aquatic life in the waters and as a result of leaks, the lithosphere is also exposed to pollution.

REFERENCES

1. Barkov Yu.V, Sisolyatin V.M. Novie napravleniya ispolzovaniya nefti i prirodnoqo qaza. Dj. Neft, qaz и biznes. 2001, №6, pp. 98-124
2. Property document of the project on modernization and reconstruction of the Oil Refinery named after H.Aliyev. Baku.2017, 83 p
3. Robinson P.R. Petroleum processing overview. In: Hsu CS, Robinson PR, editors. Practical advances in petroleum processing. New York: Springer. 2006, Vol.1, pp. 1–78
4. Gruia A. Recent advances in hydrocracking. In: Hsu CS, Robinson PR, editors. Practical advances in petroleum processing. New York: Springer. 2006, Vol.1, pp. 219–256
5. Froment G.F. Modeling in the development of hydrotreatment processes. Catal. Today. 2004, pp. 43–54
6. Technological regulations of installation №501 (hydrotreating unit) of the Heydar Aliyev Oil Refinery. pp. 15-26
7. Davidova S.L.,Teplyakov V.V. Ekoloqiceskie problemi neftepererabotki: Uceb, Razresenie. M. RUDN. 2010, pp. 54-67
8. Mahmudov C.M. Technology of production areas and industrial ecology. Baku. 2006, pp. 78-95
9. Nuraliyeva R.N. Economic and ecological problems of development of fuel and energy complex of Azerbaijan. Baku. 2010, pp. 127-134
10. Ahmadov Sh., Muradov N. Ecology. Atmospheric pollution. Baku. 2008, pp. 55-57
11. Suxanov V.P. Pererabotka nefti. Ucebnik- vissaya skola. 1974, 211p
12. Ancheyta J., Speight J. Hydroprocessing chemistry. In: Ancheyta J, Speight JG, editors, Hydroprocessing of heavy oils and residua, 1st ed. Boca Raton, FL: CRC Press/Taylor & Francis. 2007, pp. 35–50
13. Aliyev M.A., Huseynov A.G., Karimov K.S., Huseynova U.Y. Economics and management of oil and gas industry. Baku. 2016, 61p
14. Maharamov A.M., Bayramov M.R. Petrochemistry and petrochemical synthesis. Baku University Publishing House, Baku. 2006, 48 p

15. Anton A.M. Hydrotreating of oil fractions .299 p https://www.researchgate.net/publication/304479774
16. Hajiyeva S.R., Shamilov N.T., Samadova A.A. Effective treatment of industrial wastewater formed in the oil refining industry by the coagulation method. News of ANAS, Science. 2021, pp. 80-83
17. Novruzov S.A. Organic chemical technology and industrial ecology. Baku. 2006, pp. 123-124
18. Aliyev M.A., Huseynov A.G., Karimov K.S. Economics and management of the oil and gas industry. Baku. 2016, 45 p
19. Ajamov K.Y., Bagirova N.N., Mammadkhanova S.A, Huseynova E.A. Technology of preparation of catalysts and adsorbents. Baku. 2011, pp. 181-182
20. Maharamov A.M., Bayramov M.R., Mammadov I.G., Bayramova G.M. Processing of hydrocarbon raw materials. Chashyoglu, Baku. 2012, pp. 159-160

ЭКСПРЕСС-ОПРЕДЕЛЕНИЕ ОБЪЕМНЫХ ЭКОТОКСИЧНЫХ ВЕЩЕСТВ ВСТОЧНЫХ ВОДАХ, ОБРАЗУЮЩИХСЯ В ПРОЦЕССЕ ВОДОРОДНОЙ ОЧИСТКИ НЕФТЯНЫХ МАСЕЛ

А.М.Гусейнли [0000-0002-4265-0445,], *Г.И.Байрамов*
Бакинский Государственный Университет
atlashuseynli@yahoo.com

В статье проведен анализ определения количества растворенных экотоксикантов в пробе промышленных сточных вод, полученных в процессе водородной обработки нефтяных масел. В процессе гидрирования образуются различные виды отходов в зависимости от природы каждого соединения, содержащегося в нефтяных дистиллятах. Любые газообразные, жидкие, твердые отходы, образующиеся в процессе водородной очистки нефтяных дистиллятов нефтеперерабатывающей промышленностьй, в разной степени негативно воздействуют на окружающую среду. Одним из основных направлений наших научных исследований является экологическая оценка воздействия на окружающую среду сточных вод, образующихся в процессе водородной обработки нефтяных дистиллятов. На основании полученных результатов проведена оценка воздействия сточных вод на окружающую среду. Количество летучих экотоксикантов в пробе сточных вод определено спектральными методами и приведено в таблице. Использовали хромато-масс-спектрометрию для полициклических ароматических углеводородов, оптическую эмиссионную спектрометрию для металлов, спектрометрию для фенолов, красителей и фтора, нефелометрию для определения мутности и гравиметрию для общее количество взвешенных частиц. На основании полученных результатов можно оценить воздействие на окружающую среду сточных вод, образующихся в ходе технологического процесса на установке очистки водорода.

Ключевые слова: *нефтяные дистилляты, очистка водорода, спектральный метод,экотоксиканты, сточные воды.*

NEFT YAĞLARININ HİDROGENLƏ TƏMİZLƏNMƏSİ PROSESİNDƏ YARANAN TULLANTI SULARININ TƏRKİBİNDƏ OLAN EKOTOKSİKANT MADDƏLƏRİN SPEKTRAL ÜSULLARLA TƏYİNİ

A.M.Hüseynli. $^{0000-0002-4265-0445}$*, Q.İ.Bayramov*
Bakı Dövlət Universiteti
atlashuseynli@yahoo.com

Məqalədə neft yağlarının hidrogenlə təmizlənməsi prosesi zamanı alınmış sənaye çirkab sularından götürülmüş nümunədə həll olunmuş ekotoksikantların miqdarının təyini təhlil edilir. Hidrogenləşmə prosesi zamanı neft distillatlarının tərkibində olan hər bir birləşmənin təbiətindən asılı olaraq müxtəlif növ tullantılar əmələ gəlir. Neft emalı sənayesi tərəfindən neft distillatlarının hidrogenlə təmizlənməsi prosesi zamanı əmələ gələn hər bir qaz, maye, bərk tullantılar ətraf mühitə müxtəlif yollarla mənfi təsir göstərir. Elmi tədqiqatlarımızın əsas istiqamətlərindən biri neft distillatlarının hidrogenlə təmizlənməsi prosesində əmələ gələn tullantı sularının ətraf mühitə təsirinin ekoloji qiymətləndirilməsidir. Alınmış nəticələr əsasında tullantı sularının ətraf mühitə təsiri qiymətləndirilmişdir. Çirkab su nümunəsindəki uçucu ekotoksikantların miqdarı spektral üsullarla müəyyən edilmiş və cədvəldə göstərilmişdir. Biz polisiklik aromatik karbohidrogenlər üçün qaz xromatoqrafiyası-kütləvi spektrometriya metodundan; metallar üçün optik emissiya spektrometriya üsulu; fenollar, boyalar və flüor üçün spektrometriya üsulu; bulanıqlıq üçün nefelometriya üsulu; ümumi asılı hissəciklər üçün qravimetriya üsulundan istifadə etmişik. Alınmış nəticələr əsasında hidrogen təmizləyici qurğuda texnoloji proses zamanı əmələ gələn tullantı sularının ətraf mühitə təsirini qiymətləndirmək mümkündür.

Açar sözlər: *Neft distillatları, hidrogenlə təmizləmə, spektral metod,ekotoksikant maddələr, tullantı suları.*

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NEW SIMPLE METHOD FOR THE DETERMINATION OF TRACE LEVEL COPPER (II) USING 1- [2- (ALLYLAMINO) -1-METHYLETHYL] THIOUREA IN PRESENCE OF HYDROFOB AMINES BY MOLECULAR ABSORPTION SPECTRAL METHOD IN THE UV AND VISIBLE REGION

P.R.Mammadov $^{0000-0002-9512-6719}$,*T.A.Javadzade* $^{0000-0003-3327-4430}$, *A.R.Sucayev* $^{0000-0001-6890-2324}$,*R.E.Mammadova*[1], *F.M. Chiragov* $^{0000-0002-2677-9046}$
Baku State University[1]
Institute of Chemistry of Additives named after Academician A.M.Guliyev[2]
poladazer@gmail.com

Cu(II) with 1- [2- (allylamino) -1-methylethyl] thiourea the rapid reacts to form orange complex and also it to form to form brownish complexes in presence of the phenanthroline (Phen) and α,α' - dipyridine (α,α' -dip). The absorption spectra of the Cu(II) - AMTIC system is a curve with the maximum absorbance at 415 nm and molar absorption coefficient of $1.95 \cdot 10^4$ *l* mol^{-1} cm^{-1}*. The absorption spectra of the Cu(II)- AMTIC- Phen and Cu(II) -AMTIC - α,α'-dip systems is a curve with the maximum absorbances at 437 nm and 443 nm and molar absorption coefficients of* $2.94 \cdot 10^4$ *l* mol^{-1} cm^{-1} *and* $2.81 \cdot 10^4$ *l* mol^{-1} cm^{-1}*, respectively. The absorbance was linear for 0.25–2.07 mkg* ml^{-1} *of Cu(II) in the Cu(II)- AMTIC system and 0.12 –2.56 mkg* ml^{-1} *and 0.18–2.45 mkg* ml^{-1} *of Cu(II) in the Cu(II)-AMTIC- Phen and Cu(II)-AMTIC- α,α'-dipsystems, respectively. The proposed methods was successfully used in the determination of Cu(II) in several synthetic mixtures. The relative standard deviation (n = 5) was 0%–2.0%, for Cu(II), indicating that this methods are highly precise and reproducible. The results obtained agree well with synthetic mixture samples analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES).*

Keywords: *copper, 1- [2- (allylamino) -1-methylethyl] thiocarbamide, phenanthroline (Phen) and α,α' - dipyridine.*

INTRODUCTION

A copper is used as a conductor of heat and electricity, as a building material and as a constituent of various metal alloys_such as in jewelry, cupronickel used to make marine hardware and coins and constantan used in strain gauges and thermocouples for temperature measurement. Although copper (II) ions are extremely important for several biological processes, their levels in some. While trace copper ions (II) promote rancidity and off flavors in nutrients, copper accumulation in the liver is a characteristics of Wilson's disease, producing neurological and psychiatric defects situations are indications of a problem or disease in many living systems or environments.Therefore, it is clear that in the arsenal of analysts there must be simple and rapid methods to determine copper in a wide concentration range with the highest possible sensitivity accuracy[1].

A simple sensitive and selective methods for determination of trace copper has been required. Sophisticated techniques, such as inductively coupled plasma mass spectrometry (ICP-MS) [2-4], inductively coupled plasma atomic emission spectrometry (ICP-AES) [5-6], inductively coupled plasma optical emission spectrometry (ICP-OES) [7-8], atomic absorption spectrophotometry (AAS) [9-10], electrochemical [11-13] and spectrophotometry[14-15] have widely been applied to the determination of copper in various samples. Some factors such as initial cost of instrument, technical know-how, consumable and costly maintenance of technique restrict the wider applicability of spectrophotometric methods, particularly in laboratories with limited budget in developing countries and for field work. In the literaturs wide variety of spectrophotometric methods for determination of Cu(II) have been reported, each chromogenic system has its advantages and disadvantages with respect to sensitivity, selectivity and convenience [16-22]. Many reagents used in photometric methods for the determination of Cu(II) contain sulfur in the molecule. Therefore, the synthesis of new sulfur content of organic reagents, the study of their complexation with Cu(II) is an urgent task. In this work, a reagent 1- [2- (allylamino) -1-methylethyl] thiocarbamide (AMTIC) was synthesized according to the method of and a color reaction of AMTIC with Cu(II) and in the presence of hydrofob amines - phenanthroline (Phen) and α,α′ - dipyridine was carefully studied. The aim of present study is to develop a simpler spectrophotometric method for the trace determination of Cu(II) with AMTIC and in the presence of hydrofob amines - phenanthroline and α,α′ - dipyridine solutions.

EXPERIMENTAL PART

The absorbance of solutions was measured with a Perkin Elmer (United States) (Model: Lambda-40) double-beam UV/VIS spectrophotometer and with a KFK-3 photoelectrocolorimeter (Russia), with 1 cm matched quartz cells. The pH values of solutions was controlled on the ionomer I-121 with glass electrode customized by standart bufer solutions.

A Perkin Elmer (United States) (Model: Optima-2100 DV) Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) was used for comparing the results.

Chemicals and reagents

All chemicals solvents used were of analytical reagent grade or the highest purity available. Doubly distilled de-ionized water was used throughout. Glass vessels were cleaned by soaking in acidified solutions of $KMnO_4$ or $K_2Cr_2O_7$, followed by washing with concentrated HNO_3 and rinsed several times with deionized water.

Copper (II) standard solutions (10^{-2} M)

A 10^{-2} M 100 ml stock solution of copper (II) was prepared by dissolving 0.06355 g of copper (purity 99.98%) in nitric acid by warming, evaporating the solution to dryness, dissolving the residue in hydrochloric acid, evaporating the solution to half its volume, cooling and diluting with water to 100 ml in calibrated flask . Working solutions were prepared by appropriate dilution of standard solution with water.

1- [2- (allylamino) -1-methylethyl] thiocarbamide

The 1- [2- (allylamino) -1-methylethyl] thiocarbamide reagent was synthesized according to the known method . The NMR spectroscopic data of 1- [2- (allylamino) -1-methylethyl] thiocarbamide: ^{1}H NMR spektrum:(CCL_4, **δ**.m.h) 9.48$_3$(2H,NH_2), 7.21d(1H, NH), 3.22m(2H,CH_2), 2.01m (1H,NH), 2.64-2.89 d(2H,CH_2), 1.50-3.03 m (1H,CH), 1.10 s (3H,CH_3), 1.10 s (3H_1,CH_3), 5.15 m (1H-C-N- sis), 5.17m (1H_1-C-N-trans), 5.83 m (1H-C-N). ^{13}C NMR Spektrum: 186, 52.0, 53.7, 55.5, 116.2, 134.2, 184.7.

The solution of 1- [2- (allylamino) -1-methylethyl] thiocarbamide reagent was prepared by dissolving the requisite amount of AMTIC in a known volume of ethanol. More dilute solution of the reagent was prepared as required.

Phenanthroline (Phen) and α,α′ - dipyridine (α,α′ - dip)

$1 \cdot 10^{-2}$ M solutions of phenanthroline and α,α′ - dipyridine was preparing by dissolving the requisite amounts of these substancies in distilled water and ethanol(1:1).

Aqueous ammonia solution

A 100 ml solution of aqueous ammonia was prepared by diluting 10 ml of concentrated NH_3 (28%–30%) ACS grade with distilled water. The solution was stored in a glass bottle.

EDTA solution

A 100 ml stock solution of EDTA (0.1% w/v) was prepared by dissolving 128 mg of ethylenediaminetetraacetic acid, disodium salt dehydrate in 100 ml distilled water.

Other solutions

Solutions of a large number of inorganic ions and complexing agents were prepared from their grade, or equivalent grade, water soluble salts.

RESULTS AND DISCUSSION

Copper (II) ion with 1- [2- (allylamino) -1-methylethyl] thiocarbamide the rapid reacts to form orange complex and also it to form brownish complexes in presence of phenanthroline and α,α′ - dipyridine solutions.

Absorption spectra

The absorption spectra of the Cu(II)- AMTIC is a curve with the maximum absorbance at 415 nm and an average molar absorption coefficient of $1.95 \cdot 10^{4}$ l mol^{-1} cm^{-1} in aqueous media. The absorption spectra of the Cu(II)-AMTIC- Phen and Cu(II)-AMTIC- α,α′-dipsystems is a curve with the maximum absorbances at 437 nm and 443 nm and average molar absorption coefficients of $2.94 \cdot 10^{4}$ l mol^{-1} cm^{-1} and $2.81 \cdot 10^{4}$ l mol^{-1} cm^{-1} in micellar media, respectively (fig. 1).

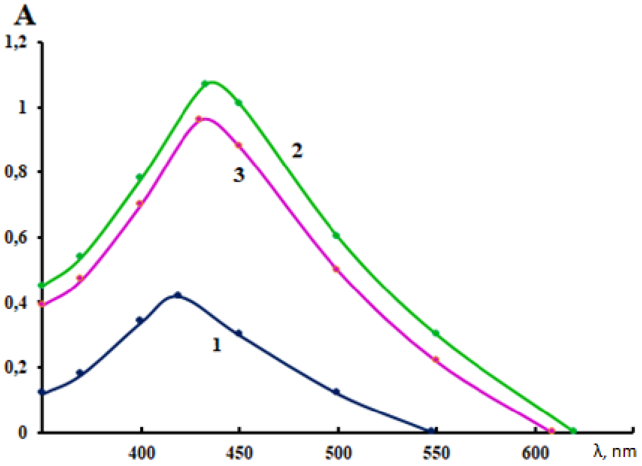

Fig.1. Absorption spectra of Cu(II)- AMTIC(1), Cu(II)-AMTIC-α,α′-dip (2) and Cu(II)-AMTIC- Phen(3).

Effect of acidity. Effect of the various pH 0-12 studied, pH 4.9,0-6,2 found to be the best acid for the Cu(II) AMTIC system and pH 4,2-5,6 found to be the best acid for the Cu(II)AMTIC- Phen and Cu(II) AMTIC-α,α′-dip systems at room temperature (25±5)^0 C. The absorbance of the reagent solution and the all systems depends on the medium pH; therefore, the absorption spectra are studied relative to a blank experiment against the background of control experiment (AMTIC and AMTIC +X), which was prepared in the same conditions (fig. 2).

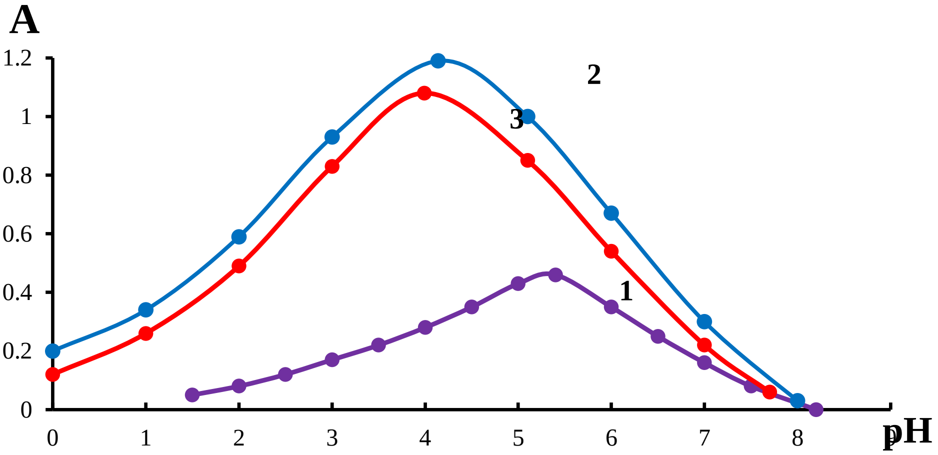

Fig.2. Effect of acidity . Cu(II)- AMTIC(1), Cu(II)-AMTIC-α,α′-dip (2) and Cu(II)-AMTIC- Phen(3).

Effect of time. The reaction is fast. Constant maximum absorbance was obtained after 10 min for Cu(II)-AMTIC system in aqueous media and 5 min for Cu(II)-AMTIC- Phen and Cu(II)-AMTIC- α,α′-dipsystems in micellar media, respectively.

Effect of temperature**.** The absorbance at different temperatures, 0–80^{0}C, of a 25 ml solution of all systems was measured according to the standard procedure. The absorbance was found to be strictly unaltered through-out the temperature range of 10–40^{0}C. Therefore, all measurements were performed at room temperature (25 ±5)^{0}C.

Stoichiometry. The component ratio in the complexes was found using the isomolar series method, the relative yield method by Starik and Barbanel and the equilibrium shift method . All the methods showed that the component ratio were 1:2 in the Cu(II)- AMTIC system and 1:2:1 in the Cu(II)- AMTIC-Phen and Cu(II)-AMTIC-α,α′-dipsystems. The number of protons displaced upon complexation was determined by the Astakhovs method, and the indicated component ratio in the complexes was confirmed.

Effect of the reagent and phenanthroline and α,α′ - dipyridine concentration. Different molar excesses of AMTIC and phenanthroline and α,α′ - dipyridine were added to a fixed Cu(II) concentration and the absorbance was measured according to the standard procedure. It was observed that a 1 mkg/ml of copper metal (optical path 1 cm in length), the reagent and phenanthroline and α,α′ - dipyridine molar ratios produced a constant absorbance of Cu(II)- AMTIC-Phen and Cu(II)-AMTIC- α,α′-dipsystems. For all subsequent measurements, 2 ml of 2·10^{-4} M AMTIC reagent and 4ml of 2·10^{-4} M phenanthroline and α,α′ - dipyridine was added.

Analytical performance of the methods

Calibration curve

The effect of metal concentration was studied over 0.01–100 mkg ml^{-1}, distributed in four different sets (0.01–0.1, 0.1–1, 1–10 mkg ml^{-1}) for convenience of the measurement. The absorbance was linear for 0.25 –2.07 mkg ml^{-1} of Cu(II) in the Cu(II)- AMTIC system and 0.12–2.56 mkg ml^{-1} and 0.18–2.45 mkg ml^{-1} of Cu(II) in the Cu(II)-AMTIC- Phen and Cu(II)-AMTIC- α,α′-dipsystems, respectively. From the slope of the calibration graph, the average molar absorption coefficient was found to be $1.95\cdot10^4$ l mol^{-1} cm^{-1} for Cu(II)- AMTIC system and $2.94\cdot10^4$ l mol^{-1} cm^{-1} and $2.81\cdot10^4$ l mol^{-1} cm^{-1} in the Cu(II)-AMTIC- Phen and Cu(II)-AMTIC- α,α′-dipsystems, respectively. The selected analytical parameters obtained with the optimization experiments are summarized in table 1.

Table 1

Selected analytical parameters obtained by optimization experiments

Parameters	Studied range	Selected value		
		Cu(II)- AMTIC	Cu(II)- AMTIC- Phen	Cu(II)-AMTIC- α,α′ - dip
Wavelength, λ_{max}(nm)	200-800	415	437	443
Wavelength , λ_{opt} (nm)	-	400	440	440
pH	0 - 12	5-6	4-5	4-5
Time , h	1 - 24h	5 - 10 min	5-6 min.	5-6 min.
Temperature , °C	0 - 80 °C	25 ± 5 °C	25 ± 5 °C	25 ± 5 °C
Cu(II): AMTIC:X	1:10- 10:1	1:2	1:2:1	1:2:1
Molar absorption coefficient , l mol^{-1} cm^{-1}	-	$1.95\cdot10^4$	$2.94\cdot10^4$	$2.81\cdot10^4$
Linear range, mkg ml^{-1}	0.01-10	0.25 –2.07	0.12–2.56	0.18–2.45
lgβ	-	10.23	12.56	11.78
Sandell's sensitivity ,mkg cm^{-2}	0.1 - 10	7	5	5
Relative Standard	0 -5	0 -2	0 -2	0 -2

Precision and accuracy

The precision of the present method was evaluated by determining different concentrations of Cu(II) (each analyzed at least five times). The relative standard deviation (n = 5) was 0%–2.0%, for 0.1–8 mkg of Cu(II), indicating that this method is highly precise and reproducible. The Sandell's sensitivity for Cu(II) were found to be 6 mkg cm^{-2} in Cu(II)- AMTIC system and 5 mkg cm^{-2} , 6 mkg cm^{-2} in the Cu(II)-AMTIC- Phen and Cu(II)-AMTIC- α,α′-dip systems, respectively.

Effect of foreign Ions

The effect of foreign ions on complexation of Cu(II) with AMTIC in the absence and in the presence of third components. It was found that in the presence of third parties the selectivity of the reactions of complex education increases significantly (table 2): these reagents are more selective for spectrophotometric determination of Cu(II) in comparison with the reagents known from literature [12].The effect of cations, anions and complexing agents on the determination of only 1 mkg ml^{-1} of Cu(II) was studied. The criterion for interference was an absorbance value varying by more than 5% from the expected value for Cu(II) alone. The results are given in table 2.

Table 2

Tolerance limits of foreign ions, tolerance ratio [Species(x)]/Cu (w/w)

Species x	Cu(II) - AMTIC	Cu(II) -AMTIC-Phen	Cu(II) AMTIC-α,α′ - dip	[26]
Na(I)	210	285	260	100
K(I)	220	300	270	100
Mg(II)	270	350	330	100
Ca(II)	270	350	330	100
Cr(III)	255	340	340	70
Fe(III)	60	80	80	10
Sr(II)	80	100	95	100
Cd(II)	200	290	280	100
Hg(II)	210	315	300	100
Mo(II)	210	285	280	10
As(III)	260	340	330	100
Zn(II)	235	280	280	100
Ba(II)	200	260	260	10
Al(III)	75	130	125	100
Cs(III)	225	295	290	100
Pb(II)	60	100	100	10
Ni(II)	100	140	120	10
Pb(II)	195	230	215	10
Cl^-	750	70	70	1000
$C_2O_4^{2-}$	240	270	270	1000
CH_3COO^-	40	70	70	500
PO_4^{3-}	140	170	160	500
CN^-	110	130	130	500

Applications

The Cu(II)-AMTIC-α,α′-dipsystem was successfully applied to the determination of Cu(II) in a series of synthetic mixtures of various compositions (table 3).

Determination of Cu(II) in synthetic mixtures

Several synthetic mixtures of varying compositions containing Cu(II) and diverse ions of known concentrations were determined by the present method using EDTA as a masking agent; and the results were found to be highly reproducible. The results of synthetic mixtures analyses by the spectrophotometric method were found to be in excellent agreement with those obtained by ICP-OES. The results are given in Table 3. Accurate recoveries were achieved in all solutions.

General Procedure

To synthetic mixtures samples of varying compositions containing 1-2 mkg ml^{-1} Cu(II) in 25 ml volumetric flask was mixed with 2 ml of $2{\cdot}10^{-4}$ M AMTIC reagent solution and 4ml of $2{\cdot}10^{-4}$ α,α′-dipsolution followed by the addition of 5 ml stock solution of EDTA (0.1% w/v). The mixture was diluted up to the mark with pH 5 buffer solutions. After 5 min the absorbance was measured at 440 nm against a corresponding reagent blank. The copper (II) content in the synthetic mixtures sample was determined using a concurrently prepared calibration graph.

Table 3

Determination of Cu (II) in synthetic mixtures

Sample	Composition of mixture (mkq/ml)	Proposed method			ICP-OES	
		Cu(II) mkq/ml		Recovery ± s[b] (%)	Cu(II) mkq/ml Found	Recovery ± s (%)
		Added	Found[a]			
A	Cu^{2+}	1.5 2.0	1.51 2.02	101 ± 0.2 102 ± 0.2	1.50 2.01	100 ± 0.2 101 ± 0.2
B	As in A + Ca^{2+}(25)+ Fe^{3+}(25)	1.5 2.0	1.52 2.04	102 ± 0.3 104 ± 0.2	1.51 2.02	101 ± 0.3 102 ± 0.2
C	As in B+Mg^{2+} (25)+Co^{3+} (25)	1.5 2.0	0.51 2.03	101 ± 0.4 103 ± 0.2	0.52 2.02	102 ± 0.4 102 ± 0.2
D	As in C +Cr^{3+}(25)+Ca^{2+} (25)	1.5 2.0	1.48 2.02	97 ± 0.3 102 ± 0.2	1.49 2.01	97 ± 0.3 101 ± 0.2
E	As in D +K^{+}(25)+Hg_2^{2+} (25)	1.5 2.0	1.49 2.02	98 ± 0.2 102 ± 0.1	1.495 2.025	99 ± 0.1 101 ± 0.1

[a] Average of five analysis of each sample

[b] The measure of precision is the standard deviation (s).

CONCLUSION

The absorption spectra of the Cu(II) - AMTIC system is a curve with the maximum absorbance at 415 nm and molar absorption coefficient of $1.95{\cdot}10^{4}$ l mol^{-1}

cm^{-1}. The absorption spectra of the Cu(II)- AMTIC- Phen and Cu(II) -AMTIC - α,α′-dip systems is a curve with the maximum absorbances at 437 nm and 443 nm and molar absorption coefficients of $2.94{\cdot}10^4$ l mol^{-1} cm^{-1} and $2.81{\cdot}10^4$ l mol^{-1} cm^{-1}, respectively.

The absorbance was linear for 0.25–2.07 mkg ml^{-1} of Cu(II) in the Cu(II)-AMTIC system and 0.12 –2.56 mkg ml^{-1} and 0.18–2.45 mkg ml^{-1} of Cu(II) in the Cu(II)-AMTIC- Phen and Cu(II)-AMTIC- α,α′-dipsystems, respectively.

The proposed methods was successfully used in the determination of Cu(II) in several synthetic mixtures. The relative standard deviation (n = 5) was 0%–2.0%, for Cu(II), indicating that this methods are highly precise and reproducible. The results obtained agree well with synthetic mixture samples analyzed by inductively coupled plasma optical emission spectrometry.

In the present work, a simple, rapid, sensitive and selective methods was developed for the determination of Cu(II) in difficult sample matrices. Therefore, this methods will be successfully applied to the monitoring of trace amounts of Cu(II) in industrial and natural samples.

REFERENCES

1. Podchainova V.N., Simonova L.N.Analytical Chemistry of Elements.Copper. M: Nauka. 1990, 279 p
2. Vladislav Chrastný, Michael Komárek.Copper determination using ICP-MS with hexapole collision cell. Chemical Papers 63. 2009,№5,pp.512–519.https://doi.org/10.2478/s11696-009-0057-z
3. Juliana A., Nunes A. , Bruno L., Batista A. , Jairo L., Rodrigues A. , Naise M. Caldas B , José A. G.Neto b & Fernando Barbosa Jr . A Simple Method Based on ICP-MS for Estimation of Background Levels of Arsenic, Cadmium, Copper,Manganese, Nickel, Lead, and Selenium in Blood of the Brazilian Population. Journal of Toxicology and Environmental Health, Part A. 2010, pp.878–887. https://doi.org/10.1080/15287391003744807
4. Alkas F.B., Shaban J.A., Sukuroglu A.A., Kurt M.A., Battal D., Saygi S. Monitoring and assessment of heavy metal/metalloid concentration by inductively coupled plasma mass spectroscopy (ICP-MS) method in Gonyeli Lake, Cyprus. Environ. Monit. Assess. 2017, pp.1–8. doi: 10.1007/s10661-017-6222-x
5. Jamie Kern,Laura Mathiason.The determination of copper, zinc, and lead in human teeth using inductively coupled plasma atomic emission spectrometry (ICP-AES). Concordia College Journal of Analytical Chemistry .2012, pp. 33-39. http://dept.cord.edu/chemistry/ccjac/2012
6. Mohammad Reza Ganjali, Mohammad Reza Pourjavid ,Leila Haji-Agha Babaei,Masoud Salavati-Niasari.Ultra-trace monitoring of copper in environmental and biological samples by inductively coupled plasma atomic emission spectrometry after separation and preconcentration by using octadecyl silica membrane disks modified by a new schiff's base. Quim. Nova. 2004.Vol. 27, № 2, pp.213-217. https://doi.org/10.1590/s0100-40422004000200008
7. Marcia S., Rocha, Marcia F, Mesko, Fagner F. Silva, Rodrigo C. Sena, Maria Cristina B. Quaresma,Thiago O. Ara ujo and Lindomar A. Reis Determination of Cu and Fe in fuel ethanol by ICP OES using direct sample introduction by an ultrasonic

nebulizer and membrane desolvator. J. Anal. At. Spectrom., 2011, Vol. 26, pp. 456–461. https://doi.org/10.1039/c0ja00096e

8. Ryley Burgess,Agilent Technologies.Determination of Copper in Green Olives using ICP-OES. Agilent Technologies, Inc. 2018 Printed in the USA, April 1, 2018. https://www.agilent.com/cs/library/applications/5991-9125en-cu-olives-icp-oes-application.pdf

9. Serkan Şahan,Uğur Şahin Determination of Copper(II) Using Atomic Absorption Spectrometry and Eriochrome Blue Black R Loaded Amberlite XAD-1180 Resin. CLEAN. Soil, Air, Water. 2010, pp. 485–491. https://doi.org/10.1002/clen.200900303

10. Gianfranco Corbini ,Elena Dreassi, Luisa Chiasserini , Matteo Maria Girolamo ,Pierfrancesco Mellace.Determination of copper by AAS in tear fluid of patients with keratoconus.ELSEVİER .Analytical Biochemistry.2021, pp.1-5. doı: 10.1016/j.ab.2021.114174

11. Wu, K.-H.; Lo, H.-M.; Wang, J.-C.; Yu, S.-Y.; Yan, B.-D. Electrochemical detection of heavy metal pollutant using crosslinked chitosan/carbon nanotubes thin film electrodes. Mater. Express .2017, pp. 15–24. https://doi.org/10.1166/mex.2017.1351

12. Pudza M.Y., Abidin Z.Z., Abdul-Rashid S., Yasin, F.M., Noor, A.S.M., Abdullah J. Selective and simultaneous detection of cadmium, lead and copper by tapioca-derived carbon dot–modified electrode. Environ. Sci. Pollut. Res. 2020, pp.1–10. doi: 10.1007/s11356-020-07695-7

13. Chong Jin Mei , Nor Azah Yusof and Shahrul Ainliah Alang Ahmad. Electrochemical Determination of Lead & Copper Ions Using Thiolated Calix[4]arene-Modified Screen-Printed Carbon Electrode Chemosensors .2021, 9, 157, pp. 1-14. https://doi.org/10.3390/chemosensors9070157

14. Chaisuksant R., Palkawong Na Ayuthaya W., Grudpan K. Spectrophotometric determination of copper in alloys using naphthazarin. *Talanta*. 2000, pp. 579–585. https://doi.org/10.1016/S0039-9140(00)00534-8

15. Vadiraj K.T , Belagali S.L.Spectrophotometric determination of copper(II) in industrial effluent samples using sulfanilic acid as a ligand. Bulgarian Chemical Communications. 2014, Vol.46, №3, pp447-451. http://bcc.bas.bg/BCC.2014/BCC-3256-Vadiraj-46-3-447-451.pdf

16. Tekale P., Tekale S, Lingayat S, et al. Extractive Spectrophotometric Determination of Copper (II) using 1–phenyl–1– hydrazonyl–2–oximino propane–1, 2–dione. Science ResearchReporter.2011,№1,pp.83–87

17. Ch. Kavitha, M. Sarath Babu, K. Saraswathi., "Spectrophotometric Determination of Copper as Copper Piperazine", International Letters of Chemistry, Physics and Astronomy. 2013, Vol. 13, pp. 205-209. doi: 10.18052/www.scipress.com/ilcpa.13.205

18. Karthikeyan J, Naik P.P, Shetty A.N. A rapid extractive spectrophotometric determination of copper (II) in environmental samples, alloys, complexes and pharmaceutical samples using 4–*N*, N(dimethyl) amino] benzaldehydethiosemicarbazone. *Environmental Monitoring and Assessment*. 2011;176(1) , pp. 419–426. doi: 10.1007/s10661-010-1593-2

19. Hashem E.Y., Seleim M. M., El-Zohry A.M. Spectrophotometric determination of copper(II) in pharmaceutical,biological and water samples by 4-(2'-

benzothiazolylazo)-salicylic acid. Journal of Applied Spectroscopy. 2011, Vol. 78, № . 4, pp. 586- 593. doi: 10.1007/s10812-011-9502-1

20. Madan P.U, Barhate V.D. Extractive spectrophotometric determination of copper (II) using 2–(5– bromo–2– oxoindolin–3–ylidene) hydrazine carbothioamide as an analytical reagent. European Journal of Biomedical and Pharmaceutical sciences. 2016,pp.392–396.https://storage.googleapis.com/journaluploads/ejbps/article_issue/volume_3_april_issue_4/1459420615.pdf
21. Turkoglu O., Soylak M. Spectrophotometric Determination of Copper in Natural Waters and Pharmaceutical Samples with Chloro (phenyl) glyoxime. Journal of the Chinese Chemical Society. 2005, pp. 575–579
22 Shaikh B., Barache U.B, Anuse M.A., et al. 4–(4'–Nitrobenzylideneimino)-3–methyl–5–mercapto–1, 2, 4–triazole, A New Chromogenic Reagent for Extractive Spectrophotometric Determination of Copper (II) in Pharmaceutical and Alloy Samples S. *Afr J Chem*. 2016, pp.157–165 doi:https://doi.org/10.1002/jccs.200500085

НОВАЯ ПРОСТАЯ МЕТОДИКА ОПРЕДЕЛЕНИЯ СЛЕДОВЫХ КОЛИЧЕСТВ МЕДИ (II) С ИСПОЛЬЗОВАНИЕМ 1-[2-(АЛЛИЛАМИНО)-1-МЕТИЛЭТИЛ] ТИОКАРБАМИДА В ПРИСУТСТВИИ ГИДРОФОБНЫХ АМИНОВ МОЛЕКУЛЯРНО-АБСОРБЦИОННО- СПЕКТРАЛЬНЫМ МЕТОДОМ В УФ И ВИДИМОЙ ОБЛАСТЯХ

П.Р.Мамедов$^{0000-0002-9512-6719}$ *, Т.А.Джавадзаде*$^{0000-0003-3327-4430}$*, А.Р.Суджаев*$^{0000-0001-6890-2324}$*, Р.Э.Мамедова*[1]*, Ф.М.Чирагов*$^{0000-0002-2677-9046}$
Бакинский Государственный Университет
Институт химии присадок имени академика А.М. Гулиева
poladazer@gmail.com

Ион меди, входя в скоростную реакцию с 1-[2-(аллиламино)-1-метилэтил] тиокарбамидом (АМТIС) образует жёлтовато-коричневый комплекс, а в присутствии фенантролина и α,α'-дипиридина образует коричневый комплекс. Максимум светопоглощения системы Cu(II)-АМТIК наблюдается при 460 нм.и при этом молярный коэффициент светопоглощения равен $1.82{\cdot}10^4$ *л моль*$^{-1}$ *см*$^{-1}$*. В системах Cu(II)-АМТIК-Фен и Cu(II)-АМТIК-α,α'-дип максимум светопоглощения наблюдается при 476 или 473 нм, и молярный коэффициент светопоглощения соответственно равны* $2.53{\cdot}10^4$ *л моль*$^{-1}$ *см*$^{-1}$ *и* $2.38{\cdot}10^4$ *л моль*$^{-1}$ *см*$^{-1}$*. Линейность оптической плотности для ионов меди в системах Cu(II)-АМТIК-Фен и Cu(II)-АМТIК-α,α'-дип наблюдается при 0.168-2.29 мкг мл*$^{-1}$ *и 0176-2232 мкг мл*$^{-1}$*интервалах соответственно. Предложенные методики были удачно применены для определения меди в нескольких синтетических смесях. Относительная стандартная погрешность определения меди 0-2%, что указывает на высокую точность и воспроизводимость метода. Полученные результаты были сопоставлены с результатами индуктивно связанной плазмы – оптической эмиссионной спектроскопии (ИСП-ОЭС) в синтетических смесях.*

Ключевые слова: *Cu(II), 1-[2-(аллиламино)-1-метилэтил]тиомочевина, фенантролин , α,α'-дипиридин.*

UB VƏ GÖRÜNƏN OBLASTDA MOLEKULYAR ABSORBSİON SPEKTRAL METOD İLƏ MİS (II) İONUNUN İZ MİQDARININ 1- [2- (ALİLAMİNO) -1-METİLETİL] TİOKARBOMİD İLƏ HİDROFOB AMİNLƏR İŞRAKINDA YENİ SADƏ TƏYİNİ METODİKASI

P.R.Məmmədov $^{0000-0002-9512-6719}$ *,T.Ə Cavadzadə* $^{0000-0003-3327-4430}$*, Ə.R.Sucayev*$^{0000-0001-6890-2324}$*,R.E.Məmmədova, F.M.Çıraqov*$^{0000-0002-2677-9046}$
Bakı Dövlət Universiteti
Akademik Ə.M.Quliyev adına Aşqarlar Kimyası Institutu
poladazer@gmail.com

Cu(II) ionu 1- [2- (alilamino) -1-metiletil] tiokarbomid (AMTIC) ilə sürətlə reaksiyaya girərək qəhvəyi-sarı rəngli kompleks əmələgətirir və həmçinin fenantrolin və α, α ' - dipiridin iştirakında isə qəhvəyi rəngli komplekslər əmələ gətirir. Cu(II)- AMTIC sisteminin işıq udma spektrində maksimum 460 nm dalğa uzunluğunda müşahidə olunur və molyar udma əmsallı $1.82{\cdot}10^{4}$ *l mol*$^{-1}$ *sm*$^{-1}$ *bərabərdir. Cu(II)-AMTIC- Phen və Cu(II)-AMTIC- α,α′-dip sistemlərinin işıq udma spektrlərində maksimumlar 476 nm və 473 nm dalğa uzunluqlarında müşahidə olunur və molyar udma əmsalları isə uyğun olaraq* $2.53{\cdot}10^{4}$ *l mol*$^{-1}$ *cm*$^{-1}$ *and* $2.38{\cdot}10^{4}$ *l mol*$^{-1}$ *sm*$^{-1}$ *qiymətlər alır. Optiki sıxlığın xəttiliyi Cu(II) üçün 0.234–2.31 mkg ml*$^{-1}$ *miqdar intervalında Cu(II)- AMTIC sistemində və 0.168–2.242 mkg ml*$^{-1}$ *və 0.176–2.232mkg ml*$^{-1}$ ^{1} *miqdar intervallarında isə uyğun olaraq Cu(II)-AMTIC- Phen və Cu(II)-AMTIC- α,α′-dip sistemlərində müşahidə olur. Təklif olunan metodikalar misin (II) bir neçə sintetik qarışıqlarda təyinində uğurla tətbiq olunmuşdu. Nisbi standart kənara çixma Cu(II) təyini üçün 0% -2.0% olmağı, bu üsulların yüksək dəqiqliyinin və təkrarlığının olduğunu göstərir. Alınan nəticələr induktiv əlaqəli plazma optik emissiya spektrometriyası (ICP-OES) üsulu ilə sintetik qarışıq nümunələrin analizinin nəticələri ilə müqayisə edilmişdir.*

Açar sözlər: *Cu(II), 1- [2- (alilamino) -1-metiletil] tiokarbamid, fenantrolin və α, α ' - dipiridin.*

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DETERMINATION OF THE RADIATION BACKGROUND ON THE TERRITORY OF AZERBAIJAN REPUBLIC AND THE STUDY OF THE DEACTIVATION OF CONTAMINATED SOILS

H.N.Shiraliyeva 0000-0003-1172-5341
ANAS Institute of Radiation Problems
s.hecer25@gmail.com

Sources that generate high dose rates include high mountain massifs in the western regions of the country (0.85-3.75 μSv/h), interior granite-marble facings of underground transport communications (Baku Metro stations) and radionuclides in stone building materials, several nationally important (mainly in Baku) architectural buildings. gray, brown-red and black granite-marble coverings of entrance stairs and front walls, commemorative plaques, monuments, obelisks (0.15-0.85 μSv/h), production and consumption radioactive sources used in industrial, educational and research institutions, households they belong. It was also revealed that the absorbed dose power of total radioactive radiation (0.15-3.75 μSv/h) is much higher than AL (Allowable Limit), as a result of radiometric measurements, and there are local areas where the level of alpha radiation is 0.03-0.35 Bq_{eq}/cm^2. When using a reagent (HNO_3, HCl or NaOH) or a mixture (HNO_3-HCl) to clean contaminated soils, it was determined that the amount of radionuclides in the soil decreases in inverse proportion to the increase in the amount or concentration of the reagent, as well as to the increase in the amount of water with which the soil is washed.

***Keywords**: radioactive background, absorbed dose, dose rate, alpha and gamma radiation.*

INTRODADUCTION

Soil contamination with radionuclides is a planetary problem that has arisen as one of the unintended side effects of the development of nuclear technology over the past decades. Physical treatment of soils contaminated with radionuclides requires the implementation of extremely expensive and difficult processes. Such microscopic fungi retain radionuclides in the soil and weaken their migration and, as a result, prevent groundwater pollution, applying mineral fertilizers before planting in soils lightly contaminated with radionuclides and, as a result, weakening the processes of migration of radionuclides from soil to plants, bioremediation are discussed in the scientific literature, and the implementation of these measures is carried out. extensive information about the need for the creation of complex technologies with the joint activity of soil scientists, and biologists [1-4] has been interpreted.

Since it is not appropriate to throw the waste of radiochemistry production and research directly into the sewage line, this waste can be collected in separate containers and treated as waste water of the technological process after all the radionuclides contained in it are captured in order to comply with the requirements of the relevant sanitary norms and regulations. The radionuclide wastes separated in the cleaning process, as well as radioactive substances and nuclear materials that have been officially used and have expired, with reduced activity, should be handed over to the "Isotope" special combine in agreement with the control bodies[5-9].

Scientific expeditions were conducted to study the distribution of natural radionuclides and the power of the exposure dose caused by them in the mountainous areas of Azerbaijan.

EXPERIMENTAL PART

"Thermo Eberline R020 SI" (Thermo Electron Co., USA) dosimeter, "PRM-470CG" (Tesla Systems Ltd., USA) gamma ray counter, "InSpector 1000" (Canberra Co, USA-France) radiometer-dosimeter, "Radiagem 2000" (Canberra Co, USA-France) alpha, beta, gamma, neutron from radiation radiometer-counters, ИСП-РМ1401К-01 IP65 (Polimaster-Minsk, Belarus) search gamma-neutron radiometer-dosimeter, "IdentiFINDER" (Thermo Scientific Co., AFR-USA) and "GR-135 Plus" (Exploranium Co., USA-Canada) isotope determination portal radiometer-dosimeters were used.

The described devices are certified according to the ISO 9001 standard on the verification of measuring instruments by the Metrology Institute of the State Agency for Antimonopoly and Consumer Market Control of the European Union and the Republic of Azerbaijan.

When the indication of the scale of the device increases during the search for a radioactive source, when sound or vibration signals are generated, the scale indicator increases to find the source, the radioactive source is buried by moving the detector up and down at the point where the maximum signal or scale indicator is observed by moving in the direction of the strength of the sound or vibration signals, or the hidden place is revealed.

In order to conduct radio monitoring in the required total time, time interval (day, month, year, years), all measurements are carried out at the same place (same places) where monitoring is carried out, with relatively small (several times smaller than the total time required for radio monitoring) time intervals. The received indicators are immediately recorded in the monitoring log for further comparative analysis and use in obtaining logical results.

"Chemically pure for analysis" reagents (Merck kGaA /Germany/, VWR PROLABO /France/, Lachema /Czech Republic/, AO "База №1 Химреактивов" /RF/) during the experiments were used. Bidistilled water obtained from GFL-2304 bidistilator has a density of 1.4 g/cm_3 at 20^{o}C, 67% nitric acid and crystalline granular sodium hydroxide 0.2 M, 0.5 M, 1.0 M and 2.0 M, density at 200C is 1.19 g/cm3. cm3, 0.4 M, 1.0 M, 2.0 M and 4.0 M solutions of 38% hydrochloric acid were prepared for analysis.

RESULTS AND DISCUSSION

Azerbaijan "On radiation safety of the population" [2], the permissible value of the average annual dose for the population is 1 mSv, which is equal to the dose intensity of 0.115 or approximately 0.12 μSv/hour for the population living in that area.

The results of radiometric measurements carried out in the country's territories show that the intensity of total radioactive radiation, that is, the rate of the absorbed dose (0.03-0.12 μSv/h) does not exceed the Permissible Limit /PL = 0.12 μSv/h) in many areas of the country. The level of alpha radiation for the soils of the country's regions is 0-0.03 Bq_{eq}/cm^2.

It was revealed that the absorbed dose power of total radioactive radiation (0.15-3.75 µSv/h) is much higher than PL as a result of radiometric measurements, and there are local areas where the level of alpha radiation is 0.03-0.35 Bq_{eq}/cm^2. Sources of high dose rate include cold and thermal springs with acidic radioactive radon (0.85-3.75 µSv/h) filtered from high mountain massifs in the western regions of the country, interior granite-marble linings of underground transport communications (Baku Metro stations) and radionuclides in stone building materials. , gray, brown-red and black granite-marble coverings of entrance stairs and front walls of several nationally important (mainly in Baku) architectural buildings, memorial plaques, monuments, obelisks (0.15-0.85 µSv/h), industrial, educational and scientific production and consumer radioactive sources used in research institutions and households belong.

Radiometric measurements were carried out on the mountain breast of Dalidag ridge, Bagirsagh village, Kalbajar region (coordinates: 39^{o} 56^{I} 026^{II} N /latitude/ and $45^{o}57^{I}$ 562^{II} E /longitude/, 2338 meters above sea level). The value of radioactive background (0.10 - 0.15 mkSv/h) and alpha background in the surrounding areas is 0 - 0.01 Bq_{eq}/cm^2. The value of the radioactive background is 0.10-0.15 mkSv/h and the value of the alpha background is 0-0.01 Bq_{eq}/cm^2 in the areas 2337 meters above sea level at the coordinates of Bagirsag village at the 39^{o} 56^{I} 024^{II} N /latitude/ and $45^{o}57^{I}$ 587^{II} E /longitude/ on the mountain breast of Dalidag range.

At the coordinates 39^{o} 56^{i} 268^{ii} N and $45^{o}57^{i}417^{ii}$ E, at an altitude of 2203 meters above sea level ("Istisu sanatorium"), the value of radioactive background is 0.12 - 0.14 mkSv/hour and the value of alpha background, 0 - 0.01 Bq_{eq}/cm^2, at the coordinates 40^{o} 02^{i} 001^{ii} N and $45^{o}59^{i}388^{ii}$ E, at an altitude of 1605 meters above sea level, the value of the radioactive background in the surrounding areas is 0.15 - 0.17 mkSv/hour and the value of the alpha background is 0 - 0.01 Bq_{eq}/cm^2, at the coordinates 40^{o} 02^{I} 328^{II} N and $46^{o}00^{I}591^{II}$ E, in the "Lower Hot-Su" area at an altitude of 1580 meters above sea level the value of the radioactive background is 0.11 – 0.12 mSv/hour and the value of the alpha background is 0 – 0.01 Bq_{eq}/cm^2.

At the coordinates 39^{o} 55^{I} 410^{II} N and $45^{o}58^{I}140^{II}$ E, 39^{0} 55^{I} 410^{II} N and $45^{o}58^{I}150^{II}$ E, 39^{0} 55^{1} 420^{11} N and 45^{o} 58^{1} 130^{11} E, 39^{o} 58^{1} 150^{11} N and 45^{o} 58^{1} 150^{11}E 2386 m above sea level in the area near mountains the radioactive background is 3.75 µSv/hour and the alpha background value is 0.05 – 0.12 Bq_{eq}/cm^2 is observed, that is a high radioactive radiation background anomaly.

A reagent (HNO_3, HCl or NaOH) or a mixture (HNO_3-HCl) was used to treat contaminated soils.

The regularities of the 2-stage deactivation processes of samples of soil (200 g) contaminated with uranyl nitrate as a model sample with a mixture of nitrogen and hydrochloric acid solutions are presented in the following pictures (fig.1, /1st stage/, fig. 2 /2nd stage/).

It is possible to reduce the amount of uranium isotopes in those soils up to 2000 times with the 2-stage deactivation processes of soil samples with the activity of ^{238}U, ^{235}U, $^{234,236}U$ isotopes in the ratio of 1200:400:20 by extraction with a mixture of nitric and hydrochloric acid solutions and then with 1 liter of distilled water (table 1).

It can be seen from the obtained laws, that when individual reagents (HNO_3, HCl or NaOH) or their mixtures (HNO_3-HCl) are used for the extraction of contaminated soils, the amount or concentration of the reagent increases, as well as inversely proportional to the increase in the amount of water with which the soil is washed, there is a decrease in the amount of radionuclides in the soil [7-10].

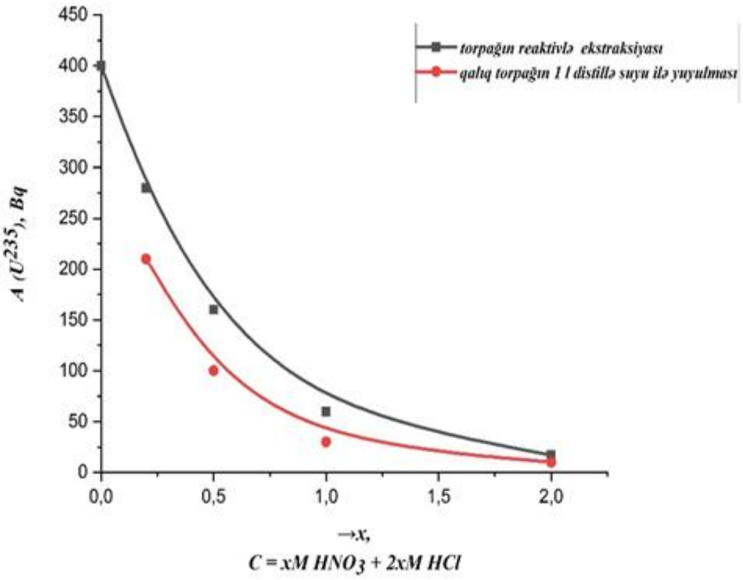

Fig. 1. Reduction of ^{235}U isotope in the soil as a result of leaching of samples of soil (200 g) contaminated with uranyl nitrate by extraction with nitric and chloride acid mixture solutions and then with 1 l. distilled water (stage 1).

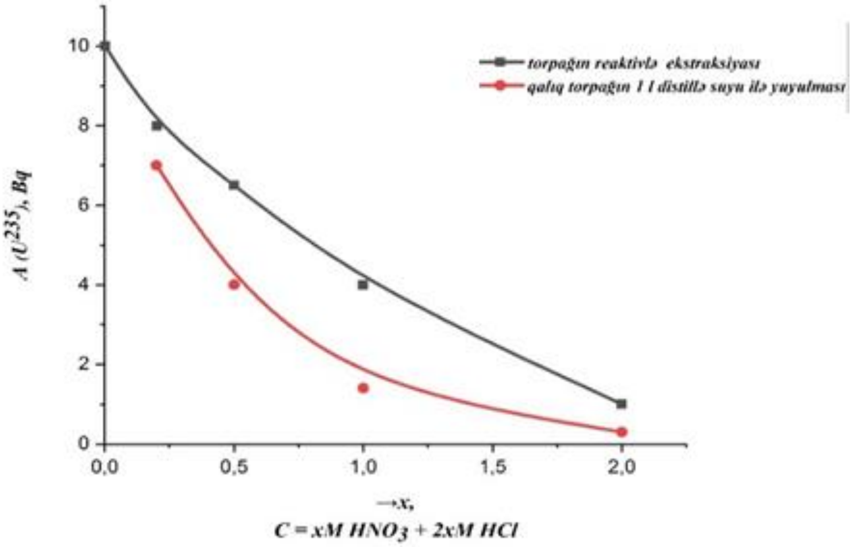

Fig. 2. Reduction of ^{235}U isotope in the soil as a result of leaching of samples of soil (200 g) contaminated with uranyl nitrate by extraction with mixture of nitric and hydrochloric acid solutions and then with 1 l. distilled water (stage 2).

The 2-stage deactivation process of soil contaminated with uranyl nitrate waste with a mixture of nitric and hydrochloric acid solutions and then with distilled water (or with an aqueous solution of sodium alkali) is a more effective cleaning method compared to deactivation with aqueous solutions of separate reagents, as well as compared to all existing prototypes is assigned. It is possible to carry out complete deactivation (DC = 1200-2000) of soil contaminated with nuclear material waste with this method.

Table 1.

Results of deactivation of 200 gram soil samples contaminated with uranyl nitrate (specific activity of ^{238}U, ^{235}U and $^{234,236}U$ radioisotopes 1200, 400 and 20 Bq, respectively) with a mixture of nitric and hydrochloric acids solution.

n, mol (n HNO_3 +2n HCl in 1 l. water)	1st stage				2nd stage				Other way for 2nd stage			
	The soil sample is extracted with $nHNO_3$+2nHCl solution for 1 hour and the soil residue is washed with 1 liter of distilled water for 1 hour				The soil residue is extracted with $nHNO_3$+ +2nHCl solution for 1 hour and the final soil residue is washed with 1 liter of distilled water for 1 hour				The soil residue is extracted with $nHNO_3$ + 2nHCl solution for 1 hour and the final soil residue is extracted with nNaOH (M) solution for 1 hour			
	A1 ^{238}U, Bq	A1 ^{235}U, Bq	A1 $^{234,236}U$ Bq	DC_1	A2 ^{238}U, Bq	A2 ^{235}U, Bq	A2 $^{234,236}U$ Bq	DC_2	A2′ ^{238}U, Bq	A2′ ^{235}U, Bq	A2′ $^{234,236}U$ Bq	$DC_{2'}$
0.2	650			1.85	21			57	17			70
		210		1.9		7		57		5		80
			12	1.7			0.3	70			0.2	100
0.5	370			3.3	14			85	11			110
		100		4.0		4		100		3		133
			7	2.9			0.2	100			0.1	200
1.0	130			9.2	6			200	4			300
		30		13		1.4		333		1		400
			3	6.7			0.05	400			0.03	667
2.0	30			40	1.1			1100	1			1200
		10		40		0.3		1330		0.3		1330
			1	20			0.01	2000			0.01	2000

Note: Ai - U in the remains of the soil sample after the development stages specific activity of isotopes;

DC_i – the deactivation coefficient of the soil sample after the processing stages (from the development stage of the special activity of the initial soil sample the ratio of the subsequent soil residue to the specific activity);

d_i – water obtained after the stage of gravity separation of pomegranate-disperse of the original soil sample after separation of the radioactive soil fraction decrease in mass (percentage of the original soil amount).

CONCLUSION

As a result of radiometric measurements, it was also found that there are local areas where the absorbed dose of total radioactive radiation (0.15-3.75 µZv/h) is much higher than YVH, and the level of alpha radiation is 0.03-0.35 Bq_{eq}/cm^2. When using a reagent (HNO_3, HCl or NaOH) or a mixture (HNO_3-HCl) to clean contaminated soils, it was determined that the amount of radionuclides in the soil decreases in inverse proportion to the increase in the amount or concentration of the reagent, as well as to the increase in the amount of water with which the soil is washed.

REFERENCES

1. Law of the Republic of Azerbaijan on radiation safety of the population. Heydar Aliyev, President of the Republic of Azerbaijan. Baku city, December 30, 1977. #423-IQ. Published in "Legislative Collection of the Republic of Azerbaijan". With changes dated 31.03.1998, 25.03.2003, 04.03.2005, 03.03.2006 .Vnesh Expert Service. 11p
2. Ilyasova Kh.N. Colloidal characterization and sorption of cobalt (II) and cadmium ions from model solutions on modified bentonite Kh.N.Ilyasova, A.I.Yagubov, M.M.Muradova [et al.] Azerb. Chemical Journal .2017, №1, pp.34-37
3. Mammadov Kh.F., Shiraliyeva H.N., Allahverdiyev R.G., Garibov G.R. Research of radiation background and distribution of radioactive elements in soil areas of Azerbaijan Scientific Achievements of Modern Society. XII International Scientific and Practical Conference, –Liverpool. July 22-24,2020, pp. 34-40
4. Mammadov Kh. F.,Shiraliyeva H.N.,Mehtiyev E.I Study of purification processes of soil contaminated with uranyl nitrate. 2021, Vol.132, №3, pp. 132-135
5. Zhu Y.G. Soil contamination with radionuclides and potential remediation .Y.G.Zhu, G.Shaw Chemosphere.2000, Vol.41, pp.121-128
6. Dmitriev S.A.,Barinov A.S., Kuptsov V.M.Method for cleaning sandy soils from radionuclides Patent RU 2388084 C1. 27.04.2010, Bull. № 12
7. Dmitriev S.A., Barinov A.S., Kuptsov V.M.The method of reagent decontamination of soils from cesium radionuclides. Patent RU 2399975 C1. 20.09.2010, Bull.№ 26
8. Dmitriev S.A., Prozorov L., Kuptsov V.M. The method of reagent cleaning of soils from cesium radionuclides .Patent RU 2361301 C1.10.07.2009, Bull. № 19
9. Kondakov V.M., Kozyrev A.S., Zubkov A.A., Semenov E.N. Vashchenko E.B. A method for monitoring the safety of radioactive waste storage sites. Patent RU 2260215 C2.10.09.2005, Bull. № 25

ОПРЕДЕЛЕНИЕ РАДИАЦИОННОГО ФОНА НА ТЕРРИТОРИИ АЗЕРБАЙДЖАНСКОЙ РЕСПУБЛИКИ И ИЗУЧЕНИЕ ДЕЗАКТИВАЦИИ ЗАГРЯЗНЕННЫХ ПОЧВ

Х.Н.Ширалиева 0000-0003-1172-5341
Институт Радиационных Проблем НАНА
s.hecer25@gmail.com

К источникам, генерирующим высокие мощности дозы, относятся высокогорные массивы в западных районах страны (0,85-3,75 мкЗв/ч), внутренняя гранитно-мраморная облицовка подземных транспортных коммуникаций (станции Бакинского метрополитена) и радионуклиды в каменных строительных материалах, ряде объектов общегосударственного значения. (преимущественно в Баку) архитектурные сооружения. серые, коричнево-красные и черные гранитно-мраморные покрытия входных лестниц и фасадных стен, памятные доски, памятники, обелиски (0,15-0,85 мкЗв/ч), радиоактивные источники производства и потребления, используемые в промышленных, образовательных и научных учреждениях, в бытовых условиях они принадлежат . В результате радиометрических измерений также было выявлено, что мощность поглощенной дозы суммарного радиоактивного излучения (0,15-3,75 мкЗв/ч) значительно *выше YVH, а также имеются локальные участки, где уровень альфа-излучения составляет 0,03-0,35 Бкэкв. /см^2. При использовании реагента (HNO3, HCl или NaOH) или смеси (HNO3-HCl) для очистки загрязненных почв установлено, что количество радионуклидов в почве уменьшается обратно пропорционально увеличению количества или концентрации реагента. , а также к увеличению количества воды, которой промывается почва.*

Ключевые слова: *радиоактивный фон, поглощенная доза, мощность дозы, альфа- и гамма-излучение.*

AZƏRBAYCAN RESPUBLİKASI ƏRAZİSİNDƏ RADİOAKTİV FONUN TƏYİNİ VƏ ÇİRKLƏNMİŞ TORPAQLARIN DEZAKTİVASİYASININ TƏDQİQİ

H.N. Şirəliyeva 0000-0003-1172-5341
AMEA Radiasiya Problemləri İnstitutu
s.hecer25@gmail.com

Yüksək doza gücü yaradan mənbələrə ölkənin qərb ərazilərindəki hündür dağ massivləri (0.85-3.75 µZv/saat), yeraltı nəqliyyat kommunikasiyalarının (Bakı Metropoliteni stansiyalarının) interyer qranit-mərmər üzlükləri və daş tikinti materiallarında radionuklidlər, bir neçə ölkə əhəmiyyətli (əsasən Bakı şəhərində) memarlıq binalarının giriş pilləkənlərinin və ön divarlarının boz, qəhvəyi-qırmızı və qara qranit-mərmər örtükləri, xatirə lövhələri, abidələr, obelisklər (0.15-0.85 µZv/saat), sənaye, təhsil və elmi-tədqiqat müəssisələrində, məişətdə istifadə olunan istehsalat və istehlak təyinatlı radioaktiv mənbələr aiddirlər. Radiometrik ölçmələr nəticəsində ümumi radioaktiv şüalanmanın udulan doza gücünün (0.15-3.75 µZv/saat) YVH-dən xeyli yüksək olduğu, alfa şüalanma səviyyəsinin 0.03-0.35 Bq_{eq}/sm^2 təşkil etdiyi lokal ərazilərin mövcud olduğu da aşkar edilmişdir. Çirklənmiş torpaqların təmizlənməsi üçün reaktivdən (HNO_3, HCl və ya NaOH) və ya qarışıqdan (HNO_3-HCl) istifadə etdikdə reaktivin miqdarının və ya qatılığının artmasına, həmçinin sonra həmin torpağın yuyulduğu suyun miqdarının artmasına tərs mütənasib olaraq torpaqda radionüklidlərin miqdarının azaldığı müəyyənləşdirilmişdir.

Açar sözlər: *radioaktiv fon, udulan doza, doza gücü, alfa və qamma şüalanma.*

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PROCUREMENT OF JET FUELS BASED RECYCLED PRODUCTS

*A.A.Mammadova, G.Ch.Dadayeva*0000-0001-6801-4255
Azerbaijan State Oil and Industrial University
memmedovafsane@mail.ru

Article is devoted to the increasing of the quality indicators of the secondary oil processing's products by adding them to engine fuels. Thermal cracking light gas oil (TCLGO) and hydrocracking light gas oil (HLGO) fractions were chosen as a raw material in research work. A mixture of TCLGO: HLGO fractions in the ratio of 1:3 - 1:5 was prepared and their catalytic conversions were studied. Catalytic conversion products of products are separated into the fractions in atmospheric and vacuum units and analyses is conducted. In order to improve the quality of catalytic conversion products, hydrogen cleaning and deep hydrogenation were applied. Moreover, temperature, pressure of process and velocity rate of raw materials were studied and 2 hours of catalytic conversion process with 1% of catalytic leads to the increasing of the yield of diesel fraction up to 44%. The products from the catalytic conversion of the light gas oil mixture of thermal cracking and hydrocracking can be recommended as a high-quality aviation and diesel fuel components with a density of 807 kg/m3 in the 190-270℃ fraction after hydrogenation and 833 kg/m3 in the 270-350°C fraction, respectively.

Keywords: *motor fuels, diesel fraction, furfural, light gas oil, thermal cracking, hydrocracking, catalyst, nickel kieselguhr, hydrogenation.*

INTRODUCTION

One of the important issues is increasing the reserves of motor fuels due to the use of petroleum recycling products. However, it is needed to improve their performance quality indicators before the adding to fuel distillates. The applications of hydrogen-free methods to improve the quality of recycling products are effective methods in this field [1-3]. For example, the purification of diesel fraction of coking, a combination of its extraction with furfural and chemical reaction with another component was used. Furthermore, technologically and economically advantageous of this method has been shown [4].

In order to improve the quality of fuel distillates obtained from recycling processes, extensive re-search has been carried out for the catalytic conversion of the complex of highly reactive hydrocarbons (unsaturated and aromatic) [4-6]. In addition, it has been shown that the use of aluminum-organic complexes as a catalyst in alkylation and oligomerization reactions leads the conducting of the process at low temperature and at liquid phase [7, 8].

The continuous tightening of the demand for increasing the stock of motor fuels and their quality creates restrictions. Thus since 2000 diesel fuel with a sulfur content of no more than 0.035% use in economically developed European countries. In 2005, it is planned to reduce this indicator up to 0.005% and 2009 to 0.001%. Restrictions are imposed for the total amount of aromatic hydrocarbons (15-25%) and the polycyclic hydrocarbons (2-5%) in the fuel.

Furthermore, the density of diesel fuel is limited to up to 820-840 kg/m3, and the boiling point is limited up to 350°C. It is planned to increase the cetane number to up 55 units.

EXPERIMENTAL PART

The joint catalytic conversion of thermal cracking to light gas oil (TCLGO) and hydrocracking light gas oil (HLGO) hydrocarbons has been studied. Raw materials with boiling points of 270°C were taken and conversions were carried out with the presence of nickel kieselguer catalyst. The optimal parameters of catalytic conversion (ratio of components, temperature, reaction time, catalyst concentration) were determined [8].

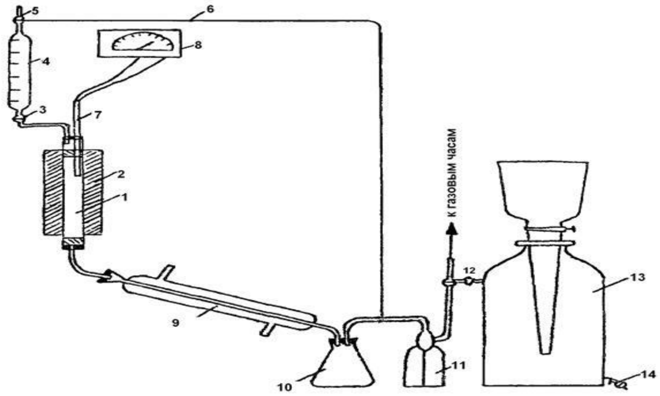

Fig.1. The principle diagram of the laboratory unit of the catalytic cracking unit 1-reactor; 2-electric heater; 3,5,12,14-crane; 4-burette; 6-regulating pipe; 7-thermocouple; 8-millivoltmeter; 9-refrigerator; 10-receiver; 11-absorber; 13-gasometr

Table 1

Fractions of atmospheric and vacuum distillation for TCLGO:HLGO(residual pressure 0.65 KPa) in the ratio of 1:3-1:5.

	Indicators	TCLGO, fraction 195-270°C	HLGO, fraction 200-270°
	Density, at 20°C, kg/m3	897.2	817.0
	Kinematic viscosity, at 20°C, mm2/s	2.3	1.9
	Crystallization temperature, °C	-35.0	-14.0
	Pour point, °C	-38.0	-15.0
	Refractive index, n_D^{20}	1.5277	1.4733
	Sulfur content (total), % mass	0.35	0.23
	Acidity, mg KOH/100ml	6.0	7.1
	Ignition temperature, °C	68.0	60.0
	Average molecular weight	201.0	185.0
	Iodine number, g J2/100 g	25.8	75.6
	Unsaturated hydrocarbons, %	20.3	55.1
	Fraction composition, °C 10% 50% 90%	201.0 231.0 256.0	217.0 219.0 254.0
	Hydrocarbon contentmass, %: Paraffin Naphtenic Aromatic	32.4 9.6 58.0	41.3 24.2 34.

As can be seen from table 3, the optimal hydrogen purification conditions of the 190-270 and 270-350°C fractions of the catalytic conversion product are at a temperature of 340°C, a pressure of 4.0-5.0 MPa, and a feed rate of 0.5 h-1 is taken.

Table 2

The field of diesel fraction after the catalytic conversion

Indicator	Temperature, °C							
	190-270			270-350			>350	Loss
	Yield, %	P_4^{20}, kq/m^3	n_D^{20}	Yield, %	P_4^{20}, kq/m^3	n_D^{20}	%, mass	%, mass
τ, hour								
1	61.2	831	1.4695	33.2	867	1.4880	3.1	1.9
2	49.1	833	1.4700	44.0	868	1.4882	4.4	2.1
3	52.0	844	1.4752	43.2	878	1.4925	2.8	1.6
4	49.3	843	1.4773	43.5	879	1.4940	3.9	2.8
Catalyst density, %								
0.5	77.0	847	1.4758	18.2	878	1.4935	2.5	1.9
1.0	49.0	835	1.4800	44.0	869	1.4878	4.6	2.1
1.5	52.6	838	1.4730	43.5	873	1.4905	2.1	1.7
2.0	49.5	833	1.4695	43.3	869	1.4867	5.2	2.5
2.5	51.2	842	1.4709	43.5	871	1.4875	4.1	1.6
3.0	51.2	835	1.4702	43.1	870	1.4886	4.5	1.9

The dependence of catalytic conversion on the time (TCLGO: HLGO =1:5, temperature 60 °C, catalyst 1%) and catalyst concentration (TCLGO: HLGO =1:5, temperature 60 °C, reaction time 2 hours) was studied by a similar method (table 2). As can be seen from table 2 1% of catalyst concentration causes increasing the yield of diesel fraction up to 44% during 2 hours. In order to meet the quality indicators of the catalytic conversion products to the perspective requirements treatment with hydrogen and deep hydrogenation process were carried out. Purification of TCLGO and HLGO fractions with hydrogen was carried out with the presence of ГКД-205 (ТШ 38-10-1199-72) catalyst in a continuously working experimental unit, giving 500 l of H_2 to each volume of raw materials.

Table 3

Indicators of catalytic conversion products of different fractions

In the reactor		Velosity rate of raw material, Hour-1	190-270 °C		270-350°C	
Temperature, °C	Pressure, MPa		Sulfur content, Mass	Iodine number	Sulfur content	Iodine number
300	3.5	0.5	0.055	1.0	0.063	1.0
300	4.0	1.0	0.001	1.0	0.053	1.8
320	4.0	1.5	0.075	0.8	0.0032	0.76
320	4.5	0.5	0.0056	0.5	0.00	0
350	4.5	0.5	0.0021	0	0.00	0

As can be seen from table 3, the optimal hydrogen purification conditions of the 190-270°C and 270-350°C fractions of the catalytic conversion product are at a temperature of 350°C, a pressure of 4.0-5.0 MPa, and a feed rate of 0.5 h^{-1} is taken.

RESULTS AND DISCUSSION

Deep hydrogenation of the fractions obtained by hydrogen purification was carried out in the presence of NiCr (GOCT 6-05-314-71) catalyst in a continuously operating experimental unit. The results of the laboratory experiments at the temperature of 4-5 MPa, the velocity raw of the race material 0, 5-1, 0 hour and the consumption of H_2 due to the raw material of 1000t/l were presented in the table 4.

According to the results, if the amount of aromatic hydrocarbons increases by 0-10% (mass) after hydro treating the 270-350°C fraction compared to the 190-270°C fraction, an increase in the cetane number is observed. At the same time, there is a relatively low combustion heat increase from 43.4 to 43.8 MC/kg. This is one of the main quality indicators of jet fuel. Similarly, after the hydrogenation process, with the increase in the boiling point of the fractions, an increase in their density and freezing temperature is observed.

Table 4

Physicochemical parameters of different fractions after hydrogenation

Indicator	Hydrogenation	
	190-270°C	270-350°C
Density, at 20°C, kg/m3	806.0	832.0
Fractional confrosition, °C:		
10%	202.0	218.0
50%	219.0	242.0
98%	252.0	353.0
Aromatic hydrocarbons, mass %	0	10
Ignition temperature, °C	69.0	74.0
Crystallization temperature, °C	-60.0	-56.0
Low heat of combustion, MC/kg	43.4	43.8
Kinematic viscosity, at 20°C, mm/s2	2.0	2.9
Height of flame without smoke, mm	21.0	24.0
Acidity, mg KOH /100 ml	yox	yox
Amount of actual resins, mg/100 ml	0,57	1.0
Naphthalene hydrocarbons, % mass	0.2	2,4
Thermal oxidation stability, the amount of sediment in 100 ml of fuel, mg	5.5	7.3
Cetane number	48.0	55.0

CONCLUSION

As a result of the conducted research, it can be noted that the 190-270 and 270-350°C fractions, which are various products of the co-catalytic conversion of TCLGO and HLGO. Thus, correct chosen optimal temperature, catalyst conversion concentration from the two products the mixture of TCLGO and HLGO after hydrogenation process enable to use them as a component for diesel fuels with cetane number of 48, 0 and 55, 0 and jet fuels with required standards.

REFERENCES

1. Rustamova M.I. Catalytic processes for obtaining high-quality motor fuels. T. Baku: Elm. 2006, 475 p
2. Rublyak K.B., Loginov S.A. Improving the motor properties of diesel fuel when mixed with light catalytic cracking gas oil Oil refining and petrochemistry. 2001, №12, pp. 13-15
3. Guseinov A.G., Musaev J. J., Sultanov S.A. et al. Catalytic cracking of hydrocarbons in coking gas oil Processes of petrochemistry and oil refining. 2004, № 3, pp. 54-57
4. Kaminsky E.F., Khavkin V., Kurganov V.M. and others.Dearomatization of middle distillates - a promising technology for improving the environmental properties of diesel fuels World of oil products. 2000 ,№2. pp.9-11
5. Zhou Young. Han Chong-ren/ Progress in Catalyst and process development for low sulfur and low aromatic diesel production Acta Petrol. Sin. Petrol. Process. 2003, №2. pp. 9-11
6. Shiyouhuagong gooling Xuexiao xuebao Li DongshenDing Guoping Xu Xiaonaing and etc. J.Petrochem Univ .2000,№ 1,pp. 28-32
7. Kotov S.V., Moiseev I.K., Shabanova F.V. Olefin oligomers: methods for obtaining and using components of fuels and oils in lachestve Neftekhimya. 2003,Vol. 43, №5, pp. 323-331
8. Mitustsva T.N., Loginov S.A.,Polina E.V. et al. Improvement of the lubricating properties of diesel fuels Chemistry and technology of fuels and oils. 2002, № 5, pp. 24-25

ЗАКУПКА РЕАКТИВНОГО ТОПЛИВА НА ОСНОВЕ ВТОРИЧНОЙ ПРОДУКЦИИ

*А. А. Мамедова, Г. Ч. Дадаева*0000-0001-6801-4255

Азербайджанский Государственный Университет Нефти и Промышленности

memmedovafsane@mail.ru

В данной статье представлена информация о проведенных работах по повышению качественных показателей моторных топлив, за счет применения продуктов вторичной переработки нефти. В качестве сырья в исследовательской работе были выбраны легкий газойль термического крекинга (ЛГТК) и легкий газойль гидрокрекинга (ЛГГК).Приготовили смесь фракций ЛГТК:ЛГГК в соотношении 1:3 - 1:5 и изучали их каталитические превращения. В процессе использовали каталитический комплекс на основе металлического алюминия. Продукты, полученные в результате каталитических превращений, разделяли на фракции и анализировали в атмосферно-вакуумном приборе. Было исследовано зависимость времени, температуры и скорости подачи сырья как оптимальные условия проведения процесса. С целью повышения качества продуктов каталитической конверсии применяли водородную очистку и глубокое гидрирование. В результате при концентрации катализатора 1% и проведении каталитической конверсии в течение 2 часов, выход дизельной фракции увеличился до 44,0%. После гидрирования продуктов каталитической конверсии смеси легкого газойля термического крекинга и гидрокрекинга, рекомендуется в качестве компонентов высококачественных авиационных и дизельных топлив с плотностью 807 кг/м3 во фракции 190-270°C и 833 кг/м3 во фракции 270-350°C.

***Ключевые слова**: моторные топлива, дизельная фракция, фурфурол, легкий газойль, термический крекинг, гидрокрекинг, катализатор, никелевый кизельгур, гидрирование.*

TƏKRAR EMAL MƏHSULLARININ ƏSASINDA REAKTİV YANACAQLARIN ALINMASI

Ə.Ə.Məmmədova, G.Ç.Dədəyeva$^{0000-0001-6801-4255}$
Azərbaycan Dövlət Neft və Sənaye Universiteti
memmedovafsane@mail.ru

Təqdim olunan məqalədə neftin ikinci emalından alınmış məhsulların mühərrik yanacaqlarına tətbiq etməklə onun keyfiyyət göstəricilərinin artırılması istiqamətində görülən işlər haqqında məlumat verilmişdir. Tədqiqat işində xammal kimi termiki krekinqin yüngül qazoylu (TKYQ) və hidrokrekinqin yüngül qazoylu (HKYQ) seçilmişdir. TKYQ:HKYQ fraksiyalarından 1:3 – 1:5 nisbətində qarışıq hazırlanaraq onların katalitik çevrilmələri öyrənilmişdir. Prosesdə metallik alüminium əsasında katalitik kompleksdən istifadə edilmişdir. Katalitik çevrilmələr nəticəsində alınmış məhsullar atmosfer və vakuum qurğusunda qovularaq fraksiyalara ayrılmış və analizləri aparılmışdır. Katalitik çevrilmə məhsullarının keyfiyyətini artırmaq üçün hidrogen təmizləmə və dərin hidrogenləşdirmə tətbiq edilmişdir. Prosesin aparılmasında optimal şərait kimi zaman, temperatur və xammalın verilmə sürətindən asılılıqları tədqiq edilmişdir. Nəticədə, katalizatorun qatılığı 1 % olduqda və katalitik çevrilmənin 2 saat müddətində aparılması nəticəsində dizel fraksiyasının çıxımı 44,0 %-ə qədər artmışdır. Termiki krekinqin yüngül qazoylu və hidrokrekinqin yüngül qazoylu qarışığının katalitik çevrilməsindən alınan məhsullarının hidrogenləşmədən sonra 190-270°C fraksiyasında sıxlığı 807 kq/m^3 *və 270-350°C fraksiyasında sıxlığı 833 kq/m*^{3} *olan müvafiq olaraq yüksək keyfiyyətli aviasiya və dizel yanacağı komponenti kimi tövsiyyə oluna bilər.*

***Açar sözlər:** motor yanacaqları, dizel fraksiyası, furfurol, yüngül qazoyl, termiki krekinq, hidrokrekinq, katalizator, nikel kizelqur, hidrogenləşmə.*

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THE STUDY OF INCREASING THE QUALITATIVE INDICATORS OF ROAD BITUMENS

S.Z.Gurbanli$^{0000-0003-2911-555X}$*, A.A.Aliyeva*
Azerbaijan State Oil and İndustry University
susenqurbanli@gmail.com

The article represents the data on studies on the effect of solid additives on the physicochemical and performance properties of road bitumen. Solid additives technical carbon, waste tire recycling product, and modified forms of technical carbon have been investigated. As a result, a comparative analysis of the use of technical carbon modified with coal as an additive for the production of ROB(The viscous road oil bitumen) 60/90 bitumen revealed a positive effect of both additives on the softening point of bitumen and an increase on adhesion of the technical carbon on bitumen properties has been determined. During the addition of technical carbon to ROB 60/90 brand bitumen in different percentages, the maximum score of bitumen adhesion is 4 points when the additive is added up to 3% (mass). At the same time, from the ecological point of view, the use of technical carbon prevents pollution of the environment from waste during the use of the disposal tires.

***Keywords**: bitumen, binder, technical carbon, modification.*

INTRODUCTION

Petroleum bitumen is used in a wide range of engineering and construction materials. The quality of oil bitumen is determined by several conditions. These are penetration, softening temperature, brittleness temperature, and ductility. Softening and embrittlement temperatures control the range of bitumen's plastic state. In other words, they provide the temperature of bitumen products in the working range. It can be said that the first question that arises in almost all products using bitumen is the increase of its softening temperature and reduction of the brittleness temperature. The high quality of bitumen, in turn, affects the high quality of asphalt concrete, a composite material made of a bitumen base.

Often, to improve the quality of road bitumen, a small number of chemicals - modifying additives, mainly various types of polymer materials - are added to it [1, 2]. The use of such modified polymer materials increases the service life of road surfaces. In addition to polymers, solid additives are also added to bitumen, including mineral powders added to reduce fluidity. Such additives are classified as stabilizing additives. This can even lead to an increase in the operating temperature range. Usually, in this way, it is possible to increase the heat resistance of materials. Scientific, technical and patent literature contains information about the use of technical carbon (TC) in bituminous compositions and asphalt-concrete to improve the operational properties of these materials [3, 4].

The authors studied the feasibility of using technical carbon (TC) as well as the possibility of using technical carbon in road construction materials. Generally, technical carbon is used as an additive. At this time, it is a modified additive to organic binding materials and a solid powder emulsifier for bitumen paste. It also can be applied as a finely dispersed filler for solid bitumen mastics [5]. As a result of several studies, the effect of the inhibitory effect of technical carbon additives on the aging of bitumen was determined [6]. This effect explains the fact that technical carbon particles consist of small crystals with a graphite structure, but each one is randomly arranged. In crystals, carbon atoms are located at the junctions of regular hexagons, forming carbon lattices. [8] .The outermost incomplete valence atom in each cage binds oxygen and hydrogen to itself. At the same time, various oxygen-containing functional groups are formed on the surface of carbon particles: phenol, xenon, lactone, and carboxyl. These groups can participate in the inhibition of oxidative processes. To improve the quality characteristics of the obtained bitumen, it is usually suggested to add 1-3% (mass) technical carbon to 100% (mass) raw material [3]. It is acceptable to add technical carbon directly to the composition of the asphalt mixture. For example, when 5% technical carbon is added to bitumen, it becomes more resistant to resistance [10]. At the same time, it withstands heavy loads and high shearing presses and has more shear stability. Thus, it is recommended to add 5% technical carbon to the asphalt-concrete mixture [7].

EXPERIMENTAL PART

The main goal of the research is to study the effect of solid additives on the physicochemical and operational properties of bitumen. As solid additives, technical carbon obtained mainly from the utilization of tires and modification of technical carbon has been studied. For the production of a bituminous binder road bitumen brand, ROB (The viscous road oil bitumen) 60/90 was used. Used tires pollute the environment and cause serious environmental problems. Technical carbon (TC, soot) is a fine black or dark gray powder obtained from waste. The smallest particles of technical carbon have a complex structure consisting of carbon and amorphous pseudo-graphic crystallites. Technical carbon particles are chained or branched to form complex graphite structures.

Particle size and specific surface area of technical carbon vary in a fairly wide range. Technical carbon has an average particle diameter of 9 to 320 mcm and a specific surface area of 12 to 250 m^2/g. Functional groups with various particles are formed on the surface of technical carbon: hydroxyl, carbonyl, and xenon. After receiving the modified form of technical carbon, air partially oxidizes it in a thin layer. However, oxygen-containing groups are strongly adsorbed on the surface of technical carbon particles. Bituminous binders are obtained by the following methods. ROB 60/90 road bitumen is added to a metal cup equipped with a mixer, electric heater, and thermometer and melted at 120^0C. A certain amount of technical carbon is added during the mixing process. The mixture was stirred at this temperature for 40 minutes. The main properties of the prepared bituminous binder are determined. The properties of the bituminous binder are determined by GOST 22245-90 "Oil road bitumen". Properties of bitumen differ by the addition of technical carbon to ROB 60/90 brand road bitumen. Its modified forms are also presented in tables 2 and 3.

As can be seen from the table, the dispersion density of technical carbon is 508 kg/m^3 and the average density is 1978 kg/m^3. Technical carbon with these parameters has a positive effect on the adhesion quality of bitumen.

Table 1

Characteristics of the chosen technical carbon

Indicators	Technical carbon
Low bulk density of technical carbon kg/m^3	508
High emptiness (capacity %)	74,3
High bitumen capacity g/100 sm^3	378,3
The true density of technical carbon kg/m^3	1978
Specific adsorption surface m^2/g	200
Specific outer surface m^2/g	175

RESULTS AND DISCUSSION

The addition of technical carbon to BND 60/90 road bitumen, as well as its modified forms, are presented in tables 2 and 3.

Table 2

Properties of bitumen binder obtained by adding modified technical carbon

The amount of supplement, % (by mass)	Properties of modified bitumen			
	By ball and ring method $T_{brittleness}$, ^{0}C	Penetration at 25^0 C	Ductility, cm	Adhesion, in points
ROB 60/90	47	61	55	2
+1%	48	64	51	2
+3%	63,2	62	42	2
+5%	65,1	59	38	2

As can be seen from table 2, in the results of the analysis of the addition of modified technical carbon to bitumen at different percentages, the best softening result is obtained at a temperature of 65.1^{0}C at 5% (mass) addition. However, no change in bitumen adhesion is seen. In the application of other 1% and 2% of mass additives, despite the increase in the softening temperature, the adhesion result in both was evaluated as 2 points.

We continued our research by adding unmodified technical carbon. The obtained results are given in table 3.

* Clarification of the adhesion score of the binder to the surface of the mineral material to evaluate the adhesion.

2 - "Unacceptable", covering not less than 75% of the surface of gravel particles with a cohesive layer;

3-"Acceptable" - covering 75% of the surface of gravel particles with a cohesive layer

4 - "Good", covering 90% of the surface of gravel particles with a cohesive layer;

5 - 95% of the binder surface is covered with gravel particles.

According to tables 2 and 3, with the increase in the number of additives, there is an increase in the softening temperature in terms of the ball and ring method, and as a result, the bitumen changes from an elastic-plastic state to a viscous state. This is because when the additive is introduced into the bitumen, it is adsorbed on the surface of the particles, and as a result, the dispersed phase increases and the system thickens. With the addition of modified technical carbon, the softening temperature of the Ring and Ball method increases more than with the addition of technical carbon. To characterize the viscosity, a conventional indicator is recorded. This is the depth of penetration of the needle into the bitumen.

Table 3

Properties of bitumen binder obtained by adding technical carbon

The amount of supplement, % (by mass)	Properties of modified bitumen			
	By ball and ring method $T_{brittleness}$, ^0C	Penetration at 25 ^0C	Ductility, cm	Adhesion, in points
ROB 60/90	47	61	55	2
+1%	49,2	59	52	3
+3%	57,15	57	49	4
+5%	64,5	50	45	3

The greater the viscosity, the less the depth of penetration of the needle into the bitumen. In our study, the environment of bitumen binder combines with oils. Therefore, the penetration parameter decreases with the increase of binder in the system. Ductility at a temperature of 25^{0}C characterizes the degree of structure of the adhesive. Based on the results, it can be concluded that the ductility of the bituminous binder decreases as the additives are added each time with a greater percentage (mass). Ductility characterizes the plastic properties of binder bitumen. These properties depend on the temperature, group composition, and structure of bitumen. It decreases with a decrease in the content of oils and increases with an increase in the content of the dispersed phase in the structure. In our study, with the increase of technical carbon, there is an increase in the amount of dispersed phase, so the ductility decreases. An important feature of the bituminous binder is the adhesion of mineral materials. To determine the result of the adhesion of the bitumen binder to the mineral substance, by adding technical carbon to the bitumen binder up to 2% (mass), its adhesion to the mineral parts of asphalt concrete increases. This is explained by the fact that there are different functional groups on the surface of the technical carbon. Carboxyl, hydroxyl, and xenon-type groups can improve the adhesion properties of the material. As you increase the additive, the adhesion worsens. In the case of modified technical carbon, the adhesion of the bitumen binder to the mineral material does not occur. During the modification of technical carbon, the functional groups on its surface change, and new functional groups are formed and are no longer in contact with acidic mineral materials. In general, we can say that road bitumen with modified technical carbon (ROB 60/90) can be considered an asphalt binder. Asphalt-forming substances act as large and small-sized fillers on the surface of the mixture, connecting them and forming a monolithic lattice. Large and small-sized filters play an important role in the formation of this monolithic lattice. Therefore, asphalt binders such as matrix should have a stronger structure, water resistance, and adhesion. Asphalt binders are considered a binary dispersed system, where technical carbon is the solid phase and bitumen is the medium [9].Bitumen asphalt binders can be:

- Loose binder (bulk bitumen),

filling the intergranular space and located outside the zone of influence of physicochemical processes at the phase-environment interface;

- Adsorption-solvate layer with high physicochemical structuring on the surface of thin-layered bitumen-phase separation.

Bituminous binders have superior properties with the addition of optimally concentrated fillers (technical carbon). Technical carbon requires more of that additive than the classic asphalt binder because it has high dispersibility and a large specific surface area. The best case of quality indicators corresponds to the optimal case of additive concentration of bituminous binder with the addition of technical carbon. For technical carbon, this is 5% (mass).

CONCLUSION

As a result of the research, both additives investigated have a positive effect on the temperature resistance of bitumen The effect of modified technical carbon on the softening point of bituminous binder is better than its unmodified form. However, since modified technical carbon does not affect the adhesion properties of bitumen, it is not appropriate to add it to road bitumen ROB (The viscous road oil bitumen) (60/90) as a modified additive. Only technical carbon results are more relevant. Because even if the softening temperature is not high, the adhesion property is higher. With the addition of 3% (mass) of technical carbon, the softening temperature is 57.5^{0}C and the adhesion score is rated as 4. At the same time, with the addition of 5% (mass) technical carbon, the softening temperature was 64.5^{0}C, and the adhesion score was evaluated as 3. In this regard, the addition of 5% (mass) of technical carbon will have a good effect on the quality indicators of ROB 60/90 brand road bitumen, and technical carbon can be considered as an additive for road bitumen. At the same time, the use of technical carbon, obtained from the disposal of used tires in road construction can be seen as a possibility for solving other environmental pollution problems.

REFERENCES

1. Abdullin A.I., Emelyanycheva E.A., Prokopiy A.M. Improved bitumen-polymer binder. Herald Technological University. 2012, pp182-185
2. Filippova O. P., Mikhailova A.M. [and others]; 1. Pat. 2330057 Russian Federation, IPC C 10 C3.04. Method for producing bitumen from acid tar YAGTU. - № 2007115684.04; publ. 25.04.2007,pp180-185
3. Kotov S.V., Timofeeva G.V., and Levanova S.V., Acoust. Road bitumen with modifying additives .Chemistry and technology of fuels and oils. 2003, pp.50-52
4. Pat. 2330057 Russian Federation, IPC C 10 C3/04The method of obtaining bitumen from acid tar / O. P. Filippova, A. M. Mikhailova [and others]; YAGTU. – № 2007115684/04; publ. 25.04.2007, pp 51-52
5. Kalgin Yu.I. Road bitumen-mineral materials based on modified bitumens: monograph .Yu.I. Kalgan; Voronezh, Mrs. Archie. -build, un-t, - Voronezh: Voronezh Publishing House, state. un-ta. 2006, pp. 270- 272
6. Verstraeten J. Bituminous materials with high resistance to flow rutting. Piarc Technical Committee on Flexible Roads. 1995, pp. 85-93
7. Kovalev Ya.N, Romanyuk V.N. Encapsulation of bitumen with a chemically compatible polymer additive, properties of modified binder and asphalt concrete based on it / Science and technology in the road industry.2007, pp 29-31.

8. GOST 22245-90 Viscous oil road bitumen. Specifications-M: Publishing house of standards. 1998, pp34- 36
9. Zolotarev V.A. Influence of the properties of bitumen-polymer binders on the shear resistance of asphalt concrete. Science and technology in the road industry. 2004, pp27-30
10. Zolotarev V.A. On the information content of bitumen quality indicators. Science and technology in the road industry. 2005, pp 38-41

ИССЛЕДОВАНИЕ ПОВЫШЕНИЯ ПОКАЗАТЕЛЕЙ КАЧЕСТВА ДОРОЖНОГО БИТУМА

С.З.Гурбанлы$^{0000-0003-2911-555X}$*, А.А.Алиева*
Азербайджанский Государственный Университет
Нефти и Промышленности
susenqurbanli@gmail.com

В статье представлены данные исследований, проведенных для изучения влияния твердой добавки на физико-химические и эксплуатационные свойства дорожного битума. В качестве твердых добавок были исследованы технический углерод и модифицированный углерод, полученные в результате переработки шин. В результате сравнительного анализа применения модифицированного технического углерода в качестве добавки для получения битума марки БНД 60/90, установлено положительное влияние обеих добавок на температуру размягчения битума и только технического углерода на повышение адгезионных свойств битума. При добавлении технического углерода в битум марки БНД 60/90 в различных процентах происходит введение добавки до 3 % (по массе) с максимальным показателем адгезии битума 4 балла. Также использование технического углерода с экологической точки зрения предотвращает загрязнение окружающей среды отходами при утилизации шин.

Ключевые слова: *битум, связующее, технический углерод, модификация.*

YOL BİTUMUNUN KEYFİYYƏT GÖSTƏRİCİLƏRİNİN ARTIRILMASININ TƏDQİQİ

S.Z.Qurbanlı$^{0000-0003-2911-555X}$*, A.Ə.Əliyeva*
Azərbaycan Dövlət Neft və Sənaye Universiteti
susenqurbanli@gmail.com

Məqalədə bərk əlavənin yol bitumunun fiziki-kimyəvi və istismar xassələrinə təsirini öyrənmək üçün aparılan tədqiqatların məlumatları təqdim olunub. Bərk əlavələr kimi, təkərlərin təkrar emalından alınan texniki karbon və modifikasiya olunmuş karbon araşdırılmışdır. Nəticədə, texniki karbon ilə modifikasiya olunmuş karbonun BND 60/90 markalı bitumun alınması üçün əlavə kimi tətbiqinin müqayisəli təhlili hər iki əlavənin bitumun yumuşalma temperaturuna müsbət və yalnız texniki karbonun bitumun adgeziya xüsusiyyətiniin artmasına təsiri müəyyən olmuşdur. Texniki karbonun BND 60/90 markalı bituma müxtəlif faizlərlə əlavəsi zamanı bitumun adgeziyasının maksimal balı 4 bal olmaqla əlavənin 3 % (kütlə) qədər daxil edilməi ilə baş verir. Eyni zamanda texniki karbonun istifadəsi təkərlərin utilizasiyası zamanı ekoloji baxımdan ətraf mühitin tullantılarla çirklənməsinin qarşısını alır.

Açar sözlər*: bitum, birləşdirici, texniki karbon, modifikasiya.*

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INVESTIGATION OF BINARY Zn-Cu-O, Ni-Cu-O and Zr-Cu-O CATALYSTS BY X-RAY DIFFRACTION METHOD

*V.M.Ismayilova V.L.Baghiyev*0000-0003-1475-9571
Azerbaijan State Oil and Industry University
vagif_bagiev@yahoo.com

In this work, binary copper-containing catalysts were studied by X-ray diffraction. It has been shown that no formation of chemical compounds is observed in all the catalytic systems studied. All synthesized binary catalysts consist of two phases of initial oxides. Thus, samples of the Zn-Cu-O catalytic system consist of phases of zinc and copper oxides, samples of the Ni-Cu-O catalytic system consist of phases of nickel and copper oxides, and samples of the Zr-Cu-O catalytic system consist of phases of zirconium and copper oxides. It has been established that the crystallinity of the Zn-Cu-O and Zr-Cu-O catalytic systems increases with an increase in the content of zinc and zirconium in the composition of the binary catalyst, while for the Ni-Cu-O catalytic system, the crystallinity practically does not change with a change in the nickel atomic ratio to copper.

Keywords: *X-ray phase analysis, binary catalysts, copper oxide, zinc oxide, zirconium oxide, magnesium oxide, crystallinity.*

INTRODUCTION

At present, it is believed that hydrogen is the fuel of the future [1, 2]. There are various methods for obtaining hydrogen [3, 4]. One of the promising methods for producing hydrogen is the reaction of steam reforming of low molecular weight alcohols. Given that methanol is obtained in large quantities in Azerbaijan, the study of the reaction of steam conversion of methanol into hydrogen is of great practical importance for Azerbaijan. It is known from periodic literature that copper-based catalysts exhibit high activity in the methanol steam reforming reaction [5–7]. In this regard, in order to study the methanol steam reforming reaction, we synthesized binary copper-containing catalysts with nickel, zirconium, and copper additives. Preliminary studies have shown that the yields and distribution of methanol steam reforming products strongly depend on both the reaction temperature and the composition of binary copper-containing catalysts. This, apparently, may be due to a change in the phase composition of binary copper-containing catalysts. In this connection, the present work is devoted to the X-ray diffraction study of binary copper-containing catalysts.

EXPERIMENTAL PART

Binary copper oxide catalysts were prepared by mixing aqueous solutions of zinc, zirconium, nickel, and copper nitrate salts. The resulting mixture was evaporated and dried at a temperature of 100°C, after which it was transferred into a porcelain cup and calcined at a temperature of 200–300°C until the complete release of nitrogen oxides. After that, the catalyst was calcined at a temperature of 700°C for 10 hours.

Thus, we have prepared three catalytic systems Zn-Cu-O, Zr-Cu-O and Ni-Cu-O in each of which 9 samples were synthesized with a different ratio of the starting metals, satisfying the following conditions:

mA/nB, where A is Zn, Ni and Zr; B-Cu; m, n =1÷9; m+n=10.

X-ray studies were carried out on a Bruker D2 Phaser automatic powder diffractometer (CuKα radiation, Ni filter, 5≤2θ≥75°).

RESULTS AND DISCUSSION

The results of the conducted X-ray studies showed that only two phases are formed in the Zn-Cu-O system: ZnO and CuO. Figure 1 shows the diffraction patterns of all nine Zn/Cu ratios put together. ZnO and CuO oxides are also present at the beginning and end of these diffraction patterns. Analysis of the obtained X-ray diffraction patterns shows that all samples consist of two phases and the percentage ratio of components is preserved in all of them, as indicated by a regular change in the peak intensities in the diffraction patterns.

Fig. 2 shows X-rays of all nine ratios (mNi/nCu) put together. For comparative analysis, at the beginning and at the end of these diffraction patterns, X-ray diffraction patterns of NiO and CuO are also presented. Analysis of X-ray diffraction patterns shows that all studied samples of this catalytic system consist of three different phases of nickel oxide and one phase of copper oxide. As can be seen from fig. 2 the percentage ratio of the components is also preserved on these samples, as evidenced by the regular change in the intensities of the reflections in the diffraction patterns.

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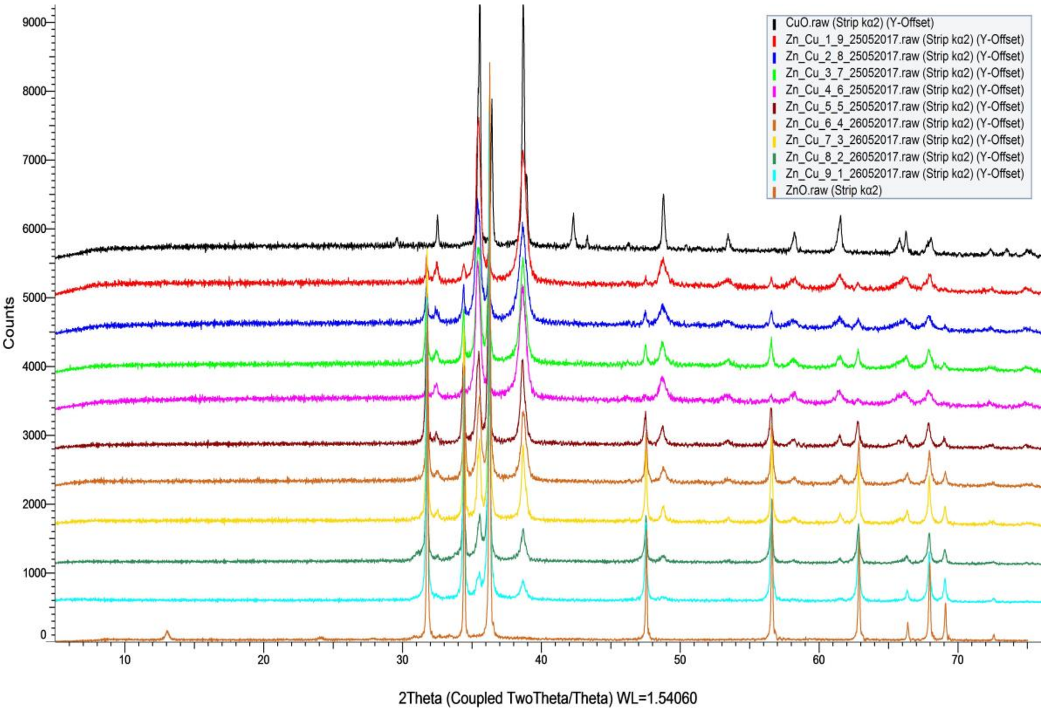

Fig. 1. X-ray diffraction patterns of zinc and copper oxides, as well as all nine samples of the Zn-Cu-O catalytic system.

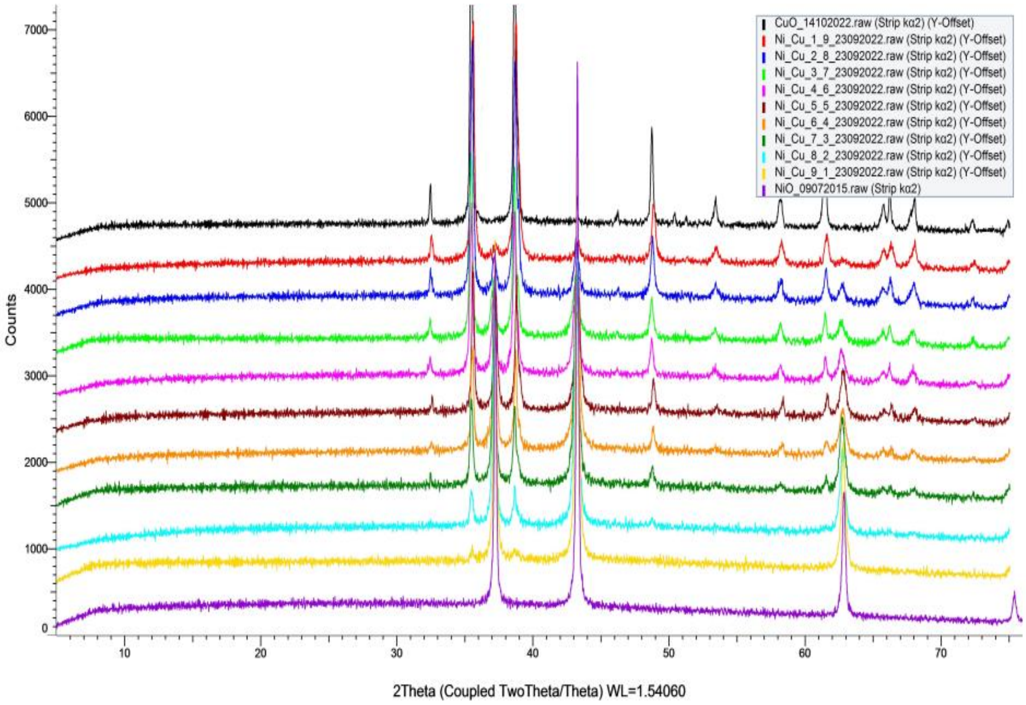

Fig. 2. X-ray diffraction patterns of nickel and copper oxides, as well as all nine samples of the Ni-Cu-O catalytic system.

Fig.3 shows the diffraction patterns of all nine ratios of the Zr-Cu-O catalyst system put together. At the beginning and at the end of these diffraction patterns, X-ray diffraction patterns of the initial ZrO_2 and CuO oxides are also presented. An analysis of the obtained diffraction patterns showed that, just as in the previous catalytic systems, only the ZrO_2 and CuO phases are formed at all ratios of the starting metals.

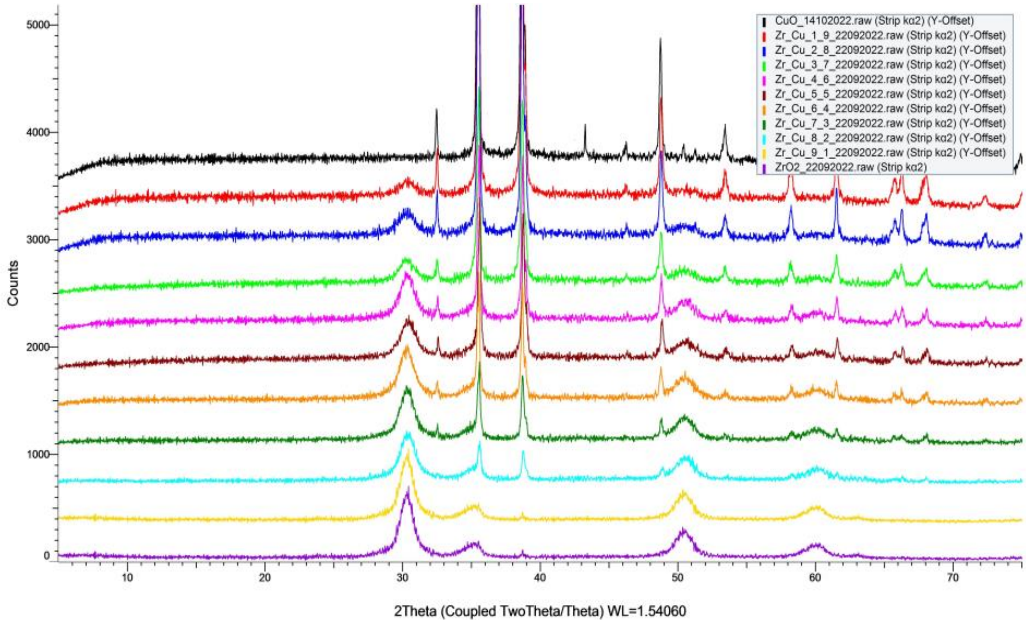

Fig. 3. X-ray diffraction patterns of zirconium and copper oxides, as well as all nine samples of the Zr-Cu-O catalytic system.

Table 1 shows the crystallographic characteristics of all phases formed during the synthesis of binary copper-containing catalysts with additions of zinc, nickel, and zirconium.

Table 1

Crystallographic characteristics of the phases formed in the catalytic systems Ni-Cu-O, Zr-Cu-O and Zn-Cu-O.

Compound	Singonia	Space group	Grid parameters			Z, number of molecules
			a, Å, α,°	b, Å, β,°	c, Å γ	
ZnO	hexagonal	$P6_3mc$	3.259	-	5.21	2
CuO	monoclinic	C12/c1	4.67	3.43	5.12	4
ZrO_2	Cubic	Fm3m	5.07	-	-	4
ZrO_2	Orthorhombic	$Pbc2_1$	5.07	5.26	5.08	4
ZrO_2	monoclinic	$P12_{1/c}1$	5.21	5.26	5.36	4
NiO	Cubic	Fm3m	4.18	-	-	4

In addition, Using the DIFFRAC.EVA program on the D2 Phaser instrument, we also calculated the degrees of crystallinity of all the forming phases, the results of which are presented in table 2. As can be seen from table 2, the crystallinity of the Zn-Cu-O and Zr-Cu-O catalytic systems with increasing zinc content and zirconium in the composition of the binary catalyst, its crystallinity increases. Thus, for the Zn-Cu-O catalytic system, the crystallinity increases from 42.9% to 93.8%, while for the Zr-Cu-O catalytic system it increases from 47.4% to 70.4%. For the catalytic system Ni-Cu-O, the crystallinity practically does not change with a change in the atomic ratio of nickel to copper.

Table 2.

Crystallinity of samples of catalytic systems Zn-Cu-O, Ni-Cu-O and Zr-Cu-O

The ratio of atoms	1-9	2-8	3-7	4-6	5-5	6-4	7-3	8-2	9-1
Zn-Cu-O	42.9	43.9	54.9	44.2	71.3	75.3	78.1	81.3	93.8
Ni-Cu-O	40.2	37.9	41.1	35.1	37.1	35.3	36.1	33.7	39.6
Zr-Cu-O	47.4	48.0	54.2	54.4	50.8	59.2	62.1	66.8	70.4

CONCLUSION

1. Binary copper containing oxide catalysts with additives of zinc, nickel and zirconium consist of two phases of the initial oxides, i.e. from oxides of zinc, nickel, zirconium and copper.
2. The degree of crystallinity of the Zn-Cu-O and Zr-Cu-O catalytic systems increases with an increase in the content of zinc and zirconium in the composition of the binary catalyst, while for the Ni-Cu-O catalytic system, the crystallinity practically does not change with a change in the nickel atomic ratio to copper.

REFERENCES

1. Xianxian Xu, Quan Zhou, Dehai Yu. The future of hydrogen energy: Bio-hydrogen production technology. International Journal of Hydrogen Energy. 2022, Vol.47, Issue 79, pp. 33677-33698
2. Simon Öberg, Mikael Odenberger, Filip Johnsson. The cost dynamics of hydrogen supply in future energy systems – A techno-economic study. Applied Energy. 2022, Vol.328, 120233
3. Canan Acar, Ibrahim Dincer. Review and evaluation of hydrogen production options for better environment. Journal of Cleaner Production. 2019, Vol. 218, pp. 835-849
4. Sukran Seker, Nezir Aydin. Assessment of hydrogen production methods via integrated MCDM approach under uncertainty. International Journal of Hydrogen Energy. 2022, Vol. 47, Issue 5, pp.3171-3184
5. Xiaofei Liu, Junwei Xu, Shuobin Li, Zijian Chen, Xianglan Xu, Xiuzhong Fang, Xiang Wang. Using XRD extrapolation method to design Ce-Cu-O solid solution catalysts for methanol steam reforming to produce H2: The effect of CuO lattice capacity on the reaction performance. Catalysis Today. 2022, Vol. 402, pp.228-240
6. Venkata D.B.C. Dasireddy. Cu–Mn–O nano-particle/nano-sheet spinel-type materials as catalysts in methanol steam reforming (MSR) and preferential oxidation (PROX) reaction for purified hydrogen production. Renewable Energy. 2022, Vol. 182, pp. 713-724
7. Woohyun Kim, K. Khaja Mohaideen, Dong Joo Seo, Wang Lai Yoon. Methanol-steam reforming reaction over Cu-Al-based catalysts derived from layered double hydroxides. International Journal of Hydrogen Energy. 2017,Vol.42,Issue 4, pp.2081-2087

ИССЛЕДОВАНИЕ БИНАРНЫХ КАТАЛИЗАТОРОВ Zn-Cu-O, Ni-Cu-O и Zr-Cu-O РЕНТГЕНОГРАФИЧЕСКИМ МЕТОДОМ

В.М.Исмайлова, В.Л.Багиев$^{0000-0003-1475-9571}$
Азербайджанский Государственный Университет Нефти и Промышленности
vagif_bagiev@yahoo.com

В работе бинарные медь содержащие катализаторы изучены рентгенографическим методом. Показано, что во всех изученных каталитических системах образование химических соединений не наблюдаются. Все синтезированные бинарные катализаторы состоят из двух фаз исходных оксидов. Так образцы каталитической системы Zn-Cu-O состоят из фаз оксидов цинка и меди, образцы каталитической системы Ni-Cu-O состоят из фаз оксидов никеля и меди, а образцы каталитической системы Zr-Cu-O состоят из фаз оксидов циркония и меди. Установлено, что кристалличности каталитических систем Zn-Cu-O и Zr-Cu-O с ростом содержания цинка и циркония в составе бинарного катализатора возрастает, в то время как для каталитической системы Ni-Cu-O кристалличность практически не меняется с изменением атомного отношения никеля к меди.

Ключевые слова: *рентгенофазовый анализ, бинарные катализаторы, оксид меди, оксид цинка, оксид циркония, оксид магния, кристалличность.*

Zn-Cu-O, Ni-Cu-O və Zr-Cu-O BİNAR KATALİZATORLARIN RENTGENOQRAFİK METODU İLƏ TƏDQİQİ

V.M.İsmayılova V.L.Bağıyev$^{0000-0003-1475-9571}$
Azərbaycan Dövlət Neft və Sənaye Universiteti
vagif_bagiev@yahoo.com

İşdə binar mis tərkibli katalizatorların rentgenoqrafik tədqiqi aparılmışdır. Tədqiq olunan bütün katalitik sistemlərdə kimyəvi birləşmələrin əmələ gəlməsinin müşahidə olunmadığı müəyyən edilmişdir. Bütün sintez edilmiş binar katalizatorlar ilkin oksidlərin iki fazasından ibarətdirlər. Beləliklə, Zn-Cu-O katalitik sisteminin nümunələri sink və mis oksidlərinin fazalarından, Ni-Cu-O katalitik sisteminin nümunələri nikel və mis oksidlərinin fazalarından və Zr-Cu-O katalitik sistemin nümunələri isə sirkonium və mis oksidlərinin fazalarından ibarətdir. Müəyyən edilmişdir ki, Zn-Cu-O və Zr-Cu-O katalitik sistemlərinin kristallikliyi binar katalizatorun tərkibində sink və sirkoniumun miqdarının artması ilə artır, Ni-Cu-O katalitik sistemi üçün isə nikelin misə olan atom nisbətinin dəyişməsi ilə kristallik praktiki olaraq dəyişmir.

***Açar sözlər**: Rentgen faza analizi, binar katalizatorlar, mis oksidi, sink oksidi, sirkonium oksidi, maqnezium oksidi, kristallik.*

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METHODICS OF TECHNICO-ECONOMICAL ESTIMATION OF RADIATION TECHNOLOGY APPLICATION (REVIEW)

Z.I.Iskenderova
Institute of Radiation Problems, Ministry of Science and Education
zenfira_iskenderova@mail.ru

This review is devoted to analyses of main aspects of radiation technology application, including the main sources of radiation technology, calculation of productivity radiation technology, evaluation of economical indicators of radiation facilities. Several types of a radiation sources can be used for the implementation of radiation-chemical processes. These include mixed neutron gamma radiation from nuclear reactors, "mantel" type reactor radiation (the zone where the chemical process is carried out is separated from the active zone), the use of fission shells (nuclear-chemical process), isotopes (as sources of gamma and electron radiation) and charged particles, mainly electrons includes accelerators.

Keywords: *radiation technology, irradiation sources, electron accelerator, isotopes as ^{60}Co and ^{137}Cs.*

INTRODUCTION

Radiation-chemical technologies have a number of advantages for the implementation of energy-intensive processes. It is possible to carry out these processes at low temperatures, since ionizing radiation energy is used for the initial chemical processes to occur. Since radiation-chemical processes do not contain additional chemicals (catalysts, etc.), and high temperatures, so the danger of fire and explosion is eliminated. These processes can be easily adjusted by changing the radiation dose. These technologies are an effective way to treat large-scale systems (wastewater, waste gases, etc.) containing small amounts of toxic waste. Radiation sources have the ability to provide more energy to the system in a short time (electron accelerators) [1-16].

Several types of a radiation sources can be used for the implementation of radiation-chemical processes. These include mixed neutron gamma radiation from nuclear reactors, "mantel" type reactor radiation (the zone where the chemical process is carried out is separated from the active zone), the use of fission shells (nuclear-chemical process), isotopes (as sources of gamma and electron radiation) and charged particles, mainly electrons includes accelerators. Various evaluations have been conducted on the use of these sources, but these studies remain at a preliminary level.

1. The main sources of radiation technology

Radiation sources practically used in radiation-chemical technology are divided into 2 groups: isotope radiation sources - ^{137}Cs and ^{60}Co, electronic accelerators. The specific activity of the currently used ^{60}Co isotope is 1.85-3.7 TBk/g (50-100 Ku/g), and the specific activity of the ^{137}Cs isotope is 0.925 TBk/g (25 Ku/g). For this reason, the ^{60}Co isotope is more widely used in industry. There are other differences between the ^{60}Co isotope and the ^{137}Cs isotopes. The energy of gamma rays emitted by ^{60}Co isotope is 1.25 MeV, and the energy of gamma rays emitted by ^{137}Cs isotope is 0.66 MeV. The half-lives of these isotopes are 5.27 years and 30.174 years, respectively. The internal absorption of isotope matrices does not reach 10% for the ^{60}Co isotope, and 50% for the ^{137}Cs isotope. The biggest difference between them is that the exposure dose rate in the gamma radiation of the ^{60}Co isotope is about 5 times greater than the dose rate of the

^{137}Cs isotope radiation. There is no big difference between the prices of these isotopes ~1 \$/Ku.

Based on the above data, the most commonly used source of gamma radiation in the water purification process is ^{60}Co, but

1. ^{60}Co dose rate strength is insufficient in many cases. It cannot provide the necessary technological output (speed).
2. The half-life of ^{60}Co is 5.27 years. This means that the source loses its activity by 12.5% every year.
3. For the above reasons ^{60}Co is mostly used in scientific research and pilot projects.
4. In many cases, the decomposition of toxic waste proceeds more rapidly in an oxygen environment. For this reason, it is more effective to carry out possible processes in the gas phase. But in this case, the absorption of radiation energy is less effective.
5. The difference between electron accelerators and the application of the ^{60}Co isotope is that the dose power of e-accelerators is several orders of magnitude higher. But even in this case, as the dose strength increases, the rate of recombination reactions of radical's increases, so their participation in the breakdown of molecules weakens.

$$[R]^2M = G\cdot\mathcal{J}\cdot 10^{-2}$$

Here, R is the concentration of radicals, G is the radiation-chemical yield, and J is the dose rate.

$$R = \sqrt{\frac{G\mathcal{J}\cdot 10^{-2}}{M}}$$

$$R\sim\mathcal{J}^{\frac{1}{2}}$$

That is, the concentration of radicals is directly proportional to the square root of the dose.

6. Another difference between electron accelerators and ^{60}Co isotope sources is that the electrons have a shorter escape distance in the medium. For this reason, the energy absorbed per unit distance $\left(\frac{dE}{dx}\right)$ during irradiation with e-accelerators is greater.

2, Calculation of productivity radiation technology,

Radiochemical technology is a specific branch of chemical technology. For this reason, special methods have been developed for calculating the productivity of radiation-chemical facilities .

The productivity of the radiation-chemical plant can be calculated by the following expression.

$$Q = 3{,}6\cdot 10^3 P\mu/D \text{ (kg/h)} \qquad (1)$$

here, P is the power of the ionizing source (kW), D is the absorbed dose (kGy), and μ is the utilization factor of the source power. It should be noted that the value of the μ parameter is 0.2-0.4 for gamma radiation, and 0.4-0.8 for electron radiation, or

$$Q = 3{,}73\cdot 10^{-4} GMP\mu \text{ (kg/h)} \qquad (2)$$

here, G is the radiation-chemical yield of the occurring process (molecul/100eV), M is the molecular weight of the substance.

Table 1

Energy losses during water irradiation of electrons of different energies

Electron energy, MeV	0,50	1,00	1,50	2,00
Energy loss, MeV·cm^2/g	4,35	3,50	3,25	3,00
Running distance, cm	0,20	0,50	0,80	1,20

It should be noted that the dependence of radiation-chemical output on the dose rate and the absorbed dose should be taken into account when using the last expression. Therefore, expression (1) is more universal. The dependence calculated by the expression (1) between the price of the dose required for different productivity and the power of the device is linear.

For example, if the productivity is 10^4 kg/h, the cost of the required dose is ~$5\cdot10^2$ kGy, and a device of ~10^4 kW is required. If the productivity is 10^5 kg/h, then this value is 10^3 kW.

3. Evaluation of economic indicators of radiation-chemical facilities

A methodology for calculating technical and economic indicators for electronic accelerators was developed in [31]. The cost of the used electron accelerator (K_S) depends on the energy of the electrons and the strength of the electron beam.

$$K_S = \delta E\sqrt{N}$$

here N is the power of the electron beam (kW), δ is the proportionality factor and varies in the range of 22-80 for different electron accelerators. E is the electron energy (MeV).

Basic funds for the creation of a radiation-technical facility consist (K_{RTf}) of the following components.

$$K_{RTf} = K_S + K_{RM} + K_N + K_K + K_T$$

K_{RM} – cost of radiation protection works, K_N – transport costs, K_K – costs of communication works, K_T – costs of construction and installation works.

Some of these costs are included in the price of the electron accelerator. Therefore, the cost of creating a radiation-chemical facility is mainly determined by the price of the electron accelerator.

Operating costs of the radiation facility are mainly determined by depreciation costs. This is about 15% of the radiation-technical facility. As a result, the productivity of the radiation-technical device is determined by the following general expression.

$$Q_{RTf} = 3{,}6 \cdot qk_1k_2T_S \quad \text{tons/year}$$

here, k_1 is the loading coefficient of the device, k_2 is the working time coefficient, T_S is the operating time of the device (hours/year)

$$q = \mu\mu^* \cdot N/D_{min} \quad \text{(kg/h)}$$

μ is the source power utilization coefficient, μ* is the coefficient characterizing the power loss of the electron beam, D_{min} is the minimum permissible dose value (kGy) for a specific radiation process.

As a result, the following expression is obtained between the productivity of the device and the total costs based on electronic accelerators.

$$X = \frac{\sigma E D_{min}}{\sqrt{N} T_s \mu}$$

Table 2

Prices for cleaning mixtures under the influence of electronic accelerators

Compounds	kW/1000 US 1 gal
Benzene	0,53
Toluene	0,43
Xylene	13
Phenol	0,47
Methylene blue	0,22
Trichlorethylene	0,52
Tetrachlorethylene	26
Chloroform	212
Carbon tetrachloride	0,55
Vinyl chloride	0,52

The implementation of the economic evaluation of the commercial device used for the purification of waste water by the combined electron beam and coagulation method is given in .

With this method, the cost of the dose required for the treatment of the water mass consisting of a mixture of industrial wastewater with a volume of 3,000 m^3 per day and domestic water with a volume of 4,000 m^3 per day is 3.5 kGy and 2 "Elektron-19" type with an electron accelerator power of 300-350 kW radiation sources were used. The power of an electron accelerator is 200 kW, the energy of electrons is 1 MeV, the width of the output window is 2 m, the coefficient of technical utilization is 0.85, u.w.f. 80% and the working period is 12 years. Before irradiation, the water mass undergoes chemical treatment, coagulation process saturated with iron sulfate, and finally sedimentation and sediment removal process, etc. exposed.

Table 3

Capital costs and running costs for setting up a commercial electron beam facility

Type of costs	Costs	Prices, US $
Capital investment	Two cascade electronic accelerator - "Elektron 23"	1 500 000
	Building and biological protection	1 500 000
	Basic (non-radioactive) equipment	1 100 000
	Auxiliary equipment	20 000
	Total costs for construction materials and equipment	1 880 000
	Project works	50 000
	Assembly, configuration and commissioning	180 000
	Total capital expenditure	2 110 000
Annual running costs	Depreciation	190 000
	Current costs of equipment and building maintenance	170 000
	Accelerator power and cooling	110 000
	Chemical reagents including air	70 000
	Salary of employees	90 000
	Total annual running costs	630 000

Treatment of waste water by combined electron beam and coagulation method is estimated at 0.25 $/m^3. The cost of cleaning with available methods is 0.45-0.65 $/m^3. As it can be seen, it is economically more profitable to treat waste water using the above-mentioned combined method. Table 3 provides information on the costs required for the construction of an electron accelerator used for the combined treatment process.

CONCLUSION

1. The obtained results can be used for calculation of productivity of applied radiation sources and evaluation of economical indicators of the process.
2. The provided review shows the perceptivity of radiation technology based on application of electron accelerators and isotope sources for the various purposes – for the modification for the polymer materials, treatment of waste waters and study of degradation toxic components in environment and other economical sectors.

REFERENCES

1. Krayushkin V.V. On the issue of optimization of radiation installations with electron accelerators. Atomic Energy,.1980, Vol.48, pp.94-98
2. Zorrilla M.V. Chemical dechlorination for the treatment of PCBs present in transformer oil (Sovtol-10): parameter study / Velazco, P.P., Villanueva, G.R., Van Langenhove, H.U. AFINIDAD.2013,Vol. 70, № 563, pp.206-211
3. Troyanowicz M. Application of ionizing radiation in decomposition of organic pollutants in waters and wastes / Bojanowska-Czajka, A., Kciuk, G. European water. 2012, Vol. 39, pp.15-26
4. Trifan A. Transformation of polychlorinated biphenyls (PCBs) into non-hazardous products by electron beam treatment / Calinescu, I., Martin, D. Rev. Chim. 2009, Vol. 60, №10, pp.1053-1055
5. National Implementation Plan under the Stockholm Convention on POPs. Republic of Azerbaijan. 2007-2020, pp.46-107
6. Marchich M., Maryev V.A. Environmentally sound management and disposal of polychlorinated biphenyls (PCBs) in the Republic of Azerbaijan.UNIDO. May 2013, pp.20-64.
7. Kong J. Dechlorination of polychlorinated biphenyls in transformer oil using UV and visible light / Achari, G., Langford, C. Journal of Environmental Science and Health.2013, Vol. 48, pp. 92-98
8. Junrong J. Chong F., Deming Z. Kinetics of 2-chlorobiphenyl reductive dechlorination by Pd-fe^0 nanoparticles / MATEC Web of Conferences. 2016, Vol. 61, pp.1-5
9. Gurbanov M.A., Gurbanov A.H., Abdullayev E.T. Radiation technology application for cleaning of water from admixtures of phenol, PAC and PCBs Institute of Nuclear Physics Academy of Science of Uzbekistan. International Conference Nuclear Science and its Application. Uzbekistan: Samarkand. 2012, pp.396-398
10. Aliyeva G. Organochlorine pesticides and polychlorinated biphenyls in air and soil across Azerbaijan. Kurkova, R., Hovorkova, I., Klanova, J., Halsall, C. Environmental Science and Pollution Research, Special Issue Brno.2012,Vol.19, pp.1953–1962
11. Aliyeva G., Halsall C., Alasgarova, Kh., Avazova M., Ibrahimov Y., Aghayeva

R.The legacy of persistent organic pollutants in Azerbaijan:an assessment of past use and current contamination. Environ Sci Pollut Res. 2013, Vol.20, pp.1993–2008

12. Singh R. Radiation induced degradation of polychlorinated biphenyls (PCB`s) pollutants in paints scrapings/ Khandal, R., Singh, G.Journal of Environmental Science and Eng.2009, Vol.51, №1, pp.73-80
13. Nerubatskaya Yu.D. Radiation oxidation of isopropyl alcohol in hydrocarbon media/ Sazonov A.B. Advances in Chemistry and Chemical Technology. 2013, Vol.27, №.6, pp. 50-54
14. Kurbanov M.A., Jamalov I.J., Alieva S.G. Investigation of the photochemical decomposition of PCB-containing oils by UV spectroscopy. VIII conference on "Radiation studies and their practical aspects" dedicated to the 65th anniversary of Academician M.K. Karimov. Baku: 2013, pp. 144-145
15. Gurbanov M.A. Study of transformation regularities of polychlorinated biphenyl (PXB) oils under the influence of γ-rays.Abdullayev E.T., Gurbanov A.H. Chemical problems. 2010, №. 2, pp. 292-295
16. AzPatent, a20160036. Radiation-adsorption method of purification of industrial wastewater from phenolic compounds. 31.08.2017, Bulletin №8, 8 p

МЕТОДИКА ТЕХНИКО-ЭКОНОМИЧЕСКОЙ ОЦЕНКИ ПРИМЕНЕНИЯ РАДИАЦИОННЫХ ТЕХНОЛОГИЙ (ОБЗОР)

З.И.Искендерова
Институт Радиационных Проблем Министерства науки и образования
zenfira_iskenderova@mail.ru

Настоящий обзор посвящен анализу основных аспектов применения радиационных технологий, в том числе основных источников радиационных технологий, расчету производительности радиационных технологий и оценке экономических показателей радиационных установок. Для реализации радиационно-химических процессов могут быть использованы несколько типов источников излучения. К ним относятся смешанное нейтронно гамма-излучение ядерных реакторов, излучение реакторов «мантального» типа (зона, в которой осуществляется химический процесс, отделена от активной зоны), использование оболочек деления (ядерно-химический процесс), изотопы (в качестве источников гамма-излучения и электронного излучения) и заряженных частиц, в основном ускорители электронов.

Ключевые слова: *радиационная технология, источники облучения, ускоритель электронов, изотопы* ^{60}*Co и* ^{137}*Cs.*

RADİASİYA TEXNOLOGİYASININ TƏTBİQİNİN TEXNİKİ-İQTİSADİ METODİKASI (ICMAL)

Z.İ.İskəndərova
Elm və Təhsil Nazirliyinin Radiasiya Problemləri İnstitutu
zenfira_iskenderova@mail.ru

Bu icmal radiasiya texnologiyasının tətbiqinin əsas aspektlərinin, o cümlədən radiasiya texnologiyasının əsas mənbələrinin təhlilinə, radiasiya texnologiyasının məhsuldarlığının *hesablanmasına, radiasiya qurğularının iqtisadi göstəricilərinin qiymətləndirilməsinə həsr edilmişdir. Radiasiya-kimyəvi proseslərin həyata keçirilməsi üçün bir neçə növ radiasiya mənbələrindən istifadə edilə bilər. Bunlara nüvə reaktorlarından qarışıq neytron qamma şüalanması, "mantel" tipli reaktor şüalanması (kimyəvi prosesin aparıldığı zona aktiv zonadan ayrılır), parçalanma qabıqlarının istifadəsi (nüvə-kimyəvi proses), izotoplar (qamma və elektron şüalanma mənbəyi kimi) və yüklü hissəciklər, əsasən elektron sürətləndiricilər daxildir.*

Açar sözlər: *radiasiya texnologiyası, şüalanma mənbələri, elektron sürətləndirici,* ^{60}*Co və* ^{137}*Cs izotopları.*

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DETERMINATION OF VANADIUM(V) ION BY ITS CONCENTRATION IN DIFFERENT OBJECTS WITH SORBENTS SYNTHESIZED ON THE BASIS OF A POLYMER MATRIX

M.B.Hasanova[0000-0002-9566-1295]
Azerbaijan State Oil and İndustry University
m.hesenova.74@mail.ru

The article studies, polymer chelating sorbents obtained by modifying of maleic anhydride with styrene and maleic anhydride with methacrylic acid copolymers with various amines and esters for determination of vanadium(V)) ion by condensation in different objects. The synthesized. sorbents and their complex compounds with vanadium(V) ion were studied by scanning electromicroscopy and thermogravimetric analysis methods. The sorption capacity of the vanadium(V) ion by the obtained sorbents was studied, the effect of the pH of the medium,the concentration of metal ions, and the ionic strength of the solution on the solidification of the metal with chelating sorbents was studied. The time dependence of sorption was investigated, and the moment of sorption equilibrium was determined.

Keywords: *maleic anhydride, styrene, methacrylic acid, chelating sorbent, sorption, desorption.*

INTRODUCTION

For the materials used in various industries to meet the necessary demand, controlling the number of components included in their composition with high precision is considered one of the main stages of the modern production process. To ensure the necessary sensitivity and selectivity of methods for determining the amount of vanadium (V), which is a representative of metal ions dispersed in biological objects, sorption methods of separation and concentration are used [1-4]. Separation and concentration methods are widely used in analytical practice to ensure the necessary sensitivity and selectivity of several determinations.

The small amount of microcomponents determined in objects with high metrological characteristics makes the analysis even more difficult, and in some cases, it makes it impossible to obtain reliable analysis results. One of the prospective solutions to the mentioned problem is the development of complex analysis methods that include the initial sorption solidification stage [5-6].

EXPERIMENTAL PART

Equipment. The acidity of the solution was monitored with a glass electrode on a PHS-25 ion meter. The optical density was measured on a KFK 2 photocolorimeter (l =1 cm). The thermal stability of sorbent and sorbent-metal chelates was measured on a NETZSCH STA 449F3 STA449F3A-0836M derivatograph. At the same time, the synthesized sorbents and their chelates with vanadium (V) were also studied with a JSM 6610LV electron microscope.

Solutions, reagents, sorbent. Reagents of chemically pure grade were used. A solution of vanadium (V) (10^{-2} M) was prepared by dissolving an exact weighed portion of the ammonium vanadate salt in distilled water according to method [14]. Working solutions were obtained by diluting the original. The required pH values were maintained with

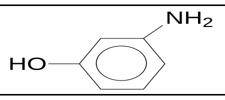
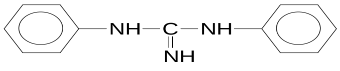
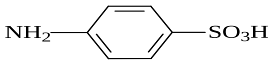
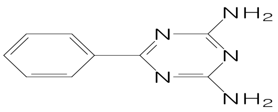
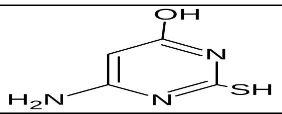
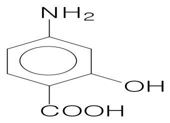
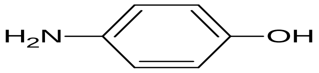
HCl, NaOH solutions and ammonia-acetate buffer solutions. To maintain a constant ionic strength, a KCl solution was used.

Experimental technique. Sorption was studied under static conditions. When studying sorption under static conditions, a solution of vanadium (V) was introduced into a graduated test tube with a ground stopper, and an ammonium acetate buffer solution was added to create the necessary acidity to a volume of 20 ml. Besides, 0.05 g of sorbent was introduced, the tube was closed with a stopper and left for 2 h, then the solution was decanted.In the eluate, the concentration of vanadium (V) was determined by the photometric method using a reagent based on pyrogallol. The concentration of vanadium (V) was calculated using a calibration curve.

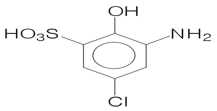
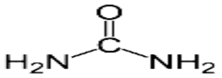
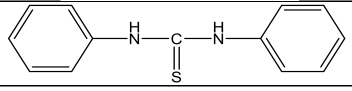
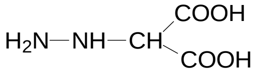
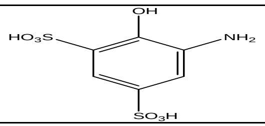
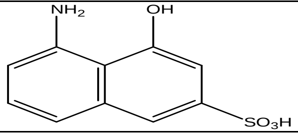
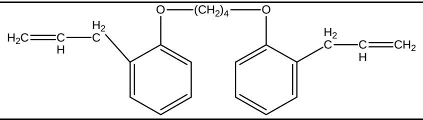
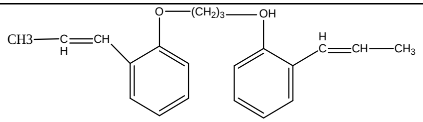
To carry out the solidification process, chelatig sorbents obtained on the basis based on and ethers based on maleic anhydride-styrene and maleic anhydride-methacrylic acid copolymers according to the method known in the literature were studied. The reaction was carried out in a sand bath at a temperature range of 80-100 ^{0} C with continuous stirring. Since the reaction takes place in an aqueous medium, the anhydride groups contained in the copolymer are hydrolyzed. Discontinuous carbonylamine is obtained from the interaction of formaldehyde and monomer (amine) in the system. The removed carbonylamine interacts with the carboxyl groups in macromolecules, and the removed amine fragment enters the macromolecule[4,7]. Studies were conducted using pyrogallol based azo compounds for spectrophotometric determination after the solidification process [8]. Synthesized sorbents and their complex compounds formed with vanadium(V) ion were studied by scanning electron microscopy and thermogravi-metric analysis methods. The monomers used to modify the polymer matrix are shown in table 1.

Table 1

Amine fragments used in the synthesis of sorbents

Conventional symbol and name of the monomer	Monomer
MS1 m-amino phenol	
MS2 (MMA1) N, N´- diphenylguanidine	
MS3 p-amino sulfonic acid	
MS4 2,4-diamine-6-phenyl-triazine-1,3,5	
MS5 4-amino-2-thiouracil	
MS6 (MMA2) 4-amino salicylic acid	
MS7 p-amino phenol	

Continue of table 1

MS8 2-hydroxy-3- sulfo-5 chloro aniline	
MS9 urea	
MS10 Diphenyl thiourea	
MS11 Molon acid dihydrazide	
MS12 2-Amino phenol-4,6-disul - futuric acid	
MS13 1-amino-2-hydroxy-4-sulfoacid-naphthalene	
MS14 2-allylphenol ether	
MS15 2-propenylphenol ether	

MS – maleic anhydride-styrene copolymer, MMA – maleic anhydride-methacrylic acid copolymer.

RESULTS AND DISCUSSION

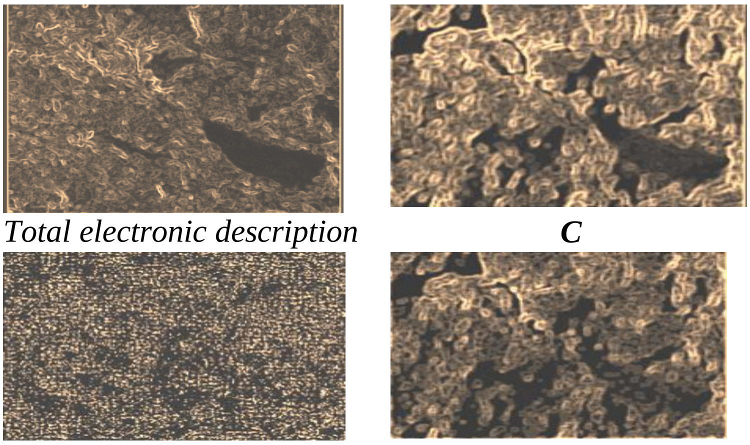
One of the sorbents synthesized in this work is the MS8 sorbent (a polymer sorbent synthesized on the basis of maleic anhydride - styrene copolymer and 2-hydroxy-3-sulfo -5-chloro aniline monomer) and the complex compounds formed by this sorbent with vanadium ion, Japan's JOEL was studied in the JSM-6610 scanning electron microscope of the company. An X-MAX electron spectrometer attached to the micros-cope shows the chemical composition, amount, and distribution of the elements in the sample. That is, with this method, it is possible to determine both the distribution map and the amount of elements (table 2).

The distribution of S and C is reflected in the element distribution map obtained as a result of sorbent's electron microscope study. According to the distribution result, S is homogeneously distributed, and C completely repeats the electronic image (fig. (1a)). According to the distribution map of elements in the chelate complex formed by vanadium with polymer sorbent, it is observed that it contains C, S, O and V. According to the distribution map of the complex, S, O, V are homogeneously distributed (fig. (1b)). As can be seen from the picture, the distribution of *C* −completely reproduces the electronic image. This shows that the sorbent is an organic compound.

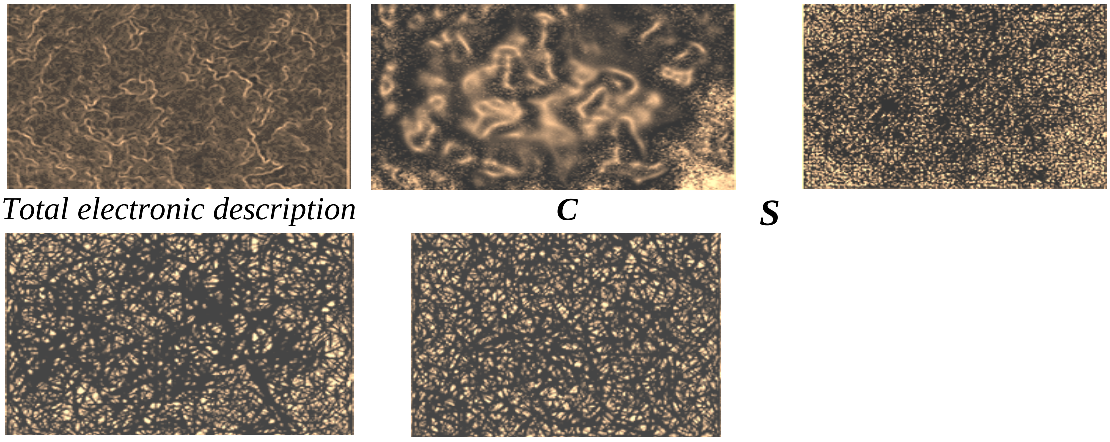
Table 2

The results of the scanning electron microscope study of the sorbent synthesi-zed on the basis of the MS8 fragment and the complex compound produced by this sorbent with the vanadium (V) ion

Sorbent					Chelate complex				
Element	Weight %	Atom %	Comp. %	Formula	Element	Weight %	Atom%	Comp. %	Formula
C	26.98	33.08	98.84	CO_2	C	26.85	33.04	98.71	CO_2
Al	0.18	0.10	0.33	Al_2O_3	S	0.39	0.20	1.08	SO_3
S	0.23	0.11	0.57	SO_3	Cl	0.21	0.09	0.00	
Cl	0.25	0.11	0.00		V	0.13	0.01	0.05	V_2O_5
O	72.36	66.62			O	72.42	66.67		
Complete	100.00				Complete	100.00			



a)



b)

Fig. 1. Distribution map of elements in the sorbent (a) synthesized on the basis of maleic anhydride-styrene copolymer and 2-hydroxy-3 sulfo-5-chloro aniline fragment and its complex compound formed with vanadium (V) ion (b).

Research using thermogravimetric analysis method. As a result of the research, the sorbent was studied before and after sorption using the gravimetric analysis method .

As can be seen from the described thermogram, the studies were carried out in an air atmosphere between 20~800 ^{0} C. At this time, the complex nature of the process occurring in the thermogram of the sorbent and the complex compound formed by it with the vanadium(V) ion is a multi-stage thermo-oxidative structure disintegration process of the polymer. 91.78 % weight loss occurs in this polymer sorbent from the beginning to the end of the process, that is, in the temperature range of 20~800 ^{0} C (fig.2). The results obtained from the thermogram of the polychelate depicted in fig.3 show that after the sorption process certain changes occur in both the TQ and DTA curves of the indicated polymer. Unlike the primary polymer, the chelate complex formed by the sorbent synthesized based on maleic anhydride - styrene copolymer and MS10 (diphenylthiourea) fragment with vanadium are observed at 167 ^{0} C in the DTA curve (in the primary polymer, this effect is observed at 183 ^{0} C and the corresponding peak has a lower intensity happens) an endoeffect that can be considered intensive is observed. Unlike the primary polymer, maleic anhydride – styrene copolymer and In the DTA curve of the chelate complex formed by the synthesized sorbent MS10 (diphenylthiourea) fragment with vanadium, an endoeffect that can be considered intense is observed at 167^{0}C (in the primary polymer this effect is observed at 183^{0}C and the corresponding peak has a lower intensity) [9-10].

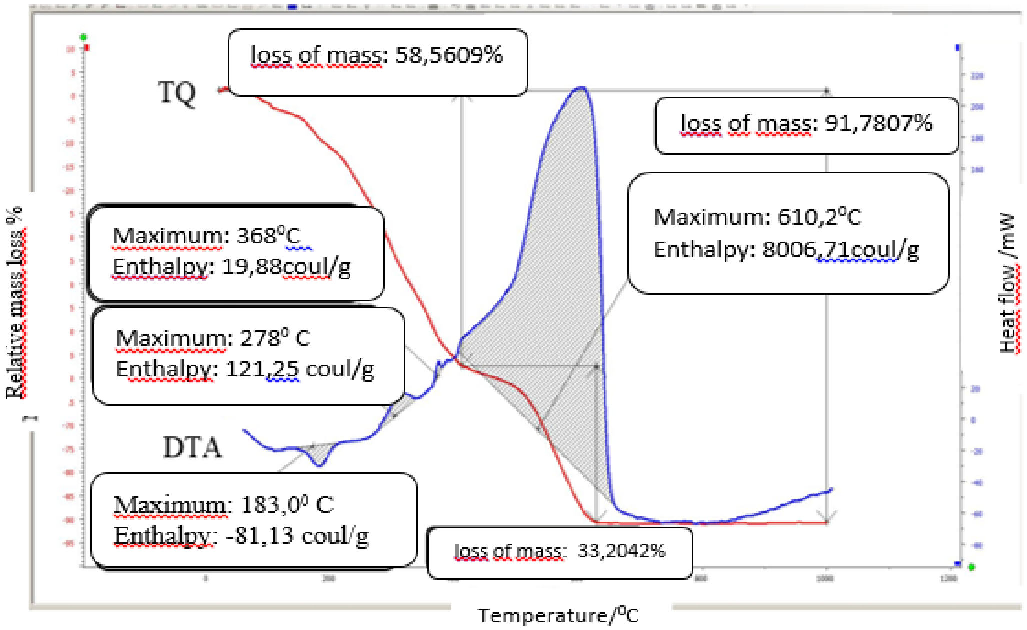


Fig. 2. DTA and TQ curves of sorbent based on maleic anhydride-styrene copolymer and MS10-diphenylthiocarbamide fragment.

analysis methods, the vanadium sorption capacity of the sorbents was studied. The influence of the pH of the environment, the concentration of metal ions, and the ionic strength of the solution on the solidification of metal with chelating sorbents was studied. The time dependence of sorption was investigated, the moment of sorption equilibrium was determined and the obtained experimental results are shown in the table below (table 3).

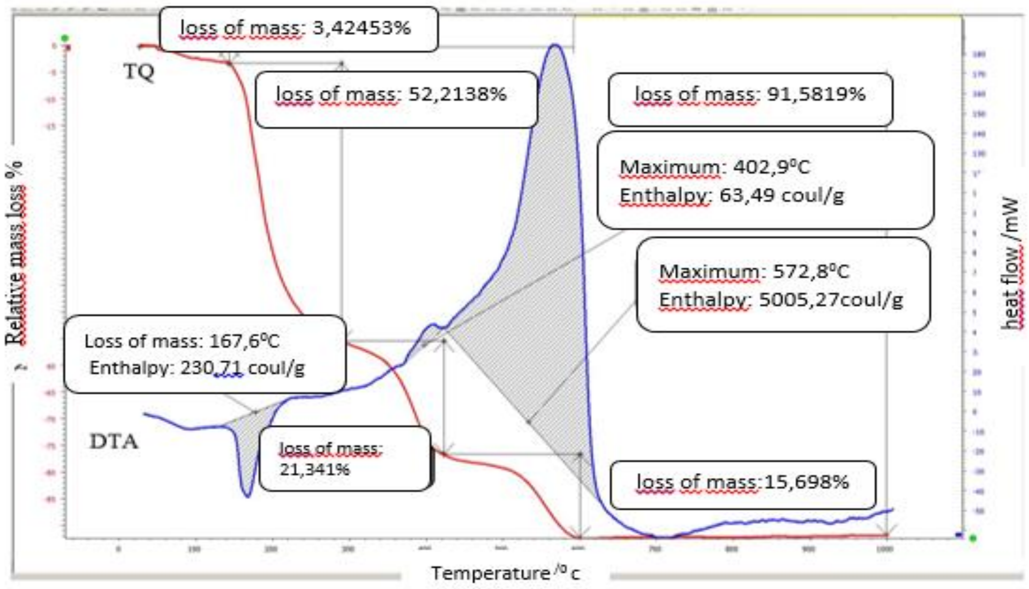


Fig. 3. DTA and TQ curves of chelation of maleic anhydride-styrene copolymer and MS10-diphenylthiourea fragment-based sorbent with V(V) ion.

The desorption of the sorbed vanadium (V) ion from the absorbent was studied separately in each system . For this purpose, the effect of different mineral acids of the same concentration ($HClO_4$, H_2SO_4 , HNO_3 , HCl) on sorption was also studied. Before determining the amount of desorption of adsorbed vanadium (V) from sorbents , the - acid that has a better effect on the desorption process (optimal acid) is determined, then the optimal concentration of the optimal acid that has the maximum effect on desorption is determined . The results of the experiment show that absorbed vanadium ions are perchlorate from MS2 , MS3, MS5, MS6, MS10, MMA2 sorbents, sulfate from MS4, MS12, MS13, MS14 sorbents, chloride from MS7 sorbent, MS1, MS8, MS9, MS11, MS15, MMA1 sorbents. and they are maximally desorbed under the influence of nitric acids.

Table 3

Vanadium (V) ion sorption indicators of sorbents

Sorbent	pHopt.	Time, hour	μ*, mol/l	ST, mg/g	Sorb. degree. %
MS1	4	2.0	0.6	241.0	89
MS2	4	2.0	0.6	191.0	75
MS3	4	2.0	0.8	256.2	92
MS4	4	1.0	1,2	259.1	95
MS5	4	2.0	0.6	267.6	97
MS6	4	2.0	0.8	265.2	95
MS7	4	1.0	0.6	241.4	89
MS8	4	2.0	0.4	202.0	90
MS9	5	2.0	0.8	265.2	97
MS10	4	2.0	0.8	263.5	96
MS11	4	2.0	0.6	163.2	60
MS12	4	1.0	0.6	248.5	91
MS13	4	1.5	0.8	249.0	91

Continue of table 3

MS14	5	1.5	0.8	158.0	58
MS15	5	2.0	0.6	240.4	88
MMA1	5	2.0	0.6	253.3	93
MMA2	5	1.0	0.6	242.8	89

After determining the optimal conditions of sorption and desorption, microquantities of vanadium(V) ions were concentrated in environmental objects (clay , mountain rock and river water) and new, effective sorption-photometric determination methods were developed. The obtained results are reflected in table 4.

Table 4

.Methods of determination of vanadium(V) by condensation in environmental objects with synthesized sorbents

Object	Sorbent	Included done , µg / l	It has been found $\overline{x} \pm \frac{t_P S}{\sqrt{n}}$, mkg / l
mountain rock	MS3	–	2 , 9 0±0.1 2
		5.00	7,98 ±0,2 5
		10.00	1 1 , 87 ±0. 1 3
		15.00	16.21 ± 0.09
Object	Sorbent	Sorbian photometric method, µg/ml	A tom-absorption assay meto du µg/ml
clay	MS5	0.288 ±0.02	0.275±0.04
Object	Sorbent	By sorption-photometric method determined V, µg/l	V determined by γ-spectroscopy, µg/l (ICP-OES Thermo ICAP 7400 DUO)
river water	MMA1	2, 8 1±0.029	2.88±0.031
river water	MMA2	2.076±0.003	2.080±0.005

The determination methods are simple, characterized by good reproducibility, ensure the accuracy of the results during the analysis of real objects (this was confirmed using addition, atomic absorption, and γ-spectroscopy analysis methods).

The conducted research shows that the proposed sorbents are useful for sorption-photometric determination of vanadium(V) [11-13].

CONCLUSION

1. Maleic anhydride-styrene and maleic anhydride methacrylic acid copolymers with various amines and ethers, seventeen polymer-based chelating sorbents were synthesized for the selective solidification of vanadium(V) ions physico-chemical indicators, including spectral and thermal characteristics, and analytical characteristics of the process were determined .
2. The effect of various factors (acidity of the environment, duration of sorption, ionic strength, and metal density) was studied to determine the optimal conditions for the sorption of vanadium with the 17 studied sorbents. The sorption capacity of sorbents for

vanadium was calculated and it was determined that MS5, MS10, MS6, MS8 and MS4 sorbents have the highest sorption capacity. The relationship between the sorption capacity and the donor atoms in the sorbent was considered. It was determined that as the number of S, N, O donor atoms increases, the sorption capacity of the sorbent for vanadium (V) increases.

3. Optimum conditions of sorption with synthesized polymers, degrees of element separation, sorption capacities of sorbents were compared, the possibility of desorption with small amounts of various mineral acids and the prospects of practical use of the studied sorbents in the analysis of natural and technical objects were shown. From these sorbents, the optimal conditions for quantitative desorption of vanadium by mineral acids were determined.
4. Vanadium (V) in natural and wastewater, mixed methods including a preliminary sorption concentration step (with subsequent spectrophotometric detection) have been developed. The proposed methods provide correct results, which are confirmed by "addition", atomic absorption spectroscopy, passport results and "spectroscopy $\gamma -$" methods.

REFERENCES

1. Aliyeva R.A., Chyragov F.M., Gamidov S.Z. Sorption study of copper (II) with a polymer sorbent. Journal of Chemical Problems, Baku. 2006, № 4, pp. 161-163
2. Aliyev E.G., Bakhmanova F.N., Gamidov S.Z., Chyragov F.M. Concentration of lead(II) with a chelating sorbent containing metaphenylenediamine fragments. Applied chemistry and biotechnology. 2020, T.10, №. 1, pp.107-113
3. Basargin N.N., Magerramov A.M., Gadzhieva S.R., Bakhmanova F.N., Gamidov S.Z., Aliyeva T.I., Chyragov F.M. "Determination of uranium(VI) in natural waters after preliminary concentration with a sorbent containing fragments of m-amino phenol". Journal of analytical chemistry. 2013, Tom 68, № 2, pp. 136-139
4. Aliyeva R.A., Gamidov S.Z., Chyragov F.M. Study of sorption of Zn(II) by chemically modified synthetic sorbent.Vestnik BU. 2007, №. 2, pp. 28-34
5. Jiang Y., Yin X., Luo X., Yu L., Sun H., Wang N. Shiny Mathews Sorption of vanadium (V) on three typical agricultural soil of the Loess Plateau, China. Environmental pollutants and bioavailability. 2019, Vol. 31, №. 1, pp.120–130
6. Mandal B., Barman M.K., Srivastava B. Extraction Chromatographic Method of Preconcentration, Estimation and Concomitant Separation of Vanadium (IV) with Silica Gel-Versatic 10 Composite. Journal of Chromatographic Science. 2014, Vol.52, issue 9 pp.1135–1144
7. Myasoedova G.V, Savvin S.B Chelating sorbents. Moscow: Nauka. 1984, 173 p
8. Magerramov A.M., Gadzhieva S.R., Bakhmanova F.N., Gamidov S.Z., Chyragov F.M. Concentration of uranium(VI) with a chelating sorbent and photometric determination with 2,3,4-trihydroxy-3'-nitro-4'-sulfoazobenzene. Journal of analytical chemistry. 2011, T. 66, №. 5, pp. 480-483
9. Tarutina L.I. and Pozdnyakova F.O. Spectral analysis of polymers. Leningrad, Chemistry. 1986, 248 p
10. Elliot A. IR spectra and structure of polymers. Moscow, Mir. 1972, 159 p
11. Magerramov A.M., Alieva R.A., Alieva Z.M, Bahmanova F.N., Chyragov F.M.. Concentration of thorium (IV) with a chelating sorbent. Zavodskaya laboratoriya. Diagnostika materialov, 2018, Vol.84, №.3, pp.21–24
12. Aliyev E.H., Bahmanova F.N., Hamidov S.Z., Chyragov F.M. Lead (II) concentration

by a chelating sorbent containing meta-phenylenediamine fragments. Proceedings of Universities. Applied Chemistry and Biotechnology. 2020, 10(1), pp.107-113

13. Alieva R.A., Mirzai J.I., Abdullaeva K.S., Bahmanova F.N., Hamidov S.Z., Chyragov F.M. Determination of molybdenum (VI) in natural waters after concentration with a sorbent containing m-aminophenol fragments. Zavodskaya laboratoriya, Diagnostika materialov. 2014, № 1, pp. 15-19
14. Korostelev P.P. Preparation of solutions for chemical analytical work. M.Science. 1964, 261 p.

ОПРЕДЕЛЕНИЕ ИОНА ВАНАДИЯ (V) МЕТОДОМ КОНЦЕНТРИРОВАНИЯ В РАЗЛИЧНЫХ ОБЪЕКТАХ С СОРБЕНТАМИ, СИНТЕЗИРОВАННЫМИ НА ОСНОВЕ ПОЛИМЕРНОЙ МАТРИЦЫ

М.В.Гасанова[0000-0002-9566-1295]
Азербайджанский Государственный Университет
Нефти и Промышленности
m.hesenova.74@mail.ru

В статье исследованы полимерные хелатообразующие сорбенты, полученные в результате модификации сополимеров малеинового ангидрида стиролом и метакриловой кислотой различными аминами и эфирами для определения иона ванадия(V) методом концентрирования в различных объектах. Синтезированные сорбенты и их комплексные соединения с ионом ванадия(V) изучены методом сканирующей электромикроскопии и термогравиметрического анализа. Исследована сорбционная способность полученных сорбентов с ионом ванадия(V), изучено влияние pH среды, концентрации ионов металла и ионной силы раствора на концентрацию ионов ванадия(V) хелатообразующими сорбентами. Исследована зависимость сорбции от времени и определен момент наступления сорбционного равновесия.

Ключевые слова: *малеиновый ангидрид, стирол, метакриловая кислота, хелатирующий сорбент, сорбция, десорбция.*

POLİMER MATRİSA ƏSASINDA SİNTEZ OLUNMUŞ SORBENTLƏRLƏ VANADİUM(V) İONUNUN MÜXTƏLİF OBYEKTLƏRDƏ QATILAŞDIRILARAQ TƏYİNİ

M.B.Həsənova[0000-0002-9566-1295]
Azərbaycan Dövlət Neft və Sənaye Universiteti
m.hesenova.74@mail.ru

Məqalədə malein anhidridi-stirol və malein anhidridi-metakril turşusu sopolimerlərinin müxtəlif aminlər və efirlərlə modifikasiyası nəticəsində alınmış polimer xelatəmələgətirici sorbentlərlə vanadium(V) ionunun müxtəlif obyektlərdə qatılaşdırılaraq təyini tədqiq edilmişdir. Sintez olunmuş sorbentlər və onların vanadium(V) ionu ilə əmələ gətirdiyi kompleks birləşmələr, skaneredici elektromikroskopiyası, termoqravimetrik analiz metodları ilə tədqiq edilmişdir. Alınmış sorbentlərin vanadium(V) ionunun sorbsiyaetmə qabiliyyəti tədqiq edilmiş, metalın xelatəmələgətirici sorbentlərlə qatılaşdırılmasına mühitin pH-nın, metal ionlarının qatılığının, məhlulun ion qüvvəsinin təsiri öyrənilmişdir. Sorbsiyanın zamandan asılılığı araşdırılmış, sorbsiya tarazlığının yaranma anı müəyyən edilmişdir.

Açar sözlər: *malein anhidridi, stirol, metakril turşusu, xelatəmələgətirici sorbent, sorbsiya, desorbsiya.*

ATTENTION FOR AUTHORS!

“Azerbaijan Journal of Chemical News” approved by the Higher Attestation Commission under the President of Azerbaijan Republic and it is included to the list of journals and periodicals that should be published by major scientific results of dissertations in Azerbaijan Republic.