

UDC 543.4:54.412:541.49

**EXTRACTION OF NICKEL (II) PICRATE FROM SOLID PHASE
WITH ORGANIC REAGENTS****L.M. Maharramova, N.E. Jabbarova, M.Y. Abdullayeva**

*Azerbaijan State University of Oil and Industry,
Azadlig 20, Baku, AZ-1010, Azerbaijan
e-mail: mayaabdullayeva@hotmail.com*

Received 04.05.2023

Accepted 25.07.2023

Abstract: *The present work is dedicated to the very important area of analytical chemistry—extraction-photometric determination of ions from a solid phase. We carried out studies on the extraction of nickel picrate (NiPik2) from the solid phase using solutions of tetrahalobicyclic reagents of the acetylene series with a dicarbonyl bridge in the side chain (L1, L2, L3, L4) of chloroform. New organic ligands were synthesized and their physicochemical properties - melting point, molecular weights, as well as their optical density studied. A new technique for the extraction-photometric determination of the nickel ion from the solid phase was developed. It found that new organic reagents (L1-L4) exhibit high extraction ability (0.11-0.64 mg/l) of Ni ions from the solid phase. When comparing the extraction activity of the studied reagents, it was revealed that the ability to extract organic ligands of tetrahalobicyclic reagents (L1-L4) changes in the following order: L4 > L3 > L1 > L2. Magnetic field increased nickel extraction by 3-4%.*

Keywords: *extraction, nickel (II) picrate, organic reagents, equilibrium, optical density, equilibrium, a magnetic field.*

DOI: 10.32737/2221-8688-2023-3-221-228

Introduction

One of the simplest and most accessible, but at the same time, effective methods of separation and concentration, in particular, metal ions, is extraction. Extraction is the process of extracting appropriate substances from various objects with solvents. The objects from which the respective compounds are extracted can be solids and liquids. Therefore, extraction processes are divided into extraction in the solid-liquid system and extraction in liquid-liquid system (liquid extraction), in other words, depending on the state of aggregation of the contacting phases, several extraction options are distinguished.

Extraction from the solid phase is a widely used method of separation and preconcentration in analytical chemistry due to rapidity, high efficiency, and the possibility of combination with various physicochemical and

chemical methods for determination of analytes of various nature [1–4].

According to the type of interaction with the substance to be extracted, extractants are divided into neutral and ion-exchange. Neutral extractants are organic substances whose molecules are capable of forming coordination bonds (donor-acceptor type) with the extracted ion, stronger than the bonds of water molecules, that is, the solvation energy of the extractant molecules exceeds the hydration energy. Ion-exchange extractants include organic acids and their salts or organic bases and their salts, capable, upon contact with an aqueous solution, of exchanging an inorganic cation or anion, which is part of the extractant, for an inorganic cation or anion, which is in solution. In this case, the condition for the extraction to proceed is higher hydration energy of the ions passing

from the organic phase to the aqueous one, as compared to the ions extracted from the aqueous solution. The extractants of this group are called liquid ion exchangers and are divided into cation-exchange and anion-exchange depending on the type of exchanged ions [5-11].

Solid phase extraction (SPE) is a fast sample preparation method that uses a sorbent (solid stationary phase) to concentrate and separate the target component or components, followed by elution (washout) with a suitable solvent.

For many years, liquid extraction, precipitation, centrifugation, column and thin layer chromatography have been the main methods for isolating, purifying, and concentrating analytes. Such preparation of samples is a lengthy and multi-stage process that requires the consumption of a large amount of extra pure (does not introduce impurities!) solvents and reagents, additional equipment and labor costs.

An excellent alternative to liquid-liquid extraction is solid phase extraction. Large volume samples can be processed using relatively small amounts of solids, which, in turn, require a small volume of solvents for the subsequent desorption of concentrated compounds, therefore, there is no need for additional evaporation and the risk of sample contamination is significantly reduced.

SPE is characterized by wider possibilities for varying the nature and strength of sample interactions with the sorbent and eluent than for liquid-liquid extraction, as a result of which more selective and quantitative isolation or finer purification of the components of interest is carried out. Due to specific interactions, each of

the analyte compounds can be selectively concentrated and recovered or separated from interfering components.

Advantages of TFE:

- high degree of extraction of target compounds (> 80%)
- excellent reproducibility and selectivity
- significant reduction in sample preparation time compared to liquid-liquid extraction
- possibility of process optimization
- ease of use
- saving of expensive solvents

Various methods are used for the analytical control of nickel (II) content in various environmental objects. Among them, the most widely used are photometric methods, which are characterized by high sensitivity, accuracy, and simplicity of the equipment used [12–16].

Analytical studies of transition metals in this direction have not yet been studied in detail, and there is not enough information about this in the world scientific literature. Therefore, studies on the extraction of ions from the solid phase with the help of organic ligands are very topical. From an analytical point of view, the separation of ions from the solid phase is of great importance for the development of technology to obtain pure, chemically pure, pure for analysis, and ultrapure metal salts [17- 19].

In this regard, chloroform solutions of new synthesized organic reagents (L_1 , L_2 , L_3 , L_4), which are tetrahalogen-containing hydrophobic organic compounds of the bicycloquinone type with an acetylene fragment, were used to extract Ni (II) from the solid phase, and an appropriate method was proposed for the quantitative extraction of photometric determination of Ni (II) from the solid phase.

Experimental part

1. Determination of the degree of extraction - Nickel A-ion from the solid phase by organic ligands L_1 - L_4 .

Preparation of solutions: organic ligands shown in table 1. $L_1=71.2$ mg; $L_2=59.6$ mg; $L_3=106.2$ mg; $L_4=109.6$ mg was dissolved in 200 ml of chloroform (CHCl_3) and a 10⁻³ molar solution was prepared. Chemically pure nickel picrate (NiPic_2) was used for extraction.

2. Determination of the optical density of organic ligands L_1 - L_4 .

Dried at 110-115⁰C salt of nickel picrate in the form of a powder weighing 100-200 mg was poured into a conical flask and 25 ml of chloroform solutions of organic ligands L_1 - L_4 with a concentration of $1 \cdot 10^{-3}$ - $2 \cdot 10^{-3}$ M were added. The solution was stirred with a magnetic stirrer for 3 hours at a temperature of 18 – 20⁰ C. Then after 15 min. samples were taken from the organic phase in a volume of 2 ml and the optical density was determined - A on a Spekol device ($l=1.0$ cm, $\lambda=375$ nm). Using an

anhydrous solution (CHCl_3 : $\text{CHCN} = 1:1$) of picric acid, the nickel ion content in the solid phase was determined by extraction with organic ligands L_1 - L_4 .

3. Extermination of the period of establishment of chemical equilibrium in the process of nickel ion extraction by organic ligands.

The greenish-yellow organic phase was studied spectrophotometrically at the maximum wavelength $\lambda_{\text{max}}=375$ nm. For this to happen, we took 100–200 mg of dried nickel picrate salt (NiPik_2) and used solutions of L_1 , L_2 , L_3 , L_4 in chloroform at room temperature (18–20°C) and determined the period of establishment of

chemical equilibrium between the phases (τ).

100–200 mg of nickel (II) picrate salt powder was poured into a 100 ml conical flask, and 25.0 ml of 10^{-3} M chloroform solution L_1 was added to it. After inserting a magnetic stirrer into the flask, the neck of the flask was closed with a polished stopper. Stirring was carried out for 5 hours. Every 30 min. the concentration of the organic phase (A) was measured on a Spekol-10 spectrophotometer ($l=5.0$ cm, $\lambda=375$ nm). The above procedures were carried out by mixing $1 \cdot 10^{-3}$ M chloroform solutions of L_1 - L_4 organic ligands in a vessel for various time intervals and investigated the time of chemical equilibrium (τ) between the phases.

Results and its discussion

Some physicochemical characteristics of organic reagents of the bicycloquinone type with tetra halogen, acetylene fragments are shown in Table 1.

It can be seen from the obtained experimental data (Table 2) that nickel picrate (NiPik_2) is extracted from the solid phase into

the organic phase by the ligand L_1 -R=76%, L_2 - up to 70.60%, L_3 - up to 89.11%, L_4 up to 95.35%. The amount of Ni ion from 0.49 mg to 0.65 mg was determined by the extraction-photometric method, and it can be concluded that the ability to extract organic ligands (L_1 - L_4) is arranged in a row as follows $L_4 > L_3 > L_1 > L_2$.

Table I. Physicochemical properties of L_1 - L_4 organic ligands

Formula and name of organic ligands (L_1 - L_4)	Temperature of melting, $^{\circ}\text{C}$	Infrared spectra, cm^{-1}	Yield, %
$\text{C}_{13}\text{H}_{10}\text{Cl}_4\text{O}_2$- 1,2,3,4-tetrachloro-7,8-quinone-5-(3-methyl-oxy-1-butyl)bicyclo[2,2,2]octene-2 (L_1)	141	3400 =O-H 2225 -C \equiv C- 1760 =C=C 1600 >C=C 760 \equiv C-Cl	86.2
$\text{C}_{13}\text{H}_{10}\text{Cl}_4\text{O}_2$- 1,2,3,4-tetrachloro-7,8-quinone-5-ethynyl-bicyclo[2,2,2]octene-2 (L_2)	89	3320 \equiv C- 2125 -C \equiv C- 1760 =C=O 1545 >C=C< 760 \equiv C-Cl	81.0
$\text{C}_{13}\text{H}_{10}\text{Br}_4\text{O}_3$- 1,2,3,4-tetrabromo-7,8-quinone-5-(4-methyl-4-oxy-2-pentenyl) bicycle [2,2,2]octene-2 (L_3)	170	3420 \equiv C-H 2235 -C \equiv C- 1765 >C=O 1605 >C=C< 680 \equiv C-Br	62.7
$\text{C}_{14}\text{H}_{12}\text{Br}_4\text{O}_3$- 1,2,3,4-tetrabromo-7,8-quinone-5-(4-methyl-oxy-2-pentenyl)bicyclo[2,2,2] octene-2 (L_4)	150	3410 \equiv C-H 2240 -C \equiv C- 1765 >C=O 1610 >C=C< 675 \equiv C-Br	52.0

Table 2. Maximum extraction of nickel picrate by chloroform solutions L₁ -L₄ from the solid phase, $\tau=2.5$ h, $\lambda_{\max}=375$ nm, $l=5.0$ cm

Organic ligands	Optical density, A	Ni, mg/l	Extraction, R, %
L ₁	0.29	0.49	76.01
L ₂	0.27	0.46	70.62
L ₃	0.34	0.57	89.11
L ₄	0.34	0.65	95.35

The study of the chemical equilibrium of the nickel ion extraction process with organic ligands showed that in the case of the L₁, L₂ ligand, complete chemical equilibrium between the phases is established after 3 hours, and in

the case of L₃, L₄ - after 2.5 hours. The resulting chemical equilibrium is not even disturbed by magnetic stirring for 5 hours and remains unchanged (figure1).

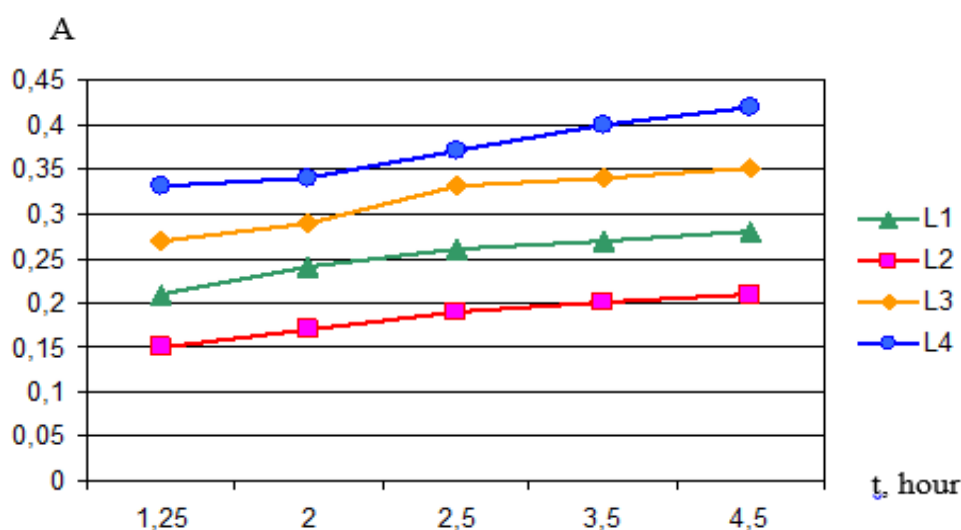


Fig.1. Change of optical density (A) over time for organic ligands - L₁, L₂, L₃, L₄

It is of interest to study the change of optical density (A) over time for organic ligands - L₁, L₂, L₃, L₄ extraction of the nickel ion by the photometric method with chloroform solutions of organic ligands - L₁-L₄ concentration $0.25 \cdot 10^{-3}$ - $2 \cdot 10^{-3}$ M in a strong magnetic field. The equilibrium between the phases is established after 90 minutes, and the extraction of nickel into the organic phase increases by 3-4%. The results obtained are presented in Table 3.

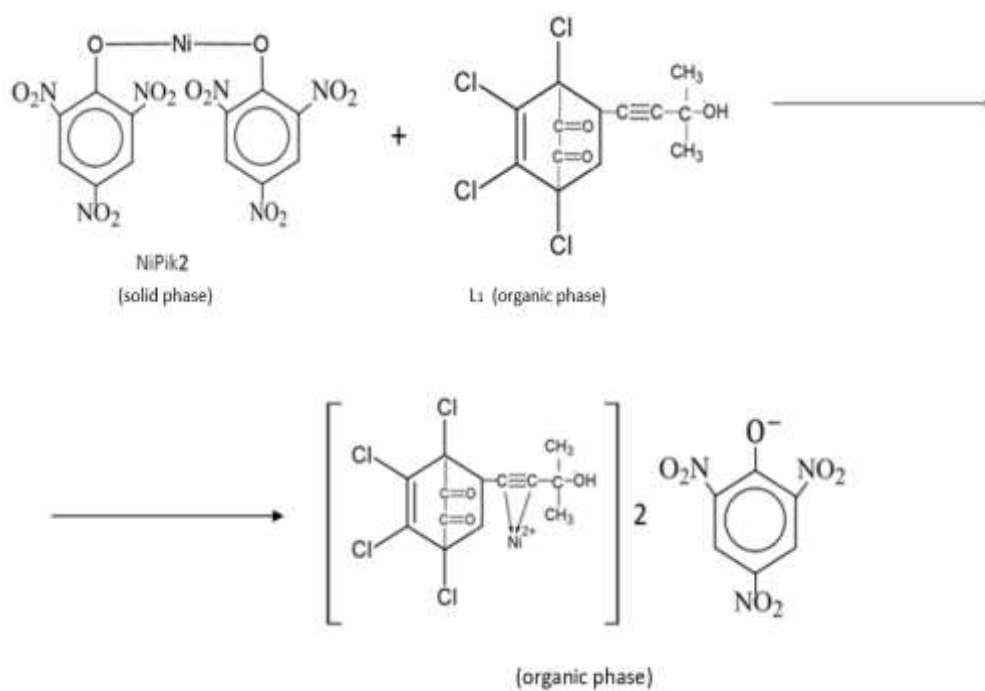
Table 3 shows that nickel picrate salts are extracted from the solid phase into the organic phase in the amount of 0.13-0.64 mg/l, forming macromolecular associates with ligands.

The process of transition from the solid

phase to internal complexation with metal ions by extraction of ligands - members that form the internal complex, or the dissolution of metal salts is mainly controlled by the following factors in stages: - for example, depending on the structure of organic ligands containing halogen atoms, the acetylene fragment ($-C \equiv C-$), functional groups $\equiv N$, $=NH$, $-NH_2$, $-OH$, $=C=O$, $-S-$, $=NOH$, etc., internal complex compounds are formed and, since the center creates a coordination bond with the transition metal- ion, these organic ligands diffuse to the pores of the metal salt in the solid phase. After a certain time, chemical equilibrium occurs between the phases.

Table 3. Physical and chemical characteristics of organic ligands and degree of nickel ion extraction in a magnetic field

Organic ligands, L _n	Concentration, C·10 ⁻³ M	Optical density, A	Quantity Ni ²⁺ , mg/l	Extraction, R, %
C ₁₃ H ₁₀ Cl ₄ O ₂ L ₁	0.25	0.07	0.13	19.75
	0.50	0.15	0.24	38.72
	0.75	0.22	0.36	57.62
	1.00	0.27	0.49	78.00
	1.25	0.27	0.49	78.00
	1.50	0.27	0.49	78.00
C ₁₃ H ₁₀ Cl ₄ O ₂ L ₂	0.25	0.11	0.12	19.4
	0.50	0.13	0.22	36.8
	0.75	0.21	0.34	56.2
	1.00	0.25	0.45	73.6
	1.25	0.25	0.45	73.6
	1.50	0.25	0.45	73.6
C ₁₃ H ₁₀ Br ₄ O ₃ L ₃	0.25	0.08	0.14	26.01
	0.50	0.17	0.28	48.02
	0.75	0.20	0.43	69.03
	1.00	0.33	0.56	91.05
	1.25	0.33	0.56	91.05
	1.50	0.33	0.56	91.05
C ₁₄ H ₁₂ Br ₄ O ₃ L ₄	0.25	0.09	0.16	26.81
	0.50	0.19	0.32	50.62
	0.75	0.28	0.48	94.43
	1.00	0.36	0.64	98.25
	1.25	0.36	0.64	98.25
	1.50	0.36	0.64	98.25

**Fig. 2.** Scheme of nickel ion extraction from the solid phase by organic ligands

At this time, the metal salt dissolves and is extracted into the organic phase. The chemical equilibrium between the liquid organic ligand and the solid phase depends on many

factors, such as temperature, surface of the metal salt, which is the solid phase, i.e. on the micron size of the particles, the phase structure of the crystal, the variety of salt-forming anions with metal ions, the ionic radius of the metal. Aside from this, it also depends on the time of phase contact, the amount of acetylene fragment (-C≡C-) and functional groups in tetrahaloorganic ligands, and the energy of formation of metal salts.

Finally, there is a transition from the solid phase to the liquid (anhydrous) phase with tetrahalogenbenzoquinone organic ligands (L₁,

L₂ L₃ L₄), i.e., transition metal salt ions interact with molecules of organic ligands, forming macromolecular ions - associates and are extracted into a liquid organic phase due to diffusion. Due to the acetylene (-C≡C-) fragment contained in hydrophobic organic ligands, the dissolution of the nickel picric salt (NiPik2) and its extraction into the organic phase can be considered as the formation of a macromolecular ion, an associate. The scheme of formation of such an associate is shown in the diagram (Figure. 2).

Conclusions

Thus, based on the results of the studies carried out, a new procedure for the extraction of transition metal salts with organic ligands of tetrahalobicyclic reagents L₁, L₂, L₃, L₄ into the organic phase has been developed.

The physicochemical characteristics of organic ligands were studied. The optical density of organic ligands and the degree of extraction of nickel ions from the solid phase were determined, which is more than 95%. It found that the magnetic field has a positive effect on the degree of nickel ion extraction

from the solid phase by organic ligands.

On the basis of the results obtained, a flow diagram of the extraction process with organic ligands was proposed.

The proposed technique makes it possible to obtain ultrachemically pure salts of nickel and other metals, as well as the synthesis of some organic substances by interfacial catalysis. In addition, the developed technique opens up opportunities for studying the mechanism of the extraction process from the solid phase.

References

1. Byrne K. Toxicity of local anesthetic agents. *Trends in Anaesthesia and Critical Care*. 2013, vol. 3, no. 1. pp. 25-30.
2. Tarhan F., Antep M., Merdivan M. Vortex assisted in situ ionic liquid dispersive liquid-liquid microextraction for preconcentration of uranyl ion in water samples before spectrophotometric detection. *J. Radioanal. Nucl. Chem.* 2019, vol. 320, no. 1, pp. 1-7.
3. Khiat M., Pacheco-Fernández I., Pino V., Benabdallah T., Ayala J.H., Afonso A.M.. A guanidinium ionic liquid-based surfactant as an adequate solvent to separate and preconcentrate cadmium and copper in water using in situ dispersive liquid-liquid microextraction. *Anal. Methods*. 2018, vol. 10, no. 13. pp. 1529-1537.
4. Didukh S.L., Losev V.N., Mukhina A.N., Maksimov N.G., Trofimchuk A.K. Sorption-photometric determination of iron using silica with functional groups of nitroso-P-salt and nitroso-N-salt. *Journal analytical chemistry*. 2017, vol. 72, no. 1. pp. 50-56.
5. Morosanova M.A., Morosanova E.I., Anisimov D.I., Zolotov Yu.A. Using silicatitania xerogels for solid phase spectrophotometric determination of fluoride in oral hygiene products. *Current Analytical Chemistry*. 2015, vol. 11, no. 4. pp. 291-299.
6. Abdullayeva M.Y., Habibov I.A. Improvement of the electrical properties of synthetic liquid dielectric for pulse capacitors. *EUREKA, Physics and Engineering*, 2020, (6), pp. 13-18.
7. Smirnova S.V., Samarina T.O., Ilin D.V., Pletnev I.V. Multielement determination of trace heavy metals in water by microwave-induced plasma atomic emission spectrometry after extraction in

- unconventional single-salt aqueous biphasic system. *Anal. Chem.* 2018, vol. 90, no. 10. pp. 6323-6331.
8. Freire M.G., P.J. Carvalho, R.L. Gardas, I.M. Marrucho, L.M.N.B.F. Santos, J.A.P. Coutinho. Mutual Solubilities of Water and the Hydrophobic Ionic Liquids. *J. Phys. Chem. B.* 2008, vol. 112, no. 6. pp. 1604-1610.
 9. Popov I.V., A.L. Tchougreff. Applying group functions to description of ionic liquids. // *Comput. Theor. Chem.* 2017, vol. 1116. pp. 141-150.
 10. Ismaiel A.A., Aroua M.K., Yusoff R. Cadmium (II)-selective electrode based on palm shell activated carbon modified with task-specific ionic liquid: kinetics and analytical applications. *Int. J. Environ. Sci. Technol.* 2014, vol. 11, pp. 1115-1126.
 11. Sun X., H. Luo, S. Dai. Mechanistic investigation of solvent extraction based on anion-functionalized ionic liquids for selective separation of rare-earth ions. *Dalton Trans.* 2013, vol. 42, no. 23, pp. 8270-8275.
 12. Larsson K., Binnemans K. Selective extraction of metals using ionic liquids for nickel metal hydride battery recycling. *Green Chem.* 2014, vol. 16, no. 10, pp. 4595-4603
 13. Tagashira Sh. Surfactant Gel Extraction of Metal Ammine Complexes using SDS and KCl at Room Temperature, and a Small-angle X-ray Diffraction Study of the Surfactant Phase. *Solvent extraction research and development.* 2013, vol. 20, pp. 39-52.
 14. Teng Hongni. Extraction separation of BSA in aqueous two-phase systems of anionic and cationic surfactant mixtures. *Journal of dispersion science and technology.* 2011, vol. 32, no. 6, pp. 829-833.
 15. Aliyev S.G., Ismaylova R.A., Suleymanov E.I., Magarramova L.M., Sultanzadeh S.S., Askerova Z.G., Zalov A.Z. Spektrofotometric investigation of complex formation of nickel(II) with 2-hidroxy-5-nitrothiophenol and aminophenol. *IJISSET International Journal of Innovative Science, Engineerring Technology.* 2018, vol. 5, issue 3, pp. 192-206.
 16. Zalov A.Z., Iskenderova K.O., Askerova Z.G., Hajiyeva A.B. Spektrometric study of nickel(II) complexes with 2-hidroxythiophenol and its derivatives in the presence of hydrophobic amines. *Chemical problems.* 2021, vol.19, no. 4, pp. 224-231.
 17. Zalov A.Z., İsgenderova K.O., Askerova Z.G. Spektrometric research into interaction nickel (II) with 1-(2-pyridylazo)-2-hidroxy-4-mercaptophenol and aminophenols. *Chemical Problems.* 2021, no. 3 (19), pp. 150-159.
 18. Rudometkina T.F., Ivanov V.M. Photometric determination of large amounts of nickel and copper in natural and industrial objects in the form of ethylenediaminetetraacetates. *Moscow University Bulletin, Chemistry,* 2011, vol. 52, no. 3, pp. 204-208. (In Russian).
 19. Shilykovskaya D.O., Elokhov A.M. Extraction-spectrophotometric determination of nickel with 4-(2-pyridylazo)resorcinol in the neonol AF 9-10-water system. *Bulletin of the Perm University, Chemistry,* 2021, no. 4, pp. 223-233. (In Russian).

ЭКСТРАКЦИЯ ПИКРАТА НИКЕЛЯ(II) ИЗ ТВЕРДОЙ ФАЗЫ ОРГАНИЧЕСКИМИ РЕАГЕНТАМИ

Л.М. Магеррамова, Н.Э. Джаббарова, М.Я. Абдуллаева

Азербайджанский Государственный Университет Нефти и Промышленности,
Азадлыг 20, Баку, AZ-1010, Азербайджан
e-mail: mayabdullayeva@hotmail.com

Аннотация: Настоящая работа посвящена весьма важной области аналитической химии – экстракционно-фотометрическому определению ионов из твердой фазы. Проведены исследования по экстракции пикрата никеля (NiPik_2) из твердой фазы с использованием растворов тетрагалогенбициклических реагентов ацетиленового ряда с дикарбонильным мостиком в боковой цепи (L_1, L_2, L_3, L_4) в хлороформе. Разработана новая методика экстракционно-фотометрического определения иона никеля из твердой фазы. Определено, что новые органические реагенты (L_1 - L_4) проявляют высокую экстракционную способность (0.11-0.64 мг/л) ионов Ni из твердой фазы. При сравнении экстракционной активности изучаемых реагентов установлено, что способность к экстракции органических лигандов тетрагалогенбициклических реагентов (L_1 - L_4) изменяется в ряду следующим образом $L_4 > L_3 > L_1 > L_2$. Магнитное поле увеличивает экстракцию никеля на 3-4%.

Ключевые слова: экстракционная способность, пикрат никеля (II), органические реагенты, твердая фаза, равновесие, магнитное поле.

NİKEL(II) PİK RATIN BƏRK FAZADAN ÜZVİ REAKTİVLƏRLƏ EKSTRAKSİYASI

L.M. Məhərrəmovə, N.E. Cabbarova, M.Y. Abdullayeva

*Azərbaycan Dövlət Neft və Sənaye Universiteti,
Azadlıq 20, Bakı, AZ-1010, Azərbaycan
e-mail: mayaabdullayeva@hotmail.com*

Xülasə: Təqdim olunan iş analitik kimyanın çox mühüm sahəsinə - ionların bərk fazadan ekstrasion-fotometrik üsulla təyin edilməsinə həsr edilmişdir. Yan zəncirində dikarbonil körpüsü olan asetilen fraqmentli üzvi liqandların (L_1, L_2, L_3, L_4) xloroformlu məhlullarından istifadə etməklə nikel (II) pikratın (NiPik_2) bərk fazadan ekstraksiyası tədqiq edilmişdir. Bu məqsədlə yeni üzvi liqandlar sintez edilmiş və onların fiziki-kimyəvi xassələri - ərimə temperaturları, molekul kütlələri, həmçinin optiki sıxlıqları tədqiq edilmişdir. Nikelin (II) pikratın bərk fazadan yeni ekstrasion-fotometrik təyini metodikasını işlənilib hazırlanmışdır. Müəyyən edilmişdir ki, yeni üzvi tetrahalogenbitsiklik reagentlər (L_1 - L_4) nikel (II) ionlarını bərk fazadan yüksək ekstraksiya etmək qabiliyyətlərinə (0.11-0.64 mg/l) malikdirlər. Tədqiq edilən reagentlərin ekstraksiya etmək qabiliyyətlərini müqayisə etdikdə müəyyən edilmişdir ki, sintez edilmiş üzvi liqandlarının (L_1 - L_4) ekstraksiya qabiliyyətləri aşağıdakı kimi dəyişir $L_4 > L_3 > L_1 > L_2$. Nikelin ekstraksiyasını maqnit sahəsi 3-4 % artırır.

Acar sözlər: ekstraksiya qabiliyyəti, nikel (II) pikrat, üzvi reagentlər, bərk faza, tarazlıq, maqnit sahəsi.