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Короткоживучий ізотоп ^{99m}Tc , похідний внаслідок розпаду радіоізоотопу ^{99}Mo , є основним інструментом ядерної медицини, за допомогою якого здійснюється 85 % всіх діагностичних сканів у світі. Для вирішення проблеми виділення ізотопів ^{99}Mo запропоновані пробопідготовка та метод вилучення Mo , який входить в комплекси, що містять нітрат з трибутилфосфатом (ТБФ), з матриць, які містять молибден, методом надкритичної екстракції діоксидом вуглецю (СФЭ-СО_2). Запропонована теорія опису розчинення Mo в розбавленій азотній кислоті за допомогою моделі Русел і Джокерів

Ключові слова: надкритичний діоксид вуглецю, надкритична екстракція, ізотопи молибдену

Короткоживучий ізотоп ^{99m}Tc , производный вследствие распада радиоизотопа ^{99}Mo , является основным инструментом ядерной медицины, с помощью которого осуществляется 85 % всех диагностических сканов в мире. Для решения проблемы выделения изотопов ^{99}Mo предложены пробоподготовка и метод извлечения Mo , входящего в нитратсодержащие комплексы с трибутилфосфатом (ТБФ), из молибденсодержащих матриц методом сверхкритической экстракции диоксидом углерода (СФЭ-СО_2). Предложена теория описания растворения Mo в разбавленной азотной кислоте с помощью модели Русел и Джокеров

Ключевые слова: сверхкритический диоксид углерода, сверхкритическая экстракция, изотопы молибдена

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THE STUDY OF SUPERCRITICAL EXTRACTION OF COMPLEXES OF MOLYBDENUM WITH CARBON DIOXIDE

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1. Introduction

The importance of the activities in this field is connected with a necessity to search new, radiation safe methods of obtaining the medical isotopes of wide application. One of the candidates for such application is the Mo isotopes which serve as initial material for obtaining the Tc medical isotopes [1]. Due to this, the use of the method of super-critical extraction with carbon dioxide [2] for separation of metal isotopes [3]

constitutes an interest. Ideally, this method allows obtaining the Tc medical isotope from the corresponding Mo isotope.

2. Literature review and problem statement

The method of uranium ions and lanthanides extraction from solid samples in the medium of supercritical carbon dioxide (SC-CO_2) with fluorinated β -dyketone was first

described in 1993 [4]. The paper demonstrates that such method can be used for extraction of metals (actinides) from different materials.

Interest in research in this field is stipulated by the fact that application of this method can noticeably decrease volumes of liquid waste peculiar to modern technologies.

Use of carbon dioxide (CO₂) as a “solvent” is caused by the fact that it possesses the relatively low critical parameters ($T_{cr}=31\text{ }^{\circ}\text{C}$ and $P_{cr}=7.3\text{ MPa}$, $\rho_{cr}=0.47\text{ g/cm}^3$), is non-toxic, explosive and fire safe, easily accessible and low-cost. Moreover, it is almost not subject to radiolysis [2]. Decrease of pressure and/or decrease of temperature turn the supercritical fluid into gas thus providing recycling of solvent and separating the extracted elements in the dry and compact form.

A large volume of research on SCE-CO₂ extraction has been conducted from 1993 till present time. During that period reviews on extraction of many complexes of metals in the form of β -dyketones [5] and other compounds [6] were published.

In the process of SCE-CO₂, the extracted material is dissolved in SC-CD and can be extracted by the method of fluid blowdown into a separate volume and decrease of pressure in it till atmospheric. This method of extraction allows separating metal complexes containing all natural set of isotopes. The possibility of uranium isotopes separation in the process of SCE-CO₂ was first realized in the paper [7] where the process was conducted in the heterogeneous temperature field. That is why such method of metal isotopes separation, and in particular Mo, constitutes practical interest as it gives the possibility to obtain the necessary isotopes till their transformation into radioactive condition.

Chemical complexes of Mo soluble in SC-CO₂ should be prepared in order to conduct the SCE-CO₂ extraction of Mo isotope.

The paper [8] studied extraction of molybdenum from sulfuric solutions with the use of supercritical carbon dioxide instead of organic solvents. However, in the process of extraction pressure of SC-CO₂ constituted the value 25 MPa which exceeds the pressure used in [7].

It is known that such Mo complexes which can be effectively extracted under pressures slightly exceeding the critical P_{cr} constitute the biggest practical interest.

One of the types of such complexes is complex of nitric acid Mo salts with tributyl phosphate (TBP).

In order to obtain the soluble in SC-CO₂ Mo complexes, solubility of Mo in acids should be studied and conditions of formation of salts complexes of these metals with TBP should be determined.

Mo is badly extracted with diluted TBP from nitrate solutions under liquid extraction [9]. However, good extraction of nitrate complexes of Mo in SC-CO₂ determines the interest for research of their extraction.

That is why the paper presents the results of research of metallic Mo dilution, formation of complexes of Mo with TBP and their supercritical fluid extraction with carbon dioxide.

3. Purpose and task of research

The purpose of this paper is to describe the probe-preparation of molybdenum complexes and conduct their supercritical fluid extraction with carbon dioxide.

The following tasks were set in order to achieve the aim of research:

- provide a short description of the isotopic composition of Mo and indicate those its isotopes which are essential for medicine;
- describe the relation of Mo to different acids in order to determine the acid with optimal ability to form complexes soluble in SC-CO₂;
- study the dependence of metallic Mo solubility in nitric acid and residual content of Mo in nitric acid solution on time;
- provide a mathematical model for description of residual content of Mo in diluted nitric acid;
- study the formation of Mo complexes under interaction of nitric acid solutions of Mo with TBP and conduct their SCE-CO₂ extraction.

4. Materials and methods of research

4.1. Molybdenum, its isotopes and their chemical properties

Natural molybdenum constitutes a mixture of isotopes with mass 92, 94, 95, 96, 97, 98 and 100 [10]. The volume of each isotope described above contains correspondingly 5,86; 9,12; 15,70; 16,50; 9,45; 23,75 and 9,62 %. Fig. 1 presents the volume circle diagram of molybdenum isotopes content. As it goes from the figure – natural molybdenum has the largest percent content of ⁹⁸Mo.

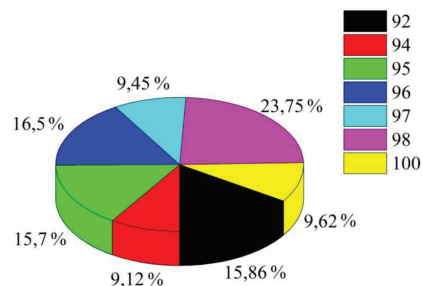


Fig. 1. Content of Mo isotopes in natural Mo

Radioactive isotopes with mass 90, 91, 93, 99, 101, 102, 105 [10] were obtained for molybdenum. However, the most important place in this list is occupied by ⁹⁹Mo ($T_{1/2}=66\text{ h}$, radiates β -particles and γ -rays) which is the mother nucleus of ^{99m}Tc, widely used in present-day medicine for radio-isotope methods of diagnostics and treatment of cancer diseases [11].

Tc isotopes can be obtained by irradiation of molybdenum containing samples in the slow neutrons flux or by their extraction in the process of processing of spent nuclear fuel (SNF) of nuclear reactors [10].

Radionuclide methods of research and treatment are widely used in different areas of medicine. Technetium isotopes ⁹⁵Tc ($T=20\text{ h}$), ^{95m}Tc ($T=61\text{ days}$), ⁹⁶Tc ($T=4.28\text{ days}$) are short-living and constitute interest as radioactive tags while analyzing technetium in natural probes and for research of chemical properties of technetium [11]. Short-living ^{94m}Tc isotope is needed for positron-emission tomography as it emits positrons with high output while decaying.

Short-living isotope ^{99m}Tc ($T_{1/2}=6.04\text{ hours}$, 94 % decays within 24 hours) is the main instrument of nuclear medicine. Movement of the isotope over the organism and

its accumulation in the diseased organs is easily fixed with radiometric equipment. Besides this it has a small period of half-excretion from the organism (less than one day for most compounds), which allows conducting a secondary examination of the same object within short periods of time without damage to human health.

Since the Tc isotopes are derivatives from Mo, the different methods of Mo extraction become paramount. Traditional methods of Tc extraction are widely used in industrial scales. These include extraction of technetium from the spent nuclear fuel of power reactors and waste of the nuclear industry enterprises, extraction of ^{99m}Tc from the irradiated by neutrons military uranium, obtaining of ^{99}Tc and ^{99m}Tc by molybdenum irradiation with reactor neutrons [11]. In medical practice, special technetium isotopes generators are used in which ^{99m}Tc is obtained under β -decay of the daughter nuclide ^{99}Mo .

The described methods are rather effective and widespread. However, they are not free from deficiencies which include radiation danger, complexity and multiple stages of processes, formation of hazardous waste.

Thus, a search of alternative, low-waste, radiation safe method of Tc extraction is the relevant task of the present days. Due to this deep research of Mo extraction by super-critical carbon dioxide (SC-CO_2) from different matrixes for further extraction of its radioactive isotopes for the purpose of its use in medical practice and technological tasks is needed.

4. 2. Dissolubility of molybdenum in acids

Molybdenum is stable in hydrochloric and sulfuric acids under low temperatures but slowly corrodes at 80–100 °C. Nitric acid itself or in mixture with hydrochloric and sulfuric acids – oxidizes and dissolves metallic Mo. Metallic Mo is quickly dissolved in nitric acid when heated. Mixtures from five volumes of HNO_3 , three volumes of H_2SO_4 and two volumes of water serve as a good Mo solvent. Molybdenum is stable in cold solutions of alkali, but is eroded a little when heated [12, 13].

Molybdenum is oxidized in the solutions containing the oxidant – oxygen, HNO_3 . Solutions become of blue color under lack of oxidant. Under excess of nitric acid, precipitation of molybdenum acid of different composition takes place: molybdenum monohydrate H_2MoO_4 or $\text{MoO}_3 \cdot \text{H}_2\text{O}$ (white or light-yellow color, crystalline form – hexagonal), molybdenum dihydrate $\text{H}_2\text{MoO}_4 \cdot \text{H}_2\text{O}$ and $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$ (yellow color, crystalline form – monocline), super-molybdenum acid H_5MoO_6 and $\text{HMoO}_4 \cdot 2\text{H}_2\text{O}$ (white, crystalline form), and others [14].

Molybdenum acid is dissolved in hydrochloric and sulfuric acids. Diluted HCl dissolves well the compact metal: loss of mass 20–30 % within 18 hours. Dilution in the concentrated HCl is slower, loss of mass 0.34 % within 18 hours under temperature 110 °C [13].

4. 3. Solubility of molybdenum in nitric acid

The residual content of molybdenum in nitric acid solutions in the form of different compounds is researched in [15, 16]. In Fig. 2, the curve 1 shows the dependency of residual content of Mo on the concentration of nitric acid under temperature 20 °C. As it follows from the picture under small concentration of HNO_3 , molybdenum dissolves weakly. With the increase of acid concentration its solubility increases and reaches maximum under concentration ~5 mole/l, which corresponds to the concentration of 70 g/l. Further with the growth of acid concentration abrupt decrease of molybdenum solubility is observed.

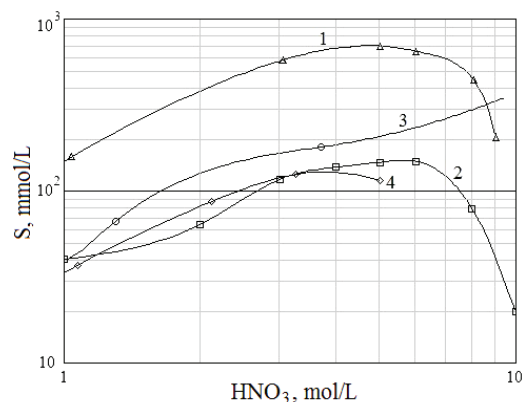


Fig. 2. Dependence of residual content of molybdenum S on the concentration of nitric acid: 1 – residual content of Mo in the solution of nitric acid [15, 16] under temperature 20 °C; 2 – residual content of Mo in the dissolved in nitric acid Mo hydrate [17] under temperature 20 °C; 3, 4 – residual content of Mo in the dissolved in nitric acid Mo dehydrate under temperature 25 °C and 26 °C correspondingly [17]

Curve 2, Fig 2 describes the residual content of Mo in the dissolved in nitric acid Mo monohydrate under the temperature 20 °C (period of balance establishment is 18 days) [17]. As it follows from the data presented in the figure, the residual content of Mo in the solution increases with the growth of acid concentration to the maximum value, which is reached under 6 M HNO_3 and is equal to 150.0 mmole/l. Further increase of the concentration of nitric acid results in a sharp decrease of Mo content. For 1 M HNO_3 under the temperature 20 °C the residual content of Mo constitutes the value of about 40.0 mmole/l.

Solubility of Mo dihydrate in nitric acid is described by curves 3, 4 in Fig. 2 which are built based on experimental points taken from different sources [17]. Curves 3, 4 describe the content of Mo which is included in the composition of Mo dihydrate, dissolved in 1M HNO_3 nitric acid under temperatures 25 °C (curve 3) and 26 °C (curve 4). Under the mentioned temperatures the residual content of Mo constitutes the value of about 40 mmole/l. Based on interpolation of reference data [17], we will consider that with decrease of temperature from 25–26 °C to 20 °C, similarly to Mo mono-hydrate, the solubility of Mo dihydrate in the nitric acid increases slightly. Such increase of solubility of Mo dihydrate in nitric acid presumably should occur synchronously with the change of the total content of Mo in the solution with the decrease of temperature [15, 16]. Therefore, we assume that under 20 °C the content of Mo included in the composition of Mo dehydrate dissolved in 1 M nitric acid is characterized by the value of 45–50 mmole/l.

Comparison of solubility of Mo dihydrate and monohydrate in the nitric acid under its concentration about 1 mole/l and temperature 20 °C demonstrates their approximate conformity, that is the mutual residual content of Mo in mono-hydrate and dihydrate constitutes the value of about 80 mmole/l.

Data on the solubility of super-molybdenum acid in nitric acid solutions are absent. That is why we will assume that dissolved in 1M HNO_3 under 20 °C super-molybdenum acid will provide residual content of Mo in the solution not lower than Mo dihydrate, as the first is the closest product of the second [15].

Thus based on the data presented above, the quantity of Mo monohydrate, Mo dihydrate and super-molybdenum acid

can be dissolved in the diluted nitric acid, which contains approximately equal quantities of Mo, totally estimated with the value of about 120 mmole/l.

The rest of Mo in the solution (about 30 mmole/l) falls, obviously, on molybdenum acids of the different content and structure [15].

4. 4. Dependence of Mo wire weight on the time of dissolving in nitric acid

A number of experiments were conducted in order to investigate the solubility of Mo in the diluted nitric acid. In the first set of experiments Mo dilution rate in the diluted nitric acid was investigated. For this purpose molybdenum wire with the weight of 0.48 g was placed in a flask with 4 ml of 1.0 mole/l nitric acid solution. Wire weight was measured step-by-step in order to determine its diminution within 16 days till its full dilution. Dilution was conducted in the thermostat under a constant temperature of 25 °C, the vessel with the nitric acid solution was kept closed. Measurement of Mo wire weight diminution was conducted by means of high precision electronic analytical scales AT-50. Final wire weight constituted 0.086 g. Dependence of Mo wire weight diminution on solution time is shown in Fig. 3 in the form of light circles (○) connected by a curve line.

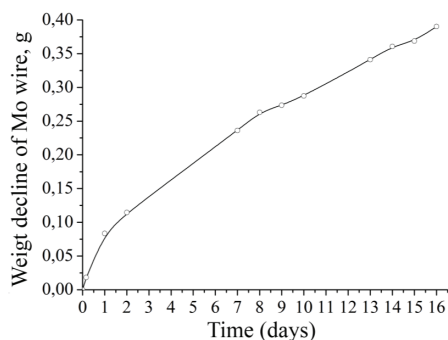


Fig. 3. Dependence of Mo wire diminution on solution time

Based on the dependence presented in Fig. 3 it can be concluded that the dilution of Mo is going linearly with time at a rate of 21 mg/24 hours. As it goes from Fig. 3, Mo will be fully diluted after 18–19 nautical days.

4. 5. Dependence of residual content of Mo in the nitric acid solution on dilution time

In order to determine the quantity of Mo transferred into nitric acid, X-ray analyzer KRAB-3YM was used. The quantity of readings of each sample of the solution within the determined period of time (40 sec) was measured by means of X-ray analyzer, starting from the first day of Mo wire solution.

Molybdenum wire with the weight of 1.4 g was used in the experiment on determination of Mo content in the nitric acid solution. Nitric acid, in the same way as in the first set of experiments, constituted 1 mole/l solution of nitric acid with the volume of 16 ml. The wire was dissolved in the diluted nitric acid in the weighing bottle closed with a grounded plug within 28 days. Weighing bottle with wire was placed in the thermostat in which temperature T=25 °C was kept. On the days marked in Fig. 4, 2 drops of the solution were placed on a paper filter, dried and then the content of Mo was determined three times based on the quantity of readings on

the x-ray analyzer. Results of measurements were averaged and based on the obtained data diagrams of the dependence of Mo content in nitric acid solution on time of dilution were built.

Fig. 4 demonstrates the dependence of Mo content in the nitric acid solution on dilution time. Experimental points are connected by a curve line which qualitatively demonstrates the quasi-periodic dependence of Mo content in nitric acid solution on time of dilution [18].

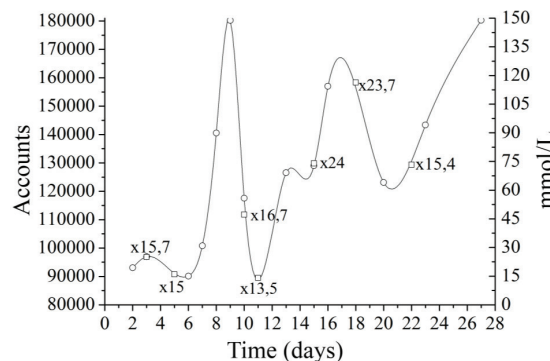


Fig. 4. Dependence of Mo content in 1 mole/l nitric acid solution (□) on time of dilution. Markers (◆) demonstrate the content of Mo in the complex, molybdenum acids+tributyl phosphate in different periods of time

The obtained quasi-periodic dependence can be explained by the fact that crystal sediment of white and light-yellow color precipitates after reaching the saturation of all Mo contained in the solution in the form of its different compounds (for example molybdenum and super-molybdenum acids).

Then after precipitation, the process of Mo entering in nitric acid solution repeats again till next saturation is reached.

The presence of sediment of white and light-yellow color indicates presumably the formation of Mo mono-hydrate, dehydrate and super-molybdenum acid in the nitric acid solution. Presented in [6, 7] analysis of Mo extraction into 100 % tributyl phosphate confirms the first assumption and also gives the basis to suppose the existence in the solution of at least such compounds as molybdenum mono-hydrate (H₂MoO₄); molybdenum dihydrate H₂MoO₄·H₂O; super molybdenum acid (H₅MoO₆) with relative content: [H₂MoO₄]:[H₂MoO₄·H₂O]:[H₅MoO₆]=1:x:y, where in accordance with the data from Fig. 2 the values x and y can possess the values from about a unit to several units.

4. 6. Three-trophic model of molybdenum dilution in the diluted nitric acid

The above assumption on the existence of at least, three types of molybdenum acid in the nitric acid solution allows assuming the following three-trophic [19] distribution of roles between them: molybdenum acid is a victim; dimolybdenum acid is a predator, into which the molybdenum acid is turned as a result of water molecule connection; supra-molybdenum acid is a super-predator, appearing from the predator by connection of hydroxyl group OH⁻.

The layout of such three-trophic system is presented in Fig. 5.

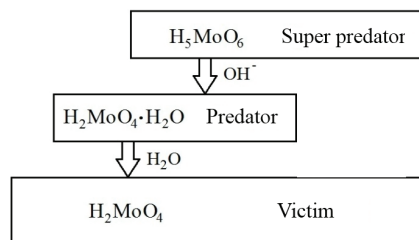


Fig. 5. Three-trophic system of forming the molybdenum acids in the nitric-acid solution

System of equations of motion describing the three-trophic system in the dimensionless form is the following [19]:

$$\begin{aligned} \frac{dy_0(x)}{dx} &= \frac{y_0(x)}{\zeta} \left(1 - y_0(x) - \frac{y_1(x)}{\beta_1 + y_0(x)} \right), \\ \frac{dy_1(x)}{dx} &= y_1(x) \left(\frac{y_0(x)}{\beta_1 + y_0(x)} - \delta_1 - \frac{y_2(x)}{\beta_2 + y_1(x)} \right), \\ \frac{dy_2(x)}{dx} &= \epsilon y_2(x) \left(\frac{y_1(x)}{\beta_2 + y_1(x)} - \delta_2 \right), \end{aligned} \quad (1)$$

where $y_0(x)$, $y_1(x)$, $y_2(x)$ – content of Mo in molybdenum (victim), dimolybdenum (predator) and supra-molybdenum (super-molybdenum) acids correspondingly; $x=1/t_0$ – dimensionless time; t_0 – characteristic process time; ϵ , β_1 , β_2 , δ_1 , δ_2 – parameters of the task which are constant positive numbers. The condition of constraints of their limits with one is imposed on the parameters δ_1 , δ_2 which corresponds to the survival of some participants of the trophic chain. The difference of the life time scale of the chain participants is determined by the parameters ζ , ϵ . Depending on the values of the system parameters, the system (1) can describe a large number of different dynamic modes including the chaotic [19].

Dynamic modes were found for 1 mole/l nitric acid solution by the method of system (1) parameters selection which provide the most adequate description of experimentally obtained dependencies of the total content of Mo on time

$$y(x) = y_0(x) + y_1(x) + y_2(x).$$

As an example of parameters selection, Fig. 6, 7 demonstrate dependence diagrams of the total content of Mo in nitric acid solution on time, calculated based on the three-trophic model (full lines) for different values of the initial weight of molybdenum wire. Points in the figure demonstrate experimentally measured values of the total content of Mo in nitric acid solution. Good coincidence of experimental points with the analytical model is observed. Axis to the right in Fig. 7, 7 demonstrates the residual content of Mo in 1 mole/l nitric acid solution and is built based on comparison of the obtained experimental data with data in Fig. 2.

Fig. 6 presents the results of numerical calculation of the system of equations (1) for the total content of Mo in nitric acid solution on time of dilution of Mo wire with the weight of 0.48 g under approximate parameters values: $\zeta=6.6$, $\epsilon=0.6$, $\beta_1=0.999$, $\beta_2=0.95$, $\delta_1=0.32$, $\delta_2=0.15$. The initial content of Mo in MC is specified by the following values: $y_0(0)=0.01$, $y_1(0)=0.01$,

$y_2(0)=0.01$. Typical time is equal to $t_0=7.6 \cdot 10^{-2}$ days and the unit of measure of the total content of Mo – $5.8 \cdot 10^{-4}$ mmole/l.

The analysis of the obtained numerical calculations demonstrates that usage of three-trophic models within the 15 % measurement error of Mo content in nitric acid solution matches the experimental data.

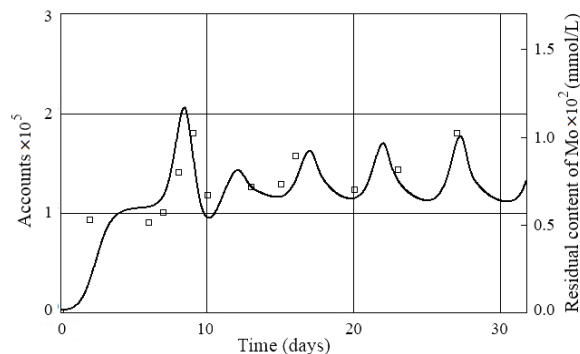


Fig. 6. Dependencies of the total content of Mo in nitric acid solution on time of dilution of Mo wire with the weight of 0.48 g, solution volume 4 ml

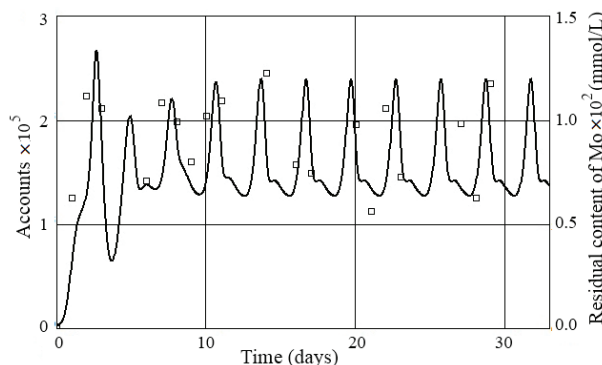


Fig. 7. Dependencies of the total content of Mo in nitric acid solution on time of dilution of Mo wire with the weight of 1.4 g, solution volume 16 ml

4.7. Interaction of nitric acid solution of Mo with tributyl phosphate and formation of molybdenum complexes diluted in SC-CO₂

In order to form the molybdenum soluble in complex, TBP (tributyl phosphate (C₄H₉O)₃PO (TBP) [12]) was used which proved itself during the research of SFE-CO₂ of uranium from natural minerals [20].

Solution of TBP in kerosene was used in this paper for the formation of molybdenum complexes dissolved in SC-CO₂.

In order to determine the effectiveness of formation of Mo complex with TBP, 3 ml of 33 % TBP with kerosene was added into a selected volume of nitric acid solution equal to 1 ml and stirred up. After sedimentation the solution was divided into two fractions, upper of which consisted of TBP with kerosene. 1 ml of the solution from the upper fraction was placed on a filter paper and dried. After this the obtained sample was studied for the content of Mo on the X-ray analyzer KRAB-3YM. Time of exposure on the KRAB-3YM constituted 40 seconds. Points (♦) in Fig. 4 correspond to the content of Mo multiplied by the number presented near each point. Results of measurement point to the formation of Mo complexes with TBP. However, estimation shows that a small part of the initial content of Mo in

nitric acid solution, with the value of about 5–7 % participates in the formation of complexes. This efficiency index of Mo complexes extraction by TBP solution can be compared with Mo extraction characteristics from 1 mole/l of HNO_3 with the solution of TBP [16] of the same concentration.

TBP (HMoO_3NO_3) and 2TBP(H_2MoO_4) complexes form during the interaction of molybdenum-containing nitric acid solution with TBP, in which molybdenum monohydrate and dihydrate are involved correspondingly and also the complex $2\text{TBP}\cdot(\text{H}_2\text{MoO}_3(\text{NO}_3)_2)$ on the basis of supra-molybdenum acid [15, 16].

These complexes, due to the presence of adjoined molecules of TBP, are well dissolved in SC-CO_2 . That is why research of the effectiveness of the molybdenum SFE-CO_2 , depending on the usage of different combinations of modifiers and means of extraction constitutes the interest.

Thus, interaction of nitric acid solution of Mo with TBP results in the formation of Mo complexes soluble in SC-CO_2 , which hold 5–7 % of Mo from its initial content in the solution.

5. Supercritical fluid extraction of molybdenum complexes

As one of the samples of the molybdenum complexes SFE-CO_2 we will present the list of conducted measures and used modifiers.

Mother solution consisted of 0.2 ml of TBP with Mo into which 0.1 ml of acetylacetone (AAC) and 0.05 ml of water were added. The obtained solution was placed in the reactor for extraction in SC-CO_2 . Dilution of Mo complexes in SC-CO_2 was conducted under temperature $T=40^\circ\text{C}$, pressure $P=16\text{ MPa}$ and time of probes exposure in the extraction chamber $t=30\text{ min}$.

After exposure of probes in the facility extraction chamber, the extract was though on five paper filters with a diameter of 20 mm each. After that filters were dried and analyzed of the X-ray analyzer KRAB-3YM. Anode voltage on the X-ray tube of the X-ray analyzer constitutes the value of 35 kV. Exposition for determination of the Mo content constitutes 40 s. Measurement of each of five paper filters was conducted three times, then the obtained data were averaged.

List of modifiers variations and means of Mo complexes extraction is presented in Table 1.

Table 1

Content of Mo in the extract under different variations of modifiers and means of extraction

№	Modifier				% of Mo extraction
	TBP	AAC	water	alcohol	
1	0.2 ml	–	–	0.6 ml IA	18 %
6	0.2 ml	0.4 ml	0.05 ml	–	19 %
3	0.2 ml	0.6 ml	0.05 ml	–	22 %
2	0.2 ml	0.7 ml	0.05 ml	–	24 %
8	0.2 ml	–	0.05 ml	–	26 %
4	0.2 ml	–	0.05 ml	0.1 ml of hexane	27 %
7	0.1 ml	0.1 ml	–	–	52 %
1	0.2 ml	0.6 ml+DD 0.3 ml+DD	0.05 ml	–	61 %
9	0.2 ml	0.1 ml	0.05 ml	–	90 %

Note: IA – isopropyl alcohol; DD – double dumping

As it goes from the table the biggest activity of Mo extraction – 90 % is reached under the ratio of modifiers: 0.2 ml of TBP+Mo, 0.1 ml of acetyl acetone and 0.05 ml of water.

Thus the present section demonstrates the possibility of SCE-CO_2 extraction of Mo complexes. It is determined that the largest efficiency of Mo extraction constitutes the value of 90 % and is reached when using the modifiers of acetylacetone and water in the ratio: 0.2 ml TBP+Mo; 0.1 ml of AAC; 0.05 ml of water.

6. Discussion of the results

Thus, the present paper presents the experimental research of super-critical extraction of the molybdenum complexes with carbon dioxide. Molybdenum has a number of isotopes some of which are unstable and due to this have practical application in medicine and technology. In order to separate Mo isotopes it was offered to use the method of SCE-CO_2 similar to the method used for uranium isotopes separation. In order to realize the method of SCE-CO_2 it is necessary to create Mo complexes soluble in SC-CO_2 . Therefore the paper presents the analysis of Mo solubility in different acids in order to determine the acid with optimal ability to create complexes soluble in SC-CO_2 . Based on the analysis, the solution of 1.0 mole/l nitric acid was selected. The research showed that the metallic Mo is dissolved in acid losing weight almost linearly with the growth of time. At this precipitation from three types of molybdenum acids appears in the solution: molybdenum monohydrate (H_2MoO_4), molybdenum dehydrate ($\text{H}_2\text{MoO}_4\cdot\text{H}_2\text{O}$) and supra-molybdenum acid (H_5MoO_6). The analysis of the probes on X-ray analyzer KRAB-3YM in order to determine the residual content of Mo showed the quasi-periodic dependence of Mo content in nitric acid solution on time of dilution. In order to explain the obtained time dependence, the three-trophic model of Mo dilution in the solutions of nitric acid which quantitatively describes the experimental results is proposed. It is shown that molybdenum called acids create Mo complexes which are well-soluble in SC-CO_2 . It is shown that extraction efficiency is about 90 % for different ways of extraction and under various modifiers. The obtained results on SCE-CO_2 extraction of Mo complexes turn to be promising for resolution of the problem of separate extraction of Mo isotopes for further fabrication of medical isotopes by the method of their activation with neutrons.

7. Conclusions

1. Mo isotopes are shown after irradiation of which with slow neutrons the radioactive nuclides of technetium with the mass 94, 95, 96, 99 appear as a result of radioactive decay. Radioactive nuclides of technetium isotopes are used in modern medicine for radiation methods of diagnostics and treatment of cancer diseases.

2. It is shown that Mo mono-hydrate, Mo dehydrate and supra-molybdenum acid with an approximately equal content of Mo are dissolved in the diluted nitric acid.

3. When dissolving the Mo wire in the diluted nitric acid a near-linear dilution time dependence of decrease of wire weight was shown.

4. Quasi-periodic dependence of residual content of Mo in nitric acid solution on time of dilution was discovered. In the short initial time interval this dependence is a non-linear

curve, growing from some start value till a certain level. When reaching this level the curve undertakes irregular oscillations, with amplitudes lower than starting.

5. In order to describe quasi-periodic in time dissolution of Mo in the diluted nitric acid the three-trophic model was offered. The model is based on the presence of three types of Mo acid in the nitric acid solution in about the same ratio: molybdenum monohydrate (H_2MoO_4), molybde-

num dehydrate ($H_2MoO_4 \cdot H_2O$) and supra-molybdenum acid (H_5MoO_6). The analysis of numerical calculations demonstrates that the use of three-trophic model within 15 % error corresponds to the experimental data.

6. It is shown that the largest efficiency of Mo extraction reaches 90 % when using modifiers of acetyl-acetone and water in the ratio: 0.2 ml of TBP+Mo, 0.1 ml acetyl-acetone and 0.05 ml of water.

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