

SUPERCRITICAL FLUID EXTRACTION OF MOLYBDENUM COMPLEXES AND ITS ISOTOPES WITH CARBON DIOXIDE

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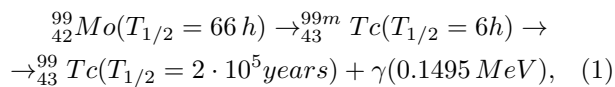
Separation of molybdenum complexes and its isotopes by supercritical fluid extraction (SFE) with carbon dioxide was experimentally investigated. The type of modifier, which provides increasing the efficiency of the metal and its isotopes separation, was determined. Extraction of molybdenum isotope complexes was carried out in the updated SFE-U unit at a constant value of the initial pressure $P = 20$ MPa and constant temperatures of the upper ($T_1 = 35$ °C) and bottom ($T_2 = 45$ °C) flanges of the extraction chamber. The exposure time of the extract and the level along the extraction chamber height, from which the eluent was sampled, were set in the experiments. It is shown, that at a certain sampling height and at certain exposure times, change in the natural content of Mo isotopes in the extracts takes place.

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1. INTRODUCTION

As it is known, natural molybdenum consists of a mixture of 7 stable isotopes [1, 2]: ⁹²Mo (occurrence 14.84%), ⁹⁴Mo (9.25%), ⁹⁵Mo (15.92%), ⁹⁶Mo (16.68%), ⁹⁷Mo (9.55%), ⁹⁸Mo (24.13%), and ¹⁰⁰Mo (9.63%).

The most significant place in the list of isotopes takes ⁹⁹Mo and its application in medical practice is well studied [3]. It is the mother nucleus of ^{99m}Tc ($T_{1/2}=66$ h, emits β -particles and γ -rays). The decay scheme of ⁹⁹Mo has the form [3]:



where γ – quanta with energy of 0.1405 MeV are emitted as a result of ^{99m}Tc decay.

^{99m}Tc isotope in the form of various pharmaceuticals is used in medical diagnostics for visualization of thyroid and salivary glands, heart and large vessels, skeleton, brain tumors, urinary organs, etc.

^{99m}Tc isotope generated as a result of the decay (1) has a sufficiently long lifetime – $2 \cdot 10^5$ years and is rapidly removed from the body [3].

Start of production and organizing the application of ^{99m}Tc isotope in Ukraine are relevant objectives due to the large number of cancers compared to world standards. According to the Bulletin of the National Cancer Registry of Ukraine, 135714 cancers were detected in 2016 without taking into account Lugansk and Donetsk regions, the Autonomous Republic of

Crimea and Sevastopol. 52.4% of the detected cases were attributed to the I and II stages, which have a high degree of medication-based treatment.

Therefore, ^{99m}Tc isotope is an extremely necessary means for detecting cancer at an early stage.

Production of mother ^{99m}Mo isotope can be realized as a result of [4]:

- reaction of ²³⁵U nuclear fission in ²³⁵U(n,F)^{99m}Mo reaction in nuclear reactors by thermal neutron fluxes;

- ⁹⁸Mo(n, γ)⁹⁹Mo neutron capture reactions, where it is required to use the expensive enriched isotope ⁹⁸Mo for increasing the yield of ⁹⁹Mo ;

- direct production of ^{99m}Tc in the reaction ¹⁰⁰Mo(ρ ,2n)^{99m}Tc using enriched ¹⁰⁰Mo (enrichment degree - up to 99%;

- ¹⁰⁰Mo(n, γ)⁹⁹Mo reactions, where intense photon fluxes, generated as a result of deceleration of an accelerated electron beam by heavy metals, dislodge photon neutrons out of ¹⁰⁰Mo target;

- reactions of fission of the uranium isotope ²³⁸U by photons ²³⁸U(γ ,F)⁹⁹Mo.

As you can see, to obtain a medical isotope ^{99m}Tc you can use slow neutrons of nuclear reactors or electron accelerators for high energies, which significantly complicates the process itself and increases the cost of the desired product.

One of the ways for mother isotope production is using the well-proven methods of generation enriched isotopes ⁹⁸Mo or ¹⁰⁰Mo, however, the cost of these isotopes is quite high.

Therefore, search for inexpensive methods of

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^{98}Mo or ^{100}Mo isotopes separation is today an urgent task.

Producing molybdenum by supercritical fluid extraction with carbon dioxide (SFE- CO_2) was studied experimentally and theoretically in a number of studies [5, 6]. In these studies molybdenum was extracted with tributyl phosphate solutions from nitric acid solutions [5]. The molybdenum extraction was of low efficiency due to its low solubility in dilute nitric acid, as well as due to its occurrence in nitric acid solutions in the form of various compounds [5, 6].

In this regard, to increase the efficiency of molybdenum extraction it is required to search for new modifiers during extraction.

This paper presents the results of experimental studies of the supercritical fluid extraction with carbon dioxide of non-nitric acid complexes of molybdenum and its isotopes at a vertical temperature gradient.

2. MATERIALS

For SFE- CO_2 extraction an acetylacetone-based molybdenum solution was prepared. Molybdic acid (AR) was used as the source of molybdenum. The initial solution was obtained in Soxhlet apparatus using 100 ml of acetylacetone (CP) and 10 g of molybdic acid powder placed in a filter paper bag. After 20 cycles of Soxhlet apparatus operation, the upper vessel was completely filled with distilled acetylacetone and the remaining extract was extracted for further experiments. The concentration of the obtained molybdenum solution was about 25 mg/ml.

3. EXTRACTION OF MOLYBDENUM BY SFE- CO_2 METHOD

SFE- CO_2 extraction was carried out on SFE-U unit using reactors with volumes of 50 and 100 ml. The initial extract in quantity of 100...300 mg was applied on filter paper and placed in the reactor. After reaching a pressure within the range of 15...20 MPa at a temperature of 40°C, the sample was kept under these conditions within 20 to 60 minutes. Supercritical fluid was discharged through a restrictor into a conical chamber (CC) with a volume of 1.5 cm³ covered with the filter paper. Since molybdenum complex in the supercritical fluid is in a dissolved state at a pressure of more than 15 MPa, it is required to add carbon dioxide to the reactor during eluent discharge to maintain the pressure above 15 MPa, while preventing the molybdenum complex from deposition on the walls of the reactor.

As the pressure decreased, carbon dioxide together with the extracted material froze as a result of supercooling and filled the volume of CC. After filling the CC volume with a solid eluent the conical chamber was freed from it and the discharge of a new batch of eluent continued in a similar mode. The resulting solid eluent was placed in a glass, where CO_2 was evaporated releasing the extract.

4. DETERMINATION OF THE EXTRACTION EFFICIENCY

To determine the efficiency of extraction, as well as the effect of pressure, exposure time and additives on it we used the method of weighing and the method of measuring the concentration of molybdenum using an X-ray fluorescence analyzer. Loss of mass of the extract applied to the filter paper was determined with an accuracy of 0.1 mg using scales AN-50. The concentration of molybdenum was determined before and after the extraction using the X-ray analyzer KRAB-3UM. Transition from x-ray data to concentration was carried out with help of a calibration curve obtained using a solution of molybdic acid in hydrochloric acid.

5 ml of the initial solution contained 1 mmol of molybdenum was used for calibration. By diluting the initial solution, four reference concentrations were obtained with a content of 4/5, 3/5, 2/5, and 1/5 of the initial one. To increase the reliability of measurements, the solution with a concentration of 1/5 of the initial one was diluted in half.

Samples for measurement were obtained by applying 0.05 ml of these solutions on filter paper, followed by drying. The resulting calibration dependence is shown in Fig.1, where experimentally measured points are marked with markers.

Calibration line $y = a + bx$ in Fig.1 was obtained by the least squares method in the MATCAD, where $a = 627.823$, $b = 300.059$. The values of the statistical coefficients are presented in Table 1.

Table 1. The values of the statistical coefficients at plotting the calibration line $y = a + bx$

Correlation coeff., $\text{corr}(x, y)$	0.9861
$R_2, \text{corr}(x, y)^2$	0.972
Covariance, $\text{cvar}(x, y)$	27.694
Standard Error, $\text{stderr}(x, y)$	18.824

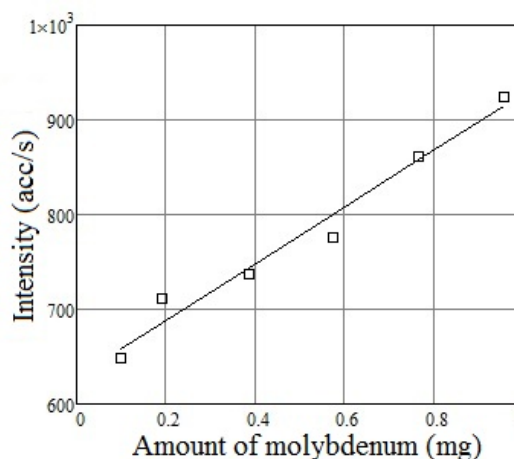


Fig.1. Calibration line of dependence of the number of readings of the X-ray analyzer KRAB-3UM on the content of molybdenum in reference solutions

The relative deviation of the experimental points from the calibration line Δy (%) is within the range of $-3.5 \leq \Delta y \leq 3.1$.

The relative calibration error is determined by Standard Error and is of the order of 2.3%.

Analysis of the results of SFE-CO₂ extraction of molybdenum has indicated that the efficiency of molybdenum separation decreases sharply, when the pressure of the extract decreases below 20 MPa.

Besides, the effect of extract exposure time on the efficiency of SFE-CO₂ extraction was investigated.

The results of study the dependence of the efficiency of SFE-CO₂ extraction of molybdenum on the extract exposure time are presented in Fig.2.

Line of the dependence of the quantity of the extracted molybdenum on the extract exposure time $y = a_1 + b_1x$ in Fig. 2 was obtained by the least squares method in the MATCAD, where, $a_1 = 0.359$, $b_1 = 6.428 \cdot 10^{-3}$. The values of statistical coefficients are presented in Table 2.

Table 2. The values of the statistical coefficients at plotting the calibration line $y = a_1 + b_1x$

Correlation coeff., $\text{corr}(x, y)$	0.8928
$R_2, \text{corr}(x, y)^2$	0.797
Covariance, $\text{cvar}(x, y)$	2.408
Standard Error, $\text{stderr}(x, y)$	0.072

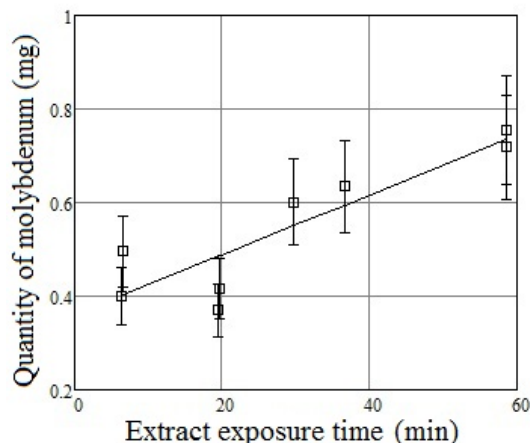


Fig.2. The quantity of the extracted molybdenum versus the exposure time of the extract

The relative deviation of the experimental points from the line of the dependence of the quantity of the extracted molybdenum on the extract exposure time Δy (%) range within $-18.9 \leq \Delta y \leq 16.5$.

The relative error in determining the quantity of extracted molybdenum is determined by Standard Error, it includes the calibration error and is of the order of $2.3\% + 0.072/0.55 \cdot 100\% = 15.4\%$.

Analysis of Fig.2 shows, that at a pressure of 20 MPa the quantity of the extracted molybdenum increases linearly with increasing the extraction time.

5. REACTOR OF THE EXPERIMENTAL UNIT FOR ISOTOPE SEPARATION

Experiments on study of SFE-CO₂ complexes of molybdenum isotopes were carried out on a laboratory SFE-U supercritical fluid extraction unit, which

had been previously used for separation of uranium isotopes [7].

The pressure of supercritical carbon dioxide in the unit could raise up to 20.0 MPa and the temperature of the bottom and upper flanges of the reactor was maintained at a given level in the range (20...50)°C using adjustable heaters. In the experiments the temperature of the bottom flange was set above the temperature of the upper one. The layout of the reactor elements is shown in Fig.3.

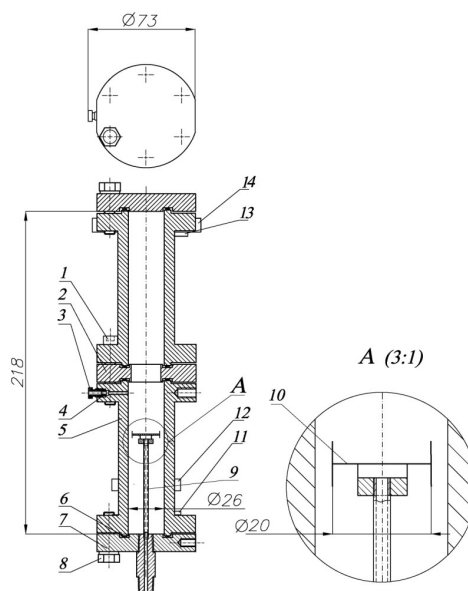


Fig.3. The layout of the reactor elements: 1. Bolt; 2. Middle flange; 3. Fitting; 4. Sealer; 5. Housing; 6. Filler; 7. Bottom flange; 8. Bolt; 9. Tube; 10. Intake; 11. Temperature sensor of the bottom flange; 12. Heating element of the bottom flange; 13. Temperature sensor of the upper flange; 14. Heating element of the upper flange

The tube 9 concentrically located in the housing 5 in Fig.3 is made of stainless steel with a diameter of 6.1 mm and a wall thickness of 1 mm. At the end of the tube there is an intake device 10 (see A in large scale in Fig.3.) in the form of an umbrella, which allows to dose the part of the extract from the reactor by reducing the pressure in it. The pressure is reduced to about 4.0 MPa. During the discharge of eluent carbon dioxide was added to the reactor in order to maintain a pressure above 15 MPa and to prevent the complex deposition on the walls of the reactor. The intake in each set of experiments was located at a given distance from the bottom flange of the reactor.

6. PROCEDURE FOR CARRYING OUT EXTRACTION

On the SFE-U unit with a reactor, the layout of which is shown in Fig.3, the extraction was carried out according to the procedure as follows:

- filter paper with the initial extract applied on it in quantity of 100 to 300 mg was placed in the reactor;

- the upper flange of the reactor was heated to $T_1=35^\circ\text{C}$, the bottom flange – to $T_2=45^\circ\text{C}$;

- the pressure of carbon dioxide in the reactor was set at 20.0 MPa;

- the extract exposition in the reactor constitutes 0,5; 1; 2 hours;

- the extract was discharged in CC of volume 1.5 cm^3 .

The separation of the extract was carried out through the intake device 10, the inlet of which was located at a distance of 150 and 50 mm from the bottom flange of the reactor.

7. DETERMINATION OF EXTRACTION EFFICIENCY

The initial sample of the solution (before the SFE- CO_2 extraction) and the samples obtained as a result of the SFE- CO_2 extraction were analyzed for the content of molybdenum isotopes using the spectra obtained on a high-resolution mass-spectrometer with ionization in inductively coupled plasma ICP-MS ELEMENT 2 [8].

The data on the natural content of Mo isotopes are presented in Table 3: column 2 – reference data; column 3 – data obtained on the high-resolution mass-spectrometer.

As you can see, the comparison of two columns of this Table indicates the full compliance of the reference data and data obtained during the extraction on the mass-spectrometer.

Table 3. *The comparative content of molybdenum isotopes in the sample and in the initial solution*

Mo	Natural content,%	The content in the initial solution, %
92	14.84	14.8063 ± 0.1429
94	9.25	9.31356 ± 0.19903
95	15.92	15.90653 ± 0.19113
96	16.86	16.62644 ± 0.19945
97	9.55	9.64547 ± 0.17835
98	24.13	24.01053 ± 0.44074
100	9.63	9.69117 ± 0.0978

The data on the content of Mo isotopes in the eluent depending on the level of the eluent sampling and the extraction time are presented in Table 4.

The data in Table 4 will be analyzed graphically. The results of the analysis of the Mo isotopes content in the eluent depending on the level of eluent sampling and the time of extraction are presented in Fig.4.

Table 4. *The content of Mo isotopes in the eluent depending on the eluent sampling point and the extraction time*

Mo	a)	b)
	L=15 cm, 60 min, %	L=5 cm, 30 min, %
92	15.0315 ± 0.11479	14.78538 ± 0.28476
94	9.63151 ± 0.13789	9.28773 ± 0.09753
95	15.66674 ± 0.28077	116.01984 ± 0.10342
96	16.52582 ± 0.11608	16.60246 ± 0.23393
97	9.61914 ± 0.123	9.41784 ± 0.12812
98	23.91133 ± 0.24912	24.30584 ± 0.37178
100	9.61396 ± 0.09693	9.58088 ± 0.05751

Mo	c)	d)
	L=5 cm, 60 min, %	L=5 cm, 120 min, %
92	14.8421 ± 0.16045	15.33418 ± 0.29948
94	9.23206 ± 0.15126	10.04887 ± 0.18899
95	15.90277 ± 0.24931	15.54153 ± 0.29700
96	16.50179 ± 0.24224	16.53139 ± 0.32962
97	9.52157 ± 0.19548	9.35543 ± 0.14426
98	24.48921 ± 0.37556	23.81031 ± 0.52268
100	9.51049 ± 0.19916	9.37829 ± 0.18021

In Fig.4 the confidence interval for measuring the isotope content is given by horizontal segments, which are located on a vertical segment passed through the corresponding mass value of the Mo isotope. Tabular values of the natural content of Mo isotopes in Fig.4 are shown with a cross. It follows from a comparison of Figs.4, a, c, that during the extract exposition for 1 hour at a temperature gradient in the reactor of $\gamma_{15} = (T_2 - T_1)/L = 10/15 = 0,667^\circ\text{C/m}$, Mo isotopes with masses (92, 94) are enriched and the isotope with a mass 96 is depleted in comparison with their natural content.

At a large temperature gradient of $\gamma_5 = 10/5 = 2^\circ\text{C/m}$ and at the same extract exposure time there is no change in the eluent isotopic composition compared to natural one.

In the case of a large temperature gradient in the reactor γ_5 , changing the isotopic composition of Mo over time is a fairly long process. It is noticeable when the extract exposition lasts for 2 hours. In this case, there is a stronger effect of changing the isotopic composition, compared with a small temperature gradient. For example, in Fig.4, d, isotopes with masses (92, 94) are more enriched than in the case of Fig.4, a, and heavier isotopes (95, 97, 100), in contrast to the small temperature gradient, where there is no enrichment, become depleted in comparison with the natural composition.

8. CONCLUSIONS

Separation of molybdenum complexes and its isotopes by the SFE-CO₂ method was studied in this paper. The type of modifier, the fluid exposure time and the pressure in the reactor were determined at which the most efficient separation of the metal and its isotopes was guaranteed. A set of experiments on the extraction of molybdenum isotope complexes was carried out in the upgraded SFE-U unit at a constant pressure P=20 MPa and constant temperatures of the bottom (T₂=45°C) and upper T₁=35°C) flanges of the extraction chamber. In each of the experiments the exposure time of the extract and the level of the height of the eluent sampling from the extraction chamber were varied.

Based on the performed experiments we can draw the following conclusions:

1. Deviation of the Mo isotopes content from the natural one in the eluent is observed at a low temperature gradient and at the extract exposure for 1 hour: isotopes 92, 94 are poorly enriched and isotope 96 is depleted.

2. At a large temperature gradient, when the fluid exposition constitutes 1 hour, no change in the isotopic composition of the eluent is observed.

3. At a large temperature gradient the isotopes with small masses (92, 94) have greater enrichment compared to the case of a small temperature gradient. At that, heavier isotopes (95, 97, and 100) in contrast to the case of a small temperature gradient, where only isotope 96 is depleted, become depleted in comparison with the natural composition.

4. Apparently, no changes in the isotopic composition in case b) is explained by insufficient exposure time of the fluid.

In conclusion, the authors express gratitude to Kazarinov Yu.G. for participating in the experiments and their processing.

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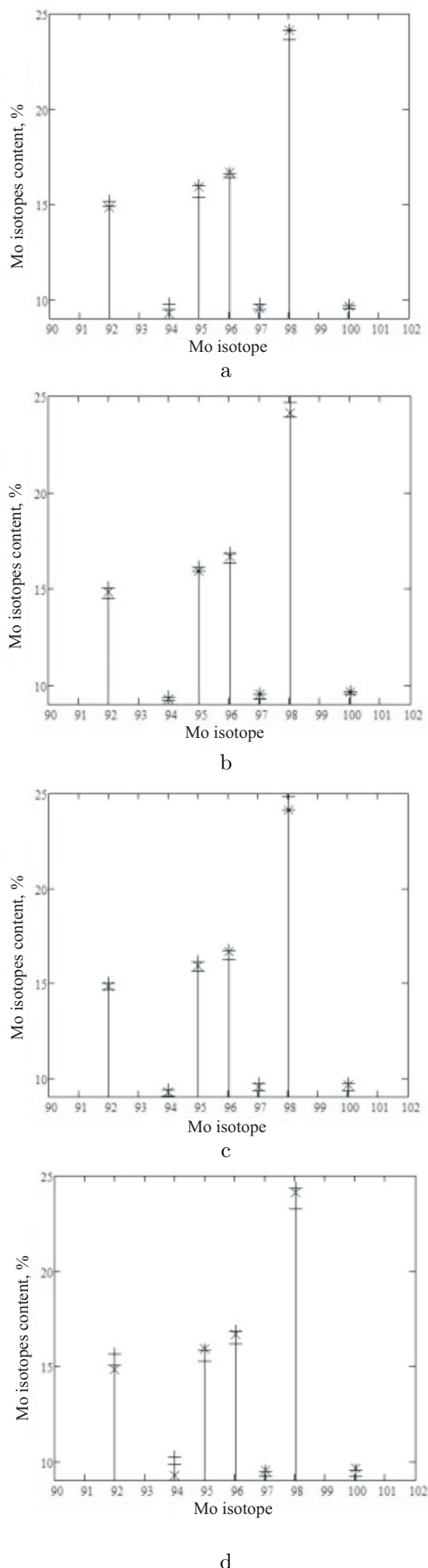


Fig.4. Mo isotopes content in the eluent versus the level of eluent sampling and the extraction time

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СВЕРХКРИТИЧЕСКАЯ ФЛЮИДНАЯ ЭКСТРАКЦИЯ ДИОКСИДОМ УГЛЕРОДА КОМПЛЕКСОВ МОЛИБДЕНА И ЕГО ИЗОТОПОВ

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Экспериментально исследовано выделение комплексов молибдена и его изотопов методом сверхкритической флюидной экстракции диоксидом углерода. Определен вид модификатора, который обеспечивает повышение эффективности выделения металла и его изотопов. Экстракция комплексов изотопов молибдена проводилась в модернизированной установке СФЭ-У при постоянном значении начального давления $P = 20$ МПа и постоянных значениях температур верхнего $T_1 = 35$ °С и нижнего $T_2 = 45$ °С фланцев экстракционной камеры. В экспериментах задавались время выдержки экстракта и уровень по высоте экстракционной камеры, откуда проводился отбор элюента. Показано, что на определенной высоте отбора пробы и при определенных временах выдержки в экстрактах наблюдается изменение природного содержания изотопов Мо.

НАДКРИТИЧНА ФЛЮІДНА ЕКСТРАКЦІЯ ДІОКСИДОМ ВУГЛЕЦЮ КОМПЛЕКСІВ МОЛІБДЕНУ І ЙОГО ІЗОТОПІВ

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Експериментально досліджено виділення комплексів молібдену і його ізотопів методом надкритичної флюїдної екстракції діоксидом вуглецю. Визначено вид модифікатора, який забезпечує підвищення ефективності виділення металу і його ізотопів. Екстракція комплексів ізотопів молібдену проводилася в модернізованій установці СФЕ-У при постійному значенні початкового тиску $P = 20$ МПа і постійних значеннях температур верхнього $T_1 = 35$ °С і нижнього $T_2 = 45$ °С фланців екстракційної камери. В експериментах задавалися час витримки екстракту і рівень по висоті екстракційної камери, звідки проводився відбір елюента. Показано, що на певній висоті відбору проби і при певних часах витримки в екстрактах спостерігається зміна природного вмісту ізотопів Мо.