SEPARATION OF FISSION ^{99}Mo BY ALPHA-BENZOIN OXIME PRECIPITATION IN NITRIC MEDIUM

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ABSTRACT

Since 2009, the production of generators ^{99}Mo/^{99m}Tc suffers a crisis of global supply due to technical problems of the two reactors which account for 64% of world production of fission ^{99}Mo. By the project of Brazilian Multipurpose Reactor (RMB), the Brazilian government invests in the construction of the first multipurpose reactor suitable for the domestic production of ^{99}Mo from LEU targets in order to supply of fission ^{99}Mo in the coming decades. The IPEN started the research of the technology and production of fission ^{99}Mo from acid and alkaline dissolutions of Low Enriched Uranium (LEU) targets as well as other used radioisotopes in nuclear medicine. This work is part of the research of the technology of the fission ^{99}Mo from acid dissolution of the LEU targets that is being developed at the IPEN. In this study the separation of the Mo by precipitation with alpha-benzoin oxime in nitric medium and the recovery by dissolution were investigated. The precipitation studies were performed by batch assays with nitric solution of Mo(VI), containing ^{99}Mo tracer, and uranyl ions. Influence of concentration of permanganate from 0.03 to 2.5%, dissolution temperature at 30°C and 150°C and the uranium concentration from 74 g.L^{-1} to 115 g.L^{-1} was studied. Results indicated that the precipitation of Mo with alpha-benzoin oxime from nitric medium is highly efficient, and its recovery by dissolution with basic solution of H_2O_2 gave a high yield.

1. INTRODUCTION

Several used radiopharmaceuticals in nuclear medicine in the areas of diagnostic imaging and radiotherapy are obtained from produced radioisotopes in nuclear reactors or particle accelerators. Among these, the fission ^{99}Mo from the nuclear reactors stands out as one of the main because produces the ^{99m}Tc which is the most widely used radioisotope in diagnostic. The ^{99m}Tc marks easily a reactive set becoming itself a radiopharmaceutical. Since 2009, the production of generators ^{99}Mo/^{99m}Tc suffers a crisis of global supply due to technical problems of the reactors of the two largest producers which account for 64% of world production of fission ^{99}Mo. Nowadays, the world production of ^{99}Mo does not meet the existing demand. By the project of Brazilian Multipurpose Reactor (RMB) [1], the Brazilian government invests in the construction of the first multipurpose reactor suitable for the domestic production of ^{99}Mo from LEU targets in order to supply of fission ^{99}Mo in the coming decades. The IPEN started

the research of the technology [2, 3] and production of fission ^{99}Mo from acid and alkaline dissolutions of Low Enriched Uranium (LEU) targets [4, 5] as well as other used radioisotopes in nuclear medicine.

This work is part of the research of the separation and purification technology of the fission ^{99}Mo from acid dissolution of the LEU targets that is being developed at the IPEN. The separation of Mo by the precipitation with alpha-benzoin oxime from nitric solution containing U ions and the recovery by dissolution were investigated.

2. EXPERIMENTAL

2.1. Materials

Molybdenum(VI) solutions of concentration 63 and 72 mg.L^{-1} in 1 mol.L^{-1} HNO$_3$ were prepared by the dilution from the aqueous solution of Na$_2$MoO$_4$ with HNO$_3$. The ^{99}Mo sample, which was provided by the Center of Radiopharmacy (CR) - IPEN/CNEN, was added into the Mo solutions and used as tracer. Potassium permanganate solutions of concentration from 0.03% to 2.5% were prepared by the dissolution of KMnO$_4$ in distilled water. The solution of 2% alpha-benzoin oxime was prepared by the dissolution in 0.4mol.L^{-1} NaOH, and at the moment of addition in the Mo solution. Solutions of 1% H$_2$O$_2$ were prepared in 0.2 mol.L^{-1} and 0.4 mol.L^{-1} of NaOH. All used chemical reagents were analytical grade.

2.2. Precipitation of the Molybdenum and Dissolution

In volume of 7 mL of nitric solution of Mo (containing ^{99}Mo tracer) was added 2.5 mL of KMnO$_4$, under manual agitation. The mixture was rest for 5 min, afterward 2 mL of the 2.0% alpha-benzoin oxime/0.4 mol.L^{-1} NaOH solution, under manual agitation, were added to precipitate the Mo(VI) ions. During 5 min was maintained a low agitation to avoid decantation. The white precipitate was filtrated with Whatman n° 41 filter paper. A washing step was carried out with 2 mL of 0.1 mol.L^{-1} HNO$_3$ (three times) and 1 ml of 0.1 mol.L^{-1} HNO$_3$ (twice).

For dissolution of the Mo precipitate, the filter paper with the precipitate was transferred to a capped glass vial and 1 mL of 1% H$_2$O$_2$/0.4 mol.L^{-1} NaOH was added. Then it was heated and after the resulting yellow solution was removed and transferred to another vial. Another 1 mL of 1% H$_2$O$_2$/0.2 mol.L^{-1} NaOH was added to the capped glass vial and it was heated again. The second resulting yellow solution was removed and added to the first yellow solution. The Mo precipitate was totally dissolved.

The Fig. 1 illustrates the flowsheet of the Mo precipitation process with alpha-benzoin oxime and dissolution that was used. All experiments were performed in duplicate at least and the mean values were presented.
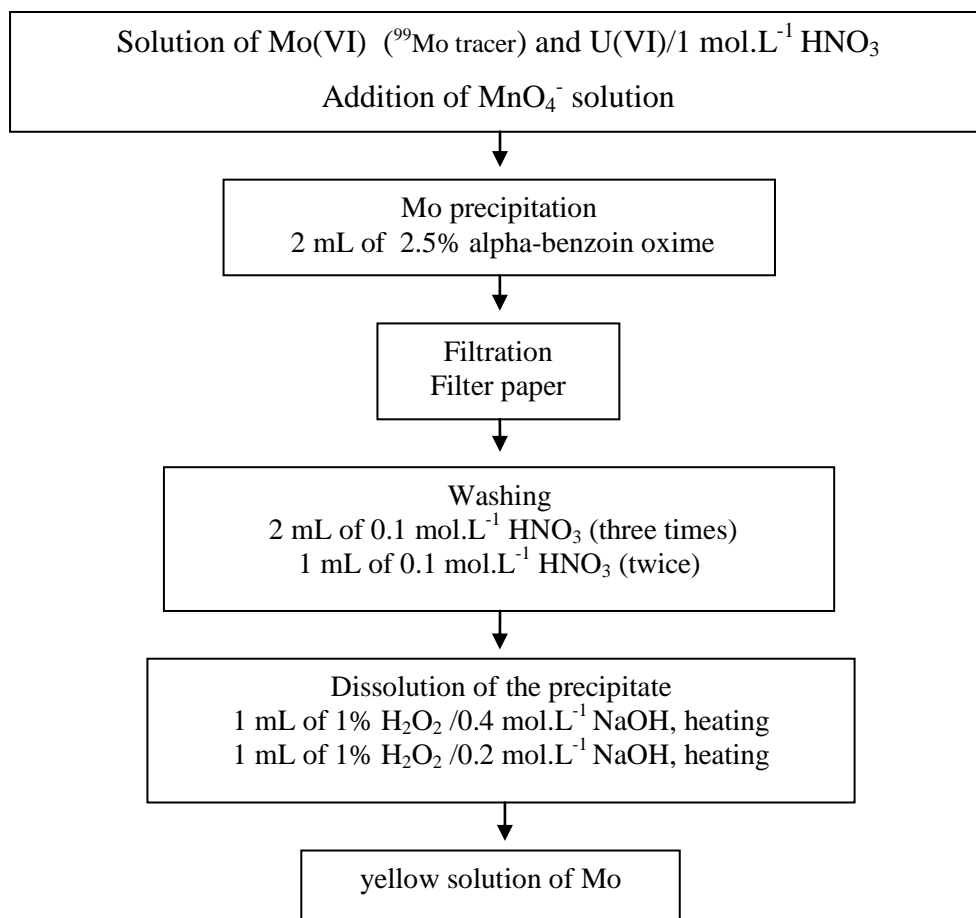
Solution of Mo(VI) ([99]Mo tracer) and U(VI)/1 mol.L^{-1} HNO$_3$
Addition of MnO$_4^-$ solution

$\downarrow$

Mo precipitation 2 mL of 2.5% alpha-benzoin oxime

$\downarrow$

Filtration Filter paper

$\downarrow$

Washing 2 mL of 0.1 mol.L^{-1} HNO$_3$ (three times) 1 mL of 0.1 mol.L^{-1} HNO$_3$ (twice)

$\downarrow$

Dissolution of the precipitate 1 mL of 1% H$_2$O$_2$ /0.4 mol.L^{-1} NaOH, heating 1 mL of 1% H$_2$O$_2$ /0.2 mol.L^{-1} NaOH, heating

$\downarrow$

yellow solution of Mo

Figure 1. Flowsheet of the separation process of the Mo(VI) ions from 1 mol.L^{-1} HNO$_3$ by the precipitation with alpha-benzoin oxime. Dissolution of the Mo precipitate.

2.3. Influence of MnO$_4^-$ concentration

Mo(VI) solutions of concentration 71 mg L^{-1} in 1 mol.L^{-1} HNO$_3$ were used for the study of influence of permanganate. The investigated concentrations were 0.03%, 0.3% and 2.5%. After the addition of 2 mL of each permanganate solution, the Mo(VI) ions of each Mo solution were precipitated with alpha-benzoin oxime in according to the described procedure in the 2.2. The activities of the [99]Mo tracer in the Mo initial solution and in the filtered solution were then subjected to gamma counting at the energy of 739 keV using a HPGe detector, Canberra, at the CR/IPEN/CNEN. The yield of precipitation was calculated by the equation (1).

$$\text{Precipitation yield \%} = (1 - C_f/C_i)*100 \qquad (1)$$

Where C_f is the gamma counting of the filtered solution and C_i is the gamma counting of the initial solution.

2.4. Influence of Dissolution Temperature

A volume of 2.5 mL of the 0.03% permanganate was added in the Mo(VI) solution of concentration 63 mg L^{-1} in 1 mol.L^{-1} HNO$_3$ and after 2.0 mL of 2% alpha-benzoin oxime in order to obtain the Mo precipitate. This precipitate was filtered, washed and the dissolution temperature was investigated. Two temperatures were verified, 30°C (heating for 5 min) and 150°C. The heating at 150°C was brought to the boiling of the solution for only 3 s. The activities of the ^{99}Mo tracer in the Mo initial solution and in the dissolution solution were then subjected to gamma counting at the energy of 739 keV using a HPGe detector, Canberra, at the CR/IPEN/CNEN. The recovery yield was calculated by the equation (2).

$$\text{recovery yield } \% = C_d/C_i * 100 \tag{2}$$

Where C_d is the gamma counting of the dissolution solution and C_i is the gamma counting of the initial solution.

2.5. Influence of U concentration

A volume of 2.5 mL of 0.03% KMnO$_4$ was added in the Mo(VI) solution of concentration 63 mg L^{-1} in 1 mol.L^{-1} HNO$_3$ containing U(VI) ions and after 2.0 mL of 2% alpha-benzoin oxime were added in order to obtain the Mo precipitate. The precipitate was filtered, washed and dissolved at 150°C. Three concentrations of U(VI) ions were investigated, 74 g.L^{-1}, 110 g.L^{-1} and 115 g.L^{-1}. The activities of the ^{99}Mo tracer in the Mo initial solution and in the filtered solution were then subjected to gamma counting at the energy of 739 keV using a HPGe detector, Canberra, at the CR/IPEN/CNEN. The yield of precipitation was calculated by the equation (1) and the recovery yield by the equation (2).

3. RESULTS AND DISCUSSION

Table 1 shows the precipitation yield obtained to each quantity of used permanganate. This reagent is added to the Mo solution in 1 mol.L^{-1} HNO$_3$ in order to guarantee the oxidation state 6+ of the Mo. All permanganate concentrations precipitated quantitatively the Mo ions, however the precipitate from the 2.5% solution was brown and black instead of white. An excess of permanganate in the precipitant medium probably reduced the Mn^{7+} to the Mn^{4+}, contaminating the white precipitate of the Mo with manganese oxide, MnO$_2$. During the study was verified that the solution of permanganate can be added dropwise to the Mo solution under manual agitation until that the pink permanganate color remains in the solution. The pink permanganate color in the Mo solution guarantees that all Mo are as Mo(VI) ions.

**Table 1. Precipitation yield of Mo(VI) from the
1 mol.L^{-1} HNO$_3$ solution with 2% alpha-benzoin
oxime.**

MnO$_4^-$, % concentration	Precipitate	Yield %
0.03	white	99 ± 1
0.3	white	99 ± 1
2.5	brown and black	99 ± 1

Table 2 shows the recovery yield of the white precipitate of Mo by dissolution according to the procedure described in the 2.4. The dissolution was total when a temperature of 150°C was applied and 87% of initial quantities of Mo was recovery.

**Table 2. Recovery yield of Mo(VI) by the
dissolution of the Mo precipitate.**

Precipitate	Temperature	Yield %
white	30°C	31 ± 3
white	150°C	87 ± 5

Table 3 shows the values of precipitation yield of Mo obtained in the presence of U(VI) ions. The precipitation was carried according to the procedure described in the 2.5. The Fig. 2 illustrates the steps of filtration and washing of the precipitation process in the presence of 74 g.L^{-1} of U. In the studied conditions, no interference was observed in the precipitation and the Mo(VI) was quantitatively separated from the nitric solution containing 74 g.L^{-1} U(VI) ions and the recovery yield by dissolution with basic solution of H$_2$O$_2$ was of 85%. The low values of precipitation yield for concentration of U(VI) ions of 110 g.L^{-1} and 115 g.L^{-1} indicated that the U interfered in the Mo precipitation.

**Table 3. Precipitation yield of Mo(VI) from the
1 mol.L^{-1} HNO$_3$ solution containing U(VI) ions and
recovery yield of dissolution.**

Precipitate	U(VI), g.L^{-1}	Precipitation yield %	Recovery yield %
white	74	99 ± 1	85 ± 5
yellow	110	30 ± 5	-----
yellow	115	36 ± 5	-----

Figure 2. Filtration step of the precipitate of Mo with alpha-benzoin oxime in the presence of U(VI) ions and the washing step of the same precipitate, respectively.

4. CONCLUSIONS

In the studied conditions in this work, the results indicated that the precipitation of Mo with alpha-benzoin oxime from nitric medium containing U ions is highly efficient, and its recovery by dissolution with basic solution of H_2O_2 gave a high yield up to 74 g.L^{-1} of U(VI).

ACKNOWLEDGMENTS

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