A Study on Separation of $^{99}$Mo from Neutron-irradiated UO$_2$ by Precipitation as Ammonium Molybdophosphate

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1. Introduction

Technetium-$^{99m}$, the short-lived (6.0 h) daughter nuclide of $^{99}$Mo, is used extensively in diagnostic medicine because of the advantages of its short half-life, $\gamma$-ray emission of moderately low energy (140 keV) and ease of combination with many medicines. The total amount of $^{99}$Mo consumed in radiopharmaceuticals has increased so rapidly in the past few years$^{11}$ that the production and the supply of $^{99}$Mo are one of the most important missions of an organization for radioisotope production.

Molybdenum-$^{99}$ having enough high specific activity for the medical application can be produced by nuclear fission of $^{235}$U. For the separation of $^{99}$Mo from fission products have been reported various methods such as adsorption on alumina column$^{3}$, solvent extraction with di (2-ethylhexyl) phosphoric acid$^{10}$ or the precipitation by $\alpha$-benzoinoxime$^{6}$. Those methods, however, include time-consuming and complicated procedures or have an danger of radiation decomposition of organic materials. In this work, a new, simple and practical separation method was developed, which based on the selective precipitation of fission-produced $^{99}$Mo. Uranium dioxide having a high melting point (2800°C) to tolerate temperature elevation during irradiation was neutron-irradiated and fission-produced $^{99}$Mo was precipitated as ammonium molybdophosphate from a solution of irradiated UO$_2$ in concentrated HNO$_3$. The salt precipitates even from HNO$_3$ solution of high concentration and so the whole process can be simplified. To explore this method, the quantity of H$_3$PO$_4$ and NH$_4$OH to form ammonium molybdophosphate, the reaction temperature, the standing time of the precipitate, the U concentration and the purification of product by recrystallization were studied in connection with the chemical yield of $^{99}$Mo.

2. Experimental and Results

2.1 Materials

(1) HNO$_3$: 14M, 7M and 2M
(2) (NH$_4$)$_6$Mo$_7$O$_{24}$: 0.24M in 8M NH$_4$OH
(3) NH$_4$OH: 15M and 8M
(4) H$_3$PO$_4$: 0.43M
(5) $^{99}$Mo tracer: Molybdenum-$^{99}$ solution (carrier free) of about 0.1 mCi/ml
(6) UO$_2$: Pelleted UO$_2$ enriched in $^{235}$U up to 2.3%
(7) U (natural isotopic composition) solution: 0.36M in 7M HNO$_3$
(8) ZrOCl$_2$: 0.06M

2.2 Factors influencing recovery of $^{99}$Mo
Sample solutions, which consist of 20 ml of 7M HNO₃ and 2 ml of (NH₄)₆Mo₇O₂₄ solution tagged with ⁹⁹Mo, were prepared. To one of the solutions, 0, 0.1, 0.5, 1.0 and 5.0 ml of H₃PO₄ were stepwisely added, while 0, 1, 3, 5 and 7 ml of 15M NH₄OH were added to another solution after addition of 1 ml of H₃PO₄ solution. After each addition, the solutions were stirred for 1 min and then allowed to stand for 15 min. A small aliquot of supernatant liquid was taken from each solution and subjected to γ-ray spectrometry with an NaI (Tl) (3 in. φ x 3 in.) scintillation detector together with an aliquot of the original solution. The percentage of ⁹⁹Mo precipitated was determined by measuring the photopeak of 740 keV γ-ray. The increase of H₃PO₄ up to 1 ml increased the recovery of ⁹⁹Mo to about 40%, but it did not give any effect further. The addition of NH₄OH in the presence of H₃PO₄ showed better results and gradually increased the recovery of ⁹⁹Mo till 83%. In order to recover ⁹⁹Mo more effectively, the effects of heating and standing were studied. Five milliliters of NH₄OH and 1 ml of H₃PO₄ were added to 22 ml of a sample solution with stirring, while the solution was kept at 50 or 80°C in hot water. After 15, 30, 60 and 120 min, the percentage of precipitated ⁹⁹Mo was determined by the similar way described above.

The elevation to 50°C of precipitation temperature enhanced the ⁹⁹Mo chemical yields from 79% to 93%, but the elevation to 80°C and the prolonged standing of the mixed solution did not show any significant effects on the precipitation percentage of ⁹⁹Mo, which remained nearly constant around 93% during the standing of 120 min.

From these results, the addition of 2 ml of H₃PO₄ and 5 ml of 15M NH₄OH to about 20 ml of a sample solution at 50°C, and standing for 15 min were chosen as the optimal conditions and the separation of ⁹⁹Mo from irradiated UO₂ was carried out as follows.

2.3 Separation of ⁹⁹Mo from fission products

Uranium dioxide of 1.3 mg was enclosed in an quartz ampoule and irradiated in JRR-3 (2×10¹⁵n/cm²sec) for 288 hours. After cooling for 5 days, irradiated UO₂ was dissolved with 10 ml of 7M HNO₃. In order to investigate the influence of U concentration on the chemical yield of ⁹⁹Mo and the contamination of other nuclides, 0, 1, 2, 3, and 4 ml portions of 0.36M U solution and 2 ml of Mo solution were added to 16 ml portions of 7M HNO₃ containing 1 ml of the fission products solution. The total volume was adjusted to 22 ml with 7M HNO₃. The separation was carried out under the optimal conditions described above and the precipitation percentage of several nuclides was determined by measuring the γ-ray spectra of supernatant liquid and precipitate with a Ge (Li)-detector (ORTEC Co. 4.8 cc). The nuclides and photopeaks taken into consideration were as follows:

140Ba 162keV; ⁹⁹Mo 181keV; ¹³²Te 230keV; ²²⁹Np 278keV; ¹³¹I 364keV; ¹⁴⁰La 487keV.

As the 230 keV photopeak of ¹³²Te and the 364 keV photopeak of ¹³¹I overlap on the photopeak of 228keV of ²²⁹Np and the photopeak of 370 keV ⁹⁹Mo respectively, the area of 230 keV due to ¹³²Te and that of 364 keV due to ¹³¹I were corrected respectively by subtrac-
ting the areas of 230 keV and 364 keV photo-peak regions determined from the peak intensity ratios of 228 keV/278 keV (\(^{239}\text{Np}\)) and 370 keV/181 keV (\(^{99}\text{Mo}\)).

The precipitation percentage of the fission products in question is almost constant through the whole concentration range of U (Fig. 1). Molybdenum-99 was recovered with yield of above 95% and the amount of troublesome nuclides such as \(^{140}\text{Ba},^{140}\text{La},^{131}\text{I}\) etc. could be greatly reduced.

2-4 Purification of \(^{99}\text{Mo}\) product by recrystallization

To remove impurities such as \(^{239}\text{Np}\) and \(^{131}\text{I}\) contained in the \(^{99}\text{Mo}\) product, the purification was attempted by recrystallization. According to the procedure described above, \(^{99}\text{Mo}\) was precipitated as ammonium molybdophosphate from a solution of \(6.6 \times 10^{-2} M\) U containing the irradiated \(\text{UO}_2\). After washing with 20 ml of 2M HNO\(_3\), the precipitate was dissolved with 5 ml of 8M NH\(_4\)OH. Two milliliters of ZrOCl\(_2\) solution was added to the solution and zirconium hydroxide containing \(^{239}\text{Np},^{99}\text{Zr}\) and other contaminants was filtered off. The filtrate was boiled for reducing the volume to about 2/3 and the concentration of NH\(_4\)OH. Then, the ammonium molybdophosphate was precipitated by adding 2g of NH\(_4\)NO\(_3\), 2 ml of H\(_3\)PO\(_4\) solution and 2ml of 14M HNO\(_3\). This purification was repeated. The final product was radiochemically pure (Fig. 2) and more than 90% of each impurity nuclide present before the purification was removed. Loss of \(^{99}\text{Mo}\) during recrystallization was about 25%.

3. Conclusion

Molybdenum-99 was recovered from HNO\(_3\) solution of neutron-irradiated \(\text{UO}_2\) as molybdophosphate precipitate with a yield of above 95% under the optimal conditions. Molybdenum-99 obtained by this process was successfully purified by recrystallization. The \(^{99}\text{Mo}\) product in the form of molybdophosphate anion \([\text{H}_4\text{P} \text{MoO}_7\text{O}_6]^{-3}\) showed an advantage of being loaded into a milking column 8 times as many as commercial \(^{99}\text{Mo}\) products in the form of MoO\(_4^{2-}\), owing to the difference of Mo atoms per unit charge. The application of this method to the practical production of \(^{99}\text{Mo}\) would ensure reasonably high yields without the drawbacks of radiation decomposition of organic reagents, or complicated or time-consuming procedures included in methods hitherto proposed. The drawback of lowering the specific activity of fission-produced \(^{99}\text{Mo}\) can be overcome practically by using \(\text{UO}_2\) of which \(^{235}\text{U}\) is enriched; 1g of \(\text{UO}_2\) (\(^{235}\text{U}\) enriched to 70%) irradiated in a neutron flux of \(3 \times 10^{13} n/cm^2 \cdot \text{sec}\) for 7 days and cooled for 1 day, can be dissolved with 7M HNO\(_3\) and adjusted to 70 ml to give a U concentration below \(6 \times 10^{-5} M\), which enables the application of the proposed method to the production of \(^{99}\text{Mo}\) of about 20 Ci having specific activity of about 20 Ci/g Mo. When higher neutron flux is available, \(\text{UO}_2\) target of lower enrichment can be used without any modification.

References

2) Tucker, W.D., Greene, W.M. and Murenhoff, A.P.: Atompraxis, 8, 163 (1962)