



TARGETS FOR THE PRODUCTION OF NEUTRON ACTIVATED MOLYBDENUM-99

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Abstract

Neutron activation of natural molybdenum is, ostensibly, the least complex route to ^{99m}Tc . However in most commercial generators the severe limitation in ^{99}Mo specific activity that the route imposes has caused manufacturers to choose the alternative fission process despite its disadvantages of being more expensive and requiring a more complex waste management strategy. The development of a newer generator technology is capable of reviving the demand for neutron activated ^{99}Mo and might encourage the production of ^{99m}Tc by countries possessing less developed nuclear infrastructures. The targets used in the (n, γ) production route consist of analytical grade molybdenum trioxide which has been further refined to remove both rhenium and tungsten trace impurities. The basic methods used by ANSTO to produce a molybdenum target capable of yielding ^{99m}Tc of high radionuclidic purity are described.

1. INTRODUCTION

The almost universal means by which ^{99m}Tc is made available for clinical use is from the elution of generators containing high specific activity fission- ^{99}Mo . The manufacture of these generators is controlled by a handful of countries with advanced nuclear infrastructures and the special capabilities of extracting pure ^{99}Mo from irradiated ^{235}U . Despite its almost total commercial dominance, this technology is expensive and is a potential hazard to the environment unless managed appropriately. Direct neutron activation of molybdenum is the least complex route of access to ^{99}Mo . Given the existence of severe limitations on the specific activity attainable, the method is still particularly suited to use in developing countries operating a research reactor but with otherwise limited resources. Solvent extraction technology [1] is the most common method for separating ^{99m}Tc from low specific activity ^{99}Mo . Produced by this technique, the ^{99m}Tc is supplied ready for 'instant' use from a central production laboratory typically at the same site as the reactor. More recently, alternative technologies have been developed in which neutron activated ^{99}Mo is incorporated in solid gel forms of zirconium or titanium molybdate [1,2,3,4] and using these technologies ^{99m}Tc is produced within a nuclear medicine clinic with an ease which is directly comparable to that of the fission ^{99}Mo generator.

The most appropriate target material for low specific activity ^{99}Mo production is molybdenum trioxide (MoO_3); neutron activation occurs via the reaction $^{98}\text{Mo}(n,\gamma)^{99}\text{Mo}$.

The most common practice is to use targets of natural abundance. The penalty associated with the irradiation of necessarily large target masses is still economically preferred to the use of enriched ^{98}Mo targets, which in any case are only capable of increasing the maximum achievable specific activity by a factor of 4. Analytical Reagent (AR) grade MoO_3 is the best choice for a target material.

2. TARGET CHARACTERISTICS

Natural molybdenum consists of seven stable isotopes; neutron activation gives rise to only three molybdenum radioisotopes - as shown in Table I.

TABLE I. RADIOACTIVE PRODUCTS FROM THE REACTOR IRRADIATION OF MOLYBDENUM

Mo Isotope	% Abundance in Natural Mo	Activation Product	Half-Life
^{92}Mo	14.84	^{93}Mo	6.9 h
^{98}Mo	24.13	^{99}Mo - $^{99\text{m}}\text{Tc}$	66.02 h-6.02 h
^{100}Mo	9.63	^{101}Mo	14.6 m

Because of the low yields and short half lives, ^{93}Mo and ^{101}Mo do not contribute significant impurities to extracted $^{99\text{m}}\text{Tc}$. On the other hand AR grade molybdenum trioxide does contain impurities [1] which ought to be removed prior to irradiation in order to minimise the formation of radionuclidic impurities in the separated $^{99\text{m}}\text{Tc}$.

For example ^{186}Re ($t_{1/2}=90.8$ h) and ^{188}Re ($t_{1/2}=16.8$ h) are formed by the $^{185}\text{Re}(n,\gamma)^{186}\text{Re}$ and $^{187}\text{Re}(n,\gamma)^{188}\text{Re}$ nuclear reactions due to the presence of a rhenium impurity in the target material. Both these radionuclidic impurities are substantially removed during the first $^{99\text{m}}\text{Tc}$ extraction and as a consequence the first $^{99\text{m}}\text{Tc}$ must always be discarded.

A process that has been used at ANSTO to reduce the rhenium level in molybdenum trioxide is given in the ANNEX hereto, however additional processing is justified to eliminate traces of tungsten.

The irradiation of tungsten* produces ^{188}W which decays to its daughter product ^{188}Re . In practice this pair $^{186}\text{W}(n,\gamma)^{187}\text{W}(n,\gamma)^{188}\text{W}\rightarrow^{188}\text{Re}$ forms a generator system within the irradiated molybdenum which, because of the chemical similarity between the elements, causes ^{188}Re to be repeatedly extracted along with $^{99\text{m}}\text{Tc}$.

Following the purification process** shown in ANNEX, the tungsten level is approximately 60 ppm. A further processing step [5] can reduce the tungsten level to less than 10 ppm.

* Because it is the product of consecutive neutron activations, the rate of ^{188}W formation varies with the square of the neutron flux; consequently ^{188}Re formation is substantially enhanced in high flux irradiations whenever a significant level of tungsten impurity exists in the molybdenum trioxide target.

**The removal of tungsten from MoO_3 relies on the preferential adsorption of tungsten by hydrated stannic oxide [6]. A small scale application of the process consists of stirring for 24 hours one litre of 0.7M $(\text{NH}_4)_2\text{MoO}_4$ pH 8-9, with 8g of $\text{SnO}_2 \cdot n\text{H}_2\text{O}$. The MoO_3 is then precipitated by the addition of concentrated HNO_3 and then calcined at 400 °C for 6 hours.

TABLE II. PRODUCTION OF ^{99}Mo BY NEUTRON IRRADIATION OF MOLYBDENUM TRIOXIDE IN THE ANSTO RESEARCH REACTOR HIFAR

Reactor Type	10 MW Thermal Research Reactor
Fuel	Enriched Uranium
Moderator	Heavy Water
Irradiation Position	Hollow Fuel Element
Thermal Neutron Flux	$0.5 - 1.0 \times 10^{14} \text{ n} \cdot \text{cm}^{-2} \text{ s}^{-1}$
Thermal Neutron Activation Cross Section	0.14 barn
Epithermal Flux Index	~ 0.12
Effective (Westcott [8]) Cross Section	1.2 barn
Effective Cross Section Corrected for Epithermal Flux Depression	0.48 barn (0.12 barn for natural target calculations)
MoO_3 Target Mass per Can	240 g
Can Type	Welded Titanium
^{99}Mo Specific Activity at Flux $1.0 \times 10^{14} \text{ n} \cdot \text{cm}^{-2} \text{ s}^{-1}$	$1.5 \text{ Ci} \cdot \text{g}^{-1}$ Molybdenum (6 day irradiation)

3. NUCLEAR CONSIDERATIONS

The thermal neutron activation cross section for $^{98}\text{Mo}(n,\gamma)^{99}\text{Mo}$ is 0.14 barns with a resonance integral of 7 barns [7]. Thermal neutron fluxes greater than $1 \times 10^{13} \text{ n} \cdot \text{cm}^{-2} \text{ s}^{-1}$ are necessary to produce specific activities of practical importance. The yields of ^{99}Mo can be significantly enhanced by epithermal neutron activation, hence the selection of the irradiation position is critical particularly in lower flux reactors. For all reactors the evaluation of the irradiation positions is essential to achieve optimum yields. Epithermal neutron enhancement of ^{99}Mo is illustrated by the results outlined in Table II.

REFERENCES

- [1] INTERNATIONAL ATOMIC ENERGY AGENCY, "Alternate Technologies for $^{99\text{m}}\text{Tc}$ Generators", IAEA-TECDOC-852 Vienna 1995.
- [2] EVANS, J.V., MOORE, P.W., SHYING, M.E., SODEAU, J.M., Zirconiummolybdate gel as a generator for technetium 99m-I. The concept and its evaluation, *Appl. Radiat. Isot.* **38** (1987) 19.
- [3] EVANS, J.V., MOORE, P.W., SHYING, M.E., SODEAU, J.M., Zirconium molybdate gel as a generator for technetium 99m-II. High activity generators, *Appl. Radiat. Isot.* **38** (1987) 25.

- [4] NARASHIMAN, D.V.S., VANAJA, P., IYER, S.P., MANI, R.S., Development of a new ^{99m}Tc generator using neutron irradiated titanium molybdate as column matrix, *Radiochim. Acta.* **42** (1987) 49.
- [5] DADACHOVA, E., Purification of molybdenum before use in technetium-99m production, Private Communication ANSTO (1997).
- [6] SEMENOV, M.I., BLOKHIN, A.A., TAUSKANOV, V.P., Use of hydrated oxides of multivalent metals for effective removal of tungsten from molybdenum compounds, *Zh. Prikl. Khim. USSR* **57** (1984) 1501.
- [7] WALKER, W.F., PARRINGTON, J.R., FEINER, F., *Chart of the Nuclides*, 14th Ed. Knolls Atomic Power Laboratory (1988).
- [8] WESTCOTT, C.H., Effective cross section values for well moderated reactor spectra, AECL407 (1957) and AECL1101 (1960).

ANNEX

PURIFICATION OF MOLYBDENUM TRIOXIDE FOR IRRADIATION

A bulk batch of 100 kg is divided into 10 kg sublots

1. The 10 kg subplot of molybdenum trioxide and 40 L distilled water are added to a 50 L container.
2. Approximately 6 L concentrated ammonia solution are added over 30 minutes with vigorous stirring.
3. The resulting solution is filtered using a coarse filter paper.
4. The solution is passed through a 2 cm diameter x 3 m long column of activated charcoal. The flow rate is $\sim 1.2 \text{ L. h}^{-1}$.
5. Sufficient concentrated nitric acid (not more than 2-3 L) is added slowly to the solution until no further precipitation occurs.
6. The resulting precipitate of hydrated molybdenum trioxide is filtered out and washed with warm distilled water.
7. The precipitate is dried at 200°C for 24 h, cooled and crushed to a fine powder.
8. The powder is heated in an oven to 380°C for 24 h. Air is blown through the oven during this stage.
9. To confirm thermal stability, 78 g of oxide is heated to 600°C in a gauged pressure vessel. The pressure generated by heating should be not greater than for the system alone.
10. After cooling the powder is stored in plastic containers prior to irradiation.
11. A sample of the purified MoO_3 is irradiated and examined for radionuclidic impurities.
12. Expiry time for the purified target is 5 y.

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