J Radioanal Nucl Chem
DOI 10.1007/s10967-012-2381-y

Feasibility study for production of ^{99m}Tc by neutron irradiation of MoO_3 in a 250 kW TRIGA Mark II reactor

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Received: 29 November 2012

Abstract The subject of this paper is to explore the possibility to obtain ^{99m}Tc from activation of ^{98}Mo, using the TRIGA Mark II low flux research reactor (Vienna, Austria). Irradiation of both natural and enriched in ^{98}Mo molybdenum oxides was compared. Aims of this work included the determination of neutron fluxes and ^{98}Mo(n, γ)^{99}Mo reaction effective cross section in the TRIGA Mark II reactor irradiation channels, calculation of ^{99}Mo specific activities, determination of optimal irradiation conditions for the subsequent ^{99m}Tc separation from MoO_3 targets using concentrating technologies.

Keywords Molybdenum · Neutron irradiation · TRIGA Mark II · Technetium · Extraction

Introduction

^{99m}Tc is a short-lived isotope and a daughter product of the β^- decay of ^{99}Mo and one of the most important radiopharmaceuticals. According to the available information from NEA/OECD [1] ^{99m}Tc is used in more than two-thirds of all diagnostic medical isotope procedures in the world. There are two basic methods of ^{99}Mo production in nuclear reactors: reaction of ^{235}U fission and reaction of ^{98}Mo neutron capture.

In the case of thermal uranium fission ^{235}U(n, f) in thermal flux of 2×10^{14} cm^{-2} s^{-1} the specific activity of ^{99}Mo obtained as a fission product is more than 37,000 GBq g^{-1} (reaction yield is 6.1 %) [2]. This high specific activity obtainable makes uranium fission technology the leading method of ^{99}Mo production.

During fission, besides ^{99}Mo about 20 longer-lived radionuclides are formed with half-lives from 0.1 to 60 days. Their total activity is hundred times higher than the activity of the obtained ^{99}Mo. The necessity of waste disposal, utilization and separation of the remaining uranium leads to some radioactive waste management and disposal issues. Another problem of the uranium fission method is that most ^{99}Mo producers use high-enriched uranium (HEU) targets, which causes nuclear security concerns. Apart from this, $\sim$5 % of formed ^{235}U fission products are different radionuclides of noble gases, some of which are used for confirmation of nuclear explosions in the international monitoring system (IMS) of the comprehensive nuclear-test-ban treaty organization (CTBTO) [3]. This leads to problems with the detection of nuclear test explosions by increasing the background of radioactive noble gases [4].

All these facts together with the aging of ^{99}Mo-producing reactors were the reason of the ^{99}Mo crisis, which occurred several years ago. According to IAEA data [5], the world shortage of ^{99}Mo was 30 % in 2010.

As an alternative, ^{99}Mo can also be produced by neutron capture reaction ^{98}Mo(n, γ)^{99}Mo. In this case, no high-level waste is formed. However, the thermal neutron cross section of the ^{98}Mo(n, γ)^{99}Mo reaction is just 0.136 barns, and therefore the production of high specific activities of ^{99}Mo cannot be obtained. On the other hand, it was shown

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Published online: 21 December 2012

Table 1 Isotopic composition of enriched MoO_3 replicated samples according to the producer's certificate (JSC "PA Electrochemical Plant")

Isotopes	^{92}Mo	^{94}Mo	^{95}Mo	^{96}Mo	^{97}Mo	^{98}Mo	^{100}Mo
Content (atomic%)	0.06	0.03	0.06	0.08	0.67	98.63	0.47

previously [6] that the effective cross section can be increased by resonance neutrons up to 0.7 barns.

The objective of this work was to study the possibility for producing technetium-99m in useful activities by activation of ^{98}Mo to ^{99}Mo, in the TRIGA Mark II (Vienna) low flux research reactor from molybdenum oxide using environment-friendly technology. Aims of the research included the determination of neutron fluxes and the ^{98}Mo(n, γ)^{99}Mo reaction effective cross section in the TRIGA Mark II reactor channels, calculation of ^{99}Mo specific activities, determination of optimal irradiation conditions and molybdenum targets irradiation time, choice and estimation of technology for ^{99m}Tc separation from the irradiated targets.

Experimental

Materials

The following materials were used:

- Analytical grade replicated samples of natural MoO_3
- Replicated samples of enriched MoO_3. Isotopic and chemical composition is shown in Tables 1 and 2, respectively
- Gold wire samples for neutron flux monitoring (Au-99.99 %)

Procedure

Twelve samples of MoO_3 were prepared for the experiments. Six of the samples were prepared from natural molybdenum (N1–N6) and another set of six samples was enriched in ^{98}Mo (E1–E6). After weighting, all samples were sealed in a polyethylene capsules. The net weight of each sample (both natural and enriched molybdenum) was 0.06 g of molybdenum. Oxide powders were evenly distributed inside of the packaging to reduce self-absorption effects. For irradiation, the MoO_3 samples were stacked vertically on the bottom of a cylindrical aluminum or cadmium shield together with gold wire neutron monitors. The cadmium and aluminum shielding had the same geometric dimensions. In case of irradiation in the "wet" central channel, the shields were additionally put into quartz cases with a fixed fishing line on top. After irradiation shields were pulled out of the channel quickly, put into a container and delivered to the gamma-spectrometry laboratory. After 2 h of cooling, the activity of ^{99}Mo in all samples was measured and recalculated back to the end of irradiation using radioactive decay law:

$$A = A_0 \cdot \exp(-\lambda \cdot t) \quad (1)$$

where A_0 is measured ^{99}Mo activity, λ—^{99}Mo decay constant, t—cooling time.

In the "dry" peripheral channel, samples were irradiated in aluminum and cadmium shielding for 10 min and in the "wet" central channel samples were irradiated only in the aluminum shielding for 60 min.

All isotopes were identified by gamma spectra. Multichannel amplitude pulse analyzer Ortec GEM-30 295-Plus with HPGe detector volume of 151 cm^3 was used for the registration of photon's gamma-emission energy and the determination of energy peak areas. All measurements were performed on a loss free counting system and all data were processed with Canberra Genie 2000 software.

The calculation of ^{99}Mo activities was done taking into account the efficiency of gamma-lines detector registration with energy 739.5 keV (analytical gamma emitting ^{99}Mo line) and gamma-photons yields:

$$A = \frac{S}{l \cdot P} \quad (2)$$

where l is efficiency of gamma-photons registration with energy of 739.5 keV, which was taken from calibration curve, P—gamma-photons yield, S—peak with energy level of 739.5 keV area in spectra of sample.

Results and discussion

^{99}Mo specific activity

The results of the experimentally determined and recalculated using Eqs. (1, 2) ^{99}Mo specific activity for defined irradiation conditions are presented in Tables 3 and 4.

Table 2 Chemical impurities of enriched MoO_3 replicated samples according to the producer's certificate (JSC "PA Electrochemical Plant")

Element	Al	Co	Cr	Cu	Fe	Mg	Mn	Na	Ni	Si	Sn	Ti	W	Zn
Content (mg/kg)	40	10	5	15	25	40	5	<50	5	100	15	10	120	30

Table 3 Results of ^{99}Mo induced activity determination in natural and enriched MoO_3 samples irradiated in the peripheral channel (10 min)

Shield material	Al	Al	Cd	Cd	Al	Al	Cd	Cd
Sample numbers	N1	N2	N3	N4	E1	E2	E3	E4
A, MBq/g	0.85	0.85	0.54	0.53	2.59	2.77	1.55	1.7

Table 4 Results of ^{99}Mo induced activity determination in natural and enriched MoO_3 samples irradiated in the central channel in aluminum shield (60 min)

Samples number	N5	N6	E5	E6
A, MBq/g	55	54	148	148

It is well known that the thermal component of the effective cross section of the ^{98}Mo(n, γ)^{99}Mo reaction is 0.136 b. Table 4 shows that the activity of ^{99}Mo in samples which were irradiated in an aluminum shield is 1.6 times higher than the activity of samples which were irradiated in the cadmium shield, effectively removing the thermal component of the neutron spectrum.

Equation (3) was used for the estimation of the thermal (I) and resonance neutron input into the activation of ^{98}Mo in the peripheral channel:

$$I = \frac{A_{\mathrm{Al}} - A_{\mathrm{Cd}}}{A_{\mathrm{Al}}} \cdot 100\ \% \tag{3}$$

where A_{Al}—activity of ^{99}Mo in target which was irradiated in aluminum shield, A_{Cd}—activity of ^{99}Mo in target which was irradiated in cadmium shield.

Results of the calculations are presented in Table 5.

According to Table 5, the input of thermal neutrons into the activation of ^{98}Mo in the peripheral channel is 35–40 % and the input of resonance neutrons is 60–65 %.

Neutron fluxes

Gold wire-detectors were used for the experimental determination of neutron fluxes in the TRIGA Mark II channels. The activation equation was used for the calculation of the total neutron flux and the sum of epithermal and fast neutrons flux (depended on shield material):

$$\varphi = \frac{A_3}{N \cdot c \cdot \delta \cdot (1 - \exp(-\lambda \cdot t))} \tag{4}$$

Table 5 Input of thermal neutrons into the activation of ^{98}Mo in the peripheral channel

$I_{(\mathrm{N1–N3})}$	$I_{(\mathrm{N2–N4})}$	$I_{(\mathrm{E1–E3})}$	$I_{(\mathrm{E2–E4})}$
36.6 %	37.48 %	41.05 %	41.73 %

where A_3—measured activities of ^{198}Au at the end of irradiation, N—number of atoms, c—content of ^{198}Au, δ—^{198}Au(n, γ)^{199}Au reaction cross section, λ—decay constant, t—irradiation time.

The results of the neutron fluxes determination are presented in Table 6.

The same method was used for the determination of the total flux in the central channel which was 1×10^{13} cm^{-2} s^{-1}.

Similar results for the neutron flux determination were obtained previously [7–9], confirming coherence of the methodology used in this work.

^{98}Mo(n, γ)^{99}Mo effective cross section

It is well known that the value of the ^{98}Mo(n, γ)^{99}Mo effective cross section depends on the sum of two components:

$$\delta^* = \delta + \xi \cdot \gamma \cdot I \tag{5}$$

where $\delta = 0.136$ barn is the cross section for thermal neutrons, I—resonance integral of ^{98}Mo infinite dilution, γ—neutron spectrum hardness, ξ—resonance integral blocking coefficient, which depends on ^{98}Mo nuclei number in unit of target volume and mean chord.

In practice, δ^* can be determined as the difference between measured values of ^{99}Mo activity in MoO_3 samples which were irradiated in aluminum and cadmium shield. Then the activation equation takes the following form:

$$\delta^* = \frac{A_{\mathrm{Mo}} \cdot M}{m_{\mathrm{Me}} \cdot N_A \cdot c \cdot \phi \cdot (1 - \exp(-\lambda \cdot t))} \tag{6}$$

where A_{Mo}—activity of ^{99}Mo taking into account registration efficiency and radiation intensity of gamma photons with energy of 739.5 keV, M—molar mass of ^{98}Mo, m_{Me}—mass of metal in MoO_3 sample, N_{A}—Avogadro constant, c—MoO_3 enrichment in ^{98}Mo, φ—neutron flux.

Results of calculations are presented in Tables 7 and 8.

Tables 7 and 8 show that the effective cross section of ^{98}Mo(n, γ)^{99}Mo reaction is increased from 0.136 barn to 0.4–0.5 barn because of resonance neutrons. In case of the IRT-T research reactor (Tomsk), where MoO_3 targets are irradiated in the central channel with a beryllium reflector, effective cross section of ^{98}Mo(n, γ)^{99}Mo reaction is about

Table 6 Results of neutron fluxes determination in the peripheral channel

	Thermal flux	Epithermal + fast fluxes	Total flux
$\phi_1, \mathrm{cm}^{-2} \cdot s^{-1}$	7.5×10^{11}	7.1×10^{9}	7.5×10^{11}

Table 7 Results of the $^{98}Mo(n, \gamma)^{99}Mo$ total effective cross section calculation in the peripheral channel

Sample number	N1	N2	E1	E2
δ^*, barn	0.6	0.59	0.48	0.51

Table 8 Results of the $^{98}Mo(n, \gamma)^{99}Mo$ total effective cross section calculation in the central channel

Sample number	N5	N6	E5	E6
δ^*, barn	0.49	0.47	0.37	0.37

0.7 barn [6]. It was also shown in the same Ref. that this increase in production cross section allows the serial production of sorption generators.

Estimation of expected ^{99}Mo specific activity

The estimation of the expected ^{99}Mo specific activity (Q) in natural and enriched MoO_3 samples for various irradiation times in the central channel was done using calculated neutron fluxes and cross sections. Calculations were done using the activation equation

$$Q = \frac{m \cdot N_A \cdot c \cdot \delta^* \cdot \varphi}{M} \cdot [1 - \exp(-\lambda \cdot t)] \quad (7)$$

Results of calculations are shown in Figs. 1 and 2.

As can be observed from Figs. 1 and 2, irradiation during 120 h in the central channel produces 16 GBq/g specific activity of ^{99}Mo for enriched samples and 5 GBq/g for natural.

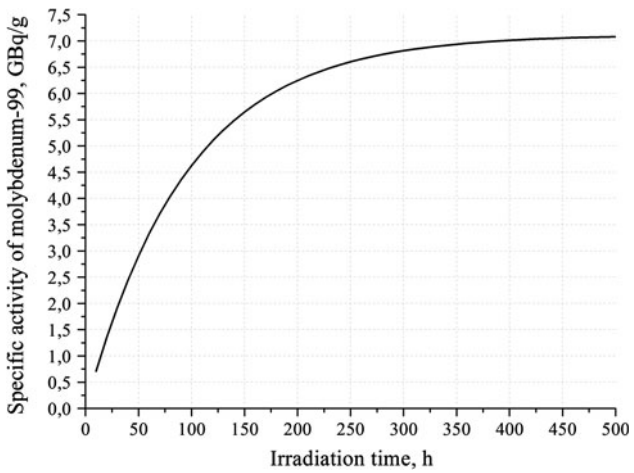

Fig. 1 Estimation of expected ^{99}Mo specific activity in natural samples irradiated in the central channel at nominal operation conditions (250 kW power)

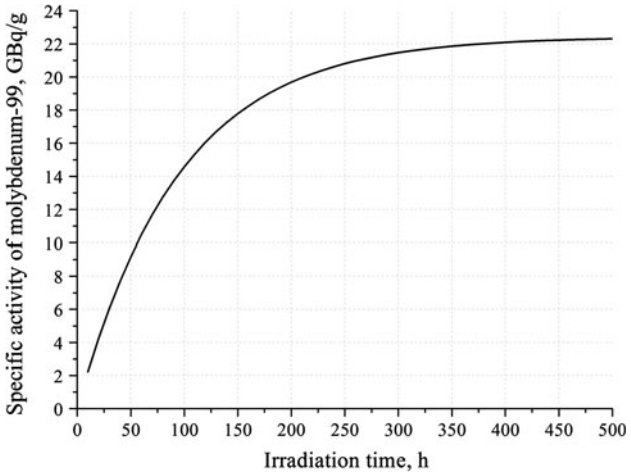

Fig. 2 Estimation of expected ^{99}Mo specific activity in enriched samples irradiated in the central channel at nominal operation conditions (250 kW power)

Extraction of ^{99m}Tc

To obtain radiopharmaceutical ^{99m}Tc with a volumetric activity of 740–1480 MBq/ml on the date of production, which is needed for diagnostic tests, from such low-activity ^{99}Mo targets, concentrating techniques should be applied. The authors think that the most appropriate and one of the most effective concentrating techniques is extraction [10].

To carry out the extraction process, irradiated MoO_3 targets are usually dissolved in KOH or NaOH in the presence of H_2O_2 [11, 12]

$$^{99}MoO_3 + 2KOH \rightarrow K_2^{99}MoO_4 + H_2O$$

After that K_2CO_3 (2.5 M solution) is added as a salting-out agent. For the separation of Tc from Mo, methyl ethyl ketone (MEK) is often used as extracting reagent [2]. ^{99m}Tc is extracted in the form of $HTcO_4$:

$$HTcO_4 + C_4H_8O + H_2O \rightarrow HTcO_4 \cdot C_4H_8O \cdot H_2O$$

At the present time there are many different types of equipment for the extraction separation of ^{99m}Tc from ^{99}Mo which work in remote control mode. The most efficient and reliable is equipment with multiple cycles of extraction and small volume of extracting reagent [10, 13]. Practice shows that the costs for ^{99m}Tc radiopharmaceuticals from an extraction generator are 3–4 times lower than the costs of similar ^{99m}Tc radiopharmaceuticals from a sorption generator. Besides this, almost no waste is formed. The scheme of the extractor with multiple extraction cycles is shown in Fig. 3. According to this scheme, the extractor consists of two coaxial columns, internal (1) and external (2). All columns are connected to an air-vacuum system via two branch pipes (5) and (6). The volumes of both columns are approximately equal and separately exceed the volume of input reagents.

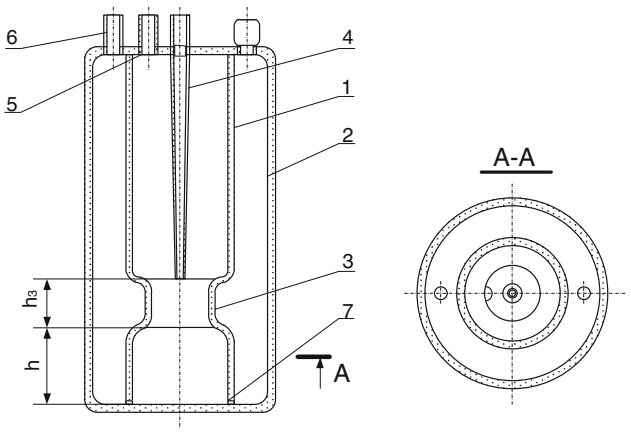

Fig. 3 Scheme of extractor in axial and cross sections

The internal column (1) has a contraction in the middle, a suction tube (4) at the top and a hole on the bottom through which the volumes of both columns communicate with each other.

Multiple extraction of ^{99m}Tc is realized by alternate transfer of extracting reagent and aqueous phase from one column to another with consequent phase immiscibility. Such transfer of liquids is reached by alternate vacuumization in columns through the branch pipes (5) and (6). Intake of the extracting reagent is realized after transfer of both phases into column (1) and their complete stratification. Extractor construction provides self-regulation of interface level and it allows maintaining extractor in shielding container without any visual control. A previous design was published in [14].

A total activity of 10 GBq of the ^{99m}Tc radiopharmaceutical is usually needed for the 1 week operation cycle of a diagnostic single crystal scintillation camera [10]. The yield of this technology is 70–80 %, so the activity of ^{99}Mo must be 13–15 GBq [14]. The usual period of any ^{99m}Tc generator use is 1 week. During this week, the activity of the ^{99}Mo parent isotope is reduced by a factor of 2.75. Taking into account the abovementioned daily demand, the initial ^{99}Mo activity in the generator on the first day of separation must be not <37 GBq. Calculations which were done on the basis of the experimental obtained values of ^{99}Mo specific activities show that the mass of natural and enriched targets which are loaded into the extractor must be 10.6 and 3.3 g, respectively.

According to calculations, 10 ml of 5 M KOH solution are needed for the dissolution of the enriched targets. After dissolution the same amount of salting-out agent is added. 20 ml of MEK is needed for the separation of ^{99m}Tc from the aqueous phase. In case of natural MoO_3 targets, volumes of solution and extracting reagent must be 58–60 and 50–60 ml respectively.

It should be noted that in case of using expensive enriched MoO_3 targets, it is necessary to carry out the subsequent regeneration for the reuse and the recovery of the target material. It can be done through precipitation by hydrogen sulfide from the used solution in form of molybdenum thiosalts [15]. In case of using cheap natural MoO_3, targets, regeneration is not reasonable. Total volume of liquid low-activity waste is about 2.5 l per year, which is not comparable with the amount and the activity of radioactive waste generated in the production of uranium-fission molybdenum.

Conclusion

The results of the experiments were neutron flux determinations in the irradiation channels of the TRIGA Mark II reactor (Vienna, Austria), feasibility of the possibility of low-waste ^{99}Mo production from two types of MoO_3 targets, namely with natural isotopic composition and enriched in ^{98}Mo, using the (n, γ)-type neutron capture reaction. An estimation of thermal and resonance neutrons input into ^{98}Mo activation process was done. The results showed that the effective cross section for the activation of ^{98}Mo in the peripheral and the central reactor channels is at the level of 0.4–0.5 barn, compared to 0.136 barn for thermal neutrons.

A technique for ^{99m}Tc production which includes 120 h irradiation of natural or enriched MoO_3 targets with masses 10.6 g (natural Mo) and 3.3 g (enriched ^{98}Mo), respectively, in the central reactor channel and subsequent separation of ^{99m}Tc using an extraction generator with multiple cycles was proposed. The expected volume activity of the separated ^{99m}Tc radiopharmaceutical would be sufficient for a 1-week work cycle of one or several (in case of enriched samples) diagnostic single crystal scintillation cameras, and therefore has a potential to ensure some local provision of ^{99m}Tc even with small power reactors as TRIGA Mark II.

Acknowledgments This research was funded by the Scholarship of the Scholarship Foundation of the Republic of Austria for undergraduates, graduates and postgraduates provided by the Österreichischer Austauschdienst (OeAD). The authors wish to thank Helmuth Böck, Dieter Hainz (Atominstitut) and Van Ingram for supporting this work. Moreover, the authors gratefully acknowledge Department of Nuclear Energy (IAEA), specially Edward Bradley, Alisa Carrigan and Yacov Barnea and Reactor Infrastructure Centre (Jozef Stefan Institute) specially Peter Stegnar for valuable scientific discussions.

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