FEASIBILITY STUDIES OF PRODUCING ^{99}Mo BY CAPTURA IN THE IEAR-1 RESEARCH REACTOR

Roberta Concilio, Arlindo Gilson Mendonça, José Rubens Maiorino.

Instituto de Pesquisas Energéticas e Nucleares, CNEN
Caixa Postal 11049 (Pinheiros)
05422-970, São Paulo, Brasil
e-mail: maiorino@net.ipen.br
amendon@net.ipen.br

Presented at the 1998 International Meeting on
Reduced Enrichment for Research and Test Reactors

October 18 - 23, 1998
Sao Paulo, Brazil

FEASIBILITY STUDIES OF PRODUCING ^{99}Mo BY CAPTURA IN THE IEAR-1 RESEARCH REACTOR

Roberta Concilio, Arlindo Gilson Mendonça, José Rubens Maiorino.

Instituto de Pesquisas Energéticas e Nucleares, CNEN
Caixa Postal 11049 (Pinheiros)
05422-970, São Paulo, Brasil
e-mail: maiorino@net.ipen.br
amendon@net.ipen.br

ABSTRACT

Everyday the production of ^{99}Mo for ^{99m}Tc generators, becomes more necessary, whose proprieties are ideal for medical diagnosis. This works presents a description and an analysis of the production of ^{99}Mo BY radioactive capture at ^{98}Mo using the research reactor IEA-R1 in 5 MW and operating 5 days a week, referring to the use of targets, separation methods, total and specific activity attained and its limitations.

INTRODUCTION

The ^{99m}Tc is an extremely important radioisotope for medicine in the area of diagnosis (lung, heart, brain, liver, thyroid gland and bones), because it presents the following characteristics:

. it has a short life of 6.02h;

. it emits a gamma radiation of low energy (140KeV) that allows an adequate penetration at the tissues besides an easy detection by gamma cameras;

. it decays by isomeric transition, so it does not emit α or β particles;

. its decay product, ^{99}Tc, has a long half life ($T_{1/2}$ = 2,14x10^5 years) and so it is little active ;

. it presents great chemical versatility to bond with several pharmaceutical products.

The ^{99m}Tc is a product of the decay of ^{99}Mo that can be produced by radioactive capture, or extracted as a product of fission from ^{235}U. The first process has the advantage of being a "clean process", better saying, it does not present fission products, making this process much more simplified and as a disadvantage of producing ^{99}Mo with low specific activity.

The capture process is nowadays used in China and Vietnam, being molybdenum trioxide the target used [1].

IPEN imports about 6300 GBq (~170 Ci) per week of ^{99}Mo from Nordion International (Canada), that is produced by fission method. The ^{99}Mo is processed and after introduced to the chromatographic ^{99m}Tc generators that will be distributed to hospital and clinics.

This study has as goal to analyze the possibilities and limitations to the production of ^{99}Mo via radioactive capture, at the IEAR-1 reactor operating at 5MW with continuous operation of 120 h, 5 days per week.

RADIOACTIVE CAPTURE AT ^{98}Mo

The process of radioactive capture for the production of ^{99}Mo is given by the reaction: $^{98}Mo\ (n,\gamma)\ ^{99}Mo$. The natural molybdenum has an abundance of 24.137% of ^{98}Mo.

The most used targets are natural molybdenum trioxide (MoO3) or enriched (> 90%) and molybdenum metal.

The cross section for radioactive capture is approximately of 0.14 barns and for the epithermic range is approximately 0.61 barns.

Targets

The countries that produce ^{99}Mo by radioactive capture irradiate MoO_3 confined in quartz flasks. At IPEN these flasks are not used because national quartz deteriorates significally the neutrons flux [2]. Molybdenum is then irradiated into aluminum rabbits, cylinders at 70mm high, 22mm diameter and 1mm width, where they lay with 30g of MoO_3 in each one. The rabbits are displayed in a way as to have to columns of 8 rabbits each covering all the active core height.

Through experiments accomplish using a beryllium irradiator, it was observed that the activities of the samples located in the position 1, 2 and 8 were sensibly smaller from other positions (Fig. 1). This event limitates the irradiation to 5 central axial positions (positions 3, 4, 5, 6 and 7) that permits the irradiation of about 300g of MoO_3 [3].

It can also be observed in Fig. 1 that the rabbits located in position 4, 5 and 6 are the ones that present more activity [3], consequently instead of using three rabbits in this position (Fig. 2a) we would use only one of 240mm high (Fig, 2b) that permits irradiation of a bigger quantity of MoO_3, besides simplifying the selective remotion of targets.

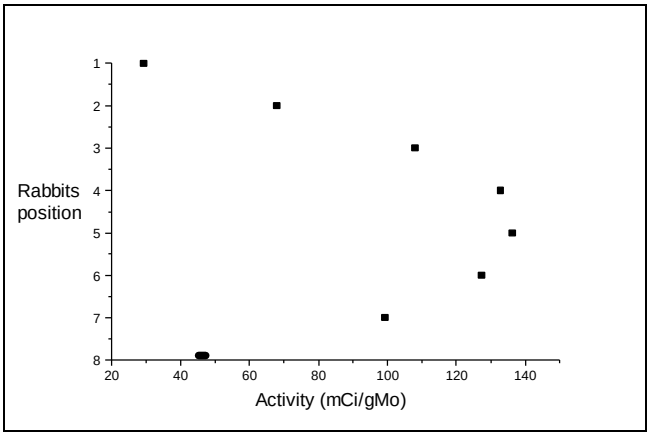

Fig. 1. Activity of the Molybdenum in each Rabbit Containing 30g of MoO_3 after 24h of Irradiation at IEAR-1 in 2MW.

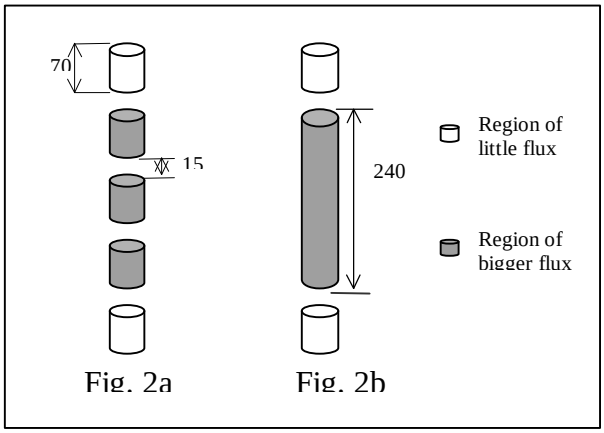

Fig. 2. Scheme of the Rabbits Inside the Irradiator

Using rabbits in the present dimensions, the specific activity presents a decrease of approximately 11% in the interior of the target due to neutron flux depression (Fig. 3) [4], so to

increase the average specific activity we propose using a rabbit with smaller diameter (approximately 10mm) or leaving a hollow in the cylinder center (Fig. 4).

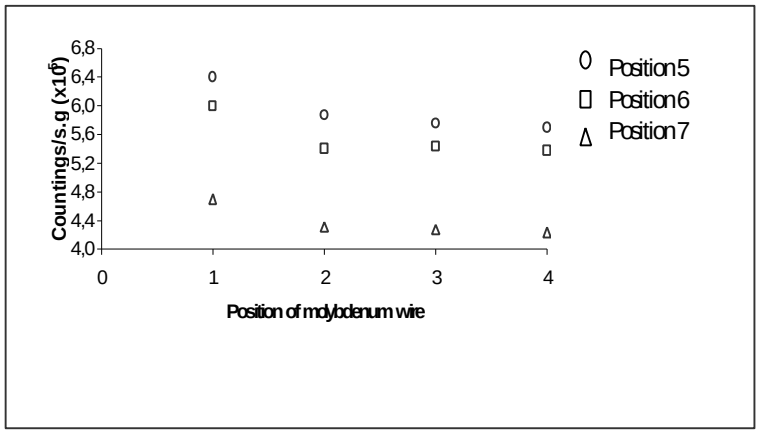

Fig. 3. Radial Reaction Rate in Samples of MoO_3 at Water Irradiation Element.Canal A,detector NaI-2 counting/s.g

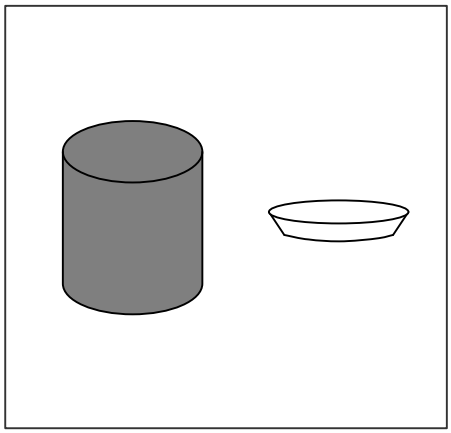

Fig. 4. Scheme of a Rabbit with a Hollow and its Lid that is Welded after Filling the Rabbit with the molybdenum.

A study was made by Yamaguchi M., Mendonça A. G., Santos A. and Osso J. A., at IEAR-1 to analyze the production perspective of ^{99}Mo production via radioactive capture [2]. Samples of MoO_3 were irradiated using beryllium irradiator (Fig. 5) and they conclude that for a continuos irradiation of 120h in 5MW the maximum specific activity is 1134.5 mCi/g Mo (positions 4, 5 and 6) for a group samples located in the region of a bigger neutrons flux ($\phi_{ept} \sim 2{,}7x10^{13}$ n/cm^2.s) and 773.9mCi/gMo (positions 3 and 7) for the other group located in the region of smaller neutron flux ($\phi_{ept} \sim 1{,}5\ x10^{13}$ n/cm^2.s).

Between 5th and 9th of May 1997 a second experiment at the reactor IEAR-1 [3] was made using beryllium irradiator placed at the center of the reactor (Fig.6) aiming increase the ephitermic flux.

The average specific activity projected to a continuos irradiation of 120h in 5MW, was of 1159,85 mCi/gMo for the samples placed at the position of larger flux ($\phi_{ept} \sim 3{,}2\ x10^{13}$ n/cm^2.s).

Post-Irradiation

Through the code ORIGEN II [5] we made a projection of chemical elements obtained after an irradiation of 120h from 1 g of natural molybdenum.

The radioisotopes formed after irradiation present short half-lives and decay to rutenium and paladium. So the radioactive dejects basically constitute of radioisotopes of long half-lives: the ^{93}Mo ($T_{1/2}$=3,5E3 years) and the ^{99}Tc ($T_{1/2}$=2,1E5 years), which do not affect significantly the quality of separated ^{99m}Tc.

The impurities associated to the target of molybdenum vary according to the supplier. In some cases we can find MoO_3 containing tungstenium as impurity, that by the reaction (n,γ) and

subsequently beta decay forms ^{188}Re that goes with technetium because of its chemical similarity. That is why one has to be careful with the target chosen.

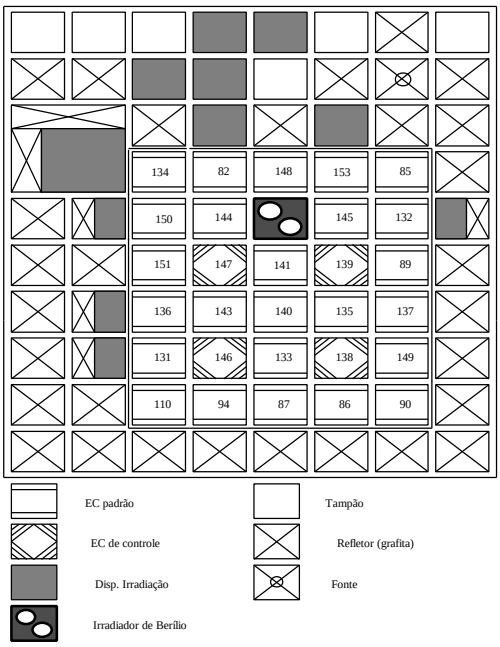

Fig. 5. Configuration of the Reactor, Illustrating the Position of the beryllium irradiator.

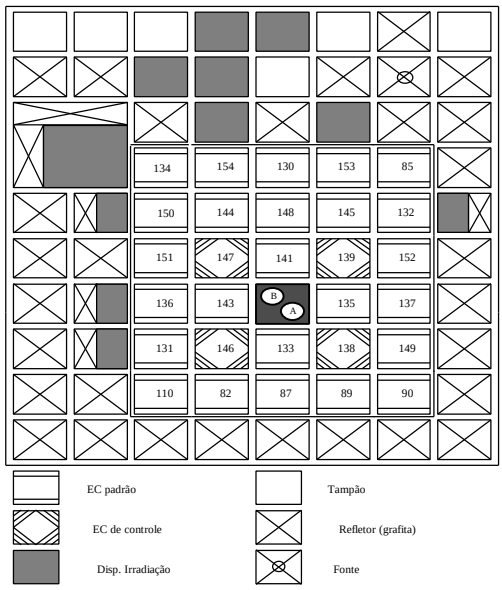

Fig. 6. Configuration of the Reactor, Illustrating the Beryllium Irradiator Placed in the Center.

Since the ^{99}Mo decays to the ^{99m}Tc that will be administrated in patients, it has to be an order of purity of approximately 98%. There are many methods of separation and purification of ^{99}Mo that vary according to the used target and the type of ^{99m}Tc generator (chromatographic, solvent extraction or sublimation). The most common ^{99m}Tc generator used by IPEN uses chromatographic that consists of a mechanism of elution: the ^{99}Mo decays to ^{99m}Tc that is eluted by a saline solution that passes through a alumina bed with fixed molybdate.

METHODS OF SEPARATION FOR A ^{99m}Tc CHROMATOGRAPHIC GENERATOR

For a target of molybdenum trioxide, the dissolution is made by the addition of a solution of ammonia hydroxide, sodium or potassium. One adds sodium hypoclorite and adjusts the pH of the solution for 1.5 – 3.0, so that the molybdenum is fixed at an alumina bed. The solution is then evaporated until it dries, having molybdenum in the form of molybdate.

For a target of molybdenum metal, the dissolution is made by adding hydrogen peroxide solution, for molybdenum metal is not easily dissolved in mineral acids, which will form molybdenum peroxide, that will convert into blue molybdenum after certain time. Then one will add sodium hydroxide solution and one will obtain sodium molybdate, which is then acidulated by the addition of chloridric acid [6,8]. One can also have a fusion with potassium nitrate, sodium peroxide or sodium carbonate, where the metal is oxidized to a soluble molybdate [7].

ACTIVITY

Using the same entry data to attain products formed after natural molybdenum irradiation, through the program ORIGEN II [5] one got the projection of values from the activities of ^{99}Mo varying irradiation time and keeping the same constant flux (table 1) and it could be concluded that a continuos irradiation of 120h is ideal, because for a longer irradiation the ^{99}Mo activity varies too little to be justified.

Table 1. Irradiation time x activity

Irradiation time (h)	**Activity (mCi/gMo)**	**Concentration (g/gMo).10^{-6}**
24	319,6	0,666
48	568,0	1,184
72	761,0	1,586
96	911,1	1,899
120	1020,0	2,142
144	1118,0	2,331
168	1189,0	2,478
192	1244,0	2,592

For an initial activity of 1160 mCi/gMo and regarding that irradiation will begin on Monday at 8 a.m. and irradiation ending will be on Saturday 8 a.m., where the material will be taken to the processing cell after a time of decay, for a preparation of gel (zirconium molybdate) and calibration will be on Monday morning 8 a.m. Then after 48 hours, the specific activity will decrease approximately 700 mCi/gMo that is equivalent to 476 mCi/gMo for besides decay; one should take into account that only 85% of molybdenum decay to ^{99m}Tc and elution yield (proportion of ^{99m}Tc present in the system that is separated during the elution) is 80%.

The relation volume/mass is proportional to specific activity, so one has to increase the volume/mass inside the ^{99m}Tc generator in order to achieve the total desirable activity, which makes impracticable the usage of the generator with molybdenum fixed onto a alumina bed.

To relieve this problem, countries like Vietnam, Australia and Thailand (table 2) are studying and developing a ^{99m}Tc generator basing on gel elution where one uses molybdenum in the form of zirconium or titanium molybdate [9,10].

Nowadays, just China produces ^{99m}Tc generators, gel type, on a commercial scale. For this a reactor of 100MW and another of 5MW are used and as a target: molybdenum trioxide.

Table 2. Study for development of ^{99m}Tc-generator gel type

	Vietnam	Australia	Thailand
Flux (n/cm^2.s)	2.0 x10^{13}	5.0 x10^{13}	2.6 x10^{13}
time (h)	100	100	50
Activity (mCi/gMo)	59.0	137.0	39.0

Inside each generator, one has 3 to 5g of zirconium molybdate with a concentration higher than 340 mgMo/g gel. Taking 5g of zirconium molybdate as a basis one has table 3.

Table 3. Activity of ^{99}Mo needed to attain ^{99m}Tc generators with 5g of gel

	^{99}Mo Activity (mCi/gMo)							
^{99m}Tc mCi	300 mg Mo/ g gel		320 mg Mo/ g gel		340 mg Mo/ g gel		360 mg Mo/ g gel	
	a	b	a	b	a	b	a	b
250	404	246	379	231	357	217	337	205
500	808	491	757	460	713	433	673	409
750	1211	736	1136	690	1069	650	1010	614
1000	1615	981	1514	920	1425	866	1346	818
1250	2019	1227	1892	1149	1781	1082	1682	1022

a: reactor exit;
b: after 48 h.

At IPEN there are researchers going on that aims to increase molybdenum concentration at gel (zirconium molybdate) and at the present time the maximum concentration attained was 260 mg Mo/g gel [11]. So considering as maximum specific activity at the exit of the reactor approximately 1160 mCi/g Mo, IPEN would have conditions of producing generators of 250 and 500 mCi (table 3). On the other hand, we intend to use 10g of gel for each ^{99m}Tc generator, what would make an elution volume of 12ml [11]. So, considering a ^{99m}Tc generator with 10 g of gel we would have the results shown in table 4. So with the same specific activity at the exit of the reactor (~1160 mCi/gMo), IPEN would have conditions to produce ^{99m}Tc generators from 250 to 1000mCi.

Table 4. Activity of ^{99}Mo needed to attain ^{99m}Tc generators with 10g of gel

	^{99}Mo Activity (mCi/gMo)							
^{99m}Tc mCi	200 mg Mo/ g gel		250 mg Mo/ g gel		300 mg Mo/ g gel		350 mg Mo/ g gel	
	a	b	a	b	a	b	a	b
250	303	184	243	148	202	123	173	106
500	606	368	485	295	404	246	346	211
750	908	552	727	442	606	368	519	316
1000	1211	736	969	589	808	491	692	421
1250	1514	920	1211	736	1010	614	865	526

a: reactor exit;
b: after 48 h.

PRODUCTION

All of ^{99}Mo for the production of ^{99m}Tc generators at IPEN is imported from Nordion International. As this radioisotope cannot be stored, because of its short half-life, if there is any problem that interrupts its production, or even transportation problems, in a few days we would not have conditions to supply the market.

With the advance of technology in medical diagnosis, the consumption of ^{99m}Tc generators (fig. 8) has significantly increased year by year (in a rate of 25% in the last 4 years) [12].

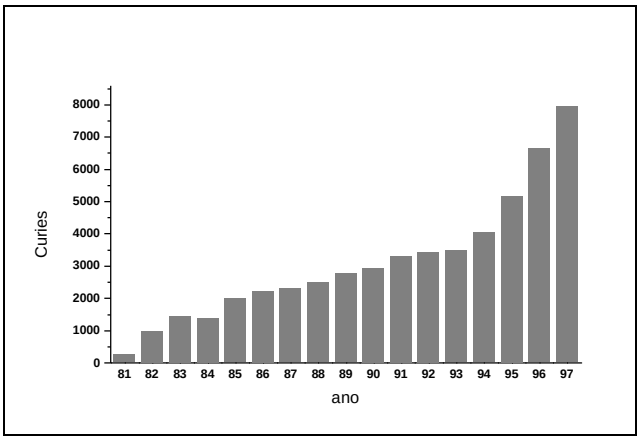

Fig 8. ^{99m}Tc Generators Supply by IPEN

The developing market is being considered together with its vulnerability for the total dependence of Nordion International, there is an urge for the research to develop methods for the production of ^{99}Mo.

CONCLUSION

Considering 1997 data (table 5) [12] one can conclude that ^{99m}Tc generators containing 5g of gel, IPEN would have conditions to produce generators of 250 and 500 mCi, which would correspond to 23.4% of the market and a reduction of annual import of approximately US$200,000.00. With the development of ^{99m}Tc generator gel type containing 10g of gel with a concentration of 260mgMo/ggel, IPEN would have conditions to produce ^{99m}Tc generators in the range of 250-1000 mCi, that corresponds to approximately 70% of the market (table 5) and a reduction of annual import of approximately US$1,000,000.00. At the end of 2.5 years this would result, an economy equivalent to the investment made to update the power of IEAR-1m.

Table 5. Production of ^{99m}Tc generators in the year of 1997

Activity (mCi)	**Number of generators produced in 1997**	**Market Participation (%)**
250	349	4.3
500	1547	19.1
750	1304	16.1
1000	2390	29.5
1250	935	11.6
1500	1132	14.0
2000	432	5.3
Total	8089	100.0

SUGGESTIONS

One can take certain measures to increase total activity, as follows:

- The usage of molybdenum metal as target, for it is 2.5 times denser than molybdenum oxide, or better saying, one would have 2.5 more material to be irradiated per cm^3. Besides, it presents a larger concentration of Mo than the MoO_3 what results in a total activity increase, or better, an economy of space at the reactor.
- The usage of rabbits 21cm high and 2cm diameter.

To increase specific activity (mCi/gMo):

- The usage of molybdenum enriched targets (increase up to 4 times)
- The increase of neutron flux and usage of rabbits with a hollow middle part (increase of approximately 10%)

REFERENCES

[1] Radioisotope Production and Quality Control. IAEA, Vienna, Technical Report Series No.128 (1971).

[2] YAMAGUCHI, M.; MENDONÇA, A.G.; SANTOS, A; OSSO, J.A; Perspectiva de Produção de ^{99}Mo via Captura Radioativa no ^{98}Mo utilizando o reator IEA-R1 a 5MW e operando 5 dias por semana, Technical Report, 1997.

[3] YAMAGUCHI, M., MENDONÇA, A.G., Análise do Experimento de Irradiação de Amostras de MoO_3 no Reator IEA-R1 Utilizando Irradiador de Berílio, Technical Report, 13th February 1997.

[4] Ricci, V., Análise de um elemento de irradiação de berílio para a produção de ^{99}Mo no reator IEAR-1, to be published.

[5] ORIGENII; Isotope Generation and Depletion Code – Matrix Exponential Method, Oak Rigde National Laboratory, Tennesse.

[6] BOYD, R.E.; Molybdenum-99: Technetium-99m
Generator, Radiochimica Acta vol. 30, p 123-145, 1982.

[7] SCADEN, E.M.; BALLOU, N.E.; Radiochemestry of Molybdenum, U.S.Naval Radiological Defense Laboratory, San Francisco, California, jan 1960.

[8] LAVI, N.; The study of conditions for the preparation and application of ^{99}Mo – ^{99m}Tc generators starting from irradiated molybdenum metal, J. Radioanal. Chem., vol. 42, 1978.

[9] LE VAN SO, Preparation of Gel Type Chromatographic Tc-99m Generators Using Titanium-Molybdate and Zirconium- Molybdate Columns Containing (n, γ) Mo-99, IAEA's Research Co-ordiantion Meeting, Bombay, India, 30 March 1990.

[10] LE VAN SO, Development of Alternative Technologies for Gel-type Chromatographic Tc99m Generator, IAEA's Research Co-ordination Meeting, Vienna, Austria, 3-6 May 1994.

[11] Osso, J., private communication.

[12] Mengatti, J., private communication.