

Article

Magnesium-Molybdate Compounds as Matrix for $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$ Generators

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Abstract: This work reports the preparation of a $^{99\text{m}}\text{Tc}$ generator based on conversion of ^{99}Mo produced by neutron irradiation, into insoluble magnesium ^{99}Mo -molybdates compounds as matrix. The effect of magnesium salt types and concentration, Mg:Mo molar ratios, pH of molybdate solutions, eluate volume as well as the addition order of molybdate and magnesium solutions' influences on the final $^{99\text{m}}\text{Tc}$ were evaluated. Polymetalates and polymolybdates salts either crystallized or amorphous were obtained depending on the magnesium salt and Mg:Mo molar ratio used in matrix preparation. $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$ generator production based on magnesium- ^{99}Mo molybdate compounds allow reduction of preparation time and eliminates the use of specialized installations. The best generator performances were attained using matrices prepared from 0.1 mol/L $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ solutions, ammonium molybdate solutions at pH 7 and at a Mg:Mo molar ratio of 1:1.

Keywords: $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$ generator; magnesium molybdates

1. Introduction

Technetium-99m ($^{99\text{m}}\text{Tc}$) is used for more than two thirds of nuclear imaging techniques because of its short 6.02 h half-life, simple decay scheme (a single 141 KeV photon), minimum whole-body dose, versatile chemistry, and availability from the $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$ generator [1-2]. This system is based on

adsorption of ^{99}Mo on an alumina column where $^{99\text{m}}\text{Tc}$ formed from decay of the ^{99}Mo is periodically eluted from the column using physiological saline, as sodium pertechnetate ($\text{Na}^{99\text{m}}\text{TcO}_4$) while $^{99}\text{MoO}_4^{2-}$ remains attached to alumina. The limited loading capacity of alumina for molybdenum (2 mg Mo/g alumina) forces the use of a uranium fission product with a high specific activity, ^{99}Mo (10^5 Ci/g Mo) [3], thus requiring sophisticated separation processing infrastructure and disposal of large amounts of radioactive wastes [4-5]. To avoid this, alternative methods of $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$ generator production have been investigated using low and medium specific activity ^{99}Mo , produced from (n, γ) nuclear reaction with natural Mo (activation method) and directly converted into insoluble substrates that can be eluted in a column. $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$ generator based on heteropolyanions such as zirconium molybdate, titanium molybdate, molybdocates, *etc.*, [6-12] have been developed by some laboratories around the world. This is due to the molybdates' matrix capacity to incorporate up to 30% in weight of ^{99}Mo [13] compared to 0.2% in traditional alumina based generators. Although these generators has opened a way of making column type $^{99\text{m}}\text{Tc}$ generator even using low and medium specific activity ^{99}Mo , the handling problems (precipitation, filtration drying, fragmentation, *etc.*) still exist because these ^{99}Mo -molybdates are mostly synthesized from ^{99}Mo , requiring sophisticated remote handling facilities and at least 6 h processing time [12,14]. To simplify the production process of these systems, we propose preparing $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$ generators based on magnesium ^{99}Mo -molybdate compounds by synthesizing magnesium molybdate compounds, followed by irradiation. This approach has three advantages: (1) it eliminates the use of specialized installations for molybdates synthesis; (2) it reduces $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$ generator preparation time and (3) it minimizes radiological contributions at $^{99\text{m}}\text{Tc}$ eluates due to the only radioisotope produced for the manganese (^{24}Mg) during magnesium molybdate compound irradiation which has a short half life: 9.46 min.

Systematic studies on $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$ generators based on magnesium ^{99}Mo -molybdate compounds were performed. The effect of six parameters on the $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$ generator performance were evaluated: magnesium concentration and salt type, Mg:Mo molar ratios, molybdates solutions and precipitated pH, and addition order of molybdate and magnesium solutions. The physical-chemical properties of magnesium molybdate compounds were also determined to relate their properties with generator performance.

2. Results and Discussion

2.1. Performances of $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$ Generators Based on Magnesium ^{99}Mo -Molybdate Compounds

Table 1 shows the performances of the $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$ generators based on magnesium ^{99}Mo -molybdate compounds prepared in this research. Results are divided into three series, in line with the type of magnesium salts used in the generator preparation: magnesium chloride hexahydrate (series A), magnesium nitrate hexahydrate (series B) and magnesium sulfate hexahydrate (series C). The generator performances were compared with those advised by the Pharmacopoeia for the $^{99\text{m}}\text{Tc}$ eluates used with medical purposes: ^{99}Mo breakthrough less than 0.015%, a minimum percentage of 95% for the radiochemical purity, a chemical purity less than 10 ppm for aluminium and pH values between 4.5 and 7.5 [15].

Table 1. Performances of $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$ generators based on magnesium ^{99}Mo -molybdate compounds.

Series	$[\text{Mg}^{2+}]$	Mg:Mo	pH ammonium molybdates	Eluate color	Eluate Volume (mL)	^{99}Mo Breakthrough (%)	$^{99\text{m}}\text{Tc}$ elution efficiency (%)	$^{99\text{m}}\text{TcO}_4^-$ (%)	Al^{3+} 10ppm	Mg^{2+} 10ppm	pH eluate	washed	Mo %	Mg %	<u>Crystalline phases</u>
A1	0.5 M	0.64:1	7	colorless	3.5	0.022	72.3	68-82	<	<	3.8-4.4	no	61.44	11.00	$\text{MoO}_3, \text{NH}_4 \text{MgCl}_3 \cdot 6\text{H}_2\text{O}$
A2	0.5 M	0.93:1	7	colorless	2	0.014	17.7	73	<	<	4.5-5	no	49.44	8.89	$\text{MoO}_3, \text{NH}_4 \text{MgCl}_3 \cdot 6\text{H}_2\text{O}$
A2w	0.5 M	0.93:1	7	colorless	2.5	0.071	31.1	75	<	<	3.3-5	yes	47.98	2.52	MoO_3
A3	0.5 M	1.08:1	7	colorless	6	0	48	89	<	<	3.2	no	67.4	17.11	$\text{MoO}_3, \text{NH}_4 \text{MgCl}_3 \cdot 6\text{H}_2\text{O}$
A3w	0.5 M	1.08:1	7	colorless	3.5	0.2	49.8	50	<	<	3.2-4.2	yes	55.97	2.51	MoO_3
A4	0.5 M	1.18:1	7	colorless	2	0.025	24.2	84-94	<	<	4.4-5.7	no	75.83	11.55	$\text{MoO}_3, \text{NH}_4 \text{MgCl}_3 \cdot 6\text{H}_2\text{O}$
A4w	0.5 M	1.18:1	7	colorless	2.5	0.0026	43.2	37-77	<	<	4.5-5	yes	47.20	4.29	MoO_3
A5	1 M	2:1	7	colorless	2	1.37	29	93	<	>	2.8-3.7	no	15.8	21.35	$\text{NH}_4 \text{MgCl}_3 \cdot 6\text{H}_2\text{O}, \text{NH}_3(\text{MoO}_3)_3, \text{NH}_4\text{Cl}$
A5w	1 M	2:1	7	colorless	3	0.035	34	93	<	<	2.2-3.1	yes	28.03	0.69	MoO_3
A6	0.5 M	2:1	7	colorless	3	0.85	52	90	<	<	4.8-5.5	no	11.28	22.27	$\text{NH}_4 \text{MgCl}_3 \cdot 6\text{H}_2\text{O}, \text{NH}_3(\text{MoO}_3)_3$
A6w	0.5 M	2:1	7	colorless	3	0.06	16	98	<	<	4.3-6.8	yes	58.81	1.62	MoO_3
A7	0.5 M	1:1	7	colorless	2.5	4.8	29.3	98	<	>	4-4.2	no	28.05	20.71	$\text{NH}_4 \text{MgCl}_3 \cdot 6\text{H}_2\text{O}, \text{NH}_3(\text{MoO}_3)_3, \text{NH}_4\text{Mo}_5\text{O}_{15}(\text{OH}) \cdot 2\text{H}_2\text{O}$
A8	0.5 M	1:2	7	colorless	2.3	0	20	84	<	<	5.2-7.2	no	47.5	18.55	$\text{NH}_4 \text{MgCl}_3 \cdot 6\text{H}_2\text{O}, \text{NH}_3(\text{MoO}_3)_3, \text{NH}_4\text{Mo}_5\text{O}_{15}(\text{OH}) \cdot 2\text{H}_2\text{O}$
A9	0.1 M	1:2	7	colorless	3.5	7.07	10	92	<	>	6.8-7	no	18.16	10.8	$\text{NH}_4 \text{MgCl}_3 \cdot 6\text{H}_2\text{O}, \text{NH}_3(\text{MoO}_3)_3, \text{MoO}_3$
A10	0.5 M	2:1	4.5	colorless	2.8	0.1	69	95	<	<	4.0-5.2	no	9.08	19.35	$\text{NH}_4 \text{MgCl}_3 \cdot 6\text{H}_2\text{O}, \text{NH}_4\text{Cl}, \text{NH}_3(\text{MoO}_3)_3$
A11	0.5 M	1:2	4.5	colorless	2.5	1.1	37	20	<	<	4.3-5.5	no	49.71	9.22	$\text{NH}_3(\text{MoO}_3)_3, \text{MoO}_3, \text{NH}_4\text{Mo}_5\text{O}_{15}(\text{OH}) \cdot 2\text{H}_2\text{O}, \text{NH}_4 \text{MgCl}_3 \cdot 6\text{H}_2\text{O}$
A11w	0.5M	1:2	4.5	colorless	3	0	20	60	<	<	5.9-6.4	yes	54.85	0.59	MoO_3
A12	0.5M	1:1	4.5	colorless	3	0.95	26.2	96	<	<	2.4-4	no	68.54		$\text{MoO}_3, \text{MoO}_3 \cdot \text{H}_2\text{O}$
B1	0.1M	0.2:1	7	colorless	2	4.24	83.9	87	<	<	2.7-3	no	27.19	5.03	amorphous, unidentified phases
B2	0.1M	0.2:1	7	yellow	2.5	1.9	87.8	91	<	<	1.7-2.6	no	19.97	3.63	amorphous, unidentified phases
B3	0.1M	0.2:1	4.5	colorless	2	1.16	77	79	<	<	2.2-4	no	21.31	2.45	amorphous, unidentified phases

Table 1. Cont.

B4	0.1M	0.2:1	4.5	yellow	2	10.74	70.1	85	<	<	2-3	no	26.05	2.89	amorphous, unidentified phases
B5	0.1M	0.2:1	10	yellow	2.5	1.8	81.3	89	<	<	2-3.6	no	26.91	2.93	amorphous, unidentified phases
B5w	0.1 M	0.2:1	10	yellow	6	0.74	76.84	83	<	<	3.8-2.6	yes			
B6	0.1 M	0.2:1	10	yellow	2.5	1.6	79.3	90	<	<	2.3-5.3	no	25.83	1.56	amorphous, unidentified phases
B6w	0.1 M	0.2:1	10	yellow	2.5	4.17	42.7	78	<	>	2.9-3.7	yes			MoO ₃ , NH ₃ (MoO ₃) ₃
B7	1 M	1:1	7	colorless	5	0	79.7	52-92	<	>	3.4-4.2	no	42.3	33.37	NH ₄ MgCl ₃ *6H ₂ O, NH ₃ (MoO ₃) ₃
B7w	1 M	1:1	7	colorless	3	0.39	55.4	98	<	<	4.6-5	yes	64.9	0.88	MoO ₃
B8	0.1 M	1:2	4.5	colorless	3	0.035	53.5	96-90	<	<	5-6.3	no	47.65		MoO ₃ , NH ₄ MgCl ₃ *6H ₂ O, (NH ₄) ₂ Mo ₃ O ₁₀
B9	0.1 M	2:1	4.5	colorless	2	1.23	57.5	99	<	<	4.3-4.8	yes		4.12	amorphous, unidentified phases, NH ₄ MgCl ₃ *6H ₂ O
C1	1 M	2:1	4.5	yellow	2.5	0.82	29	82	<	>	1-1.6	no	18.16	35.72	NH ₄ MgCl ₃ *6H ₂ O, (NH ₄) ₂ Mg(SO ₄) ₂ *6H ₂ O
C2	0.1 M	2:1	4.5	colorless	4	0.19	50	89-96	<	<	1.9-3.6	no	15.7	19.93	NH ₄ MgCl ₃ *6H ₂ O, (NH ₄) ₂ Mg(SO ₄) ₂ *6H ₂ O, NH ₄ Cl,
C2w	0.1 M	2:1	4.5	colorless	2	2.2	20	89-93	<	<	3.9-4.4	yes	74.28	0.57	MoO ₃
C3	0.05 M	2:1	4.5	yellow- clear	2	3.89	56.5	90	<	>	3.1-3.4	no	7.11	24.2	NH ₄ MgCl ₃ 6H ₂ O
C3w	0.05 M	2:1	4.5	Blue precipitated	1.5	3.8	50	81-94	≤	<	2.5-1.7	yes	34.16	2.84	amorphous, unidentified phases
C4	1 M	1:1	7	clear precipitated	2.	5.59	40.6	78	<	>	1.9-2	no	11.34	10.08	NH ₄ MgCl ₃ *6H ₂ O, (NH ₄) ₂ Mg(SO ₄) ₂ 6H ₂ O, amorphous
C4w	1 M	1:1	7	colorless	3	0.72	15	81-95	<	<	3.4-4.2	yes	69.53		MoO ₃

^{99}Mo breakthrough percentages of less than 0.015% were only obtained in the matrices prepared from: (a) 0.5 mol/L $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (series A) and b) 1 mol/L $\text{MgNO}_3 \cdot 6\text{H}_2\text{O}$ solutions (series B) using ammonium molybdate solutions at pH of 7 and a Mg:Mo molar ratio of 1:2 (Figure 1). However, $^{99\text{m}}\text{Tc}$ elution efficiencies of these generators were less than 48%, except for the matrix B7. On the other hand, the highest elution efficiencies (>70%) were obtained in the generators prepared from 0.1 mol/L $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solutions, at a Mg:Mo molar ratio of 0.2:1 and ammonium molybdate solutions at pH values between 4.5 and 10, however under these conditions, ^{99}Mo breakthrough of the eluates were more than 0.7%, apart from the matrix B7. $^{99\text{m}}\text{Tc}$ eluates of the matrices prepared preferably with Mg:Mo molar ratio of 2:1 presented radiochemical purity of more than 95% and, in general, those made from $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ solutions which satisfy the eluate pH values fixed by the Pharmacopoeia: between 4.5 and 7.5, while the eluate pH values obtained from the matrices formed with $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ were the more acid, between 1 and 3. The average elution volume of all the generators studied ranged between 2 and 3.5 mL and all $^{99\text{m}}\text{Tc}$ eluates had an Al content of less than 10 ppm. It is important to note that a high ^{99}Mo breakthrough percentage in the eluates entails the presence of Mg^{2+} in solution.

The Mo and Mg content in the generators is directly connected with: the Mg:Mo molar ratio, the type and concentration of magnesium salt used during matrix synthesis and matrix washing before irradiation. Thus the highest (75–50%) and lowest (18–7%) Mo percentages, and *vice versa* for Mg content, were recorded in the washed matrices and those prepared from $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ solutions at Mg:Mo molar ratio of 2:1 respectively.

Matrix washing caused a decrease of the $^{99\text{m}}\text{Tc}$ elution efficiencies and Mg percentage in the matrix, while an increase in magnesium salt concentration (series C) induced a drop in the $^{99\text{m}}\text{Tc}$ elution efficiency and acidification of $^{99\text{m}}\text{Tc}$ eluates. The addition order of magnesium salt and ammonium molybdate solutions, and ammonium molybdate pH in the matrix process preparation (series B) did not cause meaningful changes in $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$ generator performance.

Figure 1. Distribution of magnesium ^{99}Mo -molybdate generator performances ($^{99\text{m}}\text{Tc}$ eluate efficiency and pH, radiochemical purity) in function of ^{99}Mo breakthrough.

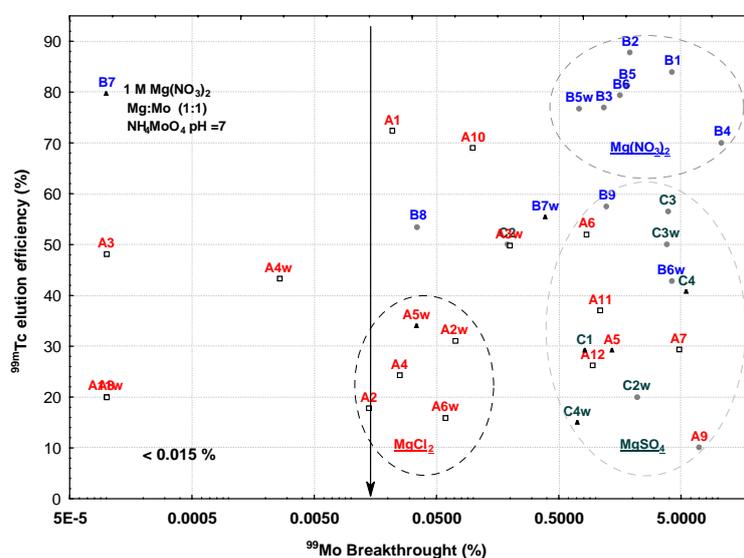
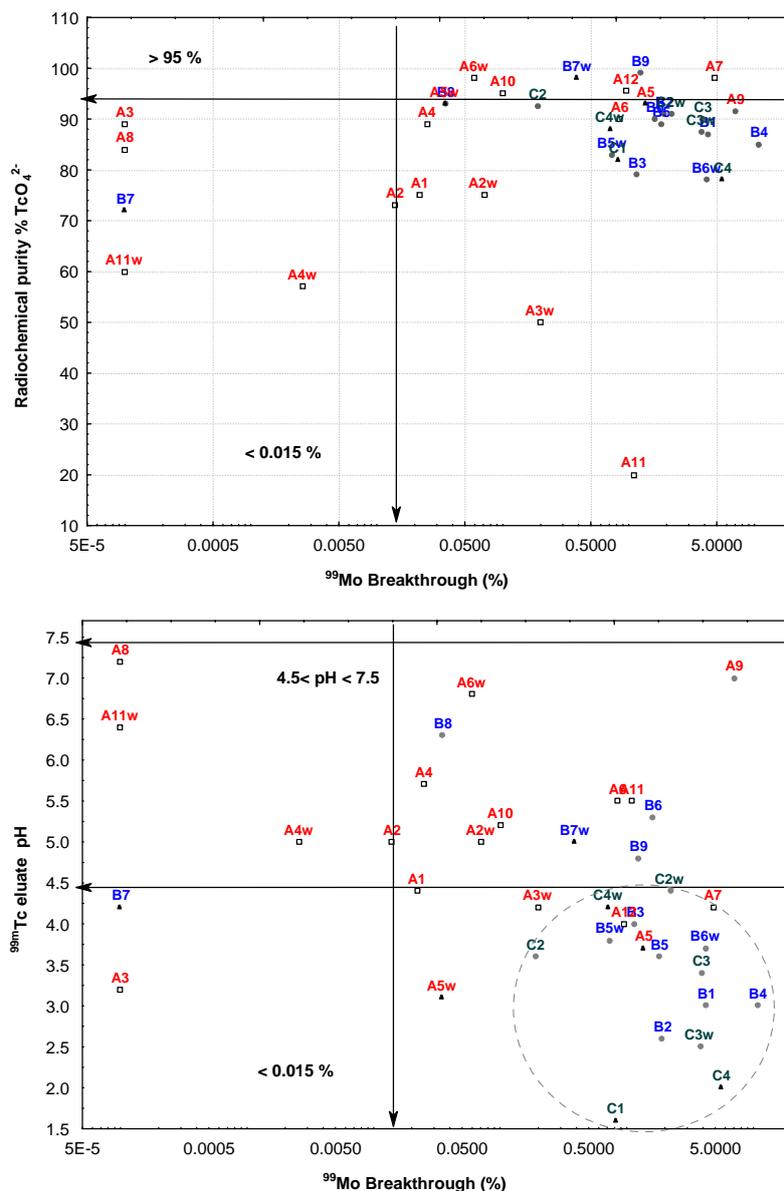


Figure 1. Cont.



^{99m}Tc eluates produced by the generators prepared from $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ solutions (series A) mostly attained the pH values established by the Pharmacopoeia: between 4.5 and 7.5, while higher acid eluates were obtained in the matrices synthesized from $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ solutions. When the Mg proportion was higher than Mo in the Mg:Mo molar ratio, ^{99}Mo breakthrough percentage increased in the ^{99m}Tc eluates and the Mo percentages in the matrix decreased. All ^{99m}Tc eluates of series A were colorless, those prepared from $\text{MgNO}_3 \cdot 6\text{H}_2\text{O}$ solutions at pH 10 or adding the ammonium molybdate solutions to magnesium salts (series B) presented a yellow coloration, while some of series C eluates showed a yellow coloring or a blue precipitate, in fact only the ^{99m}Tc eluates obtained from generator prepared with 0.1 mol/L $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ solutions were colorless.

2.2. Characterization of Magnesium Molybdate Compounds

Crystalline phases identified by XRD (see Table 1 and Figure 2a) showed that the type of magnesium salt used in preparing generator matrices determines their chemical composition. In accordance with these data, Mg-Mo compounds prepared from $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ solutions are mainly constituted of: (a) $\text{NH}_4\text{MgCl}_3 \cdot 6\text{H}_2\text{O}$, MoO_3 and $\text{NH}_3(\text{MoO}_3)_3$; (b) amorphous compounds and unidentified crystalline phases and (c) $\text{NH}_4\text{MgCl}_3 \cdot 6\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and amorphous compounds, respectively. These results are congruent with the thermogravimetric and infrared spectra shown in Figures 2b which present a characteristic pattern for each magnesium salt used. The thermal decomposition step multiples of different matrices prove the presence of compound mixtures. In series A, it is possible to identify five main causes for weight-loss, firstly water elimination of ammonium magnesium chloride hydrate ($\sim 116^\circ\text{C}$), later the transformation of NH_4MgCl_3 in $\text{Mg}(\text{OH})\text{Cl}$ and NH_4Cl ($160\text{--}170^\circ\text{C}$), after NH_4Cl decomposition ($\sim 220^\circ\text{C}$), the formation of MgO from $\text{Mg}(\text{OH})\text{Cl}$ ($350\text{--}550^\circ\text{C}$) and finally the decomposition of MoO_3 ($770\text{--}800^\circ\text{C}$) [8,16]. Three weight-losses are evident in the series B at 214 , 330 y 770°C which could be derived from NH_3Cl , $\text{Mg}(\text{OH})$ and MoO_3 decomposition respectively considering that amorphous materials and the unidentified phases (Figure 2b) are constituted by Mo , Mg , NO_3^- , NH_3 and Cl and making an analogy with the compounds formed in series A. In the case of series C, the weight-loss is fixed by the $\text{NH}_4\text{MgCl}_3 \cdot 6\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and amorphous molybdenum compound decomposition (see Table 1 and Figure 2b): dehydration ($96\text{--}130^\circ\text{C}$), elimination of $[\text{NH}_4^+]$ in NH_4MgCl_3 (167°C) and $(\text{NH}_4)_2\text{Mg}(\text{SO}_4)_2$ (451°C), decomposition of NH_4Cl ($\sim 237^\circ\text{C}$), formation of MgO ($300\text{--}400^\circ\text{C}$) and decomposition of MoO_3 (756°C) [16].

The effect of magnesium salt on forming different magnesium-molybdenum compounds during generator matrices preparation was also demonstrated by infrared analysis shown in Figure 2c. The matrix spectra prepared using $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ solutions have similar troughs in the $3500\text{--}1200\text{ cm}^{-1}$ region, but with differences in band intensities.

Figure 2. Magnesium salt effect used in the preparation of magnesium-molybdates in (a) X-ray diffraction patterns, (b) thermograms and (c) infrared spectra.

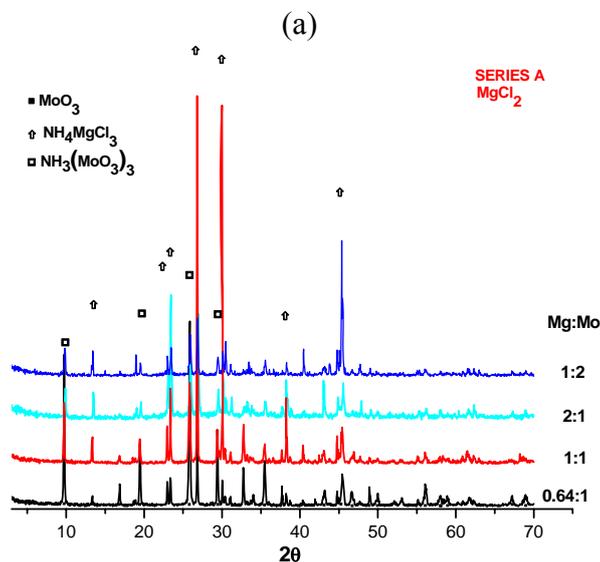
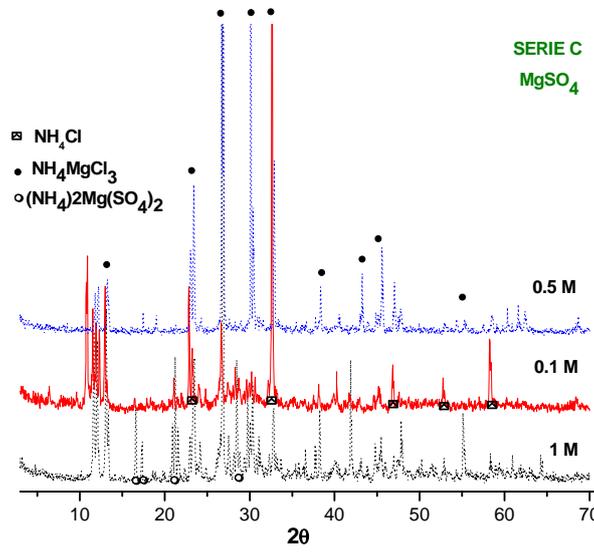
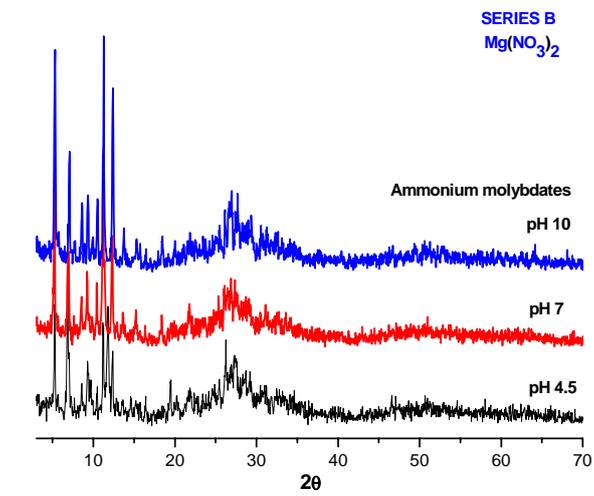


Figure 2. Cont.



(b)

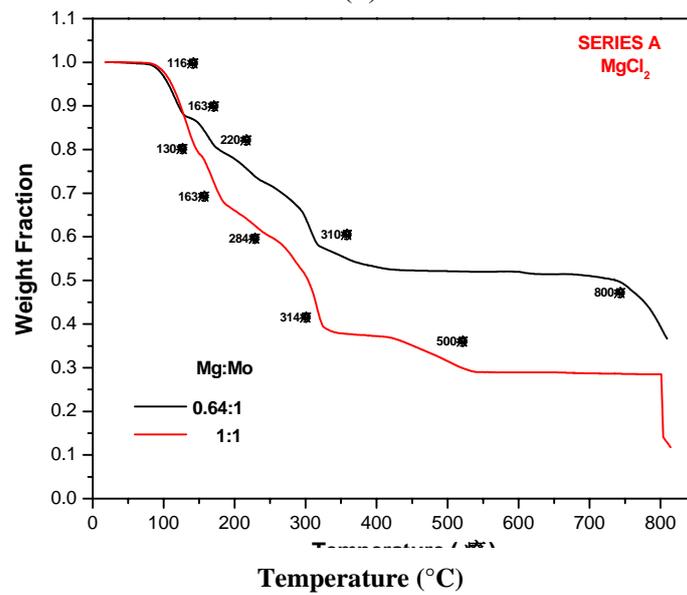
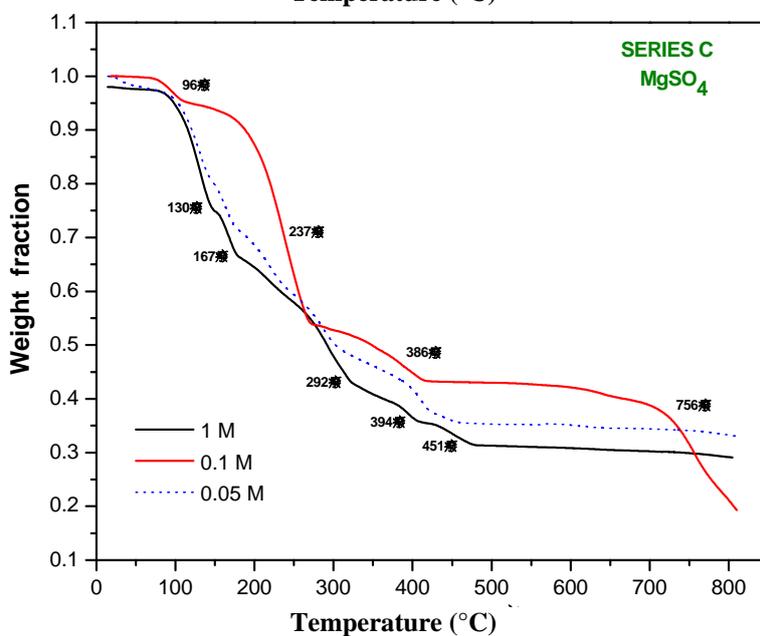
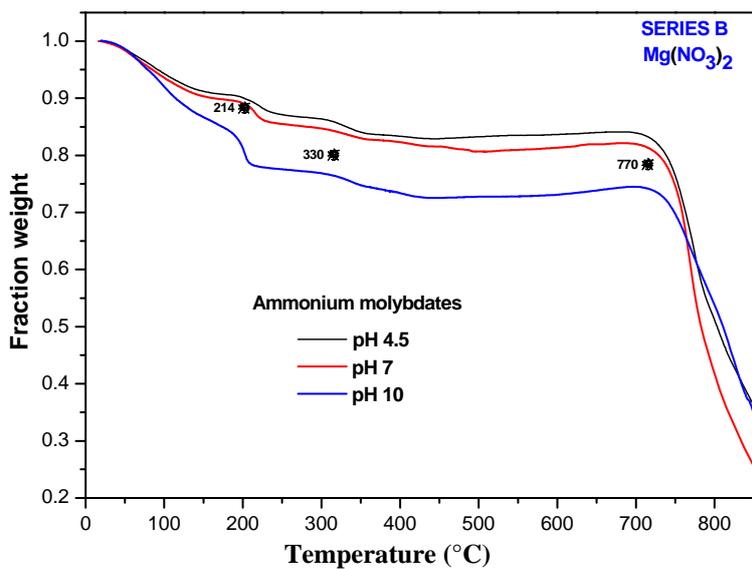
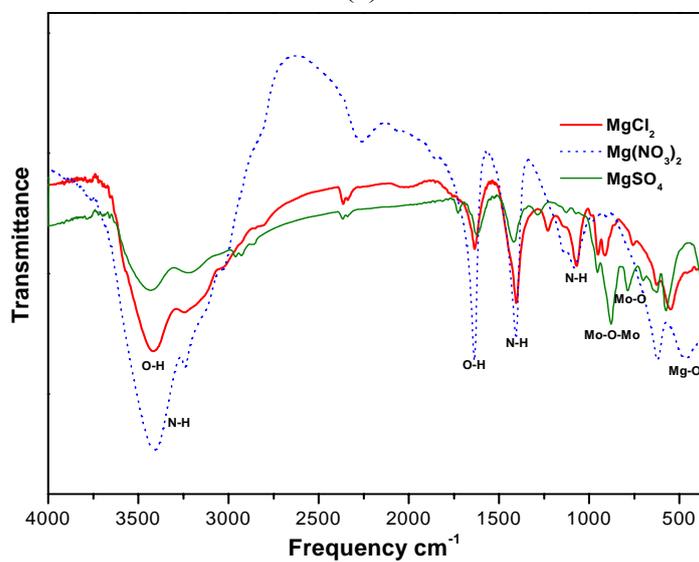


Figure 2. Cont.



(c)



In this region, ammonium and water displays strong broad N-H and O-H stretching bands between 3500 and 3300 cm^{-1} and bands at 1405 and 1640 cm^{-1} respectively [8,17-18]; while significant differences in intensities and wavenumber values and of each matrix were noted in fingerprint region (1200–400 cm^{-1}). All matrices spectra exhibit characteristic absorption bands of Mo-O-Mo vibration at 960, 910 cm^{-1} and N-H bonds at 1075 and 1220 cm^{-1} as well as a band at 620 cm^{-1} possibly originated from Mg vibrations [8,18-19]. Only the matrix prepared from $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ presented broad bands at around 470 cm^{-1} attributed to Mg-O bonds [19], and that from $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ showed characteristic bands assigned to $[\text{SO}_4^{2-}]$ (628, 700, 1075, 1130, 1287 cm^{-1}) and Mo-O vibrations at 792 and 880 cm^{-1} whereas that from $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ presented peaks 760 and 545 cm^{-1} assigned to the Mo-O vibrations and possibly to Mg-Cl bonds respectively [8,18-19].

The X-ray diffraction patterns and thermograms of a typical matrix washed and unwashed are shown in Figure 3a and 3b. The diffractograms show that the washed matrix before irradiation is constituted only by MoO_3 and the unwashed one by a mixture of MoO_3 and $\text{NH}_4\text{MgCl}_3 \cdot 6\text{H}_2\text{O}$. These data match with thermograms of the washed and unwashed matrix which have typical patterns of pure and mixed compounds respectively. Thus, washed matrices before irradiation cause soluble compounds to be removed, mainly those containing ammonium and magnesium in the matrix and conversion of the molybdenum compounds in MoO_3 . It is important to note that this behavior is independent of the type of magnesium salt used in preparing the matrix (Table 1).

The effect of matrix washing on morphology is shown in Figure 3c. The unwashed matrices present a crystalline phase soaked in an amorphous material, and the washed matrices only have the crystalline phase, constituted by rods of different thicknesses and length.

Figure 3. Generator matrix washing effect on (a) X-ray diffraction patterns; (b) thermograms and (c) morphology.

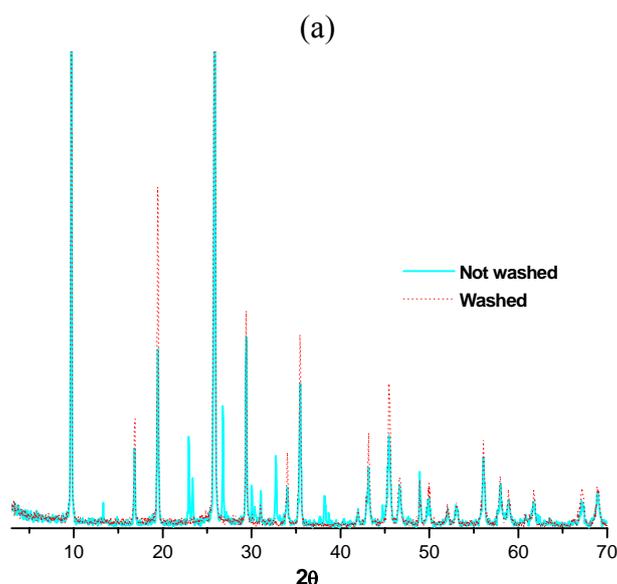
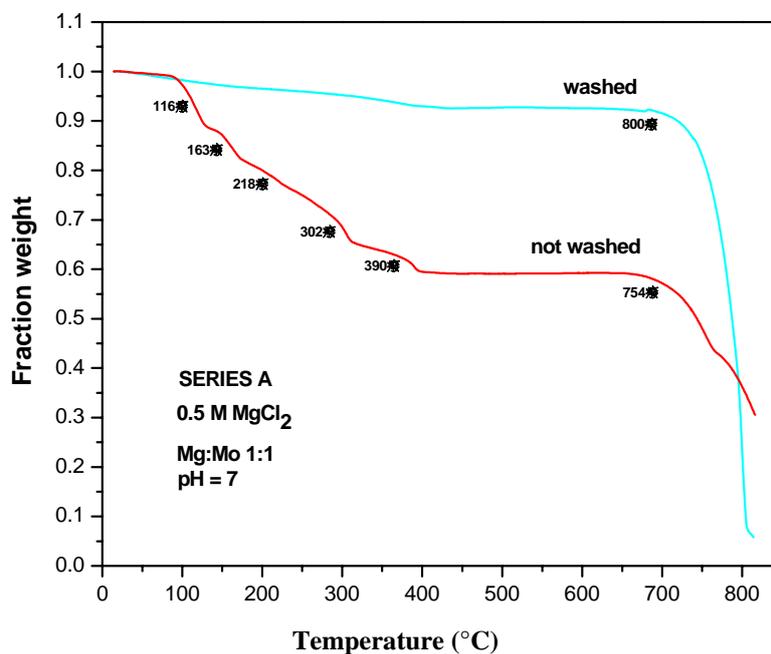
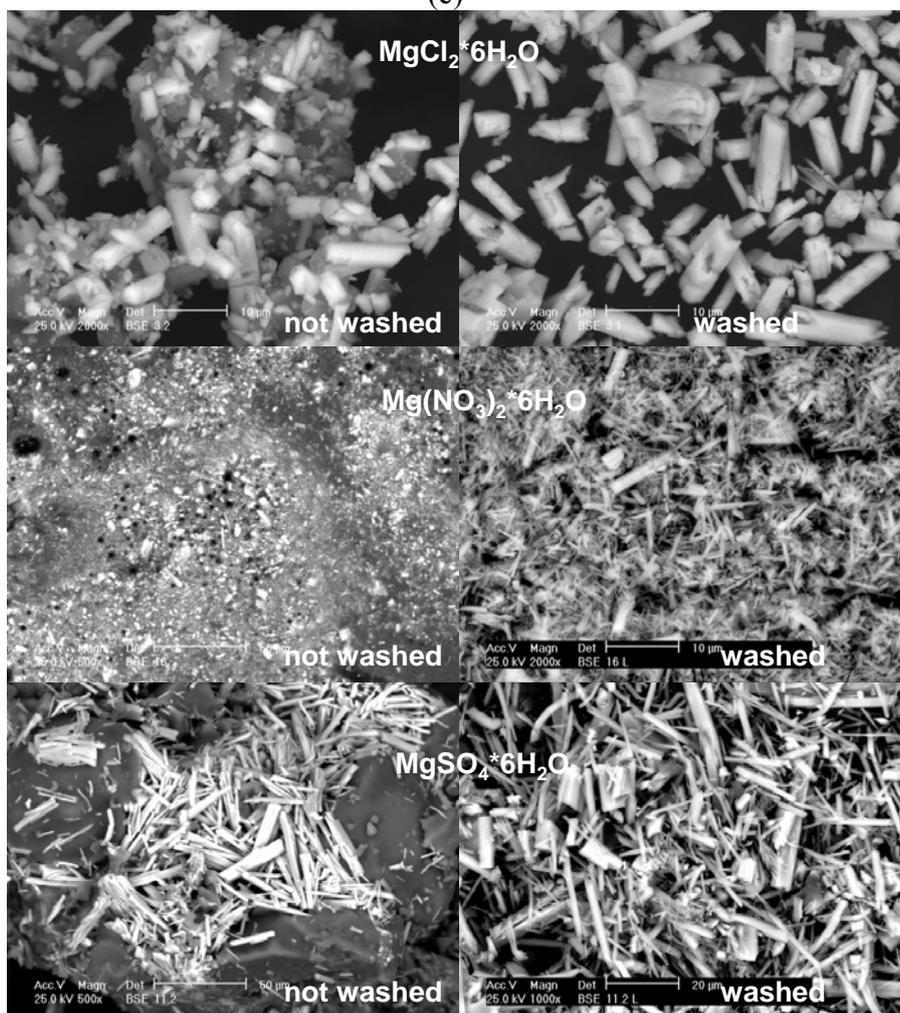


Figure 3. Cont.

(b)



(c)

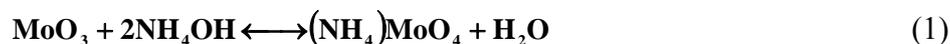


2.3. Discussion

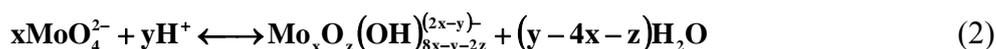
The performance of the $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$ generators based on magnesium-molybdate compounds depends upon matrix preparation and treatment methods. The latter has to be an insoluble precipitate to avoid ^{99}Mo leakage, whilst simultaneously allowing $^{99\text{m}}\text{Tc}$ release, and have a high Mo content that enables the use of low specific activities of ^{99}Mo (2.5 Ci/g) in the generator and a good thermal and radiation stability.

Magnesium molybdate is fairly soluble in water [20-21] and literature has reported obtaining magnesium molybdate precipitates, mainly used in catalysis, applied suitable thermal treatments and magnesium and molybdate concentrations. For example, Yoon *et al.* have reported magnesium molybdates precipitation from $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $(\text{NH}_4)_3\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ solutions and calcining at different temperatures (200–650 °C) [19]. Ozeki *et al.* prepared magnesium molybdate solids by concentrating a mixed solution of 0.1 mol/L sodium molybdate and 4.5 mol/L magnesium chloride [20]. Amber *et al.* obtained $\text{MgMoO}_4 \cdot \text{H}_2\text{O}$ from 0.1 mol/L Na_2MoO_4 and 0.5 mol/L MgCl_2 solutions at pH 6 treated at 155 °C for 3 days [22].

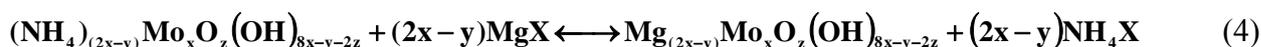
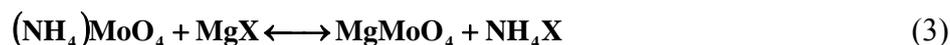
In this work, insoluble magnesium molybdate compound precipitation was favored by adjusting pH and irradiation, and not by thermal treatment. Under these experimental conditions, magnesium molybdate compounds obtained were mainly polymetalates salts such as $x\text{NH}_4\text{MgCl}_3 \cdot y\text{MoO}_3$, and polymolybdates $[\text{NH}_4\text{Mo}_5\text{O}_{15}(\text{OH})]$ (see Figure 2 and Table 2). Assuming that compound formation is the result of three steps, firstly the formation of ammonium molybdates according to reaction (1):



The molybdate ion generally exists as MoO_4^{2-} in alkaline or neutral solutions (pH > 6) while polymolybdate ions such as $[\text{Mo}_7\text{O}_{24}]^{6-}$, $[\text{Mo}_8\text{O}_{26}]^{4-}$, $[\text{Mo}_{36}\text{O}_{112}]^{8-}$ are formed in acid solutions [19,23-27]:

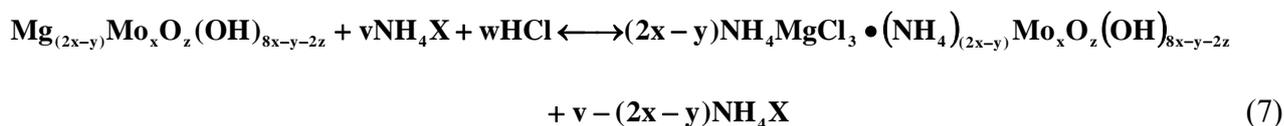


Thus the ammonium molybdate solutions prepared at pH 10 and 7 contain simply MoO_4^{2-} ions and those at pH 4.5 a mixture of polymolybdate ions where the predominant species is probably the $[\text{Mo}_7\text{O}_{24}]^{6-}$ ion [18]. In the second step, ammonium molybdates react with magnesium solutions to form magnesium-molybdates solutions. Considering these solutions pH values can vary between 8 and 4.3, the magnesium molybdates can be constituted by MoO_4^{2-} (pH > 6) or polymolybdates (pH < 6) according to:



In the last step, the magnesium molybdates are induced to precipitate by adjusting pH values of the solutions to be between 1.9 and 0.3. At pH < 2, literature has reported the presence of very large polymolybdate species like $[\text{Mo}_{36}\text{O}_{112}]^{8-}$ [23,25] or $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$ precipitation [19,28-29]. X-ray

diffraction data (see Table 2 and Figure 2) suggests polymetalates formation such as $x\text{NH}_4\text{MgCl}_3 \cdot y\text{MoO}_3$ or polymolybdates according to:



The Cl^- ion usually displaces NO_3^- and SO_4^{2-} ions [30] when magnesium nitrate and sulfate are employed in preparing magnesium molybdates; for that reason ammonium magnesium chlorides (NH_4MgCl_3) were present in all the series studied (see Table 2 and Figure 2), however mixtures of NH_4MgCl_3 and $(\text{NH}_4)_2\text{Mg}(\text{SO}_4)_2$ were also identified in matrices prepared from magnesium sulfates.

An excess of molybdenum favors polymolybdates and formation of amorphous phases whereas a surplus of magnesium the presence of ammonium magnesium salts and crystalline phases. Thus, the crystallinity degree of the compounds contained in the matrix is closely attached to $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$ generator performances. For example amorphous matrices presented the best $^{99\text{m}}\text{Tc}$ elution efficiencies (series B) while the crystalline (series A) presented lower ^{99}Mo breakthrough (see Table 1, Figure 1). Assuming that amorphous materials also consist of molybdenum oxides or polymolybdates and that the oxides and hydrous oxides of Mo(VI) exhibit cation exchange properties and show little or no anion exchange character even in acid solution [31] and ammonium magnesium salts have no adsorption properties, so the separation mechanism of the ^{99}Mo and $^{99\text{m}}\text{Tc}$ in the generators can be explained by free diffusion of $^{99\text{m}}\text{TcO}_4^-$ ion inside the matrix because the $^{99\text{m}}\text{TcO}_4^-$ anion produced in the generator is not adsorbed in the matrix and can be removed from the chromatographic column by elution with isotonic saline solution, leaving the ^{99}Mo inside. In accordance with this argument, a crystalline matrix acts as a molecular sieve preventing $^{99\text{m}}\text{Tc}$ mobility and causing generator efficiency decrease. Whereas a flexible random network (amorphous) increases generator efficiency and radiochemical purity because the matrix is more elastic but simultaneously harder and more resistant to mechanical breakdown and more difficult to dissolve. The low $^{99\text{m}}\text{Tc}$ eluate radiochemical purities obtained in some generators can be explained by Tc(VII) reduction caused by the presence of insoluble species of polymolybdates, which are strong oxidizing agents [18].

Inorganic materials are susceptible to irradiation-induced amorphization producing particularly volume changes in crystalline or amorphous phases. The main concern with large differential volume changes is that it may affect atomic bonding, local coordination, and the pathways for ion exchange, all of which can impact the release rates of radionuclides [32]. Thus the matrix amorphization caused by its irradiation could be linked to the high ^{99}Mo breakthrough obtained in generators for which matrices are mainly formed by amorphous compounds such as the series B and C.

3. Experimental

3.1. Preparation of Magnesium ⁹⁹Mo-Molybdate Compounds

Magnesium ⁹⁹Mo-molybdate compounds were formed from magnesium and molybdate solutions. The molybdate solutions were prepared from MoO₃ natural pellets, previously heated to 650 °C for 1 h and dissolved in 2 mol/L NH₄OH at a MoO₃:2NH₄OH molar ratio [8]. The pH of the formed ammonium molybdates was adjusted by adding 4 mol/L HCl and converted into magnesium molybdate by reacting with magnesium solutions. Magnesium molybdates pH were also adjusted using 4 mol/L HCl. The resulting solids were dried for 2 days using an infrared lamp and crushed in an agate mortar. One portion of magnesium molybdate precipitate was placed on a funnel to be washed using 200 mL of distilled water and the washed and unwashed solids were dried for 1 day at 40 °C in a stove. The dried magnesium molybdate were irradiated for 2 h at a neutron fluence of about $1.61 \times 10^{13} \text{ n cm}^{-2} \text{ s}^{-1}$ in the Triga Mark III Reactor (Mexico). After irradiation, about 1 g of magnesium ⁹⁹Mo-molybdate (~4.9 MBq/g) were added into a glass column (12 mm × 70 mm) containing a bed of 1 g acid alumina. The column was finally washed with 20 mL of saline solution [8,17-18]. The magnesium molybdate compounds were synthesized in duplicate at different conditions; where parameters such as magnesium salts and concentrations (MgCl₂·6H₂O, Mg(NO₃)₂·6H₂O, MgSO₄·6H₂O), Mo:Mg molar ratios, ammonium and magnesium molybdates pH and the addition order of magnesium and molybdenum solutions were evaluated (see Table 2).

3.2. Elution of Generators and Eluate Analysis

The generators were eluted with 6 mL of 0.9% NaCl every 24 h for 1 week and the following parameter of the ^{99m}Tc eluates were determined: ^{99m}Tc elution efficiency, ⁹⁹Mo breakthrough, ^{99m}Tc elution profile, ^{99m}Tc radiochemical purity, pH eluate and aluminium concentration. The ^{99m}Tc elution efficiency and the ⁹⁹Mo breakthrough were calculated from the ^{99m}Tc and ⁹⁹Mo activities measured in a CRC-10R Capintec dose calibrator and a GeHp solid state detector (Canberra 7229P) coupled to a PC-multichannel analyzer (ACUSPECT-A, Canberra, Australia). The radiochemical purity of the ^{99m}Tc eluate was determined by paper chromatography using 1 CHR (Whatman®) paper as solid phase and 85% methanol as mobile phase. The ^{99m}TcO₄⁻ R_f was 0.66–0.72. Aluminium and magnesium concentrations in ^{99m}Tc eluates were determined by the aluminon and Eriochrome Black T methods [18,33]. The eluate pH values were determined by pH paper.

3.3. Gel Characterization

Magnesium-molibdate compounds were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), infrared spectrometry, thermogravimetry and neutron activation analysis. The X-ray diffraction patterns were obtained on a Siemens D500 diffractometer for 1 h and scanned from 2.5° to 70° with steps of 0.02°. SEM imaging was performed by Philips SL30. Digital images were obtained at 5,000X, 3,000X, 1,000X and 500X magnifications in randomly selected fields. The infrared measurements were taken on a Nicole Mgna-IRTM spectrometer 550 with the samples pressed in KBr pellets. The thermogravimetric analyses were performed using a Phillips unit at a heating rate

of 10°/min under a nitrogen atmosphere [8,18]. Molybdenum and magnesium concentrations were determined by neutron activation. The procedure described in previous works was applied for molybdenum and in the case of magnesium, 50 mg of each magnesium molybdate and MgO, used as reference material, were irradiated in the Triga Mark II reactor at a neutron fluence of about $1.65 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$ for 15 s. Magnesium was determined by the 843.4 keV γ -ray of ^{27}Mg by means of a HPGe detector at a counting time of 100 s [13].

Table 2. Preparation conditions of magnesium molybdate compounds.

Series	pH Ammonium molybdates	Mg:Mo	[MgCl ₂ ·6H ₂ O] mol/L	[MgCl ₂ ·6H ₂ O] pH	pH Magnesium molybdate	Addition order
A1	7	0.64:1	0.5	0.72	0.05	Mg(NO ₃) ₂ → [MoO ₄ ²⁻]
A2	7	0.93:1	0.5	0.72	0.49	Mg(NO ₃) ₂ → [MoO ₄ ²⁻]
A3	7	1.08:1	0.5	5.9	0.3	Mg(NO ₃) ₂ → [MoO ₄ ²⁻]
A4	7	1.18:1	0.5	0.1	0.5	Mg(NO ₃) ₂ → [MoO ₄ ²⁻]
A5	7	2:1	1	5.9	1.2	Mg(NO ₃) ₂ → [MoO ₄ ²⁻]
A6	7	2:1	0.5	0.7	0.4	Mg(NO ₃) ₂ → [MoO ₄ ²⁻]
A7	7	1:1	0.5	0.7	0.5	Mg(NO ₃) ₂ → [MoO ₄ ²⁻]
A8	7	1:2	0.5	0.7	0.6	Mg(NO ₃) ₂ → [MoO ₄ ²⁻]
A9	7	1:2	0.1	0.7	0.7	Mg(NO ₃) ₂ → [MoO ₄ ²⁻]
A10	4.5	2:1	0.5	0.7	0.6	Mg(NO ₃) ₂ → [MoO ₄ ²⁻]
A11	4.5	1:2	0.5	0.7	1.8	Mg(NO ₃) ₂ → [MoO ₄ ²⁻]
A12	4.5	1:1	0.5	0.7	1.6	Mg(NO ₃) ₂ → [MoO ₄ ²⁻]
Series	pH Ammonium molybdates	Mg:Mo	[Mg(NO ₃) ₂ ·6H ₂ O] mol/L	pH [Mg(NO ₃) ₂ ·6H ₂ O]	pH Magnesium molybdate	Addition order
B1	7	0.2:1	0.1	5.5	1.1	Mg(NO ₃) ₂ → [MoO ₄ ²⁻]
B2	7	0.2:1	0.1	5.5	0.7	[MoO ₄ ²⁻] → Mg(NO ₃) ₂
B3	4.5	0.2:1	0.1	5.5	0.9	Mg(NO ₃) ₂ → [MoO ₄ ²⁻]
B4	4.5	0.2:1	0.1	5.5	0.9	[MoO ₄ ²⁻] → Mg(NO ₃) ₂
B5	10	0.2:1	0.1	5.5	1.0	Mg(NO ₃) ₂ → [MoO ₄ ²⁻]
B6	10	0.2:1	0.1	5.5	0.9	[MoO ₄ ²⁻] → Mg(NO ₃) ₂
B7	7	1:1	1	5.5	0.1	Mg(NO ₃) ₂ → [MoO ₄ ²⁻]
B8	4.5	1:2	0.1M	5.5	1.0	Mg(NO ₃) ₂ → [MoO ₄ ²⁻]
B9	4.5	2:1	0.1M	5.5	1.9	Mg(NO ₃) ₂ → [MoO ₄ ²⁻]
Series	pH Ammonium molybdates	Mg:Mo	[MgSO ₄ ·6H ₂ O] mol/L	pH [MgSO ₄ ·6H ₂ O]	pH Magnesium molybdate	Addition order
C1	4.5	2:1	1	5.4	1.0	Mg(NO ₃) ₂ → [MoO ₄ ²⁻]
C2	4.5	2:1	0.1	5.4	0.6	Mg(NO ₃) ₂ → [MoO ₄ ²⁻]
C3	4.5	2:1	0.05	5.4	0.9	Mg(NO ₃) ₂ → [MoO ₄ ²⁻]
C4	7	1:1	1	5.4	1.0	Mg(NO ₃) ₂ → [MoO ₄ ²⁻]

4. Conclusions

The performances of ^{99m}Tc generators are strongly related to the chemical composition of the matrix and consequently their preparation conditions. The magnesium molybdate compounds obtained were mainly salts of polymetalates such as $\text{NH}_4\text{MgCl}_3\cdot\text{MoO}_3$, $\text{NH}_4\text{MgSO}_4\cdot\text{MoO}_3$ and polymolybdates $[\text{Mo}_x\text{O}_z(\text{OH})_{8x-y-2z}^{(2x-y)-}]$ crystallized or amorphous. The type of magnesium salt and the Mg:Mo ratio used in the matrix preparation inhibits or favours polymetalate salts and polymolybdates amorphization. Crystalline $\text{NH}_4\text{MgCl}_3\cdot\text{MoO}_3$ were preferably obtained from $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$ solutions while amorphous compounds, probably constituted by polymetalates (see reactions 6 and 7) and unidentified crystalline phases were formed from $\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ solutions and mixtures of crystalline $\text{NH}_4\text{MgCl}_3\cdot\text{MoO}_3$ and $\text{NH}_4\text{MgSO}_4\cdot\text{MoO}_3$ and amorphous phases, also possible formed by polymetalates, were produced from $\text{MgSO}_4\cdot 6\text{H}_2\text{O}$ solutions. An excess of molybdenum or magnesium during the matrix preparation favors amorphous or crystalline phases formation respectively. The degree of ordering of Mg-Mo compounds defines the ^{99m}Tc generators performances: high ^{99m}Tc elution efficiencies were obtained from amorphous matrices while lower ^{99}Mo breakthrough by crystalline matrices. The free $^{99m}\text{TcO}_4^-$ diffusion is proposed as separation mechanism of the ^{99}Mo and ^{99m}Tc in the generators considering that polymetalates act as cation exchanges and the $^{99m}\text{TcO}_4^-$ anion produced in the generator is not adsorbed in the matrix.

$^{99}\text{Mo}/^{99m}\text{Tc}$ generator production based on magnesium- ^{99}Mo molybdate compounds allow reduction of preparation time and eliminates the use of specialized installations. The best generator performances were attained using matrices prepared from 0.1 mol/L $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$ solutions, ammonium molybdate solutions at pH 7 and at a Mg:Mo molar ratio of 1:1.

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References

1. *Technetium-99m Radiopharmaceuticals: Manufacture of Kits*; Technical Reports Series No. 466, IAEA: Vienna, Austria, 2008; pp. 7-21.
2. Verbruggen A.M. Technetium-99m radiopharmaceuticals: Current situation and perspectives. In *Trends in Radiopharmaceuticals (ISTR-2005)*; Proceedings Series, IAEA: Vienna, Austria, 2007; Volume 1, pp. 3-19.
3. Arino, H.; Kramer H.H. Fission product ^{99m}Tc generator. *Int. J. App. Rad. Isot* **1975**, *26*, 301-303.
4. Vandegrift, G.F.; Snelgrove, J.L.; Aase, S.; Bretscher, M.M.; Buchholz, B.A.; Chaiko, D.J.; Chamberlain, D.B.; Chen, L.; Conner, C.; Dong, D.; *et al.* Converting targets and processes for fission-product molybdenum-99 from high -to low-enriched uranium. In *Production technologies for molybdenum-99 and technetium-99m*; IAEA-TECDOC-1065, IAEA: Vienna, Austria, 1999; pp. 25-75.

5. Savushkin I.A.; Gourko, O.B. Tc-99m production on the basis of Central Generator and Wasteless reactor Zr-Mo Gel-Technology. In *Advances in Nuclear and Radiochemistry*. Qaim, S.M., Coenen, H.H., Eds.; Forschungszentrum Julich GmbH: Aachen, Germany, 2004; pp. 336-338.
6. Evans, J.V.; Shying, M.E. *Zirconium Molybdate Gel as a Generator for Technetium-99m*. Australian Atomic Energy Commission, AAEC/E59: Sutherland, Australia, 1984.
7. Vanaja P.; Ramamoorthy, N.; Iyer, S.P.; Mani, R.S. Development of a new ^{99m}Tc generator using neutron irradiated titanium molybdate as column matrix. *Radiochim. Acta*. **1987**, *42*, 49-52.
8. Monroy-Guzmán, F.; Cortes Romerio, O.; Díaz Velásquez, H. Titanium molybdate gels as matrix of ⁹⁹Mo/^{99m}Tc generators. *J. Nucl. Radiochem. Sci.* **2007**, *8*, 11-19.
9. El Absy, M.A.; El Nagar M.; Audah, A.I. Technetium-99m generators based on neutron irradiated 12-molybdocerate as column matrix. *J. Radioanal. Nucl. Chem.* **1994**, *183*, 339-350.
10. El Absy, M.A.; El-Bayoumy, S. The use of stannic molybdate-⁹⁹Mo as a ^{99m}Tc generator. *Isotopenpraxis* **1990**, *26*, 60-63.
11. El Kolaly, M.T. A ⁹⁹Mo/^{99m}Tc generator based on the use of zirconium molybdophosphate-⁹⁹Mo gel. *J. Radioanal. Nucl. Chem.* **1993**, *170*, 293-298.
12. Narasimhan, D.V.S.; Vanaja, K.P.; Mani, R.S. A new method for Tc-99m generator preparation. *J. Radioanal. Nucl. Chem.* **1984**, *85*, 345-356.
13. Monroy-Guzman, F.; Arriola Santamaría, H.; Ortega Álvarez, I.; Cortés Romero, O.; Díaz Archundia, L.V. Determination of Mo, W and Zr in molybdates and tungstates of zirconium and titanium. *J. Radioanal. Nucl. Chem.* **2007**, *271*, 523-532.
14. Monroy-Guzman, F.; Barron Santos E.S.; Hernandez, S. Synthesis installation of zirconium-⁹⁹Mo-molybdate gels to ⁹⁹Mo/^{99m}Tc generator. In *Synthesis and Applications of Isotopically Labelled Compounds*; Dean, D.C., Filer, C.N., McCarthy, K.E., Eds.; Wiley: England, 2004; Volume 8, pp. 325-329.
15. *Farmacopea de los Estados Unidos Mexicanos*, 9th ed.; SSA: Mexico, Mexico, 2008.
16. *Nouveau Traité de Chimie Minérale*, Pascal, P., Ed.; Masson: Paris, France, 1958, Volume IV.
17. Monroy-Guzman, F.; Diaz-Archundia, L.V.; Contreras Ramírez, A. Effect of Zr:Mo ratio on ^{99m}Tc generator performance based on zirconium molybdate gels. *Appl. Rad. Isot.* **2003**, *59*, 27-34.
18. Monroy-Guzmán, F.; Díaz-Archundia, L.V.; Hernández-Cortés, S. ⁹⁹Mo/^{99m}Tc generators performances prepared from zirconium molybdate gels. *J. Braz. Chem. Soc.* **2008**, *19*, 380-388.
19. Yoon, Y.S.; Suzuki, K.; Hayakawa, T.; Hamakawa, S.; Shishido, T.; Takehira, K. Structures and catalytic properties of magnesium molybdate in the oxidative dehydrogenation of alkanes. *Catal. Lett.* **1999**, *59*, 165-172.
20. Ozeki, T.; Murata, K.; Kihara, H.; Hikime, S. Studies on the interaction of molybdate ion and magnesium ion observed in the Raman Spectra of the Mixture Solutions. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3585-3589.
21. Essington, M.E. Formation of calcium and magnesium molybdate complexes in dilute aqueous solutions. *Soil Sci. Soc. Am. J.* **1992**, *56*, 1124-1127.
22. Amberg, M.; Günter, J.R.; Schmalle, H.; Blasse, G. Preparation, crystal structure and luminescence of magnesium molybdate and tungstate monohydrates, MgMoO₄·H₂O and MgWO₄·H₂O. *J. Sol. Stat Chem.* **1988**, *77*, 162-169.

23. Tytko, H.K.; Glemser, O. Isopolymolybdates and isopolytungstates. In *Advances Inorganic Chemistry and Radiochemistry*; Academic Press: NY, USA, 1976; Volume 19, pp. 35-40.
24. Honing, D.S.; Kustin, K. Relaxation spectra of molybdate polymers in aqueous solutions: Temperature-jump studies. *Inorg. Chem.* **1972**, *11*, 65-71.
25. Pope, M.T. *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: NY, New York, 1983; pp. 42-70.
26. Baker, L.C.W.; Glick D.C. Present general status of understanding of heteropoly electrolytes and a tracing of some major highlights in the history of their elucidation. *Chem. Rev.* **1998**, *98*, 3-50.
27. Cruywagen, Y.Y. Potentiometric investigation of molybdenum (VI) equilibria at 25 °C in 1 M NaCl medium. *Inorg. Chem.* **1980**, *19*, 552-554.
28. Sengupta, A.K. A unified approach to interpret unusual observations in heterogeneous ion exchange. *J. Coll. Inter. Sci.* **1988**, *123*, 201-215.
29. Nekovář, P.; Schrötterová, D. Liquid-liquid extraction of Mo(VI) and V(V) by Prime JMT. *J. Radioanal. Nucl. Chem.* **1998**, *228*, 95-98.
30. Jacobson, C.A. Encyclopedia of chemical reactions. *J. Chem. Educ.* **1940**, *17*, 406.
31. Fuller, M.J. Inorganic ion-exchange chromatography on oxides and hydrous oxides. *Chromatogr. Rev.* **1971**, *14*, 45-76.
32. Weber, W.J.; Ewing, R.C.; Catlow, C.R.A.; Díaz de la Rubia, T.; Hobbs, L.W.; Kinoshita, C.; Matzke, H.J.; Motta, A.T.; Nastasi, M.; Slje, E.K.H.; Vance, E.R.; Zinkle, S.J. Radiation effects in crystalline ceramics for the immobilization of high-level nuclear waste and plutonium. *J. Mater. Reser.* **1998**, *13*, 1434-1484.
33. Sandell, E.B.; Onishi, H. *Photometric Determination of Traces of Metals*; Wiley: NY, USA, 1978.

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