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Article

^{99}Mo/^{99m}Tc Generators Performances Prepared from Zirconium Molybate Gels

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^{99m}Tc pode ser produzido a partir de géis geradores de molibdato de zircônio contendo ^{99}Mo/^{99m}Tc. Estes géis são parte da matriz geradora e suas características físicas e químicas influenciam diretamente o desempenho do gerador. Neste trabalho, géis molibdato de zircônio foram sintetizados sob diferentes condições e caracterizados por análise termogravimétrica, espectroscopia de infravermelho e análise por ativação neutrônica instrumental (INAA). Nosso objetivo foi investigar e correlacionar o desempenho do gerador com as propriedades físico-químicas do gel. Os dois fatores estudados foram o pH da solução de molibdato e as condições de preparação das soluções do sal de zircônio. Diversas espécies de polimolibdato e zircônio podem ser formadas em solução, as quais podem inibir ou favorecer a formação do gel molibdato de zircônio ou as fases rica em polimolibdato (insolúvel) e de oxi-hidróxido de zircônio. O desempenho do gel gerador ^{99}Mo/^{99m}Tc está diretamente correlacionado com as estruturas do gel. Sistemas mais regulares apresentam desempenho gerador mais baixo se comparados com arranjos mais flexíveis e aleatórios. As propriedades físico-químicas dos géis, bem como seu comportamento como gerador de tecnécio-99m são apresentados e discutidos.

^{99m}Tc may be produced from ^{99}Mo/^{99m}Tc zirconium molybdate gel generators. These gels are part of the generator matrix and their chemical and physical characteristics directly influence the generator performances. In this work zirconium molybdate gels were synthesized under different preparation conditions and characterized by TGA, IR and INAA. Our goal was to investigate and correlate generator performance with the physical-chemical properties of the gel. The two factors studied were the molybdate solution pH and the preparation conditions of the zirconyl salt solutions. Several polymolybdate and zirconium species can be formed in solution which can inhibit or favor the zirconium molybdate gel formation or the insoluble polymolybdate-rich and zirconium oxy-hydroxide phases. The ^{99}Mo/^{99m}Tc gel generator performance is directly correlated with gel structures. More regular network gels present lower generator performances compared to gels with more flexible random framework. The physico-chemical properties of the gels as well as their behavior as technetium-99m generators are presented and discussed.

Keywords: ^{99m}Tc gel generator, zirconium molybdate

Introduction

^{99m}Tc is widely used as diagnostic agent in nuclear medicine and is generally produced by generator systems, where the ^{99}Mo is normally adsorbed onto an alumina column. The less strongly bound $^{99m}TcO_4^-$ is eluted with isotonic saline solutions at intervals. Nevertheless, these generators present an inherent disadvantage, because of the limited adsorption capacity of alumina for Mo(VI) that requires the use of very high specific activity of ^{99}Mo isolated from uranium fission products (~10^3 TBq g^{-1}).[1,2] To avoid this drawback, alternative methods of generator preparation using low or medium specific activities have been proposed and developed.[2,3] In particular, the incorporation of ^{99}Mo into insoluble precipitates is the most well studied approach. Heteropolyanions formed by the interaction of isopolymolybdates with atoms like zirconium, titanium, cerium, thorium, tin, etc. have been examined.[2,4-7] Using this approach the content of Mo is about 30 % inside the matrix of the generator and it is possible to use low or medium specific activity ^{99}Mo produced by neutron activation of ^{98}Mo (50-500 GBq g^{-1}).[2,8]

The properties of these generators depend basically upon the preparation conditions of ^{99}Mo-heteropolymolybdates. Factors such as the pH, the X:Mo (X = heteroatom, Zr, Ti, Th, etc.) molar ratios, Mo and Zr solution concentrations,

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the order of reactive addition, the drying temperature of the final product, etc., must be carefully studied and determined to reproduce the properties of the gel generators.[2,9] In order to find alternatives of ^{99m}Tc generator production, efficient and easy to manufacture, our laboratory has developed and evaluated the zirconium molybdate gel and its effect on generator performances.[9,10] In this work, we have studied the pH of molybdate solutions and the preparation conditions of zirconyl salt solutions used to synthesize the zirconium molybdate gels and its effect on generator performances and on the physico-chemical properties of the gel. These factors have previously only been studied by Evans and Shying,[2] who detected a decrease on the generator efficiency as the pH of molybdate solutions diminish and when the pH of zirconium oxynitrate solutions is less then 0.95. However, these authors did not present an interpretation of their results in connection with the chemistry of the reactant solutions. Our study thus has two aims: (*i*) to control the preparation of the molybdate and zirconyl solutions to obtain gels with consistent properties and (*ii*) to establish the connection between the chemistry of the reactant solutions, the physico-chemical properties of the gel and the generator performances.

Experimental

Preparation of gels

Three series of experiments were performed, in the first study, solutions of ^{99}Mo-molybdate having six different pH were evaluated. In the second experiment the zirconyl solution concentration was varied. In the third experiment the zirconyl solutions were prepared at different ageing times. Each experiment was performed by duplicated. All the gels were prepared at 1:1 Zr:Mo molar ratio (Table 1). The ^{99}Mo-molybdate solutions were obtained by thermal neutron irradiation of natural MoO_3 targets, previously heated to 650 °C for 1 h, at a neutron fluency rate of 1.61×10^{12} n cm^{-2} s^{-1} for 3 hours in the Triga Mark III reactor (Mexico). The $^{99}MoO_3$ was then dissolved in 2 mol L^{-1} NaOH and the pH of ^{99}Mo-molybdate solution was then adjusted using 4 mol L^{-1} HCl. The zirconium ^{99}Mo-molybdate gels were prepared by addition of zirconyl chloride (80 drops min^{-1}) to ^{99}Mo-molybdate solution. The gel was stirred for 10 min, its pH adjusted at 4.5 with 2 mol L^{-1} NaOH and at once air dried (< 70 °C) for about 6 hours. The dried gel was finally ground by means of water and stir to pulverize it. The gel (~ 2 g) was transferred to a glass chromatographic column (12 mm x 70 mm), packed previously with 1 g of alumina, and washed with 50 mL saline solution. The column was eluted every 24 hours using 0.9 % NaCl for 8 days. Table 1 shows the preparation conditions of zirconium-^{99}Mo-molybdate gels for each series.

Elution of generators and eluate analysis

Elution profiles were obtained by collecting fractions of 250 μL. The ^{99}Mo and ^{99m}Tc activities were measured in a CRC-10R Capintec dose calibrator and a HPGe solid state detector (Canberra 7229P) coupled to a PC- multichannel analyzer (ACUSPECT-A, Canberra). The radiochemical purity of the ^{99m}Tc eluate, that is the proportion of the total activity of the ^{99m}Tc like $^{99m}TcO_4^-$ pertechnetate ion, was determined by paper chromatography using 1 CHR (Whatman®) paper as solid phase and 85% methanol as mobile phase. The $^{99m}TcO_4^-$ R_f was 0.66-0.72. Chemical purity of eluates was determined by the arsenazo III method for zirconium and by Plasma Spectroscopy for aluminium.

Gel characterization

All of gels were characterized by thermogravimetry, infrared spectrometry and neutron activation analysis. The thermogravimetric analyses were performed using a Phillips unit at a heating rate of 10 °C min^{-1} under a nitrogen atmosphere. The infrared measurements were taken on a Nicolet Magna-IR^{Tm} spectrometer 550 with the samples pressed in KBr pellets.[9] The gel concentrations of zirconium and molybdenum were determined by means of neutron activation analysis (NAA).[8]

Table 1. Preparation conditions of zirconium ^{99}Mo-molybdate gels

Serie*	pH of ^{99}Mo-Molybdates	Concentration $ZrOCl_2.8H_2O$ / (mol L^{-1})	Ageing time $ZrOCl_2.8H_2O$	Molar ratio Zr:Mo	pH of gel
1	1.0, 2.8, 3.8, 4.5, 6.0, 7.0	0.1	1 day	1 : 1	4.5
2	4.5	0.045, 0.10, 0.5	1 day	1 : 1	4.5
3	4.5	0.1	1 h,1, 2 days	1 : 1	4.5

*Each experiment was performed by duplicated.

Results and Discussion

^{99}Mo/^{99m}Tc Generators on zirconium ^{99}Mo-molybdate gels

Elution profiles

Figure 1 summarizes the elution profiles of the gels prepared with the ^{99}Mo-molybdate solutions at six different pH values (1, 2.8, 3.8, 4.5, 6 and 7) and 0.1 mol L^{-1} $ZrOCl_2.8H_2O$ solutions (series 1). These graphs present the average data of seven elution profiles performed on each generator. The required elution volumes to extract the ^{99m}Tc from the generators prepared with ^{99}Mo-molybdate solutions at pH = 1 and 6 were about 4.7 and 7.2 mL, respectively (Table 2 and Figure 1). In the case of the series 2 data, the elution profiles of all gels look very similar to those of the series 1. All of them required between 4.2 to 4.5 mL of 0.9 % NaCl solution to elute the ^{99m}Tc. The $ZrOCl_2.8H_2O$ concentration variation apparently does not effect on the gel elution profiles. As for the gels prepared with zirconyl solutions at different ageing times (series 3), the highest elution volume (4.1- 4.3 mL) was obtained in the prepared gel with 0.1 mol L^{-1} $ZrOCl_2.8H_2O$ solution aged for 1 h, however this gel presented also the narrowest elution profile. The gels aged for 1 and 2 days required between 3.8 to 4 mL of 0.9 % NaCl solution, showing similar elution profiles. These results show that the ageing time of the zirconyl solutions in gel preparation do not have apparently an important effect on the generator elution volume. However, the elution profiles suffer slight variations on the broad curves. A broad elution curve means a more retention of the $^{99m}TcO_4^-$ in the gel.

Gel generator performances

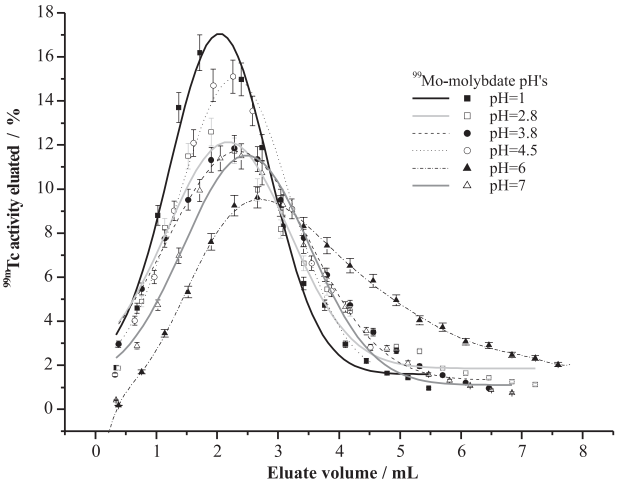

Figure 1. Effect of the pH of ^{99}Mo-molybdate solutions on the elution curves in zirconium molybdate generators.

The performances of the gel generators: elution efficiency, ^{99}Mo breakthrough (radionuclide purity) and radiochemical purity are summarized in Table 2. The results present the average data of the two generators performed for each experimental condition. Elution efficiency is the proportion of ^{99m}Tc produced in the generator that is recovered during the eluation and the percentage of the ^{99}Mo breakthrough is the proportion of the total radioactivity in the eluate that is present as ^{99}Mo.

In the series 1, the elution efficiency increased as more basic ^{99}Mo-molybdate solutions were used to prepare the gels. A maximum elution efficiency was attained using ^{99}Mo-molybdate solutions at pH = 4.5 (81 %). After this pH, the ^{99m}Tc elution efficiencies decreased until 67 % for the gels prepared with ^{99}Mo-molybdate solutions at pH = 7. The lowest elution efficiencies were obtained on the gels prepared with ^{99}Mo-molybdate solutions at pH = 6 and 7. In the case of the $ZrOCl_2.8H_2O$ concentration variation (series 2), the highest efficiency was obtained in the gel prepared with a 0.1 mol

Table 2. *Performance of ^{99}Mo/^{99m}Tc gel generators based on zirconium ^{99}Mo-molybdate

Molybdate pH	$ZrOCl_2.8H_2O$ / (mol L^{-1})	Ageing time $ZrOCl_2.8H_2O$	Elution Volume / mL	Efficiency	Mo % breakthrough	^{99m}Tc Radio-chemical purity / (%)	Zirconium / (μg mL^{-1})	Aluminum / (μg mL^{-1})	eluate pH	% Mo In gel [8]	% Zr In gel [8]	% H_2O
1	0.1	1 d	5.2	70.37	0.29	97.98	<0.2	<10	7.222	29.17	29.61	17.47
2.8	0.1	1 d	5.5	74.60	0.16	92.52	<0.2	<10	6.850	26.07	23.16	16.85
3.8	0.1	1 d	7.0	72.21	0.03	95.55	<0.2	<10	7.175	27.14	28.99	16.85
4.5	0.1	1 d	4.5	81.41	0.04	93.20	<0.2	<10	6.752	29.56	26.33	17.51
6	0.1	1 d	6.5	68.18	0.02	85.91	<0.2	<10	6.892	28.02	26.70	13.62
7	0.1	1 d	5.5	67.41	0.23	94.51	<0.2	<10	6.789	29.17	29.61	15.13
4.5	0.045	1 d	4.25	74.02	0.032	90.3	<0.2	<10	7.045	27.87	30.88	15.90
4.5	0.1	1 d	4.5	81.41	0.040	93.2	<0.2	<10	6.752	29.56	26.33	17.51
4.5	0.5	1 d	4.3	63.46	0.12	46.1	<0.2	<10	7.750	33.61	30.85	14.19
4.5	0.1	2 d	3.75	76.66	0.057	95.6	<0.2	<10	7.069	33.68	31.97	17.73
4.5	0.1	1 h	4.5	69.77	0.004	29.4	<0.2	<10	7.144	28.22	27.72	16.81

*Average data of the experiments performed by duplicated.

L^{-1} $ZrOCl_2.8H_2O$ solution (81 %) while the lowest in that prepared with 0.5 mol L^{-1} $ZrOCl_2.8H_2O$ (63 %). The use of extremely high and low $ZrOCl_2.8H_2O$ concentrations (0.045 and 0.5 mol L^{-1}) in the gel preparation produce an efficiency decrease of 10 and 20 % compared with gel prepared with 0.1 mol L^{-1} $ZrOCl_2.8H_2O$ solution. As for the gels prepared from the $ZrOCl_2.8H_2O$ solutions aged at different times (series 3), the highest and lowest efficiencies presented in the gels with 0.1 mol L^{-1} $ZrOCl_2.8H_2O$ solutions aged for 1 day (81 %) and for 1 h (69 %). The extreme times of zirconyl solution preparation that is aged $ZrOCl_2.8H_2O$ solutions for 1 h and 2 days, cause a generator efficiency decrease around 5 and 15% compared to gel prepared with 0.1 mol L^{-1} $ZrOCl_2.8H_2O$ solution aged for 1 day. This behavior can be explained from the hydrolysis of zirconyl chloride which generates different species in solution depending upon the zirconly concentration and the ageing time (See discussion).

According to the U.S. Nuclear Regulatory Comission (NRC) recommendations, the percentage of the ^{99}Mo breakthrough should not exceed 0.015 % at the time of the injection.[11] For series 1, the highest percentages of ^{99}Mo breakthrough were obtained on the gels prepared with ^{99}Mo-molybdate solutions at pH 1, 2.8 and 7 while those prepared at pH 3.8, 4.5 and 6 presented a ^{99}Mo breakthrough < 0.04 %. The lowest elution efficiencies and the highest ^{99}Mo breakthroughs appeared on the gels prepared with ^{99}Mo-molybdate solutions at extreme pH values (1 and 7) (Table 2). In the case of series 2 (Table 2), the ^{99}Mo breakthrough amount in eluents is proportional to $ZrOCl_2.8H_2O$ concentration. This behavior can be expressed by the equation 1:

$$\% \ ^{99}\text{Mo breakthrough} = 0.0317 + 0.059\,[ZrOCl_2.8H_2O] + 0.235\,[ZrOCl_2.8H_2O]^2 \quad (1)$$

Thus the highest ^{99}Mo breakthrough (0.12 %) was found in prepared gel with the highest $ZrOCl_2.8H_2O$ concentration (0.5 mol L^{-1}), and the lowest in that using 0.045 mol L^{-1} $ZrOCl_2.8H_2O$ solution which just presented 0.032 %.

The ^{99}Mo breakthrough is also function of $ZrOCl_2.8H_2O$ solution ageing used in the gel synthesis whose best theoretical curve is:

$$\% \ ^{99}\text{Mo breakthrough} = 0.004 + 0.046\,[ZrOCl_2.8H_2O] - 0.009\,[ZrOCl_2.8H_2O]^2 \quad (2)$$

The highest ^{99}Mo breakthrough percentage (0.057 %) was obtained in gels prepared with the most aged $ZrOCl_2.8H_2O$ solution (2 days) and the lowest with the solution with least ageing (0.004 %).

The radiochemical purity of ^{99m}Tc eluated practically from all gels was more than 93 %, indicating that the ^{99m}Tc was largely eluted as $^{99m}TcO_4^-$. Only three gels showed (Table 2) purities less than 90 %: (*i*) the prepared gel with ^{99}Mo-molybdate solutions at pH = 6 and whose purity was about 85 %, (*ii*) the prepared gel from 0.5 mol L^{-1} $ZrOCl_2.8H_2O$ solution, with a purity of 46.1 % and (*iii*) the prepared gel with a 0.1 mol L^{-1} $ZrOCl_2.8H_2O$ solution ageing for 1 h which presented the lowest radiochemical purity of all gels: 29.4 %.

The chemical purity of eluates was particularly important with regard to zirconium and aluminium. In all eluates, the Zr was always less than 0.2 µg mL^{-1} and in the case of Al, it was also less than 10 µg mL^{-1}. These concentrations do not exceed the recommended limits for NRC, which must be less than 20 µg mL^{-1}.[11]

The variation of molybdate solution pH and $ZrOCl_2.8H_2O$ solution preparation conditions in the gel synthesis caused no effects on the eluate pH which presented values between 6.7 and 7.7. The highest value pH (7.75) was obtained in prepared gel with the lowest $ZrOCl_2.8H_2O$ concentration: 0.045 mol L^{-1}.

Gel characterization

Thermogravimetry

All of the gels began to decompose in the 25-250 °C temperature range, which corresponds to the loss of hydration water. The gels prepared from ^{99}Mo-molybdate solutions at pH < 4.5 loose about 17 % of water whereas those prepared at pH > 6 lose between 13 and 15 % (Table 2). From 250 °C to 750 °C, the anhydrous gels do not suffer a weight-loss but when the temperature is higher that 750 °C a rapid decomposition takes places producing MoO_3 and ZrO_2.[9]

The gel thermograms of the series 2 and 3 (Table 2) present the same shape than those of series 1. They also have two stages of weight loss: the first where the gels are dehydrated between 25 and 250 °C and the second one (> 750 °C) in which the gels suffer complete decomposition.[9] The lowest (14.19 %) and highest (17.52 %) water-loss were obtained in the gel prepared from 0.5 mol L^{-1} and 0.1 mol L^{-1} $ZrOCl_2.8H_2O$ solution, respectively. As regards the effect of $ZrOCl_2.8H_2O$ solution aging (series 3), the water losses are slightly increased as more aged solutions are used. An average water-loss about 17 % was obtained in these gels.

Infrared spectroscopy

All gels present similar infrared spectra: a broad intense absorption band in the region from 3500 to 3000 cm^{-1} and a strong band at 1625 cm^{-1} characteristics of aqueous (H-O-H) bending.[9,12] The O-H bond absorbs differently depending on its environment, in particular the band from 3500 to 3000 cm^{-1} shows a widening and a lower percentage transmittance as the molybdate solution's pH increases from 1 to 7. However the gel prepared from molybdate solution at pH 2.8 presents the broader band and the lowest percentage transmittance. Thus, there are three types of bound water in these compounds: (*i*) water in the form of hydroxyl bonded to Mo atom, (*ii*) water molecules present as water of hydration inside the crystal lattice or in the adsorbed state and (*iii*) hydronium ions [$(H_3O)Cl$]. The band at 1625 cm^{-1} corresponds to the water of crystallization, the weak adsorption bands at 1400 cm^{-1} and 1045 cm^{-1} can be assigned to a complex vibration arising from interation of hydroxyl group vibrations with a Mo-O bond and to vibrations of hydroinum ions as in ions [$(H_3O)Cl$], respectively.[13] The spectra also show a weak adsorption band at 2365 cm^{-1} which practically disappears in the spectrum of the gel prepared with molybdate solutions at pH 7. This band has been assigned to Mo-O bond stretching.[9] In the fingerprint region (1000 to 400 cm^{-1}), the shape of spectra are also similar. Three adsorption bands can be identified: the first one at 890 cm^{-1}, assigned to Mo-O-Mo bonds, the second one at 740 cm^{-1} which is the less intense band, originated probably from both Zr-O and Mo-O modes and the third one, the more intense band, at 475 cm^{-1} produced possibly by the Zr-O bond.[9,14-18] The bands show a decrease of the percentage transmittance as the molybdate solution's pH is increased from 1 to 7, apart from the gel prepared with molybdate solution's pH 2.8, which shows the lowest percentage transmittance and intensities. In this gel (pH 2.8), the adsorption bands of the fingerprint region practically disappear.

The infrared spectra of series 2 (Figure 2) show the same shape that those of the series 1, except for the gel prepared from a 0.045 mol L^{-1} $ZrOCl_2.8H_2O$ solution, which presents in the fingerprint region (1000 to 400 cm^{-1}): (*i*) an medium adsorption bands at 610 cm^{-1} originated by the Mo-O bonds,[9,17] (*ii*) a displacement of adsorption bands toward lower frequencies, (*iii*) the disappearance of the peak at 740 cm^{-1} and (*iv*) an increase of intensity of the band at 1400 cm^{-1}. The gels prepared from 0.045 mol L^{-1} and 1 mol L^{-1} $ZrOCl_2.8H_2O$ solutions present a weak adsorption band at 1045 cm^{-1} produced probably by the Zr-O bond, in accordance with the spectra of pure zirconium compounds reported previously.[9] The dissimilarities on the spectra presented in Figure 2 suggest the formation of a different chemical structure when the gels are prepared from 0.045 mol L^{-1} $ZrOCl_2.8H_2O$ solutions.

The infrared spectra of series 3 are similar to those of series 1 and 2. The $ZrOCl_2.8H_2O$ solutions ageing only affect the adsorption band intensity. The lowest intensities were obtained in the gels prepared with $ZrOCl_2.8H_2O$ solutions ageing for 1 day while the highest with those ageing for 1 hour.

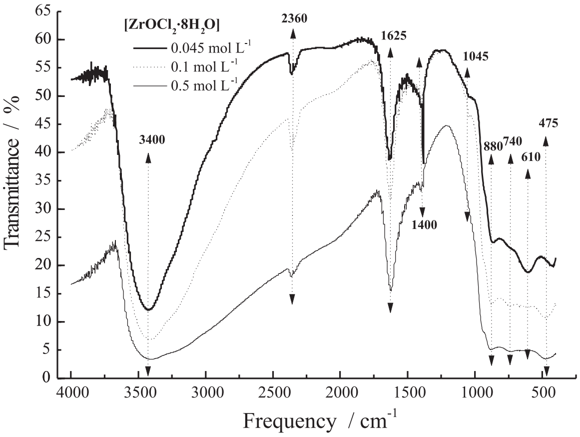

Figure 2. Infrared spectra of the zirconium molybdate gels prepared at different $ZrOCl_2.8H_2O$ concentrations (Series 2).

The Mo and Zr content in the gels (Table 2) were determined by Neutron Activation Analysis following the methodology described in previous works.[8] The zirconium molybdate gels contain about 30 % of Mo and Zr, however these percentages present slight variations depending on the molybdate solutions pH and the $ZrOCl_2.8H_2O$ solutions concentration and ageing used to prepare the gels. In the case of the molybdate solutions pH, there is no specific tendency, the largest percentage of Mo was obtained in the gels prepared at pH of 4.5 (29.5 %) while the smallest percentage at pH of 2.8 (26 %). In the case of the $ZrOCl_2.8H_2O$ solutions, the percentage of Mo increases with the concentration and ageing of these solutions. The number of oxygen and the water molecules contain in the gels depend on the preparation conditions of each gel. In consequence, the structure of these gels is subject to the different arrangements of these molecules around the Zr and Mo.

The performance of the ^{99m}Tc gel generators are directly related to the physico-chemical properties of the gel and consequently with its chemical structures. The modification of the ^{99}Mo-molybdate solutions pH used to prepare the zirconium molybdate gels alters the chemical structure of the gels because the molybdates form different species in solution. Numerous reports on acidification of molybdate solutions have suggested the occurrence of MoO_4^{2-} species at pH > 6 and the formation of polymolybdates at pH below 6 and at molybdate concentration > 10^{-3} mol L^{-1}.[19-22] However, published information is contradictory as regards the polymolybdates formed. For example, Pope[21] and Tytko and Glemser[19] have reported the formation of the heptamolybdate anion $[Mo_7O_{24}]^{6-}$ or its protonated forms ($[HMo_7O_{24}]^{5-}$, $[H_2Mo_7O_{24}]^{4-}$ or $[H_3Mo_7O_{24}]^{3-}$), as the predominant species in aqueous solution, at molybdate concentration > 10^{-3} mol L^{-1} and at pH 3 - ca.5.5. At more acid (pH 2-3) molybdate solutions, the experimental interpretations are uncertain, and they suggest the presence of a mixture of protoned heptamolybdates and octamolybdates

$[Mo_8O_{26}]^{4-}$. Finally, they report the formation of one or more very large polymolybdate species, like the anion $[Mo_{36}O_{112}]^{8-}$, at solutions acidified to about 1.8.[19,21] Honing and Kustin[20] and Cruywagen[23] suggest that at pH > 3 the molybdates form heptamolybdates and octamolybdates, while Sengupta[24] and Nekovář[25] cite as predominant species between pH 1 and 6 to the heptamolybdates and at low pH (<2) the precipitation of the MoO_3. In order to discern the presence of the different molybdate species formed under our experimental conditions, molybdate solutions were prepared at six different pHs following the same methodology used in the gel preparation. Figure 3 shows the infrared spectra of these solutions. The fingerprint region (1000 to 400 cm^{-1}) of these spectra reveals a clear difference between the solutions prepared at pH 7 and 6. It is evident that at pH 6 the MoO_4^{2-} ion is mixed with another molybdate species, and for that reason the performances of both generators (see Table 2) are slightly different as are the infrared spectra of these gels. On the other hand, the high ^{99}Mo breakthrough percentage and low efficiency of the generators at these pHs could be attributed to the rupture of the long chains of ZrO_2 units comprising a micelle by the simple MoO_4^{2-} ions, favoring the formation of smaller units with a more regular configuration which can be dissolved easier. At pH 6 this effect decreases thanks to the presence of the other molybdate species besides MoO_4^{2-} ion. In the case of the molybdate solutions at pH 4.5 and 3.8 the infrared spectra follow a similar pattern. These results suggest us that the predominant species at both pH is $Mo_7O_{24}^{6-}$ ion in accordance with the infrared spectra of the $(NH_4)_6Mo_7O_{24}\cdot H_2O$ reported previously by our group.[9] It should be noted that the infrared spectra of the gels prepared with molybdate solutions at pH 4.5 and 3.8 are also very similar however, the generator efficiencies are appreciably different: 81 % and 72 % respectively. Considering that the polymolybdates form polymeric structures based on infinite chains of MoO_x unit which are assembled around the ZrO_y unit to form the zirconium molybdate gels,[21,26, 27] it is possible to suggest that the discrepancies between the efficiencies of the gels prepared with molybdate solutions at pH 4.5 and 3.8 can originate from the different arrangements of the MoO_x unit and the ZrO_y unit. The better defined pattern of the infrared spectrum of the molybdate solution at pH 3.8 indicates that the $Mo_7O_{24}^{6-}$ ion is the only one species present in solution and therefore the structure of the heteropolymolybdate is probably better ordered than in the gels prepared with solutions at pH 4.5 where a mixture of the $Mo_7O_{24}^{6-}$ and MoO_4^{2-} ions is certainly present. At pH 3.8 the network structure is more compact producing a decrease in the elution efficiency because of the reduced pore size which limits the free diffusion of the TcO_4^- ions through the column. This conclusion agrees with that suggested by our group in the study of the effect of Zr:Mo ratio on generator performance.[9] In the case of the molybdate solutions at pH 2.6 and 1.9, the infrared spectra (Figure 3) show that molybdate species are different than those present at higher pH (> 2.6). This information indicates that the gels prepared at pH 2.8 and 1 were formed from different molybdate species and therefore their structures and the generator performances (Table 2) are different. It is possible that at low pH values the highly aggregated polymolybdate ions formed in solution inhibit the alkaline hydrolysis of the zirconium solutions to hydrous zirconia ($ZrO_2\cdot H_2O$) as well as the displacement of the aquo groups of the hydrous zirconia by the polymolybdate[9] because the large size and charge of these anions:

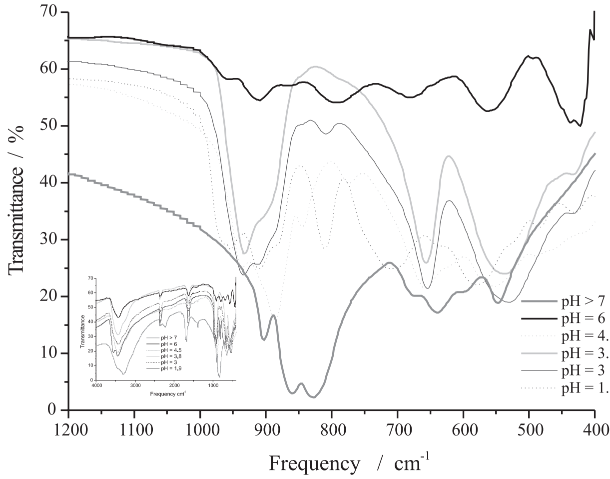

Figure 3. Infrared spectra of the molybdate solutions at different pHs.

$$ZrOOH^{+} + wMo_xO_z(OH)^{(2x-y)-}_{8x-y-2z} \longrightarrow$$
$$\longrightarrow \left[ZrO_2\cdot(x-w)H_2O\cdot Mo_xO_z(OH)^{(2x-y)}_{(8x-y-2z)}\right]^{-} + wH_2O \quad (3)$$

It has been suggested that the precipitation of zirconium oxy-hydroxide phases followed by a molybdate-rich phase when acidic molybdate solutions are used to prepare these gels, results in the formation of materials with a heterogeneous character.[2] In consequence, the eluates of the generators prepared with acidic molybdate solutions (pH 1 and 2.8) present high ^{99}Mo breakthrough percentage (see Table 2) because the polymolybdate anions are not attached to the hydrous zirconia and as a results the gels can dissolve easier.

As regards the influence of the zirconyl solutions, published information about the preparation of zirconium molybdate gels describes multiple preparation conditions of the zirconyl solutions. Evans and Shying[2] report the use of zirconium oxynitrate solutions with the pH adjusted to 1.0

by the addition of 5 mol L^{-1} ammonium hydroxide while Moore *et al.*[28] adds 3 mol L^{-1} K_2CO_3 solutions to adjust the pH of these solutions. Other approaches by Narashimhan and co-workers[29,30] and Saraswathy and co-workers [31,32] use 0.25 mol L^{-1} zirconium oxychloride solution pre-heated to 55 - 60 °C; Dadachov *et al.* [27] and Clearfield and Blessing[12] utilize 0.5 mol L^{-1} $ZrOCl_2.8H_2O$ solutions; Osso *et al.*[33] adjusts the pH at 1.5 with 3 mol L^{-1} Na_2CO_3 pre-heated to 50 ºC; Sánchez-Ocampo and Bulbulian[34] apply zirconium chloride solutions prepared from zirconium dioxide dissolved with 0.1 mol L^{-1} hydrochloric acid or metallic zirconium dissolved in concentrated hydrofluoric acid and later in concentrated hydrochloric acid adjusted the pH at 4 with 1 mol L^{-1} ammonia. Finally, in the IAEA Report "Alternative technologies for ^{99m}Tc generators",[35] several different conditions are reported, including 1.4 mol L^{-1} zirconium oxychloride solutions heated to 60-70 ºC, adjusted with HCl at pH 1.8-2.5, 0.1 mol L^{-1} solutions at pH 1.6, and 0.25 mol L^{-1} solutions. In summary, zirconium molybdate gels have been prepared from zirconium: oxynitrate, oxychloride or chloride solutions at concentrations from 0.1 to 1.4 mol L^{-1}, adjusting the solution pH values between 1 and 4 with hydroxide or carbonate solutions; and sometimes these solutions have been pre-heated between 50 and 70 °C.

It is known that when the crystalline solid $ZrOCl_2.8H_2O$ is first dissolved, at concentrations of the order of 0.01 to 1 mol L^{-1}, tetrazirconium ions of formula $Zr_4(OH)_8^{8+}$ with water of hydration pass into the solution phase. The large zirconium ion reacts with its environment and breaks down practically completely to the basic zirconyl ion $ZrOOH^+nH_2O$ produced by the hydrolysis of zirconyl chloride or of zirconyl nitrate, in accordance with the reaction:[36]

$$4ZrOCl_2 + zH_2O \rightarrow Zr_4(OH)_8^{8+}{\cdot}xH_2O + (16\text{-}x)H_2O \rightarrow 4ZrOOH^+ + 4H^+ + 8Cl^{\square} + nH_2O \qquad (4)$$

The acid strengths of the freshly prepared zirconyl chloride solution change on standing and the final pH of these solutions is nearly the same as those of hydrochloric acid solutions of the same molarity. When the acidity of zirconyl salt solutions is increased, either by concentrating it or by adding acid, hydronium ions react with the ion $ZrOOH^+$ and convert it to ZrO^{2+} which tends to combine to the tetramer specie ($Zr_4(OH)_8^{8+}$).

$$ZrOOH^+ + H_3O^+ \rightarrow ZrO^{2+} + H^+ + 2Cl^- \qquad (5)$$

When the alkalinity of these solutions increases, by addition of ammonia or sodium hydroxide, the hydrous zirconia forms:[36]

$$ZrOOH^+ + OH^- \rightarrow ZrO_2{\cdot}H_2O + (1\text{-}x)H_2O \qquad (6)$$

Nevertheless, an adjustment of pH of the zirconyl salt solutions by addition of carbonate salts can form the trioxodizirconium ion ($Zr_2O_3^{2+}$).[36]

It is difficult to carry out a comparison between our data and those reported by the literature, because the variety of preparation conditions of the zirconyl solutions used in each investigation. In addition, these conditions are not described with precision in many cases and it is not possible to know if the zirconyl solutions had been heated, aged or pH adjusted. For example, considering that the concentrations of zirconyl solutions present a pH about the same as those of hydrochloric acid solutions of the same molarity,[36] then the pH of 0.25 mol L^{-1} and 0.5 mol L^{-1} zirconyl solution, reported by some authors, can attain values about 0.6 and 0.3 respectively, after 24 hours of aging, favoring the formation of the ZrO^{2+} species. While other works cite an adjustment of the pH with carbonate salts which favor the formation of the trioxodizirconium ion ($Zr_2O_3^{2+}$). It is evident that the chemical form of the zirconium ions present before reaction with the molybdates solutions hardly influences on the final structure of the gels, as our data have shown (see Figure 2).

The ageing and the concentration of zirconyl solutions jointly can inhibit or favor the formation of $ZrOOH^+$ which is the precursor of the hydrous zirconia. At high zirconyl solution concentrations the pH is low and the formation of ZrO^{2+} is favored while at low concentration the pH increases and the $ZrOOH^+$ is preferably formed. The ageing zirconyl solutions favor the formation of $ZrOOH^+$, in the case of the low $ZrOCl_2.8H_2O$ solution concentration, while at high concentrations the most favored species is ZrO^{2+}. Thus gels prepared from 0.045 mol L^{-1} $ZrOCl_2.8H_2O$ favor the formation of ZrO_2 from $ZrOOH^+$ and therefore their structures present a more ordered framework which can act as a "molecular sieve" preventing the diffusion of the $^{99}TcO_4^-$ and causing the decrease of the generator efficiency. At 0.5 mol L^{-1} $ZrOCl_2.8H_2O$, the low pH imposed by the zirconyl concentration, inhibits the alkali hydrolysis of ZrO_2 and favor the formation of ZrO^{2+} resulting the precipitation of zirconium oxy-hydroxide phases followed by a molybdate-rich phase. The latter probably causes the increase the ^{99}Mo breakthrough percentage, the decreasing of the generator efficiency and the reduction of the [Tc(VII) O_4^-] to [Tc(IV)$^-$] ratio. While at 0.1 mol L^{-1} $ZrOCl_2.8H_2O$ a competition between the formation of species $ZrOOH^+$ and ZrO^{2+} produce gels with more random network which allow a more diffusion of the $^{99}TcO_4^-$ increasing the generator efficiency.

As regards the ageing of the zirconyl solution, the more freshly prepared solutions (1 h) present predominant species to ($Zr_4(OH)_8^{8+}$) and the oldest form a mixture of the $ZrOOH^+$ and ZrO^{2+} species, depending on the $ZrOCl_2.8H_2O$ concentration. If the proportion of $ZrOOH^+$ is more than ($Zr_4(OH)_8^{8+}$) or ZrO^{2+}, $ZrOOH^+$ will be hydrolyzed by the polymolybdate solutions and zirconium molybdate will form (See reaction 3). On the other hand, it is possible that the zirconium species and the polymolybdate ions do not react but form independent insoluble compounds causing the decrease of the generator efficiencies, the increase of the ^{99}Mo breakthrough percentage in the eluates of ^{99m}Tc and the reduction of the [$Tc(VII)O_4^-$] to [$Tc(IV)O^-$]. The presence of insoluble species of polymolybdates, which are strong oxidizing agents,[22,37] can cause therefore a decrease of the ^{99m}Tc eluate radiochemical purity by the reduction of the Tc(VII). Consequently the low radiochemical purities obtained in the generators prepared from 0.5 mol L^{-1} and 0.1 mol L^{-1} $ZrOCl_2.8H_2O$ solutions ageing for 1 day (46 %) and 1 hour (29.4 %), respectively could be connected with this fact.

The physico-chemical proprieties of the gels depend also on the distribution and amount of water in the gel. This water can be unattached to the gel or not in crystallographically defined positions, producing a decay of the performances of the generators. Gels that present infrared spectra with broad intense absorption bands in the region from 3500 to 3000 cm^{-1} and strong band at 1625 cm^{-1}, exhibit this behavior (see Figure 2).

Conclusions

The zirconium molybdate gels are amorphous materials.[9] The pH of the molybdate solution and the preparation conditions of zirconyl solutions used during the gel synthesis appreciably alter the physico-chemical properties of the zirconium molybdate gels and as a consequence the performances of the ^{99}Mo/^{99m}Tc generators.

A rigid and regular lattice (structure) of the zirconium molybdate gels acts as a “molecular sieve” preventing the mobility of the ^{99m}Tc in the gel and causing the decrease of the generator efficiency. While a flexible random network with a highly crosslinked gel increase the efficiency and the radiochemical purity of the generator because the gel is more elastic but simultaneously harder and more resistant to the mechanical breakdown, that means the gel is more difficult to dissolve. These properties are directly connected with the different chemical species of zirconium and molybdenum present during the formation of the zirconium molybdate gels. These species can inhibit or favor: (*i*) the formation of the hydrous zirconia ($ZrO_2 \cdot H_2O$) by the alkaline hydrolysis of the zirconium solutions from the molybdate solutions and (*ii*) the displacement of the aquo groups of the hydrous zirconia by the polymolybdate anions to form the zirconium molybdate gels (See reaction 3). $ZrOCl_2.8H_2O$ solution preparation conditions have a clear influence on the chemical form of eluted ^{99m}Tc. The $^{99m}TcO_4^-$ ion is preferably eluted from gels prepared with 0.1 mol L^{-1} $ZrOCl_2.8H_2O$ solution ageing for 1 day.

Three species of zirconium can be present in solutions depending of the concentration, pH and aging of the solutions: $Zr_4(OH)_8^{8+}$, $ZrOOH^+$ and ZrO^{2+}. The predominant species will determine the type of compound formed, zirconium molybdate gels ($ZrOOH^+$), soluble or insoluble compounds framed by polymolybdates and zirconium oxy-hydroxide ($Zr_4(OH)_8^{8+}$ and ZrO^{2+}).

Modification of the molybdate solution pH gives rise to the formation of different polymolybdate species. The presence of the only one molybdate species during the synthesis of the zirconium molybdate gel promotes the formation of more regular gels while a polymolybdate species mixture encourage the formation of the gels with heterogeneous structures that better the performances of the ^{99}Mo/^{99m}Tc generators. Additionally, the size and charge of the polymolybdate anions which depend on the pH of the solutions, are also an important factor to favor or inhibit the formation of the zirconium molybdate gels or of the insoluble species of polymolybdates and zirconium oxy-hydroxide which cause an increase of the ^{99}Mo breakthrough percentage in the ^{99m}Tc eluates. The best performances of the ^{99}Mo/^{99m}Tc zirconium molybdate gel generators are attained using gels with random network which allow a more diffusion of the $^{99}TcO_4^-$ increasing the generator efficiency. We suggest to prepare gels from molybdate solutions at pH 4.5, where a mixture of $Mo_7O_{24}^{6-}$ and $Mo_xO_y^{x-y-}$ ions is present, and 0.1 mol L^{-1} $ZrOCl_2.8H_2O$ solutions aged for 1 day, where the formation of $ZrOOH^+$ ions is favored.

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