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ABSTRACT

A new ^{99m}Tc generator based on zirconium molybdate gel is described. Essentially the gel is a cation ion exchanger which permits the elution of the pertechnetate ion. The high molybdenum content of this gel, its stability under self-irradiation, and the absence of organic materials during preparation provide a generator concept that eliminates high processing costs, active waste storage costs and stability problems in other types of generator.

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CHEMICAL PREPARATION; GELS; INORGANIC ION EXCHANGERS; LEACHING; MOLYBDATES; RADIOISOTOPE GENERATORS; TECHNETIUM 99; ZIRCONIUM COMPOUNDS

CONTENTS

1. INTRODUCTION

The first molybdenum-99/technetium-99m (^{99}Mo/^{99m}Tc) generator has been described by Tucker *et al.* [1958] and the history of its development at the Brookhaven National Laboratory has recently been reviewed by Richards *et al.* [1982]. The Brookhaven concept, which is the basis of most commercial medical generators, uses alumina chromatography to separate ^{99}Mo from its daughter ^{99m}Tc. Purified fission product ^{99m}Mo-molybdate is added to the alumina column where it is strongly adsorbed and from which the less strongly bound $^{99m}TcO_4^-$ is eluted at intervals.

Following this original work, Lieberman and Gemmill [1968] developed a medical generator which used ^{99}*Mo* produced by the neutron activation of ^{98}Mo (n,γ) ^{99}Mo, and for several years most commercial generators utilised this process. However, as the radionuclidic purity of the ^{99m}Tc from the fission product ^{99}Mo generators improved, there was an almost complete shift back to the fission produced material.

Boyd [1982] recently reviewed ^{99}Mo/^{99m}Tc generators and summarised the advantages and disadvantages of chromatographic generators using the two sources of ^{99}Mo. He emphasised that although chromatographic generators using fission product ^{99}Mo are widely used, the process had inherent disadvantages, particularly the high capital cost of the processing plant and the disposal of other fission products. The development of substrates, other than alumina, was suggested to enable the use of (n,γ) ^{99}Mo to avoid these problems.

For its commercial operations the AAEC required a generator which combined the advantages of the (n,γ)^{99}Mo with the convenience of the chromatographic generator.

The loading capacity of alumina for molybdate is very dependent on the method of preparation of the oxide, and on the pH of the solution which controls both the hydrolytic polymerisation of the molybdate and the surface ionisation of the alumina. The value of 2 mg Mo g^{-1} at pH 5-6 quoted by Arino and Kramer [1975] is a typical capacity. For retention of fission product ^{99}Mo with a very high specific activity (~ 10^3 TBq g^{-1}) this capacity is adequate, but attaining the required generator activities with the lower specific activity (n,γ)^{99}Mo (50-500 GBq g^{-1}), requires the use of large generators and hence large elution volumes and limited ^{99m}Tc concentrations in the eluate. Clearly, any adsorptive process using (n,γ) ^{99}Mo will share this basic restriction.

The new generator described here, overcomes the loading restrictions by using a zirconium molybdate gel. The gel contains ~ 25 wt % molybdenum compared to ~ 0.2 wt % for the typical adsorption capacity on Al_2O_3; this low specific activity (n,γ) ^{99}Mo can provide high activity generators. The gel is an insoluble cation exchanger with an open structure which allows the free diffusion of TcO_4^- and hence milking in high yield using a simple elution technique. The ^{99}Mo is chemically combined as an intrinsic part of the gel structure rather than being held by the more labile adsorption bond as in the chromatographic generator. The concept has been patented by Evans and Matthews [1978].

2. EXPERIMENTAL

2.1 Materials

All reagents were used as received. Molybdenum trioxide was of A.R. quality from the Peking Chemical Works. Zirconium oxynitrate from several sources varied in quality. Only material that was completely soluble in water was used; this requirement was met with zirconium oxynitrate supplied by Alpha Inorganics and Atomergic Chemicals (minimum 98 per cent). Material from BDH (Technical) and batches from Alpha having a high Zr/NO_3 ratio were largely insoluble and were rejected. Zirconium oxychloride (> 99 per cent) was purchased from Merck.

2.2 Gel Preparation

2.2.1 Laboratory procedure

The following procedure was adopted for the preparation of most zirconium molybdate gels in the laboratory; any departure from the method described is specified. A small sample of molybdenum trioxide (0.4 g) was irradiated in a neutron flux to provide approximately 40 MBq g^{-1} of molybdenum. This was mixed with natural molybdenum trioxide (9.6 g), dissolved in ammonium hydroxide (3 mol dm^{-3}, 50 cm^3) and the pH adjusted to 4.0 ± 0.1 with nitric acid (5 mol dm^{-3}). An equimolar zirconium oxynitrate solution was prepared and the pH adjusted to 1.0 ± 0.1 by the slow addition of ammonium hydroxide (5 mol dm^{-3}) while the solution was vigorously stirred. After standing overnight the pH fell 0.1 - 0.2 units.

The molybdate solution was added to the stirred zirconium nitrate solution and the zirconium molybdate complex precipitated as a stable suspension at a pH of about 1.8. The precipitate was vacuum filtered using a Buchner funnel and air-dried in a laboratory oven for 12 to 16 hours at 55°C. The dried product, a hard, brittle and clear or translucent glassy gel, was manually crushed and sieved and the 150 to 500 μm fraction selected for elution studies in columns.

2.2.2 Hot cell

The method used for the preparation of high activity gels in the hot cell differed considerably from the standard laboratory method described above. The technique was simplified to accommodate the limited in-cell facilities and used evaporation rather than filtration.

A quantity of MoO_3 (2.5 to 7.0 g) was weighed in the hot cell from irradiated MoO_3 (30 to 40 GBq g^{-1}) and dissolved in ammonium hydroxide (3 mol dm^{-3}). Excess ammonia was removed by evaporation to incipient dryness under an infrared lamp. In preliminary experiments further drying caused the formation of an insoluble molybdate. The ammonium molybdate was redissolved in water.

A solution of zirconium oxynitrate (10 per cent excess over equimolar) with pH adjusted to 1 ± 0.1 was prepared and placed in the hot cell. The molybdate solution was added slowly to the stirred zirconium solution. The resulting slurry was evaporated, without filtration, to dryness under an infrared lamp and the gel heated for 15 hours. The distance from the lamp to the gel had previously been adjusted to give a drying temperature of about 70°C. The dried gel was crushed through a stainless steel mesh (900 μm) and portions (~ 2 g) were loaded into generator tubes, which were then sealed and passed from the cell into shielded containers for elution studies.

2.3 Elution of Technetium-99m

The sieved gel (2 g) was placed in a generator bottle which provided a column of about 15 mm diameter and 15 mm height supported on a sintered glass frit. Bed density was normally about 1.2 to 1.3 g cm^{-3}. Physiological saline solution (9 g dm^{-3}) was passed through the column at a constant flow rate (0.8 cm^3 min^{-1}) *via* a multichannel proportioning pump placed at the exit tube. Up to ten generators could be eluted simultaneously. The normal procedure was first to wash the columns with saline (50 cm^3) and then elute with further saline (10 cm^3) at approximately twenty-four hour intervals over a number of days.

The high activity generators (30 to 40 GBq in ~ 4 g of gel) were eluted with 10 cm^3 lots of solution by gravity flow from a drip feed bottle rather than by pump. The elution times consequently varied (0.2 to 1.4 cm^3 min^{-1}).

The ^{99m}Tc activity of the eluants was determined by scintillation counting for the laboratory generators and by counting in an ion chamber for the higher activity generators. The activity was expressed as a percentage of the theoretical ^{99}Mo content of the column to obtain the elution efficiency.

2.4 Analysis

The zirconium and molybdenum contents of the eluate were determined spectrophotometrically using the Arsenazo III [Pakalns 1969] or the thiocyanate [Vogel 1961] method, respectively, or by atomic absorption. Nitrate contents were determined using an Orion nitrate ion selective electrode.

The metal and nitrate contents of the solid gels were determined on solutions obtained by dissolving the gels in HCl (10 mol dm^{-3}). The oxygen content of the gel was obtained by igniting the gel at 600°C to remove ammonium nitrate and water and dissolving to analyse metals as above. The oxygen was obtained by difference. The water content was taken to be the weight loss on drying for 24 hours at 100°C.

Thermogravimetric analysis was carried out using a Cahn microbalance programmed for a heating rate of 5°C min^{-1} under nitrogen.

3. RESULTS

3.1 Gel Preparation

On mixing the equimolar zirconium nitrate and ammonium molybdate solutions, an essentially 100 per cent yield of a viscous, thixotropic suspension of a zirconium molybdate precipitate was obtained. The consistency of the suspension varied greatly with the conditions of precipitation. Under normal conditions, vacuum filtration was a convenient method for dewatering the precipitate. The filter cake (typically 85 wt%

water) was air-dried in a laboratory oven for 12 to 16 hours at 55°C to give the final gel. The standard laboratory method gave gels that were typically yellow, clear or translucent, glassy solids.

The gels retained part of the soluble salt deposited during the evaporation step. The fraction of solution, and consequently the soluble salt removed by vacuum filtration, depended on the nature of the precipitate. This varied from a coarse granular precipitate, which was readily filtered to a semi-transparent, flocculent precipitate depending on the preparation variables, particularly the pH. Subsequently, the soluble salt content of the dried gel ranged from 20 to 40 per cent. Gels with the requisite properties of high elution efficiency and low molybdenum solubility were found invariably to originate from coarse granular zirconium molybdate precipitates. Because of the uncertainty in salt content, gels were analysed for ^{99}Mo content for use as a basis for elution efficiency calculations. The zirconium to molybdenum ratio in the gel was approximately 1:1, with all the reactant metals being precipitated.. A typical gel analysis is Mo 32, Zr 31, O 27 and water 10 wt%.

Table 1 summarises the elution efficiencies and the release of molybdenum obtained over a number of days with several gels prepared and eluted by the standard laboratory methods described in Sections 2.2 and 2.3. Typical elution profiles are shown in Figure 1.

The molybdenum dissolved in the eluate is expressed as per cent of the molybdenum content of the generator.

An investigation was made of the effect on gel performance of changes to some of the more important variables at each stage of the preparation.

3.1.1 Precipitation

Zirconium oxynitrate

Commercial zirconium oxynitrates are not true stoichiometric compounds. They vary from chalky insoluble compounds, with a low nitrate/zirconium ratio to clear, soluble, deliquescent solids with a higher nitrate ratio which lose nitric acid on standing in air. In the present work, their moisture contents varied over a wide range. Only batches which gave clear solutions were used to prepare gels.

Table 2 gives elution results obtained from gels prepared from several batches of soluble commercial zirconium oxynitrate. Where the natural pH of the zirconium nitrate solution (~ 0.3 mol dm^{-3}) differed markedly from pH 1, a portion was adjusted to pH 1 ± 0.1 and gels were prepared from both solutions in the normal way.

The Alfa Inorganics Lot A yielded a clear solution with a pH of 0.97 and was used for most studies. With the exception of the Alfa Inorganics Lot 123077 (pH 0.42), the zirconium molybdates precipitated from the solutions filtered readily and, with one exception (Alfa Inorganics Lot 091977), dried to clear yellow gels. The zirconium molybdate precipitated at pH 0.42 (Alfa Inorganics Lot 123077) peptised and formed a stable colloid which could not be filtered. When dried without filtration, the gel peptised again on contact with water and could not be eluted. The dried gels prepared from Alfa Inorganics Lot 091988 were opaque but eluted satisfactorily.

All gels prepared from zirconium nitrate solutions with pH values of 0.57 and above eluted satisfactorily, but those prepared from the higher pH solutions (~ pH 0.95) gave 5 to 10 per cent higher efficiencies. The release of molybdenum from the gels prepared from the three Alfa Inorganics batches differed but could not be correlated with the original pH.

Solution pH

A series of gels was prepared using molybdate solutions adjusted to pH values between 3 and 7 with nitric acid (5 mol dm^{-3}), before mixing with the zirconium solution. The pH of the zirconium solution was kept constant at 1 ± 0.1. After filtration the pH of the resultant mixtures varied between 1.1 and 2.8. The appearance of the final gel changed from a clear pale yellow at pH 3 to an opaque white gel at pH 7. The elution efficiencies of the gels, and the concomitant release of molybdenum, increased with increasing pH of the molybdate solution. Between pH 3 and 7, the loss of molybdenum increased by a factor of approximately 5 (Table 3).

Zr/Mo ratios

A series of gels was prepared with zirconium to molybdenum molar ratios from 1.2 : 1 to 1 : 1.3 using the standard procedure. The elution efficiencies and molybdenum releases obtained on eluting the gels are shown in Table 4. Compared with the equimolar gels, those with excess zirconium were more opaque and less coloured, showed no significant difference in elution efficiency and released less molybdenum. In addition, the precipitates obtained with the 1.2 : 1 ratio were white, and gave more stable colloidal suspensions which were difficult to filter. Gels with an excess of molybdenum had both higher elution efficiencies (15 per cent with the 1:1.3 gels) and higher releases of molybdenum, which increased with higher molybdenum content.

Use of NaOH

Gels were prepared using sodium hydroxide in place of ammonium hydroxides to dissolve the MoO_3. Gels dried at 52 and 100°C showed no significant change in elution efficiency and molybdenum release (Table 5) from those normally prepared with ammonium hydroxide. The reduced efficiency obtained when a gel was dried after the initial wash cycle was also observed with the standard ammonium hydroxide gel.

3.1.2 Drying

Effect of temperature

The effect of drying temperature on gel performance is shown in Table 6. A batch of standard zirconium molybdate was prepared and portions of the filtered material were heated in an air oven for 16 h at temperatures between 57 and 164°C. The gel, dried at ambient temperature, was allowed to stand for two days to give a clear, glassy gel. Drying temperatures up to 120°C did not significantly change the elution efficiency but, at 142°C and above, a lower yield of ^{99m}Tc was obtained. The gel dried at ambient temperature gave the highest yield.

The influence of heating on the release of ^{99m}Tc was further investigated by drying a gel at a low temperature (45°C) and then reheating portions of the gel for a further 16 hours at temperatures between 45 and 400°C. Again, the elution efficiency was not significantly changed by heating below 115°C, but decreased markedly at 165°C, and at 200°C essentially no ^{99m}Tc could be eluted (Table 7). Heating to 115°C did not significantly change the elution profile. Greater than 80 per cent of the final yield was always obtained in the first three cm^3 of a 10 cm^3 elution (Figure 2).

Alternative drying techniques

A number of alternative drying techniques are available. A preliminary evaluation has been made of some of these techniques.

(a) Evaporation

Evaporation of the zirconium molybdate slurry was used as an alternative to filtration in the hot cell preparation. The results of the laboratory evaluation of this technique (Section 2.2.2) are given in Table 8. The gels from evaporation were encrusted with salt and were more opaque than those dried after filtration. The elution efficiencies did not differ significantly from those of gels prepared under standard conditions.

(b) Rotary drying

Two batches of gel were prepared using rotary evaporation. The gel slurry, from the precipitation step, was poured into a round-bottomed flask attached to a Rotavapor rotary dryer. A stream of hot air was passed through a glass tube into the body of the flask from a Leister welding gun, while the flask was rotated slowly.

The gels dried to opaque yellow flakes which broke from the walls of the flask when dry. These gels were mechanically stable and did not deteriorate over five elutions. Their elution efficiencies were lower, the first averaged 71.2 per cent when dried over three hours and the second 67.9 per cent when dried over a shorter period (2 h).

(c) Microwave drying

A standard domestic microwave oven was used to dry two samples of zirconium molybdate filter cake prepared by the standard method. Elution efficiencies from six elutions were low and decreased with drying time. The first, dried for four minutes, averaged 56 per cent and the second, dried for six minutes, only 24 per cent. These pale yellow opaque gels gave off flashes of light during drying, presumably due to decomposition of ammonium nitrate.

(d) Freeze drying

Freeze drying was investigated briefly as a method of drying and simultaneously forming gel particles of a suitable size distribution for use in the generators. A vacuum-filtered cake (75-85 per cent water) was freeze dried overnight. The product was typically a pale yellow brittle gel formed in granular pieces with a size distribution suitable for column elution (fines ~ 10 per cent). Subsequent experiments gave products with a high fines content (60 to 80 per cent).

3.1.3 Gel sizing

In the standard procedure the gel is crushed and sieved by hand. The 150-500 μm fraction, which constituted more than 50 per cent, was used in the elution columns; less than 20 per cent of fines ($<$ 150 μm) was present. Crushing in a vibratory ball mill, even if plastic balls were used, always produced a high proportion of fines.

In a preliminary evaluation of the usefulness of gel disintegration in water as a size reduction step, dried gels were given various water treatments and eluted in the normal way. The results are shown in Table 9. Generally, the gels performed similarly to the standard ground and sieved gels, giving elution efficiencies of 70-90 per cent over six daily elutions. The amount of molybdenum released was high in the first elution but over six elutions attained equilibrium level similar to normal. The levels of molybdenum did not increase over the six elutions indicating that the gels were stable over repeated elutions. When the gel was fractured in a beaker or *in situ* using both static and flowing water, there was no significant effect on the performance. Gels immersed in water direct from the oven performed in the same way as gels allowed to cool in air for 30 minutes.

3.1.4 Effect of salt content on the gel

Infrared analysis showed that the water treatments used to fracture the gels leached most of the occluded ammonium nitrate (originally ~ 22 wt %). When these water-washed, essentially salt-free, gels were re-dried there was an almost complete loss in subsequent elution efficiencies (Table 10).

Thermal analysis of these gels (Figure 1) showed that mass was lost more rapidly when the salt was removed before analysis, indicating that they contained more water. A similar result was obtained when the zirconium molybdate precipitate was extensively washed with water before drying (Table 11). Gel prepared from unwashed precipitate, had an efficiency of 71.4 per cent but only 4.5 per cent when washed. Removal of the salt by washing had little effect on the pH of the eluate. With standard gel, the pH increased from 2.11 to 2.57 over six elutions whereas with salt-free gel it rose from 2.09 to 2.34.

3.2 Influence of Radiation

The effects of self-irradiation of the gel were simulated with external irradiation from a ^{60}Co source (1 Mrad h^{-1}). The effect on elution efficiency after irradiating the gel columns for 17 h was measured. Table 12 compares the performance of three standard gels with a gel containing 10 per cent Ce(IV) and another with 10 per cent Fe(III) in place of an equivalent amount of Zr(IV). The gels showed no loss of efficiency as a result of irradiation treatment between elutions, but the Fe(III)-Zr(IV) gel gave a lower efficiency.

The above gels were prepared by the standard method in the complete absence of organic solvents, whereas some earlier gels involved the use of acetone as a drying agent. To investigate the effect of an organic solvent, a zirconium molybdate gel was prepared and, whereas a part was dried using the standard technique, the remainder used an acetone wash, followed by drying in an air oven at 55°C, to remove the bulk of the residual solvent. A similar procedure was adopted for a gel prepared using zirconium oxychloride in place of zirconium nitrate. Irradiation markedly reduced the elution efficiencies of the gels washed with acetone (Table 13) but their efficiencies recovered slowly when the gels were allowed to stand after removal from the irradiation field. There was no significant difference between gels derived by the nitrate and chloride routes.

3.3 High Activity Generators

A series of high activity generators (30-40 GBq) was prepared and eluted to establish the stability of the gels to self-irradiation and their elution performance.

The hot-cell preparation procedure was based on a modified method (Section 2.2.2) which used an evaporation technique in place of filtration. The simple procedures necessitated by limited hot cell facilities resulted in poor product control. However, although two gels were discarded, the remainder were generally suitable for elution. Overheating and the lack of pH control were the cause of the rejections.

The elution performances of eight generators prepared from three batches of gel are given in Tables 14-16. Their elution efficiencies, based on a single 10 cm^3 elution, were significantly less than the low activity gels prepared in the laboratory. However, the second and third elutions contributed additional ^{99m}Tc, so the combined elution efficiencies were comparable with low activity gels. They did not deteriorate when eluted daily with normal saline over seven to ten days. Rinsing the generators with water between saline elutions (to remove chloride) or draining by blowing air through the column with a syringe, made no change in the elution efficiencies. An elution with water reduced the overall efficiency by up to 20 per cent (Table 14-16), but showed no further deterioration with successive elutions. Molybdenum release from the generators averaged 0.15 per cent for batch 1 gel and did not increase over the ten days of elution. Generators from batch 2 and batch 3 gels released smaller amounts of molybdenum (0.011 and 0.008 per cent respectively).

4. DISCUSSION

There are two basic requirements for generators. The first is the need for a compound of molybdenum from which the anionic $^{99m}TcO_4^-$ can be eluted and which is chemically and mechanically stable under the conditions of elution. Such requirements are shared by inorganic ion exchange materials, of which the inorganic acid salts of tetravalent metals have long been of interest [Amphlett 1964; Clearfield *et al.* 1973]. Although most interest has centred on zirconium phosphates, largely because of their insolubility and stability, Kraus *et al.* [1958] found that an amorphous zirconium molybdate displayed promising cation exchange properties. As a cation exchanger, the material could be expected to have little affinity for the TcO_4^- and, provided that the interior passageways of the molybdate are large enough to allow the large anion to diffuse out, a simple elution of this ion should be possible.

Kraus and co-workers prepared zirconium molybdate by adding zirconium(IV) solution to a solution of molybdate present in large excess. From the data for the tungstate quoted in their paper, the ratio of Zr to Mo in the final gel was 1 to 3. However, we found that the use of a large excess of molybdate gave an unstable gel and hence reduced it in our standard procedure to equimolar quantities. Gels produced by this method were amorphous, their powder X-ray diffraction patterns showed no crystal structure and their thermogravimetric analysis (TGA) spectra were structureless. The solid gels had a 1 : 1 ratio of zirconium to molybdenum and a stoichiometry approximating to a formula of $ZrO_2.MoO_3.x\ H_2O$.

The elution characteristics of standard gels listed in Table 1 clearly show that TcO_4^- is easily eluted in high yield (75-85 per cent). Further, the rate of elution of TcO_4^- under standard conditions, illustrated by the elution curve (Figure 2), gave 40 per cent elution in the first cubic centimetre indicating a fast diffusion of the large anion within the interior of the zirconium molybdate gel. The molybdenum released to the eluate was relatively low and did not increase over the life of the generators (eight daily elutions), confirming the chemical stability of the gel under elution conditions.

The chemistry of the gel precipitation is complex. Both molybdenum and zirconium undergo concentration, pH, temperature and time-dependent hydrolytic polymerisation, and also polynuclear complex formation reactions, under the conditions of precipitation.

Baes and Mesmer [1976] reviewed the hydrolysis reactions of these two metals. Equilibria involving MoO_4^{2-} and the polymolybdates are rapidly attained. Polymerisation occurs at concentrations above 10^{-4} mol dm^{-3} and low pH, with $Mo_7O_{24}^{6-}$ as the predominant species. In the precipitating molybdate acid solutions, the species $H(MoO_4)^-$, $H_2(MoO_4)$, $H_8(MoO_4)_7^{6-}$, $H_9(MoO_4)_7^{5-}$, $H_{10}(MoO_4)_7^{4-}$ and $H_{11}(MoO_4)_7^{3-}$ have been postulated. At concentrations of acid greater than several tenths molar, the principal species formed by the hydrolysis of zirconium are polynuclear $Zr_4(OH)_8^{8+}$ together with $Zr_3(OH)_4^{8+}$ and $Zr_3(OH)_5^{7+}$. Slow irreversible hydrolysis occurs at lower acidities, accompanied by an increase in polymerisation and a change in structure. Speciation in a freshly prepared solution is indefinite in such a system.

In a study of the formation of hydrous zirconia, Clearfield [1964] proposed a structure based on the condensation of the cyclic $[Zr_4(OH)_8]^{8+}$ tetramers, which occur in the crystalline state. If the tetramers are condensed under conditions which allow the formation of an organised polymer, the resultant polymer consists of zirconium atoms surrounded by eight hydroxyl groups in the form of a distorted cubic arrangement. Oxylation between these layers gives a three-dimensional structure with the general formula $[ZrO_b(OH)_{4-2b} \cdot x\,H_2O]n$.

The preparation of zirconium molybdate in Clearfield's work involved rapid precipitation to give amorphous gelatinous precipitates. Thus the formation of order in the precipitating polynuclear complexes is unlikely. Clearfield and Blessing [1972] prepared a microcrystalline compound of formula $ZrMo_2O_7(OH)_2(H_2O)_2$ by precipitation from zirconium and molybdenum aqueous reactants in the molar ratio of 1 to 2 and refluxing the amorphous molybdate gels. The structure consisted of a three-dimensional network of cross-linked chains built up of quite regular $[ZrO_3(OH)_2O_2]$ pentagonal bipyramids and distorted $[cis\text{-}MoO_4(OH)(H_2O)]$-octahedra.

Contrary to the experience of Kraus *et al.* [1958] with amorphous gels, Clearfield and Blessing [1972] found that the crystalline zirconium molybdate exhibited disappointing ion exchange properties. Furthermore, the crystalline compound was strongly hydrolysed during titration with 0.1 mol dm^{-3} (NaCl + NaOH) according to the process:

$$ZrMo_2O_7(OH)_2(H_2O)_2 + 4OH^- + (x+y-5)H_2O \rightleftharpoons ZrO_{2-x}(OH)_{2x}(H_2O)_y + 2MoO_4^{2-}$$

These observations led Clearfield and Bessing to conclude "that the amorphous zirconium molybdate gels, represented by the empirical formula $ZrMo_xO_{2+3x-y}(OH)_{2y}(H_2O)_z$ are riddled with pores and channels and contain a rich surplus of hydroxo- and aquo-surface groups bound to the metal atoms. The ion exchange function of the gels presumably depends on the acidic, protolytic character of these groups and probably involves facile cation diffusion in the loose structures".

The crystals, $ZrMo_2O_7(OH)_2(H_2O)_2$ were on the other hand, thought "to have a compact structure such as to prohibit non-disruptive cation diffusion; although they do possess acidic, metal-bonded hydro- and aquo-groups. However, alkimetric neutralisation of these protolytic groups causes a total collapse of the crystal structure *via* hydrolysis of the molybdate group and hydroxylation of Zr(IV)".

Clearly, the ion diffusion characteristics which give the amorphous gels their superior ion exchange properties are equally essential to allow passage of the TcO_4^- in the generator matrix. It has been assumed, from this experience, that crystallinity should be avoided in materials prepared for use as a generator matrix. The efficiency of elution from the present generators confirms the easy movement of TcO_4^- in the amorphous matrix.

The gels of Kraus *et al.* [1958] gave high cation exchange capacities but, during acid-base titration, tended to release significant quantities of molybdate from the gel at pH values in excess of neutral. Passage of normal saline of near neutral pH through our zirconium molybdate gel is accompanied by a steady release of protons to the eluate. The pH values of the washings and eluate were not consistently monitored during these experiments but, where measured, were usually in the range pH 2.0 - 3.0 and remained reasonably constant over the life of the generator. It seems likely that the release of protons was not associated solely with Na^+-H^+ exchange because it occurred with water washings and elutions as well as with saline. However, any hydrolytic reactions which may have occurred did not alter the gel structure under elution conditions because the molybdenum release was small and approximately constant with time. Thus, these gels were more hydrolytically stable than those of Kraus *et al.* presumably because of the lower ratio of molybdenum to zirconium.

Because of the amorphous nature of the zirconium molybdate gels, it is likely that any variation in preparation procedures will greatly influence their properties. It was important to develop standardised procedures to obtain a consistent product particularly those that control the complex speciation in the reacting metal solutions. Although a basic study of this complex system was not possible, applied studies of selected variables were essential.

The pH is important for determining the chemistry of the reactant solutions. Varying the pH of the molybdate solutions between 3 and 7 produced gels of very different characters. Compared with the normal yellow glossy gels, those obtained using the higher pH molybdate were white opaque materials having a more oxide-like appearance. The latter may have been caused by the early precipitation of zirconium oxy-hydroxide phases followed by a molybdate-rich phase to give a gel with a heterogeneous character. Compared with the normal gel, the latter exhibits a higher elution efficiency accompanied by high molybdenum solubility.

A similar trend is observed as the molybdenum to zirconium ratio is increased. This suggests that material with a molybdenum to zirconium ratio significantly greater than one is less hydrolytically stable than that with a ratio of one. This is compatible with the observations of Kraus *et al.* [1958] and Clearfield *et al.* [1973] who observed, respectively, extensive molybdenum release at pH values near neutral from their 3 : 1 and 2 : 1 gels. Thus, the formulation of the gel is a compromise between the higher activity and elution efficiency obtained with high molybdenum content and the resultant higher solubility and hence molybdenum release.

From the evaluation of different batches of zirconium oxynitrate it was found that zirconium solutions below pH 0.5 formed unstable gels on drying, which were easily peptised but, when the pH was adjusted to 1 the gels were satisfactory. Gels prepared from zirconium solutions in the pH range 0.5 to 0.75 eluted satisfactorily but with lower efficiency than gels from the same solutions but having higher pH values. The release of molybdenum on eluting these gels varied by a factor of three. Therefore, the condition of the zirconium solution undergoing slow polymerisation reactions partly dictates the nature of the final gel, but these effects require further study. At this stage of development, it is important to control and standardise the preparation of the zirconium solution to obtain gels with consistent properties.

The substitution of Na^+ for NH_4^+ in the feed solutions had no significant effect on gel properties. Ammonium nitrate present in the gel as occluded salt, produced stability problems in the drying process, but this could be avoided by substituting sodium.

The water content of the gel is an important parameter. Results showed that the gel could be dried at temperatures up to 120°C without a deterioration in elution properties. At 140°C, the effects of irreversible dehydration became apparent and resulted in the loss of elution efficiency. Heating to 200°C produced an almost complete loss of efficiency. No crystallinity was detectable in these heated gels and the loss of efficiency was presumably caused by changes in pore structure accompanying irreversible loss of water.

The presence of occluded salt in the gel played an important role in its drying characteristics. Re-drying a previously formed gel (after the soluble salts had been washed out), even at low temperatures, resulted in a catastrophic loss of efficiency. A similar effect was obtained if the salts were washed from the precipitate at the filtration stage before drying. Occluded salt, present in the gel in high concentration (~ 25 wt %) appears essential during drying for the retention of an open pore structure which is capable of allowing free diffusion of the TcO_4^- ion. The salt could provide some form of steric effect in the pores or possibly influence the reversibility of the drying process.

The air oven technique used to dry the filtered gel cake in the laboratory method and the slurry in the hot cell method was too time-consuming for use on a production scale. Conventional drying on a tray with increased drying temperatures up to 110-120°C and optimised air flow appears to be a likely solution. However, a number of alternative drying techniques were evaluated. Both the evaporation and the rotary drying techniques eliminated the slurry filtration, a cumbersome step under high activity handling conditions. Their elution efficiencies were slightly lower and their appearance differed. They were opaque and encrusted owing to the presence or increased quantity of salt. Freeze drying produced gels with variable size distributions. However, the method shows some promise and merits further development. Microwave drying gave a white opaque product with a significantly decreased elution efficiency. There is evidence that if water is removed too rapidly, the gel structure does not have time to form; this may be the cause of the poor product from microwave drying.

To ensure rapid and uniform ^{99m}Tc elution in a column, the size of the irregular gel agglomerates, which have dimensions of up to 1 cm, must be reduced. The standard method employs manual crushing, an inconvenient and dusty step under high activity conditions, particularly on a production scale. The gel is an inherently brittle product with a high level of in-built strain. When cooled in air after drying at higher temperatures, it fragments over a period of some hours.

Disintegration of the freshly dried gel rapidly accelerated when it was immersed in water [Lee 1978]. This was a satisfactory method for reducing the size of the gel for use in a column and for product performance. The factors controlling this process have not been investigated in detail. Immersing the gel at 55°C and allowing it to cool to ambient over 30 minutes had no significant effect on the particle size distribution and performance of the product. However, it was observed that gels allowed to stand for several days and then immersed in water disintegrated slowly, yielding larger particles and few fines. This suggests that on standing in air, the in-built strain of the dried gel is slowly relieved owing to a slow uptake of water. Gel fragmentation in water appears to be a promising process for gel sizing on a larger scale under high activity conditions. Factors that control the particle size distribution, particularly cooling time and water temperature, need to be clarified to optimise the process.

Another essential requirement for the gel was that it should elute satisfactorily when highly active and subject to significant self-irradiation. A problem associated with alumina chromatographic generators is the occasional low yields of ^{99m}Tc. This has been attributed by several workers, including Cifka and Vesely [1971] and Stegman [1982], to radiolytic reduction of the ^{99m}Tc (VII) to a lower valence state, (IV) or (V), which is more strongly bonded to the oxide. This effect often requires the addition of a scavenger of solvated electrons to the eluant, *e.g.* nitrate, or to the generator bed.

The elution results from high activity gel generators (up to 39 GBq ^{99}Mo) demonstrated the stability of the zirconium molybdate gels under self-irradiation. Elution efficiencies did not decrease with the number of elutions, hence the deterioration that sometimes provides low efficiencies with chromatographic generators was not observed with the gel generator. The elution efficiencies were higher than those measured in the tracer studies. The larger volume of eluant required (30 cm^3 rather than 10 cm^3) was due, at least in part, to the larger columns used (3 to 4 g rather than 2 g).

Losses in yield of ^{99m}Tc from alumina column generators during elution have been attributed to the retention of water in the system [Rhodes and Croft 1978] and to chloride ions [Boyd 1982]. This led to a dry generator operation in which residual eluant was removed from the column after each elution. These effects were not apparent in the gel generators as drainage of the bed by air-blowing had no influence on the performance (Tables 14-16).

The gel can be eluted with water since the TcO_4^- ion is not strongly held by an ion exchange mechanism, as is the case with alumina, and does not require a displacing anion. The 35 GBq generator eluted satisfactorily with water to give only slightly lower efficiencies.

Gel generators used in early drying techniques, and contaminated with acetone, lose efficiency under the influence of an external γ-radiation field [Matthews 1978]. This effect occurred with nitrate- and chloride-based gels but could be prevented by the incorporation of Ce(IV). Standard gels free from organic contamination (Table 12) did not show this effect. These results indicate the advantage of using an organic-free process for the preparation of generator material which avoids the risk of accelerated radiation-induced reduction of TcO_4^- [Molinski 1982; Deutsch *et al.* 1982 and Boyd 1982].

The retention of ^{99m}Tc elution efficiency by gels at activities up to 39 GBq and the absence of ^{99m}Tc reduction effects may be attributed to a number of causes:

. The scavenging effect of residual interstitial NO_3^- in the gel.

. The lower self-irradiation field compared to the alumina chromatographic generator. The ^{99m}Mo is spread throughout the column in the gel whereas it is held in a narrow band in the alumina.

. The electron-exchange properties of the gel. Denisova *et al.* [1966] noted that zirconium molybdate was capable of oxidising $SnCl_2$ solutions and had an electron-exchange capacity of 0.18 meq g^{-1}.

. The complete absence of organics.

The results of this study indicate that the gel concept could replace or augment the developed methods for supplying ^{99m}Tc radiopharmaceutical preparations to hospitals. The concept has the advantage of using (n,γ) ^{99}Mo, which eliminates the extensive waste disposal problems associated with fission product ^{99}Mo and the need for costly processing plant to separate the fission products and transuranics present in irradiated uranium.

In addition to its potential use as a portable generator in clinical laboratories, the gel generator shows promise for large-scale production by a centralised supplier of ^{99m}Tc. The solvent extraction generator is widely used for this purpose [Boyd 1982] but has the disadvantage of being a complicated process in which product ^{99m}Tc can be contaminated with organic residues. These produce undesirable changes in the biological reactions of the ^{99m}Tc. If the gel generator is resistant to the self-irradiation from the higher activities in the large-scale generators, then it should overcome these problems. Elution by water leads to simple post-concentration processes and extends the scope of the generator in terms of the specific activity requirements of the ^{99}Mo starting material.

Future development of the generator requires a process that is suitable for routine use in a hot cell, particularly for dewatering, drying and sizing the gel. Large gel generators must be prepared and eluted in the hot cell to test their use for centralised ^{99m}Tc production. The development of concentration techniques for ^{99m}Tc would be an advantage.

The gel used in this study is not a discrete crystalline compound but an amorphous compound whose complex structure depended on its preparation. It is important to further study and understand the complexities of the gel chemistry and how these relate to the variables of preparation and to gel properties, particularly elution characteristics. A better understanding of gel chemistry will allow optimisation of the gel generator performance in terms of efficiency, elution profile and ^{99}Mo release. Because of the complex nature of this amorphous structure, it will be necessary to control and standardise the gel preparation procedures in order to obtain a consistent product.

5. CONCLUSIONS

This study has shown that the concept of a gel generator is sound and that it has the following advantages:

- The zirconium molybdate gel can be prepared in a form which is chemically and mechanically stable under the conditions of use.
- High yield TcO_4^- can be eluted with water or saline.
- The elution technique is simple.
- The gel is stable under the self-irradiation provided by ^{99}Mo loadings in a typical portable generator.
- It appears free of radiolytic effects leading to loss of elution efficiency.
- At this stage of development, the concept meets the requirements for both a portable generator and a larger generator suitable for centralised ^{99m}Tc production. This would have the advantage of providing a unified and flexible production scheme.

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7. REFERENCES

Amphlett, C.B. [1964] - Inorganic Ion Exchangers. Elsevier, Amsterdam.

Arino, H. and Kramer, H.H. [1975] - *Int. J. Appl. Radiat. Isot.*, 26:301.

Baes, C.F. and Mesmer, R.E. [1976] - The Hydrolysis of Cations. John Wiley & Sons, New York.

Boyd, R.E. [1982] - *Int. J. Appl. Radial. Isot.*, 33:801.

Clearfield, A. [1964] - *Rev. Pure Appl. Chem.*, 14:91.

Clearfield, A. and Blessing, R.H. [1972] - *J. Inorg. Nucl. Chem.*, 34:2643.

Clearfield, A., Nancollas, G.H. and Blessing, R.H. [1973] - New Inorganic Ion Exchangers in Ion Exchange and Solvent Extraction, (eds. Marinsky, J.A. and Marcus, Y.). Marcel Dekker, New York.

Cifka, J. and Vesely, P. [1971] - *Radiochim. Acta*, 16:30.

Denisova, N.E., Boichinova, E.S. and Peregudova, [1966] - *Zh. Prikl. Khim (Leningrad)*, 39:1235.

Deutsch, E., Heineman, W.R., Zodda, J.P., Gilbert, T.W., Williams, C.C., [1982] - *Int. J. Appl. Radiat. Isot.* 33:843.

Evans, J.V. and Matthews, R.W. [1978] - Australian Patent 515,808; United Kingdom 2000361; Canadian 1,131,429; United States 4,280,053; German P28,252,16-6; French 78,173,98; Japanese PA69,739.

Kraus, K.A., Phillips, H.O., Carlson, T.A. and Johnson, J.S. [1958] - Ion Exchange Properties of Hydrous Oxides. *Proc. Second Int. Conf. Peaceful Uses of Atomic Energy,* United Nations, Geneva, 28:3.

Lee, E.J. [1978] - AAEC unpublished work.

Lieberman, E. and Gemmill, W.J. [1968] - US Patent 3,382,152.

Matthews, R.W. [1978] - AAEC unpublished work.

Molinski, V.J. [1982] - *Int. J. Appl. Radiat. Isot.*, 33:811.

Pakalns, P. [1969] - *Anal. Chim. Acta*, 44:73.

Rhodes, B.A. and Croft, B.Y. [1978] - Basics for Radiopharmaceuticals. Morby, St. Louis, p.120.

Richards, P., Tucker, W.D. and Srivastava, S.C. [1982] - *Int. J. Appl. Radiat. Isot.*, 33:793.

Stegman, J. [1982] - *Int. J. Appl. Radiat. Isot.*, 33:829.

Tucker, W.D., Greene, M.W., Weiss, A.J. and Murrenhoff, A.P. [1958] - BNL-3746.

Vogel, A.I. [1961] - Quantitative Inorganic Analysis. Longmans, London.

TABLE 1
ELUTION PERFORMANCE OF STANDARD ZIRCONIUM MOLYBDATE GELS

Gel No.	1	2	3	4	5
Elution No.	Elution Efficiency (%)*				
1	77.1	75.0	80.5	81.4	76.4
2	77.0	75.5	79.4	82.8	74.3
3	70.4	75.1	82.4	83.5	77.5
4	78.2	78.3	82.5	85.8	83.4
5	80.4	77.4	83.0	83.9	80.9
6	79.3	80.4	80.1	87.2	73.2
7	75.6	79.6	84.5		
8	82.4				
Average	77.5	77.3	81.8	84.1	77.6
	Molybdenum Release (%)				
1	0.016	0.031	0.035	0.010	0.022
2	0.011	0.030	0.011	0.010	0.025
3	0.014	0.035	0.011	0.009	0.030
4	0.010	0.025	0.013	0.010	0.015
5	0.010	0.022	0.010	0.009	0.016
6	0.009	0.020	0.012	0.007	0.019
7	0.010	0.018	0.010		
8	0.010				
Average	0.011	0.026	0.015	0.009	0.021

* Elution: standard laboratory conditions (Section 2.3); 50 cm^3 saline wash before first elution.

TABLE 2
EFFECT OF ZIRCONIUM OXYNITRATE SOURCE ON GEL PERFORMANCE

	Zirconium Oxynitrate							
Origin	Alfa Lot A	Alfa Lot 091977	Alfa Lot 123077		Atomergic Batch A		Atomergic Batch B	
Zirconium %	35.5	27.8	30.7		20.7		19.3	
Nitrate %		41.0	46.7		36.7		35.4	
Solution pH	0.97	0.75	0.42	0.96*	0.57	0.95*	0.63	0.95*
Elution No.	Elution Efficiency (%)							
1	84.2	77.1		75.1	73.4	84.5	71.8	87.7
2	81.4	70.4		78.7	72.6	86.5	73.1	86.5
3	83.1	74.9	Gel	82.3	75.3	85.3	73.5	87.7
4	86.8	75.6	Peptised	81.2	77.7	90.5	78.8	88.7
5	83.3	75.8		79.1	79.0	88.8	75.9	90.5
Average	83.8	74.8	-	79.3	75.6	87.1	74.6	88.2
	Molybdenum Release (%)							
1	0.056	0.034		0.010				
2	0.057	0.025		0.010				
3	0.060	0.025		0.009				
4	0.057	0.020		0.010				
5	0.060	0.021		0.009				
Average	0.058	0.025		0.010				

Elution: standard conditions, 50 cm^3 saline wash before first elution.

* pH adjustment with NaOH solution (3 mol dm^{-3}).

TABLE 3

EFFECT OF pH OF MOLYBDATE SOLUTION ON GEL PERFORMANCE

pH of Molybdate Solution	3	4	5	6	6.5	7
pH of Filtrate	1.1	1.3	1.3	1.5	1.7	2.8
Elution No.	Elution Efficiency (%)					
1	85.2	84.2	95.7	93.6	92.2	91.9
2	74.8	81.4	85.5	94.1	92.1	92.4
3	80.5	83.1	89.0	92.5	91.0	93.2
4	82.4	86.8	92.6	93.6	91.0	93.6
5	77.4	83.3	89.4	85.5	87.4	89.5
Average	80.1	83.8	90.4	91.8	90.7	92.1
	Molybdenum Release (%)					
1	0.017	0.056	0.067	0.088	0.088	0.15
2	0.025	0.057	0.069	0.086	0.079	0.15
3	0.023	0.060	0.063	0.082	0.081	0.11
4	0.026	0.057	0.068	0.082	0.077	0.13
5	0.033	0.060	0.069	0.081	0.089	0.11
Average	0.025	0.058	0.067	0.084	0.083	0.13

Elution: standard conditions; 50 cm^3 saline wash before first elution.

TABLE 4
EFFECT OF Zr:Mo RATIO ON GEL PERFORMANCE

Zr:Mo Ratio	1.2:1	1.1:1	1:1	1:1.1	1:1.2	1:1.3
Elution No.	Elution Efficiency (%)					
1	72.3	68.3	71.1	75.6	87.0	86.9
2	67.7	71.4	73.3	75.2	83.7	90.9
3	67.6	70.6	70.5	73.5	82.0	90.3
4	80.4	69.9	73.1	72.9	82.4	91.1
5	74.4	73.6	74.6	76.7	76.4	87.6
Average	72.5	70.8	72.5	74.8	82.3	89.4
	Molybdenum Release (%)					
1	0.067	0.044	0.036	0.076	0.076	0.14
2	0.014	0.011	0.039	0.069	0.080	0.11
3	0.010	0.011	0.044	0.072	0.079	0.12
4	0.013	0.014	0.046	0.072	0.073	0.11
5	0.022	0.022	0.043	0.050	0.091	0.10
Average	0.025	0.020	0.042	0.068	0.080	0.12

Elution: standard conditions; 10 cm^3 saline wash before first elution.

TABLE 5
REPLACEMENT OF AMMONIUM BY SODIUM IONS IN GEL PREPARATION

Gel*	1	2	3
Elution No.	Elution Efficiency (%)		
1	87.6	48.2	81.1
2	84.7	42.5	74.7
3	81.1	44.1	71.1
4	78.7	45.5	78.3
5	77.7	49.1	77.4
Average	82.0	45.9	76.5
	Molybdenum Release (%)		
1	0.025	0.040	0.035
2	0.014	0.025	0.042
3	0.011	0.022	0.035
4	0.020	0.025	0.035
5	0.010	0.012	0.025
Average	0.016	0.025	0.034

Elution: standard conditions; gels washed with 50 cm^3 saline before elution.

* Gels prepared by standard method except that NaOH was substituted for NH_4OH in preparing the zirconium and molybdenum solutions.

* Gels 1 and 2 were dried at 100°C and gel 3 at 55°C. Gel 2 was re-dried after the 50 cm^3 water wash.

TABLE 6
EFFECT OF DRYING TEMPERATURE ON GEL PERFORMANCE

Drying Temp. (°C)	Ambient	57	74	90	107	120	142	164
Elution No.				Elution Efficiency (%)				
1	92.6	81.4	76.9	82.9	79.8	74.7	51.4	36.3
2	92.3	82.8	74.3	84.3	83.4	78.5	61.5	50.5
3	91.9	83.5	77.3	82.3	86.0	77.6	67.1	54.1
4	92.1	85.8	77.2	83.8	77.7	80.1	63.6	52.3
5	92.2	83.9	78.3	83.2	79.8	78.5	61.9	49.7
6	93.0	87.2	79.5	85.0	83.4	76.5	63.0	52.9
Average	92.3	84.1	77.25	83.6	81.7	77.6	61.4	49.3
				Molybdenum Release (%)				
1	0.011	0.010	0.008	0.010	0.009	0.006	0.012	0.018
2	0.009	0.010	0.007	0.009	0.008	0.007	0.012	0.015
3	0.009	0.009	0.007	0.008	0.007	0.007	0.012	0.015
4	0.008	0.010	0.006	0.008	0.007	0.007	0.012	0.015
5	0.008	0.009	0.007	0.008	0.006	0.006	0.012	0.014
6	0.007	0.007	0.007	0.008	0.007	0.006	0.012	0.013
Average	0.009	0.009	0.007	0.008	0.007	0.006	0.012	0.015

Elution: standard conditions; 50 cm^3 saline wash.

TABLE 7
EFFECT OF HEATING ON GEL STABILITY

Temperature (°C)	45	65	86	115	165	200	268	400
Elution No.	Elution Efficiency (%)							
1	69.2	76.5	76.3	80.7	55.8	0.7	0.4	1.6
2	73.3	73.3	79.6	76.1	42.1	0.4	1.5	8.8
3	69.3	77.4	76.6	73.8				
4	68.3	83.4	81.8	79.9				
5	72.6	71.9	71.8	68.4				
Average	70.5	76.5	77.2	75.8	49.0	0.6	1.0	5.2

Elution: standard conditions; 10 cm^3 saline wash before first elution.

TABLE 8
PREPARATION USING AN EVAPORATION PROCESS

	Standard Gel	Evaporated Gel Nos.* 1	2	3	Standard Gel	Evaporated Gel Nos.* 1	2	3
Elution No.	Elution Efficiency (%)				pH of Eluate			
1	70.2	69.3	65.1	76.9	2.11	2.10	2.06	2.11
2	68.1	73.1	62.7	78.4	2.11	2.17	2.04	2.09
3	71.8	73.9	70.9	77.3	2.33	2.35	2.28	2.21
4	74.1	76.9	72.9	80.1	2.42	2.42	2.36	2.35
5	71.6	74.6	71.5	80.2	2.55	2.56	2.49	2.55
6	72.3	75.2	72.4	79.4	2.57	2.60	2.59	2.57
Average	71.4	73.8	69.2	78.7				

Elution: standard conditions; 50 cm^3 saline wash.

* Prepared as hot cell method (Section 2.2.2).

TABLE 9
GEL DISINTEGRATION ON WATER IMMERSION

Gel No.*	1	2	3	4
Elution No.	Elution Efficiency (%)			
1	77.5	73.7	81.7	74.0
2	78.4	75.4	73.4	78.4
3	71.7	79.1	71.5	79.5
4	72.1	78.1	72.9	77.2
5	79.7	78.7	74.4	77.1
6	80.0	80.8	89.0	81.0
Average	76.6	77.6	77.2	77.9
	Molybdenum Release (%)			
1	0.087	0.091	0.122	0.104
2	0.043	0.036	0.038	0.035
3	0.019	0.017	0.018	0.017
4	0.017	0.015	0.015	0.015
5	0.016	0.015	0.013	0.013
6	0.015	0.015	0.012	0.013
Average	0.030	0.030	0.040	0.030

* Gels dried in oven at 55°C then, before elution, treated as follows:

Gel No.1. Stood for 30 min to cool to room temperature, loaded into a generator and water (150 cm^3) at room temperature passed through column at 0.8 $cm^3\ min^{-1}$.

Gel No.2. Stood for 30 min, then added to beaker of water (150 cm^3) at room temperature and aged for three hours.

Gel No.3. As No.1 except that gel was at 55°C on immersion.

Gel No.4. As No.2 except that gel was at 55°C on immersion.

Elution: standard conditions; 50 cm^3 saline wash before first elution.

TABLE 10
EFFECT OF REDRYING GEL AFTER SALT REMOVAL

Gel No.*	1	2	3	4
Elution No.	Elution Efficiency (%)			
1	2.3	2.2	2.6	1.9
2	4.4	4.3	5.3	3.4
3	4.7	4.7	5.6	4.0
4	4.8	4.8	5.9	3.9
5	5.0	4.8	5.7	3.6
6	6.5	5.4	6.6	4.1
Average	4.6	4.4	5.3	3.5
	Molybdenum Release (%)			
1	0.006	0.010	0.010	0.031
2	0.053	0.067	0.041	0.029
3	0.031	0.032	0.024	0.021
4	0.019	0.027	0.017	0.015
5	0.021	0.022	0.016	0.013
6	0.022	0.022	0.012	0.015
Average	0.030	0.030	0.020	0.020

* Gels pretreated as in Table 9 and redried at 55° before elution.

Elution: standard conditions; 50 cm^3 saline wash before first elution.

TABLE 11
EFFECT OF SALT REMOVAL BEFORE GEL FORMATION

Gel Preparation	Standard	Washed*	Standard	Washed*
Elution No.	Elution Efficiency (%)		pH of Eluate	
1	70.2	3.8	2.11	2.09
2	68.1	4.3	2.11	2.12
3	71.8	4.0	2.33	2.16
4	74.1	5.0	2.42	2.20
5	71.6	5.5	2.55	2.32
6	72.3	4.6	2.57	2.34
Average	71.4	4.5		

Elution: standard conditions; 50 cm^3 saline wash before first elution.

* Gel prepared by standard method, except zirconium molybdate precipitate washed with water to remove NH_4NO_3 before drying.

TABLE 12
EFFECT OF γ-IRRADIATION ON ELUTION EFFICIENCIES OF MOLYBDATE GELS

	Gel Type	Zr/Mo	Zr/Mo	Zr/Mo	Zr/Mo* 10% Ce(IV)	Zr/Mo* 10% Fe(III)
Elution No.	Pretreatment	Elution Efficiency (%)				
1	Nil	64.3	76.0	72.5	76.4	56.0
2	Nil	71.8	71.5	71.6	64.8	49.6
3	Nil	66.9	70.8	73.7	69.9	53.7
4	Irradiation+	72.5	74.2	72.1	69.8	55.5
5	Nil	72.9	71.8	75.2	65.1	45.5
6	Irradiation+	73.9	75.5	73.6	74.7	52.0
7	Nil	73.6	73.9	75.2	69.9	47.6
8	Irradiation+	76.3	73.5	71.7	80.8	51.0

Elution: standard conditions; 50 cm^3 of saline wash before first elution.

* Gels prepared in usual fashion but substituting 10 mol % Zr with Ce(IV) or Fe(III).

+ Gels γ-irradiated between elutions for 17 hours in a 1 Mrad h^{-1} field using a ^{60}Co source.

TABLE 13
ELUTION EFFICIENCIES OF ZIRCONIUM MOLYBDATE GELS DRIED WITH ACETONE

Gel Type		Nitrate Derived		Chloride Derived*	
	Drying Method	Standard	Acetone+	Standard	Acetone+
Elution No.	Pretreatment	Elution Efficiency (%)			
1	Irradiation**	70.9	18.2	84.4	39.1
2	Irradiation**	72.3	26.6	88.7	31.2
3	Nil	80.6	60.5	87.3	57.3

Elution: standard conditions; 50 cm^3 saline wash before first elution.

* Gels prepared by the standard procedure but zirconium oxychloride substituted for oxynitrate.

+ Gels washed with acetone and air-dried at 55°C.

** Gels irradiated as in Table 12

TABLE 14
ELUTION OF HIGH ACTIVITY ZIRCONIUM MOLYBDATE GEL (n,γ)^{99}Mo
BATCH 1

Elution No.	Elution Efficiency (%)	Molybdenum Release (%)	Elution After Treatment
		Generator No.3 (24 GBq)	
	Saline/Water		
1	53		
2	73	0.20	Water rinse and air drain
3	64	0.15	
4	66		
5	57	0.33	
6	65	0.13	Water elution only
7	66		
8	66		
		Generator No.1 (31 GBq)	
	Saline		
1	68	0.16	
2	74		
3	69	0.18	Water rinse and air drain
4	69	0.16	
5	71	0.09	
6	69	0.20	
7	71	0.07	
8	71		Nil
9	71		
		Generator No.2 (38 GBq)	
	Saline		
1	71	0.19	
2	53	0.09	Water rinse and air drain
3	65	0.11	
4	66		
5	65	0.13	
6	64	0.11	
7	66		Water rinse only
8	47		
9	67		
10	66		

Elution: 10 cm^3 of saline under gravity (last three elutions of No.3 with water); washed with 10 cm^3 of saline and 10 cm^3 of water before first elution.

After elution some generators (as indicated) were rinsed with 10 cm^3 of water and interstitial water was removed with air.

Elution rates: generator 1, 0.3-0.4 cm^3 min^{-1}; generator 2, 0.5-0.6 cm^3 min^{-1}; generator 3, 0.2

TABLE 15
ELUTION OF HIGH ACTIVITY ZIRCONIUM MOLYBDATE GEL $(n,\gamma)^{99}Mo$
BATCH 2

	Elution Efficiency (%) Saline			Molybdenum
	0-10 cm^3	10-20 cm^3	Total	Release (%)
Elution No.	Generator No.1 (24 GBq)			
1	54		54	
2	57		57	
3	55		55	
4	61	7	68	
5	63	5	68	
6	60	8	68	
7	64	6	70	0.01
8	72	4	76	
Elution rate 0.7-1.3 cm^3 min^{-1}				
	Generator No.2 (29 GBq)			
1	43		43	
2	49		49	
3	56		56	
4	61	9	70	
5	57	13	70	
6	67	6	73	
7	69	5	74	0.012
8	72	5	77	
Elution rate 0.6-1.4 cm^3 min^{-1}				

Elution: 2 × 10 cm^3 lots of saline under gravity; washed with 50 cm^3 of saline and 10 cm^3 of water.

After each elution, columns rinsed with 10 cm^3 ofwater and interstitial water removed with air.

TABLE 16
ELUTION OF HIGH ACTIVITY ZIRCONIUM MOLYBDATE GEL $(n,\gamma)^{99}Mo$
BATCH 3

	Elution Efficiency (%)				Molybdenum
Elution No.	0-10 cm³	10-20 cm³	20-30 cm³	Total	Release
			Generator No.1 (34 GBq)		
1	56			56	
2	50	15	9	74	
3	58	14	7	79	
4	61	14	5	80	
5	66	9	9	84	
6	70	7	4	81	
7	67	8	4	79	0.008
Average	61	11	6	78	
			Generator No.3 (35 GBq)		
1	61			61	
2	40	16	8	64	
3	50	20	11	81	
4	64	9	3	76	
5	36	9	9	54	
6	46	6	4	56	
7	54	6	4	64	0.008
Average	50	11	7	68	
			Generator No.2 (39 GBq)		
1	44			44	
2	54	16	8	78	
3	63	15	5	83	
4	67	12	5	84	
5	73	10	3	86	
6	74	7	3	84	
7	75	7	2	84	0.007
Average	64	11	4	79	

Elution: generators No.1 and 2 were eluted with 3 × 10 cm³ lots of saline.

Generator No.3 was eluted similarly with water. Washed with 50 cm³ saline (No.3 with water) before first elution. The columns were not rinsed or drained after elution. Elution rate, 0.7-1.3 cm³ min^{-1}.

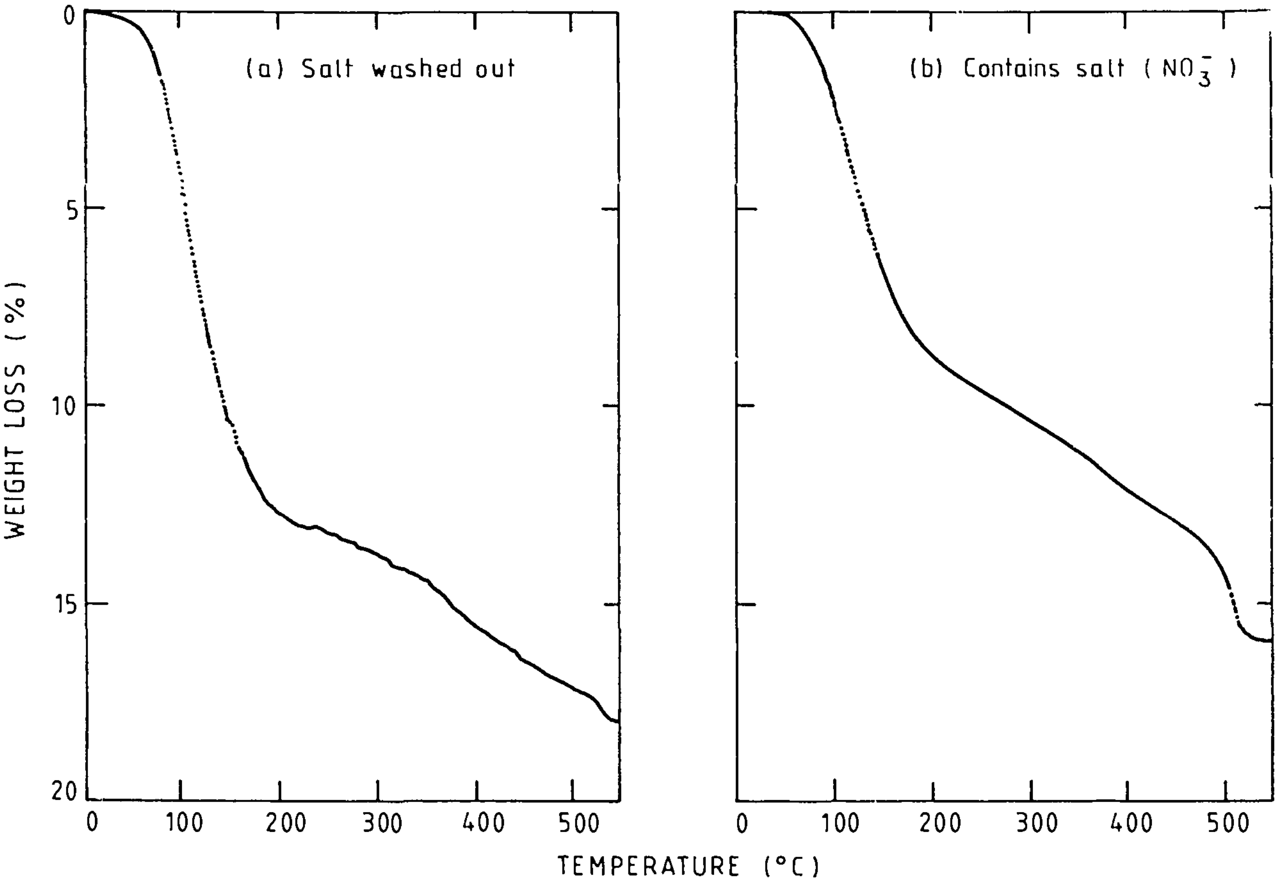

FIGURE 1 Thermogravimetric plots of zirconium molybdate gels heated at 5°C/min in flowing nitrogen. Comparison of water contents in gel containing salt and the same gel washed free of salt

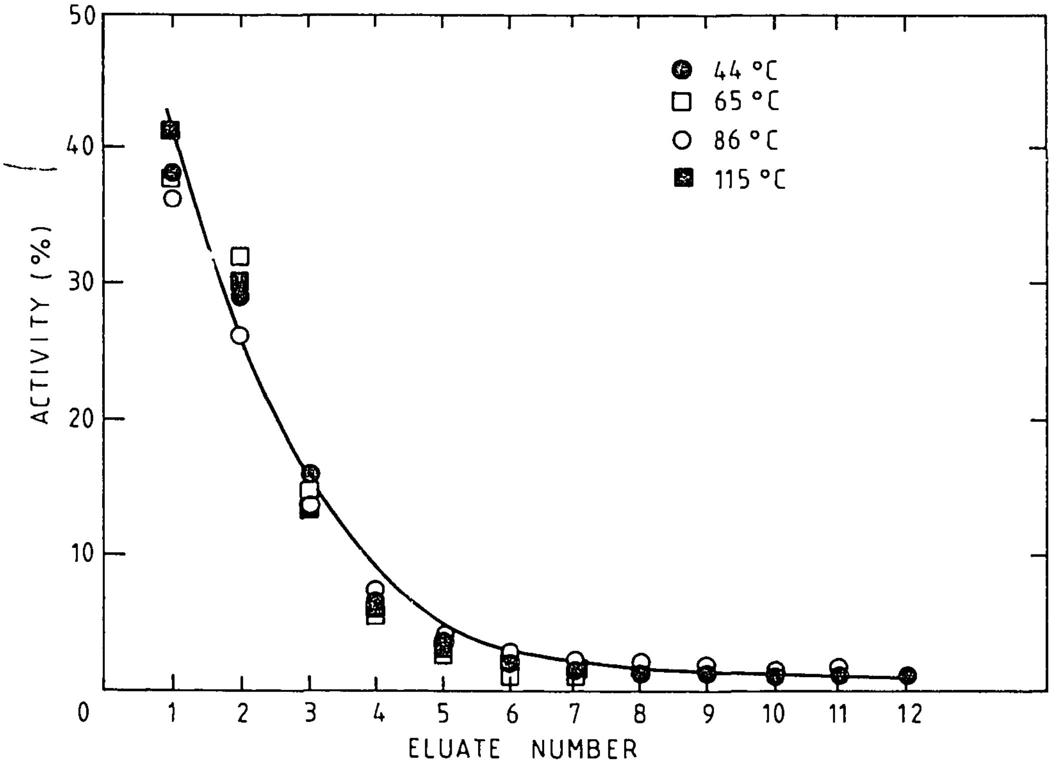

FIGURE 2 Elution profiles of zirconium molybdate gels, 2nd elution. Effect of temperature