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PREPARATION OF ZIRCONIUM MOLYBDATE GEL FOR ^{99m}Tc GEL GENERATOR

September 1988

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Zirconium molybdate gel has excellent characteristics for use as column matrix material of ^{99m}Tc generators. In this work, zirconium molybdate gels were prepared under different conditions; pH's of molybdate solutions from 2.5 to 7.0, Mo:Zr molar ratios from 0.7:1.0 to 1.3:1.0, drying temperatures from an ambient temperature to 200°C, and drying times from 1 h to 25 h. Contents of water, nitrate, molybdenum and zirconium were measured to examine the fundamental conditions in gel preparation. The Mo:Zr molar ratio was 1.0:1.0 for the most of gels obtained. A ^{99m}Tc generator was prepared with an amorphous zirconium molybdate containing a tracer level of ^{99}Mo as column matrix material. Elution of ^{99m}Tc was rapid and the average elution efficiency was 90 % for 6 ml elutions. Contents of radionuclidic impurities, Zr and Mo in the eluates, were low enough to meet the pharmacopoeia requirements for human use.

Keywords: Zirconium Molybdate Gel, Gel Preparation, Radioactive Zirconium Molybdate, ^{99m}Tc Gel Generator

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* On leave from Centre for Radioisotope Production, National Atomic Energy Agency, Indonesia

^{99m}Tc ゲルゼネレータ用ジルコニウム・モリブデン酸ゲルの調製

日本原子力研究所東海研究所アイソトープ部
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（１９８８年８月１０日受理）

ジルコニウム・モリブデン酸ゲル（以下，ゲル）は，^{99m}Tcゼネレータのカラム充塡材に適した性質をもっている。ゲル調製時の基礎条件を研究するため，ゲルを種々の条件（モリブデン酸溶液のpH；2.5～7.0，Zr：Moのモル比；0.7：1.0～1.3：1.0，乾燥温度；室温～２００℃，乾燥時間；1～２５時間）で調製し，ゲルのZr，Mo，硝酸塩および水分等の含有量を調べた。ゲルのZr：Moモル比は，ほとんど大部分のゲルが1.0：1.0であった。トレーサ量の放射性ゲルをカラム充塡材に用いて ^{99m}Tc ゲルゼネレータを調製し，$^{99m}TcO_4^-$ の溶離持性を調べた。その結果，$^{99m}TcO_4^-$ は迅速に溶離され，平均溶離効率は９０％であった。$^{99m}TcO_4^-$ 溶出液中に含まれる放射性不純物核種，Zr および Mo 量は人体投与のための医薬品基準に充分適合していることを確認した。

本報告は科学技術庁の科学技術者交流計画によっておこなわれたものである。

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1. Introduction

Technetium-99m (^{99m}Tc) is currently the most widely used radioisotope in nuclear medicine and accounts for over 85 % of all the diagnostic in vivo medical applications of radioisotopes. Usually, ^{99m}Tc is separated from its parent nuclide, ^{99}Mo; i.e. a ^{99m}Tc generator.

The first ^{99m}Tc generator[1] was developed at Brookhaven National Laboratory (BNL) in 1957 based on column chromatography over aluminum oxide which adsorbed ^{99}Mo obtained from fission products of ^{235}U. Following this BNL concept, GEMILL and LIEBERMAN[2] developed a medical generator using ^{99}Mo obtained from neutron activation of ^{98}Mo. These generators of aluminum oxide, easy to handle and capable of reliable operation, elute high purity ^{99m}Tc efficiently.

Most of the commercial ^{99m}Tc medical generators are still produced based on the concept of BNL. However, this type of generators has several disadvantages which limit its practical application. The major one is the limitation of the adsorption capacity of alumina for molybdate ions (at pH 4, 20 mg per gram of alumina)[3]. Another one is the breakthrough of a trace quantity of molybdenum due to low adsorption capacity of alumina for molybdate ions. The limitation of the adsorption capacity for molybdate ions requires the use of ^{99}Mo of high specific activity or "carrier free" ^{99}Mo in the preparation of chromatographic generators of reasonable size which allows rapid elution in small volume. In countries which have neither a nuclear reactor with sufficient neutron flux to irradiate the enriched ^{98}Mo nor technology necessary to handle fission products of ^{235}U, it is almost impossible to prepare chromatographic generators suitable for the medical use.

The increasing use of ^{99m}Tc in the field of nuclear medicine urged the development of various types of ^{99m}Tc generators. GERLIT[4] and LATHROP[5] developed solvent extraction generators based on liquid-liquid extraction. ROBSON[6] developed sublimation generators based on the difference in the sublimation temperatures between molybdenum trioxide and technetium pentaoxide. TACHIMORI[7] studied the sublimation mechanism of technetium and found that ^{99m}Tc was sublimated in the form of $^{99m}TcO_2$. An advantage of these generators is that ^{99}Mo of a low specific activity produced by the ^{98}Mo(n,γ)^{99}Mo reaction can be used to obtain a high concentration of ^{99m}Tc. One of the problems of the solvent extraction generators is that the ^{99m}Tc contains contaminants of methylethylketone (MEK) formed during the evaporation process. Another problem is a possible fire risk which would result

from the MEK vapor. The third problem is a complicated operation of the system which requires highly trained personnels. The low separation efficiency (about 25%) is one of the disadvantages of the sublimation generators. These techniques do not seem suitable for a small nuclear medicine laboratory.

The problems as mentioned above can be overcome by the use of the zirconium molybdate gel generator. The concept of this generator, which was first developed by EVANS et al.[8], is to incorporate low-specific-activity ^{99}Mo produced from the ^{98}Mo (n, γ) ^{99}Mo reaction into zirconium molybdate gels to be used as a column matrix material. The gels are obtained as amorphous precipitates on mixing aqueous solutions of ammonium molybdate and zirconium oxynitrate. This gel contains approximately 25 wt% of molybdenum, whereas 0.2 wt% of molybdenum is adsorbed on alumina. The properties of the gels vary non-reproducible depending on such preparation conditions as the pH of molybdenum and zirconium solutions, the mole ratio of molybdenum and zirconium, the order of mixing molybdenum and zirconium, and the conditions of aging, washing, and drying the precipitates.

The present work aims to elucidate the properties of zirconium molybdate gels prepared from molybdate and zirconium oxynitrate solutions under various conditions. A ^{99m}Tc gel generator is prepared by radioactive molybdate (^{99}Mo) and zirconium oxynitrate solutions. Elution characteristics of ^{99m}Tc eluted with physiological saline solution is investigated.

2. Experimental

2.1 Preparation of Zirconium Molybdate Gel

The following procedure was adopted for the preparation of zirconium molybdate gels as a standard procedure. Molybdate trioxide (15 g, Merck) was dissolved in 3 M ammonium hydroxide solution and the pH was adjusted to 4.0 with 5 M nitric acid solution. The whole solution was then diluted to 500 ml with water. The zirconium oxynitrate solution (27 g, Kanto Chemical) was dissolved in water and the pH was adjusted to 1.0 by the slow addition of 5 M ammonium hydroxide solution while the solution was stirred. This solution was diluted to 500 ml with water. The molybdate solution (40 ml) was added slowly with a pipet to the equimolar zirconium oxynitrate solution while being vigorously stirred. The precipitate obtained was vacuum filtered with a Buchner funnel, washed with 5 ml water and dried at 100°C for 6 h. The dried product was then crushed and sieved, and the

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150-500 μm (100-32 mesh) fraction was selected for analysis.

Other gels were prepared under different conditions in order to study the effect of the preparation conditions. The preparation conditions were as follows: Firstly, the pH of the molybdate solution was changed from 2.5 to 7.0, while the pH of the zirconium solution was kept at 1.0. Secondly, the Mo:Zr molar ratio was changed from 0.7 to 1.0. Thirdly, the drying temperature was changed from an ambient temperature to 200°C. Fourthly, drying time was changed from 1 h to 25 h.

2.2 Gel Analysis

2.2.1 Water Content

The Gels obtained under above mentioned conditions were dried at 70°C for 15 h before analysis. Dehydration profiles of the gels were obtained with a thermal gravimetry/differential thermal analyzer (Daini Seikosha Model SSC 560 GH). The gels were heated from 100°C to 500°C at the heating rate of 100°C/min in argon gas which flowed at the rate of 50 ml/min. The water content of gels were determined from the weight loss of the gels from 100°C to 300°C (see Fig. 1).

2.2.2 X-ray Diffraction

X-ray diffraction patterns of the gels were obtained with a Rigaku X-ray Diffractometer equipped a monochrometer of pyrolitic graphite. The X-ray intensities were measured by diffractive analysis in the range from 10 to 65 degree at the scanning speed of 2 deg/min (see Fig. 2).

2.2.3 Determination of Molybdenum, Zirconium, Oxygen and Nitrate

About 50 mg of each zirconium molybdate gel was dissolved in 2 ml of concentrated sulfuric acid and diluted to 100 ml with water. The molybdenum contents were determined with an atomic absorption spectrometer (Shimazu, model AA-670G) equipped with a graphite furnace. The maximum operation temperature was 3000°C. The calibration curve for molybdenum was obtained with a molybdenum standard solution (from 50 to 150 ppb, see Fig. 3). An aliquot of the samples (0.1 ml) was taken and diluted to 100 ml with water. Molybdenum contents in the sample solution were dtermined from the calibration curve.

Zirconium contents were determined spectrophotometrically by the arsenazo-III method[9] with a Hitachi 181 UV-VIS spectrophotometer. The calibration curve for zirconium was obtained with zirconium standard solu-

tions (from 9.4 to 47 μg/100 ml, see Fig. 4). The sample solution (0.2 ml) was transferred to 100 ml volumetric flasks containing 50 ml of concentrated nitric acid and 5 ml of 10 % urea solution. After a few minutes, 10 ml of the 0.1 % arsenazo-III solution was added to the 100 ml volumetric flask, and then the mixture was shaken, cooled in icy water, and diluted to 100 ml with water. The absorbance of the solution was measured at 665 nm against a reagent blank. Oxygen contents in the gel were calculated from a weight percent of zirconium molybdate gels.

Nitrate ion contents in the solution were determined with a nitrate-ion-selective electrode. In order to obtain a calibration curve under the same conditions as sample solutions, a 10 ml portion of 0.4 M sulfuric acid solution and 1500 ppm of zirconyl ion were added to various NO_3^- standard solutions (1-500 ppm). The pH of the solution was adjusted in the range from 9 to 10 with diluted sodium hydroxide solution. The solutions were filtered to eliminate zirconium hydroxide, $ZrO(OH)_2$. After the pH of the filtrates was adjusted from 6.5 to 8.5, lithium acetate solution (5 ml, 1 mM) was added to adjust the ion strength and then the solution was exactly diluted to 50 ml with water. Portion of the solution were transferred into a beaker and stirred. The electromotive force (e.m.f.) were measured. A calibration curve was obtained by plotting each e.m.f. reading in millivolts against logalithm of the concentration of nitrate ion (see Fig. 5). Portions (10 ml) of the sample solution containing 1-30 ppm of nitrate ion were used for the measurement of nitrate ion concentrations.

2.3 Preparation of Radioactive Zirconium Molybdate Gel

Five grams of MoO_3 was irradiated for 1 h at thermal neutron flux of 5.6×10^{13} $cm^{-2} \cdot s^{-1}$ in the JRR-4 reactor. The irradiated target was dissolved in 20 ml of 3 M ammonium hydroxide solution and the pH was adjusted to 4.0 with 5 M nitric acid solution. This solution was then added to an equimolar zirconium oxynitrate solution (pH 1.0) while being stirred. The precipitate obtained was vacuum filtered with a Buchner funnel and dried at 80°C for 6 h. Finally, the dried gel was crushed and sieved and the 150-50 μm in diameter (100-32 mesh) fraction was collected to use as a generator.

2.4 Preparation and Elution of ^{99m}Tc Gel Generator

Two grams of radioactive gel was transferred to a generator column (8 mm in diameter and 80 mm high) equipped with a sintered glass frit (G-2

size). A piece of quartz wool was placed on the top of the column. The generator was washed with 50 ml of water and then 50 ml of physiological saline solution. The ^{99m}Tc was eluted with a saline solution at a constant flow rate of 1.0 ml/min. The elution profiles of the ^{99m}Tc was determined by measuring ^{99m}Tc radioactivity in 10 ml eluates (2 ml each). The generator was eluted daily with 6 ml of saline solution.

2.5 Eluate Analysis

The ^{99m}Tc radioactivity in the eluates was measured with an ionization chamber coupled to a Capintec Radioisotope Calibrator (CRC-10 R). The ^{99}Mo in the eluate as a radioactive impurity was measured by placing the eluates in a 4 mm thick lead container. Other radioactive impurities were measured by a HPGe detector coupled to a multichannel analyzer (4095 channel, Canberra, series 35). Amounts of zirconium, molybdenum, and nitrate in the eluate were estimated from the data obtained for non-radioactive zirconium molybdate gel generator.

2.6 Determination of the Breakthrough of Molybdenum, Zirconium and Nitrate Ion

Breakthrough profiles of molybdenum, zirconium and nitrate ions were measured for a non-radioactive gel generator. A column which contained 3 g of the gel was washed continuously with 150 ml of saline solution, and the eluates were collected in every 10 ml with a fraction collector. The amount of zirconium, molybdenum and nitrate ion in the eluates were determined in the procedure described above.

3. Results and Discussion

The pH of filtrates for the gels which were prepared with various molybdate solutions (pH 2.5 to 7.9) varied between 1.2 and 2.9 (Table 1). The appearance of the gel changed from pale translucent yellow at pH 2.5 of molybdenum solution to opaque white at pH 7.0.

The appearance of the gel which was prepared with various Mo: Zr molar ratios (0.7:1.0 to 1.3:1.0) became more opaque and less colored with increasing relative content of zirconium. The pH of molybdate solution did not give large effects on the Mo:Zr molar ratios in the gels, as shown

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in Table 1.

The water content in the gel was determined from the weight lost between 100°C and 300°C (Fig. 1). The thermogravimetric curve showed rapid weight loss above 300°C, probably indicating the decomposition of a material in the gel. EVANS[10] has pointed out that the decomposed material is ammonium nitrate of a soluble salt (originally 22 %). Although gels were prepared at various pH from the molybdate solutions, the water content was approximately 4 wt% for all the gels prepared, as shown in Table 1. In this work, the water content in a gel obtained under the standard condition was about 4 wt%. This value was smaller than that of EVANS' work (10 %). This disagreement may be ascribed to the drying procedure (70°C, 15 h) before analysis of the water content. The predrying possibly caused some dehydration of the gel.

The effect of Mo:Zr molar ratio in the water content in the gel was investigated. The Mo:Zr molar ratios varied from 0.7:1.0 to 1.3:1.0, as shown in Table 2. Weight percent of water content in the gel decreased significantly as the Mo:Zr molar ratios increased.

At the ratio of 0.7:1.0, the weight percent of water was 5.6 %. At the ratio of 1.3:1.0, the weight percent of water was only 2.8 %. For other items, scattering in the data is large, so that a clear interpretation is difficult at present. The effect of drying temperature on the water content was also investigated. The drying temperature was changed from an ambient temperature to 200°C, as shown in Table 3. The weight percent of water decreased significantly as the drying temperature increased. At an ambient temperature, the weight percent of water was 9.0 %. At 200°C, the weight percent of water was smaller than 0.5 %. The effect of drying time on the water content in the gel was investigated, as shown in Table 4. No significant change in the water content was observed for the gels dried for different periods (1 h to 25 h). Water content in the gel is an important parameter. EVANS[11] studied the effect of the drying temperature on the ^{99m}Tc elution efficiency. According to his study, drying above 120°C reduces the elution efficiency of ^{99m}Tc and ^{99m}Tc is not eluted from the gel dried above 200°C. Since the water content in the gel also decreases to almost zero at temperatures above 200°C, there should be some correlation between the ^{99m}Tc elution efficiency and the water content in the gel.

Drying temperature dependences of the Mo:Zr molar ratio are summarized in Table 3. No significant difference in the Mo:Zr molar ratio of the gel was obtained. Drying time dependences of the Mo:Zr ratios are summarized

in Table 4. The molar ratios of Mo:Zr fluctuated between 1.0:1.0 and 1.0:1.4. Because the Mo:Zr molar ratio was nearly 1.0:1.0 for every gel, the stoichiometry would approximately be $ZrO_2 \cdot MoO_3 \cdot x\,H_2O$ as reported by EVANS[11].

All the gels produced under the varying conditions showed no signals due to the structure in the X-ray diffraction patterns, as shown in Fig. 2. Those gels were amorphous.

The nitrate content in the gel prepared under various conditions was listed in Table 5. According to EVANS, the nitrate content in dried gels, which were not washed before drying, was from 20 wt% to 30 wt%. In this work, the precipitates of zirconium molybdate were always washed with water before drying and the nitrate contents were found to be lower than that reported by EVANS. The presence of occluded salts in the gel is considered to play an important role in forming an open pore structure which allows easy diffusion of $^{99m}TcO_4^-$ ions from the radioactive zirconium molybdate gel.

The contents of molybdenum, zirconium, water and nitrate in the gel prepared in this work did not agree well with the results of EVANS. In order to improve the drying condition of the gel, the following procedures should be adopted. The water content should be determined from the weight loss of the gel dried at 100°C for 24 h without further predrying before analyses. The molybdenum and zirconium contents should be determined after igniting the gel at 600°C to remove the ammonium nitrate in the gel. The oxygen content can be calculated from the weight percent of zirconium and molybdenum in the gel.

To investigate the chemical stability of the gel against the saline solution, the amount of Zr, Mo and nitrate in eluates obtained from the non-radioactive gel generator (3 g) were determined. The gel components was continuously eluted with saline solution (10 ml each). The amount of Zr, Mo and nitrate was measured for these samples. As shown in Table 6, the Zr content was too small to be detected in each of the 15 fractions except for the fraction number 9 (48 ppm). The Mo content was found to be smaller than 2 ppm except for the fraction number 11 (>4.3 ppm). The Mo content was found to increase as the fraction number increased, but the content remained within the permissible limit. The nitrate content decreased slightly as the fraction number increased.

The elution characteristics of ^{99m}Tc was examined by eluting ^{99m}Tc with saline solution from a gel generator, which was prepared with the radioactive zirconium molybdate gel dried at 80°C for 6 h. The performance of the ^{99m}Tc gel generator used in this column work is shown in Table 7.

The elution profile of ^{99m}Tc obtained from the radioactive gel generator (2 g, 87 MBq or 2.345 mCi) showed a sharp peak. As seen in Fig. 6, more than 95 % of ^{99m}Tc was eluted in only 6 ml of saline solution. The mean elution efficiency (yield) of ^{99m}Tc eluted with 6 ml of saline solution was 90 %. The ^{99}Mo radionuclidic impurity in eluates was below the detection limit when measured with an ionization chamber detector. The γ-ray spectra of the eluate were measured with a HPGe detector coupled to a multichannel analyzer. A single peak of ^{99m}Tc at 140 keV was observed together with very small peaks of ^{99}Mo at 181 keV, 740 keV, and 778 keV, as shown in Fig. 7. The experimental elution of ^{99m}Tc from the gel generator (Fig. 6, 7) demonstrated that the radioactive zirconium molybdate gel prepared in the present work was an excellent column matrix for a ^{99m}Tc generator.

The final purpose of this work is to find out the optimal preparation conditions of the radioactive gel suited for the column matrix of the generator. Thus, the influence of the gel preparation conditions, particularly the dehydration, on the ^{99m}Tc elution should be investigated further in future.

The breakthrough amount of Mo, Zr and nitrate from the gel generator was examined. The amount of Mo in the eluate was estimated to be less than 1 ppm. The amount of Zr was below the detection limit. The nitrate content in the ^{99m}Tc eluate was estimated to be about 1000 ppm, which was extremely high compared with the analytical results for the non-radioactive gels. This may be due to incompleteness of washing of the radioactive gels, carried out by a remote handling in the hot cell. Thus, it is necessary to examine further the conditions for efficient removal of nitrate salts from the radioactive zirconium molybdate in the gel preparation process.

On the other hand, when we extend the work to prepare a gel generator with much higher radioactivity, it is necessary to design remote controllable crushing and sieving devices suitable for the hot-cell work and, to install them for extra safety of operators.

4. Conclusion

Zirconium molybdate gels were prepared under various conditions of pH, Mo:Zr molar ratios, drying temperatures and drying times. All of the gels prepared were amorphous. The amorphous zirconium molybdate consisted mainly of zirconium, molybdenum, oxygen and water and the composition of that was affected by the preparation conditions. The gels were stable to

The elution profile of ^{99m}Tc obtained from the radioactive gel generator (2 g, 87 MBq or 2.345 mCi) showed a sharp peak. As seen in Fig. 6, more than 95 % of ^{99m}Tc was eluted in only 6 ml of saline solution. The mean elution efficiency (yield) of ^{99m}Tc eluted with 6 ml of saline solution was 90 %. The ^{99}Mo radionuclidic impurity in eluates was below the detection limit when measured with an ionization chamber detector. The γ-ray spectra of the eluate were measured with a HPGe detector coupled to a multichannel analyzer. A single peak of ^{99m}Tc at 140 keV was observed together with very small peaks of ^{99}Mo at 181 keV, 740 keV, and 778 keV, as shown in Fig. 7. The experimental elution of ^{99m}Tc from the gel generator (Fig. 6, 7) demonstrated that the radioactive zirconium molybdate gel prepared in the present work was an excellent column matrix for a ^{99m}Tc generator.

The final purpose of this work is to find out the optimal preparation conditions of the radioactive gel suited for the column matrix of the generator. Thus, the influence of the gel preparation conditions, particularly the dehydration, on the ^{99m}Tc elution should be investigated further in future.

The breakthrough amount of Mo, Zr and nitrate from the gel generator was examined. The amount of Mo in the eluate was estimated to be less than 1 ppm. The amount of Zr was below the detection limit. The nitrate content in the ^{99m}Tc eluate was estimated to be about 1000 ppm, which was extremely high compared with the analytical results for the non-radioactive gels. This may be due to incompleteness of washing of the radioactive gels, carried out by a remote handling in the hot cell. Thus, it is necessary to examine further the conditions for efficient removal of nitrate salts from the radioactive zirconium molybdate in the gel preparation process.

On the other hand, when we extend the work to prepare a gel generator with much higher radioactivity, it is necessary to design remote controllable crushing and sieving devices suitable for the hot-cell work and, to install them for extra safety of operators.

4. Conclusion

Zirconium molybdate gels were prepared under various conditions of pH, Mo:Zr molar ratios, drying temperatures and drying times. All of the gels prepared were amorphous. The amorphous zirconium molybdate consisted mainly of zirconium, molybdenum, oxygen and water and the composition of that was affected by the preparation conditions. The gels were stable to

a saline solution. The ^{99m}Tc gel generator was prepared with the amorphous zirconium molybdate gel containing a tracer level of ^{99}Mo and the elution performance was examined by eluting ^{99m}Tc with the saline solution. The mean elution efficiency (yield) of ^{99m}Tc with 6 ml of the saline solution was 90 %. Contents of radionuclidic impurities, Zr and Mo in the eluates were low enough to meet the pharmacopoeia requirements for human use. It was confirmed from the elution experiment of $^{99m}TcO_4^-$ that the radioactive zirconium molybdate gel prepared in this work was to be used as a column matrix material for a ^{99m}Tc generator.

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The authors are grateful to Dr. E. Shikata, Dr. H. Umezawa, Dr. H. Kudo and Mr. A. Iguchi for their valuable discussions and suggestions. Sincere appreciation is expressed to Dr. N. Masaki of Solid State Physics Laboratory for his assistance in the X-ray diffraction analysis of gels and to Mr. N. Takeuchi for his help in radioactivity measurement. Many thanks are also due to all of the members in the Department of Radioisotopes for their encouragements.

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Acknowledgments

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Table 1 Effect of pH of molybdate solution on Mo, Zr, Water and oxygen contents in zirconium molybdate gels

No.	pH of Mo soln.	pH of filtrate	Mo content (wt %)	Zr content (wt %)	Mo:Zr mol ratio in gel	Water content (wt %)	Oxygen content (wt %)
1	2.5	1.2	31.1	30.1	1.0:1.0	4.3	34.2
2	3.0	1.2	28.8	33.9	1.0:1.2	4.1	30.9
3	4.0	1.3	29.5	35.9	1.0:1.2	4.2	30.4
4	5.0	1.4	31.1	32.3	1.0:1.1	4.0	32.6
5	6.0	1.6	30.3	28.3	1.0:1.0	4.0	37.4
6	7.0	2.9	28.5	34.0	1.0:1.2	4.0	33.5

Conditions : – pH of zirconium oxynitrate solution : 1.0
– Mo:Zr mol ratios = 1.0 : 1.0
– Drying temperature : 100 ℃
– Drying time : 6 h

Table 2 Effect of Mo : Zr mole ratios on Mo, Zr, Water and oxygen contents in zirconium molybdate gels

No.	Mo:Zr mole ratio in soln.	Mo content (wt %)	Zr content (wt %)	Mo:Zr ratio in gel	Water content (wt %)	Oxygen content (wt %)
1	0.7:1.0	28.3	36.8	1.0:1.3	5.6	29.3
2	0.8:1.0	19.2	34.5	1.0:1.9	4.4	41.9
3	0.9:1.0	27.4	32.1	1.0:1.2	4.1	36.4
4	1.0:1.0	33.7	46.2	1.0:1.5	4.0	16.1
5	1.1:1.0	25.4	33.7	1.0:1.4	4.0	36.9
6	1.2:1.0	33.3	29.5	1.0:0.9	3.8	33.4
7	1.3:1.0	34.5	27.2	1.0:0.9	2.8	35.4

Conditions : – pH of zirconium oxynitrate solution : 1.0
– pH of molybdate solution : 4.0
– Drying temperature : 100 ℃
– Drying time : 6 h

Table 3 Effect of drying temperature on Mo, Zr, Water and oxygen contents in zirconium molybdate gels

No.	Drying temp. (°C)	Mo content (wt %)	Zr content (wt %)	Mo:Zr ratio in gel	Water content (wt %)	Oxygen content (wt %)
1	ambient	30.3	29.2	1.0 : 1.0	9.0	31.5
2	60	29.1	27.9	1.0 : 1.0	4.8	38.2
3	80	29.7	31.1	1.0 : 1.1	4.0	35.2
4	120	29.4	29.1	1.0 : 1.0	2.9	38.6
5	150	34.2	30.0	1.0 : 0.9	2.8	33.0
6	170	31.0	29.9	1.0 : 1.0	1.8	37.3
7	200	24.5	26.0	1.0 : 1.1	<0.5	49.0

Conditions : -pH of zirconium oxynitrate solution : 1.0
-pH of molybdate solution : 4.0
-Mo : Zr mole ratio = 1.0 : 1.0
-Drying time : 6h

Table 4 Effect of drying time on Mo, Zr, Water and oxygen contents in zirconium molybdate gels

No.	Drying time (h)	Mo content (wt %)	Zr content (wt %)	Mo:Zr ratio in gel	Water content (wt %)	Oxygen content (wt %)
1	1	27.2	26.2	1.0 : 1.0	6.8	39.2
2	3	31.6	42.2	1.0 : 1.4	7.0	19.2
3	10	27.4	29.8	1.0 : 1.1	6.3	36.5
4	15	26.0	31.1	1.0 : 1.3	6.5	36.4
5	20	27.1	27.0	1.0 : 1.0	6.6	39.4
6	25	25.7	25.9	1.0 : 1.1	5.8	42.6

Conditions : -pH of zirconium oxynitrate solution : 1.0
-pH of molybdate solution : 4.0
-Mo : Zr mole ratio = 1.0 : 1.0
-Drying temperture : 100°C

Table 5 Nitrate content in the zirconium molybdate gels prepared under various conditions

pH of Mo soln	Nitrate content (wt %)	Mo : Zr ratio in soln	Nitrate content (wt %)	Drying temp. (℃)	Nitrate content (wt %)	Drying time (h)	Nitrate content (wt %)
2.5	22.2	0.7 : 1.0	15.8	ambient	5.6	1	13.7
3.0	22.4	0.8 : 1.0	17.6	60	9.5	3	13.1
4.0	17.6	0.9 : 1.0	21.7	80	9.4	10	15.8
5.0	24.0	1.0 : 1.0	21.9	120	9.7	15	11.6
6.0	22.3	1.1 : 1.1	16.5	150	8.2	20	17.5
7.0	16.0	1.2 : 1.0	27.1	170	9.3	25	21.9
—	—	1.3 : 1.0	19.4	200	10.5	—	—

Table 6 Zr, Mo and NO_3^- breakthrough from non-radioactive gel generator containing 3g of zirconium molybdate gel

No. of fraction	Zr content (ppm)	Mo content (ppm)	NO_3^- content (ppm)
1	ND	0.96	1932
2	ND	0.77	1073
3	ND	1.27	1032
4	ND	1.15	992
5	ND	1.25	1032
6	ND	1.38	915
7	ND	1.0	992
8	ND	1.39	992
9	48	1.06	992
10	ND	1.40	908
11	ND	≫4.28	953
12	ND	1.99	845
13	ND	1.26	908
14	ND	1.20	845
15	ND	1.61	908

ND : not detected

Volume of elution : 10 ml for each fraction

Table 7 Performance of ^{99m}Tc gel generator of zirconium molybdate (2g)

Elapsed time (h)	^{99}Mo in column (mCi)	^{99m}Tc in eluate (mCi)	Yield of ^{99m}Tc (%)	Mo in eluate
0	2.35	—	—	—
24	1.83	1.40	90	ND
40	1.43	1.12	91	ND
116	0.71	0.54	89	ND

ND : not detected

Elution volume : 6 ml

^{99}Mo radioactivity : 87 MBq (2.35 mCi) at calibration

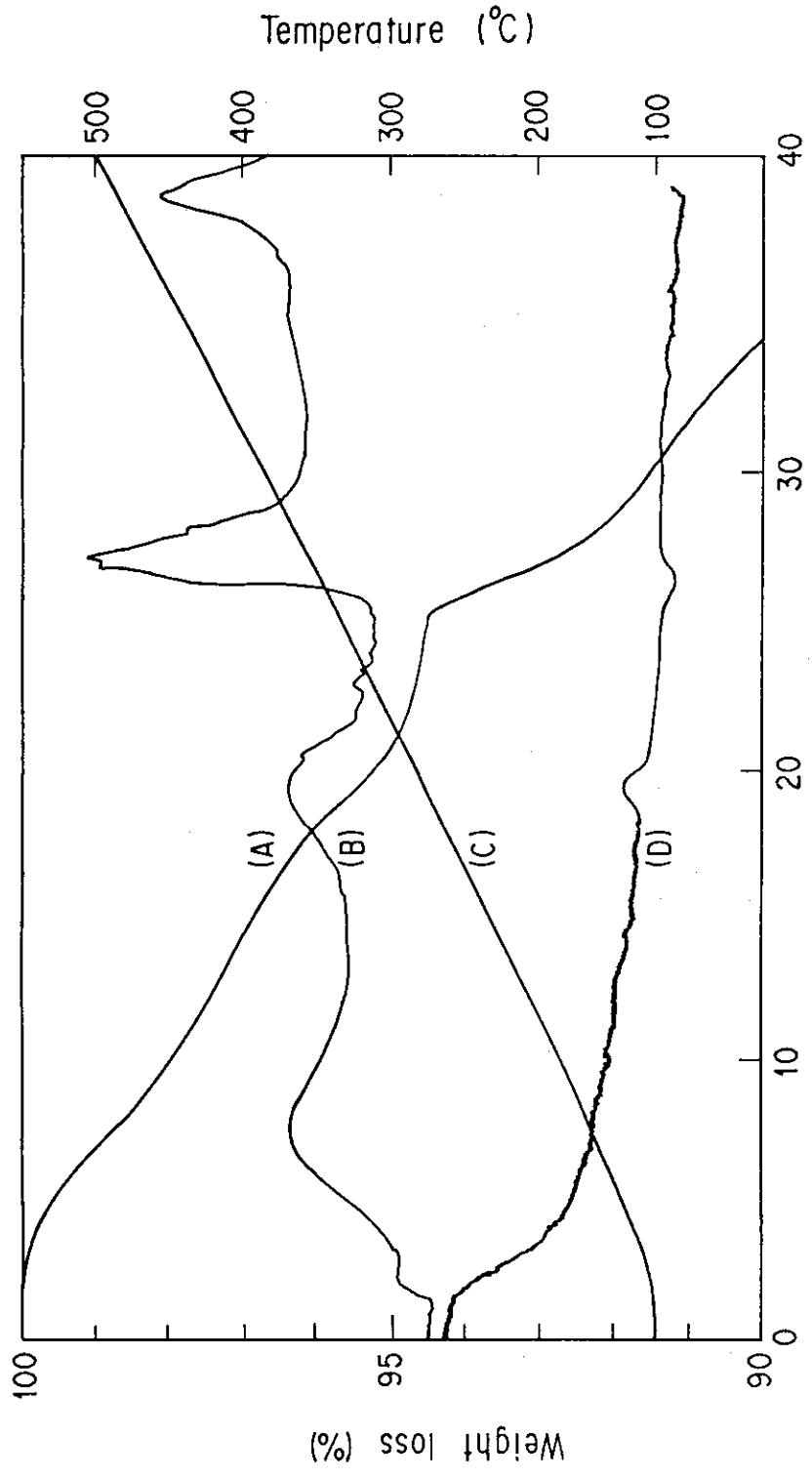

Fig. 1 Thermal Gravimetry/differential thermal analysis (TG/DTA) curve for zirconium molybdate gel

(A) : Thermal gravimetry curve (C) : Temperature curve

(B) : Differential thermal gravimetry (D) : Differential thermal analysis curve

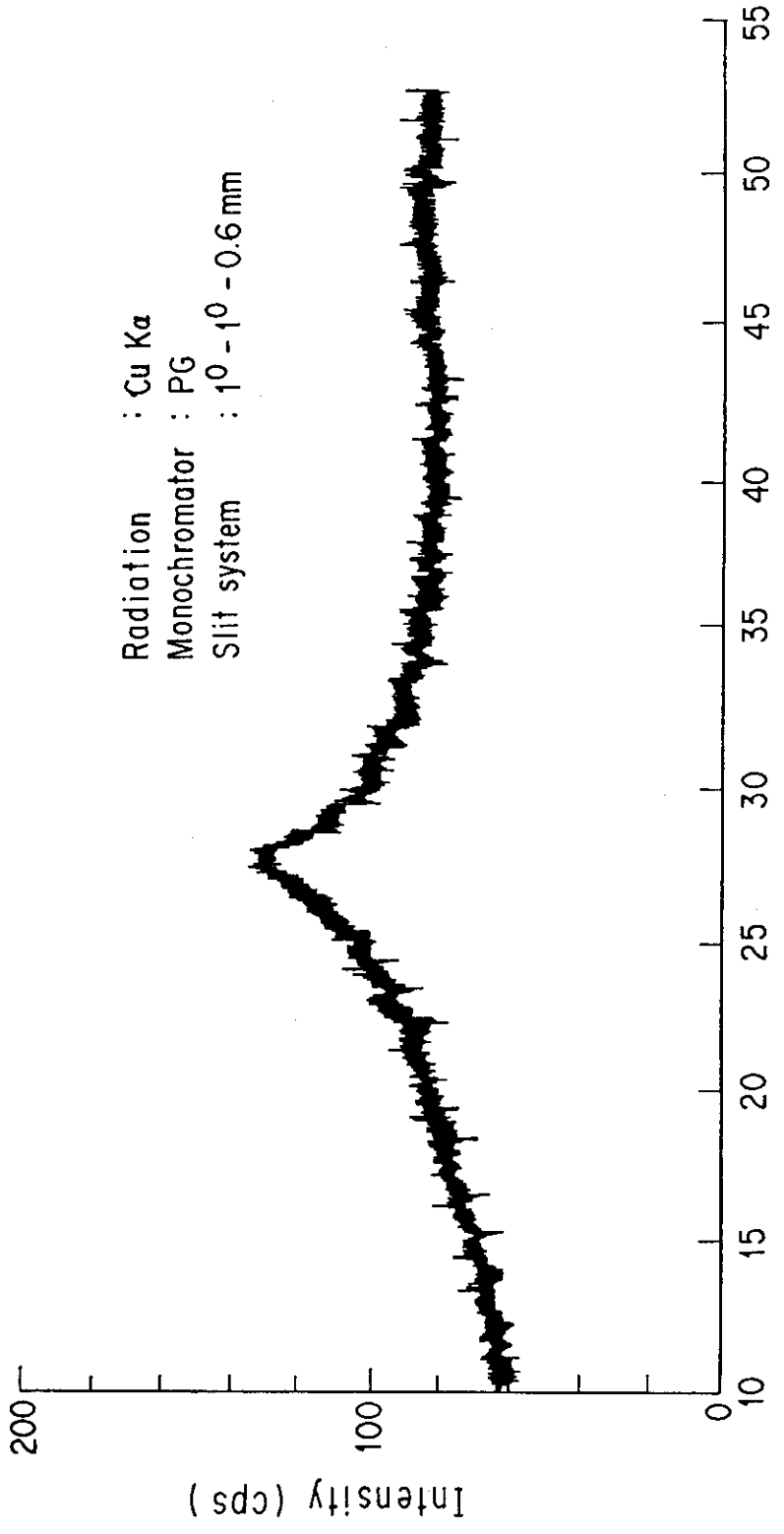

Fig. 2 X-ray diffraction pattern of zirconium molybdate gel

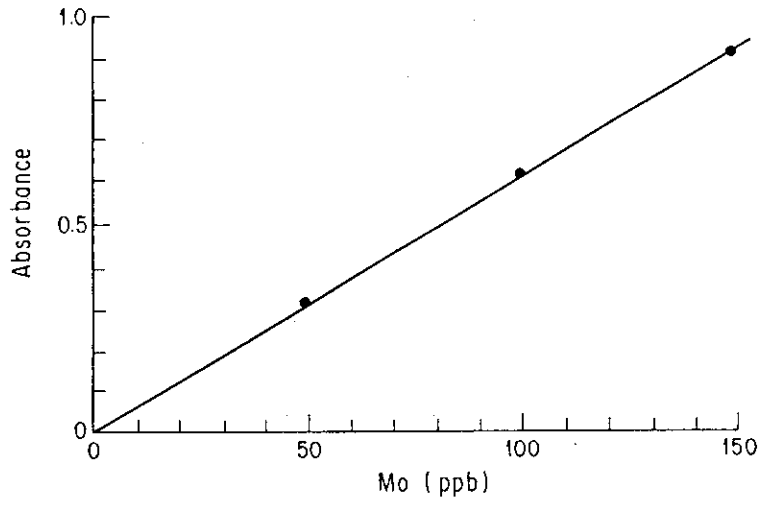

Fig. 3 Calibration curve for Mo.

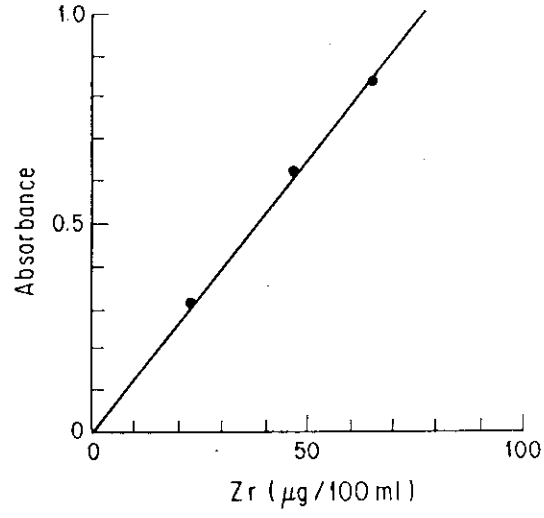

Fig. 4 Calibration curve for Zr by arsenazo - Ⅲ method

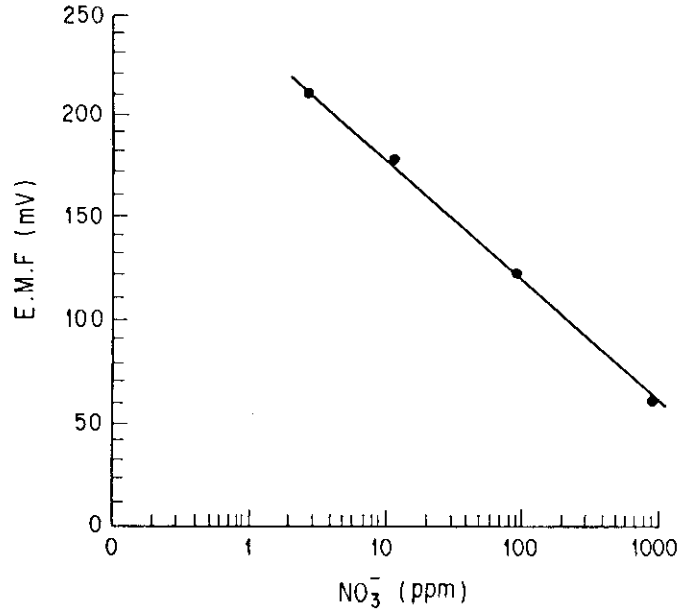

Fig.5 Calibration curve for NO_3^-

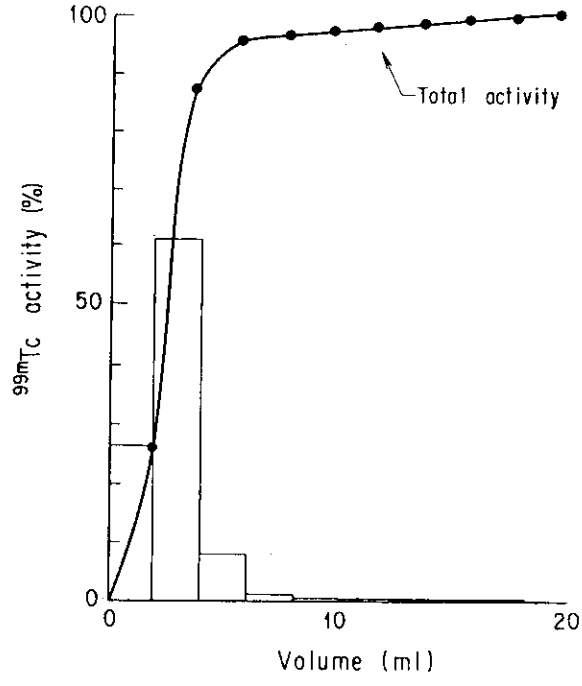

Fig.6 ^{99m}Tc elution profile obtained from radioactive zirconium molybdate gel generator

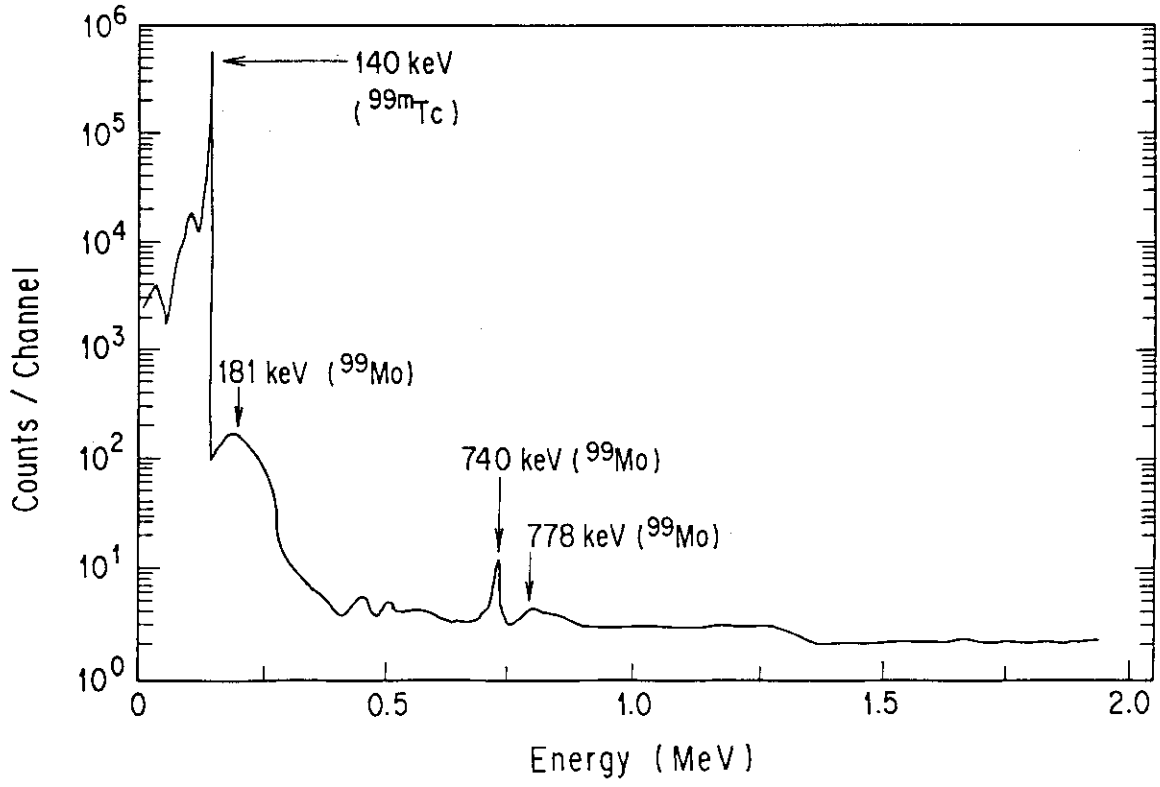

Fig. 7 Gamma ray spectrum of ^{99m}Tc eluate