Preparation and characterization of cerium(IV) tellurium molybdate gel and its application as a bed for chromatographic ⁹⁹Mo/⁹⁹ᵐTc generator

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Cerium(IV) tellurium molybdate was prepared as a new gel bed for chromatographic ⁹⁹Mo/⁹⁹ᵐTc generator. The gel material prepared with the optimum conditions was characterized with IR spectroscopy, thermal analysis, XRD, EDX and FESEM. The highest precipitation yield of ⁹⁹Mo within the formed gel was found to be 97.6% at a Ce:Te:Mo molar ratio of 1:0.2:1. The prepared ⁹⁹Mo/⁹⁹ᵐTc chromatographic column based on Ce(IV) tellurium molybdate gel bed showed a good performance. The ⁹⁹ᵐTc elution yield was 77.8±3.0% with a radionuclidic purity of ≥ 99.99%, radiochemical purity of 96.5±1.3% (as ⁹⁹ᵐTeO₄⁻) and pH-value in the range of 5-7. Molybdium and cerium levels in ⁹⁹ᵐTc eluates did not exceed 1 and 0.3 ppm, respectively, while no tellurium was detected.

1. Introduction

Chromatographic column generators of (n,γ)⁹⁹Mo/⁹⁹ᵐTc gel have low-specific activity ⁹⁹Mo, but they represent an alternative option to those of alumina loaded with higher specific-activity fission ⁹⁹Mo. Gel generators can participate in the solution of the problem of the increasing demand of ⁹⁹ᵐTc, which is used in more than 80% of nuclear medicine applications, all over the world. Among the advantages of gel generators are the easy and quick preparation of (n,γ)⁹⁹Mo solution, low cost and minimal radioactive waste.¹ Criteria for good gel generators include high-content of ⁹⁹Mo in the gel bed, high elution yield and high radionuclidic, radiochemical and chemical purities of the ⁹⁹ᵐTc eluates. Many gel materials, including acidic salts of polyvalent metals and salts of heteropolyacids, have been used as beds for ⁹⁹Mo/⁹⁹ᵐTc generators, e.g., zirconium molybdate,²–⁶ stannic molybdate,⁷ titanium molybdate,⁸ cerium(IV) molybdate,⁹ 12-molybdocerate(IV),¹⁰ 6-tungstocerate(IV),¹¹ magnesium molybdate¹² and zirconium molybdisphosphate.¹³ Zirconium molybdate is the most famous material used as a bed for ⁹⁹Mo/⁹⁹ᵐTc generators, but the synthesis and study of other gel materials constitute a renewable research filed in literature to obtain more alternatives.

For zirconium molybdate gel, replacement of 5% (molar) of zirconium with Ce(IV) enhances the ⁹⁹ᵐTc elution yield due to overcoming the reduction of ⁹⁹ᵐTc species, because of radiolysis, and oxidation of its species to ⁹⁹ᵐTeO₄⁻.¹⁴ Thus, in the present work, using such high molar ratio of cerium (IV) will be advantageous especially in case of high-⁹⁹Mo activity generators in which the radiolysis effect will be higher. In addition, adding a small ratio of tellurium (IV) was found to increase the ⁹⁹Mo uptake by the formed gel comparing with the case of CeMo gel.⁹ This work aims at the preparation of cerium(IV) tellurium molybdate gel material containing a high content of molybdenum which can be used as a new bed material for a chromatographic ⁹⁹Mo/⁹⁹ᵐTc radioisotope generator of a good performance.

2. Experimental

All the chemicals used were of AR grade. Distilled water was used for preparing solutions.

A γ-ray spectrometer composed of a multichannel analyzer (MCA) of Inspector 2000 model (Canberra Series, USA), coupled with a high-purity germanium (HPGe) coaxial detector of GX2518 model, was used for γ-radioactivity identification and measurement.

A pH-meter with a microprocessor (Hanna Instruments pH211 model, Portugal) was used for measuring pH-values of solutions. An analytical balance (A&D Engineering Inc., AND HR-202 model, USA) having dual range (42 g/0.01 mg, 210 g/0.1 mg) was used for weighing. A centrifuge (REMI Laboratory, R32A model, India) was used for centrifugation of the mixtures to efficiently separate the precipitated gel materials from the supernatants.

A UV-VIS spectrophotometer (Shimadzu, UV-160 A model, Japan) was used for detection of Ce and Mo in ⁹⁹ᵐTc eluted from the Ce(IV) tellurium molybdate–⁹⁹Mo column.

The IR spectrum was recorded with an FT-IR spectrometer (Bomem, model MB157S, Canada) in the range from 4000 to 400 cm⁻¹ at room temperature.

Thermal analysis, including simultaneous TGA and DTA, was carried out with a thermal analyzer (Shimadzu, model DTG-60H, Japan). X-ray diffraction was performed with an 18 kV diffractometer (Bruker, model D8 Advance, USA) with monochromated CuKα radiation (λ = 1.54178 Å).

Elemental analysis was performed using energy dispersive X-ray spectrometer (ISIS-300, Oxford EDX). FESEM images were taken using field emission scanning electron microscope (FESEM) (JEOL JSM-6500F, USA).

2.1. Molybdenum-99 radiotracer. ⁹⁹Mo was obtained by eluting commercial ⁹⁹Mo/⁹⁹ᵐTc generators with alumina-packed columns (Mon-Tek Generator, Monrol Nuclear Products Industry and Trade Inc., Turkey; loaded with 20 GBq on calibration date). Each column was eluted with 20 ml of 2 M NH₄ solution 20 days after the calibration date. Then the NH₄ solution was evaporated to dryness, and the residual ⁹⁹Mo was redissolved in 5 ml of 0.1 M NaOH.

2.2. Preparation of cerium(IV) tellurium molybdate (CeTeMo) gel. A 0.1 M Mo(VI) solution was prepared by dissolving 2.42 g of Na₂MoO₄·2H₂O in 20 ml of distilled H₂O

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with the addition of 2.5 ml of \(^{99}\)Mo solution along with few drops of 30% \(\text{H}_2\text{O}_2\). The volume of the \(\text{Mo(VI)}\) solution was completed to 100 ml with distilled \(\text{H}_2\text{O}\). A 0.1 M Ce(IV) solution was prepared by dissolving 6.32 g of \((\text{NH}_4)_4\text{Ce(SO}_4)_4\cdot \text{H}_2\text{O}\) in 100 ml of dilute \(\text{H}_2\text{SO}_4\) to obtain a solution of pH1. A 0.1 M Te(IV) solution was prepared by dissolving 1.60 g of \(\text{TeO}_2\) in 100 ml of 5 M \(\text{NaOH}\). Mixtures with different Ce(IV): Te(IV):Mo(VI) molar ratios were prepared by adding Mo(VI) solution dropwise to Ce(IV) solution and, then, Te(IV) solution was added dropwise to the Mo(VI)-Ce(IV) mixture. Varied volumes of the three solutions were used to obtain different molar ratios. Thereafter, pH of the final mixture was adjusted to 5.5 by using \(\text{H}_2\text{SO}_4\)/\(\text{NaOH}\) solutions. The final volume of each mixture was 50 ml. The mixtures were left for 10 h to allow the formed precipitates to settle and then were centrifuged. The supernatant of each mixture was checked radiometrically to determine the precipitation yield of \(^{99}\)Mo within the formed gel material.

The precipitated gel obtained from the mixture with the optimum Ce:Te:Mo molar ratio (i.e., the mixture with which the highest precipitation yield of \(^{99}\)Mo was achieved) was found to be that with 1 Ce: 0.2 Te: 1 Mo. The mixture with the optimum molar ratio was prepared again by adding 50 ml of 0.1 M Mo(VI) solution, containing \(^{99}\)Mo radiotracer, dropwise to 50 ml of 0.1 M Ce(IV) and then 10 ml of 0.1 M Te(IV) was added dropwise to the Mo(VI)-Ce(IV) mixture. The pH-value was thereafter adjusted to 5.5 by using \(\text{H}_2\text{SO}_4\)/\(\text{NaOH}\) solutions. The mixture was left for 10 h to allow the precipitate to settle. The mixture was then centrifuged, the supernatant was removed by decantation while the precipitate was spread as a thin layer on a watch glass and dried for 12 h at 50°C. The dried gel was pulverized to \(0.1–0.2\) mm particle size and, then, used as a column bed for a \(^{99}\)Mo/\(^{99m}\)Tc chromatographic generator. The mixture was prepared again by the same method, but without adding \(^{99}\)Mo radiotracer and with washing the dried gel with excess distilled water followed by re-drying overnight at 50°C, to characterize the prepared gel.

### 2.3. Characterization of CeTeMo gel.

The inactive prepared CeTeMo gel (with the optimum molar ratio) was characterized by IR spectroscopy, thermal analysis (TGA and DTA), XRD, EDX and FESEM.

### 2.4. Preparation of \(^{99}\)Mo/\(^{99m}\)Tc chromatographic column generator.

A 0.7 cm i.d. glass column was used as a bed for the \(^{99}\)Mo/\(^{99m}\)Tc generator. The column was provided with a small piece of glass wool, as a support for the gel bed, and a bottom stopcock. 1 g of the pulverized CeTeMo gel bed was packed into the column by settling from distilled water. The column was excessively washed with distilled water and subsequently conditioned with 50 ml of 0.9% \(\text{NaCl}\) for further elution of \(^{99m}\)Tc.

### 2.5. Elution of \(^{99}\)Mo/\(^{99m}\)Tc generator and quality control of the eluted \(^{99m}\)Tc.

Technetium-99m was firstly eluted 23 h after the conditioning time by passing 10 ml of 0.9% \(\text{NaCl}\) solution through the CeTeMo gel column. The column was eluted 14 times with different flow rates (0.25, 0.5, 0.75 and 1 ml/min) over the course of 25 days. The time between each two successive elutions was \(\geq 23\) h. The \(^{99m}\)Tc elution yield was determined by comparing the counting rates of the 140-keV peak in the \(\gamma\)-ray spectrum of the column directly before and after elution, taking the contribution of \(^{99}\)Mo to this peak into account. The elution profiles were drawn for various elution flow rates. pH-values of the eluate solutions were determined using the pH-meter.

The percent \(^{99}\)Mo content in the eluate was determined, in the case of its presence, as the contribution of the count rate of 181- or 739-keV peak in the \(\gamma\)-ray spectrum to the total count rate. The \(\gamma\)-ray spectrum of the eluate was measured directly after elution and after 5 days. The radionuclidic purity of the eluted \(^{99m}\)Tc was determined as the contribution of the count rate of 140-keV peak in the \(\gamma\)-ray spectrum of the eluate to the total count rate.

The radiochemical purity of the eluted \(^{99m}\)Tc (contribution of \(^{99m}\)MoO\(_4\) count rate to the total count rate the eluted \(^{99m}\)Tc was determined by ascending paper chromatography using Whatman no. 1 chromatographic paper and a mixture of 85% methanol + 15% \(\text{H}_2\text{O}\) as a developing solvent. The activity distribution along the chromatogram was traced using the \(\gamma\)-ray spectrometer to determine \(R_L\), where:

\[ R_L = \frac{R_{\gamma}}{R_{\text{eluate}} - R_{\text{eluate}} - R_{\gamma}} \]

The possible impurities of molybdenum, cerium and tellurium originated from the CeTeMo gel matrix, were determined in \(^{99m}\)Tc eluates spectrophotometrically using thiocyanate method (maximum absorption at 470 nm), persulfate method (maximum absorption at 320 nm), Bismuthil II method (maximum absorption at 330 nm), respectively.

### 3. Results and discussion

CeTeMo gels were prepared with different Ce:Te:Mo molar ratios. As indicated by Figure 1, precipitation yield of \(^{99}\)Mo increased gradually from 32.2% at Ce:Te:Mo molar ratio of 1:1:0.5 till reaching a first lower maximum value of 61% at the molar ratio of 0:2:1; and then, it slightly decreased to 48.5% at the molar ratio of 0:1:1. Thereafter, the precipitation yield sharply increased to a second higher maximum value of 97.6% at the molar ratio of 1:0:2:1 and then sharply decreased to 58.1% at the molar ratio of 1:0:5:1. Further change of the molar ratio to 1:1:1 yielded a precipitation yield of 52.4%. Hence, Ce:Te:Mo molar ratio of 1:0:2:1 was chosen for characterization of the prepared CeTeMo gel (via IR, thermal analysis, XRD, EDX and FESEM) and further preparation and quality control.

![Figure 1. Precipitation yield of \(^{99}\)Mo as a function of Ce:Te:Mo molar ratio used for preparing CeTeMo gel.](image-url)
control of $^{99}$Mo/$^{99m}$Tc generator. Thus, the addition of tellurium during gel preparation, with a Ce:Te:Mo molar ratio of 1:0.2:1, increased the precipitation yield of $^{99}$Mo to 97.6 %, which is markedly higher than the yields of 35.8 and 63 % $^{99}$Mo in the case of CeMo gel with Mo:Ce molar ratios of 1:1 and 2:1, respectively.9

Figure 2 shows IR spectrum of CeTeMo gel. The IR spectrum includes peaks at 501 cm$^{-1}$ (due to Te–O–Te bending mode), 874 cm$^{-1}$ (due to Mo–O stretching mode), 1401 cm$^{-1}$ (due to Ce–O–H bending mode), 1614 and 3411 cm$^{-1}$ (due to O–H bending and stretching modes of lattice water, respectively).9,18-21

Figure 2. IR spectrum of CeTeMo gel.

Figure 3 shows the TGA and DTA curves of the CeTeMo gel. There was a 8.3 % weight loss on TGA curve in the temperature range from 16 to 200°C due to the loss of lattice water with an endothermic peak on DTA curve at 71°C. The presence of lattice water in a suitable amount is important to enhance the diffusion of $^{99m}$TcO$_4^-$ through the gel material during elution.22 In the range of 200–800°C, there was another weight loss of 4.1% due to decomposition of the gel material to cerium, molybdenum and tellurium oxides, in addition to subsequent sublimation of molybdenum oxide.21,23 The thermal gravimetric behavior of CeTeMo gel resembles to a great extent that of cerium(IV) molybdate (CeMo) gel.9

Energy dispersive X-ray (EDX) spectrometric elemental analysis indicated that the prepared gel material incorporated ~27 % (wt./wt.) of molybdenum. This Mo content is considered high (where gel matrices used in $^{99}$Mo/$^{99m}$Tc generators should contain high Mo content; > 25 %) and comparable with Mo content in zirconium molybdate gels (30 %).24

Figure 4 shows the XRD pattern of the CeTeMo gel, which indicates a nearly amorphous structure (low-crystallinity structure) of the prepared CeTeMo gel. The amorphous structure is usually preferred to the rigid crystalline structure, where the latter one hinders the mobility of $^{99m}$Tc leading to a decrease in the elution yield. In addition, the amorphous structure has a more mechanical strength than the crystalline one, i.e., it is more resistant to abrasion and dissolution.25

Figure 5 shows FESEM images of the CeTeMo gel. Image (a) indicates the gel particles with a size range of ~100-200μm (~0.1-0.2 mm), while the more magnified images (b) and (c) indicates many meanders and cavities, the presence of which facilitates the diffusion of saline solution through the gel bed during $^{99m}$Tc elution.

Figure 6 compiles the elution profiles of the $^{99}$Mo/$^{99m}$Tc generator at flow rates of 0.25, 0.5, 0.75, and 1 ml min$^{-1}$. The elution yield of $^{99m}$Tc was 77.8 ±3.0 %. Thus, the average $^{99m}$Tc elution yield for CeTeMo gel is slightly higher than that for CeMo gel (75.4 %).9 Sharp elution peaks were obtained with the flow rates of 0.25, 0.5 and 0.75 (the most sharp one was obtained with the flow rate of 0.75 ml min$^{-1}$), while a relatively broad one was obtained with the flow rate of 1 ml min$^{-1}$. A maximum percent fraction of $^{99m}$Tc activity was obtained at the 2$^{nd}$ ml of eluate for the flow rates of 0.25, 0.5 and 1 ml min$^{-1}$ (49.7, 54.1 and 33.1 %, respectively), while it was obtained at the 1$^{st}$ ml of eluate for the flow rate of 0.75 ml min$^{-1}$ (82.5 %).

Radionuclidic purity of the obtained $^{99m}$Tc eluates was ≥ 99.99 %, i.e., in all cases $^{99}$Mo content in the eluate did not
exceed 1x10^{-3} \%. pH-values of 99mTc eluates ranged from 5-7. Radiochemical purity was 96.5\pm1.3 \% as 99mTcO_4\-. Chemical impurities of molybdenum and cerium in 99mTc eluates did not exceed 1 and 0.3 ppm, respectively, while no tellurium was detected.

4. Conclusion

Cerium(IV) tellurium molybdate (CeTeMo) gel was successfully prepared as a high-Mo content material with a high 99Mo precipitation yield. CeTeMo gel was used as a new bed material for a chromatographic 99Mo/99mTc radioisotope generator showing a good performance; suitable 99mTc elution yield, high radionuclidic, radiochemical and chemical purities and pH-value in the range of 5-7.

References

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