

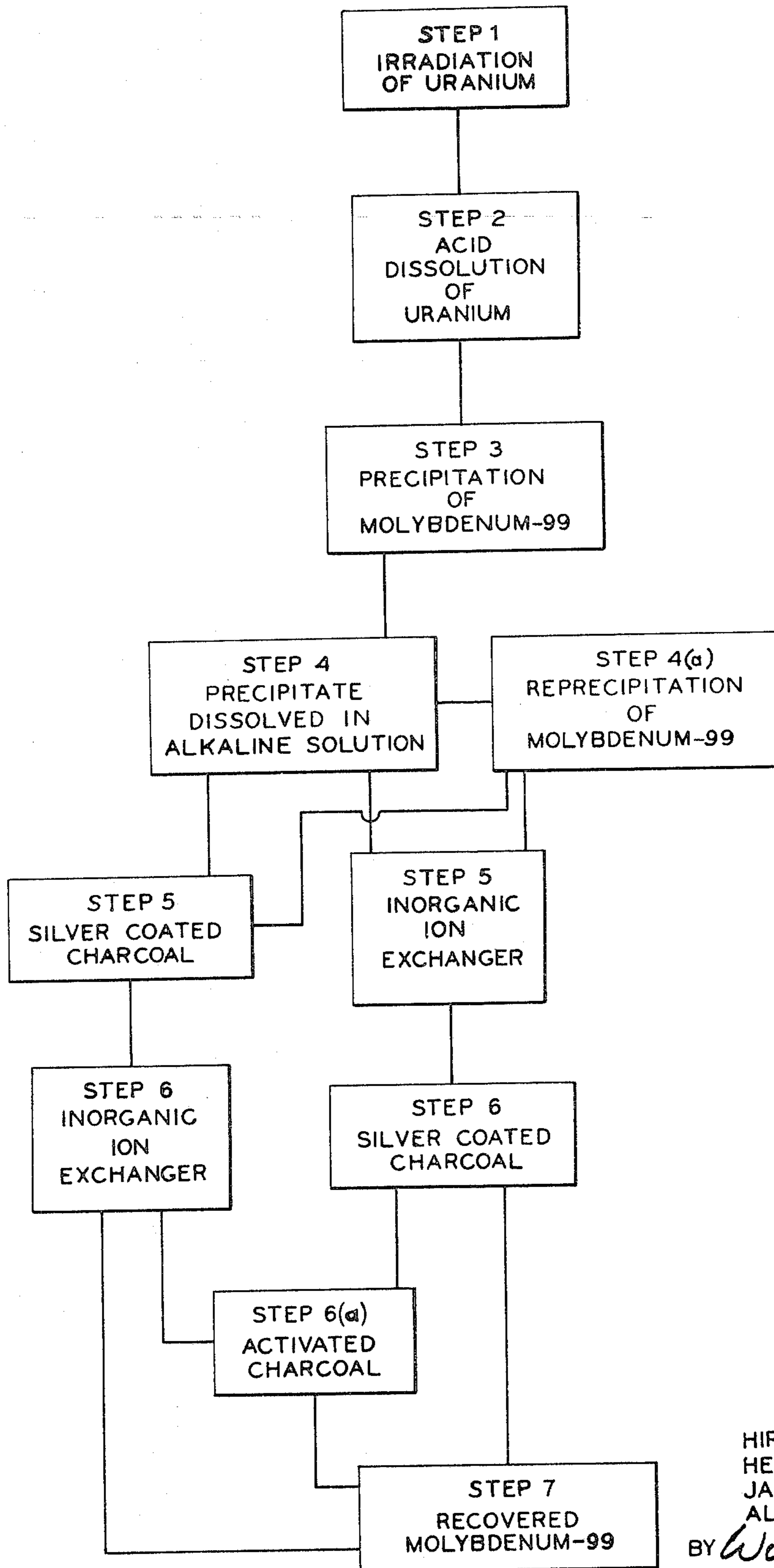
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PRODUCTION OF HIGH PURITY FISSION PRODUCT MOLYBDENUM-99

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PRODUCTION OF HIGH PURITY FISSION PRODUCT MOLYBDENUM-99

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ABSTRACT OF THE DISCLOSURE

High purity fission product molybdenum-99 is prepared by a process which comprises the steps of:

- (a) irradiating a uranium material,
- (b) dissolving the irradiated uranium material in an aqueous inorganic acid to form a solution,
- (c) precipitating molybdenum-99 by contacting the solution with alpha-benzoinoxime,
- (d) recovering the molybdenum precipitate and dissolving the precipitate in an aqueous alkaline solution,
- (e) contacting the solution containing the dissolved molybdenum-99 with adsorbents which are selective for the removal of impurities associated therewith, and
- (f) thereafter recovering radioactive molybdenum-99.

This invention relates to a process for the production of fission product molybdenum-99. In one aspect, this invention is directed to a process for producing radioactive molybdenum-99 in a high degree of purity and having a high specific activity.

Molybdenum-99 is widely used in nuclear medicine because it produces a daughter product, technetium-99m, which is used as a diagnostic tracer in in vivo diagnostic tests, for example, in brain tumor, liver, kidney, lung, and thyroid scans. For use in such radiopharmaceutical generators, molybdenum-99 (⁹⁹Mo) must be of exceptionally high order of purity, and it should have a relatively high specific activity. One of the ways that has been studied for producing ⁹⁹Mo has been by irradiating uranium in a nuclear reactor. However, one of the problems that is encountered when producing ⁹⁹Mo in this manner is that more than 50 elements and more than 100 radioactive isotopes are formed by nuclear fission. Therefore, the recovery of any single radioactive species from such a mixture can be a formidable task. Methods that have been employed heretofore for recovering ⁹⁹Mo from irradiated uranium include alumina column chromatography. However, the yield of product is small by this method, and the ⁹⁹Mo prepared is not sufficiently pure for medical use because it contains significant amounts of radioactive iodine and ruthenium. Another method that has been attempted for recovering ⁹⁹Mo involves extracting the molybdenum from acidic aqueous solution into an organic solvent containing di-2-ethylhexyl phosphoric acid. However, this method required repeated extraction and back-extraction procedures, resulting in a relatively large quantity of liquid radioactive waste that had to be disposed of.

It is therefore an object of this invention to provide a process for the preparation of radioactive molybdenum-99. A further object of this invention is to provide a process for the preparation of fission product molybdenum-99 in a high degree of purity and having a high specific activity. Another object of the invention is to provide a process for isolating molybdenum-99 from other radioactive fission products with the formation of

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a minimum amount of radioactive waste materials. A still further object of this invention is to provide a process for preparing molybdenum-99 which is suitable for diagnostic purposes. These and other objects will readily become apparent to those skilled in the art.

In its broad aspects, this invention relates to the process for the preparation of high purity fission product molybdenum-99. The process comprises the steps:

- (1) irradiating a uranium material,
- (2) dissolving the irradiated uranium material in an aqueous inorganic acid to form a solution,
- (3) precipitating molybdenum-99 by contacting the solution with alpha-benzoinoxime,
- (4) recovering and dissolving the molybdenum precipitate in an aqueous alkaline solution, and
- (5) contacting the solution containing the dissolved molybdenum-99 with at least one adsorbent for the selective removal of impurities. The adsorbents employed are (i) silver coated charcoal, (ii) an inorganic ion exchanger and/or (iii) activated carbon. Thereafter radioactive molybdenum-99 is recovered.

The invention will further be understood by reference to the drawing. The single drawing is a flow chart of a process for preparing radioactive molybdenum-99 in accordance with the teachings of this invention. As indicated, steps 1, 2, 3 and 4 encompass the irradiation, acid dissolution, precipitation and dissolution of the molybdenum-99 in an alkaline solution. Steps 5 and 6 involve contacting the alkaline solution with adsorbents. The sequence is not critical and either the silver coated charcoal or the inorganic ion exchanger can be used first. For a product of higher purity, the molybdenum can be reprecipitated in step 4(a) and the alkaline solution contacted with activated carbon in step 6(a) after proceeding through steps 5 and 6. Various holdback carriers can also be employed in steps 2, 3, 4, or 4(a) to provide a product of optimum purity.

It should be appreciated that various modifications can be made in the sequence of steps shown in the drawing. The particular sequence chosen will largely be dependent upon the degree of purity desired as well as other considerations. For example, after step 4 as shown in the drawing, one can proceed directly to step 6(a) and then to step 7. Alternatively, after step 6(a) one can return to step 4(a) and then proceed directly to steps 5 and 6 or just step 6 and step 7 or proceed through any of the indicated routes. After step 6, as shown in the drawing, one can also return to step 4(a) for an additional reprecipitation. From step 4(a) one can also go directly to steps 6(a) and 7 or through any of the other indicated routes.

Molybdenum-99 prepared in accordance with the process of this invention is highly pure and possesses a high specific activity. Purities as high as 99.9999 percent are readily obtained by the process set forth in the drawing. Moreover, as will be evident from the disclosure and examples, the entire process, after the irradiation step, is conveniently conducted in a single hot cell with the formation of a minimum amount of radioactive waste materials. Since the volume of solutions employed in the various steps is small and the specific activity of the molybdenum-99 is high, the process can be conducted quickly, efficiently and with a minimum of radioactive waste material. For example, several hundred curies of molybdenum-99 per batch can be provided and require less than eight hours of processing time. Moreover, the specific activity is greater than 10,000 curies per gram.

As indicated, the present invention involves a multi-step process for the production of fission product mo-

lybdenum-99 of a high degree of purity and having a high specific activity.

The first step of the process encompasses the irradiation of a uranium material, particularly one which is enriched in the fissionable isotope, to provide fission product molybdenum-99. Irradiation of compounds to produce fission product molybdenum-99 is a well known technique and can be effected by placing the proper compounds in the irradiation zone of a nuclear reactor, particle generator, or neutron isotopic source. Although a variety of compounds are suitable for use in the process of this invention, the preferred target is a uranium material, such as uranium-235. Other compounds can also be employed, however, it is often necessary to isolate the molybdenum component after irradiation to obtain a final product of the desired purity. Illustrative compounds which can be employed as the source of fission product molybdenum-99 include, among others, fissionable materials such as uranium-235, uranium-238, plutonium-239 and the like.

In practice, it has been observed that the uranium material can be conveniently irradiated in a nuclear reactor if the primary target is comprised of an enclosed cylindrical, stainless steel vessel, preferably having a thin, continuous, uniform layer of a fissionable material, integrally bonded to its inner walls and a port permitting access to the interior of the vessel. This type of primary target retains the advantage of the known aluminum sandwich method, namely, good heat transfer, but avoids its disadvantages. The fissionable material is deposited as a thin layer adherent on the inner surface of the cylindrical vessel. The small thickness of the layer, which may be of the order of one-thousandth of an inch thick, and its intimate contact with the vessel results in good heat transfer from the deposit to the coolant that is in contact with the exterior surface of the vessel.

In a preferred embodiment the primary target is fabricated from annealed, seamless, stainless steel tubing approximately 18 inches in length and having an outer diameter from 1 to 2 inches and a wall thickness of from about 0.03 to about 0.10 inch. The top is equipped with a port permitting access to the interior of the vessel. The port is composed entirely of metal, preferably stainless steel, and must be capable of withstanding the stresses and temperatures created during exposure of the primary target to neutrons. It has been observed that temperatures of up to about 300° C. are generated during irradiation. The primary target should be capable of withstanding temperatures of at least about 500° C. for at least one hour.

As hereinafter indicated, the primary target will contain a predetermined amount of fissionable material deposited on its inner wall. As indicated in the examples, the uranium material can be deposited electrolytically. Other methods can also be employed, if desired, to deposit the fissionable material, i.e., uranium or plutonium, onto the inner walls of the vessel. For example, the metal can be sputtered, ion plated, or evaporated, onto metal surfaces by known techniques.

In practice, for an 18 inch primary target, of 1 inch diameter, it has been observed that a maximum of about 10,000 curies of radioactivity can be produced from a cylindrical uranium coating which is 15 inches in length and has a thickness of approximately 20 milligrams of uranium per square centimeter. Such deposits weigh from about 7 to about 10 grams. Uranium thicknesses of up to about 50 milligrams per square centimeter for the same size primary targets have also been employed and are calculated to yield approximately 25,000 curies of radioactivity based upon a 15 inch coating of the length of the inner wall of a 1 inch outer diameter stainless steel tube. Such deposits weight from about 18 to about 25 grams. Another aspect is that the primary target serves as the same vessel for irradiation and chemical dissolution of the uranium. After the irradiation step, the

primary target is transferred to a hot cell for the chemical processing steps.

Through the use of the cylindrical vessel the irradiated material has its surface exposed for prompt and effective dissolution in the second phase of the process. The acid dissolution solution can be introduced through the port in the volume needed to dissolve the irradiated material. Through suitable choice of solvent the deposit can be dissolved without any effect to the vessel itself. The large surface area exposed, results in rapid dissolution, which may be 15 minutes, and therefore conserves processing time and avoids loss of product through radioactive decay. The resulting solution contains an insignificant quantity of dissolved vessel, which considerably simplifies the subsequent chemical processing and enables sophisticated separative methods to be used that result in highly-pure products.

As previously indicated, the next step in the process is the acid dissolution of the deposited inner layer. In practice, the irradiation material is conveniently dissolved by the introduction of a mixture of nitric and sulfuric acids to the cylindrical vessel through the port. The transfer of solutions and trapping of off gases are all done in a closed system. A mixture of concentrated sulfuric acid and hydrogen peroxide can also be employed but is less preferred. For the particular target described above sixty cubic centimeters of 2 normal sulfuric acid containing 2.5 cubic centimeters of concentrated nitric acid were sufficient to dissolve the uranium. Dissolution is enhanced by rotating the target while heated to 90-95° C. for approximately 45 minutes. After cooling, any resulting radioactive gaseous fission product wastes are removed from the primary target by distillation into a cold finger connected to the target and immersed in liquid nitrogen.

The dissolved uranium solution is then drained from the target into a receiver for the third step, i.e., precipitation of the molybdenum-99. It has been observed that molybdenum is selectively precipitated from the acid solution with alphanitrosoacetophenone and can therefore be conveniently separated from solution and many impurities contained therein. The dissolved uranium solution is therefore drained from the target into a bottle, the target washed with sulfuric acid and the washings added to the bottle.

Prior to the addition of the alphanitrosoacetophenone, the solution is preferably chilled in an ice bath. It is also desirable to add an amount of a reducing agent sufficient to remove radicals formed as a result of radiolysis. Aqueous solution of sodium sulfite has been found to be satisfactory although other known reducing agents can also be employed.

The alpha-benzoinoxime is then added to the solution to precipitate the molybdenum-99. In practice, a two weight percent solution of alphanitrosoacetophenone dissolved in 0.4 normal sodium hydroxide has been found to give satisfactory results. Other concentrations of alpha-benzoinoxime in alkaline solution can also be employed. After the precipitate has formed, the solution is filtered through a fritted glass column and washed with several aliquots of dilute sulfuric acid solution.

In the fourth step the precipitate is then dissolved in an alkaline solution, such as 0.6 normal sodium hydroxide. Heating the solution to about 90-95° C., while the column is vented with a charcoal filter, insures rapid and complete dissolution of the precipitate. The column is then washed with dilute sodium hydroxide and/or water. The washings and molybdenum-99 solution can then be passed through a charcoal column or silver coated charcoal column. This insures the removal of organic material from the dissolved precipitate and facilitates the second precipitation with alpha-benzoinoxime if a highly pure product is desired. For optimum results it has been found that the highest degree of radio-nuclidic purity is obtained when the molybdenum-99 is precipitated twice from solution with alphanitrosoacetophenone. While the second precipitation

is not absolutely essential, it does provide a product having the highest purity.

Additionally, before performing the second precipitation a higher yield was obtained when an oxidant, such as potassium permanganate, bromine water, and the like, was added to insure that the molybdenum was in its highest oxidation state.

The fifth step of the process of this invention involves contacting the solution containing the molybdenum-99 with one or more adsorbents for the selective removal of impurities. Two types of adsorbents have been found to be particularly useful for removing impurities and providing a molybdenum solution of the highest purity. Silver-coated charcoal and inorganic ion exchanger are both ideally suited for optimizing the purity of the desired isotope solution.

The silver-coated charcoal that is used is activated carbon that contains silver deposited thereon. The activated carbon that is employed is preferably employed as a powder, although other forms of activated carbon can be used if desired. The powder preferably has a particle size of from about 5 to about 400 mesh, and more preferably from about 50 to about 200 mesh. (The mesh size of the carbon particles is measured in accordance with the U.S. Standard Sieve Series.)

Any type of activated carbon can be employed in preparing the adsorbent. The purification efficiency appears to be about the same for all types of activated carbon, although adsorption capacity appears to vary directly with the amount of oxygen contained in the carbon. It has been found that the preferred type of activated carbon is that which is prepared from coconut shells by standard procedures.

The activated carbon can be coated with elemental silver by known techniques. For instance, the carbon can first be washed with pure water in order to eliminate all impurities, and it can then be contacted with an aqueous solution of silver nitrate, which can contain dilute acid such as nitric acid or sulfuric acid in order to prevent the silver nitrate from precipitating. A reducing agent such as sodium sulfite is added, followed by the addition of sodium hydroxide. This mixture is heated at a temperature of from about 40° to about 100° C., and preferably from about 80° to about 90° C., for a period of about 30 minutes. After cooling, the excess liquid is removed by decanting, or the like, and the activated carbon containing the coating or deposit of silver therein is washed with purified water several times. The silver coated activated carbon should be stored under water until it is used in order to prevent contamination.

In depositing the silver on the carbon the alkali is used to ensure that the maximum amount of silver is deposited, and the reducing agent is used to ensure that the silver deposited is in the elemental form, not in the form of the oxide or hydroxide.

The amount of silver deposited will normally be within the range of from about 0.01 to about 2, and preferably from about 0.1 to about 1.5, weight percent, based on weight of carbon.

The silver coated activated carbon can be used in a mixture with activated carbon (free of silver coating) as the adsorbent in the process of the invention. In many cases, the adsorption capacity is thereby increased. The proportion of activated carbon can be up to, for instance, about 70, and preferably from about 40 to 60, weight percent, based upon weight of silver-coated carbon plus activated (non-silver coated) carbon.

A more complete description of the preparation of the silver coated charcoal can be found in U.S. patent application Ser. No. 64,567 entitled, "Production of High Purity Molybdenum Using Silver Coated Carbon as Adsorbent," filed Aug. 17, 1970, and assigned to the same assignee as the instant invention.

A second adsorbent which is employed to give optimum purity is an inorganic ion exchanger. The exchanger acts

as a cation exchanger and also as a weak and strong molecular adsorption media when contacted with a base. The inorganic ion exchanger is preferential for the removal of cations and some anions. It is particularly useful for the removal from the molybdenum-99 solution of such elements as tellurium, ruthenium, silver, zirconium, rare earths and the like.

Illustrative inorganic ion exchangers include, among others, silicates, the oxides and phosphates of metals, and like materials. For example, the inorganic ion exchanger can be silica gel, zirconium oxide, aluminum oxide, iron oxide, titanium oxide, aluminum phosphate, aluminum silicates, such as molecular sieves, and the like. These inorganic ion exchangers are sold commercially and are available under such trade names as HZO-1, produced by Bio-Rad Laboratories, ABEDEM HTO produced by S.E.R.A.I. (Belgium) and the like. The solution containing the molybdenum-99 is merely contacted with the adsorbents, as for example, by passing the solution through a column in which the adsorbent is contained. It is not critical which adsorbent the molybdenum-containing solution passes through first. As indicated in the drawing, after step 4 or 4a, the solution can be contacted first with either the silver coated charcoal or the inorganic ion exchanger.

The adsorbent is employed in an amount sufficient to remove essentially all of the impurities and provide a highly pure molybdenum-99. In practice, the amount used will depend on the impurities in the alkaline solution after the molybdenum precipitate has been dissolved, the quantity of solution with which it comes in contact, and other considerations.

In order to ensure that all traces of organic compounds are removed from the molybdenum solution, it is also desirable as an additional step before recovery of the molybdenum to pass the solution through activated charcoal can also be employed after the first and before the second precipitation with alpha-benzoinoxime. This insures removal of residual organic compounds and facilitates the second precipitation step if one is employed. The molybdenum-99 is recovered from the adsorbents in the final step.

Because of the difficulty in measuring impurity levels in solutions of such high specific activity, molybdenum-technetium generators were prepared by known techniques and the technetium-99m eluate analyzed. The only impurities observed in the eluate was iodine-131 and ruthenium-103 at relative concentrations of 0.002 percent (20 microcuries impurity per 1 million microcuries of technetium-99m). The presence of holdback carriers, such as ruthenium and iodine compounds, in the precipitation step reduced the impurity level of ruthenium and iodine in the eluate to less than 0.00002 percent. While the holdback carriers can be added at various steps during the process, the ruthenium compound is most conveniently added before the precipitation or reprecipitation steps. The iodide compound is preferably added simultaneously with the stabilizer.

The holdback carriers can be introduced as solids, powders, or preferably as aqueous solution. In practice they are employed in a "holdback carrier amount." By this term is meant an amount sufficient to retain impurities and thus lower the overall impurity level of the resulting molybdenum-99 solution. In practice, amounts of from about 10 to about 200 micrograms and more preferably from about 50 to about 100 micrograms have been found adequate.

As indicated, the holdback carriers are ruthenium and iodide compounds, preferably the salts. Illustrative compounds include, among other, ruthenium chloride, ruthenium nitrate, ruthenium sulfate, sodium iodide, potassium iodide and the like.

The fission product molybdenum prepared by the process of this invention is ideally suited for the preparation of generators employing alumina substrates. In contrast

to known generators which usually take at least 2 hours to prepare, generators can be conveniently prepared in less than 5 minutes. Moreover, when fission product ^{99}Mo is loaded on alumina at pH 4 to 9 no treatment of the substrate is required, and a high activity $^{99}\text{Tc}^m$ generator that possesses a high separation factor can be obtained. By eliminating substrate treatment, the $^{99}\text{Tc}^m$ generators can be produced in much shorter times. Additionally, since fission product molybdenum-99 is employed, the resulting technetium-99m solution obtained from the generator is of a greater concentration than heretofore possible. The highest concentration usually obtained was less than 50 millicuries per milliliter. In contrast, technetium-99m can be obtained from the generators using fission product molybdenum-99 in concentrations of 1000 or higher, millicuries per milliliters.

The technetium-99m in the column or vessel which contains ^{99}Mo - $^{99}\text{Tc}^m$ activity can subsequently be isolated, e.g., milked, filtered, centrifuged or the like for technetium-99m as it is formed with an acidic, neutral or basic solution. Preferably, it has been observed that best results are obtained when the system is eluted with 4 milliliter portions of saline solutions. This is done by contacting the substrate with the desired volume of saline and collecting the liquid portion.

A further advantage characteristic of the process of this invention is that the substrate and/or the entire elution system can be sterilized, i.e., by autoclaving at the normally prescribed temperatures and pressures.

The radiometric analysis of the eluted technetium-99m indicates that it contains up to 99% of the available technetium-99m and the radionuclidic purity is greater than 99.99%. The total metal element impurity is less than 1 part per million as determined by emission spectroscopy techniques.

When the molybdenum-99 is reprecipitated with alpha-benzoinoxime and the solution contacted with activated charcoal, the radionuclidic purity is usually at least 99.99%. When only one precipitation is done and the solution contacted with the silver coated charcoal, ion exchanger and activated charcoal, the purity is also at least 99.99%. When the molybdenum-99 is precipitated twice and contacted with the three adsorbent, the purity is in excess of 99.999%.

The following examples are illustrative:

EXAMPLE I

Preparation of primary target

An 18-inch long tube of 1 inch outer diameter and constructed of annealed, seamless No. 304 stainless steel tubing (MIL-T-8504A specification) was cleaned in sulfuric acid solution and washed. Uranium enriched to 93% in ^{235}U was electroplated over a 15-inch length inside the capsule in the form of a uniform thin film of uranium oxide. The electroplating was affected by first preplating a thin-film of uranium onto the inner surface of the tube from an aqueous bath containing 0.042 molar uranyl nitrate and 0.125 molar ammonium oxalate, the pH having adjusted to 7.2 with NH_4OH . Electrodeposition was affected for 60 minutes at a current of 0.9 ampere, 1.5 volts; and a temperature of $93 \pm 1^\circ \text{C}$. Thereafter, the cylinder was removed from the plating assembly, washed with water, dried, and weighed. The final uranium deposit was made from a similar electrolytic bath as that used in the preplating step. The temperature employed was $93 \pm 1^\circ \text{C}$. and a fixed voltage of 1.5 volts. The current was cycled by means of a clock mechanism starting with 0.3 ampere, 0.6 ampere, then 0.9 ampere, then 0.3 ampere, etc. every 15 minutes. The electrolyte was circulated through the cylinder at a flow rate of 200 milliliters per hour. The electrodeposition rate was approximately 1.2 grams uranium oxide per hour. After about 8 hours, the cylinder was removed from the plating assembly, washed and dried. The ends of the cylinder were dipped in nitric acid to remove about $1\frac{1}{2}$ inches of the uranium deposit to

give an arbitrarily selected length of 15 inches of uranium deposit in the tube. The resulting film thickness was 20 mg. ^{235}U per cm^2 of tube surface, for a total deposit of 7 gm. ^{235}U . The total uranium mass was determined gravimetrically. The plated tube was then baked at 500°C . in nitrogen. The adherence of the film was checked with a vibration test. The film remained adherent despite temperature cycling between room temperature and 500°C .; the latter being well above the expected radiation temperature of 330°C . Tubes plated with uranium have been temperature-cycled and vibrated with less than 1% of the film appearing as loose powder granules.

The two end caps of the tube were heliarced in place. The sewage-type fittings that comprise the capsule seal and entry port are No. 316 S/S. The maximum allowable internal working pressure is 900 p.s.i. (ASME Code for Class B nuclear vessel at 340°C .).

The plated vessel was then filled to about one atmosphere of helium, sealed, and then leak-tested with a mass-spectrometer-type leak detector. The maximum permissible leak is 10^{-8} sec./sec. The integrity of the stainless steel seal plug (and the welds) has been verified up to 250 hours at 300°C ., and in short-duration tests at 500°C ., and also in the 214 hour Instrumented Target Experiment during which the radiation monitoring system indicated no primary capsule leakage.

EXAMPLE II

Irradiation of molybdenum-99

The reactor irradiation assembly employed was comprised of a sealed primary capsule containing uranium-235 and enclosed within a close-fitting secondary container. Heat generated in the primary was conducted through the narrow gas-gap between it and the secondary. Gas lines entering the top and bottom of the secondary allowed a helium atmosphere to be established within the container and a slow sweep of gas to be taken to monitoring equipment located on the reactor bridge. Pressure, flowrate, and radioactivity of the gas were monitored. Exit gas was filtered before venting into the reactor-building exhaust duct via a solenoid-controlled shut-off valve. The secondary container was centered in a stringer tube within the reactor core and was cooled by primary water flowing in the annulus so formed. The assembly was designed to contain about 400 curies of ^{99}Mo at removal from the reactor.

The primary target capsule, as prepared in Example I above, was then placed in a secondary capsule which was fabricated from No. 304 stainless steel sanitary tubing. A lead weight was provided for ease in placement and for ensuring that the assembly would not float in water. Two gas lines ($\frac{1}{4}$ and $\frac{1}{8}$ inch O.D. No. 304 S/S) were provided, one in the top cap and one near the lower end of the capsule. These lines supplied the helium gas which served as the heat-transfer medium between primary and secondary necessary for limiting the primary temperature to the design value of 330°C .

The upper end-cap consisted of a stainless steel "CAJON" type VCO coupling TIG-welded to the capsule body. This coupling employed a silver plated stainless steel O-ring for its seal. The O-ring was discarded after use. All welds and penetrations in the secondary capsule body were helium leak-checked.

The secondary capsule containing the primary target capsule was placed in a core stringer tube. This aluminum (No. 6061) tube provided the 0.25" gap needed for the desired cooling water speed of 3.5 ft./sec. past the secondary capsule. Primary reactor cooling water with normal gravity flow was used. Measurements in a test stand showed that at least 3.9 ft./sec. is obtained.

The stringer tube, containing the secondary and primary target, was then lowered into a nuclear reactor and irradiated at a neutron flux of 3×10^{13} n./ cm^2 sec. for 100 hours. Thereafter, the primary target was removed to a hot cell facility, the swage-type fitting opened and

the primary target connected to a self-sealing entrance port.

EXAMPLE III

Chemical processing of molybdenum-99

After the irradiated target capsule has "cooled" for a period of twenty-four hours, it is placed in liquid nitrogen for ten minutes. Thereafter, the exit port of the capsule is opened with a wrench and a tubular T transfer section equipped with a pressure gauge and two sealable exit ports at the ends of the T is attached. A 275 cubic centimeter evacuated bottle was attached to the other end of the T by means of a valve and waste fission product gases removed from the capsule—the pressure in the capsule was then maintained at less than -10 inches of mercury.

With the target capsule at room temperature, 60 cubic centimeters of 2 normal sulfuric acid containing 2.5 cubic centimeters of concentrated nitric acid were introduced by a syringe into the capsule. The target capsule was then placed on a rotating mill which was equipped with a heating source. The target was rotated and when the temperature reached 90–95° C., it was rotated for 45 minutes and the pressure was not allowed to exceed 70 pounds per square inch gauge. Thereafter the target was allowed to cool to 70° C.

The target was then clamped in a vice and a cold finger attached to the T-section. The line to the cold finger contained an alumina trap to pick up iodine. The cold finger contained calcium oxide, calcium sulfate and zeolites to pick up water, residual iodine and other radioactive waste products. The valve on the T-section was opened and the pressure reading dropped to about 10 pounds per square inch gauge. A Dewar flask surrounding the cold finger was filled with liquid nitrogen to the 2-inch level for a ten minute period. Thereafter it was filled to the 4-inch level. At the end of an additional ten minutes it was completely filled. After degassing was completed, the target pressure was less than 10 inches of mercury. The cold finger was detached after one-half hour and the target vented to the atmosphere within the hot cell by means of a syringe.

Thereafter, the target was inverted and the acid solution containing the dissolved uranium and fission products was drained into a 275 cubic centimeter plastic coated evacuated bottle by means of a valve. The target was placed on the rotating mill and 25 cubic centimeters of 0.4 N H₂SO₄ injected with a syringe. After rotating for five minutes, the target was vented to the atmosphere. The acid wash solution was drained into the plastic coated bottle and the target set aside in a designated storage area. Ten cubic centimeters of 20% Na₂SO₃ were then added to the uranium solution and the contents mixed by shaking. Thereafter, 15 cubic centimeters of 2% alpha-benzoinoxime in 0.4 N NaOH was added to precipitate the molybdenum. After shaking well, the solution was allowed to stand for five minutes. The acid concentration was about 8%. The solution was then placed in an ice bath for an additional five minutes.

The precipitate was filtered by means of a fritted glass column (medium frit) and then the bottle washed with two 20 cubic centimeter injections of 0.1 N H₂SO₄. The washings were drawn through the column by means of the adjustable vacuum line. The precipitate on the column was washed with three 10 cubic centimeter injections of 0.1 N H₂SO₄. The pressure was equalized and 10 cubic centimeters of 0.6 N NaOH (containing 1 cubic centimeter of 30 percent of H₂O₂/100 ml.) was injected into the column. When the precipitate was dissolved, it was drained into a clean bottle containing 20 cubic centimeters of water. The column was washed with 10 cubic centimeters of the NaOH solution, 10 cubic centimeters of water, and the washings added to the bottle. The solution was then passed through a 1 x 8 cm. charcoal column

and washed with 20 ml. 0.2 N NaOH. To the solution, after 5 minutes of chilling in an icebath, was slowly added 44 cubic centimeters of 9 N H₂SO₄. A 2.5% KBnO₄ solution was then added in small increments until a well defined pink or brown color was evident. After chilling in ice for 10 minutes, the KMnO₄ was reduced by the dropwise addition of freshly prepared sulfurous acid.

Immediately thereafter 15 cubic centimeters of a chilled solution of 2% alpha-benzoinoxime in 0.4 N NaOH was added, the solution shaken and placed in an ice bath for 5 minutes. The precipitate was again filtered and redissolved in the sodium hydroxide solution as indicated above. The solution was then passed through a 2 x 8 cm. column containing silver coated charcoal and a 1 x 8 cm. column containing inorganic ion exchanger, HZO produced by Bio-Rad Laboratories. The columns were washed with 25 cubic centimeters of 0.2 N NaOH. Finally, the solution was passed through a column containing activated charcoal and drained into a container.

The molybdenum solution so obtained was analyzed for concentration (millicuries/milliliters) and radionuclidic purity. The molybdenum-99 concentration was determined by gamma ray spectroscopy and found to be greater than 1000 millicuries per milliliter. The total of any other fission products was less than 1 microcurie per curie of molybdenum-99.

Although the invention has been illustrated by the preceding examples, it is not to be construed as being limited to the materials employed therein, but rather the invention is directed to the generic area as hereinbefore disclosed. Various modifications and embodiments can be made without departing from the spirit and scope thereof.

What is claimed is:

1. A process for the preparation of radioactive molybdenum-99 which comprises the steps of:

- (1) irradiating a uranium material,
- (2) dissolving said irradiated uranium material in an aqueous inorganic acid to form a solution,
- (3) precipitating molybdenum-99 by contacting said solution with alpha-benzoinoxime to form a complex of molybdenum-99 and alpha-benzoinoxime,
- (4) recovering and dissolving said complex precipitate in an aqueous alkaline solution,
- (5) contacting said alkaline solution containing dissolved molybdenum-99 with at least one adsorbent for the selective removal of impurities, said adsorbent being selected from the group consisting of (i) silver-coated charcoal, (ii) an inorganic ion exchanger, and (iii) activated carbon, and
- (6) thereafter recovering radioactive molybdenum-99 in the form of a molybdate salt.

2. The process of claim 1 wherein said uranium material is uranium oxide.

3. The process of claim 1 wherein said uranium material is uranium metal.

4. The process of claim 1 wherein said inorganic acid is a mixture of sulfuric and nitric acids.

5. The process of claim 1 wherein said inorganic acid is a mixture of hydrogen peroxide and sulfuric acid.

6. The process of claim 1 wherein said alpha-benzoinoxime contacts said solution in the presence of a stabilizer.

7. The process of claim 6 wherein said stabilizer is sodium sulfite.

8. The process of claim 6 wherein said stabilizer is sulfurous acid.

9. The process of claim 1 wherein said alkaline solution is sodium hydroxide.

10. The process of claim 1 wherein said alkaline solution is potassium hydroxide.

11. The process of claim 1 wherein the aqueous alkaline solution is acidified and then steps (3) and (4) are repeated.

12. The process of claim 1 wherein said ion exchanger is zirconium oxide.

13. The process of claim 1 wherein adsorbent (i) is employed before adsorbent (ii).

14. The process of claim 1 wherein adsorbent (i) is employed after adsorbent (ii).

15. The process of claim 1 wherein the aqueous alkaline solution is acidified after step (5) and then steps (3), (4) and (5) are repeated.

16. The process of claim 1 wherein at least one holdback carrier is employed to improve the purity of said molybdenum-99.

17. The process of claim 16 wherein said holdback carrier is a ruthenium compound.

18. The process of claim 17 wherein said holdback carrier is an aqueous solution of ruthenium chloride.

19. The process of claim 17 wherein said holdback carrier is added after step (2).

20. The process of claim 17 wherein said holdback carrier is added during step (3).

21. The process of claim 17 wherein said holdback carrier is added during step (5).

22. The process of claim 16 wherein said holdback carrier is an iodide compound.

23. The process of claim 22 wherein said holdback carrier is added after step (2).

24. The process of claim 22 wherein said holdback carrier is added during step (3).

25. The process of claim 22 wherein said holdback carrier is added after step (4).

26. The process of claim 23 wherein said holdback carrier is added simultaneously with sodium sulfite of claim 7.

27. The process of claim 1 wherein said aqueous alkaline solution is acidified and an oxidizing agent is added and then steps (3) and (4) are repeated.

28. The process of claim 27 wherein said oxidizing agent is potassium permanganate.

29. The process of claim 27 wherein said oxidizing agent is bromine water.

30. The process of claim 1 wherein the aqueous alkaline solution is acidified after step (5), and then an oxidizing agent is added and then steps (3), (4) and (5) are repeated.

31. The process of claim 30 wherein said oxidizing agent is potassium permanganate.

32. The process of claim 30 wherein said oxidizing agent is bromine water.

33. A process for the preparation of a highly pure

radioactive molybdenum-99 having a high specific activity which comprises the steps of:

- (1) irradiating uranium oxide deposited on the inner walls of a sealed stainless steel cylindrical target,
- (2) dissolving said uranium oxide in an aqueous mixture of sulfuric and nitric acids to form a solution,
- (3) adding to said solution a stabilizing amount of sodium sulfite and holdback carrier amounts of ruthenium chloride and sodium iodide,
- (4) precipitating molybdenum-99 by contacting said solution with alpha-benzoinoxime in the presence of a stabilizer to form a complex of molybdenum-99 and alpha-benzoinoxime,
- (5) recovering and dissolving said complex precipitate in an aqueous sodium hydroxide solution,
- (6) contacting said solution with silver-coated charcoal,
- (7) acidifying said solution, adding an oxidizing agent and repeating steps (4) and (5),
- (8) contacting said sodium hydroxide solution with silver-coated charcoal and zirconium oxide,
- (9) contacting said sodium hydroxide solution with activated charcoal, and
- (10) recovering said molybdenum-99 in the form of sodium molybdate.

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