

PRODUCTION OF TECHNETIUM IN MOLYBDENUM TARGET ON LINAC AND MODELING TECHNETIUM DISTILLATION

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Along with the traditional methods of molybdenum and technetium separation from target irradiated by an electron linear accelerator, the possibility of technetium stripping from aqueous solution has been considered. To achieve the required temperature we used phosphoric acid.

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1. INTRODUCTION

In nuclear medicine 80% of radiopharmaceuticals labeled with technetium- 99m [1] ($T_{1/2} = 6.02 h$, $E_{\gamma} = 140.5 keV$) are used in diagnostic studies. This determines the importance of the problem.

2. PRODUCTION OF ^{99}Mo

In production of ^{99}Mo – the parent nucleus of technetium – both molybdenum oxide and molybdenum metal are used. The most common is reactor method of ^{99}Mo production comprising irradiation of ^{235}U by neutron flux and fission of uranium nucleus [2]. Fission products contain several percent of ^{99}Mo . Another reactor way is irradiation of molybdenum oxide (monoisotopic) with a neutron flux and production of from ^{99}Mo [2]. The use of the first reactor method produces a lot of radioactive waste and requires weapons-grade uranium giving a higher yield of ^{99}Mo . In the production of molybdenum in a cyclotron [3] the reaction $^{100}Mo(p, np)^{99}Mo$ is used. Another reaction $^{100}Mo(p, 2n)^{99m}Tc$ results in direct production of ^{99m}Tc . A cyclotron method of ^{99}Mo production has not found industrial application because of the high energy costs.

An alternative to the aforementioned methods is production of ^{99}Mo on electron linear accelerator. Despite the low specific activity of the target the price of technetium dose may be lower than the one produced at the reactor. When using the linac it is desirable to use metal targets from enriched molybdenum. The production goes according to equation: $^{100}Mo(\gamma, n)^{99}Mo \rightarrow ^{99m}Tc$ (yield 89%) [4]. Earlier, the same method was used in Davydov's and Mareskin's works [5]. Although this alternative method has been described in the literature, it has not yet been used

for the industrial production of technetium. Irradiation of metallic molybdenum target of natural composition was produced by an electron accelerator with maximum energy of 35 MeV and average current of 250 mA. Brake γ - quanta were produced in the tungsten converter 1 mm thick. Maximum exposure time was 26 hours. We have used targets of natural metallic molybdenum in the form of spacers with the diameter 16 and 11 mm and thickness of 0.2 mm. The spacers had a hole in the middle to be bound with wire into bundles weighing $\sim 20...30 g$. To separate Mo and Tc targets should be dissolved.

3. DISSOLUTION OF Mo

Although the problem of metallic molybdenum dissolution has been solved in analytical chemistry, new approaches appear. Until recently, the main process was dissolution in acids. The monograph [6] has systematized the existing literature quite thoroughly, but it is metal sample weights from 0.2 to 5 g that we are interested in. Nitric, sulfuric, hydrochloric acids are used as reagents. For example, for a 0.5 g sample of the metal 20...40 ml of HNO_3 are used (1:1), i.e. the amount of acid exceeds stoichiometric one many times. For example, for a 0.5 g sample of the metal by Zelikman [7], molybdenum dissolves in nitric acid or mixtures of sulfuric and nitric acids (molybdenum cores on which the tungsten coil is wound are dissolved in the same manner). Our task was to dissolve molybdenum target, drive off the excessive acid and to dissolve the dry residue in alkali, thus obtaining a solution suitable for the work of technetium extraction generator. When dissolved in nitric acid, molybdenum forms molybdic acid as a white gel that prevents further dissolution of the metal. Since the mass of metallic molybdenum target is 20...30 gr, its

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dissolution occurs differently than of 5 gr samples due to the formation of a large volume of gel.

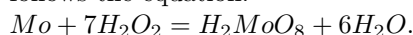
Studying the literature, we focused our attention on molybdenil sulfate reagent (MoO_2SO_4), supplied as 30% solution in sulfuric acid [8]. Apparently, there is possibility to form other molybdenile salts, probably even molybdenile nitrate. In case of rapid addition of 5-fold excess to 30 g of molybdenum (compared to stoichiometric) of nitric acid (12 M), dissolution of molybdenum takes place with formation of a small volume of sediment ($\sim 10 ml$) which does not interfere with rapidly proceeding reaction (in less than 10 min.) By addition of nitric acid portions of 10...15 ml dissolution proceeds moderately rapidly, but we cannot get rid of the sediment. In this case the target is not fully dissolved. Molybdenile nitrate forms at substantial excess of nitric acid. Given that the nitrate ion practically does not form complex compounds, first of all, we paid attention to the hydrofluoric and hydrochloric acids as an addition to the nitric acid in molybdenum dissolution. We decided to test the efficacy of ligand, fluoride ion introduced as hydrofluoric acid. We succeeded to dissolve 30 gr of molybdenum in mixture with 53 ml of 56% nitric acid and 51 ml of 40% hydrofluoric acid. Consumption of nitric acid was almost stoichiometric. After stripping of excess acids 30 g of molybdenum was concentrated in 66 ml solution.

The use of hydrofluoric acid is inconvenient, it requires tupperware withstanding heat on a hotplate.

So we decided to use hydrochloric acid. To dissolve 27.28 gr of molybdenum, which took about 2.5 hours, 54 ml of nitric acid and 123 ml of hydrochloric acid were used. In the middle of the dissolution process white precipitate appeared which dissolved after adding 20 ml of hydrochloric acid. The idea of molybdenile soluble salts formation proved fruitful. We used target dissolution in a mixture (1:1) of nitric and hydrochloric acids. Acid mixture was used to reduce the amount of residue molybdcic acid. In the presence of hydrochloric acid, as we believe, soluble molybdenile chloride forms. Dissolution of heavy molybdenum targets (20 g or more) in a mixture of hydrochloric and nitric acids 1:1 were performed repeatedly, the targets completely dissolved without solution splashing.

The authors of [9], have also used anodic dissolution of molybdenum in alkali. However, this device is quite complicated for this. The irradiated target was wrapped in nickel net for crumbling molybdenum to contact with the positive electrode. The net was attached to mixer (1000 rev/min). Thus, an acceptable rate of dissolution was provided. In recent years it has been proposed to dissolve metallic molybdenum in hydrogen peroxide. Small targets about 0.2 g were usually dissolved at moderate temperature [3]. Dissolution was carried out at temperature of $\sim 60^\circ$, adding 30...35% of peroxide portions, probably for fear of uncontrolled decomposition of peroxide compounds. In these conditions, our targets (20 g and more) did not dissolve. Dissolving 30 g of molybde-

num, we added 15...20 ml of water, a target glass was heated to 60...80° to initiate the reaction, and then brought to boiling. Peroxide was added in portions, each of not more than 10 ml to avoid splashing and foaming of the solution. When dissolving, off molybdenum acids are formed, mainly diperoxide molybdenum (H_2MoO_6) and tetraperoxide molybdenum (H_2MoO_8). These peracids contain oxygen chains $-O-O-$ instead of one atom of oxygen and as we see, are soluble in water unlike molybdcic acid. Duration of 30 gr of Mo dissolution is 2 hours and it follows the equation:



As a result of dissolution we obtain yellow-orange solution. With prolonged standing (24 h) the solution solidifies, turning into yellow-orange translucent mass. In the process of dissolution residue (presumably from molybdcic acid (H_2MoO_4)) can form, which is dissolved in an excess of the peroxide.

Prior to learning of molybdenum dissolution in peroxide, we have found out that molybdenum can be dissolved in a mixture of nitric and ortho-phosphoric acids. Since the latter has a set of actions, molybdcic acid does not precipitate from solution of phosphoric acid. We have conducted several experiments on the dissolution of Mo in hot H_3PO_4 adding nitric acid portions. Dissolution proceeds smoothly and predictably. With molybdenum solution in phosphoric acid it would be unreasonable not to try to strip Tc from the solution. However, we could not immediately decide to strip the radioactive element - technetium.

4. SIMULATION OF TECHNETIUM STRIPPING

Rhenium has been selected as a model element. Chemical properties of technetium and rhenium are close. Boiling point of technetium oxide (VII) is 310°, rhenium oxide – 359°. There is a link [10], which indicates possible stripping from sulfuric acid. Technetium is quantitatively stripped from the sulfuric acid solution under the condition that the purge gas does not contain reducing agents [11]. In our opinion, the boiling point of sulfuric acid is not sufficient to strip technetium, for 80% H_2SO_4 – 210°, and it is inconvenient to work with azeotropic mixture of 98.3%. The temperature of the phosphoric acid can easily be increased up to 350° (or even higher) without emission of harmful gases.

Solution of molybdenum oxide in phosphoric acid and aliquot of the standard solution of rhenium was placed into the Wurtz flask. Rhenium oxide was stripped using an air cooler. To create the oxidizing atmosphere potassium permanganate was added. Rhenium in the stripping was determined by emission method on ICP-spectrometer. It was shown that rhenium was stripped quantitatively from solutions of phosphoric acid. Subsequently, having learnt molybdenum dissolution in hydrogen peroxide, we added phosphoric acid to the solution and stripped rhenium. It should be born in mind that rhenium is

contained in metallic molybdenum and in all molybdenum reagents.

5. CONCLUSIONS

Method of technetium (rhenium) stripping from an aqueous solution of phosphoric acid may be an alternative to other methods for the separation of molybdenum and technetium:

- molybdenum sorption on aluminum oxide and washing out the produced technetium with saline;
- adsorption of technetium on ion exchange resin;
- extraction of technetium from molybdate alkali solution;
- sublimation of technetium from molybdenum oxide melt.

The most common way (traditional) is production of technetium on the sorption generator which is a glass column with aluminum oxide of $\sim 2\text{ ml}$. Molybdenum-99 deposits on aluminum oxide. Accumulating technetium is washed with saline. Sorption generators provide low productivity and are used at a high specific activity of the irradiated material $\sim 10^3\text{ Ci/g}$. The advantage is that they can be used directly in the hospital. Such devices are used worldwide [12]. Technetium extraction in the extraction generator is influenced by various factors, the main of which can reduce the effectiveness of extraction, it is a complex salt solution composition, presence of NO_3^- and poor contact between the aqueous and organic phases. Sublimation method mentioned above [1, 4, 13] is to dissolve a metal target, evaporate the solution and preparation of molybdenum oxide. Molybdenum oxide melts at $800\dots 830^\circ$ in a platinum boat and accumulating technetium in the form of heptaoxide is stripped in oxygen flow, however, there is no industrial technology for this process at the moment. In accelerated molybdenum-99 production at low specific activity of technological solutions, ion-exchange technetium extraction from solution of complex ionic composition on chelate resin type and technetium washing out from the resin with water or saline is of interest. In this way molybdenum-99 technology using linac is being developed in Canada now [14].

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НАРАБОТКА ТЕХНЕЦИЯ В МОЛИБДЕНОВОЙ МИШЕНИ НА ЛИНЕЙНОМ УСКОРИТЕЛЕ ЭЛЕКТРОНОВ И МОДЕЛИРОВАНИЕ ОТГОНКИ ТЕХНЕЦИЯ

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Наряду с традиционными методами разделения молибдена и технеция из мишени, облучённой на линейном ускорителе электронов, рассмотрена возможность отгонки технеция из водного раствора. Для достижения необходимой температуры использована ортофосфорная кислота.

НАПРАЦЬОВАННЯ ТЕХНЕЦІУ В МОЛІБДЕНОВІЙ МІШЕНІ НА ЛІНІЙНОМУ ПРИСКОРЮВАЧІ ЕЛЕКТРОНІВ ТА МОДЕЛЮВАННЯ ВІДГОНКИ ТЕХНЕЦІУ

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Нарівні з традиційними методами розділення молибдену і технецію з мішені, опроміненої на лінійному прискорювачі електронів, розглянута можливість відгонки технецію з водного розчину. Для досягнення необхідної температури використана ортофосфорна кислота.