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SEPARATION OF ^{99}Mo FROM ^{132}Te USING THIOUREA AS COMPLEXING AGENT. APPLICATION TO THE SEPARATION OF ^{99}Mo FROM FISSION PRODUCTS

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A radiochemical method to isolate ^{99}Mo from ^{132}Te, both produced in the fission of ^{235}U, has been developed. The method is based on the formation of a cationic complex of tellurium with thiourea in acid medium which is retained (98.7 ± 0.5)% on a cation exchange resin (Dowex 50W-X8, 100–200 mesh), while (99.8 ± 0.05)% ^{99}Mo passes through it, due to the non-formation of such complex in the same experimental conditions. The radionuclidic purity of ^{99}Mo was found to be suitable for the preparation of ^{99}Mo–^{99m}Tc generators. The retention of ^{99}Mo on an alumina column as a function of pH was investigated and the best pH range for this purpose was found to be 4.0–4.5.

Thiourea (thiocarbamide) forms complexes of the amine type with numerous heavy metals and reacts with a number of cations and anions to give colored products of analytical importance. Most of the complexes formed with thiourea are cationic.[1]

ABRÃO[1,2] verified that tellurium(IV) ions react with thiourea, leading to formation of a cationic complex which is strongly held by a cationic ion exchanger. MESTNIK[3] studied the optimum conditions of complex formation and its characterization, and verified that molybdenum does not form cationic complex with thiourea in the same experimental conditions and then it is not retained by a cation exchanger column.

Molybdenum-99 is an important radionuclide in nuclear medicine because it is the source of a short-lived daughter, ^{99m}Tc,[4] which is widely used to visualize human organs. The development of techniques which permit a safe and clear visualization of internal anatomical structures may be directly attributed to the use of this radionuclide.

The applications of ^{99m}Tc include two groups, depending on the chemical form which is administered. As sodium pertechnetate (TcO_4), it is absorbed by most of the tissues of the body and in this form it is used for cardiac dynamic studies,[5] brain tumor localization,[6] scintillographies of the brain, thyroid and salivary glands.[5] When it is in its lower oxidation states, incorporated into inorganic or organic compounds, it is used for other purposes, for example: ^{99m}Tc-human macroaggregated serum albumin is used in pulmonary scintillography[7] and blood flow studies,[8] ^{99m}Tc-fibrinogen for circulatory studies,[9,10] ^{99m}Tc–DMSA and sodium glucoheptonate for renal scintillography[11] and as

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^{99m}Tc-pyrophosphates, ^{99m}Tc-polyphosphates and ^{99m}Tc–MDP for bone scintillographies.[12]

The fact that ^{99m}Tc (6.02 h) is produced by the ^{99}Mo radioactive decay (66.0 h) makes possible its use at long distances from the production site as a generator system. The radioisotope generator is a system composed by two radionuclides: one has a longer half-life (father) which generates by radioactive decay another radioisotope with a short half-life (daughter).

The chemical separation of ^{99m}Tc from its father (^{99}Mo) is obtained rapidly by a simple process of column chromatography in which ^{99m}Tc is eluted with 0.9% NaCl solution.

Two processes are commonly used to produce ^{99}Mo: activation of ^{98}Mo with thermal neutrons and as a product of ^{235}U fission, both performed in nuclear reactors.

In the first method, ^{99}Mo is produced by ^{98}Mo irradiation with thermal neutrons according to the reaction: $^{98}Mo(n,\gamma)^{99}Mo$. It is a simple procedure but in order to obtain ^{99}Mo with high specific activity, it is necessary to use enriched targets and a thermal neutron flux larger than $10^{13} n \cdot cm^{-2} \cdot s^{-1}$, because of the low activation cross section of ^{99}Mo (0.51 barns) and the natural isotopic abundance of ^{98}Mo, 24.6%.[13]

The second method (product of ^{235}U fission) is preferred for the production of ^{99}Mo–^{99m}Tc generators, because ^{99}Mo is obtained with high specific activity and can be easily adsorbed in small Al_2O_3 columns. This allows the elution of ^{99m}Tc with high radioactive concentration. Several techniques are used for the separation of ^{99}Mo from the fission products: ion exchange, column chromatography, sublimation, solvent extraction and precipitation. The last two techniques are not suitable because of the use of organic reagents that are easy to decompose upon radiation (solvent extraction) and generally low specific activities are obtained (precipitation).

Experimental

Radioisotopes. ^{123m}Te, obtained by the $^{122}Te(n,\gamma)$ reaction; ^{132}Te and ^{99}Mo, fission products, were utilized as tracers in the studies.

Chromatographic columns. A cation exchange resin (Dowex 50W–X8, 100–200 mesh) was utilized in studies of complex retention. The retention of ^{99}Mo was verified in chromatographic acid, grade I, alumina (Merck).

Radioactivity measurements. They were performed by γ-spectrometry, using a multi-channel analyzer with 4096 channels, Ortec, 7450 Model, connected to a Ge–Li detector, Ortec.

pH measurements. They were done using a Metrohm Herisau apparatus, E350B Model.

Reagents. All reagents used were of analytic grade, Merck.

Tellurium-thiourea complex preparation and retention in cationic resin (Dowex 50W-X8, 100–200 mesh)

Preparation of the columns. 4–5 ml of cationic resin (Dowex 50W-X8, 100–200 mesh) was placed in a glass column of 9mm internal diameter. It was washed with 25 ml of 1.0N HCl and distilled water for elimination of excess acid.

Procedure for complex preparation. 0.5 ml conc. H_2SO_4 and 1.0 ml 0.4M $HONH_3Cl$ were added to 10.0 ml 10^{-3}M H_2TeO_4(^{123m}Te). The solution was heated to 80–90 °C for

Table 1
Retention of tellurium-thiourea complex on the cationic resin (Dowex-50W-X8, 100–200 mesh)

Experiment	Retention, %	
	^{123m}Te	^{132}Te
1	99.0	99.5
2	99.6	96.1
3	98.2	97.0
4	97.2	99.1
5	98.8	99.6
6	99.1	96.7
Mean retention:	98.6 ± 0.8	98.0 ± 1.6

5 minutes. 0.5 g of thiourea was added to the solution and the heating was maintained for 5 minutes. The pH of the final solution was 1.0. After 30 minutes, a sample of the complex solution was percolated through the resin, which was further washed with 25 ml of acidified H_2O (pH 1). The complex retention in the resin was measured and the values are shown in Table 1. The same procedure was used to prepare the complex with ^{132}Te. For ^{123m}Te and ^{132}Te, activity measurements were analyzed using the photopeaks 158.8 keV and 228.2 keV, respectively.

Behavior of the molybdenum + thiourea in cationic resin

The behavior of ^{99}Mo in the presence of thiourea in the same experimental conditions of tellurium-thiourea complex preparation was studied as shown before. The ^{99}Mo-thiourea solution was percolated through a cationic resin (Dowex-50W-X8, 100–200 mesh) and the ^{99}Mo activities of the loading solution, effluent and washes were measured by γ-spectrometry. The retention was determined (Table 2).

Table 2
Determination of ^{99}Mo in the effluent and washes of the columns (Dowex 50W-X8, 100–200 mesh)

Experiment No.	^{99}Mo in the effluent and washes, %
1	98.6
2	98.1
3	95.0
4	99.9
5	99.1
6	99.3
Mean retention:	98.3 ± 1.7

Application of the method for separation of Mo–Te obtained from ^{235}U fission

Irradiations. Samples of 10mg U_3O_8 were irradiated inside quartz ampoules under a thermal neutron flux of about 10^{13} n · cm^{-2} · s^{-1}, during 8 hours. After that, the samples were left cooling for a period of two days.

Process of Te–Mo separation from fission products. The samples were dissolved in 2 ml of HNO_3 (1 : 1) and the resulting solution was diluted to obtain 1N solution. It was percolated through an Al_2O_3 column (9 mm diam. and 20 mm height), where molybdenum, tellurium and iodine traces were retained. The column was washed with 50 ml of 0.1N HNO_3 to remove all residual uranium and fission products. After that, it was washed with 50 ml of distilled water and 30 ml of 0.01M NH_4OH to remove the iodine. The molybdenum and the tellurium were eluted with 30 ml of 1N NaOH.

Separation of Mo from Te using thiourea as a complexing agent. A solution of ^{99}Mo–^{132}Te was evaporated to dryness and the residue was dissolved in 10 ml of distilled water. Sulfuric acid, hydroxylamine hydrochloride and thiourea were added as mentioned before and after 30 minutes, this solution was percolated through a cationic resin. The column was washed with 25 ml water acidified with H_2SO_4 (pH approximately 1) similarly to the loading solution. The activities of ^{99}Mo and ^{132}Te of the loading solution, effluent and washing solution were measured and the average result of the retentions in six experiments was (98.7 ± 0.5)% for ^{132}Te and (0.16 ± ± 0.05)% for ^{99}Mo. Table 3 shows these results.

Analysis of the radionuclidic purity of ^{99}Mo solution. The ^{99}Mo solutions were analyzed by γ-spectrometry and the results are shown in the Results and Discussion.

Table 3
Retention of ^{132}Te-thiourea complex and ^{99}Mo on Dowex 50W-X8 resin (100–200 mesh)

Experiment No.	Retention, %	
	^{132}Te-thiourea complex	^{99}Mo
1	98.8	0.13
2	97.8	0.25
3	98.7	0.11
4	99.2	0.15
5	99.1	0.18
6	98.8	0.14
Mean retention:	98.7 ± 0.5	0.16 ± 0.05

Influence of pH in the retention of ^{99}Mo on alumina column

The adsorption of molybdenum on alumina is very interesting for ^{99m}Tc generators production.[14,15] It depends on the pH which causes changes in the chemical structure of the molybdate ion as well as in the alumina surface electric charge.[16,17,18] The influence of pH in the retention of ^{99}Mo on alumina, at pH between 2.5 to 5.5 was studied Carrier-free ^{99}Mo of low activity (< 37 KBq) was employed.

Preparation of alumina columns. Five glass columns with 0.9 cm diameter containing approximately 2 g of dry alumina were used.

Treatment of alumina. The alumina was washed with distilled water and the floating particles were poured off and rejected. For approximately 10 g of alumina, five volumes of 50 ml distilled water were used. After that, the alumina was washed four times with 25 ml of 0.1N HCl, and again, the floating particles were poured off and rejected. These columns were conditioned at different pHs, using HCl solution, so that the pH attained the values of 2.5, 3.5, 4.0, 4.5 and 5.5.

Percolation

5 ml samples of ^{99}Mo solution with pH adjusted to 2.5, 3.5, 4.0, 4.5 and 5.5 were percolated through the alumina columns, using a flow of approximately 1.0 ml/min. At the end of this operation, the columns were washed with 20 ml of distilled water acidified with HCl to a pH similar to that of the loading solution. The ^{99}Mo adsorption was determined and the results are shown in Table 4.

Table 4
Influence of the pH on the retention of ^{99}Mo on alumina columns

Experiment No.	pH of the column	Adsorption of ^{99}Mo, %
1	2.5	88.9
2	3.5	95.3
3	4.0	99.2
4	4.5	99.4
5	5.5	80.2

Elution of ^{99m}Tc

Five ml of ^{99}Mo solution obtained by the method presented in this paper was adjusted to pH 4.5 and percolated through a glass column, 0.9 cm in diameter, containing 2 g of alumina (pH similar to the loading solution). The column was washed with 20 ml of water acidified with HCl (pH 4.5). After that, the column was again washed with 0.9% NaCl solution getting pH 5. Finally, ^{99m}Tc was eluted with 3 ml of 0.1N NaCl and the product was analyzed by γ-spectrometry (Fig. 1).

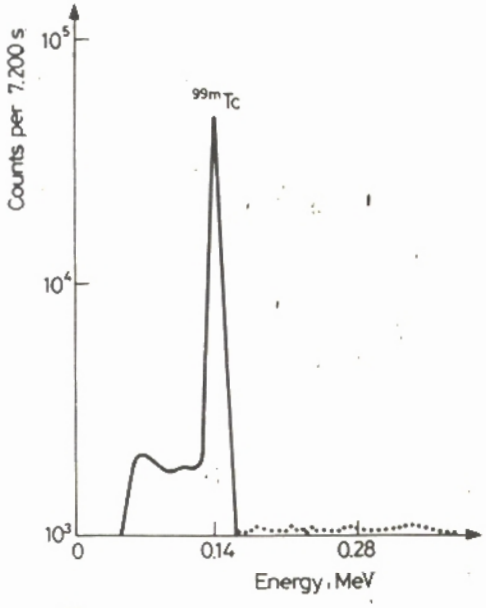

Fig. 1. Gamma-ray spectrum of ^{99m}Tc solution soon after the generator elution with 0.9% NaCl solution

Results and discussion

Retention of tellurium-thiourea complex in the cationic resin (Dowex-50W-X8, 100–200 mesh)

The results presented in Table 1 show that the mean retention of the ^{123m}Te and ^{132}Te-thiourea complexes in the resin were: $(98.6 \pm 0.8)\%$ and $(98.0 \pm 1.6)\%$, respectively, while $(98.3 \pm 1.7)\%$ of ^{99}Mo percolated appears in the effluent and washing solutions (Table 2). This fact shows that ^{99}Mo does not form cationic complex with thiourea under these conditions. Therefore, ^{99}Mo is collected in the effluent.

Separation of ^{99}Mo–^{132}Te and radionuclidic analysis of the product (^{99}Mo)

Table 3 shows that the separation of ^{99}Mo–^{132}Te was achieved with good results, since average retentions of the six experiments for ^{132}Te was $(98.7 \pm 0.5)\%$ and only $(0.16 \pm 0.05)\%$ of ^{99}Mo was retained in the column.

Radionuclidic purity. It is important that ^{99}Mo presents a high radionuclidic purity because it will be used to produce ^{99m}Tc generators and the nature of the contamination of ^{99m}Tc eluted from the generators is determined by the production process of the father (^{99}Mo).

In this work, the radionuclidic impurities found in the ^{99}Mo solutions were:

$^{131}I = 1.7 \cdot 10^{-3}$ KBq/MBq ^{99}Mo,

^{103}Ru = not detected,

$^{132}Te = 3.0 \cdot 10^{-2}$ KBq/MBq ^{99}Mo.

These results are satisfactory because they are below the estabilished limits for ^{99}Mo fission used in ^{99m}Tc generators.[19]

These limits are: $^{131}I < 5 \cdot 10^{-2}$ KBq/MBq ^{99}Mo

$^{103}Ru < 5 \cdot 10^{-2}$ KBq/MBq ^{99}Mo

$^{132}Te < 5 \cdot 10^{-2}$ KBq/MBq ^{99}Mo

Influence of pH in the retention of ^{99}Mo on alumina columns

The analysis of Table 4 indicates that the maximum retention of ^{99}Mo occurs with pH around 4.0–4.5. It also shows the tendency of a fast decrease in the retention at higher pH, while at lower pH, the retention decreases slowly.

At low Mo concentrations, ($< 10^{-3}$M), and in acid solutions,[14,20,21] molybdenum appears on the alumina surface as MoO_4^{-2}, while at higher concentrations, as isopolymolybdates. In the experiments reported in this paper, dilute solutions were used, that is, $C_{Mo} < 10^{-3}$M. Therefore, it can be considered that Mo(VI) is present in the

monomeric state (MoO_4^{-2}), regardless of the pH of the solution. Thus, its retention in alumina occurs in the form of MoO_4^{-2} for all pH studied.

One more analysis of Table 4 shows that the tendency to sharp decrease in absorption at a region closer to neutral to basic pH (pH 5.5) can be explained by the fact that the alumina surface is neutral or negative in this region, not adsorbing the molybdate ions.[14]

Our results agree with the ones obtained by GONZALES et al.[22] and LEVI.[23]

Elution of ^{99m}Tc

From the results we can conclude that the eluted ^{99m}Tc has satisfactory radionuclidic purity and it is adequate to medical purpose. The γ-spectrum of the eluted ^{99m}Tc is shown in Fig. 1.

Conclusions

We can conclude that the method established in this work can be used for the separation of ^{99}Mo–^{132}Te, obtained in ^{235}U fission. Therefore, the method may be applied to separate ^{99}Mo from the fission products. ^{99}Mo had an adequate radionuclidic purity when uranium oxide was irradiated for only 8 hours. However, if the irradiation requires longer periods, it is necessary to apply a more accurate control. This statement is also valid for the eluted ^{99m}Tc solutions. Yet, the ^{99}Mo obtained is retained in alumina columns at pH around 4.0–4.5, which is suitable for the preparation of ^{99m}Tc generators.

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