CRP ON "DEVELOPING TECHNIQUES FOR SMALL SCALE INDIGENOUS MOLYBDENUM-99 (MO-99) PRODUCTION USING LOW ENRICHED URANIUM (LEU) FISSION OR NEUTRON ACTIVATION."

FINAL REPORT

Status Report on Technical Progress for LEU-Based ^{99}Mo Production at IPEN-CNEN/SP, Brazil – Modified Cintichem Process

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Abstract

Due to the increasing needs for nuclear medicine in Brazil and the world shortage of ^{99}Mo observed since 2008, IPEN-CNEN/SP-Brazil decided to develop its skills for producing ^{99}Mo through the route of ^{235}U fission. This decision was based on: (i) the well-established laboratory for producing ^{99m}Tc generators already in operation in IPEN and responsible for the Brazilian market supply; (ii) the availability of LEU by the Brazilian Enrichment Laboratory; (iii) the established capacity to prepare targets of U-Al alloys; (iv) the availability of some human resources in uranium chemistry; (v) the possibility of operating the IEA-R1 for at least ten years more; and (vi) the recent ongoing project of the CNEN to construct a new research reactor. IAEA agreed to the participation of Brazil in the CRP dealing with the indigenous production of ^{99}Mo in 2010. This paper will present an update of the project at IPEN, showing the efforts of the different groups towards the goal of producing ^{99}Mo through the fission of LEU ^{235}U targets employing the modified Cintichem process. It will present the results of the preliminary experiments dealing with the acid dissolution of metallic U targets; the separation of ^{99}Mo from some fission-produced impurities, comprising the precipitation with α-benzoin oxime and purification in HZO and activated charcoal columns and the separation of ^{131}I for use as primary radioisotope. It will also present the configuration of the new reactor project in Brazil and the calculations concerning the amount of the fission products generated in the ^{235}U targets in the real conditions projected for this reactor. During this period Brazil participated in the meeting held by IAEA in Chile in 2010 with 5 researchers and one researcher went to a visit to ANL and Y-12 installations in the USA under the support of IAEA.

1. INTRODUCTION

IPEN (Instituto de Pesquisas Energéticas e Nucleares or Nuclear and Energy Research Institute) is the biggest nuclear research institute of the Brazilian Nuclear Commission CNEN (Comissão Nacional de Energia Nuclear or National Nuclear Energy Commission). IPEN, located in the city of Sao Paulo, produces almost all radiopharmaceuticals used in Brazil. IPEN has a research pool type reactor of 5 MW (IEA-R1) and two cyclotrons for producing radioisotopes for nuclear medicine use.

The Radiopharmacy Center of IPEN-CNEN/SP-Brazil has an established radioisotope production program to supply radiopharmaceuticals to the nuclear medicine community in Brazil. IPEN provides radiopharmaceuticals for more than 350 users (hospitals, clinics, etc.) in the country. These radiopharmaceuticals are prepared with radioisotopes produced in both a nuclear reactor and cyclotron accelerators. IPEN has a research reactor, so called IEA-R1m that nowadays operates at 4.5MW for 60 hours continuously.

Among the radioisotopes used for medical application, ^{99m}Tc is the most used, responsible for more than eighty percent of the total applications and is delivered in the form of homemade ^{99}Mo/^{99m}Tc generators. IPEN imports all the ^{99}Mo used in Brazil and up to 2009 the principal supplier

was Nordion from Canada. At that time IPEN imported 450 Ci (6-days calibration) per week of ^{99}Mo. Nowadays IPEN imports nearly 390 Ci of ^{99}Mo every week from different suppliers.

In the past, IPEN developed the route for producing ^{99}Mo by neutron activation of ^{98}Mo targets in the IEA-R1 Research Reactor. IPEN has a processing cell for this ^{99}Mo production route, using the gel generator technique but it was demonstrated to be not feasible to the size of medicine application needs existing in Brazil.

Due to the increasing needs of the nuclear medicine in Brazil and the world shortage of ^{99}Mo observed since 2008, IPEN decided to develop its skills for producing ^{99}Mo through the route of ^{235}U fission. This decision was based on: (i) the well-established laboratory for producing ^{99m}Tc generators already in operation in IPEN and responsible for the Brazilian market supply; (ii) the availability of LEU (20 wt%) by the Brazilian Enrichment Laboratory; (iii) the established capacity to prepare targets of U-Al alloys; (iv) the availability of human resources in uranium chemistry; (v) the possibility of operating the IEA-R1 for at least ten years more; and (vi) the intention of the CNEN to construct a new research reactor.

2. ^{99}Mo PROJECTS AT IPEN

The reactor produced radioisotope program started at IPEN in 1959 with the production of ^{131}I and since then all the efforts were made towards the development of methods for the production of the desirable radioisotopes. Since 1981 IPEN produces and distributes ^{99m}Tc generators with imported fission-produced ^{99}Mo and in-house developed technology of chromatographic alumina based generators. In 1996 IPEN started a project aiming the nationalization of the production of ^{99}Mo through the ^{98}Mo(n,γ)^{99}Mo reaction and developing the MoZr gel generator technology. Two different targets were tested: metallic Mo and MoO$_3$ in the form of powder or molten. The targets were irradiated for a definite length of time with low neutron fluxes and inside a Be irradiator located at the reactor core with the highest possible flux. A successful technology was developed for the preparation of the gel and a hot processing cell was assembled for the routine preparation of MoZr gel and gel generators. The Quality Control group validated the generators, approving the required quality and generators up to 11.1 GBq (300 mCi) could be produced with reactor power of 5 MW. Unfortunately, the reactor could not reach the power required for the start of the clinical trials with the generator, 5 MW. Nowadays, even if the reactor operates at this power, the nuclear medicine market requires generators of higher activities. Studies are under way aiming the concentration of the ^{99m}Tc activity eluted from the gel generator. However, this project made it possible to upgrade the reactor power to 4.5 MW and nowadays it is possible to produce at least 50% of the Brazilian demand of ^{131}I.

Figure 1 shows the distribution of ^{99}Mo/^{99m}Tc generators by IPEN in the last decade. The growing demand was interrupted in 2009 due to the crisis in ^{99}Mo supply.

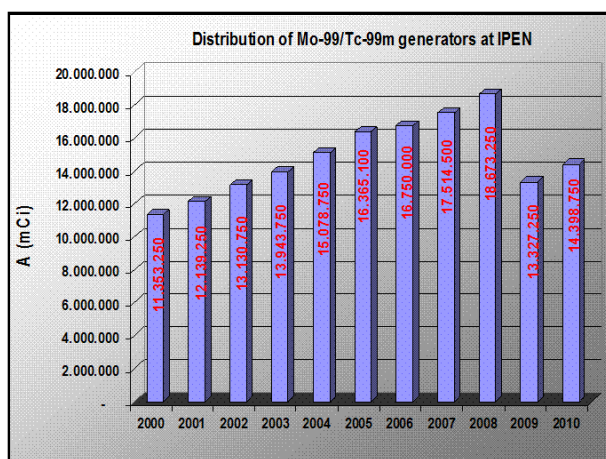FIG. 1. Distribution of ^{99}Mo/^{99m}Tc generators by IPEN.

Before the ^{99}Mo supply crisis that started in 2008, IPEN's main ^{99}Mo supplier was Nordion, Canada, reaching nearly 450 Ci every week. To overcome this supply crisis IPEN chose 3 approaches: short, medium and long term solutions.

The short term solution was to diversify the suppliers of ^{99}Mo. Nowadays IPEN has contracts with 4 suppliers: Argentina, South Africa, Nordion (Canada) and recently IRE (Belgium), providing a total of 390 Ci of ^{99}Mo every week. In the past the production of ^{99}Mo/^{99m}Tc generators was done once a week, nowadays there are 3 productions every week, with a total of 360 generators. This modification and the better use of ^{99m}Tc by the physicians led to a reduction on the demand of ^{99}Mo in Brazil.

The medium term solution was the production of ^{99}Mo through the ^{98}Mo(n,γ)^{99}Mo reaction, the separation of ^{99m}Tc and delivery of ^{99m}Tc solutions to the physicians in the form of ^{99m}TcO$_4^-$ or labeled kits with ^{99m}Tc. The IEA-R1m reactor at IPEN was recently upgraded to 4.5 MW and it is expected to operate at 5 MW in 2012. In this situation, nearly 50 Ci of ^{99m}Tc could be produced every week and delivered to clinics and hospitals in the region of São Paulo. The target is MoO$_3$ and ^{99m}Tc is separated by solvent extraction with a separation yield of 80%. A hot cell is being assembled and production is expected to start before June 2012.

The long term solution is the production of ^{99}Mo through the fission of low enriched uranium (LEU) targets. This solution is only possible due to the decision of the Brazilian government of constructing a new nuclear reactor, the so called BMR (Multipurpose Brazilian Reactor). The reactor will have a power of 30 MW and will be constructed at Iperó, a city 100 km from São Paulo.

The BMR has a defined site and a conception project to all the buildings, including the Radioisotope production facility. Other radioisotopes will be produced, such as ^{131}I, ^{153}Sm, ^{177}Lu, ^{166}Ho, ^{32}P, ^{188}W and ^{90}Y. The goal of this project is to produce 1000 Ci of ^{99}Mo with a pre calibration of 6 days.

The routes of ^{99}Mo production are being developed: (1) alkaline dissolution of U-Al LEU targets and (2) acid dissolution of metallic LEU targets (Figure 2).
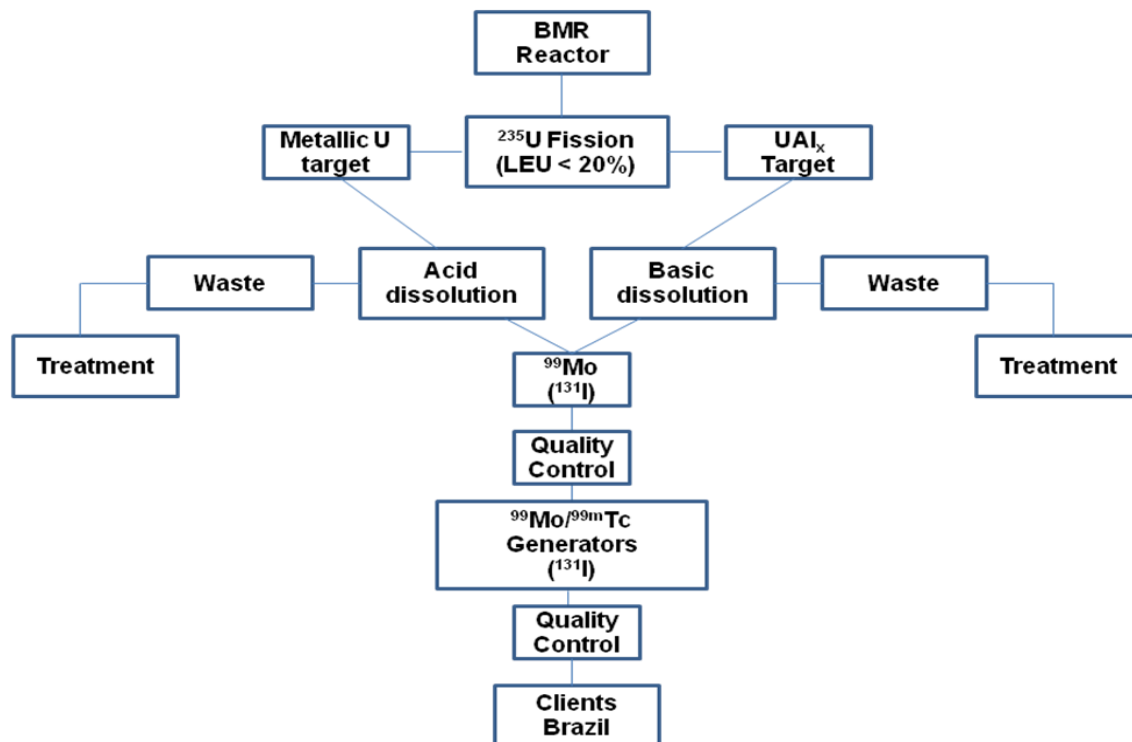

FIG. 2. *Long term alternatives for the production of ^{99}Mo and distribution of ^{99m}Tc via LE^{235}U in the BMR.*

The first approach had an input from IAEA in collaboration with Argentina in the beginning of the 90's and IPEN has the technology of preparing U-Al targets and also experience in the separation and purification of ^{99}Mo.

The second approach was made possible with the inclusion of Brazil in the CRP on "Developing techniques for small scale indigenous molybdenum-99 (^{99}Mo) production using low enriched uranium (LEU) fission or neutron activation". The objectives of joining this CRP were to obtain technical information about the production of ^{99}Mo from the fission of ^{235}U by irradiating LEU targets already made available from this CRP and to get the support from IAEA and the developers of technology in order to get access to the technical information involved in the production of ^{99}Mo, such as preparation of the U target, waste management, the chemical process of the irradiated U target, purification of ^{99}Mo and quality control of the final product. This information will help in the decision on the production route that will be adopted by IPEN in Brazil.

Brazil joined this CRP late, in June 2010, but a great amount of work has been done, especially in the chemical separation process, the so-called modified Cintichem process. The interaction and technical cooperation was also made possible through IAEA. These efforts will be specified in this report.

Several groups are involved in this project at IPEN: (1) target group connected to the fuel element production center; (2) chemical separation and quality control group; (3) waste management group; (4) radiological protection group; (5) neutronic group and (6) project group.

3. WORK RELATED TO THE CRP

3.1. PARTICIPATION IN MEETINGS

IPEN participated in the "Technical Meeting on developing techniques for small scale indigenous molybdenum-99 production using low enriched uranium fission or neutron activation - Specific Waste and Quality Issues" that took place between November 9-12, 2010 in Santiago, Chile. Five participants from IPEN were at the meeting, 2 of them paid by IAEA. From the 5 participants, 3 belong to the chemical separation and quality control group, 1 from waste management and 1 from targetry.

One researcher from IPEN participated of the "Consultancy Meeting on non-HEU based ^{99}Mo Production Technology and Infrastructure" with the following schedule:

- 27–28 June 2011 at Argonne National Laboratory, ANL, Chicago, USA, that dealt with the modified Cintichem process
- 30 June–1 July 2011 at B&W Y-12 National Security Complex, Knoxville, USA, that dealt with the metallic U (LEU) target preparation process

3.2. MODIFIED CINTICHEM PROCESS

The study of the modified Cintichem process was split into 4 processes: (1) Dissolution of metallic U targets; (2) Precipitation of Mo with alpha-benzoin oxime (α-Bz); (3) column purification of Mo and (4) Recovery of ^{131}I.

Some definitions were needed for developing the chemical process. The amount of carrier impurities was calculated for the fission of LEU targets leading to 1000 Ci of ^{99}Mo with 6 days of pre calibration. These values are shown in Table 1.

TABLE 1. MASS OF MAIN METALLIC LEU FISSION PRODUCTS

Nuclide	Mass (g)
Mo	5.51E-02
Pu	8.65E-03
Np	7.96E-05
I	1.09E-02
Ru	4.89E-02
Rh	1.32E-03
Zr	8.13E-02
Sr	3.90E-02
Te	1.90E-02
Y	9.16E-03
Mo	5.51E-02
Pu	8.65E-03

During the studies several radioactive tracers (Table 2) were prepared by irradiating adequate targets at the IEA-R1m reactor. Other radioactive tracers were used coming from the routine production, such as ^{99}Mo and ^{131}I.

TABLE 2. RADIOACTIVE TRACERS PRODUCED AT IPEN'S REACTOR

Target	Tracers	Half-life
TeO_2	^{121}Te; ^{123m}Te	154 d; 120 d
$ZrOCl_2$	^{88}Zr; ^{95}Zr	85 d; 65.5 d
$RuCl_3$	^{97}Ru; ^{103}Ru	2.88; 39.6 d

3.2.1 Dissolution of metallic U targets

Few preliminary experiments were performed with the dissolution of metallic U targets. Crude foils of U were provided by the targetry group with a thickness of few mm and mass of 13 g. The non-irradiated foils were dissolved with 6 mol.L^{-1} HNO$_3$ with some I- carrier and ^{131}I tracer. The time of dissolution was long due to the thickness of the foil, taking nearly 4 hours to complete dissolution. The solution and off gas were used for evaluating the recovery of ^{131}I and also to study the presence of U in the precipitation and purification of Mo.

3.2.2 Precipitation of Mo with α-Bz

Initially, a mimetic of the acid dissolution process of LEU foils was performed in acidic media using 2 mL of 1mol.L^{-1} HNO$_3$, 2% α-benzoin oxime (α-Bz) as precipitant agent and (0.1 mol.L^{-1}) NaOH /1%H$_2$O$_2$ as dissolver solution. Moreover, 0.5 mL of a Mo carrier solution (MoO$_3$ 10-30 mg/mL) and 2.5% KMnO$_4$ solution were added to the reaction in order to simulate both the macroscopic precipitation of ^{99}Mo and LEU foils dissolution, respectively.

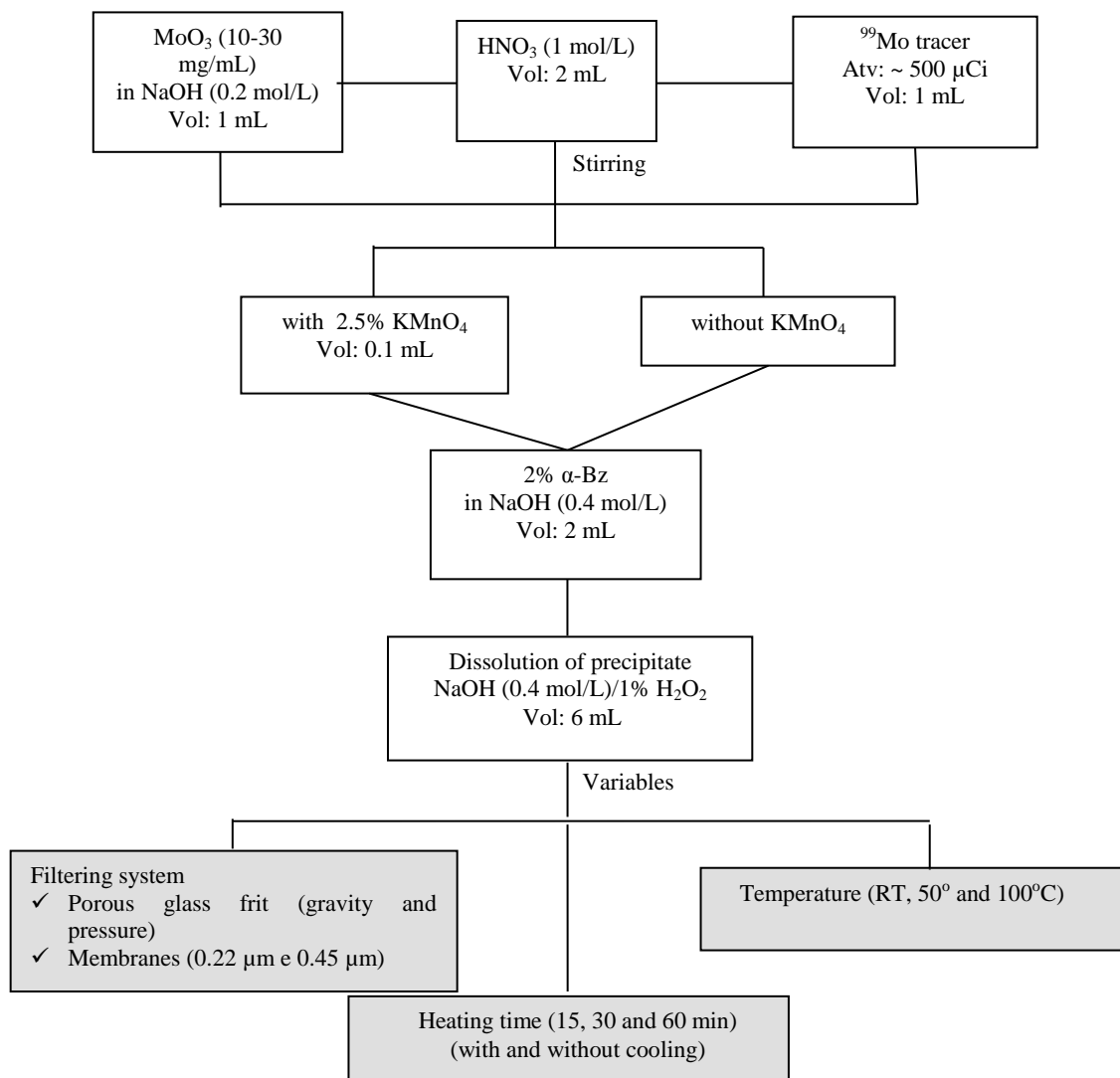The initial experiments were performed as described in Figure 3.

FIG. 3. Diagram of the preliminary experiments for the precipitation of Mo with α-Bz.

The chosen filtering system was a glass frit filtration as seen in Figure 4.

FIG. 4. Glass frit filtering device for Mo-α-Bz.

The preliminary results showed that, besides using a glass filter, there was the need of using pressure to filter the solution and that the best results were achieved by heating the solution to 100°C for 15 min and letting the solution to cool down before the filtration. This effect is shown in Table 3.

TABLE 3. EFFECT COOLING DOWN THE SOLUTION CONTAINING Mo AND α-Bz BEFORE FILTRATION

Condition	% precipitation	% recovery
With cooling	98.72	95.27
Without cooling	76.00	57.85

The following parameters were then evaluated but this time heating the solution to 50°C: the α-Bz/Mo ratio, the Mo carrier content, the concentration of the dissolution solution and the heating time at 50°C. The filtration was carried out using a glass frit filtration unit. Samples were taken before the precipitation of ^{99}Mo, from the filtrate, precipitate washing and dissolution. The precipitation and recovery yields of ^{99}Mo were measured by γ-ray spectroscopy using an HPGe detector.

The highest yields of ^{99}Mo precipitation and recovery yields (98.72% and 95.27%, respectively), were reached out under the initial conditions with low mass of Mo. When the mass of Mo was increased, the results started to decrease. The first change was the concentration of NaOH used in the preparation of the α-Bz and in the dissolution of the precipitate. The results are shown in Figure 5.
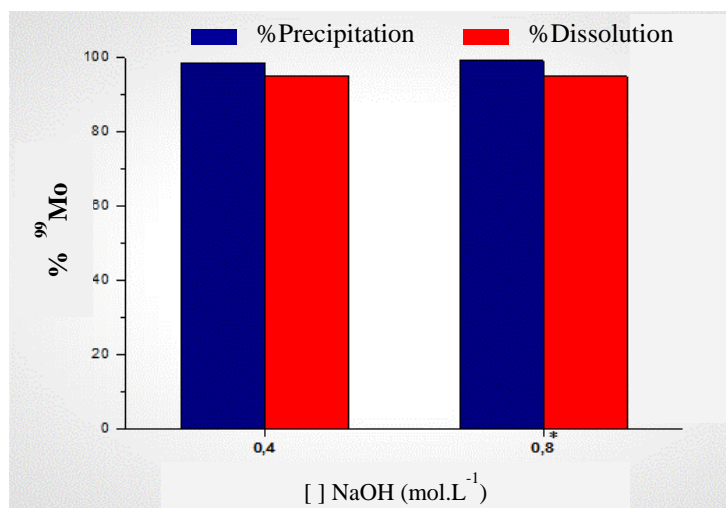
FIG. 5. Effect of the concentration of NaOH in the precipitation and dissolution of Mo-α-Bz.

From this point 0.8 mol.L^{-1} NaOH was employed in the experiments. Figure 6 shows the effect of the time of heating the solution at 50°C during the precipitation.
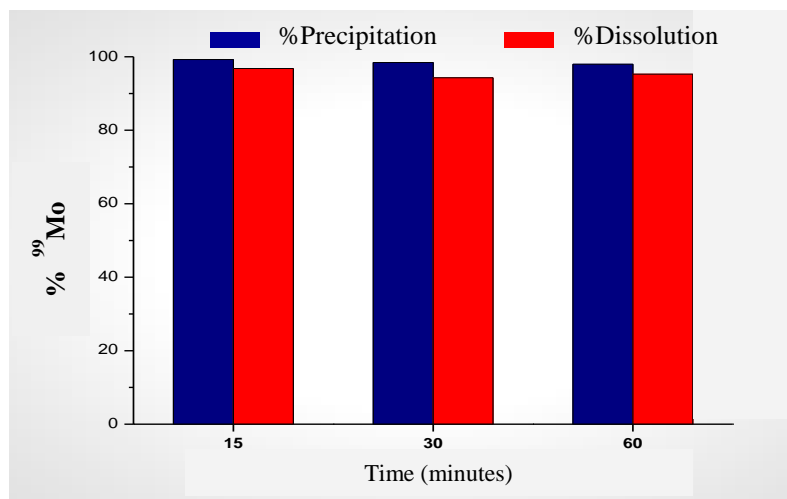

FIG. 6. Effect of the time of heating in the precipitation and dissolution of Mo-α-Bz.

The best results were achieved with 50 min of heating. The effect of the mass ratio α-Bz/Mo can be seen in Figures 7, 8, 9 and 10. Figure 7 still used a solution of 2% of α-Bz and 5 mg of Mo carrier. In Figures 8 to 10 the concentration of α-Bz was 6% and the mass of Mo carrier was varied.
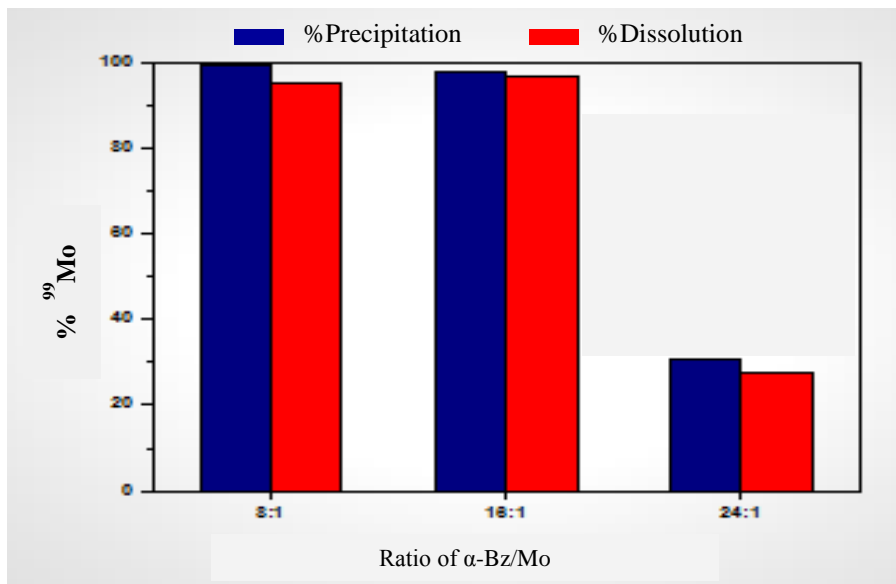
FIG. 7. Effect of the mass ratio of α-Bz/Mo in the precipitation and dissolution of Mo-α-Bz (2% of α-Bz and 5 mg of Mo).
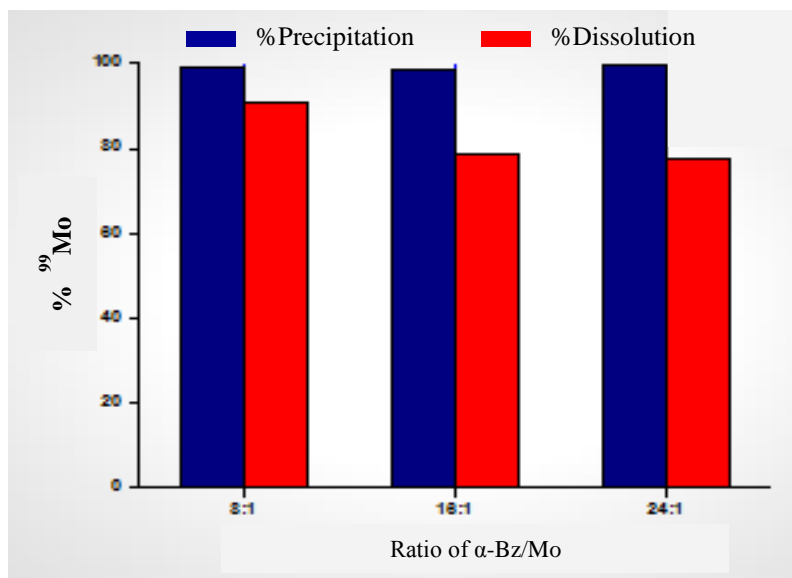

FIG. 8. Effect of the ratio of α-Bz/Mo in the precipitation and dissolution of Mo-α-Bz (6% of α-Bz and 5 mg of Mo).
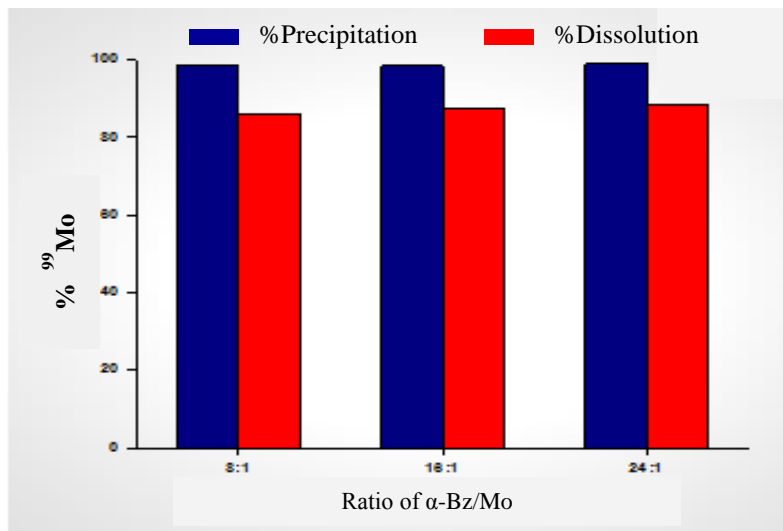
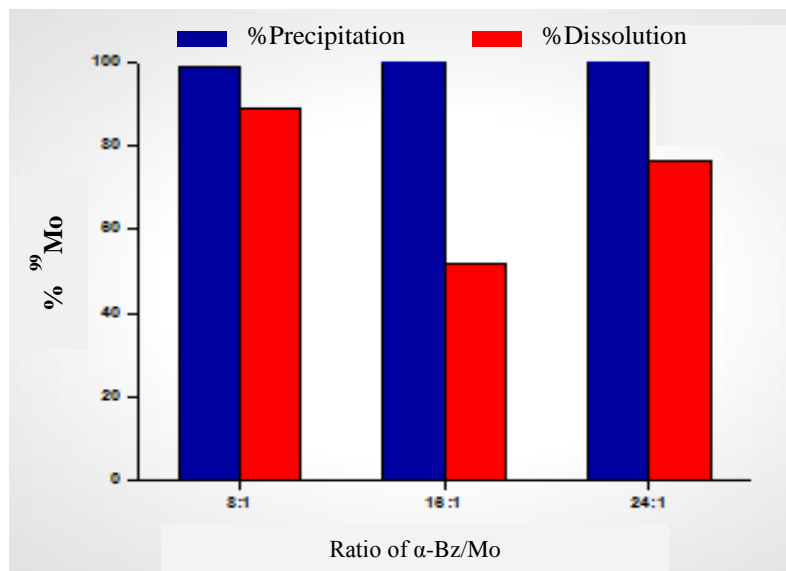*FIG. 9. Effect of the ratio of α-Bz/Mo in the precipitation and dissolution of Mo-α-Bz (6% of α-Bz and 10 mg of Mo).*

FIG. 10. Effect of the ratio of α-Bz/Mo in the precipitation and dissolution of Mo-α-Bz (6% of α-Bz and 15 mg of Mo).

As can be noticed, ^{99}Mo precipitation is above 98% even at the highest α-Bz/Mo ratio evaluated (24:1). Differences among recovery rates were largely dependent on the characteristics of the precipitates. A sharp decrease of both ^{99}Mo precipitation and recovery rates can be observed for the highest amount of Mo carrier studied (Figure 11), which corroborates with the reaction stoichiometry.
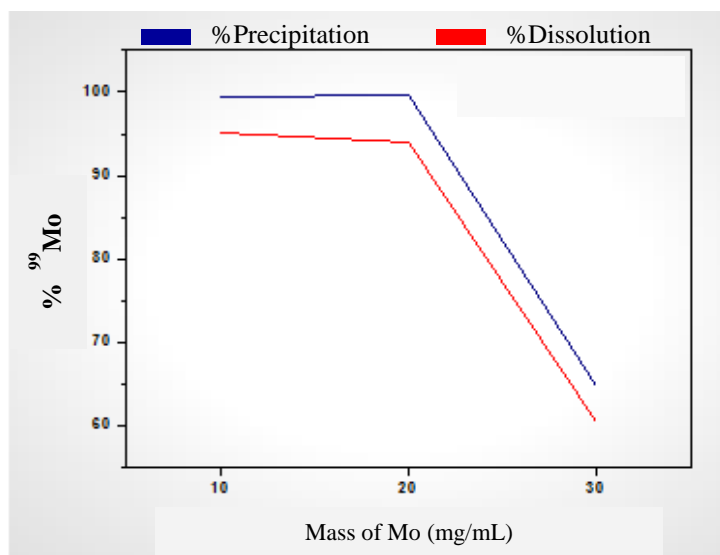
FIG. 11. Effect of the mass of Mo in the precipitation and dissolution of Mo-α-Bz.

A Fractional Factorial Design of resolution V was held as an early step within a statistical strategy for optimizing the overall process of precipitation and recovery of ^{99}Mo. In this sense, both significance and magnitude of the independent variables effects [α-Bz/Mo molar ratio, Mo carrier content, reaction time and temperature, and cooling time of the reaction mixture] as well as their interactions were evaluated for the recovery yields of ^{99}Mo. Upper and lower limits were established for the five independent variables under analysis. The definition of the experimental matrix and the subsequent statistical analysis were performed using the computer program Statgraphics Plus (Statistical Graphics Co., Rockville, MD, USA). Also three experimental runs were added to the basic experimental design (16 experiments) in order to estimate the experimental error, thus allowing the analysis of the statistical significance in the mathematical model as well as the variables under study. The statistical significance and magnitude of each independent variable and their interactions were obtained through the analysis of variance and multiple linear regressions, respectively.

The results showed that temperature, reaction time and their interactions are inversely proportional to the percentages of both precipitation and recovery of ^{99}Mo. The α-Bz/Mo ratio has an inverse effect, which means that the greater the α-Bz ratio used in the model, the higher the percentage of ^{99}Mo precipitation and recovery.

A statistical design of an optimal response surface type (Central Composite Design) was used as a tool of analysis with these preliminary results. The results can be seen in Figures 12, 13 and 14.
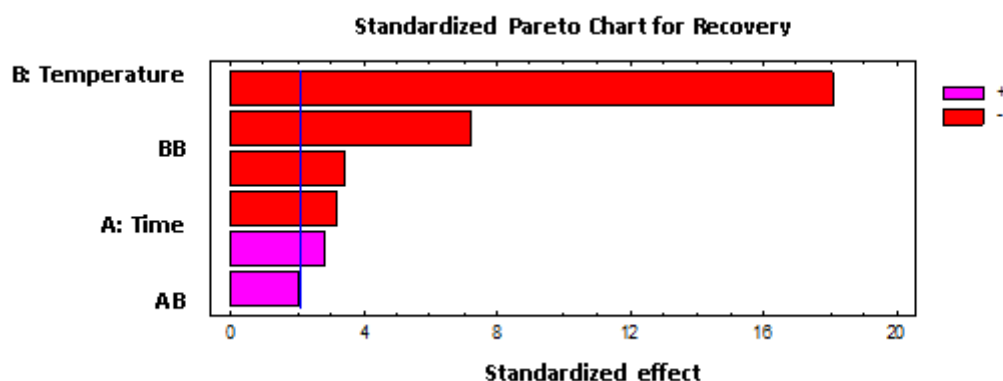

FIG. 12. Statistical significance of the variables in the percentage of ^{99}Mo precipitation.
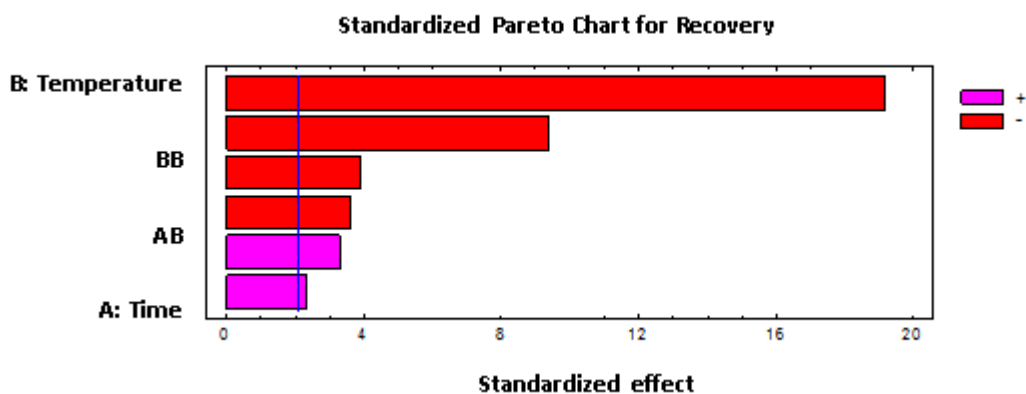
FIG. 13. Statistical significance of the variables in the percentage of ^{99}Mo recovery.
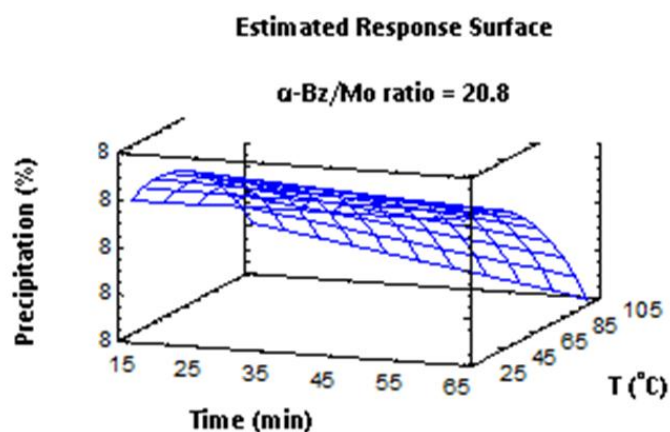
FIG. 14. Representation of the ^{99}Mo precipitation surface response at constant α-Bz/Mo ratio (20.8).

These results were useful for minimizing the number of experiments performed.

The overall procedure for the precipitation of Mo with α-Bz was concentration of α-Bz 6%, concentration of NaOH 0.8 mol.L^{-1}, temperature 50°C, 15 min of heating and cooling prior to filtration and ratio of α-Bz/Mo higher than 8.

The influence of some contaminants was also evaluated, such as I, Te, Ru and Zr using radioactive tracers. Figure 15 shows the effects and behaviour of the presence of I and Te in the solution.

FIG. 15. Effect of the presence of I and Te in the precipitation and dissolution of Mo-α-Bz.

There is no change in the behavior of Mo but almost half of I is carried with Mo after the precipitate dissolution.
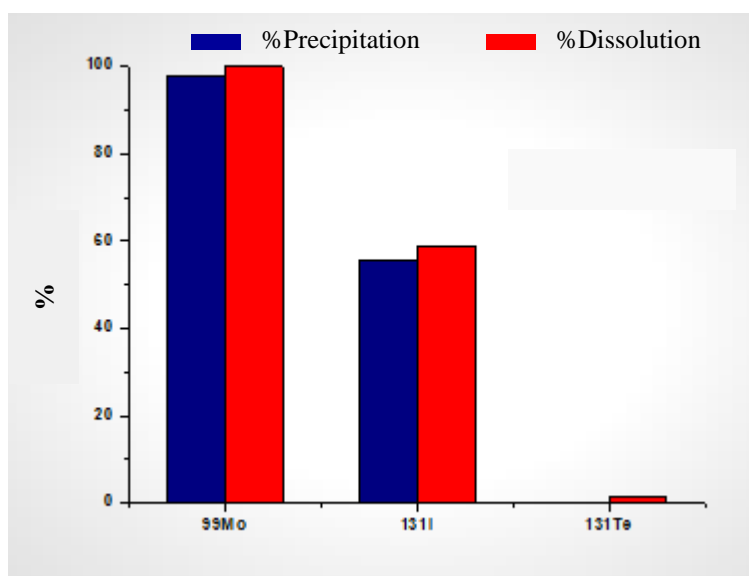
3.2.3. Column purification of Mo

Based on published protocols of the modified CINTICHEM process, the purification step of [99]Mo coming from fission LEU foils is performed by adsorption chromatography containing activated charcoal (AC), activated charcoal containing silver (AC-Ag) and hydrous zirconium oxide (HZO). The expected behavior is the elution of Mo and retention of impurities such as I, Te, Zr and Ru.

The experiments started with the study of the behavior isolated of Mo, with the addition of contaminants and with the solution coming from the dissolution of the Mo-α precipitate.

Table 4 shows the characteristics of the AC columns used in this work.

TABLE 4. CHARACTERISTICS OF AC COLUMNS

	Column 1	Column 2	Column 3	Column 4	Column 5
Material	AC (grain)	AC (powder)	AC (powder)	AC grinded	AC grinded
Size (Φ x h)	13 mm x 20 cm	10 mm x 18 cm	10 mm x 18 cm	9 mm x 9,5 cm	10 mm x 18 cm
Filling	5 cm of CA	5 cm of CA	5 cm of CA	3,5 cm of CA	4,5 cm of CA
Assembling	Frit – CA – glass wool	Glass wool – CA – glass wool	Glass wool – CA – glass wool	Glass wool – CA – glass wool	Glass wool – CA – glass wool
Washing	20 mL H_2O	20 mL H_2O	*	**	**
Condicioning	50 mL 0.2 $mol.L^{-1}$ NaOH	50 mL 0.2 $mol.L^{-1}$ NaOH	50 mL 0.4 $mol.L^{-1}$ NaOH	50 mL 0.4 $mol.L^{-1}$ NaOH	50 mL 0.4 $mol.L^{-1}$ NaOH
Flow	3 $mL.min^{-1}$	3 $mL.min^{-1}$	3 $mL.min^{-1}$	2 $mL.min^{-1}$	3 $mL.min^{-1}$

The use of the columns showed that AC had to be grinded, so only columns 4 and 5 were further employed. Table 5 shows the effect of the variation of the concentration of NaOH on the retention of Mo and I.

TABLE 5. EFFECT OF NaOH CONCENTRATION ON THE RETENTION OF Mo AND I ON AC

Eluent	^{99}Mo elution	^{131}I retention	Elution volume
0.2 mol.L^{-1} NaOH	62.1%	12.1%	20 mL
0.4 mol.L^{-1} NaOH	95.1%	14.7%	20 mL

The best results were achieved with 0.4 mol.L^{-1} of NaOH. Table 6 shows the effects of the variation of the mass of Mo.

TABLE 6. EFFECT OF Mo MASS ON AC

Mass of Mo carrier	^{99}Mo elution	Elution volume
5 mg	95.1%	20 mL
20 mg	96.9%	20 mL
30 mg	96.4%	20 mL

Mo is not retained when the carrier mass was increased. Figure 16 shows the behavior of Mo, I and Te on AC with or without the presence of 2.5 % solution of KMnO$_4$.
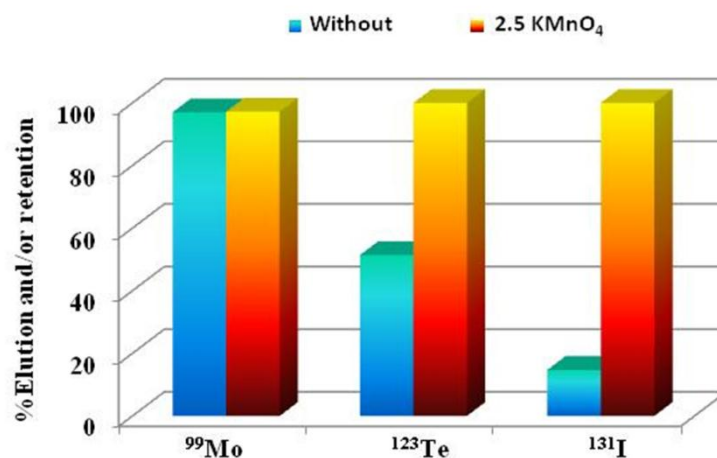

FIG. 16. Behavior of Mo, I and Te on AC with and without KMnO$_4$.

The presence of KMnO$_4$ was important to increase the retention of I and Te. Table 7 shows the characteristics of the HZO columns used in this work.

TABLE 7. CHARACTERISTICS OF HZO COLUMNS

	Column 1	Column 2	Column 3
Material	HZO	HZO	HZO
Size (Φ x h)	14 mm x 20 cm	13 mm x 12 cm	10 mm x 18 cm
Filling	5 cm of HZO (~ 11.4 g)	3 cm of HZO (~ 5 g)	4.5 cm of HZO (~ 5 g)
Assembling	Glass wool – HZO – glass wool	Glass wool – HZO – glass wool	Glass wool – HZO – glass wool
Washing	100 mL of H_2O	50 mL of H_2O	50 mL of H_2O
Condicioning	50 mL of 0.2 mol.L^{-1} NaOH	50 mL of 0.4 mol.L^{-1} NaOH	50 mL of 0.4 mol.L^{-1} NaOH
Flow	3 mL.min^{-1}	2 mL.min^{-1}	1.5 mL.min^{-1}

The columns employed were commercial from Biorad. Table 8 shows the effect of the variation of the concentration of NaOH on the retention of Mo and I.

TABLE 8. EFFECT OF NaOH CONCENTRATION ON THE RETENTION OF Mo AND I ON HZO

Eluent	^{99}Mo elution	^{131}I retention	Elution volume
0.2 mol.L^{-1} NaOH	91.5%	14.9%	20 mL
0.4 mol.L^{-1} NaOH	96.8%	0.04%	20 mL

The best concentration was 0.4 mol.L^{-1} of NaOH even if the retention of I was reduced. Table 9 shows the effects of the variation of the mass of Mo.

TABLE 9. EFFECT OF Mo MASS ON HZO

Mass of Mo carrier	^{99}Mo elution	Elution volume
5 mg	98.5 ± 2.4%	20 mL
20 mg	94.1 ± 2.1%	20 mL
30 mg	94.7 ± 0.1%	20 mL

There was a slight increase on the retention of Mo when the carrier mass was increased. Figure 17 shows the behavior of Mo, I and Te on HZO with or without the presence of 2.5 % solution of $KMnO_4$.
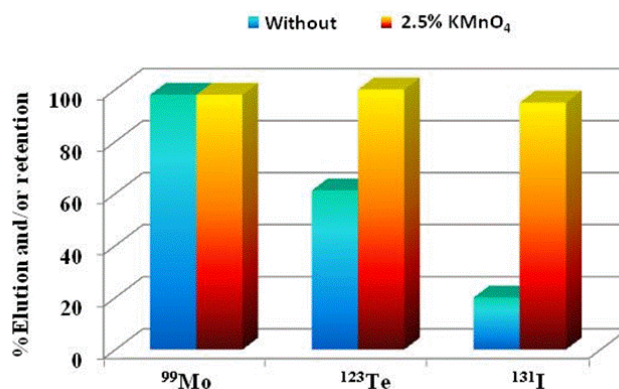
FIG. 17: Behavior of Mo, I and Te on HZO with and without KMnO$_4$.

The presence of KMnO$_4$ was also important to increase the retention of I and Te on HZO. Table 10 shows the characteristics of the homemade AC-Ag columns used in this work.

TABLE 10. CHARACTERISTICS OF AC-Ag COLUMNS

	Column 1	Column 2
Material	AC-Ag	AC-Ag
Size (Φ x h)	15 mm x 19.5 cm	10 mm x 18 cm
Filling	5 cm de CA (grinded)	5 cm de CA/Ag (~ 0.2 – 0.07 mm / 50 – 200 mesh)
Assembling	Glass wool -AC- Ag-glass wool	Glass wool -AC- Ag-glass wool
Washing	After assembling	Before assembling
Condicioning	50 mL of 0.4 mol.L^{-1} NaOH	50 mL of 0.4 mol.L^{-1} NaOH
Flow	2 mL.min^{-1}	4.5 mL.min^{-1}

Figure 18 shows the behavior of Mo, I and Te on homemade AC-Ag columns.
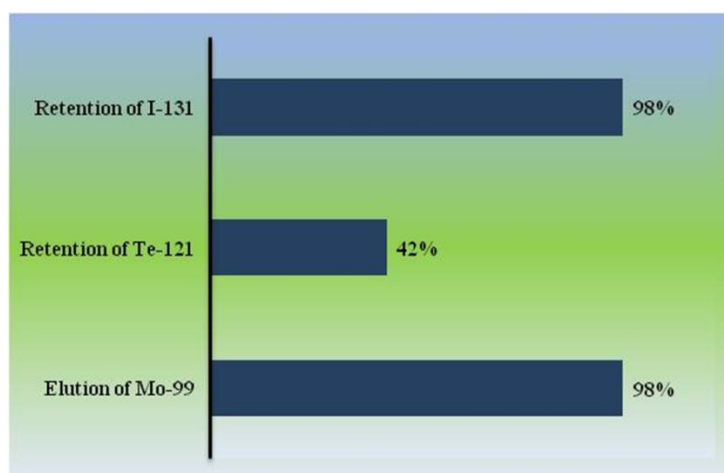

FIG. 18. Behavior of Mo, I and Te on homemade AC-Ag columns.

The homemade AC-Ag columns had good retention of Te and I and low retention of Mo. A commercial solid-phase extraction cartridge (OnGuard® II Ag) previously conditioned with 20 mL of H_2O was used in the same separation for comparison. The elution of ^{99}Mo in the silver cartridge was less than in the AC-Ag column (<93% in the cartridge compared to 98% in the column). The retention of the ^{121}Te was better in the cartridge (about 80%) than in the column (42%) whereas the retention of ^{131}I was the same in the two systems, showing that the silver is efficient to hold back this radionuclide.

Table 11 shows the characteristics of the tandem columns (AC/HZO/AC-Ag) used in this work.

TABLE 11. CHARACTERISTICS OF TANDEM COLUMNS

	Column 1	Column 2	Column 3
Material	AC/HZO/AC-Ag	AC/HZO/AC-Ag	AC/HZO/AC-Ag
Size (Φ x h)	10 mm x 20 cm	10 mm x 20 cm	10 mm x 20 cm
Filling	3 cm AC; 3 cm HZO; 3 cm AC-Ag	3 cm AC; 3 cm HZO; 3 cm AC-Ag	3 cm AC; 3 cm HZO*ZrO_2; 3 cm AC-Ag
Assembling	Glass wool – CA – Glass wool – HZO Glass wool – CA/Ag – Glass wool	Frit – CA - Glass wool – HZO – Glass wool – CA-Ag – Glass wool	Frit – CA - Glass wool – HZO – Glass wool – CA-Ag – Glass wool
Washing	30 mL de H_2O	50 mL de H_2O	-
Condicioning	50 mL of 0.4 mol.L^{-1} NaOH	50 mL of 0.4 mol.L^{-1} NaOH	70 mL of 0.4 mol.L^{-1} NaOH
Flow	0.5 mL.min^{-1}	0.5 mL.min^{-1}	3.5 mL.min^{-1}

*Homemade HZO

Table 12 and 13 show the behavior of Mo, I and Te in the tandem columns prepared with commercial HZO and homemade ZrO_2, respectively.

TABLE 12. BEHAVIOUR OF Mo, I, AND Te, IN THE TANDEM COLUMN PREPARED WITH HZO

Flow	^{99}Mo elution	^{121}Te retention	^{131}I retention
0.5 mL.min^{-1}	55.4%	55.1%	94.3%
Pressure (sirynge)	83.8%	40.4%	64.2%

TABLE 13. BEHAVIOUR OF Mo, I, AND Te, IN THE TANDEM COLUMN PREPARED WITH HOMEMADE ZrO_2

Flow	^{99}Mo elution	^{121}Te retention	^{131}I retention
3,.5 mL.min^{-1}	97.7%	25.5%	95.2%

It can be seen that the tandem column assembled with HZO needed some pressure to increase the elution of Mo, decreasing the retention of I. On the other hand the tandem column assembled with homemade ZrO_2 achieved very good results without using pressure.

Some experiments were performed using the samples generated from the precipitation step containing a mixture of ^{99}Mo and contaminants being further purified using a home-made chromatographic column containing activated charcoal (AC), activated charcoal containing silver (AC-Ag) and HZO. Tables 14 and 15 showed the results of the behavior of a solution containing only carrier and tracer of Mo and a solution containing carrier and tracer amounts of Mo, I, Te, Zr and Ru, respectively.

TABLE 14. OVERALL ^{99}Mo SEPARATOPM AND PURIFICATION YIELDS

Precipitation (%)	Dissolution of Precipitate (%)	Column Purification (%)	Total Process Yield (%)
		^{99}Mo	
99.7	96.0	98.0	93.8

TABLE 15. OVERALL ^{99}Mo AND CONTAINMENTS SEPARATION YIELDS

Precipitation (%)	Dissolution of Precipitate (%)	Column Purification (%)	Total Process Yield (%)
		^{99}Mo	
86.0	~100	93.4	80.3
		^{131}I	
74	~100	91	67.3
		^{123m}Te	
100	41.6	41.9	17.4
		^{95}Zr	
44.6	57.7	89	51.3
		^{103}Ru	
18.6	~100	35.9	6.7

It can be concluded that the process gives high recovery yields of ^{99}Mo when there is no contaminants in solution. There is a decrease with the presence of contaminants and it is also observed that high amounts of I and Zr still remain with ^{99}Mo. A previous separation of I can reduce this contamination.

3.2.4. Recovery of ^{131}I

It is an objective of the ^{99}Mo project to also recover and use the ^{131}I produced in the fission of LEU targets. Three different approaches are being developed: The recovery on the off gas of the U dissolution, the recovery in the solution after the dissolution of U by column adsorption and by an electrochemical method.

The off gas method employs ceramic microspheres of alumina containing metals as Cu and Ag. The best results so far were achieved with Ag microspheres giving 42 % of retention and ~100% of recovery in 0.2 mol.L^{-1} NaOH. Good preliminary results with Cu were obtained.

The recovery in the U solution employs several absorber materials such as ion exchange resins, Ag and Cu microspheres, and activated charcoal and commercial cartridges. Reasonable results were achieved with AC.

The electrochemical approach is a new one and preliminary experiments with carrier I, Mo and Te are encouraging.

4. CONCLUSIONS

The project of production of ^{99}Mo through the fission of low enriched uranium (LEU) targets is a reality at IPEN-Brazil. The participation in this CRP allowed Brazil to start the project, especially the chemical process of separation and purification of ^{99}Mo after the dissolution of metallic LEU targets. The participation in the meetings in Chile and USA was very important, from the learning point of view and also opening doors for future cooperation.

Brazil is planning to continue the project assembling a cold pilot plant that will be upgraded for use of tracers of the most important nuclides. There is also provision of hot cells in the BMR for this methodology in the future.

There are still some areas where the assistance of IAEA is necessary:

- The delivery of some natural U foils to Brazil, from Korea and /or USA
- The delivery of a dissolver to Brazil from USA
- Technical visit to Y-12. Brazil has 2 fellowships to be used up to April 2012
- Waste management assistance, especially from Australia
- Economical and technical assistance to assemble a pilot plant