

## COMPARISON BETWEEN A COMMERCIAL SOLID-PHASE EXTRACTION CARTRIDGE AND A HOME-MADE SILVER CONTAINING CHARCOAL COLUMN: PURIFICATION OF Mo-99 FROM I-131 AND Te-121

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### ABSTRACT

Among the radioisotopes used for medical application in Nuclear Medicine,  $^{99m}\text{Tc}$ , readily available from the elution of  $^{99}\text{Mo}/^{99m}\text{Tc}$  generators, is the most used, responsible for more than eighty percent of the total applications. These generators use the  $^{99}\text{Mo}$  radioisotope that is produced in nuclear reactors and IPEN imports all the  $^{99}\text{Mo}$  used in Brazil, mainly from Canada (Nordion). Due to the increasing needs of the Nuclear Medicine in Brazil and the world shortage of  $^{99}\text{Mo}$  observed since 2008, IPEN decided to construct a new research reactor named Brazilian Multipurpose Reactor (BMR) as well as to develop the production of  $^{99}\text{Mo}$  through the route of  $^{235}\text{U}$  fission using a CINTICHEM modified separation process. The  $^{99}\text{Mo}$  obtained from this process contains some contaminants and need to be purified. The aim of this work is to compare the preliminary results of the purification step of the solution containing  $^{99}\text{Mo}$  and the contaminants,  $^{131}\text{I}$  and  $^{121}\text{Te}$  in the silver containing charcoal column and a solid-phase extraction cartridge. The purification process of  $^{99}\text{Mo}$  coming from fission LEU foils was performed by adsorption chromatography using a home-made activated charcoal containing silver column (AC-Ag) and a commercial solid-phase extraction cartridge (OnGuard® II Ag). High yields of  $^{99}\text{Mo}$  elution and high retention of  $^{131}\text{I}$  were achieved in the AC-Ag column and silver cartridge but  $^{121}\text{Te}$  was more retained in the cartridge than in the AC-Ag column.

### 1. INTRODUCTION

Technetium-99m ( $T_{1/2} = 6$  h;  $\gamma$ -ray energy = 140 keV) is the most widely used radioisotope in Nuclear Medicine. The popularity of  $^{99m}\text{Tc}$  is also due to its low cost, low radiation exposure to patients, high quality imaging and reliable availability in the form of Molybdenum-99/Technetium-99m generators ( $^{99}\text{Mo}/^{99m}\text{Tc}$ ). Currently  $^{99m}\text{Tc}$  is exclusively produced from the decay of its 66 h half-life parent  $^{99}\text{Mo}$  [1].

$^{99}\text{Mo}$  can be produced in research reactors by  $(n,\gamma)$  reaction with  $^{98}\text{Mo}$  or by fission of  $^{235}\text{U}$  ( $n,f$ ) reaction. Activation method is rather simple and inexpensive but gives low specific activity. On the other hand, fission method is complex and expensive but gives high specific activity [2]. Most  $^{99}\text{Mo}$  is produced by fissioning of highly enriched uranium (HEU in  $^{235}\text{U}$ ) in a reactor. The Institute of Energetic and Nuclear Research (IPEN-CNEN/SP) imports all the  $^{99}\text{Mo}$  used in Brazil and the principal supplier is Nordion from Canada. This  $^{99}\text{Mo}$  quantity represents almost 4% of the world overall production

In 2009, a shortage in the delivery of  $^{99}\text{Mo}$  had started due a shutdown in the reactor of Nordion, affecting IPEN's production of  $^{99\text{m}}\text{Tc}$  generators. To overcome the problems associated with the import of  $^{99\text{m}}\text{Tc}$  generators or fission  $^{99}\text{Mo}$ , such as availability of hard currency, increase in the price of  $^{99}\text{Mo}$ , import policies, delay and changes in supply schedule, the indigenous production of  $^{99}\text{Mo}$  in the country is justified [1,3]. Since then, IPEN decided to develop its skills for producing  $^{99}\text{Mo}$  through the route of  $^{235}\text{U}$  fission from low enriched uranium (LEU) targets. This decision is based on: (i) the well established laboratory for producing  $^{99\text{m}}\text{Tc}$  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 some human resources in uranium chemistry; (v) the possibility of operating the IEA-R1 for at least ten years more; and (vi) the recent intention of the CNEN to construct a new research reactor, called Brazilian Multipurpose Reactor (BMR).

To reduce nuclear-proliferation concerns, the International Atomic Energy Agency (IAEA), Vienna, initiated a program of development of techniques to reduce the use of high enriched uranium (HEU) by substituting for low enriched uranium (LEU) fuel and targets. So, in the beginning of 2010 Brazil started participating in the Coordinated Research Project: "Developing Techniques for Small Scale Indigenous  $^{99}\text{Mo}$  Production using LEU Fission or Neutron Activation" implemented by the IAEA. The CRP aims to assist recipients to research, test and evaluate the LEU modified CINTICHEM (USA) process with LEU foil targets, and neutron activation of natural molybdenum oxide targets and utilization of gel generators.

In the CINTICHEM process, the metallic U target is dissolved in nitric acid. After the target is dissolved, the solution is prepared (by the addition of several reagents) for molybdenum precipitation with alpha-benzoinoxime ( $\alpha\text{-BO}$ ). Following precipitation, the precipitate is collected, washed, and redissolved. The redissolved molybdenum solution is then passed through two additional purification steps through ion exchange columns [4]. Various quality controls of the purified  $^{99}\text{Mo}$  solution have to do to verify if the  $^{99}\text{Mo}$  is apt to medical use and to produce  $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$  generators. There are some nuclides that can be contaminants in the  $^{99}\text{Mo}$  solution like zirconium, ruthenium, rhodium, tellurium and iodine. The aim of this work is to compare the preliminary results of the purification step of the solution containing  $^{99}\text{Mo}$  and the contaminants, Iodine-131 ( $^{131}\text{I}$ ) and Tellurium-121 ( $^{121}\text{Te}$ ) in a home-made charcoal containing silver column and a solid-phase extraction cartridge.

## 2. METHODOLOGY

Based on published protocols of the modified CINTICHEM process [3], the purification step of  $^{99}\text{Mo}$  coming from fission LEU foils was performed by adsorption chromatography using a home-made activated charcoal containing silver column (AC-Ag) and, for comparison, a commercial solid-phase extraction cartridge OnGuard® II Ag (Dionex Corporation, EUA).

In this system, both in the column or in the cartridge, the expected behavior for Mo is that it is eluted with the passage of NaOH, while it is expected that other elements, Te and I are retained in both media.

## 2.1 Specifications of the Column and Commercial Cartridge

In the study, the size of AC-Ag column was 10 mm in diameter and 180 mm high and the carbon-coated-silver adsorbent was prepared in accordance with the literature following the procedure [5]:

- (1) Transfer 70 g of 50-200 mesh coconut charcoal into a 500 mL beaker.
- (2) Wash charcoal with water and discard fines. Repeat washing 4-5 times.
- (3) Place beaker on stirring-heater. Add magnet. Start stirring gently.
- (4) Add 30 mL of 10%  $\text{AgNO}_3$  in  $0.1 \text{ mol.L}^{-1}$   $\text{HNO}_3$ , 8 mL of a 5%  $\text{Na}_2\text{SO}_3$  and 80 mL of  $1 \text{ mol.L}^{-1}$  NaOH, successively.
- (5) Heat at  $80 - 90^\circ\text{C}$  for 30 min. Cool.
- (6) Discard supernate. Wash the substrate with water 4 - 5 times. Store the substrate (AC-Ag) under water.

In order to fill the column a small glass wool cork was placed. Then, 5 cm of AC-Ag was spilled and a second glass wool cork was placed. It was conditioned with  $0.4 \text{ mol.L}^{-1}$  NaOH, whereas the commercial solid-phase extraction cartridge (OnGuard® II Ag) was conditioned with 20 mL of  $\text{H}_2\text{O}$ .

## 2.2 Loading Sample Solutions

In the purification experiments, individual and combined behavior of tracers were carried out with  $^{99}\text{Mo}$ ,  $^{131}\text{I}$  and  $^{121}\text{Te}$  on the chromatography column and extraction cartridge. The loading sample solutions compositions were:

- (I) 5 mg of Mo carrier ( $\text{MoO}_3$ ) and 0.5 mL of  $^{99}\text{Mo}$  tracer, pH 14 (total volume: 1.0 mL);
- (II) 0.5 mL of  $^{131}\text{I}$  tracer, pH 14;
- (III) 5 mg of Te carrier and 100  $\mu\text{L}$  of  $^{121}\text{Te}$  tracer, pH 14 (total volume: 600  $\mu\text{L}$ ),
- (IV) 5 mg of Mo carrier, 0.5 mL of  $^{99}\text{Mo}$ , 0.5 mL of  $^{131}\text{I}$ , 5 mg of Te carrier and 100  $\mu\text{L}$  of  $^{121}\text{Te}$  tracer, pH 14 (total volume: 2.1 mL).

## 2.3 Elution and Analyses

The loading sample solutions were passed through the AC-Ag column (at a flow rate of about 4.5 mL/min) and the extraction cartridge (under pressure) and collected. Then, the column

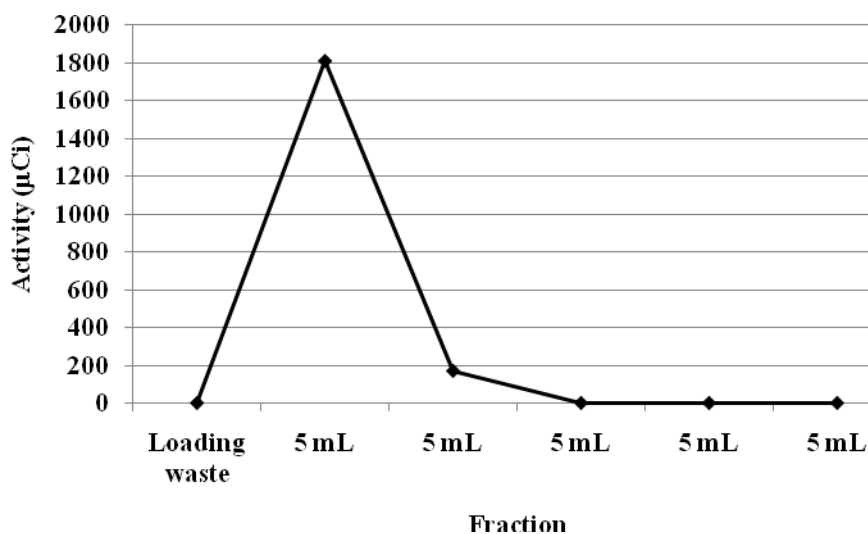
and cartridge were eluted with  $0.4 \text{ mol.L}^{-1}$  NaOH collecting fractions of 5 mL each one in a final volume of 25 mL.

The elution and retention yields of the solutions I and II were measured by a dose calibrator (Capintec<sup>®</sup>) and solutions III and IV by gamma-ray ( $\gamma$ -ray) spectroscopy using a high-purity germanium (HPGe) detector. In this case, the parameters like geometry and time were constant for the same counting.

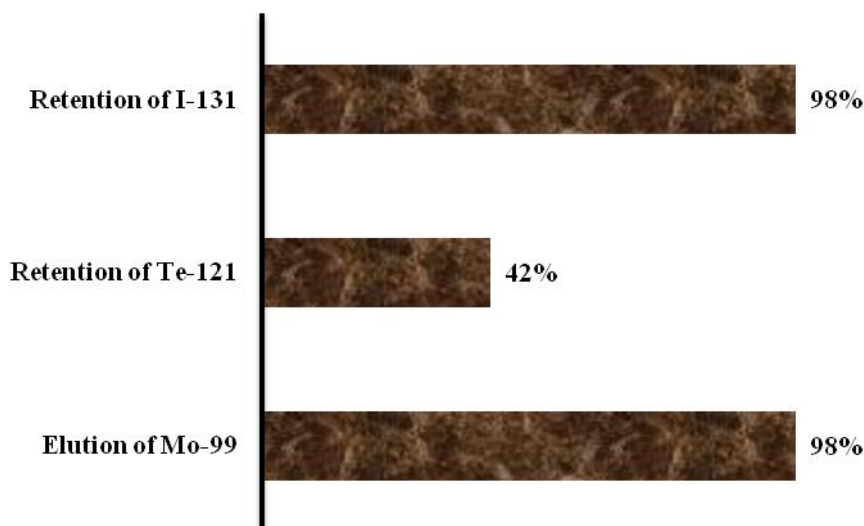
## 4. RESULTS

### 4.1 Activated Charcoal Containing Silver Column (AC-Ag)

Figure 1 shows the elution curve of  $^{99}\text{Mo}$  in a home-made charcoal containing silver column (AC-Ag). The radionuclide was eluted in the first 10 mL of NaOH (fractions 1 and 2). The behavior of the loading solutions I, II and III also were studied in the AC-Ag column, and the results are shown in Fig. 2.



**Figure 1. Elution curve of the loading sample of  $^{99}\text{Mo}$  in a AC-Ag column.**



**Figure 2. The elution and/or retention behavior of the  $^{99}\text{Mo}$ ,  $^{131}\text{I}$  and  $^{121}\text{Te}$  radionuclides in the AC-Ag column.**

How can be seen in the Fig. 2, the silver column was efficient to hold back the radionuclide  $^{131}\text{I}$  in the column (98% of retention), not intervening in the retention of  $^{121}\text{Te}$  (42% of retention) or elution of  $^{99}\text{Mo}$  (98% of elution).

#### 4.2 The Commercial Solid-Phase Extraction Cartridge (OnGuard® II Ag)

The separation of the materials by ion exchange chromatography is based on the ions differential and reversible adsorption from the mobile phase by the exchange group from the matrix. The solid-phase extraction cartridge OnGuard II Ag (Dionex) is a cation-exchange resin in silver form with the Sulfonic ( $\text{R-SO}_3^-$ ) active group (matrix), capacity of 2.0 – 2.2 mEq/cartridge (1 cc) and pH ranging from 0 to 14.

For these characteristics and for the affinity between iodine (in the chemistry form of iodide,  $\text{I}^-$ ) and silver, one can expect a good retention of the radionuclide  $^{131}\text{I}$  in this cartridge and a good percentage of elution of the other elements, such as  $^{99}\text{Mo}$  and  $^{121}\text{Te}$ . Because of this high affinity already known, the loading solution II (only  $^{131}\text{I}$ ) was not passed through the cartridge. The Tab. 1 shows the results obtained for the solutions I, III and IV.

**Table 1. The elution and/or retention behavior of the studied load solutions.**

Load solution	Elution		Retention	
	<sup>99</sup> Mo	<sup>121</sup> Te	<sup>131</sup> I	
I	92.3%	-	-	
III	-	75.6%		
IV	89.7%	80.2%	98%	

How can be seen in the Tab. 1, the elution of <sup>99</sup>Mo in the silver cartridge was less than in the AC-Ag column (<93% in the cartridge compare to 98% in the column). The retention of the <sup>121</sup>Te was better in the cartridge (about 80%) than in the column (42%) whereas the retention of <sup>131</sup>I was the same in the two systems, showing that the silver is efficient to hold back this radionuclide.

## 5. CONCLUSIONS

The behavior of the elements <sup>99</sup>Mo and <sup>131</sup>I was similar in the activated charcoal containing silver column (AC-Ag) as in the solid-phase extraction cartridge (OnGuard II), both efficient to retain <sup>131</sup>I, being only 2% of this radionuclide eluted with 0.4 mol.L<sup>-1</sup> NaOH. The only difference found was the retention of <sup>121</sup>Te that was better in the extraction cartridge than in the AC-Ag column.

## ACKNOWLEDGMENTS

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