2024 International Nuclear Atlantic Conference – INAC 2024
Escola de Guerra Naval, Rio de Janeiro, RJ, May 6 - 10, 2024

ISBN: 978-65-594-1256-3

Determination of the total retention capacity of ^{99}Mo in anionic extracting agent

I. M. Yamazaki[1], D. S. Moreira, M. S. Dias, J. A. Seneda, M. F. Koskinas

yamazaki@ipen.br

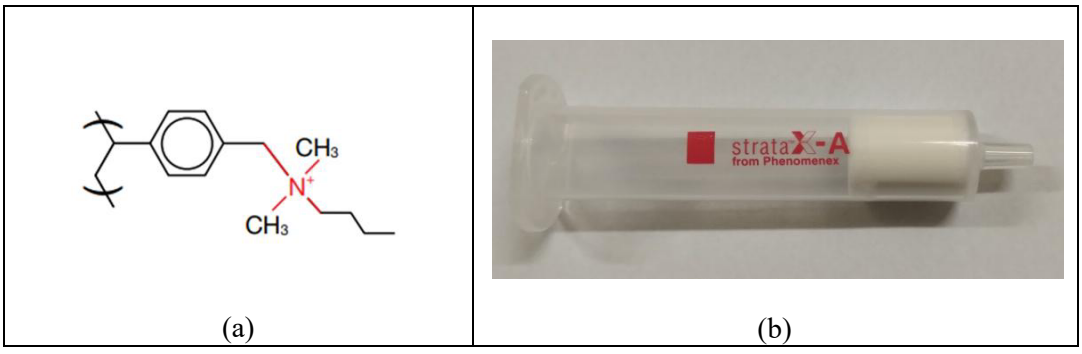
IPEN-CNEN/SP
Avenida Professor Lineu Prestes, 2242
Cidade Universitária, São Paulo - SP
CEP 05508-000

1. Introduction

The Nuclear Metrology Laboratory (LMN) of IPEN-CNEN/SP is developing a research project on the study of analytical techniques for the determining the radioactive impurities emitting alpha and beta particles, in radiopharmaceuticals produced by the Radiopharmaceutical Center (CR) of IPEN. This project started with the determination of impurities present in ^{99}Mo, used as a ^{99m}Tc generator, by means of radiochemical separation using anion exchange resins. This work presents the study of the anionic extracting agent Stracta X-A, produced by Phenomenex [1], widely used in quality analyses, in order to validate its total exchange capacity in the retention of ^{99}Mo (Solid Phase Extraction (SPE) technique). The quantitative stoichiometric calculation of the Stracta X-A extracting agent, used to the analysis of ^{99}Mo associated with the natural Mo carrier, was obtained by determining the breakthrough curve (BT) [2] and the number of chemical equivalents.

2. Methodology

The extracting agent Stracta-X-A, is a stratified compound with composite materials formed by two or more layers of ionic-type resins. It consists of a tube with 6.0 mL capability of which 1.6 mL with 500 mg of polymeric extracting agent - SPE, Stracta X-A. When used in analytical separation and purification studies involving molybdenum chemistry [3], the chemical mechanism of ion exchange is what predominates in the process [4]. The main retention mechanisms of Stracta-X-A, resin are: π-π links, hydrophobic interactions and ion exchange reactions, due to its stratified molecular structure [4]. The extracting agent molecule, Stracta X-A, associated with the quaternary di-methylbutyl amine functional group is shown in Fig 1a and in Fig 1b the SPE column containing the extracting agent is presented.



(a) (b)

Figure 1. a) Molecule of the extracting agent Stracta X-A; b) SPE tube containing the extracting agent.

In the retention of Mo* (where Mo* is ^{99}Mo +Mo_{nat}), as Molybdate ($Mo^*O_4^{2-}$), the main mechanism acting is ion exchange, presented in equation 1 (pH > 6.0) and in equation 2 (2<pH<6.0), the R- symbology is used to simplify the molecule associated with the functional group.

$$2\ R\text{-}OH\ +\ MoO_4^{2-}\ \rightarrow\ R_2MoO_4\ +\ 2OH^- \qquad (1)$$

$$R\text{-}OH\ +\ HMoO_4^-\ \rightarrow\ R\text{-}HMoO_4\ +\ OH^- \qquad (2)$$

In the analytical process for the determination of the stoichiometry of the Mo*, the retention mass of the Mo* ion in the extracting agent was obtained by the following steps:

1. Formation of the MoO_4^{2-} ion in aqueous medium, requiring pH > 8.0 for its retention in the extracting agent [4].

2. Percolation of the ^{99}Mo loading solution associated with Mo_{nat}., in the extracting agent,

3. Elaboration of the BT curve of the Mo*, using radiometric techniques,

4. Determination of the ^{99}Mo retention mass associated with Mo_{nat} by means of mathematical integration calculations of the area in the BT curve.

Initially, the chemical behavior of Mo_{nat} as a function of pH in the extracting agent was studied using the chromatographic cycle of ion exchange consisting of:

1. Washing the column with milliQ water, (conductivity 3.8 μScm^{-1} at 25° C), to eliminate minor particulates and improve the distribution of the compound to the column,

2. Conditioning with NaOH 4.0 g L^-,

3. Sorption and elution of the analyte,

To obtain the breakthrough curve, the same procedures used in the radiochemical separation of ^{99}Mo indicated in the European Pharmacopoeia [5] were followed, and two charge solutions were prepared, load A solution used as standard and load B solution to be percolated. The elution procedure was:

1. Washing the column with milliQ water, (conductivity 3.8 μScm^{-1} at 25° C), to eliminate minor particulates and improve the distribution of the compound to the column,

2. Conditioning with 4.0 g L^{-1} NaOH solution,

3. Percolation of the load solution, concentration 0.00086 Mo $g.mL^{-1}$, collecting the effluent in fractions of 0.5 mL each.

The effluent analysis of ^{99}Mo solution was performed in an HPGe gamma spectrometer, selecting the 739 keV gamma emission of ^{99}Mo. The breakthrough curve was constructed using the peak area of ^{99}Mo, normalized by its A load standard solution versus volume (mL) of effluent.

By means of the breakthrough curve, the amount of Mo^* and the number of equivalents were determined according to the equation 3.

$$Ne = m/(mol/k) \quad (3)$$

Where:
Ne = Number of equivalents.
m = Mass of anionic ion MoO_4^{2-}
k = number of electronic charges (2)

3. Results and Discussion

The studies of the chemical equilibrium conditions, as shown in the Fig 2, which were obtained by the curve of pH versus volume (mL), indicated that 15 mL of H_2O milliQ was enough for washing and 5 mL of NaOH for the conditioning of the extracting agent. In the sorption of 1.0 mL of Mo_{nat} (2.42 $g.L^{-1}$), followed by its elution with 1 mL of NaOH, it was observed the drop of the pH in the region from 40 to 42 mL but it was not found less than 11, maintaining in the alkaline region, in order to prevent Mo polyacids to be formed. It was necessary to maintain the formation of the MoO_4^{2-} ion [4].

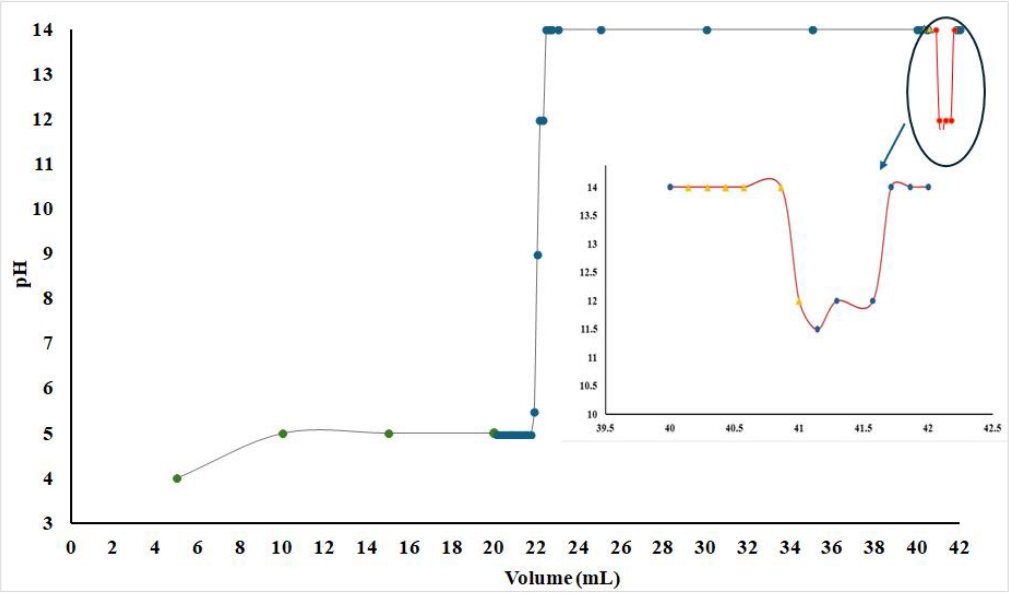


Figure 2. Chromatographic cycle (pH versus mL) obtained with a SPE Cartridge Stracta-X-A 1.6 mL extracting agent: H_2O washing (green, 5-20 mL) - NaOH conditioning (blue, 20-40 mL) - Mo sorption (yellow, 40-41 mL) - NaOH elution (blue, 41-42 mL).

For the determination of the total exchange capacity of the extracting agent, by means of the breakthrough curve, was analyzed the region of interest for stoichiometric calculations obtained by numeric integration. The total exchange capacity of Mo had its limit determined between the break point in 2.75 mL and the beginning of Mo percolation, showed in the Fig. 3. It was obtained a mass of 0.0024g of the Mo* retained. This result determines the chemical equivalents to the Mo* which is equal to the chemical equivalents to the extracting agent (1:1), which was 5 x 10^{-5}, obtained by equation 3.

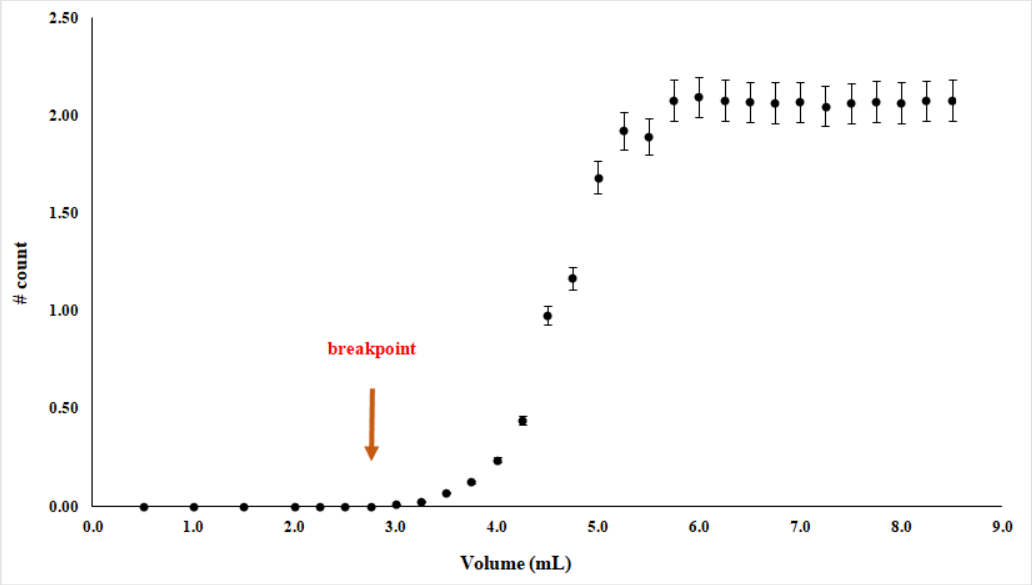


Figure 3 - Breakthrough curve for ^{99}Mo.

4. Conclusions

In this work, the chemical equivalent of the extracting agent was determined using the recovery of chemical equivalence methods and radiometric techniques with ^{99}Mo. The breakeven point was determined at 2.75 mL, showing that only one cartridge SPE resin it is enough to retain all the Mo*. The analytical technique applied in this work can be useful to understand the retention mechanism in other extracting agents.

Acknowledgements

The authors would like to thank the staff of the Radiopharmaceutical Center of IPEN-CNEN/SP for providing the ^{99}Mo solution.

References

[1] Phenomenex Stracta X-A. https://www.phenomenex.com ; access in 02/18/24.

[2] Chowdhury, Z. Z., Hamid, S. B. A., and Zain, S. M. "Evaluating design parameters for breakthrough curve analysis and kinetics of fixed bed columns for Cu(II) cations using lignocellulosic wastes," BioRes. 10(1), 732-749, 2015. https://bioresources.cnr.ncsu.edu/resources/evaluating-design-parameters-for-breakthrough-curve-analysis-and-kinetics-of-fixed-bed-columns-for-cuii-cations-using-lignocellulosic-wastes/, access in 02/18/24.

[3] Scaden, E.M. et al, "The radiochemistry of molibdenium",1960.

[4] Mohammad, R. F. et al, "Targeted elimination of molybdenum ions from a leaching solution with the ability of radiated grafting GMA-PAN nanofibers, Scientific" Reports, (2024)

[5] European directorate for the quality of medicines and healthcare, 2014. "Sodium Molybdate (^{99}Mo) Solution (Fission)", Ph. Eur. 8.0, pp. 1088-1089 (2014).