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

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Abstract: The Nuclear Metrology Laboratory (LMN) at IPEN-CNEN/SP is developing a research project aimed at studying analytical techniques for determining radioactive impurities, emitting alpha and beta particles. This project started with the determination of impurities present in ^{99}Mo, which is used to obtain the radiopharmaceutical ^{99m}Tc by means of radiochemical separation in the ^{99}Mo/^{99m}Tc generator. The study of the anionic extracting agent Strata X-A widely used in quality analysis, was realized by means a breakthrough curve in order to validate its total exchange capacity for Mo. The breaking point was determined at (2.75 +/- 0.14) mL, showing that just one 0.5 g Strata X-A cartridge is sufficient to retain 1.0 mL of a (Na_2MoO_4+ ^{99}Mo) solution in concentration of 2.42 g L^{-1}.

Keywords: ^{99}Mo, anionic extracting agent, breakthrough curve.

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Determinação da capacidade de retenção total de ^{99}Mo em agente extrator aniônico

Resumo: O Laboratório de Metrologia Nuclear (LMN) do IPEN-CNEN/SP está desenvolvendo um projeto de pesquisa voltado ao estudo de técnicas analíticas para determinação de impurezas radioativas, emissoras de partículas alfa e beta. Este projeto teve início com a determinação de impurezas presentes no ^{99}Mo, utilizado para obtenção do radiofármaco ^{99m}Tc, por meio de separação radioquímica em gerador de ^{99}Mo/^{99m}Tc. Este trabalho apresenta o estudo do agente extrator aniônico Strata X-A, amplamente utilizado em análises qualitativas, a fim de validar sua capacidade de troca total para ^{99}Mo, utilizando curva de breakthrough. O ponto de ruptura foi determinado em (2,75 +/- 0,14) mL, mostrando que apenas um cartucho Strata X-A de 0,5 g é suficiente para reter uma solução de 1,0 mL de (Na_2MoO_4+ ^{99}Mo) em uma concentração de 2,42 g L^{-1}.

Palavras-chave: ^{99}Mo, agente extrator aniônico, curva de breakthrough.

1. INTRODUCTION

The Nuclear Metrology Laboratory (LMN) at IPEN-CNEN/SP is developing a research project on the study of analytical techniques for the determining the radioactive impurities emitting alpha, beta and gamma radiations, in radiopharmaceuticals produced by the Radiopharmaceutical Center (CR) of IPEN.

This project started with the determination of impurities present in ^{99}Mo, which is used to obtain the radiopharmaceutical ^{99m}Tc by means of radiochemical separation at ^{99}Mo/^{99m}Tc generators. This work investigated the applicability of the widely used anion-exchange resin Strata X-A [1] for the determination of its total exchange capacity for ^{99}Mo with carrier Mo natural, by means of the breakthrough curve integration [2]. The choice of this resin was based on the study made by Said [3] of several anion exchange resins.

In this work, the pH was also investigated to certificate that after the retention of ^{99}Mo into the anion exchange resin, the eluent maintained the alkalinity.

The methodology described in the European Pharmacopeia [4] for determination of impurities in ^{99}Mo was used in this study.

2. MATERIALS AND METHODS

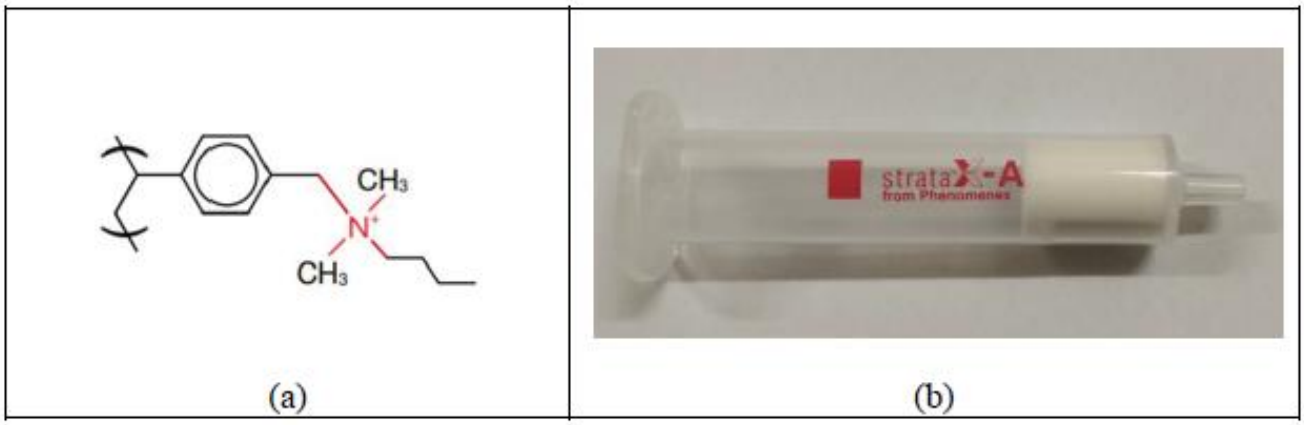
In this study, all reagents used were of analytical grade and the experiments were performed in the sequence described below, at room temperature and pressure.

2.1. Strata X-A anion exchange cartridge

The anion exchange cartridge Strata X-A is a stratified composite material produced by Phenomenex [1]. Strata X-A cartridge consists of a tube with 6.0 mL capability in two or

more layers in which 1.6 mL with 500 mg of strong anion exchange functionalized polymeric sorbent, which can be used for separation and purification of molybdenum [5]. The predominant mechanism for retaining Mo* (where Mo* represents the combined isotopes ^{99}Mo and Mo natural carrier) is ion exchange [6, 7]. The structural formula contains a quaternary di-methylbutyl amine functional group that is showed in Fig. 1a. Fig. 1b shows a photo of cartridge containing the extracting agent.

Figure 1: a) Structural formula of the extracting agent Stracta X-A; b) Cartridge containing the extracting agent.



Source: (a) Phenomenex Strata X-A [1] ; (b) Photo by Author.

In the retention of Mo*, as Molybdate ($Mo^*O_4^{2-}$), the main mechanism acting is ion exchange, according to equation 1 (pH ≥ 6.0) and equation 2 (2<pH<6.0).

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

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

The R- symbol is used to represent the polymeric chain of the resin.

2.2. Chromatographic cycle curve, pH versus volume

The experimental method to obtain the chromatographic cycle curve pH versus volume was carried out employing one cartridge of the Stractra X-A resin. Initially, before passing the Mo solution, the column was cleaned using milli-Q water (conductivity 3.8 $\mu S.cm^{-1}$ at) 25 °C, to remove any impurities or minor particulates and to improve the

distribution of the compound into the column that could interfere with the analysis. This step ensures a clean baseline and improves the distribution of the Mo* compound within the column.

Following the cleaning step, the column was conditioned with a solution of NaOH, 4.0 g L-1. This conditioning step likely serves two purposes: 1) to adjust the Stracta X-A pH to a specific value suitable for Mo capture, and 2) to obtain activate sites (containing the functional groups) on the extracting agent for optimal interaction with Mo.

The core of the experiment involves sorption and elution. The Mo containing sample was loaded into the column, allowing Mo* to interact with the Stracta X-A resin. This interaction involving ion exchange leads to the sorption of Mo by the extracting agent.

A crucial aspect of this study is monitoring the pH of the eluent. After the conditioning step, the passage of 1.0 mL of MoO42– solution through the cartridge was done. By the end, 5 mL of NaOH 4.0 g L-1 were added. In all steps, the eluent was collected in fractions of 0.1 mL each and the flow rate was kept less than 1.0 mL.min-1. The pH was measured with pH indicator strips.

A three steps curve was obtained to establish the pH range for the retention of the molybdate ion: 20 mL of H2O milliQ washing, increase of the pH to the NaOH solution value, passage of 1.0 mL of Mo nat and increase of the pH with 5 mL of NaOH.

2.3. Breakthrough curve

The breakthrough (BT) curve investigates the radiochemical separation of ^{99}Mo using a chromatographic technique constructed following procedures outlined in the European Pharmacopoeia (EP) [4] to assess the column's efficiency in retaining Mo. Two charge solutions were prepared, load A solution used as standard and load B solution to be percolated. The effluent analysis of ^{99}Mo solution was performed in an HPGe gamma spectrometer, selecting the 739 keV gamma emission of ^{99}Mo. The BT curve was

constructed using the peak area of ^{99}Mo, normalized by its A load standard solution, versus volume (mL) of effluent.

The procedure was: 1) Washing the column with milliQ water (conductivity of 3.8 μS cm^{-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 B load solution, with Mo concentration of 0.00096 g.mL^{-1}, collecting the effluent in fractions of 0.5 mL each. The flow rate was kept less than 1.0 mL.min^{-1} for all steps.

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:

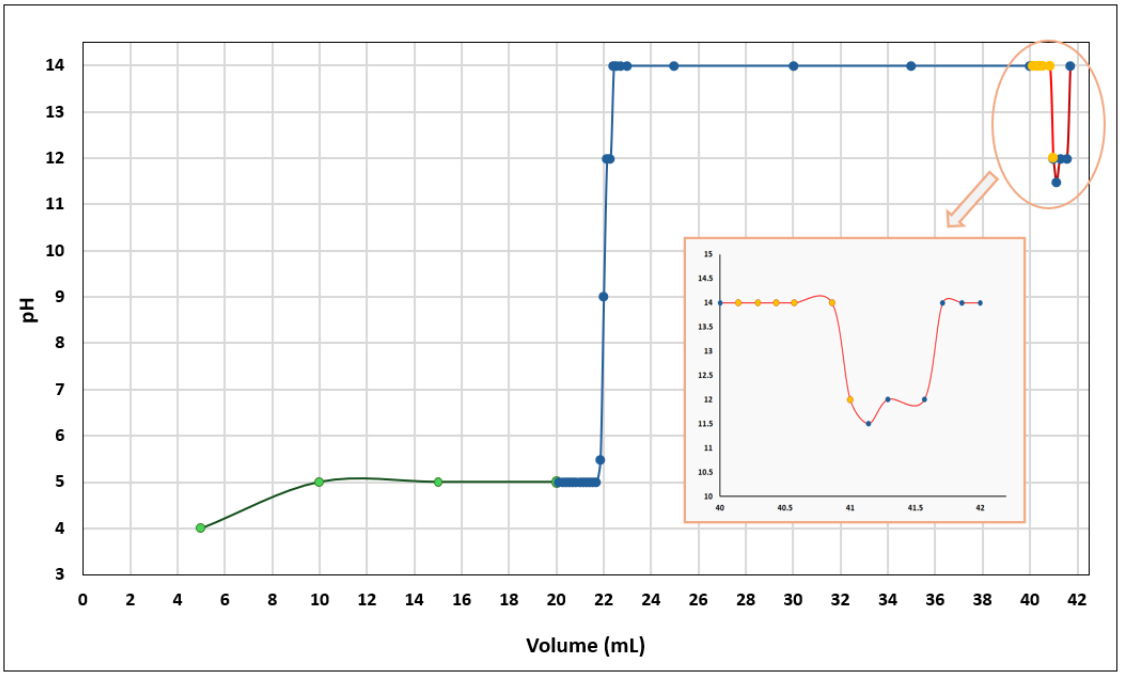
1. Formation of the MoO_4^{2-} ion in aqueous medium, requiring pH > 8.0 for its retention in the extracting agent [4].
2. Percolation of the ^{99}Mo loading solution associated with Mo_{nat}, in the extracting agent.
3. Elaboration of the BT curve of the Mo*, using radiometric techniques. The breakpoint was defined when effluent measurements showed the presence of the ^{99}Mo.
4. Finally, the mass of Mo* retained was determined by mathematically integrating the area under linear (concentration of load B until Breakpoint) and the BT curve.

3. RESULTS AND DISCUSSIONS

The studies of the chemical equilibrium conditions, as shown in Fig. 2, which were obtained by the curve of pH versus volume (mL), indicated that 11 mL of H_2O milliQ was enough for washing and 5 mL of NaOH 4.0 g.L^{-1} for the conditioning of the extracting agent. In the sorption of 1.0 mL of Mo_{nat} (0.96 g L^{-1}) followed by its elution with 1.0 mL of NaOH, it was observed the drop of the pH in the region from 40 to 42 mL but it was not found pH

less than 11, maintaining the extraction media in the alkaline region, in order to prevent polymolybdate ions to be formed.

Figure 2: pH variation of eluent of a Strata-X-A cartridge: 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).

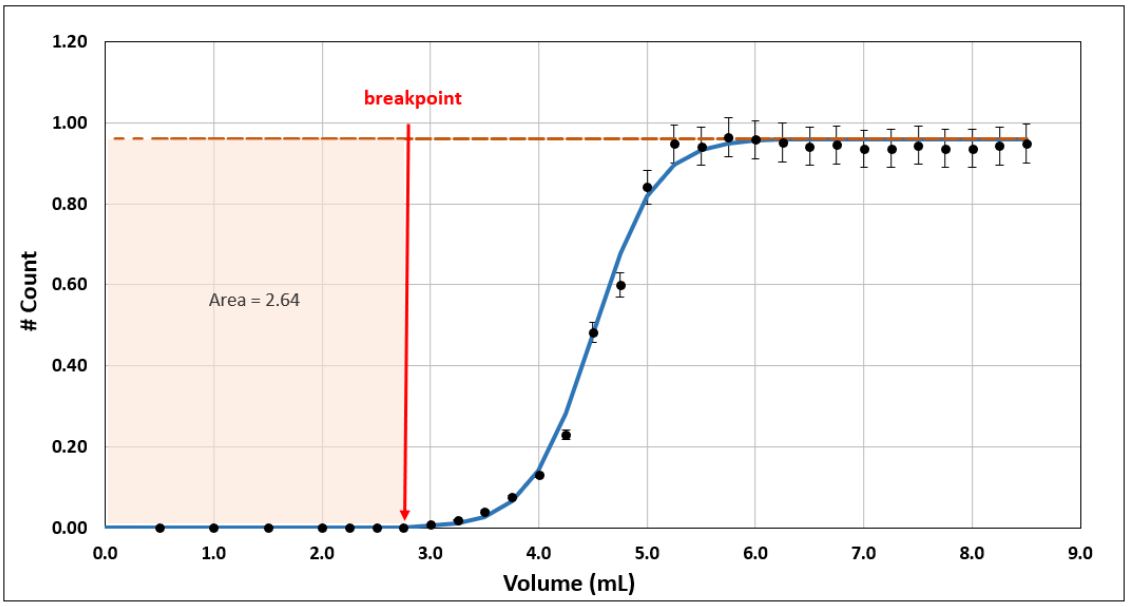


Source: Author.

The quantitative stoichiometric calculation of the Strata X-A extracting agent, used to the analysis of ^{99}Mo with the natural Mo carrier, was obtained by determining the breakthrough curve (BT).

The BT curve was obtained adjusting the experimental data to a sigmoide curve given by $f(x) = \frac{L}{1+e^{-k(x-x_0)}}$ function´s midpoint. Using the Excel software with Solver algorithm-analysis tools, these parameters were determined and the following values were obtained: L=0.962; k = 3.67; x_o = 4.54. The breakthrough curve for ^{99}Mo is shown in Fig. 3.

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



Source: Author.

For the determination of the total exchange capacity of the extracting agent, (breakpoint was adopted as the limit for stoichiometric calculations), by means of the breakthrough curve, the region of interest for stoichiometric calculations obtained by numeric integration was analyzed. The total exchange of Mo had its limit determined between the breakpoint in (2.75 ± 0.14) mL and the beginning of Mo percolation, showed in the Fig. 3, normalized by its A load standard solution versus volume (mL) of effluent. It was obtained a mass of (2.64 ± 0.10) mg of Mo* retained.

4. CONCLUSIONS

In this work, the total retention capacity for Mo in anionic extracting agent StrataX-A was studied. By means of the breakthrough curve, the breakpoint was determined as (2.75 ± 0.14) mL, showing that only one 0.5 g Strata X-A cartridge is sufficient to retain the

Mo present in 1.0 mL of Na_2MoO_4 solution which contains the ^{99}Mo with an activity of 370 MBq.

Although this study was carried out with an activity of 370 MBq, other activity can be used, as long as the concentration of Mo atoms in the sample does not exceed 2.42 g L^{-1}

ACKNOWLEDGMENT

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CONFLICT OF INTEREST

All authors declare that they have no conflicts of interest.

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