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DETERMINATION OF THE IMPURITIES Al, Mn, Fe, Ni, Cu and Zn IN NUCLEAR GRADE URANIUM BY ICPOES

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ABSTRACT

Uranium compounds are specially produced for use in nuclear reactors and must meet strict physical and chemicals specifications. The current study discusses the separation of Al, Mn, Fe, Ni, Cu and Zn from uranium compounds and their quantitative determination using inductively coupled plasma optical emission spectrometry. To avoid interference effect caused by uranium in the spectroscopic emission lines of elements of interest, the chromatographic behavior of TBP impregnated macroporous Amberlite XAD-4 column was investigated. The break through curves of uranium obtained showed maximum retention of up to 11 grams of uranium and the elution curves for the elements showed reproducible recovery rate of 90% on 50 mL elution. Synthetic samples of nuclear grade uranium prepared with the addition of 250 µg/g of U of the above individual elements were used to verify the performance of the method. The method showed a recovery rate of 80 to 90% for the elements under study.

1. INTRODUCTION

Uranium compounds produced specifically for use in nuclear reactors should conform to strict chemical and physical specifications. The maximum level of impurities, a requirement for safety and performance of a nuclear fuel should be assured by means of accurate analytical techniques. The centers of production, research and development, commonly employ the inductively coupled plasma optical emission spectrometry (ICP OES) and mass spectrometry (ICP MS) techniques for multi-elemental determination [1-4]. Spectroscopic interferences of the uranium emission lines, superimpose over those impurities preventing the direct application of the spectroscopic techniques in their quantification. One way to overcome this difficulty is to perform chemical separations to isolate the impurities from uranium and subsequently carry out the measurements. Publications detailing uranium separation by liquid-liquid extraction using TBP solvent are well known [5-8]. Some investigations are carried out with the use of combined techniques of solvent extraction and adsorption on solid phase. Some works are performed using combined techniques of solvent extraction and adsorption on solid phase [9,10].

The current study was developed at IPEN to establish a method for separation and quantification of impurities in uranium matrix. In the present study, reversed-phase partition chromatography separation of uranium from impurity elements was carried out using XAD-4/TBP. The impurities in the fuel element (FE) arise from the manufacturing process and must be quantified and tracked so that the fuel can be used in nuclear reactor. ASTM [11] and IPEN establish a rigid requisite about the impurities concentration of uranium compounds to be accepted as nuclear fuel. This specification is applied to about 28 inorganic elements. Elevated concentrations of impurities can harm the efficiency of the nuclear fuel.

Ensuring and assuring the quality of environmental chemistry and manufacturing processes of the FE as well as nuclear facilities, this work conforms to the guidelines of the Brazilian Nuclear Program (PNB), which include: a) to meet the legal rand program requirements of the safeguard of nuclear requirements and program requirements of the safeguard of nuclear materials of the Brazilian-Argentine Agency for Accounting and Control of Nuclear Materials (ABACC); b) to satisfy the demand that involves the production line of fuel element UAl_2 precursor of radiopharmaceuticals products; c) to meet the demand for new technical and scientific developments in technologies for the chemical characterization and production of ^{99}Mo; d) to expand the production capacity of radiopharmaceuticals.

2. MATERIALS AND METHODS

The preparation of chromatographic columns and the analytical technique used are described below.

2.1 Preparation of the Extraction Chromatographic Column and Analytical Technique Used

The column was prepared stirring 300g of Amberlite XAD-4 resin (20-60 mesh) on 460 mL of TBP dissolved in acetone, followed by heating during 24h in a furnace (60^oC) until complete evaporation of acetone. The amount of TBP impregnated was 150% (v/m).

The slurry packing technique was adopted for packing the impregnated resin inside a glass column (22cm X 1.8 cm i.d). Immediately prior to the use, the column was conditioned with 150 mL of 5.5M HNO_3 at a flow of 2 mL min^{-1}.

Analyses were carried out using an ICP OES Spectro Flame M120 Spectro Analytical Instruments, with a Meinhard concentric nebulizer, using four-point calibration with a set of standard solutions analytical grade (Merck).

The following lines (nm) were used: Al 396.152, Cu 324.754, Fe 259.837, Mn 294.920, Ni 241.476, Zn 334.502, and U 409.01.

2.2 Tests Performed with the Chromatographic Columns

The following tests were carried out with this system:

a) Evaluation of the retention capacity of uranium: about 220 mL of 50.004 g L^{-1} of uranium solution prepared from a standard nuclear grade U_3O_8 chemical was percolated at a flow rate of 1 drop per second and 22 fractions consisting of 10 mL were collected and measured by ICP OES for quantification of uranium.

b) Determination of the volume and recovery factor for the impurities: 10 mL of a solution containing 500 µg of Al, Cu, Fe, Mn, Ni, Zn were prepared in triplicate from 1000 mg L^{-1} stock standard solutions from Merck . In order to obtain the same chemical condition for the elements, the solution was evaporated to dryness on a hot plate at 80 °C and the final residue was taken up with 10 mL of 5.5 M HNO_3. The solution was percolated through the column at a rate of one drop per second. The effluent solution was collected in fractions of 10 mL and analyzed by ICP OES.

c) Determination of the recovery factor in the presence of uranium matrix by preparing a synthetic uranium samples in triplicate: a sample of 40.0 mL was taken from a standard uranium solution (50.004 g L^{-1}) and to this aliquot, 0.50 mL of the standard solutions 1000 mg L^{-1} of the elements Al, Cu, Fe, Mn, Ni, Zn (spectra pure grade, Merck Chemical) were added. This solution was evaporated to dryness in a hot plate fixed to $80^{o}C$ and then the residue was taken up with 10 mL of 5.5 M HNO_3. This solution was percolated through the chromatography column at a rate of one drop per second. The effluent solution was collected in centrifuge tubes in 15 fractions. Each fraction consisting of 10 mL was measured by ICP OES for quantification of the elements of interest.

3. RESULTS AND DISCUSSION

The uranium breakthrough curve determination was performed by the percolation of uranium solution. As the uranium solution percolates down the column, the complexes of uranium as $UO_2(NO_3)_2$ 2TBP [6] are formed and trapped in the active sites of the resin. Uranium in excess failed to establish a chemical balance and also could not find available active sites and thus continuously eliminated in the effluent solution. This behavior was observed from the fraction corresponding to 160 mL of uranium as is evident from Figure 1. On the other hand the other elements that form part of the solution does not form stable complexes with TBP and are eliminated in the effluent solution as can be seen in Figure 1. Thus, after percolation of the whole solution, the complex of uranium is fully retained in the column and the elements of interest are collected together in a small volume of effluent solution.

In the fraction corresponding to 220 mL the concentration of uranium is practically invariant to the fraction corresponding to 250 mL as shown in Figure 1. From 220 mL of uranium solution percolated through the column, the break through curve shows that the column is saturated. This corresponds to retention of 11 g of uranium in the column. Thus, it is demonstrated that the column is effective for the retention of uranium in quantities 4-5 times above the required amount, 2 g of uranium, to prepare samples for measurement of elements of interest.

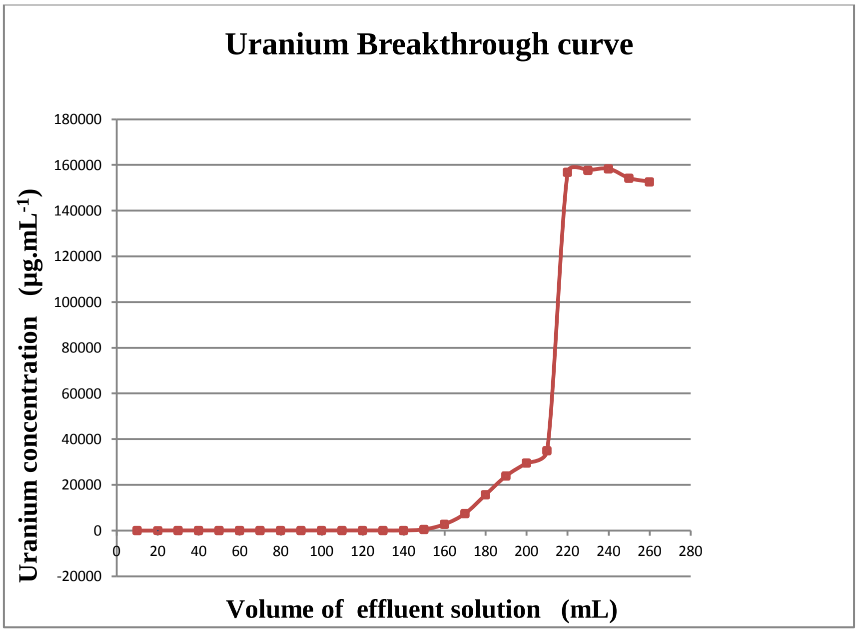

Figure 1. Uranium Breakthrough curve

Figures 2 and 3 represent graphically the impurities elution curves for each study discussed and described in the item 2.2 b and c. The curves are composed by overlapping measures for the tests performed in triplicate for each study discussed in b) and c). The graph shows the elution behavior for Ni, Cu and Zn. The other elements follow the same behavior, and are not presented here to avoid overlapping of lines. The numbers placed next to the symbols of the elements in the legend indicate the numbers corresponding to the replicates.

The examination of these curves show:

1. the maximum recovery of the of elements was between 20 and 50 mL
2. the quantitative elution of the elements occurred in up to 50 mL
3. there was shift in the position of volume
4. the first 10 mL has no amounts of the elements under study.
5. the elution of the elements elements for both studies presented the same behavior of elution.

Despite of the shifting and expansion of the curves, the recovery factor ranged from 70 to 90% in both cases.

The presence of uranium of in the solution has not affected the ability and the quality of the separation of the impurities by the chromatographic column, since uranium was retained in the upper part of the column as a yellow band, corresponding to about one third of the total length of the column.

This study shows that there is a great robustness and reproducibility of the method of separation employed.

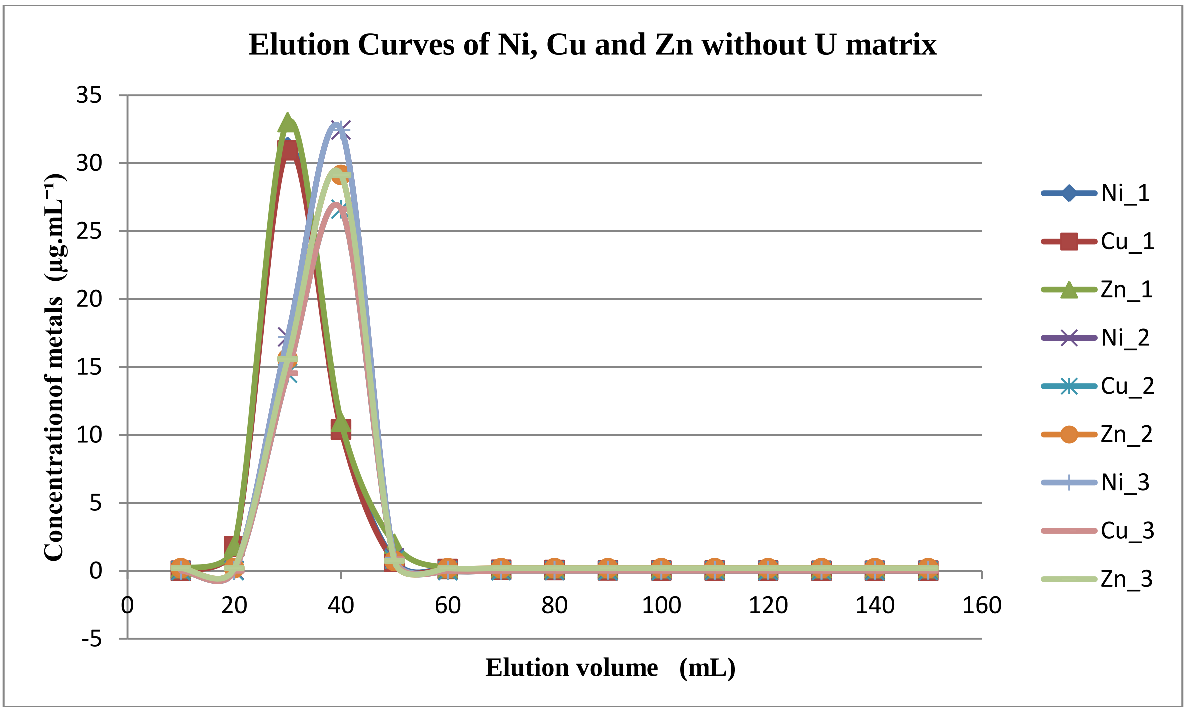

Figure 2. Elution curve of Ni, Cu, Zn in the system XAD-4/TBP without uranium matrix

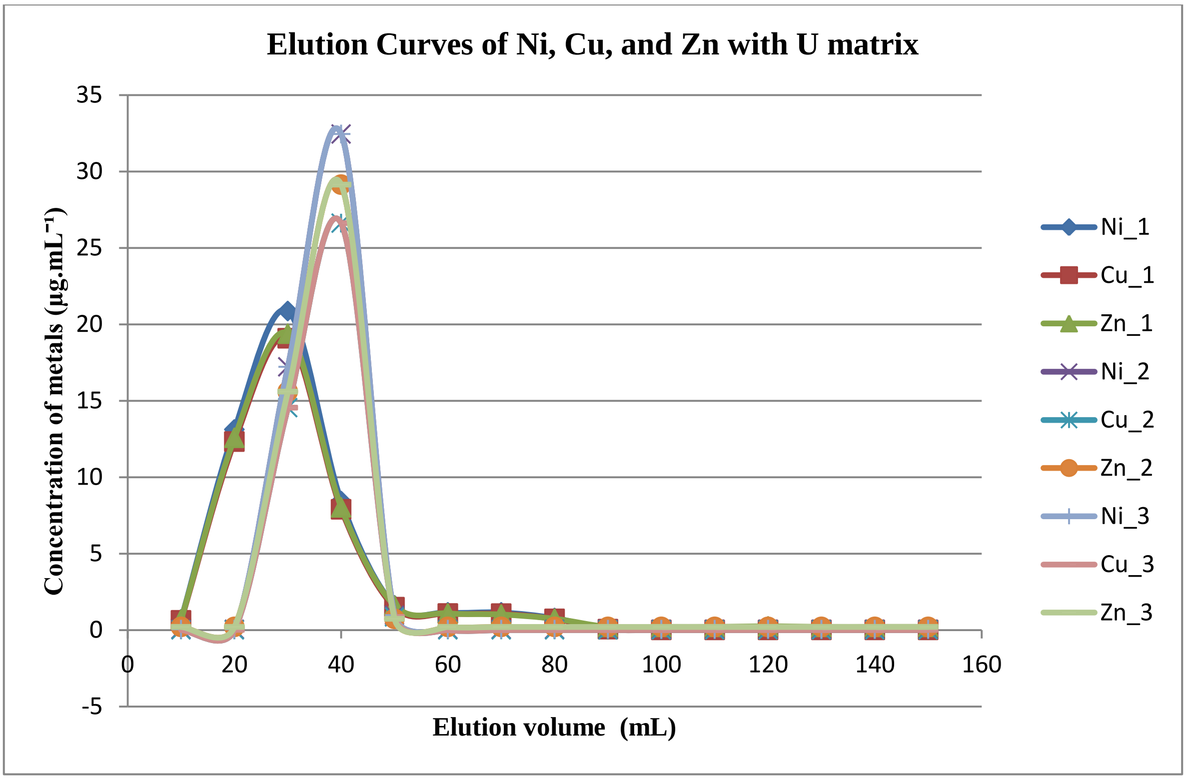

Figure 3. Elution curve of Ni, Cu, Zn in the system TBP/ XAD-4 with uranium matrix

4. CONCLUSIONS

A preliminary analysis showed that the methodology developed for the analysis of impurities in uranium matrix is feasible and the technique of extraction chromatography with the system TBP/XAD-4 for uranium separation and preconcentration of elements of interest is extremely fast and efficient and can be applied in the routine analysis. The amount of TBP impregnated in Amberlite XAD, was shown to be a key parameter for obtaining high yield retention of large amounts of uranium in a small volume of resin. This high yield of the chromatographic column reflected in the quantitative separation of uranium from the interest elements, allowing ICP-OES measurements, with good signal strength and interference-free spectrum of uranium. The development of a column of small size allowed ergonomic adjustments. This also enabled the reduction of waste generation during the analysis, resulting in an environmental gain. Future studies should continue in order to apply the method for the determination of other elements of interest to the fuel element.

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