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AVAILABILITY OF U-238 AND Th-232 PRESENT IN PHOSPHOGYPSUM USED IN AGRICULTURE: PRECISION AND ACCURACY OF THE METHODOLOGY

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ABSTRACT

Phosphogypsum (PG) can be classified as Technologically Enhanced Naturally Occurring Radioactive Material (TENORM), and it is obtained as a residue of the phosphate fertilizer industry. PG presents in its composition radionuclides of the natural U and Th series: mainly Ra-226, Ra-228, Th-232, Pb-210 and Po-210. The Brazilian producers stock the PG in dry stacks, posing risks to the surrounding environment. A possible solution to this problem is to reuse PG in agriculture; however, it is necessary to ensure that the radionuclides present in the PG will not be available to the agricultural products. This study is part of a research project sponsored by Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP - 2010-10587-0) entitled “Availability of metals and radionuclides in tropical soils ammended with phosphogypsum”, and its objective is to evaluate the reliability of an optimal methodology to determine U-238 and Th-232 in samples of soils amended with PG through percolation with water. The methodology comprises a sequential radiochemical separation of the radionuclides present in the leachate. The UTEVA resin was used for the purification and separation of U-238 and Th-232, and the final activity concentrations were determined by alpha spectrometry. The precision and accuracy of the methodology were checked by measuring standard reference material. The results obtained for the relative error and relative standard deviation varied respectively from 2.34 % to 5.92 % and 6.10 % to 6.21 % for uranium, and from 0.42 % to 3.13 % and 9.68 % to 10.97 % for thorium.

1. INTRODUCTION

Phosphogypsum (PG), a residue of the phosphate industry, is classified as Technologically Enhanced Naturally Occurring Radioactive Material (TENORM) or as a NORM waste. It is obtained in the phosphate fertilizer industry, during the attack of the phosphate rock with sulphuric acid for the production of phosphoric acid [1]. The ratio of PG to phosphoric acid is 5:1 - to each ton of phosphoric acid, five tons of PG are produced [2].

PG presents in its composition radionuclides of the natural U and Th decay series: mainly Ra-226, Ra-228, Th-232, Pb-210 and Po-210, while other radionuclides, such as U, originally present in the phosphate rock, migrate to the phosphoric acid [1,3,4]. It is estimated that the Brazilian production of PG had reached the amount of approximately 5.5 million tons [5]. The Brazilian producers stock the PG in dry stacks, posing risks to the surrounding environment: leaching and contamination of water systems, workers direct exposure to gamma radiation, inhalation of gas Rn-222 and public direct exposure by inhalation of atmospheric dust formed from erosion of stacks [6]. In Brazil TENORM industries are subjected to the recommendations given by Comissão Nacional de Energia Nuclear (CNEN), which include compliance with the radiological protection regulations [7,8].

One possible solution to this environmental problem is to reuse PG in agriculture as a soil conditioner. The Brazilian regulatory body (CNEN) established exemption limits for the use of PG in agriculture or cement industry: the Ra-226 and Ra-228 activity concentration should be below 1 Bq g^{-1} [9]. However, for its safe application, it is necessary to ensure that the radionuclides present in the PG will not be available to the agricultural products. This paper aims to determine the availability of U-238 and Th-232 in samples of soils amended with PG through percolation with water. This study is part of a research project sponsored by Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP - 2010-10587-0) entitled "Availability of metals and radionuclides in tropical soils ammended with phosphogypsum". The methodology comprises a sequential radiochemical separation of the radionuclides present in the leachate with specific resins, based in the IAEA's draft document [10]. Initially, the resins TEVA and UTEVA were used for the purification and separation of Th-232 and U-238, respectively, but the results obtained for the accuracy were not satisfactory for Th. Better results were achieved by using only the resin UTEVA for the purification and separation of both radionuclides. In any case, the final activity concentrations were determined by alpha spectrometry. The precision and accuracy of the methodology were checked by measuring standard reference materials.

2. MATERIALS AND METHODS

The precision and accuracy of the methodology using the resins TEVA and UTEVA were determined by using standard solution from Instituto de Radioproteção e Dosimetria (IRD), with activity concentration of 3.24±0.48 Bq kg^{-1} for U-238 and 0.80±0.12 Bq kg^{-1} for Th-232. The analysis was performed in triplicate. The initial solution was spiked with 449.4 mBq of U-232 and 311.8 mBq of Th-229, as tracers for the determination of the chemical yield of the radiochemical process and a known amount of the standard solution.

The samples were evaporated to dryness, re-dissolved with 20 mL of 3 M HNO_3, and percolated on TEVA resin from Eichrom, preconditioned with 20 mL of 3M HNO_3. Then the resin was washed with 10 mL of 3M HNO_3, followed by 5 mL of 2.5 M HNO_3. Under these conditions, the thorium is retained in the column while uranium and other interfering radionuclides such as radium are eluted. The thorium was eluted from TEVA resin by the addition of 20 mL of 9M HCl and 5 mL of 6M HCl.

The TEVA resin has as active component an aliphatic quaternary amine, as shown in Fig. 1. The TEVA resin capacity factor for uranium and thorium is presented in Fig. 2.

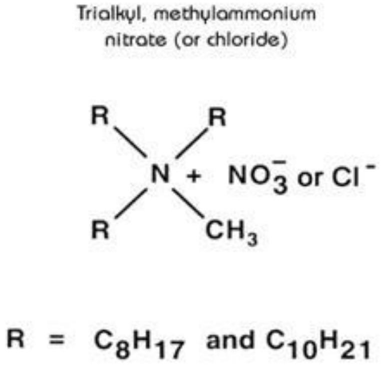

Figure 1: TEVA resin's active component [11].

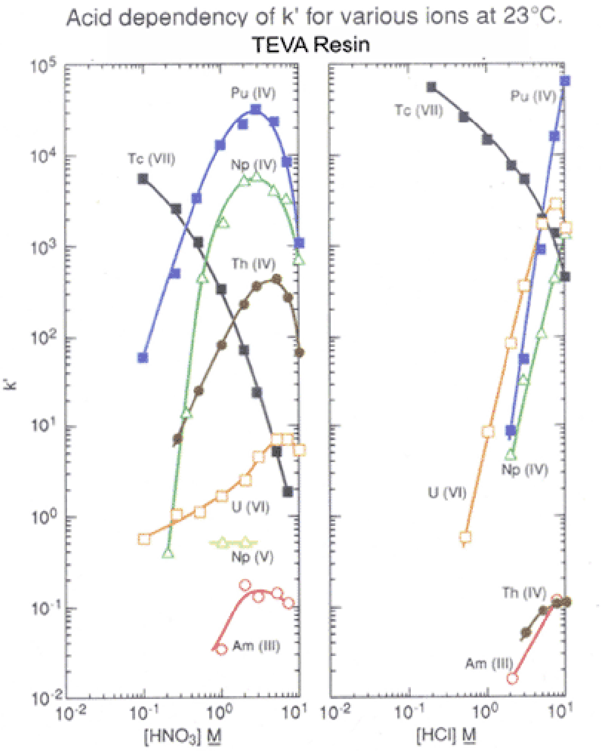

Figure 2: TEVA resin's capacity factor in HNO_3 and HCl [11].

The eluted solution containing uranium was percolated on UTEVA resin from Eichrom, preconditioned with 20 mL of 3 M HNO_3. Then the column was washed with 10 mL of 3M HNO_3, followed by 5 mL of 9 M HCl. Under these conditions, the uranium is retained in the column and separated from other interfering radionuclides such as radium. The uranium was eluted from UTEVA resin by addition of 30 mL of 0.01 M HCl.

The UTEVA resin has as an active component diamyl amylphosphonate, as shown in Fig. 3. This structure forms nitrate complexes in the presence of actinides. The UTEVA resin capacity factor for uranium and other radionuclides is presented in Fig. 4.

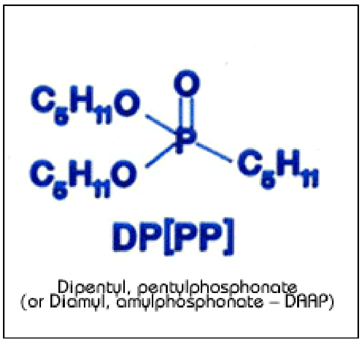

Figure 3: UTEVA resin's active component [11].

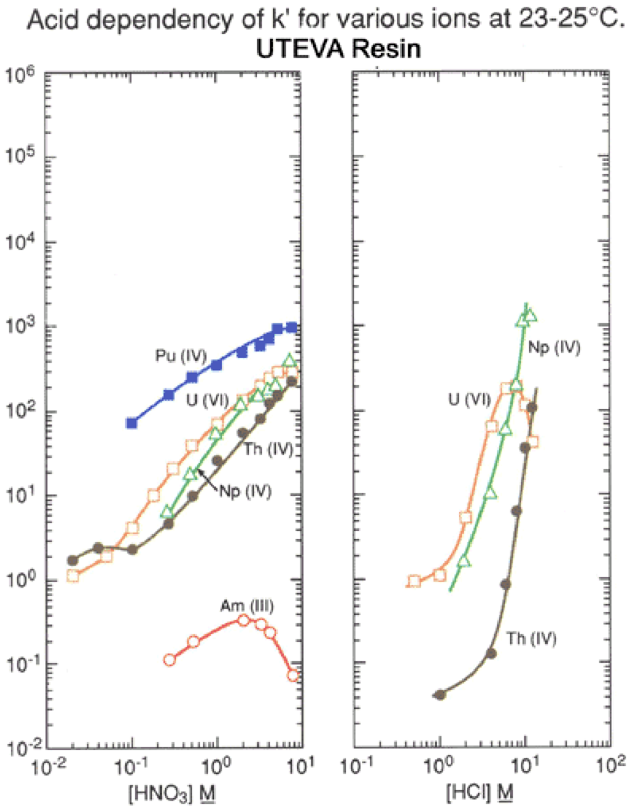

Figure 4: UTEVA resin's capacity factor in HNO_3 and HCl [11].

The final solutions containing thorium and uranium, respectively, were evaporated to dryness and re-dissolved with 10 mL of a 10% $(NH_4)SO_4$ solution at pH 2. Then the solutions were electroplated on a stainless steel disc by applying an electric current of 1.0 A during one hour. [12]. One minute before the end of electrodeposition, it was added 1 mL of concentrated NH_4OH [13].

The alpha counting was performed by using a surface barrier detector Alpha Analyst from Canberra. The stainless steel discs were counted for 80.000 seconds.

Since the results obtained for the accuracy of thorium by using this methodology were unsatisfactory, some changes were undertaken in order to improve the method. Casacuberta, et al. [13] obtained good results for the separation and purification of uranium and thorium by using only the UTEVA resin. Therefore a new methodology was implemented, in which the initial solution containing uranium and thorium was percolated on the UTEVA resin previously conditioned with 20 mL of 3 M HNO_3, washed twice with 5 mL aliquots of 3 M HNO_3, and finally with 5 mL of 9 M HCl. Under these conditions, both radionuclides were retained in the resin. Thorium is eluted firstly by passing 25 mL of a solution of 5 M HCl – 0.05 M oxalic acid. Finally, uranium was removed from the resin by adding 20 mL of 0.01 M HCl.

To determine the precision and accuracy of this new methodology, a standard solution from IRD, with activity concentration of 1.52±0.23 Bq kg^{-1} for U-238 and 1.60±0.24 Bq kg^{-1} for Th-232 was used. This analysis was performed in quadruplicate. The performance of the methodology was also checked by using the standard reference material IAEA-385 Irish Sea

Sediment, with activity concentration of 29 Bq kg^{-1} for U-238 and 33.7 Bq kg^{-1} for Th-232. In this case, the analysis was performed in triplicate.

3. RESULTS AND DISCUSSION

The results obtained for the precision and accuracy for the determination of uranium and thorium in standard solution from IRD, by using the first methodology with the resins TEVA and UTEVA, are presented in Table 1. The relative error was evaluated by the equation (1).

$$\textit{Relative Error} = \frac{\left| MV - CV \right|}{CV}\, 100 \tag{1}$$

Where MV is the mean value and CV is the certified value.

The relative standard deviation was evaluated by the equation (2):

$$\textit{Relative Standard Deviation} = \frac{SD}{MV}\, 100 \tag{2}$$

Where SD is the standard deviation and MV is the mean value.

Table 1: Precision and accuracy by using TEVA and UTEVA resins and standard solution from IRD

Radionuclide	Mean value (Bq kg^{-1})	Certified value (Bq kg^{-1})	Relative error (%)	Relative standard deviation (%)	Chemical yield (%)
U-238	3.13±0.21	3.24±0.48	3.40	6.71	69-80
Th-232	1.22±0.15	0.80±0.12	52.50	12.30	12-36

The results present good accuracy and precision for U-238, besides high chemical yield. On the other side, Th-232 results presented good precision, but not good accuracy. The recovery yield for thorium was also not so high.

The results obtained for the precision and accuracy for the determination of uranium and thorium in the standard solution from IRD, by using the second methodology with the UTEVA resin, are presented in Table 2.

Table 2: Precision and accuracy by using UTEVA resin and standard solution from IRD

Radionuclide	Mean value (Bq kg^{-1})	Certified value (Bq kg^{-1})	Relative error (%)	Relative standard deviation (%)	Chemical yield (%)
U-238	1.61±0.10	1.52±0.23	5.92	6.21	84-88
Th-232	1.55±0.17	1.60±0.24	3.13	10.97	13-29

The accuracy and precision for U-238 are similar for the two methodologies and in good agreement with the certified value. The major differences are for Th-232, which presented much better results for accuracy by using only UTEVA resin, even though the chemical yield has not improved.

The results obtained for the precision and accuracy for the determination of uranium and thorium in standard reference material IAEA-385 Irish Sea Sediment, by using the second methodology with the UTEVA resin, are presented in Table 3.

Table 3: Precision and accuracy by using UTEVA resin and standard reference material IAEA-385 Irish Sea Sediment

Radio nuclide	Mean value (Bq kg^{-1})	Certified value (Bq kg^{-1})	95% Confidence interval (Bq kg^{-1})	Relative error (%)	Relative standard deviation (%)	Chemical yield (%)
U-238	29.68±1.81	29	28-30	2.34	6.10	65-97
Th-232	33.56±3.25	33.7	32.8-33.9	0.42	9.68	15-30

By analyzing the IAEA-385 standard reference material, good accuracy and precision were obtained for both U-238 and Th-232. The thorium chemical yield was similar to the one obtained with the other methodologies and samples.

4. CONCLUSIONS

Uranium results presented satisfactory accuracy, precision and chemical yield, for the two methodologies studied. It is worth to mention that in both methods, UTEVA was the resin used for the U purification.

For thorium, better results for the accuracy were obtained by using UTEVA resin instead of TEVA resin. The chemical yield was not as good as the one obtained by Oliveira and Carvalho [12] and Casacuberta, et al. [13], which used similar methodology.

It is concluded that the second methodology is more reliable to be applied in the main study, with advantages of being substantially faster and using a smaller quantity of chemical reagents.

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