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A COMPARATIVE STUDY USING DIFFERENTS RESINS TO DETERMINE THORIUM ISOTOPES

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ABSTRACT

Thorium is a naturally occurring radioactive element that is widely distributed in the crust of the Earth. This element is very common in mineral formations in regions with high levels of natural radioactivity, therefore, its determination in environmental samples is important. Thorium isotopes (^{228}Th, ^{230}Th, and ^{232}Th) were determined in a reference material, the IAEA Soil 327 sample, to validate the two methods employed using different resins. The initial preparation with acid dissolution is the same to both, in the first is used anion exchange resin (DOWEX 1x2) and electrodeposition in silver planchets. And in the second method is used a specific chromatographic resin (TEVA) and cerium fluoride microprecipitation. At the end both analysis are quantified by alpha spectrometry. The two methods the results obtained were satisfactory for the reference material used, with relative error of less than 4% for ^{228}Th, ^{230}Th, and ^{232}Th. The main differences found between them were spectrums resolutions, time and cost of analysis.

1. INTRODUCTION

Thorium is a radioactive element that occurs naturally in low concentrations in the Earth's crust. It is pure form is a silvery-white heavy metal that is about as dense as lead. In nature, almost all thorium is thorium-232, although several additional isotopes can be present in small amounts. Of the 26 known isotopes of thorium, only 12 have half-lives greater than one second, and of these only 3 have half-lives sufficiently long to warrant a concern [1].

The most important thorium isotopes are ^{232}Th and ^{228}Th of the natural thorium series and ^{234}Th and ^{230}Th which are decay products of natural uranium series [2].

Thorium is generally a health hazard only if it is taken into the body. External gamma exposure is not a major concern because thorium emits only a small amount of gamma radiation [1].

The longer-lived naturally occurring isotopes of thorium are all alpha emitters so the alpha spectrometry technique can be used to quantify them directly [3].

The electrodeposition is very used on the preparation of thorium samples. Electrodeposition is one of more possibilities for application of electro-gravimetric methods to determine of a trace amount of radionuclides [4].

An alternative method of preparing actinide alpha counting sources was developed instead of electrodeposition. The method uses micro-precipitation with cerium fluoride and provides a quicker, simpler way of preparing alpha counting sources in routine, production-type laboratories that process many samples daily [5].

In this study thorium isotopes, ^{228}Th, ^{230}Th, and ^{232}Th, were determined in a reference material, the IAEA Soil 327 sample, to validate the two methods employed using electrodeposition in silver planchets and cerium fluoride microprecipitation.

2. EXPERIMENTAL

The Reference Material IAEA- Soil 327 [6] was analyzed to compare the methods using different resins to determine thorium radisotopes. Approximately 2 g of sample were dissolved with three concentrate acids (nitric, perchloric, and hydrofluoric) for both methods. The ^{229}Th tracerwas added in the sample solution containing thorium to determine the chemical recuperation. For the first method the final solution was evaporated and the salts dissolved with 8 M nitric acid for determination using anion exchange resin (DOWEX 1x2) and electrodeposition. For the other method, the salts were dissolved with 3 M nitic acid and the determination of Th radioisotopes were done using the specific chromatographic resin (TEVA) and microprecipitation..

2.1. Method 1: Anion exchange resin (DOWEX 1x2) and electrodeposition

Radiochemical Th separation was carried out using Dowex 1x2 anion exchange resin pre-conditioned with 8 M nitric acid. The sample in nitric media was percolated through anion column Dowex 1x2 resin. Thorium was retained and eluted with concentrated hydrochloric acid.

The eluted solution was dried on a hot plate and the salts dissolved with the electroplating solution at pH 2.3. The electroplating solution was prepared using concentrated sulfuric acid, 0.3 M sodium sulfate and deionized water.

The radioisotopes were electrodeposited on polished silver planchets using an electrical current of 1.0 A during 90 minutes. The Th radisotopes were analyzed in an Alpha Analyst spectrometer

with 12 PIPS (Passivated Implanted Planar Silicon) detectors (counting efficiency 18%), and Genie 2000/Alpha Analyst spectroscopy systems, from Canberra Industries for 200,000 seconds.

2.2. Method 2: Chromatographic resin (TEVA) and micropecipitation

Radiochemical Th separation was carried out using the TEVA, that is a specific chromatographic resin, pre-conditioned with 3 M nitric acid. The sample in nitric media was percolated through TEVA resin. Thorium was retained and eluted with 6 M HCl and 9 M HCl.

The eluted fraction was microprecipitated with a solution of Cerium Fluoride. The precipitate obtained was filtered using a polypropylene filter with 0.1 μm porosity and 2.5 cm diameter and dried under a lamp.

The Th radisotopes were analyzed in an Alpha Analyst spectrometer with 12 PIPS (Passivated Implanted Planar Silicon) detectors (counting efficiency 18%), and Genie 2000/Alpha Analyst spectroscopy systems, from Canberra Industries for 200,000 seconds.

3. RESULTS AND DISCUSSION

The chemical recovery of thorium analysis was 85 % for method 1 (DOWEX 1x2) and 88 % for method 2 (TEVA). The activity concentrations of ^{228}Th, ^{230}Th, and ^{232}Th radioisotopes in the IAEA- Soil 327 obtained after radiochemical separations are presented in the Table 1.

Table 1: Results for different methods – IAEA-Soil 327

Radionuclide	Method 1 Bq/kg	Method 2 Bq/kg	Recommended Value Bq/kg	95% Confidence Interval
^{228}Th	37.0 ± 1.7	37.3 ± 1.6	38.2	37.2 – 39.2
^{230}Th	33.3 ± 1.5	33.2 ± 1.6	34.1	32.4 – 35.8
^{232}Th	37.6 ± 1.7	37.2 ± 1.5	38.7	37.2 – 40.2

The relative error (RE) was used as a measure of precision. RE is expressed as a percentage and has no units. The RE for analysis are present in the Table 2.

Table 2: The relative error

Radionuclide	RE (%) Method 1	RE (%) Method 2
^{228}Th	3.14	2.36
^{230}Th	2.35	2.69
^{232}Th	2.84	3.86

By the results obtained these methodologies can be considered effective and efficient, since they presented relative error less than or equal to 4 %.

The main differences found between the method using exchange resin (DOWEX 1x2) and electrodeposition, and the specific chromatographic resin (TEVA) and microprecipitation are spectrum resolutions. The microprecipitation showed a spectrum with not good resolution.

However, the time and cost of analysis using the specific chromatographic resin (TEVA) and microprecipitation is smaller and less expensive about the method exchange resin (DOWEX 1x2) and electrodeposition.

Typically, the method using TEVA resin takes two to three days while the other method takes up to six days. Besides the method using the ion exchange resin spends larger amounts of acids due to the large volume of the resin and at the end of the analysis still has the value of the silver planchets for electrodeposition which makes it more expensive.

The method for the determination of actinides and strontium in amples has been developed at the Savannah River Site Environmental Lab (Aiken, SC, USA) that could be used in emergency response situations. The method utilizes a rapid acid digestion method and a streamlined column separation process with stacked TEVA, TRU and Sr resin cartridges. Alpha emitters were prepared using cerium fluoride microprecipitation for counting by alpha spectrometry [7].

Quantitative methods for the determination of actinides have been developed for environmental samples. The procedures include aggressive dissolution, separation by anion-exchange resin, separation and purification by extraction chromatography (e.g., TRU, TEVA and UTEVA resins). Anion-exchange has proved to be a strong tool to treat large volume samples, and extraction chromatography shows an excellent selectivity and reduction of the amounts ofacids [8].

3. CONCLUSIONS

Although exchange resin (DOWEX 1x2) and eletrodeposition technique requires a refined chemical process in relation to the chromatographic resin (TEVA) and microprecipitation technique, that requires little treatment of the sample, both methods presented high precision and good accuracy in the results.

After validation using Reference Material IAEA- Soil 327, it was possible to conclude that both methods are suitable for determination of thorium radisotopes.

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