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RADIOCHEMICAL DETERMINATION OF URANIUM FOR ENVIRONMENTAL SAMPLES BY OPEN TUBULAR LIQUID CHROMATOGRAPHY AND ALPHA SPECTROMETRY*

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ABSTRACT. Uranium-series analyses are an essential component of many research projects in Earth and environmental science and also for the protection of public health. In this work a simple and fast method for the determination of uranium isotopes using open tubular liquid chromatography and alpha spectrometry is described. The uranium standard solution was acidified at pH 1 with hydrochloric acid before separation. A strong base anion resin Dowex AG 1X8 was used for the separation of target compounds. The elution of uranium at different concentrations of hydrochloric acid (0.05; 0.10 and 0.15 M) was tested. After its separation from thorium, the uranium is electrodeposited onto stainless steel discs and then measured by alpha spectrometry. The measurements were performed using an ORTEC SOLOIST alpha spectrometer with PIPS (Passivated Implanted Planar Silicon) detector and the data acquisition was made by ASPEC-927 Dual Multichannel. The results of performed experiments showed that Dowex AG 1X8 resin is a selective sorbent for uranium and it can be used for the preconcentration of uranium isotopes from different aquatic samples.

Keywords: *uranium, separation, open tubular liquid chromatography, alpha spectrometry*

INTRODUCTION

The identification and determination of uranium isotopes is an important tool for the environmental studies and for the protection of public health [1-3]. Radium and uranium from soil and building materials are the main sources for indoor radon, a radioactive gas considered at this time as the second cause of the lung cancer risk [4-7]. The identification and the quantification of uranium isotopes require a proper separation of each isotope and high purification of them in order to obtain highly accurate results. Alpha-particle

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spectrometry is one of the measurement technique used for the determination of uranium isotopes [8-10]. The main advantages of this method are the low background and the good resolution. The current techniques for the uranium separation and purification require sample dissolution with strong acids, precipitation and ion exchange [11, 12]. A proper combination of some of these techniques allows obtaining a very good separation of uranium.

Ion exchange is successfully applied to the separation and determination of radionuclides in the pure form of complex mixtures. In the recent years this method has found wide application due to its simplicity, speed and high degree of purity obtained.

The aim of this work is to develop a selective radiochemical separation method of uranium from thorium using Dowex AG 1X8 resin and to quantify it by alpha spectrometry after electrodeposition onto stainless-steel discs.

RESULTS AND DISCUSSION

The tests were carried out on simulated waste samples containing a known activity of uranium isotope, in order to check the efficiency of the separations. The resin used in this work was Dowex AG 1X8 (100-200 mesh) that is a Type I strong base anion resin containing 4% divinylbenzene (DVB). Its structure is based on a microporous copolymer of styrene and DVB that results in maximum resistance to oxidation, reduction, mechanical wear and breakage. The resin active principle consists in the quaternary ammonium ($-NR_3^+$) groups which are capable of binding chloride complexes of UO_2^{2+} (e.g. $UO_2Cl_4^{2-}$). Uranium may be separated with an anion exchanger, since in 9M HCl uranium forms a negatively charged complex $[UO_2Cl_4]^-$ that may be trapped on the anion exchanger, while the other elements pass through the column.

The uranium recovery was calculated after its passing through the home made columns. In order to evaluate the efficiency of the separation method by alpha spectrometry, alpha sources were prepared by electrodeposition. In Table 1 are presented the recoveries obtained for samples 1-12 which are the samples obtained using the pretreatments of column filled with Dowex resin described in Table 2.

As it could be observed from Figure 1, for the first separation column, the higher uranium recovery (98.3%) was obtained for the sample 5 by eluting with 0.10M HCl at room temperature, while the lowest recovery (62.0%) was obtained for sample 1 by eluting with 0.05M HCl heated. The other values are inside of this range.

The results from Figure 1 prove that the eluent HCl concentration is an important recovery parameter. The best results were obtained for tests at room temperature. The increase of eluent temperature encourages the recovery process for around 0.10M HCl concentration of eluent.

Table 1. The uranium recoveries obtained for samples 1-12.

Sample no	Amount added (Bq/sample)	Amount found (Bq/sample)	Recovery (%)
1	5.6	3.5	62.0
2	4.5	3.9	87.0
3	9.6	6.5	68.0
4	11.9	11.4	95.9
5	11.9	11.7	98.3
6	11.9	10.0	84.4
7	11.8	8.5	72.4
8	8.0	6.8	85.3
9	9.4	6.9	73.7
10	14.7	14.3	97.4
11	7.5	7.5	99.7
12	9.6	8.5	88.8

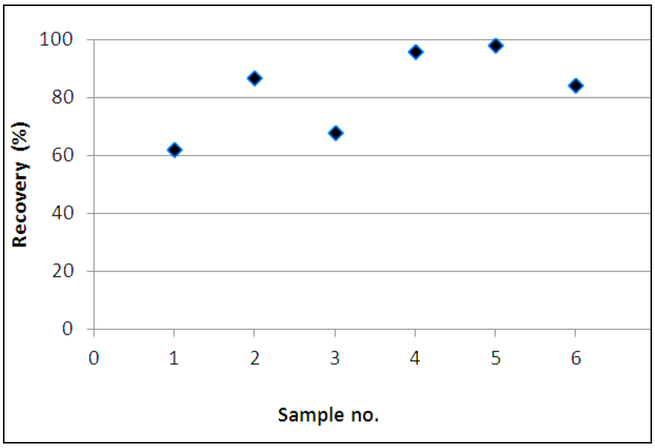

Figure 1. The recovery obtained for the first column conditioning (washed with 0.10M HCl and 9M HCl). Samples 1-6.

The second column recovery offers us interesting results which are represented in the chart of Figure 2. We could observe a generally good positioning of the achieved values ranged around of 90% recovery for tests at room temperature.

The highest recovery value (99.71%) was achieved for the sample 11 obtained by eluting with 0.10M HCl at room temperature meanwhile the lowest recovery (72.40%) was obtained for sample 7 by eluting with 0.05M HCl heated. It can be observed the same situation as in the case of first column conditioning: the HCl concentration of eluent influences the recovery process. The best results were obtained for 0.10M HCl concentration of eluent at room temperature.

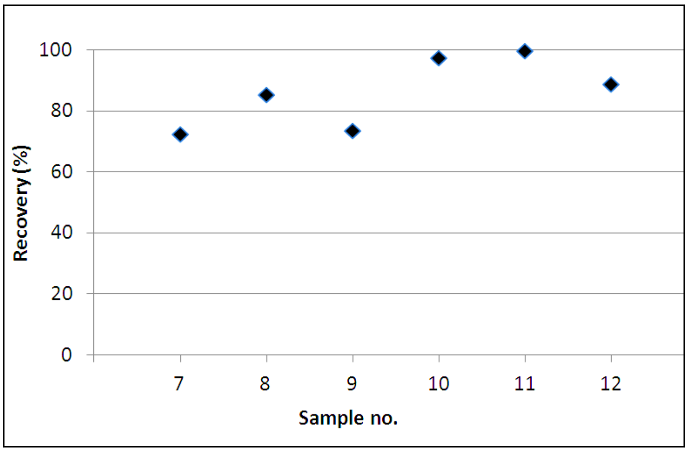

Figure 2. The recovery obtained for the second column conditioning (the resin kept 12 hours in 9M HCl). Samples 7-12.

The main energies of U isotopes are: ^{238}U - 4196 KeV, ^{234}U - 4777 KeV, and ^{235}U - 4679 KeV. The Figure 3 illustrates the ^{238}U, ^{234}U and ^{235}U activities (counts). Also it can be observed that the two peaks representing the ^{238}U and ^{234}U are not equal as they should be (secular equilibrium), so we can conclude that the used U is depleted uranium.

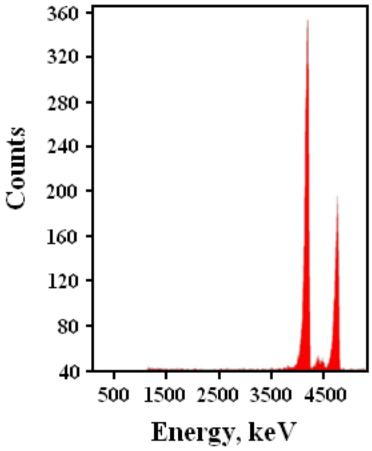

Figure 3. The obtained uranium alpha spectrum.

No thorium could be found in any of the final solutions; the main energies of thorium isotopes are: ^{232}Th – 4007 KeV, 3952 KeV and ^{230}Th – 4682 KeV, 4615 KeV [13]. Therefore we can conclude that a very good separation of uranium from thorium have been obtained.

This investigation proves that the recovered U isotopes feature a high purity related to a high uranium recovery. This fact demonstrates that the performed analysis method is suitable for the environmental U determinations.

CONCLUSIONS

The uranium separation and determination from samples is a very important tool in environmental studies. A very good uranium recovery in the separation process is required due to its low concentration in environmental samples.

The highest recovery obtained for uranium separation by open tubular liquid chromatography was 99.71% by conditioning the resin 12 hours in 9M HCl and then eluting with 0.10M HCl at room temperature. The lowest recovery obtained was 62% by conditioning the column with 0.10M HCl and 9M HCl and then eluting with heated 0.05M HCl. The recovery percent increases significantly with the increasing of the eluent HCl concentration around 0.10M. The alpha spectrum do not show any traces of added thorium, we can state that a very good separation of uranium from thorium have been done.

Our future work will be focused on applying this method on real samples and also testing other resins for uranium separation by open tubular liquid chromatography.

EXPERIMENTAL SECTION

In this work we used a strong basic anion exchange resin, Dowex AG 1X8 (100-200 mesh) purchased from Sigma-Aldrich. All chemicals were analytical grade.

The performance of methodology was checked by using uranium standard solutions. The solutions were prepared by dissolution of uranyl nitrate $UO_2(NO_3)_2{\bullet}6H_2O$ (99.99%, purchased from Merck Company) in 9M HCl solution. In this way the uranyl nitrate was converted to chloride form.

A very good separation between uranium and thorium is required taking into account the environmental applications. We prepared a low activity mixed solution of these two radionuclides. Therefore, a known quantity of thorium (1 Bq/sample) obtained from a $Th(NO_3)_4{\bullet}5H_2O$ salt was added to uranium solutions from Table 1 in order to check the selectivity of the performed separation protocol for uranium.

The standard solution was acidified at pH 1 with hydrochloric acid before the uranium separation. The resin is completely hydrated prior to column packing and then it is washed using a mobile phase that will cause the greatest swelling.

In this paper two different ways for resin conditioning were used. The first one, the conditioning was accomplished by washing the column loaded with Dowex 1X8 resin with 0.10M HCl and then with 9M HCl. The second conditioning was made by washing the same type of resin with pure H_2O and after, keeping the resin for about 12 hours in 9M HCl. In Table 2 are presented the two column conditionings and the eluents of different HCl concentrations at different temperatures used for uranium and thorium elution process. The columns used in this work are 7 cm length and 1 cm internal diameter. The same volume of standard solutions was used for every uranium and thorium separation. The uranium anionic complexes should be retained on the resin and thorium should pass through the column. A solution of 9M HCl was passed through the column for washing any traces of other possible elements retained on the column, including thorium.

For the elution of uranium through columns, different temperatures for eluents were tested using different aqueous solutions of hydrochloric acid (0.05; 0.10 and 0.15 M) (Table 2). The same volume of eluent (20 mL in two stages) was used for all separations. The elution was performed at a rate of 5-6 drops per minute. The room temperature was about 22°C.

The samples obtained after elution were electrodeposition onto stainless steel discs. The measurements of uranium isotopes were performed with alpha spectrometer with an ORTEC SOLOIST alpha spectrometer with PIPS (Passivated Implanted Planar Silicon) detector (1200 mm^2 size).

Table 2. The column conditioning and the used eluents.

Sample No	Dowex 1X8 Column Conditioning	Eluent
1	Washed with 0.1M HCl and then with 9M HCl	0.05 M HCl heated to boiling point
2		0.10 M HCl heated to boiling point
3		0.15 M HCl heated to boiling point
3		0.05 M HCl at room temperature
5		0.10 M HCl at room temperature
6		0.15 M HCl at room temperature
7	Kept 12 hours in 9M HCl and then loaded into the column.	0.05 M HCl heated to boiling point
8		0.10 M HCl heated to boiling point
9		0.15 M HCl heated to boiling point
10		0.05 M HCl at room temperature
11		0.10 M HCl at room temperature
12		0.15 M HCl at room temperature

The resolution of the detector is 19 KeV and the data acquisition was made by ASPEC-927 Dual Multichannel.

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