

SOLID-PHASE EXTRACTION FOR THE SEPARATION OF ACTINIDES FROM RADIOACTIVE WASTE

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ABSTRACT

For the characterisation of conditioned radioactive waste, the actinides to be analysed must be separated from matrix components, if possible, element-specific. Microwave pressure digestion is a time-saving digestion method for radioactive waste samples. The partitioning of the actinides from the liquid samples are carried out with the aid of solid-phase extraction. For the experiments, on the one hand, commercially available extraction resins such as Actinide™, TRU™, UTEVA™ and TEVA™ Resin from Eichrom were used. On the other hand, an extraction resin with Cyanex 301 produced in-house was tested specifically for actinide-lanthanide partitioning. It was possible to separate 99.4 % of the lanthanides by a two-stage partitioning process. A partitioning run using the Eichrom resins was successfully adapted to the waste matrices and automated with the aid of a laboratory robot. It is particularly meaningful to perform a prior matrix partitioning with Actinide™ Resin A semi-quantitative qualification of the sample is possible by the α -analysis of the actinide fraction. The extractant, which was eluted from the column together with the actinides, was destroyed oxidatively by means of a newly developed technique using microwave pressure digestion.

INTRODUCTION

The characterisation of actinides in solid radioactive waste samples is only possible if the waste matrix is destroyed before and as result a liquid sample is obtained. With the aid of microwave pressure digestion all kind of radioactive waste matrices can be destroyed effective in a time-saving manner [1]. The enrichment and partitioning of the actinides in these liquid sample was performed by solid-phase extraction. A separation scheme using Eichrom resins developed by Horwitz et al. [2,3,4] was tested with the actinides Thorium, Uranium, Neptunium, Plutonium, Americium, Curium and the lanthanide Europium. These separations had been carried out for aqueous standard solutions first and had to be adapted to different kinds of radioactive waste matrices e.g. concrete, ion exchange resins, filter dusts, slurries and sander grains. With respect to future options for destroying actinides by transmutation it is also essential to carry out an actinide-lanthanide partitioning which was not considered in Horwitz separation scheme. These considerations and experiments with different kinds of radioactive waste matrices led to a successfully tested partitioning scheme, which is presented in the conclusions

This paper does not go into details on the experiments with the resins impregnated with Cyanex 301 for lanthanide separations, which are described in Reference [1].

EXPERIMENTAL

The experiments on the Eichrom resins were carried out both with radioactive standard solutions and with solutions containing radioactive waste matrices. The solutions were transferred to the different columns containing 1g (for Actinide™ Resin) or 0.7g (for TEVA™, UTEVA™ and TRU™) resin. The columns were washed with several mineral acids [1,4] and the actinides were then eluted (see also results and discussion).

The destruction of DIPEX™, which is eluted together with the actinides from Actinide™ Resin, was first realised by the addition of 5 mL 30 % H₂O₂ and 0.5 mL 0.2 M NaVO₃ as catalyst [5]. An other possibility to destroy DIPEX™ was to undergo a microwave decomposition with 5 mL HNO₃ and 1.5 mL H₂O₂. The microwave, which was used, was a mega 1200 of MWS. There was no catalyst necessary for this method. The microwave program, which was used for this dissolution and the temperature and pressure data are shown in Figure 1.

The final determination of the separated actinides was performed with the aid of alpha spectrometry. Electrodeposition on a nickel plated brass target (Ø 50 mm) with NH₄Cl proved to be a suitable method for the preparation of samples with minimum possible layer thickness. For the measurement of samples in a grid chamber a stainless steel target with a diameter of 200 mm was used.

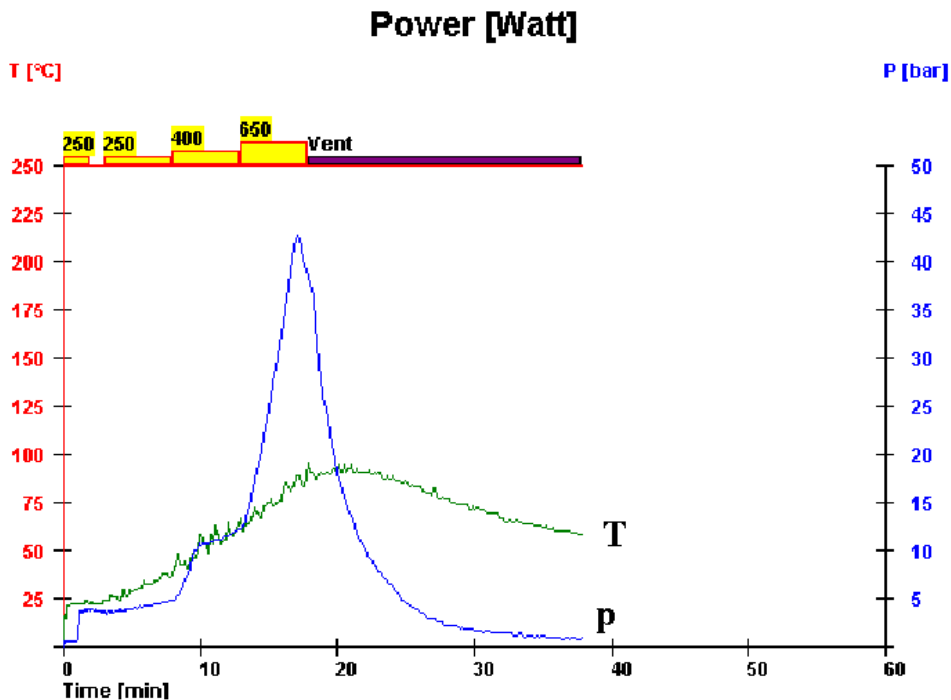


Fig. 1: Microwave program with temperature and pressure data for the DIPEX™ destruction

RESULTS AND DISCUSSION

Results with Actinide Resin

All actinides and lanthanides can be separated from matrix components with Actinide Resin. 100 mg ascorbic acid was added to the sample to reduce potential Fe(III) to Fe(II) so that iron was not extracted by the column. The extraction of Fe(III) would have caused an earlier breakthrough of trivalent actinides and lanthanides which was undesired. The liquid sample in 2M HCl was transferred to a column with Actinide™ Resin. The column was washed with 5 mL 2M HCl, 5 mL 2 M HCl / 0.5 M HF and 5 mL H₂O. The actinides and lanthanides were eluted with 15 mL isopropanol together with the extracting agent DIPEX™. Due to the very high distribution ratio of all actinides and lanthanides on this column it was not possible to elute the radionuclides with a mineral acid or even with an other complexing agent containing the same functional group as the resin [5]. Therefore the DIPEX™-actinide-complex had to be destroyed for further separation steps.

First of all the recovery rates of different actinides were determined on Actinide™ Resin. Standard actinide solutions were used for these experiments and 1 mL of the isopropanol fraction was measured with LSC. The recovery rates were reproducible > 80 % for all requested radionuclides (see Table I). The same recovery rates were obtained with concrete or ion exchange resin samples. These samples came out of the microwave decomposition with a concentration of 5 M HNO₃. It was not necessary to converse into HCl to receive the same good recovery rates so that the samples could be utilised at once.

Table I: Recovery rates of actinides on Actinide™ Resin

Radionuclide	Recovery rate
²³⁹ Pu	91 ± 5 %
²⁴¹ Am	96 ± 2 %
²³³ U	93 ± 4 %
²³⁷ Np	86 ± 6 %
²⁴⁴ Cm	104 ± 5 %
²³² Th	83 ± 5 %

It was possible to prepare 1 mL of the isopropanol fraction directly for α-measurement to have a first look on the actinides, which are present in the sample. A quantitative analysis could even be carried out when 100 μL of the fraction was prepared together with 2 mL of a 1 % Zapon lacquer solution on a stainless steel target (∅ 200 mm) for α-measurement in a grid chamber. A more time-consuming electrodeposition was not necessary.

As mentioned before it was necessary to destroy the extracting agent DIPEX™ for the next separation steps. The isopranoanol fraction was first evaporated and then heated on a hot plate with H₂O₂ and NaVO₃. This method led to a black residue, which had to be treated the described way another three times. This destruction step was very difficult to handle because of the exothermic reaction and was thus also very time consuming. It was replaced by the destruction with HNO₃ and H₂O₂ using a microwave decomposition. This step could be carried out in one hour. After evaporation a residue was obtained which contained mainly amorphous parts and methylenediphosphonic acid but no DIPEX™. This residue was dissolved in 2 M HNO₃ / 1 M Al(NO₃)₃ and put into the next separation steps without any problems. It was even shown that the recovery rates after the destruction in the microwave were higher than the rates received with the other method (see Table II).

Table II: Recovery rates of the actinides after different destruction methods of DIPEX™

Radionuclide	Recovery rate after destruction with H ₂ O ₂ and NaVO ₃	Recovery rate after microwave decomposition
²³⁷ Np	90 ± 3 %	85 ± 5 %
²⁴¹ Am	77 ± 7 %	85 ± 5 %
²³³ U	65 ± 5%	90 ± 4 %
²³⁹ Pu	65 ± 6 %	90 ± 6 %

Results with TEVA[®] Resin

The actinides Neptunium and Thorium can be separated distinctively on a TEVA™ Resin column. The sample should be in 2 M HNO₃ / 1 M Al(NO₃)₃. 100 mg ascorbic acid and 2 mL 0.6 M ferrous-sulfamate solution have to be added to reduce Neptunium completely to Np(IV) and Plutonium to Pu(III). TEVA™ Resin can only extract the tetravalent actinides and after washing with different mineral acids (see Table III), Thorium can be eluted with 9M HCl and Neptunium with 0.02 M HNO₃ / 0.02 M HF.

Experiments were carried out with standard solutions including known activities and real waste matrices e.g. concrete, ion exchange resin. As expected the recovery rates for Neptunium and Thorium in standard solutions were around 95 % (see Table III). The addition of ascorbic acid had to be increased if waste matrices including Fe(III) are used. This factor was easy to handle, but Thorium caused a problem in real waste matrices. 70 % of Thorium was found after the sample was rinsed through the column (see Table III). Thorium appears always in its stable oxidation state +4 so there was no need to add another oxidation or reducing agent. That meant that the Thorium was not completely extracted by the resin. We supposed that the waste matrix components influenced the extraction of Thorium on TEVA™ Resin. Cleaning the sample from

matrix components with Actinide™ Resin led to the same result. After the destruction of DIPEX™, phosphoric acid residues remained which disturbed the extraction of Thorium on TEVA™ Resin. This effect could not be inhibited by the addition of more Al(NO₃)₃ which normally complexes phosphate ions.

Table III: Comparison of the recovery rates in standard and real waste solutions of different actinides on TEVA™ Resin

Rinsed Solution	Recovery rate Am [%]		Recovery rate U [%]		Recovery rate Pu [%]		Recovery rate Th [%]		Recovery rate Np [%]	
	St.	RW	St.	RW	St.	RW	St.	RW	St.	RW
Sample	95	92	80	78	90	90	--	70	--	--
2.5 M HNO ₃ / 0.1 M Fe(II)- sulfamate	3	3	15	16	5	5	--	--	--	--
2.5 M HNO ₃	--	--	--	--	--	--	--	--	--	--
9 M HCl	--	--	--	--	--	--	90	15	--	--
6 M HCl	--	--	--	--	--	--	3	--	--	--
0.02 M HNO ₃ / 0.02 M HF	--	--	--	--	--	--	--	--	95	90

St. = Standard solution

RW = Real Waste solution

Results with UTEVA Resin

It is possible to separate Uranium and also Thorium on UTEVA™ Resin. The washing fraction of TEVA™ Resin can be used without any further treatment. After washing with 3M HNO₃ and converting to HCl system Thorium is eluted with 5 M HCl and Uranium is eluted with 0.1 M HCl.

We made experiments with standard and real waste solutions both for Uranium and Thorium, which delivered non satisfying results with TEVA™ Resin. As can be seen in Table IV Uranium was eluted with good recovery rates of 95 % respectively 90 %. Again we found Thorium in the rinsed sample solution. But in this case it was only 10 % and it was possible to analyse the Thorium quantitatively by the addition of a Thorium spike.

Table IV: Comparison of the recovery rates in standard and real waste solutions of different actinides on UTEVA™ Resin

Rinsed Solution	Recovery rate Am [%]		Recovery rate U [%]		Recovery rate Pu [%]		Recovery rate Th [%]	
	St.	RW	St.	RW	St.	RW	St.	RW
Sample	93	91	--	--	92	89	--	10
3 M HNO ₃	3	3	--	--	5	5	--	--
9 M HCl	--	--	--	--	--	--	--	--
5 M HCl	--	--	--	--	--	--	80	65
0.1 M HCl	--	--	95	90	--	--	--	--

St. = Standard solution
 RW = Real Waste solution

Uranium/Thorium separations on UTEVA™ Resin with and without using Actinide™ Resin as a cleaning step were carried out to show the effectiveness of Actinide™ Resin. Five radioactive samples with different matrices (ion exchange resin (Lewatit M500), U/Th-precipitate (containing Fe, Ca), U/Th-sludge (containing Fe, Ca, Al), U/Ni-sludge (containing Fe, Ca, Al, Ni) and sander grains (mineral)) were decomposed and used for these separations. Table V shows the recovery rates for Uranium (²³²U) with and without using Actinide™ Resin.

Table V: Recovery Rates for ²³²U after the separation with UTEVA™ Resin

	Recovery rates (²³² U) with Actinide™ Resin	Recovery rates (²³² U) without Actinide™ Resin
U/Th-precipitate	65 %	89 %
U/Th-sludge	63 %	83 %
U/Ni-sludge	77 %	88 %
ion exchange resin	63 %	31 %
sander grains	69 %	90 %

Using Actinide™ Resin before UTEVA™ Resin delivered similar recovery rates (ca. 65%) for all matrices. It has to be annotated that at the time when this work was performed the microwave destruction method for DIPEX™ was not developed yet. Because of the experiences we made with this destruction method we can postulate that the recovery rate would be around 90%. The

experiments without Actinide™ Resin show in four cases the same recovery rates (ca. 88%). Hence, the ion exchange matrix provides a low recovery rate of only 31% without using the Actinide™ Resin, which can be increased up to 63%. This is very important especially if the Uranium (or Thorium) content of a sample is close to its detection limit. Another great advantage of using the Actinide™ Resin was the smaller half width of the Thorium peaks in the obtained α -spectras. This can be explained by a better separation of the matrix components, which interfere otherwise with the electrodeposition.

Results with TRU[®] Resin

It is possible to separate Plutonium from Americium, Curium and lanthanides. First 1 mL 2.5 M NH₂OH·HCl and 100 μ L 2.5 M NaNO₂ has to be added to oxidise Pu(III) to Pu(IV) because only Pu(IV) is extracted by TRU™ Resin. Hydroxylamine hydrochloride stabilises Fe(II) in solution which was added as ferrous sulfamate before. This is very important otherwise Fe(II) is oxidised to Fe(III) by sodium nitrite and causes then an early breakthrough of Americium.

Table VI shows that there were the same good recovery rates for standard and real waste solutions. This Resin did not cause any problems.

Table VI: Comparison of the recovery rates in standard and real waste solutions of different actinides on TRU™ Resin

Rinsed Solution	Recovery rate Am [%]		Recovery rate Cm [%]		Recovery rate Pu [%]	
	St.	RW	St.	RW	St.	RW
Sample	--	5	--	--	3	4
2 M HNO ₃	--	--	--	--	--	--
2 M HNO ₃ / 0.1 M NaNO ₂	--	--	--	--	--	--
0.5 M HNO ₃	--	--	--	--	--	--
9 M HCl	--	--	--	--	--	--
4 M HCl	92	85	104	90	--	--
0.1 M oxalic acid	--	--	--	--	95	90

St. = Standard solution

RW = Real Waste solution

CONCLUSION

In order to separate actinides (Neptunium, Thorium, Uranium, Americium and Plutonium) and lanthanides from dissolved radioactive waste, we tested a separation scheme presented in Figure 2 successfully. With this partitioning run the actinides and lanthanides were separated from matrix components on Actinide™ Resin. It was possible to have a first look at the actinides after this separation with the aid of α -spectrometry. We developed a new microwave destruction method of DIPEX™, the extracting agent of Actinide™ Resin, which is also eluted from the column. This method delivered recovery rates > 80% in an acceptable destruction of one hour. Furthermore we showed with an easy Uranium/Thorium separation on UTEVA™ Resin the advantages of using Actinide™ Resin as a cleaning step for more complex and different kind of matrices. For Thorium the half width of the peaks in the α -spectras were reduced and for some matrices the obtained recovery rates increased.

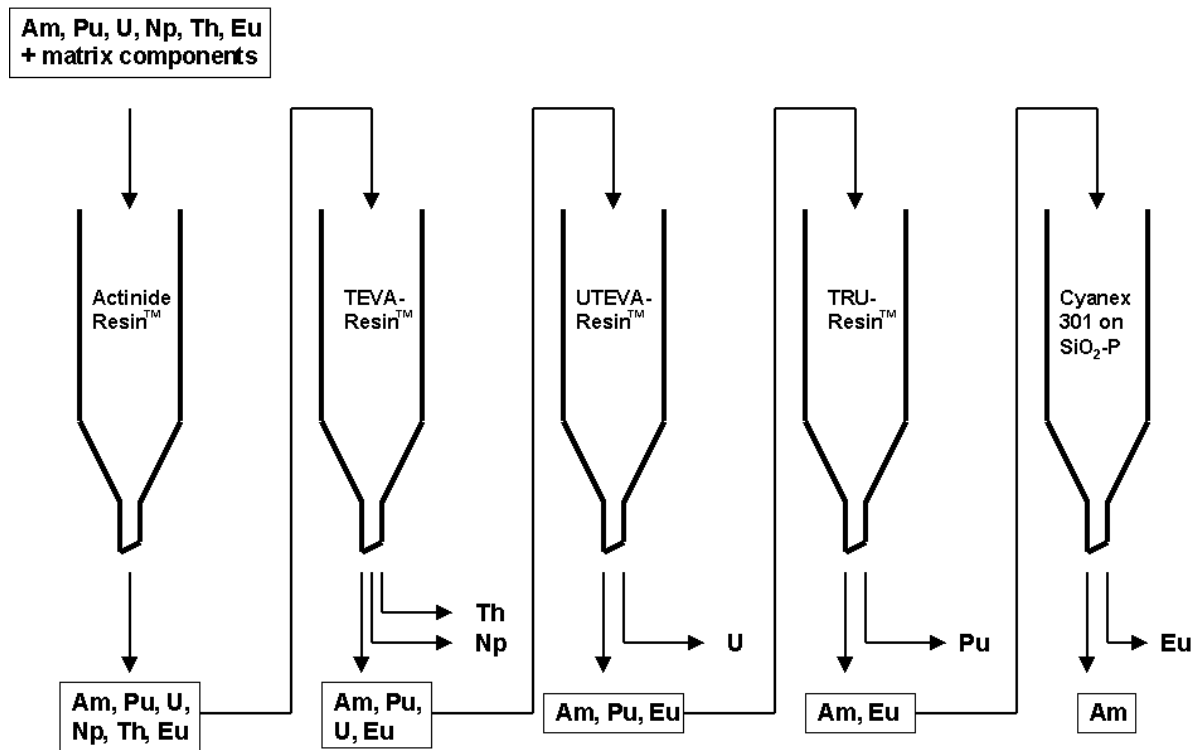


Fig. 2: Separation scheme for the actinide-separation from radioactive waste with Eichrom-resins and for the actinide-lanthanide-partitioning with an extraction resin with Cyanex 301

Neptunium was separated on TEVA™ Resin of the other radionuclides. The separation of Thorium caused problems on this Resin because its extraction was on the one hand influenced by matrix components. After a cleaning step with Actinide™ Resin on the other hand the extraction of Thorium was inhibited by remaining phosphoric acid residue. Therefore Uranium and Thorium were separated from Americium, Plutonium and lanthanides on UTEVA™ Resin with a high recovery rate of 90% for Uranium. Acceptable 65% of Thorium were found in the Thorium

fraction. It was also possible to separate Americium (Curium and the lanthanides) and Plutonium on TRU™ Resin (recovery rates of 80-95%).

The separation of the lanthanides was successfully carried out with an in house-made resin containing Cyanex 301. 99.4% of the lanthanides were separated by a two stage partitioning process.

The whole separation scheme can be automated with the aid of a laboratory robot system. This is already realised in our laboratories and guarantees a quick partitioning process with a minimum dose rate for the laboratory worker.

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