



# Rapid americium separations from complex matrices using commercially available extraction chromatography resins

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## Abstract

A method for rapid separation of americium from complex matrices by use of two commercially available extraction chromatography resins is reported. TRU resin is capable of purifying americium/lanthanides together from Group 1, Group 2 and transition metals. TRU resin tolerated high loadings of iron, aluminium, calcium sodium and potassium. TEVA resin purified americium/lanthanides by elution with ammonium thiocyanate. Decontamination factors > 20,000 were achieved within one working day. The affinity of TEVA resin for americium, curium and lanthanides as a function of ammonium thiocyanate concentration is reported. The possibility of americium/lanthanide separations on LN resin has been explored.

**Keywords** Americium · Curium · Separation · Extraction Chromatography

## Introduction

Extraction chromatography has become a popular method for the separation of americium from the lanthanide elements. These separations are considered especially difficult due to the similar physiochemical properties of these elements [1]. The separation of americium from curium represents an even greater challenge [2]. These separations are important due to their applications in nuclear fuel reprocessing [3], environmental monitoring [4] and nuclear forensics [5].

Several publications have documented the affinity of the commercially available Eichrom resins for lanthanides and actinides [6–12].

LN resin is a 40% (w/w) loading of the phosphorus based extractant bis(2-ethylhexyl) hydrogen phosphate (HDEHP) onto 25–53 µm particles Amberchrom CG-71 [13]. There is evidence from previously reported weight distribution ratios and capacity factors that americium/lanthanide separation

may be possible at low (<0.5 M) nitric acid concentrations [12].

TRU resin is based upon a 40% (w/w) loading of the extractant octyl(phenyl)-*N,N*-dibutyl carbamoyl methyl phosphine oxide (CMPO) dissolved in tributyl phosphate (TBP) on the polymer Amberchrom CG-71 [14, 15]. It has been shown to be able to separate americium and the lanthanides together as a group from many other elements with a high tolerance for contaminants that may be considered typical in environmental samples such as iron, calcium, aluminium, sodium and potassium [7].

TEVA resin is a 40% (w/w) loading of the quaternary ammonium salt A336 upon the same polymer. The preferential binding of SCN<sup>-</sup> to actinides over lanthanides has been utilised for the separation of trivalent actinides (An(III)) from trivalent lanthanides (Ln(III)). Ln(III) are unretained on the column when eluted with 1 M NH<sub>4</sub>SCN/0.1 M formic acid, An(III) can then be stripped using 0.25–2 M HCl [6].

This work describes a rapid method for the separation of americium from a simulated complex matrix by the sequential use of TRU and TEVA columns. The matrix was simulated to be representative of those typical in nuclear fuel reprocessing, environmental monitoring and nuclear forensics samples. The possibility of americium/lanthanide separations by the application of elution profiles of low molarity (<0.5) nitric acid on LN resin and the possibility of americium/curium separations using high molarity

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(4–5 M) ammonium thiocyanate on TEVA resin have also been explored.

## Experimental

### General

All radionuclides used were provided from calibrated stocks in the School of Chemistry, University of Manchester or otherwise AWE. Micropipettes of 2–10  $\mu\text{L}$ , 10–100  $\mu\text{L}$ , 20–200  $\mu\text{L}$  and 0.1–1 mL were calibrated on a 4 decimal place balance with  $> 18 \text{ M}\Omega$  deionised water in the temperature range 18–22  $^{\circ}\text{C}$  and were found to be within their stated range. All acid solutions were made from analytical grade concentrated solutions and were diluted with  $> 18 \text{ M}\Omega$  deionised water.

Gamma counting was performed using a Canberra 2020 coaxial HPGe gamma spectrometer with an Ortec DSPEC-50 multi-channel analyser energy and efficiency calibrated for the geometry used. Gamma spectroscopy was performed against a standard of known activity counted in the same geometry and Am-241 was quantified using the diagnostic photon energy of Am-241 (59.5 keV).

The estimated uncertainty on measurements of active isotopes, quantified by gamma spectroscopy, is 5% based on standard uncertainty multiplied by a coverage factor  $k=2$ , providing a level of confidence of approximately 95%.

ICP-MS analysis was performed on an Agilent 7500cx spectrometer. Multiple standards for each element in the range 1–100 ppb were used for ICP-MS quantification. All reagents and solvents used were of standard analytical grade.

The estimated uncertainty on the measurements of stable isotopes quantified by ICP-MS is 10% based on a standard uncertainty multiplied by a coverage factor  $k=2$ , providing a level of confidence of approximately 95%.

### Batch experiments

Resin (100 mg) was prepared according to the manufacturer's instructions. The resin was added to a solution containing a known quantity of the stated radionuclides in the stated solvent and vortex mixed at 2000 rpm for 60 min. The acid solution was drained and the resin and solution reweighed to allow for the application of a mass correction in the weight distribution calculation. The solution was transferred to a standard measurement geometry and counted by gamma spectroscopy.

## Column separation

A standard plastic column, with an internal diameter of 7 mm, was packed to a 39 mm height using 0.7–0.8 g of each of the TRU and TEVA resins. These dimensions were chosen to emulate the size of many pre-loaded commercially available EXC resin columns available from Eichrom.

The TRU column was loaded with a minimum volume of solution containing 50–100 Bq of Am-241, 50 mg of stable Fe(II), Al(III), Ca(II), Na(I), K(I), and 1 mg of stable Be(II), Sr(II), Cd(II), Cs(I), Ba(II), Y(III), Mo(VI), Ce(III), Pr(III), Nd(III), Sm(III), Tb(III) and Ag(I) generated from their nitrate salts or otherwise purchased as a certified standard from Essex Scientific Laboratories Ltd, UK. All elements were at natural isotope abundances.

The columns were eluted with the stated elution profiles with a flow rate of 1 mL/min controlled by the use of a vacuum box. The fraction which contained the majority of the americium eluted from the TRU column was redissolved in 4 M ammonium thiocyanate/1% formic acid and loaded onto the TEVA column in a minimal volume.

Each fraction was collected and made to a standard geometry before being counted by gamma spectroscopy. A small aliquot was removed and diluted for analysis of stable isotopes by ICP-MS.

## Results and discussion

### Batch studies

The affinity of TEVA resin for the isotopes to be extracted from solution has been characterised by the weight distribution ratio ( $D_w$ ) parameter (Eq. 1).

$$D_w = \frac{(A_0 - A_s) \text{ mL}}{A_0 \text{ g}} \quad (1)$$

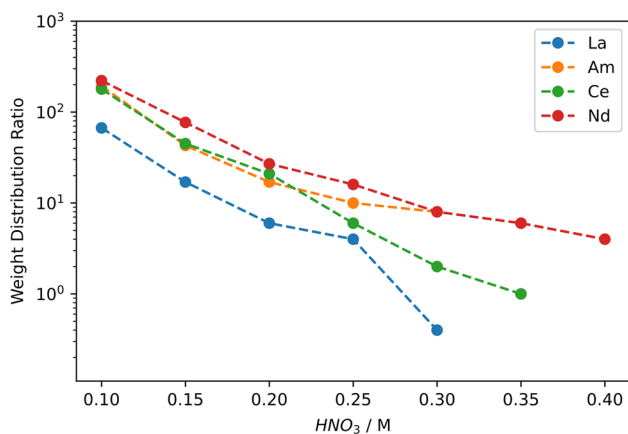
$A_0$  = initial activity

$A_s$  = activity post extraction

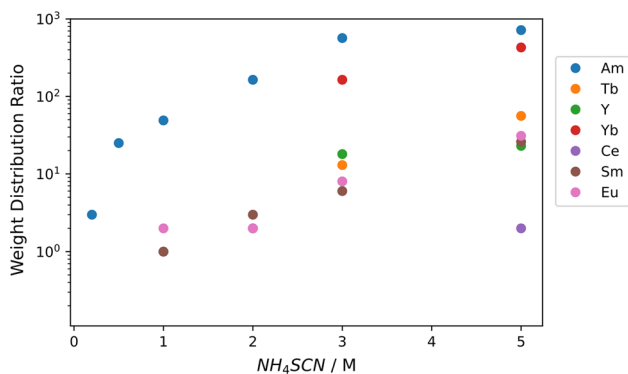
mL = volume of solute

g = mass of resin

This metric was decided upon because it is prevalent in the literature [2, 6, 13, 16–24] and hence provides a suitable point of comparison between the results given here and those previously reported.  $D_w$  is also readily converted into other common measures of extraction capability such as capacity factor ( $k'$ ) and free column volumes (FCV) for comparison



**Fig. 1** Weight distribution ratio for americium and lanthanides on LN resin as a function of nitric acid concentration

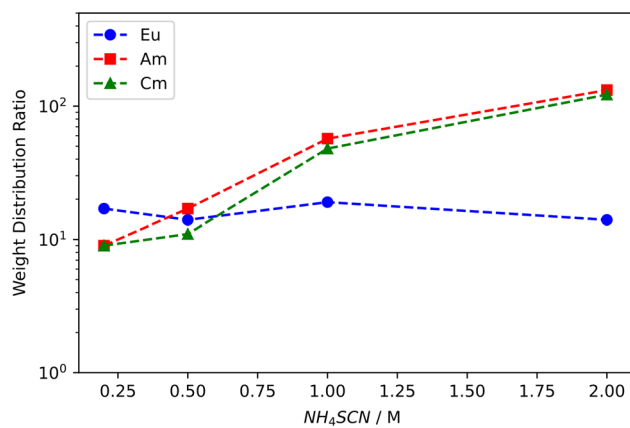


**Fig. 2** Weight distribution ratio for elements as a function of ammonium thiocyanate concentration

between batch experiment systems and column experiments [25].

Figure 1 shows  $D_w$  for americium and lanthanides on LN resin. As can be seen at low nitric acid concentrations there are significant differences in the resins affinity for americium by comparison with lanthanides implying the potential for separation by column chromatography.

Figure 2 shows  $D_w$  for americium, yttrium and several lanthanides on TEVA as a function of ammonium thiocyanate concentration. As can be seen there is a higher affinity for americium over all lanthanides and yttrium at every concentration. The quaternary ammonium salt A336 which serves as the extractant on TEVA extracts the metals by anion exchange. The preferential binding of  $\text{SCN}^-$  to



**Fig. 3** Weight distribution ratio for europium, americium and curium as a function of ammonium thiocyanate concentration

actinides over lanthanides provides the basis for the separation [6, 26].

Figure 3 shows similar data for europium, americium and curium. The preference for actinides over lanthanides is observed as expected. Little difference is seen in  $D_w$  for americium vs curium however at 2 M ammonium thiocyanate concentration  $D_{\text{Am}} = 132$  and  $D_{\text{Cm}} = 122$  providing a separation factor of 1.1.

## Column studies

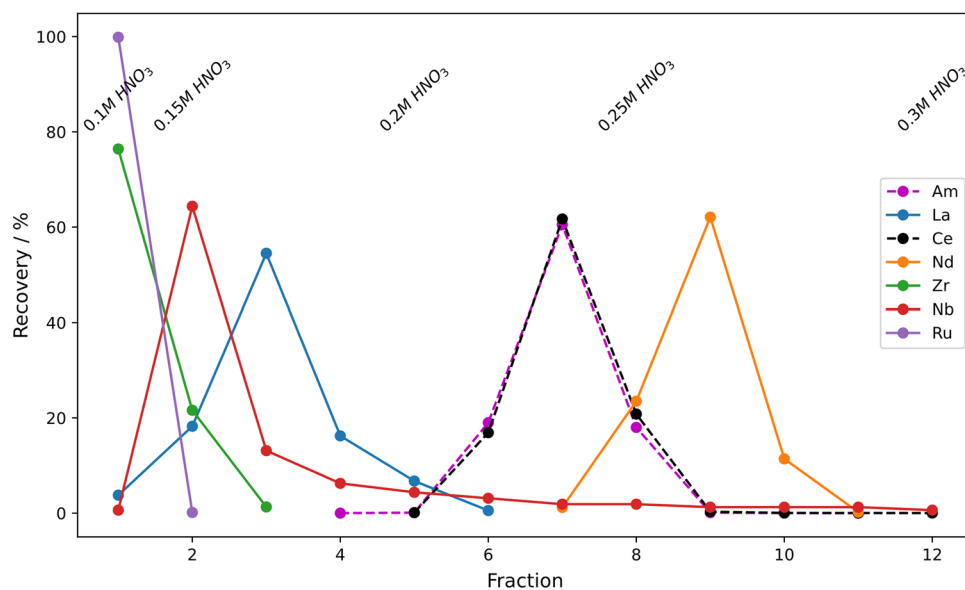
Decontamination factor (Eq. 2) is a measure of the purification of the component that is to be extracted and the equation is frequently used in radiochemical separations:

$$\text{DF} = \frac{\frac{P_{\text{final}}}{P_{\text{initial}}}}{\frac{I_{\text{final}}}{I_{\text{initial}}}} \quad (2)$$

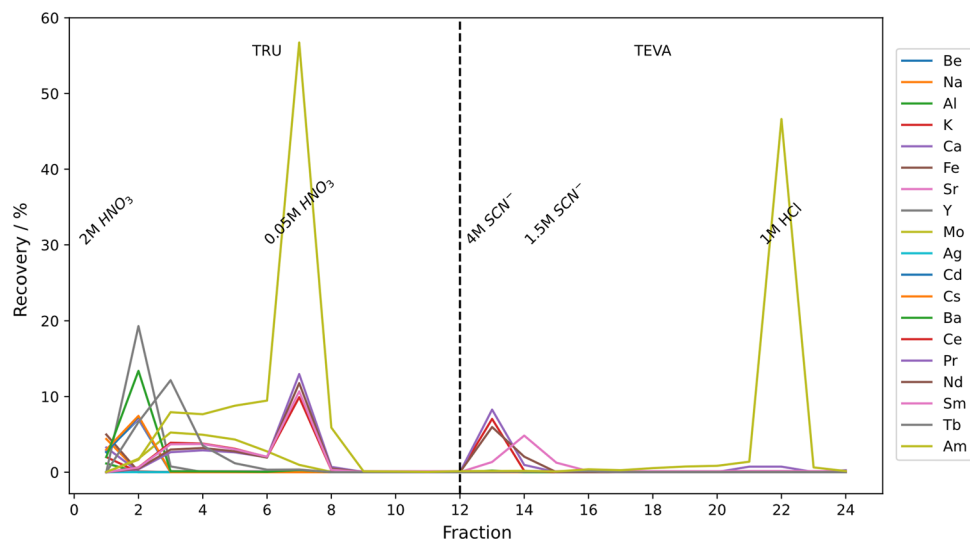
where  $P$  represents the product and  $I$  the contaminant, both of which are commonly expressed in units of activity in the case of radioactive nuclides or alternatively in units of concentration [20]. DF has been used to quantify purification of americium from the complex matrix in the present work.

Figure 4 displays the elution profile for americium and a simulated matrix of transition metals and lanthanides on LN resin. An elution profile of low molarity nitric acid was chosen to try and exploit the differences in  $D_w$  between americium and lanthanides observed and reported in Fig. 1. Good separation from transition metal

**Fig. 4** Elution profile for americium and simulated matrix elements from LN resin column



**Fig. 5** Elution profile for americium and simulated matrix elements on TRU/TEVA column stack

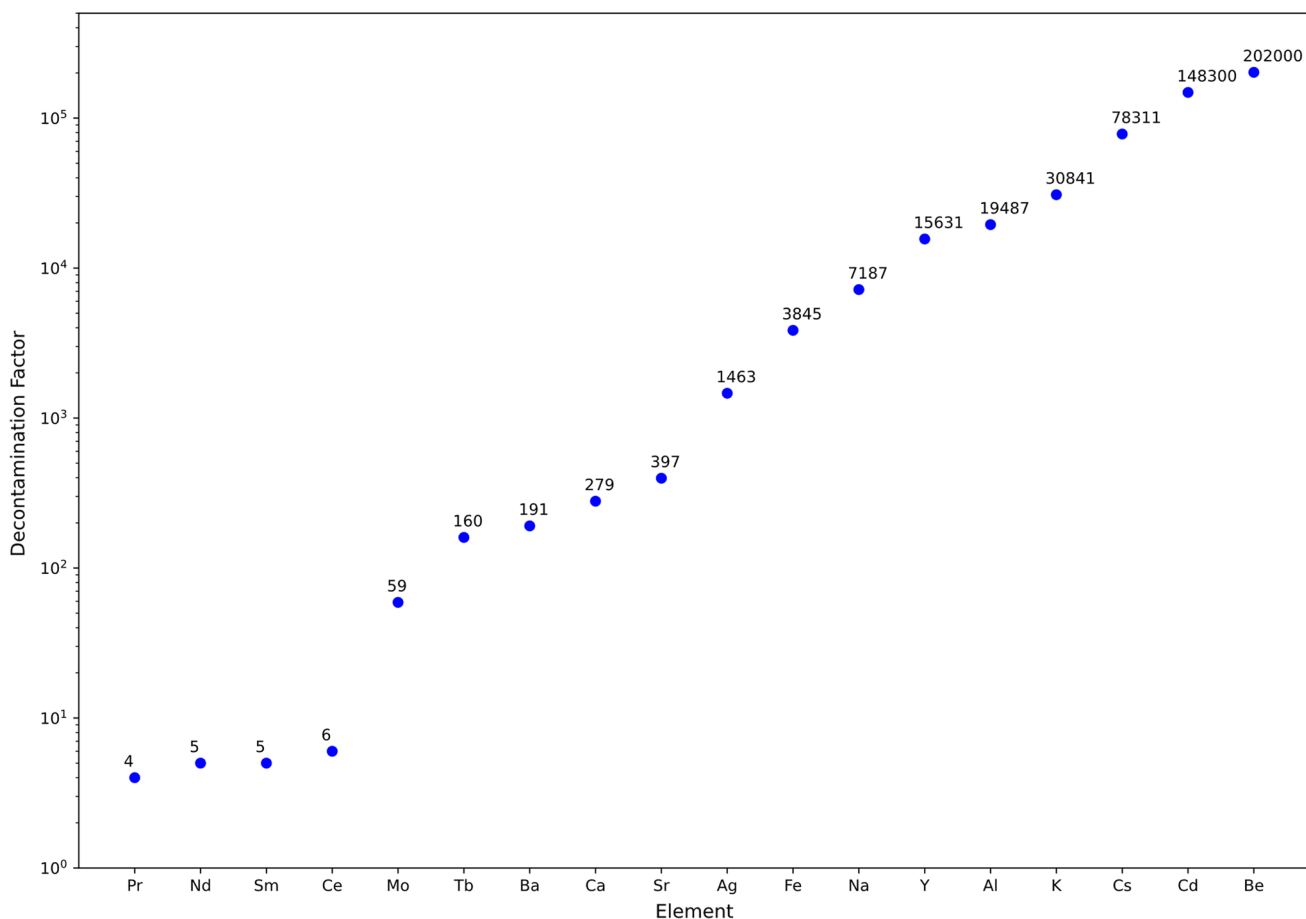


was observed as is to be expected. Separation from lanthanum and neodymium was achieved however no separation of americium from cerium was possible.

Figure 5 displays the elution profile for americium and the simulated matrix on TRU and TEVA columns respectively. As can be seen good separation from non-lanthanides is achieved on the TRU column and then the americium/lanthanide separation is achieved on the TEVA column as expected [6, 7]. This result is quantified by the decontamination factors displayed in Figs. 6 and 7.

There is some bleed through of americium on the TRU column totalling 35.5% of the total applied across the first 6 fractions before 63% is retrieved across two fractions by elution with 0.05 M nitric acid.

The fraction containing the majority (57%) of the americium (fraction 7) was applied to the TEVA column. A highly purified fraction comprising 47% of the americium originally applied to the initial TRU column was retrieved from the TEVA column by elution with 1 M hydrochloric acid (Fig. 5).



**Fig. 6** Decontamination factor for americium over simulated matrix elements on TRU column

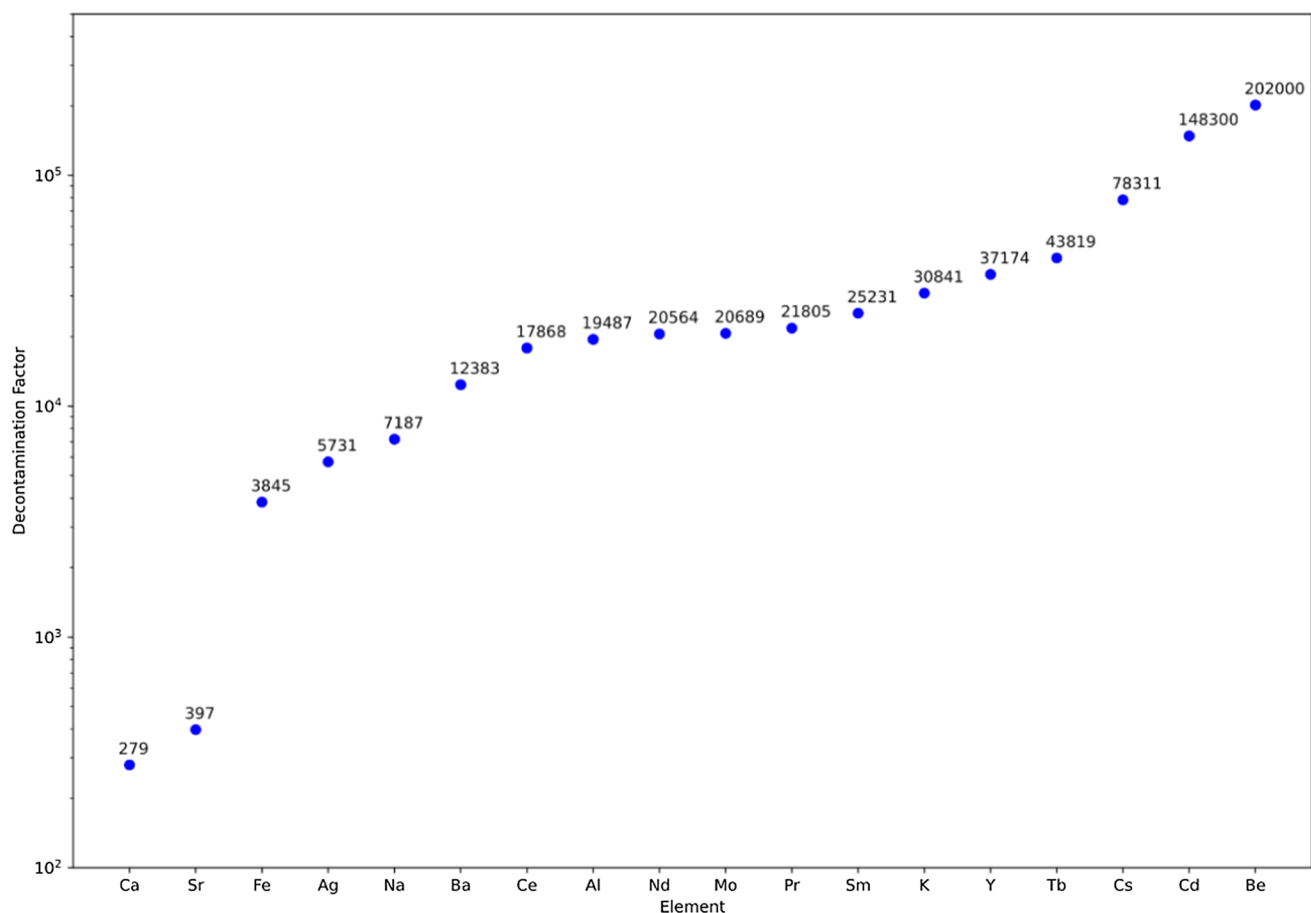
Only calcium and strontium could not be sufficiently purified by this method indicating that these elements may need to be removed prior to its application although they seemingly did not impede the purification of americium from the other simulated matrix elements. These elements would not be plated out alongside americium by electrodeposition and so would cause no impediment to quantification by alpha spectrometry (Fig. 8).

## Conclusion

The distribution coefficients for americium and a selection of lanthanides/transition metals as a function of low molarity nitric (0.1–0.4 M) nitric acid on LN resin have

been reported. Significant differences in distribution coefficient between americium and lanthanides at these low molarities were the basis for a separation by column chromatography. Good separation of americium from transition metals, lanthanum and neodymium were obtained. No separation of americium from cerium was possible.

The distribution coefficients for americium, curium, yttrium and a selection of lanthanides as a function of ammonium thiocyanate concentration on TEVA resin have been reported. The resin showed good discrimination for americium over lanthanides at high (4 M and above) concentrations of ammonium thiocyanate. A distinguishable  $D_w$  between americium and curium leading to a separation factor of 1.1 was seen at 2 M ammonium thiocyanate concentration. Future work should aim to study the effect

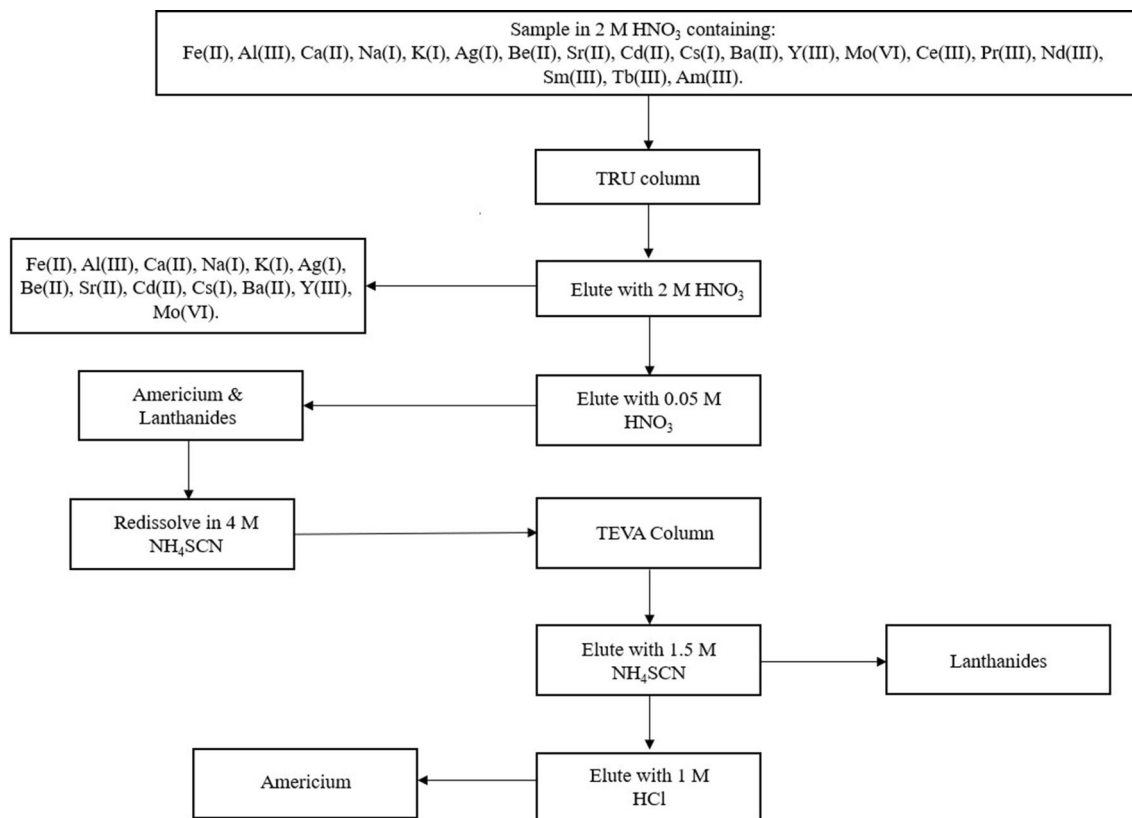


**Fig. 7** Decontamination factor for americium over simulated matrix elements on TEVA column

of raising this concentration from 2 up to 5 M as the trend suggests that the disparity in affinity may increase as is the case with americium/lanthanide separations.

A powerful and rapid method for the separation of americium from complex matrices has been documented in the form the sequential use of two commercially available extraction chromatography resins. Firstly the resin TRU was used to filter out Group 1, Group 2 and transition metal elements. The remaining aliquot containing americium

and lanthanides was purified by the use of a TEVA column eluted with ammonium thiocyanate followed by HCl. The method led to excellent decontamination factors of  $> 20,000$  for americium/lanthanides. Each column took 60 min to run with a flowrate of approximately 1 mL/min achieved by use of vacuum box, a dramatic improvement over the *ca.* 0.2 mL/min under gravity. The increased flowrate meant that the method and quantification were easily deliverable within one working day.



**Fig. 8** Separation scheme for purification of americium from complex matrix

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