THE SEPARATION OF SOME FISSION PRODUCTS AND ACTINIDES ON PAPER TREATED WITH LIQUID ANION EXCHANGER

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INTRODUCTION

Process solutions in many stages of the aqueous reprocessing of nuclear fuels are mostly contaminated with a few fission products such as Ce, Zr and Ru which form a series of partly extractable complexes. A simple method of analyzing the U and Pu products or waste solutions is the separation of the nuclides by paper chromatography. The method can easily be modified to separate other substances such as corrosion products, alloy components or additives.

Some earlier work on fission product separation by paper chromatography was done by GÖTTE AND PÄTZE[1] with HCl as eluent and by CROUTHAMEL AND FUDGE[2] with HF. KELLER[3] successfully separated some of the actinides with alcohol–acid mixtures. TESTA[4] used amine-impregnated paper and cellulose in a series of experiments and separated rare earths.

Most of the transition elements form more or less stable complexes in acid or salt solutions. KRAUS AND NELSON[5] established the anionic character of such complexes in strong acids or electrolyte solutions. Liquid anion exchangers have been extensively studied to evaluate their extraction properties in liquid–liquid extraction. The knowledge of the extraction coefficients for the extraction of metals by amines allows the prediction of the R_F values of these metals using paper impregnated with liquid amines. Likewise, extraction coefficients (E) may be predicted from R_F values. The following correlation has been proposed by MARTIN AND SYNGE[6]

$$E = k\left(\frac{1}{R_F} - 1\right)$$

Some extraction coefficients for tri-n-octylamine (TOA) are given in Fig. 1. High coefficients indicate small R_F values in corresponding systems on paper.

EXPERIMENTAL

Paper

Schleicher and Schüll paper No. 2034b Mgl was used. Strips, 2 × 30 cm, were dipped for 15 min in a TOA/xylene solution. After gentle drying a film of ion exchanger is left on the paper.

Amine

Tri-*n*-octylamine is a weak base, with a water solubility of less than 0.01 %, but is soluble in many organic solvents. The amine was diluted with xylene to molarities ranging from 0.05 to 0.5. To eliminate reactions between the amine and the eluent, all amine solutions were pre-equilibrated with the corresponding eluent. In every case the amine nitrate should be formed quantitatively.
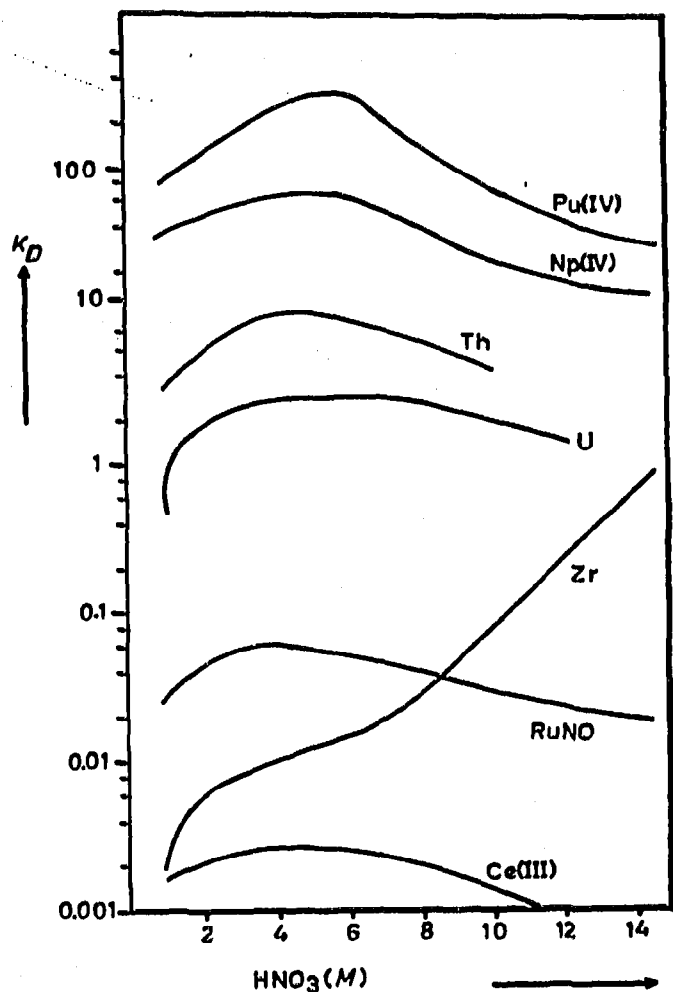

Fig. 1. Distribution coefficients of some nuclides for extraction with 0.45 M (20 vol.%) tri-*n*-octyl-amine/xylene.

Radionuclides

The following nuclides in the nitrate form were used: [91]Y, [144]Ce, [95]Zr, [106]Ru, [228]Th, [231]Pa, [233]U, [237]Np, [239]Pu, and [241]Am. Ru was present as a mixture of nitrosyl nitrates. The transformation into the nitrate form should be carried out with special care in the case of Zr and Pa so that oxalate and fluoride ions are completely removed. In some cases we added non-radioactive carrier. The metal concentrations were about 5 μg/μl and the activities 50 μC/ml. About 5 μl were applied to a paper strip.

Chromatography

The elution time required by ascending chromatography ranges from 20 min

to about 12 h depending on the composition of the eluent (to reduce the time, the runs were stopped at 15 cm). The chromatograms were developed by colour reactions and/or counting methods. U, Th, La and Ce may be shown up with 0.1 % morin (La with NH_3), Mo and U by $K_4Fe(CN)_6$, Zr with 0.1 % alizarin or β-nitroso-α-naphthol and Ru by ammonium sulfide. Counting the radioactivity is advantageous: a methane gas flow proportional detector was mounted on a scanner. The ultra-thin 2 in. window gives a good efficiency even for α radiation. α- and β-activity may be recorded separately by scanning first on the α plateau and then on the $\alpha + \beta$ plateau of the detector covering the slot with a thin foil to absorb the α radiation. This means that in some cases there is the additional possibility of quantitative determination even if the nuclides are not separated on the paper.

RESULTS

HNO_3 as eluent

In aqueous reprocessing nitric acid is mostly used as the dissolution agent. The R_F values of the fission products studied with HNO_3, as eluent, range from 0.85 to 1. This means that nitrate complexes are not very stable and the species present prefer the aqueous phase and a good separation is not achieved.
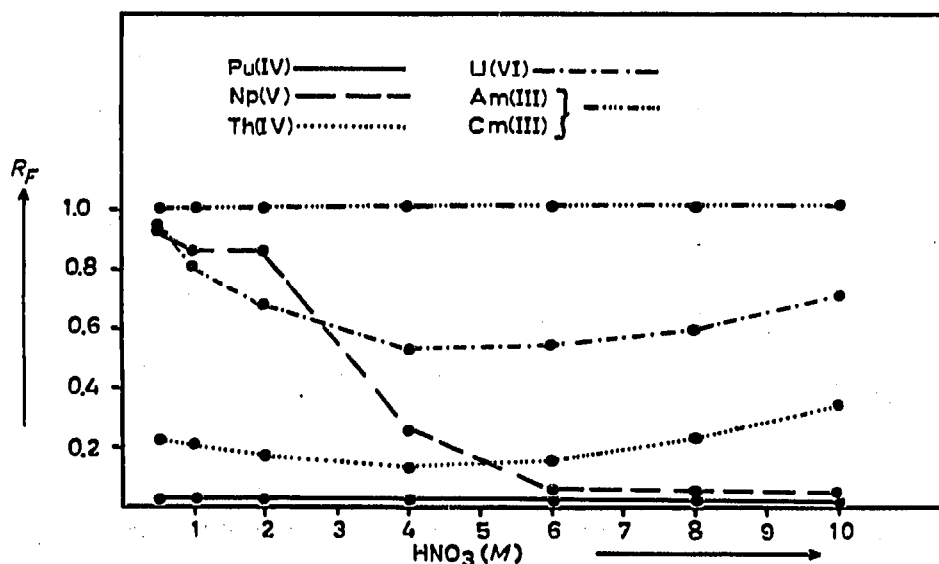

Fig. 2. R_F values of actinides as a function of HNO_3 concentration. Paper treated with 0.1 M TOA.

The actinides, however, are well separated (see Fig. 2). The R_F values for 2 M and 8 M HNO_3 are given in Table I. Pu(IV) and Np(V) were stabilized by addition of $NaNO_2$. Np(V), however, is not stable at high acid concentrations in the presence of NO_2^- ions. The disproportionation 2 $NpO_2^+ + 4$ $H^+ \longleftrightarrow Np^{4+} + NpO_2^{2+} +$ 2 H_2O is acid dependent. Moreover, the Np(IV) formed by this reaction seems to be oxidized partly by the nitrite ion and not by the nitric acid. Our stock solution (4 M HNO_3), for example, had 56 % Np(V), 27 % Np(IV) and 17 % Np(VI), whereas the same solution with 0.05 M $NaNO_2$ (24 h equilibrium) had 84 % Np(VI) and 16 %

Np(IV) (the identification of the oxidation states is discussed later). The reaction $Np^{4+} + NO_2^- + H_2O \longrightarrow NO + NpO_2^+ + 2 H^+$, being acid dependent, would be suppressed with increasing acid concentration. Accordingly, an 8 M HNO_3 solution of Np with 0.05 M $NaNO_2$ had 65 % Np(VI) and 35 % Np(IV).

TABLE I

R_F VALUES OF ACTINIDES ELUTED WITH 2 M AND 8 M HNO_3

Actinide	R_F	
	2 M HNO_3	8 M HNO_3
Pu(IV)	0.03	0.03
Th	0.18	0.24
U(VI)	0.68	0.60
Np(V)	0.86	(0.20)*
Pa/Am/Cm	1	1

* Np(VI).

Nitrate salts as eluents

Replacement of the hydrogen ion by large cations surrounded by water molecules generally increases the distribution coefficients of the metal ions which are forced into the organic phase by salting-out effects. When nitrate salts are used instead of HNO_3 as eluent the overlapping spots are separated.

We used NH_4NO_3, $LiNO_3$ and $Al(NO_3)_3$ solutions with a constant 0.5 M HNO_3 concentration to prevent hydrolysis of the metal complexes. $LiNO_3$ (Fig. 3) and $Al(NO_3)_3$ (Fig. 4) give good separations. Y, La, Ce(Zr), and U can be separated with 4 M $LiNO_3$.

The mixture of RuNO-nitrate and nitro complexes considered here would re-establish equilibrium composition only slowly if any of the components are removed by extraction. The half-times of the nitration and denitration reactions are in the
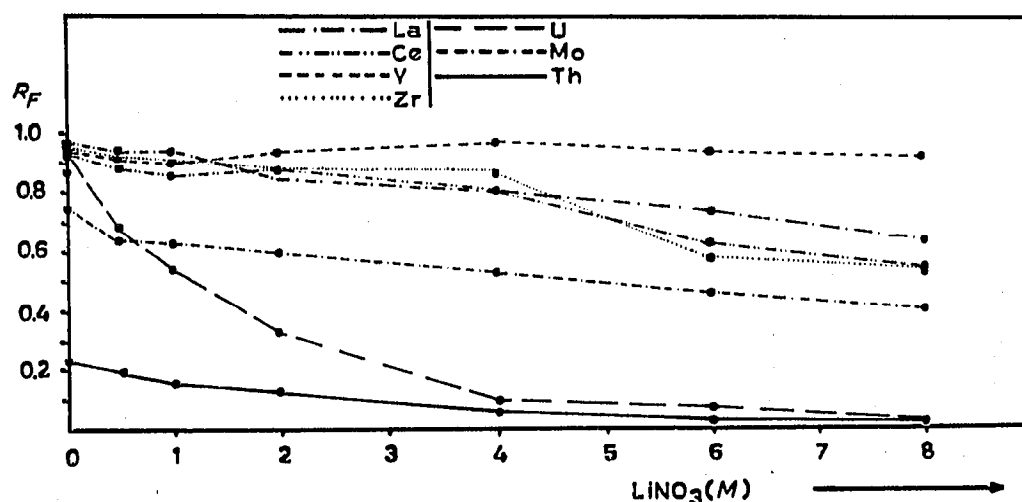

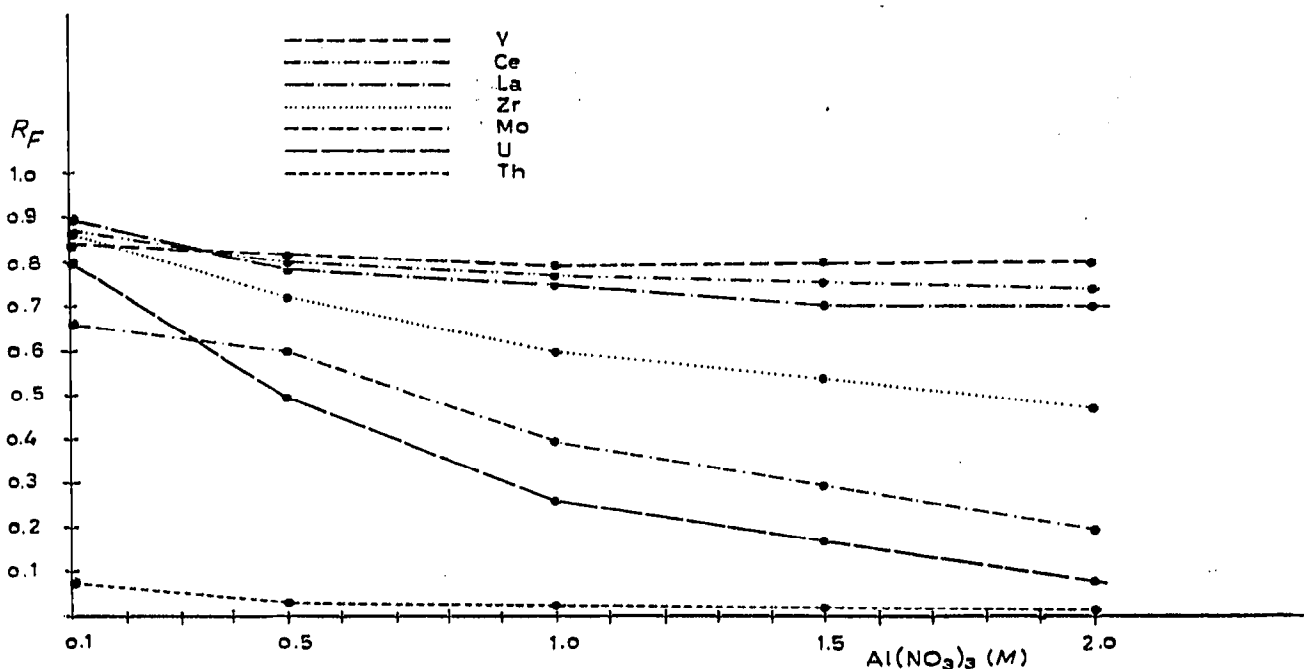Fig. 3. R_F values as a function of $LiNO_3$ concentration (0.5 M HNO_3); 0.1 M TOA.

Fig. 4. R_F values as a function of $Al(NO_3)_3$ concentration (0.5 M HNO_3); 0.1 M TOA.

order of minutes. This results in extensive tailing on the paper during elution. To eliminate the tailing, Ru should not move at all ($R_F \sim 0$). This is achieved with 0.1 M $Al(NO_3)_3$ (Fig. 5). The separation of Ru, Zr/Nb, Ce and U is possible at about 0.5 M $Al(NO_3)_3$ + 0.5 M HNO_3. A high amine concentration on the paper is necessary.

Actinides

We first determined the R_F values of the nuclides at their most stable oxidation state, *i.e.* Th(IV), U(VI), Np(V), Pu(IV) and Am(III). The eluents were NH_4NO_3, $LiNO_3$ and $Al(NO_3)_3$ solutions with constant 0.5 M HNO_3 (Fig. 6). Pu and Np(V) are stabilized by NO_2^-.
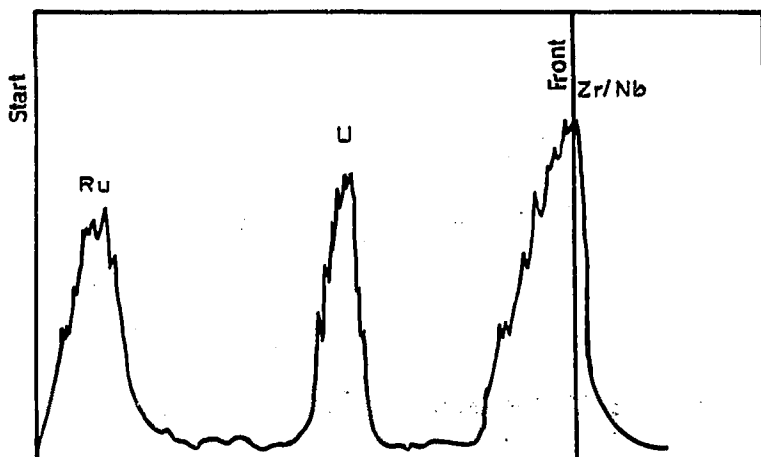

Fig. 5. Scanner plot, separation of Ru, Zr, U. Eluent: 0.1 M $Al(NO_3)_3$ + 0.5 M HNO_3. Paper treated with 0.5 M TOA.

With o.5 M LiNO$_3$ + o.5 M HNO$_3$ (o.1 M amine) the R_F values found are as follows:

	R_F
Am/Cm	1
Np(V)	o.85
U(VI)	o.70
Th	o.20
Pu(IV)/Pa	o

The separation of Pu, Am, and Cm by a similar simple method is possible[7]. Pa solutions must be free of fluoride ions, otherwise the R_F would increase to o.9–1. High amine concentrations on the paper lower the R_F values; the separation, however, will not be improved.
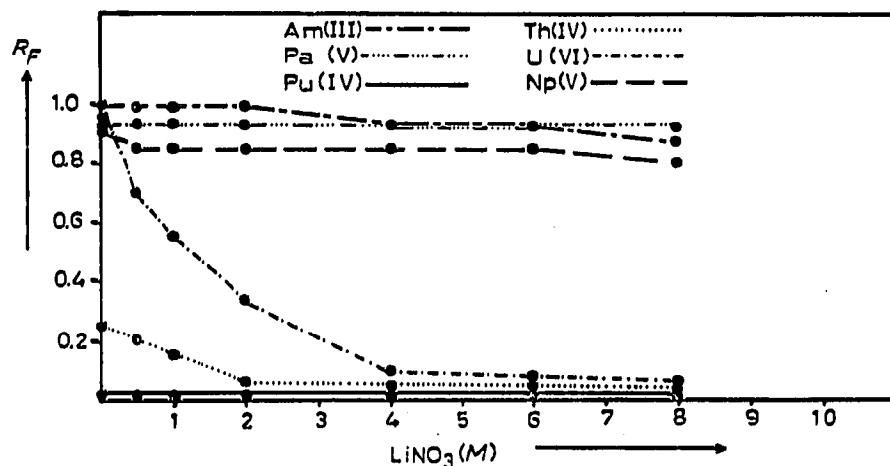

Fig. 6. R_F values of actinides as a function of LiNO$_3$ concentration (o.5 M HNO$_3$); o.1 M TOA.

Identification of different oxidation states

Np and Pu are stable in several oxidation states. A simple quantitative analysis of the proportions of the different oxidation states in a solution is possible by paper chromatography on amine paper, provided the eluent and paper are not participating in any redox reaction.

Neptunium

The eluent should not contain more than 1 M HNO$_3$ to avoid oxidation or disproportionation. The R_F values of Np(IV), Np(V) and Np(VI) are sufficiently different to allow separation with o.5 M NH$_4$NO$_3$ + o.5 M HNO$_3$ and quantitative determination by α- or β-counting (Fig. 7, Table II).

Np(IV) was prepared by reduction with Fe(II) sulfamate, Np(V) by oxidation to Np(VI) and reduction with NaNO$_2$ and Np(VI) by oxidation with Ce(IV).

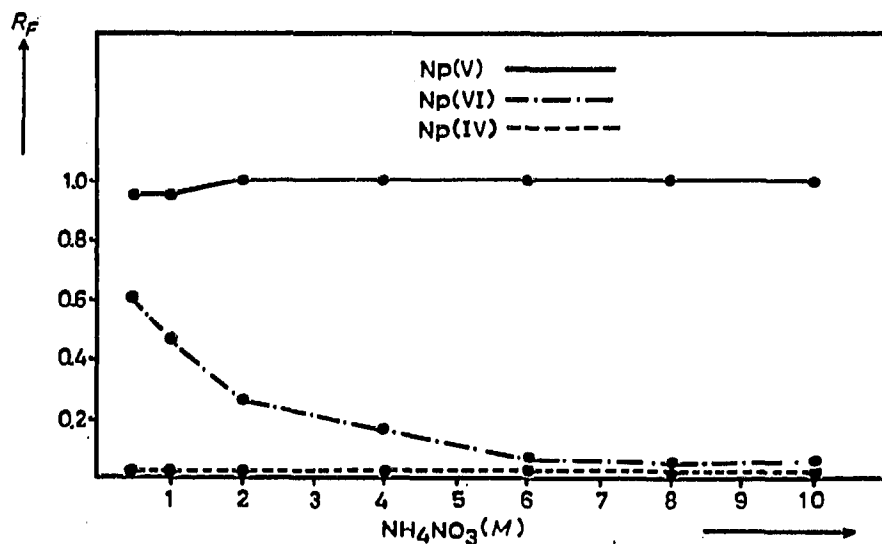Fig. 8 shows the analysis of a chromatogram by cutting the strip into 1 cm sections and counting the activity.

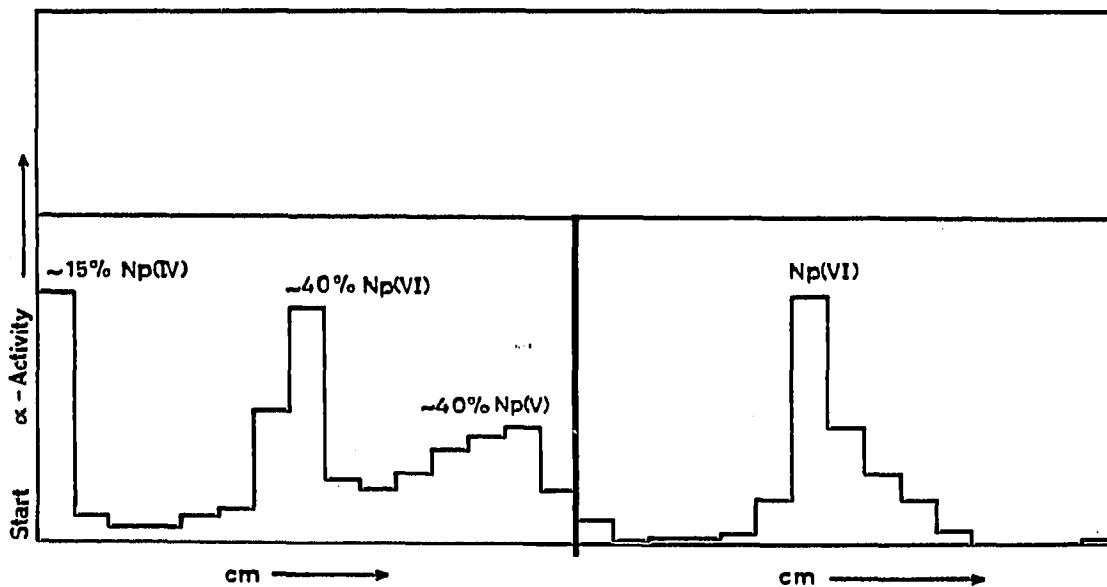Fig. 7. R_F values of Np in different oxidation states. Eluent: NH_4NO_3 + 0.5 M HNO_3; 0.1 M TOA.

Fig. 8. Analysis of a Np solution. Left: stock solution, 6 M HNO_3 + 0.02 M $NaNO_2$. Right: 6 M HNO_3 + Ce(IV).

TABLE II

R_F VALUES OF Np(IV), Np(V) AND Np(VI) WITH NH_4NO_3 AND HNO_3 AS ELUENT
Paper treated with 0.1 M TOA.

NH_4NO_3 (M)	R_F			HNO_3 (M)	R_F		
	$Np(IV)$	$Np(V)$	$Np(VI)$		$Np(IV)$	$Np(V)$	$Np(VI)$
0.5	0	0.90	0.56	0.5	0	0.95	0.85
1	0	0.90	0.46	1	0	0.90	0.80
2	0	0.90	0.26	2	0	0.88	0.63
4	0	0.90	0.17	4	0	0.81	0.20
6	0	0.88	0.13	6	0	0.75	0.15
8	0	0.85	0.10	8	0	0.65	0.20
10	0	0.85	0.08	10	0	0.63	0.32

Plutonium

NH_4NO_3 is also suitable as eluent for the identification of Pu oxidation states. The R_F values of the single species are plotted in Fig. 9. Pu(III) was reduced by Fe(II) sulfamate, Pu(IV) stabilized by $NaNO_2$ and Pu(IV) oxidized by Ce(IV).
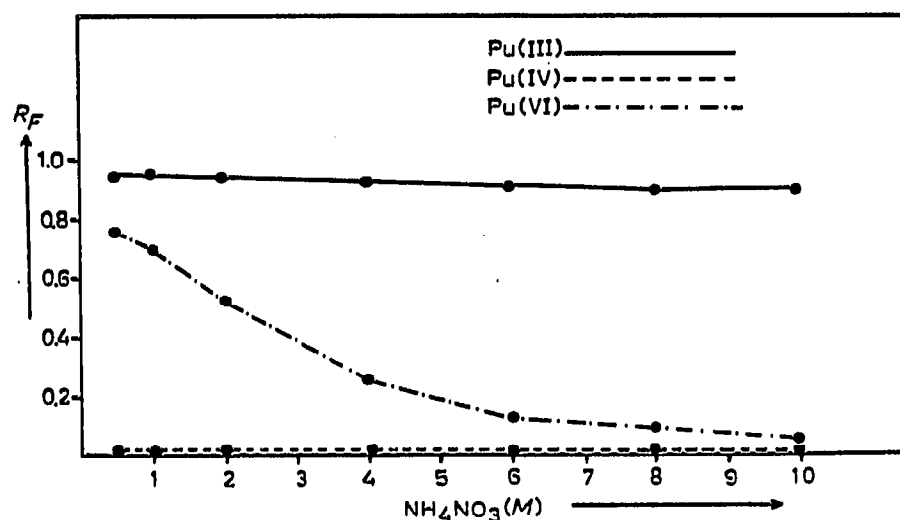

Fig. 9. R_F values of Pu in different oxidation states. Eluent: NH_4NO_3 + 0.5 M HNO_3; 0.1 M TOA.

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SUMMARY

After treatment of paper with a liquid anion exchanger (tri-*n*-octylamine) the differences in the stability of the metal complexes may be used to improve the analytical separation of some important fission products and actinides by paper chromatography. The R_F values of Y, La, Ce, Zr, Ru and Th, Pa, U, Np, Pu, Am with nitric

acid and nitrates as eluents are given. Quantitative determination by scanning the radioactive nuclides is possible and some methods are proposed. The oxidation states of Np and Pu are identified by their different R_F values. The composition of mixtures with different valency states of the metals may be determined quantitatively.

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