RADIOCHEM.RADIOANAL.LETTERS 48/1/ 61-70 /1981/

SOLVENT EXTRACTION STUDIES USING TETRACYCLINE AS A COMPLEXING AGENT, XI. EXTRACTION OF PROTACTINIUM. SEPARATION OF ^{233}U FROM ^{233}Pa AND THORIUM. SEPARATION OF ^{233}Pa FROM THORIUM

M. Saiki, F.W. Lima

Radiochemistry Division, Instituto de Pesquisas
Energéticas e Nucleares, C.P. 11049, 01000,
São Paulo, SP Brasil

Received 9 April 1981
Accepted 17 April 1981

Separation of ^{233}U from irradiated thorium and from ^{233}Pa is accomplished by solvent extraction using tetracycline /TC/ as a complexing agent and diethylenetriaminepentaacetic acid as a masking agent. For the separation of ^{233}Pa from thorium, sodium fluoride is used to mask the complexation reaction Th-TC. Benzyl alcohol is used as an organic solvent.

INTRODUCTION

Previous papers of this series on radioanalytical applications of tetracycline /TC/ have described separations of uranium from neptunium[1], thorium[2], scandium and lanthanide elements[3], and from other elements[4].

This systematic study is now extended to the separation of ^{233}Pa formed in β-decay of ^{233}Th after thermal neutron irradiation of ^{232}Th, and to the separation of ^{233}U from irradiated ^{232}Th and simultaneously from ^{233}Pa.

EXPERIMENTAL

All reagents used were of analytical grade purity.

TC-benzyl alcohol solutions, at a concentration of 0.01M in TC, were used for the extraction experiments.

A 4.9X10^{-3}M sodium fluoride solution was used as a masking reagent for the complexation reaction of protactinium with TC to allow the extraction of thorium into the TC-benzyl alcohol phase. Diethylenetriaminepentaacetic acid /DTPA/ solution, at a concentration of 2.5x10^{-3}M, was the masking agent for protactinium and thorium, allowing the extraction of uranium into the organic phase. Water used to prepare the solution was first deionized in a mixed bed ion-exchanger and next distilled from a quartz apparatus. The benzyl alcohol phase was previously saturated with water and vice versa. Solutions of TC in benzyl alcohol were prepared by dissolving tetracycline hydrochloride in the organic reagent. Fresh solutions were prepared for each experiment.

Tracer solution of carrier-free ^{233}Pa/V/ was prepared by the irradiation of thorium hydroxide in a thermal neutron flux corresponding to 6x10^{12} n.cm^{-2}.sec^{-1} for about 8 h. The irradiated thorium hydroxide was then dissolved with some drops of concentrated hydrochloric acid and the solution allowed to stand for 20 h. The ^{233}Pa formed by the β-decay of ^{233}Th was then separated on an anion exchanger /Amberlite CG-400, Type II/ according to Krauss et al.[5]. ^{233}Pa is retained by the exchanger while thorium passes through the column. ^{233}Pa retained by the exchanger was eluted with 0.2M hydrochloric acid and the ^{233} solution was kept in 8M HCl in a polyethylene flask. The final tracer solution for the extraction experiments was prepared by evaporating to dryness 250 μl of the 8M HCl solution of ^{233}Pa and dissolving the residue with dilute $HClO_4$.

Check for thorium
was performed by usi
solutions of ^{234}Th w
using uranyl nitrate
as that used for the
$^{232+234}$Th solutions:
changer resin, eluti
acid and a checking
the percolated solut
detector coupled to
of ^{234}Th was practic
rium was retained by
^{233}Pa.

The presence of o
^{233}Pa solution was v
Ge/Li/ detector coup

Tracer solution o
diluted to 8.6x10^{-5}M
minute per μg of ^{233}

Polyethylene ware
traction funnels, wh
the extraction glass
at a concentration o
ligible during the 3
on the glass walls w
procedure.

The organic phase
hol; the aqueous pha
vestigated in 0.10M
volume of the aqueou
aqueous phase was ad
diluted $HClO_4$ or NaC

For extraction bo
stirrer for 30 min a

Check for thorium in the ^{233}Pa carrier-free solutions was performed by using a ^{234}Th tracer solution. Carrier-free solutions of ^{234}Th were prepared according to Abrão[6] using uranyl nitrate solutions. The same set of operations as that used for the preparation of ^{233}Pa was applied to $^{232+234}$Th solutions: percolation through the anion-exchanger resin, elution of the resin with 0.2M hydrochloric acid and a checking for ^{234}Th by counting the resin and the percolated solution in a well-type NaI/Tl/ 7.5x7.5 cm detector coupled to a multichannel γ-analyzer. Percolation of ^{234}Th was practically complete, indicating that no thorium was retained by the anion-exchanger together with ^{233}Pa.

The presence of other radioactive impurities of the ^{233}Pa solution was verified by γ-ray spectrometry using a Ge/Li/ detector coupled to a 4096-channel analyzer.

Tracer solution of ^{233}U /Amersham-Searle Co./ was diluted to 8.6×10^{-5}M in uranium, giving 4000 counts per minute per μg of ^{233}U, in a proportional gas-flow counter.

Polyethylene ware was used throughout except the extraction funnels, which were of Pyrex glass. Attack of the extraction glass funnels by the masking reagent NaF, at a concentration of about 5×10^{-3}M, was practically negligible during the 30-min shaking time. Adsorption of ^{233}Pa on the glass walls was also negligible during the extraction procedure.

The organic phase was 5 ml of 0.01M TC in benzyl alcohol; the aqueous phase was a solution of the element investigated in 0.10M $NaClO_4$ /supporting electrolyte/. The volume of the aqueous phase was also 5 ml. The pH of the aqueous phase was adjusted by adding known volumes of diluted $HClO_4$ or NaOH solution.

For extraction both phases were stirred with a mechanical stirrer for 30 min at 25.0±0.5 °C. After equilibration the phases were separated by centrifugation and 1 ml from each phase was withdrawn for counting ^{233}Pa on a single-channel analyzer coupled to a 5.0x4.4 cm well-type NaI/Tl/ detecto

Thorium concentration in each phase was determined as described previously[7].

The extraction of uranium was studied by using natural uranium or ^{233}U solutions. The natural uranium concentrati in each phase, was determined by epithermal neutron activation analysis[8]. For the determination of ^{233}U the soluti was transferred onto stainless steel planchets, by means of a micropipette, and evaporated to dryness under an infrared lamp. ^{233}U was counted in a proportional gas-flow counter. Each value for ^{233}U in the organic or aqueous phase was the mean of counting values of triplicate planchets prepared as described.

RESULTS AND DISCUSSION

^{233}Pa and uranium are not extracted into pure benzyl alcohol, without TC, as shown in Table 1. The same is valid for thorium[7].

Fig. 1. shows that the extraction equilibrium for ^{233}Pa is reached very fast as was also observed for thorium using the same extraction system[7].

The experimental points on Fig. 1. correspond to the same straight line which was checked by statistical "t" and "F" tests[9] at a confidence level of 95%.

Separation of ^{233}Pa from thorium and of ^{233}U from ^{233}Pa and thorium

Fig. 2. presents the extraction curves of protactinium, thorium and uranium /uranyl/ as function of pH, showing

---

Fig. 1. Distribut
function
120 min;
II* indic
in the aq
ly

that separation c
sible by multiple

However, the
can be achieved
with NaF, as show
justed before the
ments were carrie
After the additio
librium was attai

tion and 1 ml from each
^{3}Pa on a single-channel
ll-type NaI/Tl/ detector
ase was determined as

udied by using natural
ral uranium concentratio
ithermal neutron acti-
tion of ^{233}U the solutio
l planchets, by means
o dryness under an in-
proportional gas-flow
organic or aqueous
es of triplicate plan-

ted into pure benzyl
ble 1. The same is valid

n equilibrium for ^{233}Pa
served for thorium using

l. correspond to the
d by statistical "t"
l of 95%.

d of ^{233}U from ^{233}Pa

curves of protactinium,
ction of pH, showing

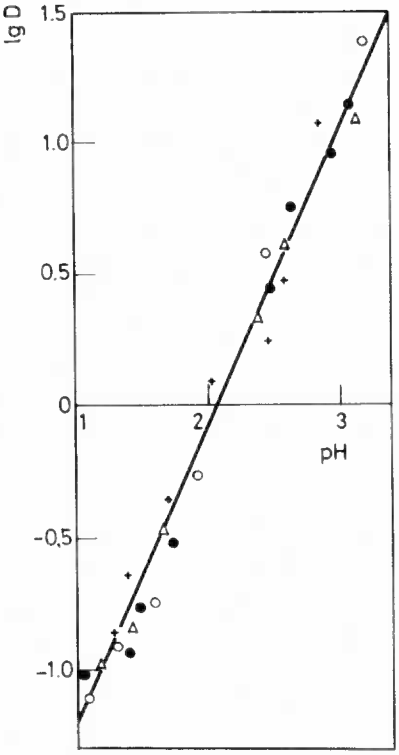

Fig. 1. Distribution ratio /log D/ of ^{233}Pa vs pH as a function of shaking time. I*: /●/ - 10 min; /+/ - 120 min; II*: /o/ - 10 min; /Δ/ - 120 min. I* and II* indicate whether ^{233}Pa was initially present in the aqueous phase or the organic phase, respectively

that separation of the three elements would only be possible by multiple extraction.

However, the separation of protactinium from thorium can be achieved by masking the Pa-TC complexation reaction with NaF, as shown in Fig. 3 and Table 2. The pH was adjusted before the addition of sodium fluoride. pH measurements were carried out using a Hellige model 7/60 pH-meter. After the addition of sodium fluoride and after the equilibrium was attained, the pH was measured with a Merck pH

TABLE 1

^{233}Pa and uranium extraction into benzyl alcohol without tetracycline

Protactinium		Uranium	
pH	E	pH	E
0.75	1.9	0.95	1.0
1.06	1.9	1.80	0.3
1.67	2.5	3.15	0.4
2.55	2.5	4.30	0.1
2.88	1.7	5.95	0.1
3.39	0.8	6.40	0.2

$[U] = 5.0 \times 10^{-5}$M; ^{233}Pa, carrier-free, $[NaClO_4] = 0.10$M. Shaking time: 30 min; temperature: 25.0±0.5 °C; E = percentage of element in the organic phase

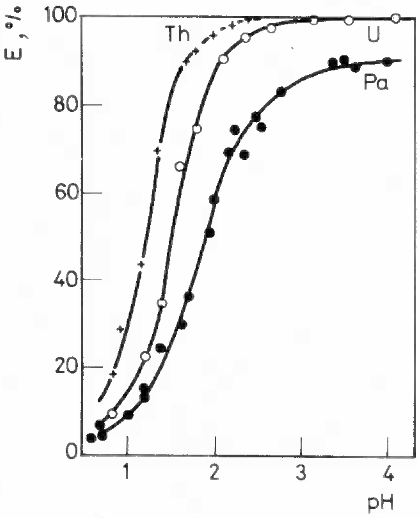

Fig. 2. Extraction curves for thorium, uranium and protactinium. $[TC] = 0.010$M; $[Th] = 5.0 \times 10^{-4}$M; $[U] = 7.0 \times 10^{-5}$M; $[NaClO_4] = 0.10$M; shaking time = 30 min; temperature = 25.0±0.5 °C

benzyl alcohol without
ne

ranium

	E
	1.0
	0.3
	0.4
	0.1
	0.1
	0.2

ee, [$NaClO_4$] = 0.10M.
25.0±0.5 °C; E = percent
e

rium, uranium and protac-
n] = $5.0x10^{-4}$M; [U] =
0M; shaking time = 30 min;

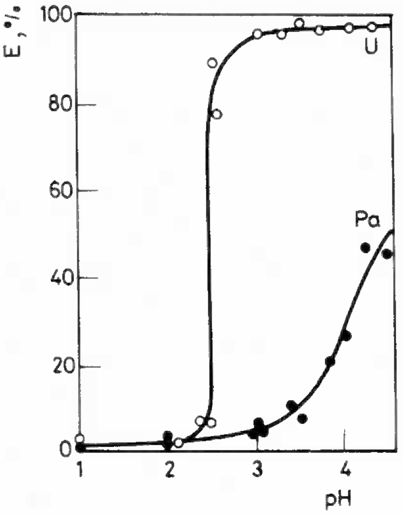

Fig. 3. Extraction curves for thorium and ^{233}Pa using NaF as a masking agent. [NaF] = $4.9x10^{-3}$M; [Th] = $2.0x10^{-5}$M; [$NaClO_4$] = 0.10M; [TC] = 0.010M

TABLE 2

Separation of ^{233}Pa from thorium by using TC-benzyl alcohol solution and NaF as a masking agent

E of Th	E of ^{233}Pa
95.2	3.8
96.2	3.9
95.9	4.4
92.6	5.3
94.9	4.4
Mean 95.0±1.4	4.4±0.6
Separation factor = 430	

pH = 3.0; [NaF] = $4.9x10^{-3}$M; [TC] = 0.010M;
[Th] = $2.0x10^{-5}$M

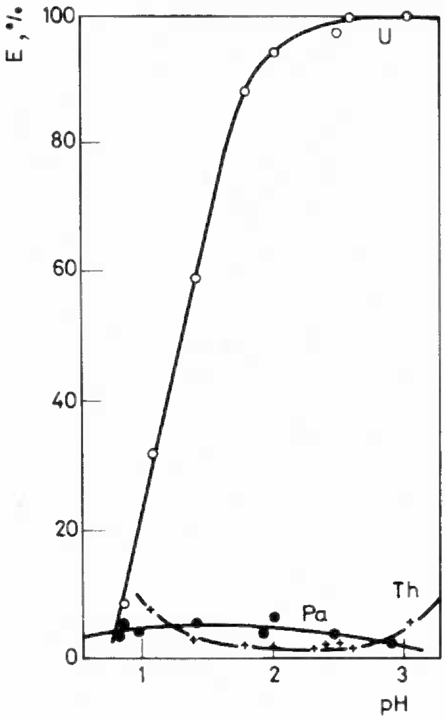

Fig. 4. Extraction curves for uranium, thorium and ^{233}Pa using DTPA as a masking agent. $[DTPA] = 2.5\times10^{-3}M$; $[U] = 7.0\times10^{-5}M$; $[Th] = 5.0\times10^{-4}M$; $[TC] = 0.010M$

indicator paper in order to avoid the attack of the glass electrode by fluoride ions.

If ^{233}Pa is allowed to decay to ^{233}U in the chain $^{232}Th/n,\gamma/^{233}Th \xrightarrow{\beta^-} {}^{233}Pa \xrightarrow{\beta^-} {}^{233}U$, uranium can be easily separated from thorium and protactinium. The complexation reactions Pa-TC and Th-TC are masked with DTPA, and the extraction of ^{233}U into the organic phase TC-benzyl alcohol can be accomplished. Fig. 4. shows such a separation.

*

The authors

the samples of

Engineering, IP

REFERENCES

1. M.J.C. Nasta
29 /1977/ 61.

2. M. Saiki, F.W
/1977/ 67.

3. M. Saiki, F.W
/1977/ 1.

4. M. Saiki, F.W
/1978/ 53.

5. K.K. Krauss,
78 /1956/ 269

6. A. Abrão, Chr
of Thorium an
and Hydrofluo
thorium and C
São Paolo, Br
/IEA-Pub-217/

7. M. Saiki, F.W

8. L.T. Atalla,
607.

9. V.V. Nalimov,
to Chemical A

ium, thorium and ^{233}Pa
gent. [DTPA] = 2.5x10^{-3}M;
.0x10^{-4}M; [TC] = 0.010M

the attack of the glass

o ^{233}U in the chain
^{233}U, uranium can be
protactinium. The
Th-TC are masked with
into the organic phase
shed. Fig. 4. shows such

The authors are grateful to Laborterapica Bristol for the samples of tetracycline and to the Center of Chemical Engineering, IPEN, for the ^{233}U tracer.

REFERENCES

1. M.J.C. Nastasi, F.W. Lima, Radiochem. Radioanal. Lett., 29 /1977/ 61.

2. M. Saiki, F.W. Lima, Radiochem. Radioanal. Lett., 29 /1977/ 67.

3. M. Saiki, F.W. Lima, Radiochem. Radioanal. Lett., 30 /1977/ 1.

4. M. Saiki, F.W. Lima, Radiochem. Radioanal. Lett., 35 /1978/ 53.

5. K.K. Krauss, G.E. Moore, F. Nelson, J. Am. Chem. Soc., 78 /1956/ 2692.

6. A. Abrão, Chromatographic Separation and Concentration of Thorium and Rare Earths from Uranium, Using Alumina and Hydrofluoric Acid. Preparation of Carrer-Free Radiothorium and Contribution to the Fission Rare Earths. São Paolo, Brasil, Instituto de Energia Atômica, 1970 /IEA-Pub-217/.

7. M. Saiki, F.W. Lima, J. Radioanal. Chem., 50 /1979/ 77.

8. L.T. Atalla, F.W. Lima J. Radioanal. Chem., 20 /1974/ 607.

9. V.V. Nalimov, The Application of Mathematical Statistics to Chemical Analysis, Pergamon Press, Oxford, 1963.